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East Yard Communities For Environmental Justice
COALITION FOR CLEAN AIR
EARTHJUSTICE

August 10, 2022

VIA: ELECTRONIC MAIL ONLY (mmorris@aqmd.gov)

Re: Comments on Proposed Amended Rule 1178 (Further Reductions of VOC Emissions from Storage Tanks at Petroleum Facilities)

Dear Mr. Morris,

The undersigned organizations submit these comments on Proposed Amended Rule 1178. While we appreciate the South Coast Air Quality Management District's ("Air District") consideration of various leak prevention and detection methods detailed in our December 2021 letter, we are concerned about the Air District's methodologies in evaluating the feasibility and cost-effectiveness of several control methods and the Air District's failure to evaluate other key rule reforms. These issues are detailed below and warrant that the agency reevaluate its recommendations.

This long overdue regulatory update presents a critical opportunity for the Air District to strengthen this rule to reduce toxic volatile organic compound ("VOC") emissions from storage tanks at petroleum facilities. For far too long, communities burdened by these massive storage tanks have been waiting for the agency to take action to reduce emissions. Accordingly, the Air District should thoroughly evaluate available technologies and amendments to ensure a robust rule that secures the maximum amount of VOC reductions possible from these sources.

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1. The Air District's Cost-Effectiveness Analysis Must Focus on Maximizing Emissions Reductions and Consider the Localized Benefits of Reducing VOCs.

In evaluating the cost-effectiveness of various leak prevention and detection methods to reduce VOCs, the agency used a general $30,000 per ton of VOC threshold established under the 2016 Air Quality Management Plan ("AQMP").[1] The agency's use of a general threshold to eliminate potential emissions reductions measures is unauthorized. Moreover, the agency's cost effectiveness approach fails to prioritize maximizing emissions reductions and to consider the localized benefits from reducing VOC emissions.

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[1] South Coast Air Quality Mgmt. Dist., PowerPoint Presentation at Proposed Amended Rule 1178 Working Group Meeting No. 5, at 12 (July 14, 2022) [hereafter "Working Group Meeting No. 5 Presentation"].

Under Health and Safety Code section 40440.8, the agency must consider a range of enumerated factors when proposing rule amendments that have the potential to "significantly affect air quality or emissions limitations," including "probable costs," "cost effectiveness of alternatives," and "emission reduction potential of the rule or regulation."[2] The section does not authorize the agency to use a general "threshold" to determine what alternatives would not be cost effective and to remove them from consideration despite their significant emission reduction potential.

Moreover, the agency's approach to cost effectiveness (i.e., the price per ton of emission reductions) ignores the localized benefits associated with reducing VOCs. These emissions expose nearby residents to a range of toxic air contaminants, including benzene, toluene, ethylbenzene, and xylene, that are known to cause a range of acute and chronic health conditions.[3] In fact, the Community Emissions Reductions Plans ("CERPs") developed under Assembly Bill 617 are intended to deliver air quality benefits directly to overburdened communities that "experience social and economic disadvantages that add to their cumulative burdens."[4] Accordingly, the agency's cost effectiveness analysis must consider these localized benefits for residents in Wilmington, Carson, and West Long Beach given that this rulemaking is due in part to the agency's commitments under the CERP for these areas.

2. The Air District's Reliance on a 2016 Cost-Effectiveness Threshold is Arbitrary and Misleading. The Cost-Effectiveness Threshold Must Reflect 2022 Dollars.

Even if the Health and Safety Code authorized the agency to use a general threshold, the agency's approach is arbitrary. As noted, the agency used a $30,000 per ton of VOC threshold established under the 2016 AQMP.[5] This cost-effectiveness threshold, however, would be about $36,000 per ton of VOC in 2021 dollars.[6] While setting the cost effectiveness threshold in the past, the agency then actively considers current equipment, labor, and other installation costs in 2022 dollars. The Air District's approach results in an unequal, arbitrary comparison where costs are inflated and likely to exceed a more than half-decade old cost-effectiveness threshold.

In response to this concern, staff contended the updated cost-effectiveness figures in the draft 2022 AQMP have not been approved by the Governing Board and therefore could not be used in this rulemaking. However, the cost-effectiveness thresholds summarized in the AQMPs are designed to serve as guidance and for general planning purposes—these values are not binding on each subsequent rulemaking, which requires a tailored socioeconomic impact assessment.[7] The nonbinding effect of thresholds articulated in the AQMP is confirmed by both the Health and Safety Code and the agency's statements in the most recent 2022 AQMP.

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[2] Cal. Health & Safety Code § 40440.8(b)(1)-(6).

[3] Cal. Off. of Env't Health Hazard Assessment, *Analysis of Refinery Chemical Emissions and Health Effects*, at 20 (Mar. 2019) (Attached as Exhibit 7).

[4] South Coast Air Quality Mgmt. Dist., *Community Emissions Reduction Plan: Wilmington, Carson, and West Long Beach*, at 1-1 (July 19, 2019).

[5] Working Group Meeting No. 5 Presentation, *supra* note 1, at 12.

[6] South Coast Air Quality Mgmt. Dist., *2022 Draft Air Quality Management Plan*, at 4-63 [hereafter "2022 AQMP"].

[7] Cal. Health & Safety Code §§ 40922, 40440.8.

Under Health and Safety Code section 40703, for example, in adopting a regulation, the agency "shall *consider*, pursuant to Section 40922, and make available to the public, its findings related to the cost effectiveness of a control measure, as well as the basis for the findings and the considerations involved."[8] Similarly, under Health and Safety Code section 40440.8, when amending a rule the agency considers the analysis performed under Section 40922 to assess "the availability and cost-effectiveness of alternatives to the rule or regulation."[9] Other than reviewing and disclosing the cost effectiveness of alternatives listed in the AQMP, nothing in these sections binds the agency to a particular cost effectiveness threshold.

Finally, in the 2022 AQMP, the agency acknowledges the need to update these cost figures at the rulemaking stage, noting that "to account for normal inflation that occurs every year, these [cost effectiveness] values will be adjusted to the dollar year used for socioeconomic modeling in each subsequent rulemaking."[10] Accordingly, even if thresholds were authorized in considering the cost effectiveness of a proposed measure, the agency would be required to update the cost effectiveness threshold for this rulemaking to reflect 2022 figures.

3. The Air District Failed to Evaluate Higher Control Efficiency for Non-Combustion Systems and the Installation of Vapor Recovery Systems on All Fixed and Floating Roof Tanks.

In assessing the effectiveness of vapor recovery systems, staff reviewed annual performance tests showing greater than 99% efficiency for a combustion vapor recovery unit.[11] Based on the evaluation of "other records of performance tests" and initial performance testing, staff concluded that vapor recovery systems are achieving a 98% emission control efficiency.[12] As a result, staff recommends requiring an "overall control efficiency of at least 98% by weight for combustion emission control systems."[13]

The Air District, however, did not evaluate an equal or higher efficiency standard for non-combustion systems that collect and process vapors through carbon adsorption. According to U.S. EPA, "[w]hen properly designed, operated and maintained, carbon adsorbers can achieve high VOC removal efficiencies of 95 to *99 percent* at input VOC concentrations of between 500 and 2,000 ppm in air."[14] This efficiency rate is confirmed by manufacturers, such as APC Technologies whose activated carbon systems "can provide 98-99%+ control efficiency."[15]

Additionally, the Air District failed to consider requiring the installation of vapor recovery systems for all fixed and floating roof storage tanks in the region. According to agency statistics

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[8] Cal. Health & Safety Code § 40703.
[9] Cal. Health & Safety Code §§ 40922, 40440.8.
[10] 2022 AQMP, *supra* note 6, at 4-63.
[11] Working Group Meeting No. 5 Presentation, *supra* note 1, at 14.
[12] *Id.*
[13] *Id.*
[14] EPA, Air Pollution Control Cost Manual Section 3.1, *Chapter 1: Carbon Adsorbers* at 1-1 (7th ed. Oct. 2018), https://www.epa.gov/sites/default/files/2018-10/documents/final_carbonadsorberschapter_7thedition.pdf (Attached as Exhibit 4); *see also* TIGG, *What Is Activated Carbon?*, https://tigg.com/resources/activated-carbon-knowledge-base/what-is-activated-carbon/ (Attached as Exhibit 10).
[15] *APC Technologies,* CarbonPure Adsorption Systems Datasheet, https://www.apctechnologies.net/pdf/APC-CarbonPure.pdf (Attached as Exhibit 11).

presented during the July 15, 2021, working group meeting, there are at least 308 fixed roof storage tanks with vapor recovery systems, in addition to 250 internal floating roof and 290 external floating roof storage tanks in the region.[16] However, during the July 14, 2022, working group meeting staff identified a total of 267 fixed roof tanks with vapor recovery systems rather than 308.[17] The agency neglected to explain this discrepancy and failed to consider the installation of vapor recovery systems on all storage tanks lacking these controls. As noted in previous comments, operators can connect several storage tanks to a single vapor recovery unit, thus providing for cost savings as operators reduce fugitive VOC emissions.[18]

4. The Air District's Secondary Seals Analysis Relied on Misleading Cost Data and Equipment Life and Ignored Secondary Seals for Exempt Domed External Floating Roof Tanks.

In evaluating costs for secondary seals for internal floating roof tanks, the agency concludes that it would not be cost effective to require secondary seals on at least 31 tanks with internal floating roofs. The agency's analysis is problematic for several reasons.

First, the agency did not conduct a market assessment to evaluate costs for seal installation. Rather, staff used costs from the Rule 1178 rulemaking in 2001 and "adjusted to 2022 dollars."[19] The agency does not detail the specific costs from 2001 that it considered in its assessment.

Second, staff based its analysis on a secondary seal equipment life of 20 years without providing any evidentiary support for its determination.[20] In fact, secondary seals have a much higher equipment life of 25 or more years according to several manufacturers.[21]

Finally, the agency fails to consider the installation of secondary seals on domed external floating roof tanks built before January 1, 2002, that are currently exempt under Rule 1178 and the potential emission reductions from requiring these controls.[22]

For these reasons, staff should revise its analysis and proposed recommendation to require secondary seals on internal floating roofs, as well as domed external floating roof tanks presently exempt under Rule 1178.

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[16] South Coast Air Quality Mgmt. Dist., PowerPoint Presentation at Proposed Amended Rule 1178 Working Group Meeting No. 2, at 19 (July 15, 2021) [hereafter "Working Group Meeting No. 2 Presentation"].

[17] Working Group Meeting No. 5 Presentation, *supra* note 1, at 14.

[18] EPA, *Lessons Learned from Natural Gas STAR Partners: Installing Vapor Recovery Units on Storage Tanks*, at 1 (Oct. 2006), https://www.epa.gov/sites/default/files/2016-06/documents/ll_final_vap.pdf (Attached as Exhibit 1).

[19] Working Group Meeting No. 5 Presentation, *supra* note 1, at 15.

[20] *Id.*

[21] *See, e.g.*, ATECO Tank, *Secondary Seal – 3 Type*, https://atecotank.com/floating-roof-seal/external-floating-roof-seals/secondary-seal-3-type/ (typical service life for their secondary seals is 15-25 years) (Attached as Exhibit 12); *CTS, CTS20 Secondary Compression Plate Seal at pdf p. 11*, http://svimx.com/wp-content/uploads/2017/05/03_Tank-seals-datasheets-CTS-UK.pdf (expected service life for their secondary seal is "in excess of 30 years.") (Attached as Exhibit 13).

[22] S. Coast Air Quality Mgmt. Dist., Rule 1178(j)(2).

5. The Air District Relied on a Flawed Cost-Effectiveness Analysis to Exclude External Floating Roof Tanks from Doming Requirements and Focused Solely on Crude Oil Tanks.

In evaluating doming external floating roof tanks, staff included costs for labor and crane rental, among other expenses.[23] Staff also added a 20% increase in labor costs for unionized labor, and based its cost-effectiveness analysis on a 25-year equipment life and annual reported emissions inventories from 2020. Based on these factors and the resulting cost-effectiveness determination, of the 43 affected crude oil tanks, only 31 tanks with a diameter of less than 180 feet would be required to install domes. The agency's analysis is flawed in several ways.

First, the Air District failed to consider whether all facilities subject to Rule 1178 would be required to use unionized labor to install domes and does not explain how the agency arrived at a 20% increase to account for unionized labor costs. The agency does not detail whether some of the facilities would use their own employees to perform some or all the installation work or whether current workforce shortages might allow the use of non-unionized labor.[24] Moreover, the agency does not consider that Rule 1178 applies to a range of petroleum facilities, including those engaged in storage operations, that may not be required to use unionized labor.[25]

Second, the Air District assumes a 25-year equipment life for domes in evaluating cost effectiveness. The agency provides no evidentiary support for its equipment life determination. In fact, available information confirms that geodesic domes are known to have a service life of 50 or more years in some cases.[26]

Third, the Air District relies on reported annual emissions inventories from 2020 in assessing potential reductions. The agency fails to explain how these emissions are representative of typical releases from these storage tanks and unaffected by turnarounds or reduced operations caused by the pandemic. Moreover, the agency's own Fluxsense study confirms these emissions inventories underreport actual emissions from storage tanks, but staff's analysis here does not account for these discrepancies and the additional reductions that could occur from doming.[27]

Finally, there are at least 290 external floating roof tanks in the region.[28] However, the agency focuses on 43 crude oil external floating roof tanks for doming but provides no explanation for ignoring hundreds of other tanks of similar construction from consideration. As detailed in previous comments, the geodesic dome over a floating roof prevents wind-induced evaporative

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[23] Working Group Meeting No. 5 Presentation, *supra* note 1, at 18.
[24] Cal. Health and Safety Code § 25536.7(5)(A), (6)(A).
[25] Cal. Health and Safety Code § 25536.7 (applies to sources engaged in processes described under the North American Industrial Classification System Code 324110 (crude oil refining) or 325110 (petrochemical manufacturing)).
[26] *Managing Your Aluminum Dome Asset*, Tank Storage Magazine (Apr. 20, 2020), https://www.tankstoragemag.com/2020/04/20/managing-your-aluminum-dome-asset/ (Attached as Exhibit 8).
[27] Johan Mellqvist et al., *Emission Measurements of VOCs, NO2, and SO2 from the Refineries in the South Coast Air Basin Using Solar Occultation Flux and Other Optical Remote Sensing Methods* (Apr. 11, 2017) (Attached as Exhibit 3).
[28] Working Group Meeting No. 2 Presentation, *supra* note 16, at 19.

losses.[29] Most rim seal vapor losses for external floating roof tanks stem from wind effects.[30] The agency should reconsider its decision to exclude hundreds of storage tanks from doming requirements given the potential for additional emission reductions.

6. The Air District Dismissed Suspension Systems for Internal Floating Roof Tanks Based on Flawed Analysis and Failed to Consider Requiring These Systems for New Proposed Tanks.

In evaluating cable suspension systems for internal floating roofs, the Air District focused on retrofits for existing tanks. Based on costs and 2020 air emissions inventories, the agency determined that it would not be cost effective to retrofit all internal floating roof tanks.[31] The agency's consideration of suspension systems for internal floating roof tanks is inadequate.

The agency's analysis does not detail the labor or other costs considered, including whether labor costs were also increased by 20% to account for unionized labor, which as detailed above might not be applicable to all facilities subject to the rule. Nor did the agency explain how its use of 2020 annual emissions data would be an appropriate measure given pandemic slowdowns, facility turnarounds, and Fluxsense findings concerning emissions underreporting. Finally, the agency focused solely on retrofits and did not consider whether to require that all new proposed internal floating roof tanks use suspension systems.

7. The Air District Improperly Dismissed Open Path Monitoring and Gas Sensors Based on an Improper Cost Effectiveness Analysis and Neglected to Consider Other Alternatives.

In evaluating, continuous emissions monitoring options, the Air District concludes that open path monitoring and gas sensors would not be cost-effective based on the $30,000 cost effectiveness threshold developed by the agency in 2016.[32] In particular, gas sensors had a cost effectiveness threshold between $44,800 and $53,000 per ton of VOC reduced and open path monitoring had a cost effectiveness of $30,700 that is slightly above the agency's threshold.[33] The agency's conclusions are arbitrary and unsupported.

As noted above, the agency's use of inflated 2022 cost data that is then compared to a 2016 cost effectiveness threshold is unauthorized and leads to arbitrary results. Moreover, the agency used a 20-year equipment life factor when evaluating open path devices.[34] But the agency does not disclose whether it obtained that information from surveying manufactures or whether it is speculating on expected equipment life. At a minimum, the agency should provide some evidentiary support for its use of that equipment life figure.

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[29] Maine Dep't of Env't Protection, *Measurement and Control of Emissions from Aboveground Petroleum Storage Tanks*, at 50 (Jan. 1, 2021), https://mainebeacon.com/wp-content/uploads/2021/01/Report-to-the-Joint-Standing-Committee-on-the-Environment-and-Natural-Resources.pdf (Attached as Exhibit 9).

[30] *Id.* at 31.

[31] Working Group Meeting No. 5 Presentation, *supra* note 1, at 20.

[32] *Id.* at 32.

[33] *Id.*

[34] *Id.*

Finally, the Air District neglects to consider other alternatives, such as Method 325A/B that could be cost effective under the agency's approach.[35] At a minimum, the agency should evaluate Method 325A/B and the potential emissions reductions.

8. The Air District Failed to Consider Bi-Weekly Third-Party Monitoring of Storage Tanks with OGI Cameras and Increased Method 21 Inspections.

In evaluating potential changes to storage tank leak inspections, staff considered monthly and weekly third-party monitoring with an OGI camera. The agency determined that weekly monitoring of individual tanks would have a cost effectiveness of $44,400 per ton of VOC, which would be above the Air District's $30,000 per ton cost-effectiveness threshold.[36] Consequently, staff recommended only partial weekly inspections of 15 individual tanks and a tank farm overview using an OGI camera or alternatively operators can implement an approved continuous monitoring system.[37]

The Air District's proposed updates to Rule 1178's leak detection provisions are inadequate. In evaluating tank inspections using an OGI camera, the agency failed to consider the cost effectiveness of requiring individual tank inspections occurring every two weeks. OGI cameras are useful in that they can assist in detecting large leaks.[38] Additionally, the agency failed to consider also increasing the frequency of Method 21 inspections, which are currently required to occur on a quarterly basis and are critical in identifying leaks at or below 500 parts per million ("ppm"). These leaks can be cumulatively considerable if left unidentified and unaddressed for months at a time.

9. The Air District Failed to Evaluate Various Other Necessary Updates to Rule 1178 that Would Result in Additional Emissions Reductions.

There are several other necessary amendments raised in the December 6, 2021, comment letter that staff failed to evaluate without any explanation. In particular, staff should assess the following to ensure that proposed amendments to Rule 1178 achieve the maximum amount of reductions possible. The agency should not leave any potential strategies to reduce emissions unaddressed. Communities have waited far too long for the agency to update this regulation to reduce emissions from storage tanks at petroleum facilities.

First, staff ignored necessary changes to portable storage tank requirements. Under current Rule 1178, portable storage tank operators are exempt from conducting performance tests to ensure that emissions controls are properly functioning. Specifically, Rule 1178 does not require operators to conduct performance tests when operators install or modify emissions controls, or

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[35] EPA, *Method 325a—Volatile Organic Compounds From Fugitive And Area Sources: Sampler Deployment and VOC Sample Collection* (Jan. 14, 2019) (Attached as Exhibit 5); EPA, *Method 325b—Volatile Organic Compounds From Fugitive And Area Sources: Sampler Preparation and Analysis* (Jan. 14, 2019) (Attached as Exhibit 6); *see also* 40 C.F.R. § Pt. 63, App. A.

[36] Working Group Meeting No. 5 Presentation, *supra* note 1, at 33.

[37] *Id.* at 35.

[38] Hazem Abdel-Moati, et al., *New Optical Gas Imaging Technology for Quantifying Fugitive Emission Rates*, International Petroleum Technology Conference (Dec. 6, 2015), https://doi.org/10.2523/IPTC-18471-MS (Attached as Exhibit 2).

change operating parameters in a way that affects control efficiency. Rule 1178 only requires operators to take weekly EPA Method 21 measurements to determine whether emissions are below the leak threshold. Rule 1178's exemption for portable storage tanks is unwarranted.

Second, staff ignored a lower leak threshold for tank inspections using EPA Method 21. As noted in previous comments, the Air District's leak threshold under Rule 1178 is 500 ppm. In contrast, BAAQMD's leak threshold under Regulation 8, Rule 5 is 100 ppm. The agency should require a lower leak threshold triggering repairs and other corrective action.

Finally, staff ignored requiring reinspections of tanks with leaks above the applicable threshold after corrective action. Operators should be required to reinspect repairs to ensure that the leak remains below the applicable threshold. Otherwise, there is no assurance that the leak is under control and might not be addressed until a subsequent quarter.

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We appreciate your time and attention to the concerns raised in this comment letter. We welcome the opportunity to discuss these issues with you in more detail.

Sincerely,

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INDEX OF EXHIBITS
IN SUPPORT OF
COMMENTS ON PROPOSED AMENDED RULE 1178

Exhibit No.	**Description**
1	EPA, *Lessons Learned from Natural Gas STAR Partners: Installing Vapor Recovery Units on Storage Tanks* (Oct. 2006)
2	Hazem Abdel-Moati, et al., *New Optical Gas Imaging Technology for Quantifying Fugitive Emission Rates*, International Petroleum Technology Conference (Dec. 6, 2015)
3	Johan Mellqvist et al., *Emission Measurements of VOCs, NO2, and SO2 from the Refineries in the South Coast Air Basin Using Solar Occultation Flux and Other Optical Remote Sensing Methods* (Apr. 11, 2017)
4	EPA, Air Pollution Control Cost Manual Section 3.1, *Chapter 1: Carbon Adsorbers* (7th ed. Oct. 2018)
5	EPA, *Method 325A – Volatile Organic Compounds and Area Sources: Sampler Deployment and VOC Sample Collection* (Jan. 2019)
6	EPA, *Method 325B – Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis* (Jan. 2019)
7	Cal. Off. of Env't Health Hazard Assessment, *Analysis of Refinery Chemical Emissions* (Mar. 2019)
8	*Managing Your Aluminum Dome Asset*, Tank Storage Magazine (Apr. 20, 2020)
9	Me. Dep't of Env't Prot., *Report to the Joint Standing Committee on the Environment and Natural Resources: Measurement and Control of Emissions from Aboveground Petroleum Storage Tanks* (Jan. 2021)
10	TIGG, *What Is Activated Carbon?*
11	APC Technologies, CarbonPure Adsorption Systems Datasheet

Exhibit No.	**Description**
12	ATECO Tank, *Secondary Seal – 3 Type*
13	CTS-Netherlands, CTS20 Secondary Compression Plate Seal Datasheet

EXHIBIT 1

Lessons Learned
from Natural Gas STAR Partners

Installing Vapor Recovery Units on Storage Tanks

Executive Summary

There are about 500,000 crude oil storage tanks in the United States. These tanks are used to hold oil for brief periods of time in order to stabilize flow between production wells and pipeline or trucking transportation sites. In addition, the condensate liquids contained in produced gas that are captured by a mist eliminator filter/coalescer ahead of the first compressor station in transmission pipelines are often directed to a storage tank as well. During storage, light hydrocarbons dissolved in the crude oil or condensate—including methane and other volatile organic compounds (VOC), natural gas liquids (NGLs), hazardous air pollutants (HAP), and some inert gases—vaporize or "flash out" and collect in the space between the liquid and the fixed roof of the tank. As the liquid level in the tank fluctuates, these vapors are often vented to the atmosphere.

One way to prevent emissions of these light hydrocarbon vapors and yield significant economic savings is to install vapor recovery units (VRUs) on storage tanks. VRUs are relatively simple systems that can capture about 95 percent of the Btu-rich vapors for sale or for use onsite as fuel. Currently, between 7,000 and 9,000 VRUs are installed in the oil production sector, with an average of four tanks connected to each VRU.

Natural Gas STAR partners have generated significant savings from recovering and marketing these vapors while at the same time substantially reducing methane and HAP emissions. Partners have found that when the volume of vapors is sufficient, installing a VRU on one or multiple storage tanks can save up to $606,800 per year and payback in as little as two months. This Lessons Learned study describes how partners can identify when and where VRUs should be installed to realize these economic and environmental benefits.

Technology Background

Underground crude oil contains many lighter hydrocarbons in solution. When the oil is brought to the surface and processed, many of the dissolved lighter hydrocarbons (as well as water) are removed through a series of high-pressure and low-pressure separators. The crude oil is then injected into a storage tank to await sale and transportation off site; the remaining hydrocarbons in the oil are emitted as vapors into the tank. The same principles apply for condensate, which accumulates as a result of the conditions within the pipelines and is removed ahead of the first compressor station. The recovered condensate, which contains dissolved light hydrocarbons, is routed to a storage tank where the dissolved light hydrocarbons are emitted as vapors. These vapors are either vented, flared, or recovered by vapor recovery units (VRUs). Losses of the remaining lighter hydrocarbons are categorized in three ways:

- ★ Flash losses occur when the separator or heater treater, operating at approximately 35 pounds per square inch (psi), dumps oil into the storage tanks, which are at atmospheric pressure.
- ★ Working losses refer to the vapor released from the

Economic and Environmental Benefits

Method for Reducing Natural Gas Losses	Volume of Natural Gas Savings (Mcf/yr)	Value of Natural Gas Savings ($/yr) [1]			Implementation Cost ($)	Other Costs ($)	Payback (Months)		
		$3 per Mcf	$5 per Mcf	$7 per Mcf			$3 per Mcf	$5 per Mcf	$7 per Mcf
Installing Vapor Recovery Units (VRUs) on Oil Production Storage Tanks	4,900—96,000	$13,965— $273,600	$23,275— $456,000	$32,585— $638,400	$35,738— $103,959	$7,367— $16,839	6 — 37	4 — 23	3 — 16

[1] Assumes 95% of the annual volume of gas lost can be recovered using a VRU.

- changing fluid levels and agitation of tank contents associated with the circulation of fresh oil through the storage tanks.

- Standing losses occur with daily and seasonal temperature changes.

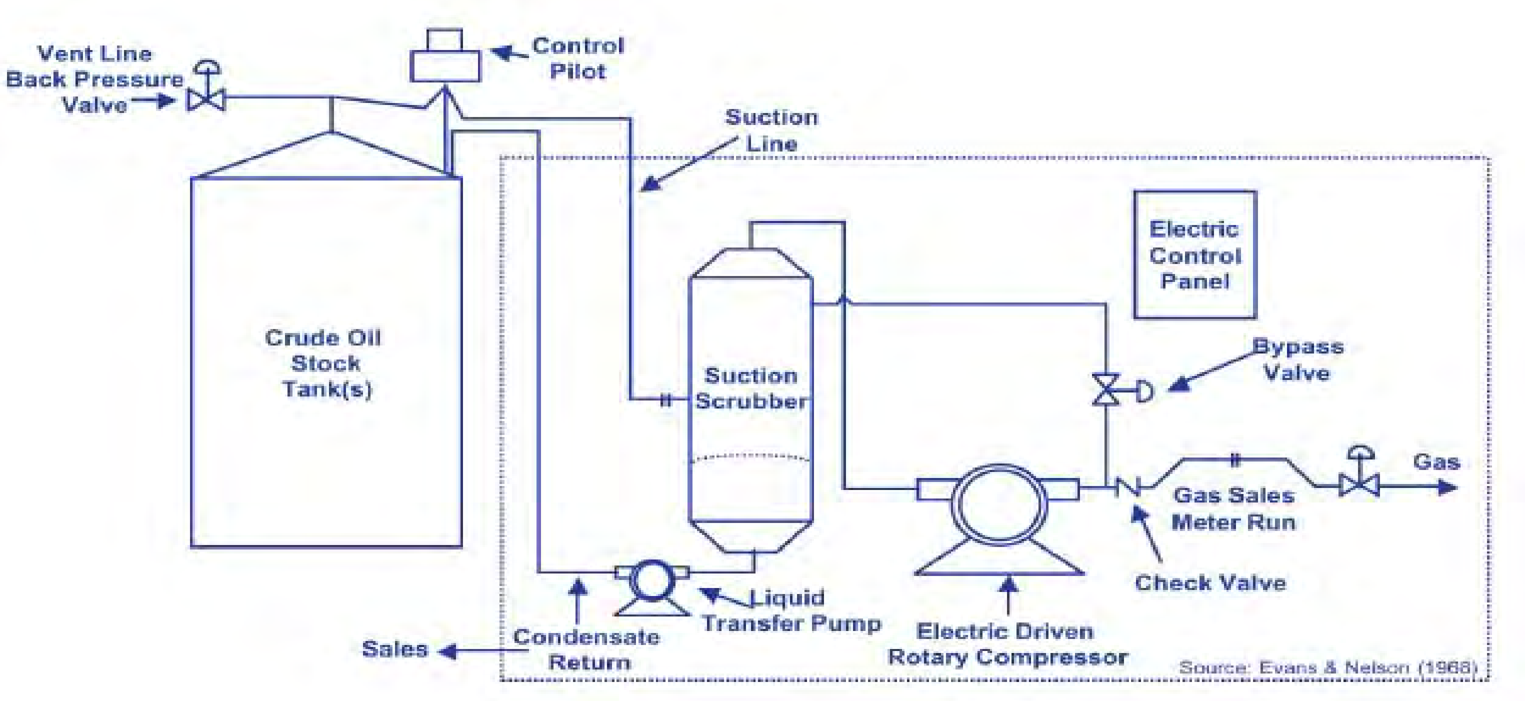
The volume of gas vapor coming off a storage tank depends on many factors. Lighter crude oils (API gravity>36°) flash more hydrocarbon vapors than heavier crudes (API gravity<36°). In storage tanks where the oil is frequently cycled and the overall throughput is high, more "working vapors" will be released than in tanks with low throughput and where the oil is held for longer periods and allowed to "weather." Finally, the operating temperature and pressure of oil in the vessel dumping into the tank will affect the volume of flashed gases coming out of the oil.

The makeup of these vapors varies, but the largest component is methane (between 40 and 60 percent). Other components include more complex hydrocarbon compounds such as propane, butane, and ethane; natural inert gases such as nitrogen and carbon dioxide; and HAP like benzene, toluene, ethyl-benzene, and xylene (collectively these four HAP are referred to as BTEX).

VRUs can recover over 95 percent of the hydrocarbon emissions that accumulate in storage tanks. Because recovered vapors contain natural gas liquids (even after condensates have been captured by the suction scrubber), they have a Btu content that is higher than that of pipeline quality natural gas (between 950 and 1,100 Btu per standard cubic foot [scf]). Depending on the volume of NGLs in the vapors, the Btu content can reach as high as 2,000 Btu per scf. Therefore, on a volumetric basis, the recovered vapors can be more valuable than methane alone.

Exhibit 1 illustrates a VRU installed on a single crude oil storage tank (multiple tank installations are also common). Hydrocarbon vapors are drawn out of the storage (stock) tank under low-pressure, typically between four ounces and two psi, and are first piped to a separator (suction scrubber) to collect any liquids that condense out. The liquids are usually recycled back to the storage tank. From the separator, the vapors flow through a compressor that provides the low-pressure suction for the VRU system. (To prevent the creation of a vacuum in the top of a tank when oil is withdrawn and the oil level drops, VRUs are equipped with a control pilot to shut down the compressor and permit the back flow of vapors into the tank.) The vapors are then metered and removed from the VRU system for pipeline sale or onsite fuel supply.

Exhibit 1: Standard Stock Tank Vapor Recovery System



Source: Evans & Nelson (1968)

Economic and Environmental Benefits

VRUs can provide significant environmental and economic benefits for oil and gas producers. The gases flashed from crude oil or condensate and captured by VRUs can be sold at a profit or used in facility operations. These recovered vapors can be:

- ★ Piped to natural gas gathering pipelines for sale at a premium as high Btu natural gas.
- ★ Used as a fuel for onsite operations.
- ★ Piped to a stripper unit to separate NGLs and methane when the volume and price for NGLs are attractive.

VRUs also capture HAPs and can reduce operator emissions below actionable levels specified in Title V of the Clean Air Act. By capturing methane, VRUs also reduce the emissions of a potent greenhouse gas.

Decision Process

Companies using fixed roof storage tanks can assess the economics of VRUs by following five easy steps.

Step 1: Identify possible locations for VRU installation.

Virtually any tank battery is a potential site for a VRU. The keys to successful VRU projects are a steady source and adequate quantity of crude oil or condensate vapors along with an economic outlet for the collected product. The potential volume of vapors will depend on the makeup of the oil or condensate and the rate of flow through the tanks. Pipeline connection costs for routing vapors off site must be considered in selecting sites for VRU installation.

Step 2: Quantify the volume of vapor emissions.

Emissions can either be measured or estimated. An orifice well tester and recording manometer (pressure gauge) can be used to measure maximum emissions rates since it is the maximum rate that is used to size a VRU. Orifice meters, however, might not be suitable for measuring total volumes over time due to the low pressures at tanks. Calculating total vapor emissions from oil tanks can be complicated because many factors affect the amount of gas that will be released from a crude oil tank, including:

1. Operating pressure and temperature of the separator dumping the oil to the tank and the pressure in the tank;
2. Oil composition and API gravity;
3. Tank operating characteristics (e.g., sales flow rates, size of tank); and
4. Ambient temperatures.

There are two approaches to estimating the quantity of vapor emissions from crude oil tanks. Both use the gas-oil ratio (GOR) at a given pressure and temperature and are expressed in standard cubic feet per barrel of oil (scf per bbl).

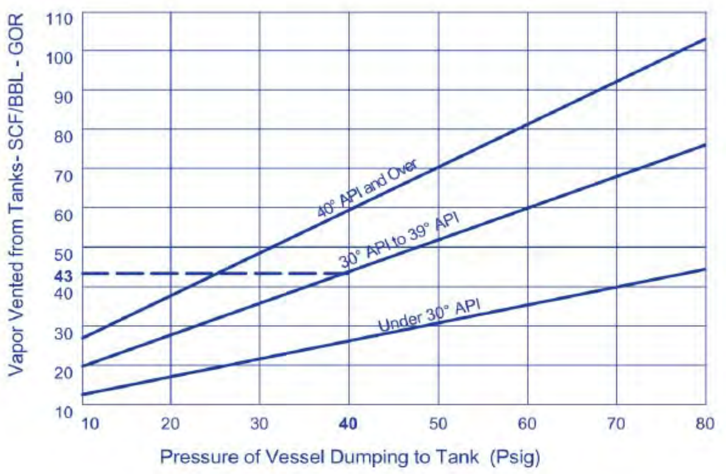
This process is applicable to all compressor designs. The less common overhung compressors have a single seal, and switching from wet to dry seals would yield half the savings of doing the same for a beam type compressor.

The first approach analyzes API gravity and separator pressure to determine GOR (Exhibit 2). These curves were constructed using empirical flash data from laboratory studies and field measurements. As illustrated, this graph can be used to approximate total potential vapor emissions from a barrel of oil. For example, given a certain oil API

Five Steps for Assessing VRU Economics:

1. Identify possible locations for VRU installation;
2. Quantify the volume of vapor emissions;
3. Determine the value of the recovered emissions;
4. Determine the cost of a VRU project; and
5. Evaluate VRU project economics.

Exhibit 2: Estimated Volume of Storage Tank Vapors



gravity (e.g., 38°) and vessel dumping pressure (e.g., 40 psi), the total volume of vapors can be estimated per barrel of oil (e.g., 43 scf per bbl). Once the emissions rate per barrel is estimated, the total quantity of emissions from the tank can be determined by multiplying the per barrel estimate by the total amount of oil cycled through the tank. To continue the example above, assuming an average throughput of 1,000 barrels per day (bbl per day), total emissions would be estimated at 43 Mcfd (Exhibit 3).

Exhibit 3: Quantity (Q) of Hydrocarbon Vapor Emissions

Given:
API Gravity = 38°
Separator Pressure = 40 psi
Oil Cycled = 1,000 bbl/day
Vapor Emissions rate = 43 scf/bbl (from Exhibit 2)

Q = 43 scf/bbl x 1,000 bbls/day = 43 Mcfd

The shortcoming of this approach is that it does not generate information about the composition of the vapors emitted. In particular, it cannot distinguish between VOC and HAP, which can be significant for air quality monitoring, as well as determining the value of the emitted vapors.

The second approach is to use the software package E&P Tank version 2.0. This is the modified version of the previous software; the American Petroleum Institute (API) introduced several changes in this model which made it more user-friendly. Partners in the Natural Gas STAR Program have recommended E&P Tank as the best available tool for estimating tank battery emissions. Developed by API and the Gas Research Institute (now the Gas Technology Institute), this software estimates emissions from all three sources—flashing, working, and standing—using thermodynamic flash calculations for flash losses and a fixed roof tank simulation model for working and standing losses. An operator must have several pieces of information before using E&P Tank, including:

1. Separator pressure and temperature.
2. Separator oil composition.
3. Reference pressure.
4. Reid vapor pressure of sales oil.
5. Sales oil production rate.
6. API gravity of sales oil.

E&P Tank also allows operators to input more detailed information about operating conditions, which helps refine emissions estimates. With additional data about tank size, shape, internal temperatures, and ambient temperatures, the software can produce more precise estimates. This flexibility in model design allows users to employ the model to match available information. Since separator oil composition is a key input in the model, E&P Tank includes a detailed sampling and analysis protocol for separator oil. Future versions of the software are being developed to estimate emissions losses from production water tanks as well.

Step 3: Determine the value of the recovered emissions.

The value of the vapors recovered from VRUs and realized by producers depends on how they are used:

1. Using the recovered vapors onsite as fuel yields a value equivalent to the purchased fuel that is displaced–typically natural gas.
2. Piping the vapors (NGL—enriched methane) to a natural gas gathering pipeline yield a price that reflects the higher Btu content per Mcf of vapor.
3. Piping the vapors to a processing plant that will strip the NGLs from the gas stream and resell the NGLs and methane separately should also capture the full Btu content value of the vapors. Exhibit 4 illustrates a method of calculating the value of the recovered vapors using an average price of $7.00 per Mcf (for pipeline quality natural gas at 1,000 Btu per scf). Where the

Exhibit 4: Value of Recovered Vapors

R = Q x P
R = The gross revenue
Q = The rate of vapor recovery (Mcf/day)
P = The price of natural gas

Calculate:
Q = 41 Mcfd (95% of 43 from Exhibit 3)
P = $7.00/Mcf
R = 41 Mcfd x $7/Mcf =
$287/day
$8,800/month
$105,600/year

Methane Content of Natural Gas

The average methane content of natural gas varies by natural gas industry sector. The Natural Gas STAR Program assumes the following methane content of natural gas when estimating methane savings for Partner Reported Opportunities.

Production	79 %
Processing	87 %
Transmission and Distribution	94 %

Btu content of the vapors is higher, the price per Mcf would be higher.

Step 4: Determining the cost of a VRU project.

The major cost elements of VRUs are the initial capital equipment and installation costs and operating costs.

VRU systems are made by several manufacturers. Equipment costs are determined largely by the volume handling capacity of the unit; the sales line pressure; the number of tanks in the battery; the size and type of compressor; and the degree of automation. The main components of VRUs are the suction scrubber, the compressor, and the automated control unit. Gas measurement is an add-on expense for most units. Prices for typical VRUs and related costs are shown in Exhibit 5.

When sizing a VRU, the industry rule-of-thumb is to double the average daily volume to estimate the maximum emissions rate. Thus, in order to handle 43 Mcfd of vapor (Exhibit 3), a unit capable of handling at least 86 Mcfd should be selected.

Nelson Price Indexes

In order to account for inflation in equipment and operating & maintenance costs, Nelson-Farrar Quarterly Cost Indexes (available in the first issue of each quarter in the *Oil and Gas Journal*) are used to update costs in the Lessons Learned documents.

The "Refinery Operation Index" is used to revise operating costs while the "Machinery: Oilfield Itemized Refining Cost Index" is used to update equipment costs.

To use these indexes in the future, simply look up the most current Nelson-Farrar index number, divide by the February 2006 Nelson-Farrar index number, and, finally multiply by the appropriate costs in the Lessons Learned.

Partners who have installed VRUs and VRU manufacturers report that installation costs can add as much as 50 to 100 percent to the initial unit cost. Installation costs can vary greatly depending on location (remote sites will likely result in higher installation costs) and the number of tanks (larger VRU systems will be required for multiple tanks). Expenses for shipping, site preparation, VRU housing construction (for cold weather protection), and supplemental equipment (for remote, unmanned operations) must also be factored in when estimating installation costs.

Operations and maintenance (O&M) expenses vary with the location of the VRU (sites in extreme climates experience more wear), electricity costs, and the type of oil

Exhibit 5: Vapor Recovery Unit Sizes and Costs

Design Capacity[1] (Mcfd)	Compressor Horsepower[2]	Capital Costs[3] ($)	Installation Costs[3]	O&M Costs ($/year)
25	5—10	20,421	10,207—20,421	7,367
50	10—15	26,327	13,164—26,327	8,419
100	15—25	31,728	15,864—31,728	10,103
200	30—50	42,529	21, 264—42,529	11,787
500	60—80	59,405	29,703—59,405	16,839

[1] Assumes design capacity is double average vapor recovery rate.
[2] Assumes compressor discharge to a 100 psi or less sales line or fuel gas system.
[3] Cost information provided by Natural Gas STAR partners and VRU manufacturers.

produced. For instance, paraffin based oils can clog the VRUs and require more maintenance.

Step 5: Evaluate VRU Project Economics.

Installing a VRU can be very profitable, depending on the value of the recovered vapors in the local market. Exhibit 6 calculates the simple payback and Internal Rate of Return (IRR) for VRU sizes and costs listed in Exhibit 5. Using an estimate of the value of recovered vapors of $7.00 per Mcf, the potential returns are attractive, particularly for the larger units.

When assessing VRU economics, gas price may influence the decision making process; therefore, it is important to re-examine the economics of installing vapor recovery units as natural gas prices change. Exhibit 7 shows an economic analysis of installing a 100 Mcfd vapor recovery unit at different gas prices.

Lessons Learned

The use of VRUs can profitably reduce methane emissions from crude oil storage tanks. Partners offer the following lessons learned:

★ E&P software can be an effective tool for estimating the amount and composition of vapors from crude oil tanks.

★ Vapor recovery can provide generous returns due to the relatively low cost of the technology and in the cases where there are market outlets for the high BTU vapors.

★ VRUs should be installed whenever they are economic, taking into consideration all of the benefits—environmental and economic.

★ Because of the very low pressure differential between

Exhibit 6: Financial Analysis for VRU Project

Design Capacity (Mcfd)	Installation & Capital Costs[1] ($)	O&M ($/Year)	Value of Gas[2] ($/Yr)	Payback[3] (months)	Internal Rate of Return[4] (%)
25	35,738	7,367	30,300	19	58
50	46,073	8,419	60,600	11	111
100	55,524	10,103	121,360	6	200
200	74,425	11,787	242,725	4	310
500	103,959	16,839	606,810	3	567

[1] Unit cost plus estimated installation cost of 75% of unit cost. Actual costs might be greater depending on expenses for shipping, site preparation, supplemental equipment, etc.
[2] 95% of total gas recovered at $7 per Mcf x 1/2 design capacity x 365 days
[3] Based on 10 percent discount rate.
[4] Calculated for 5 years.

Exhibit 7: Gas Price Impact on Economic Analysis

	$3/Mcf	$5/Mcf	$7/Mcf	$8/Mcf	$10/Mcf
Value of Gas Saved	$52,011	$86,686	$121,360	$138,697	$173,371
Payback Period (Months)	16	9	6	6	5
Internal Rate of Return (IRR)	70%	136%	200%	231%	294%
NPV (i=10%)	$93,947	$213,440	$332,934	$392,681	$512,174

the storage tank and the compressor, large diameter pipe is recommended to provide less resistance to the gas flow.

- ★ A VRU should be sized to handle the maximum volume of vapors expected from the storage tanks (a rule-of-thumb is double the average daily volume).
- ★ Rotary vane compressors are recommended for VRUs to move the low volume of gas to low pressures.
- ★ It is very important to choose reliable, sensitive control systems, because the automated gas flow valves must be opened and closed on very low pressure differences.
- ★ Include methane emissions reductions from installing VRUs in annual reports submitted as part of the Natural Gas STAR program.

One Partner's Experience

Chevron USA Production Company installed eight vapor recovery units in 1996 at crude oil stock tanks. As a result, Chevron has realized an estimated reduction in methane emissions of 21,900 Mcf per year from each unit. At today's gas price of $7 per Mcf, this corresponds to approximately $153,300 in savings per unit, or $1,226,400 for all eight units. The capital and installation costs were estimated to be $240,000 ($30,000 per unit) in 1996 or the equivalent of $324,000 ($40,500 per unit) in 2006 dollars. This particular project would have realized a payback in just over 3 months in 2006.

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**United States
Environmental Protection Agency
Air and Radiation (6202J)
1200 Pennsylvania Ave., NW
Washington, DC 20460**

October 2006

EPA provides the suggested methane emissions estimating methods contained in this document as a tool to develop basic methane emissions estimates only. As regulatory reporting demands a higher-level of accuracy, the methane emission estimating methods and terminology contained in this document may not conform to the Greenhouse Gas Reporting Rule, 40 CFR Part 98, Subpart W methods or those in other EPA regulations.

EXHIBIT 2

ARTICLE NAVIGATION

New Optical Gas Imaging Technology for Quantifying Fugitive Emission Rates

Hazem Abdel-Moati; Jonathan Morris; Yousheng Zeng; Petroula Kangas; Duane McGregor

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Abstract

The U.S. Environmental Protection Agency (EPA) has promulgated regulations governing the detection and repair of equipment leaks that cause fugitive emissions of volatile organic compounds (VOC). These regulations are embedded in various emission standards and are generally referred to as Leak Detection and Repair (LDAR) programs. The primary method used currently in the U.S. to detect leaks is EPA Method 21.[1] Method 21 requires operators to use portable instruments, typically a Flame Ionization Detector (FID) or a Photon Ionization Detector (PID), to "sniff" around the circumference of individual equipment components (e.g., valves, flanges, pump seals, etc.)[2] . If the detector reading (parts per million or PPM) is higher than target thresholds, the component is deemed to be leaking and it must be repaired within a certain time. Fugitive VOC emissions from a facility are calculated based upon the PPM readings (referred to as screening values or SVs) and empirical correlations between SVs and mass emission rates.[2] Because the leak check is performed on each individual component basis, the implementation of a Method 21 based LDAR program is tedious, labor intensive, and prone to errors.

Optical gas imaging (OGI) technology has been developed and can be used to detect VOC leaks from process equipment. The OGI technology allows operators to use a specially designed Infrared (IR) video camera to see VOC plumes leaking from components that are not visible to the naked eye. Detecting VOC leaks using OGI is more efficient than Method 21 because leak checking using OGI is visual, making detection faster, and can be performed over an area instead of component-by-component. The OGI method allows operators to detect larger leaks easily and more frequently, achieving the same environmental benefit with a lower cost. For this reason, the OGI method is also referred to as "Smart LDAR". In December 2008, U.S. EPA promulgated the "Alternative Work Practice" (AWP) rule allowing operators to use OGI for LDAR compliance.[3] However, the AWP rule requires operators to continue to perform leak checks using Method 21 at least once a year.

Skip to Main Content

Although OGI can be very effective in detecting leaks, it does not provide a quantitative measure of leak rate. This has been one of the shortcomings of OGI from a regulatory perspective, thereby hindering its adoption as a true alternative to Method 21. This paper describes development of quantitative OGI (QOGI) technology. Existing OGI camera technology is the basis the new GOCI technology. If an OGI camera detects a leak, then, the operator can apply the new QOGI technology quantify the mass leak rate from the captured video images.

Keywords: US government, new optical gas imaging technology, air emission, detection, HSSE standard, concentration, emission rate, OGI, ionization detector, leak rate

Subjects: HSSE & Social Responsibility Management, Environment, HSSE standards, regulations and codes, Air emissions

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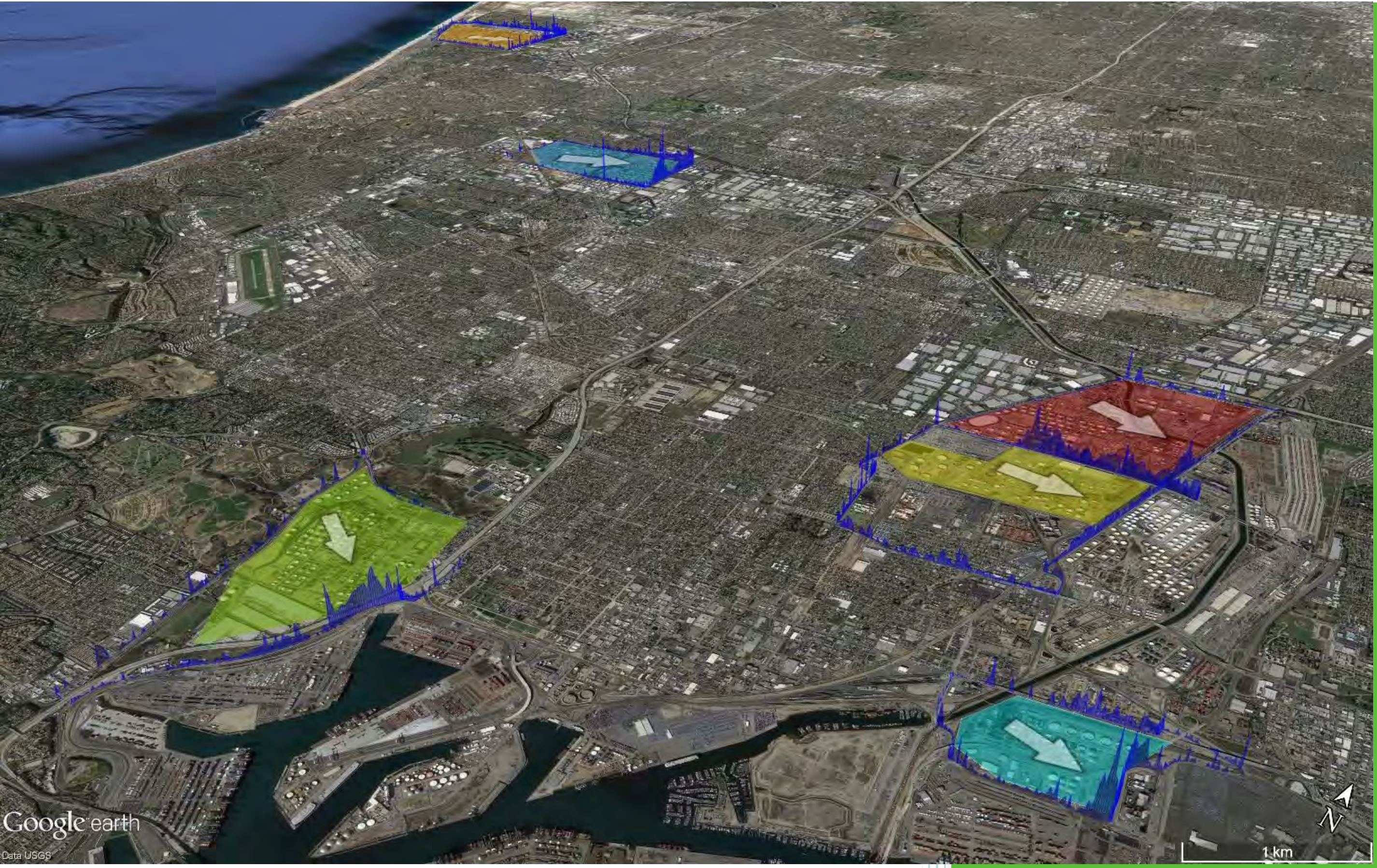
EXHIBIT 3

2015

Emission Measurements of VOCs, NO_2 and SO_2 from the Refineries in the South Coast Air Basin Using Solar Occultation Flux and Other Optical Remote Sensing Methods



FluxSense

FINAL REPORT

FluxSense Inc

11 April 2017

Date: 11 April 2017

Title: Emission Measurements of VOCs, NO_2 and SO_2 from the Refineries in the South Coast Air Basin Using Solar Occultation Flux and Other Optical Remote Sensing Methods

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FluxSense Inc is subsidiary of FluxSense AB (www.fluxsense.se; San Diego, CA). FluxSense started as a spin-off company from research conducted at Chalmers University of Technology in Sweden and has been active for more than 10 years. FluxSense has carried out more than 100 industrial site surveillances in Austria, Belgium, Denmark, France, Middle East, Netherlands, Norway, Sweden and the US.

[Cover: Visualization of alkane plume transects (blue curves) from Solar Occultation Flux (SOF) measurements conducted at the six refineries for this study during similar wind conditions. The apparent height of the blue line is proportional to the integrated vertical column concentration expressed in mg/m^2. White arrows indicate wind directions during these measurements. Image mapped on Google Earth © 2016.]

Executive summary

BACKGROUND

Accurate characterization of facility-wide emissions from industrial sources on a real or near-real time basis is critical for developing effective control strategies to improve regional air quality, promoting compliance, and reducing exposure for nearby communities. To improve the understanding of such emissions in the South Coast Air Basin (SCAB), the South Coast Air Quality Management District (SCAQMD) has sponsored a series of measurement projects to study industrial emissions using Optical Remote Sensing (ORS) methods. The projects include experimental studies of emissions from refineries, oil depots, treatment facilities, oil wells, gas stations, fuel islands and barges. In addition, SCAQMD has sponsored technology demonstration and validation studies to assess potential uncertainties of different optical techniques through side-by-side measurements of real sources and controlled source gas releases.

Numerous research studies using ORS conducted in the US and worldwide (including a 2013 pilot project sponsored by SCAQMD) suggest that measured emissions of VOCs from industrial facilities are larger compared to emission inventory estimates developed based on accepted reporting conventions. Given the large number of refineries and other industrial activities in the SCAB, it is therefore very important to evaluate novel measurement methods for detecting and quantifying industrial emissions directly.

This report presents the results of a two and a half month long measurement campaign aimed at characterizing and quantifying emissions of VOCs, NOx, and SO_2 from six major refineries in the SCAB. The measurements spanned from August 28 to November 11 2015, with up to 15 individual measurement days at each site. Additionally, a detailed eight day long measurement study inside the tank farm of one of the refineries was conducted to quantify emissions from the tank farm, locate potential leak sources, and validate the SOF technique by comparative measurements to other ORS methods.

Mobile surveys using two ORS techniques, namely SOF (Solar Occultation Flux) and Mobile SkyDOAS (Differential Optical Absorption Spectroscopy), were conducted around the refineries' perimeters to estimate facility-wide emission fluxes of VOCs, SO_2 and NO_2. These ORS techniques were complemented by extractive optical methods, including MeFTIR (Mobile extractive Fourier Transform Infra-Red spectroscopy) and MWDOAS (Mobile White cell DOAS) to map ground concentrations of alkanes, methane and aromatic VOCs and to calculate inferred fluxes for methane and aromatics. The required wind information was collected using a stationary wind-LIDAR (LIght Detection and Ranging; which provides vertical wind profiles) and conventional wind mast measurements.

SOF is a proven technique employed by FluxSense in over 100 fugitive emission studies around the world. In Europe the SOF technique is considered Best Available Technology (BAT) for measurements of fugitive emission of VOCs from refineries (Barthe *et al.* 2015), and in Sweden it is used together with tracer correlation and optical gas imaging to annually screen all larger refineries and petrochemical industries. In Swedish facilities, ORS emission measurements are conducted annually for at least ten days, during different seasons, in order to obtain a good representation of the annual mean. These measurements represent the total emission flux coming from the entire refinery, divided into sub parts such as process areas, crude oil storage, product storage tanks, water treatment facilities, flares, and loading operations. In the study presented here, such sub-area measurements were demonstrated for the tank farm of Refinery A.

The estimated uncertainty for the SOF emission measurements is typically 30 % for total site emissions, and usually slightly higher for individual sub-parts. The estimated measurement uncertainties have been verified in several (blind and non-blind) controlled source gas release experiments (including the one performed during this study and discussed elsewhere) and in side-by-side measurements with other techniques. The uncertainties in the total refinery emissions of BTEX and CH_4 obtained from inferred fluxes are larger than for the direct flux measurements of alkanes. Ideally, the gases should be well mixed in the plume for this method to work the best, but in reality there will be a stronger weighting towards low elevated sources (tanks) compared to higher elevated ones (process units) depending on the measurement geometry. Based on canister samples collected in several European refineries in the past, we know that typically the BTEX fraction is higher in the process units (10-15 % of total VOCs) compared to tank farms (5-10 % of total VOCs). The inferred BTEX flux will consequently be a low estimate of actual BTEX emissions because plumes from tanks are usually located closer to the surface, while plumes from process areas can extend further up into the atmosphere. In this study the overall BTEX to alkane ratio was 0.11.

RESULTS

Table ES.1 shows the measured hourly emission rates (kg/h) of various gaseous species from the refineries investigated during this study. The emissions presented in table ES 1 represent median values of all valid transects obtained during the two and a half month study period. The BTEX and CH_4 emission values have been extrapolated from concentration ratios of these species to alkanes measured at ground level and scaled with direct alkane emission measurements by SOF. It should be noted that, rather consistently for all the refineries, the BTEX emissions are typically one tenth of the total VOC emissions, while CH_4 emissions are on average two thirds of the alkane emissions.

Table ES.1. Median values of all measured site emissions during the 2015 SCAQMD survey. The fluxes of alkanes, SO_2 and NO_2 are obtained from direct measurements, while BTEX and CH_4 are inferred from gas ratio measurements. Note that benzene is part of BTEX.

Measured Refinery SCAQMD Survey 2015	**N Days**	**Alkane Flux** [kg/h]	**SO_2 Flux** [kg/h]	**NO_2 Flux** [kg/h]	**BTEX Flux** [kg/h]	*Benzene Flux [kg/h]*	**CH_4 Flux** [kg/h]
Refinery A	15	269	62	66	24	*3.4*	167
Refinery B	5	70	53	31	11	*1.1*	53
Refinery C	4	244	37	57	37	*8.2*	142
Refinery D	7	164	17	34	16	*1.6*	79
Refinery E	7	244	53	63	31	*2.7*	207
Refinery F	4	139	37	18	10	*0.8*	57
Sum		**1130**	**259**	**269**	**129**	*18*	**705**

In Table ES.2 the measured emission data for the various sites has been normalized by the corresponding crude oil capacity for each facility and compared to the reported emission inventories. The table shows that the measured VOC emission factors for the studied refineries range from 0.017 % to 0.045 % (mass emission per mass capacity of crude). SOF measurements carried out in other well-run refineries typically show average VOC emission factors of 0.03 % to 0.1 %. Thus, according to this data, the refineries in the SCAB are generally performing well, with relatively low emission compared to their capacity. However, as highlighted in Table ES.2, significant differences exist between measured and reported inventory emissions for VOCs and, for all refineries combined, the overall discrepancy between measured and reported inventory values was a factor of 6.2. For benzene the corresponding overall discrepancy ratio was about 34, although the magnitude of BTEX emissions was relatively small. Refinery C stands out with a measured benzene emission being more than twice as high as the next refinery in order. The measured SO_2 and NO_2 emissions are much closer to, and in some instances lower than, those reported in the inventories. In Table ES 2, the reported annual emissions have been divided by 12 to obtain a monthly inventory value to compare to the measured monthly median emissions from this survey. Hence, the discrepancies and emissions factors are representative for September 2015 (the time-period when the majority of the ORS measurements were performed).

Table ES.2. VOC emission factors normalized by the corresponding crude oil capacity for the various sites, and ratios between measured values and reported inventories for the 2015 SCAQMD survey.

Measured Refinery Representative of September 2015	**Crude capacity 2015***		**Measured Monthly Emission for Sept. 2015**	**Emission Factor****	**Discrepancy factor (Measured/Reported^2)**			
	bbl/day	**Tons^1/mo**	**Alkanes+BTEX Tons^1/mo**	**Alkanes+BTEX %**	**Alkanes+ BTEX**	**SO_2**	**NO_2**	**Benzene**
Refinery A	257300	1086215	214	0.020 %	6.4	1.2	1.0	43
Refinery B***	139000	586801	59	0.045 %	8.3	1.5	0.8	33
Refinery C***			205		11.8	2.7	1.1	202
Refinery D	104500	441156	132	0.030 %	10.5	1.7	1.1	39
Refinery E	269000	1135608	201	0.018 %	5.4	1.7	0.8	38
Refinery F	149500	631128	109	0.017 %	2.7	1.1	0.3	3.2
Overall****	**919300**	**3880908**	**919**	**0.024 %**	**6.2**	**1.5**	**0.83**	**34**

* Crude capacity data is obtained from the 2016 California Energy Commission report.

** Mass emission per mass capacity of crude oil.

*** Crude capacity for Refinery B and Refinery C are reported together since Refinery B processes the crude oil and the Refinery C upgrades intermediate products to finished products.

**** The overall discrepancy values are calculated from the total sum of reported and measured emissions, respectively. The overall emission factor is based on the sum of measured emissions for all refineries relative to the total capacity. Reported annual values have been divided by 12 to obtain a monthly inventory value to compare to the measured monthly average emissions from this survey. The comparisons are representative for September 2015 (the time-period when most of the measurements were performed).

[1] metric tons.

[2] Note that total nitrogen oxides (NO_x) are reported while only the NO_2 fraction was measured by SkyDOAS.

ORS measurements were also conducted for eight days inside the tank farm of one of the refineries listed above. The objective of this part of the study was to demonstrate the capability of real time ORS techniques to identify and quantify emissions and potential gas leak sources inside a refinery. Several storage and crude oil tanks were identified as VOC emitters, including a large underground reservoir containing vacuum gas oil (VGO).

While conducting measurements inside one of the refineries, our mobile optical methods identified an area characterized by elevated alkane concentrations of about 70,000 ppb, in contrast to the ten to a few hundred ppb normally measured downwind of similar sources. An infrared gas imaging camera (FLIR) was used to visualize and confirm alkane gas emissions through a shallow pool of water on the ground. Once the leak was discovered, the refinery staff took swift action to investigate and repair the source of the leak. The investigation discovered a pinhole-size leak in a pipeline buried 30 cm below the ground. After the leak was repaired additional ORS measurements were conducted to verify that the problem was resolved. This event illustrates how mobile ORS measurements combined with conventional gas imaging can quickly identify an unknown leak and allow it to be fixed before any serious complications may occur.

Within this project we also conducted a separate study to compare the SOF readings to those of other ORS techniques such as DIAL (Differential Absorption Lidar) and long-path FTIR through side-by-side measurements on various tanks inside one of the refineries. The agreement between emissions from different tanks and reservoirs inside the refinery measured by SOF and DIAL was excellent (within 10-20 %). As part of the SOF, DIAL and long-path FTIR technology comparison and validation, a blind gas release experiment was also carried out using a controlled source emitting 2-25 kg/h of odorless propane at the flat open parking lot of the Angels stadium in Anaheim, CA. In this study, the SOF measurements consistently underestimated the true emissions by 35%, but showed excellent correlation for the different release rate configurations (R^2 ~98%). The detailed results of this technology inter-comparison study are compiled and presented in a separate report.

DISCUSSION

A common concern when comparing measured emissions with those reported in the inventories is that the reported data are calculated for a full year while measurements are typically conducted over a limited time period. This may impact uncertainties when translating measured emission rates to annualized values, as external environmental parameters such as wind, temperature and solar insolation, affect tank emissions. An additional concern is whether a sufficient number of measurements (and measurement days) have been sampled to eliminate the influence of any intermittent emissions due to tank cleaning, maintenance, flaring, etc. To address these concerns, we carefully analyzed the frequency distributions (histograms) of the measured emissions and wind data, and studied how they may be impacted by seasonal variations in meteorological conditions. In addition, the effect of ambient temperature and wind speed on tank emissions was investigated. For this study we concluded that variations in emissions resulting from environmental changes are relatively small and within the uncertainties of the SOF and SkyDOAS measurements.

The observed differences between measured emissions and reported inventories (based on the US EPA AP-42 standard) are considerably higher than what can be explained by measurement uncertainties alone, or incomplete diurnal and seasonal sampling. Refineries and tank farms are complex environments with a large number of components and numerous potential leak sources (e.g. tank seals, valves, gauges, flares, vapor recovery units, etc.). Many of these components can show degrading performance over time, and to appropriately account for the impact of non-ideal performance in emission inventory reporting is, we believe, an impossible task. Nevertheless, EPA's AP-42 system provides valuable insights for a specific facility on the production and abatement techniques applied and on what emission level the site could reach given ideal performance of all installations. Comparing measured emissions to ideal performance levels could therefore provide a basis for benchmarking of different refineries or sites.

OUTLOOK

Studies conducted in the SCAB, the Bay Area, Texas, and other places worldwide, show that field measurements provide a reliable way to determine actual emissions of VOCs and other pollutants from refineries and various industrial sites. Accurate estimates of VOC and other pollutant emissions from industrial sources are crucial for improving air quality models, to guide air pollution mitigation strategies, promote successful compliance strategies, and reduce exposure for nearby communities.

In our experience, the observed difference in fugitive VOC emissions between measured and inventory estimates is a general issue for the petroleum industry worldwide. We believe that a possible path forward could be to conduct monitoring in parallel with continued AP 42 based reporting, and to use the measurements to guide and verify the efficiency of the emission reduction efforts at the industrial sites.

Future longer-term ORS studies spanning over different seasons can be conducted in order to alleviate concerns stemming from comparison of emissions measured over limited-time to annual emissions reported through the inventories. Additionally, future studies could combine ORS measurements and site-specific emission modeling performed for inventory calculations. A better dialog between scientists conducting the measurements and the facility operators could also be crucial to improve our understanding of how site activities may affect measured emissions.

Traditional Leak Detection and Repair (LDAR) is an important practice to control and limit unplanned VOC emissions from refineries and to identify potential leak sources. The ORS techniques used in this study have demonstrated their ability to quickly quantify and map refinery emissions and to identify potential air pollution sources within a facility. Using real time measurements, refinery personnel and air quality regulators can enhance LDAR programs by prioritizing LDAR activities. Addressing the most concerning issues first is important to reduce occupational risks for refinery workers, avoid public hazard exposures, and limit the economic losses due to unplanned evaporation of refinery products.

A continued path towards improved air quality involves a good understanding of current emission levels and sources. Repeated and systematic emission measurements will be an important tool for benchmarking industry’s environmental performance as well as for sustaining and verifying efficient emission improvement plans, ultimately resulting in cleaner air and a better environment.

Acronyms, Units and Definitions

Acronyms used in this report

ASOS	Surface Weather Observation Stations
BPD	Barrels per day
BTEX	Sum of Benzene, Toluene, Ethyl Benzene and Xylene
DOAS	Differential Optical Absorption Spectroscopy
FTIR	Fourier Transform InfraRed
LDAR	Leak Detection And Repair
LIDAR	Light Detection and Ranging
MWDOAS	Mobile White cell DOAS
MeFTIR	Mobile extractive FTIR
SOF	Solar Occultation Flux
SCAB	South Coast Air Basin
SCAQMD	South Coast Air Quality Management District
VOC	Volatile organic compound, used interchangeably for non-methane VOC

Units

Air temperature	degrees C
Atmospheric Pressure	mbar
Relative Humidity	%
Wind direction	degrees North
Wind speed	m/s
Column	mg/m^2
Concentration	mg/m^3
Flux	kg/h

Unit Conversions

1 lbs = 0.4536 kg
1 kg/h = 52.9 lbs/day
1 bbl = 159 l
1 bbl/day = 5.783 kg/h (crude oil)
1 (short) ton = 907.2 kg
1 kton/year = 104 kg/h
1 klbs/year = 0.052 kg/h

Definitions

Alkane or alkanes are considered to be all non-methane alkane species.

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1 Introduction and Background

Industrial volatile organic compound (VOC) emissions contribute to significant formation of ground level ozone which is formed through atmospheric chemical reactions of volatile organic compounds (VOCs) and nitrogen oxides NO_x in the presence of sunlight, often called photo chemical smog. Elevated ozone concentrations are known to reduce crop yields and constitute a public health concern.

Larger metropolitan areas in the US, including the South Coast Air Basin, have trouble meeting ozone standards since anthropogenic sources tend to be concentrated in urban areas, including both mobile and stationary sources. VOC emissions from the latter category, i.e. refineries, petrochemical industries and solvent use, are typically dominated by evaporative losses from storage tanks and process equipment, so called fugitive emissions. Industrial NO_x and SO_2 emissions, on the other hand, occur primarily from external combustion sources. These channeled emissions are quite well understood since they come from relatively few places in an industrial site and since they can be monitored using conventional technology. Evaporative losses of VOCs can potentially occur in every unit in which petroleum products are stored, processed or transported. Units that are malfunctioning, in need of maintenance, or irregularly operated can have drastically elevated emissions without giving any indication. These types of irregular emissions can remain unnoticed if measurements of diffuse emissions are not made.

The industries typically estimate their emissions with emission factors calculated using methods and formulas described in AP-42, Compilation of Air Pollutant Emission Factors (US-EPA 2013). New Technologies for quantitatively measuring these types of VOC emissions exist but have so far only been applied at limited facilities. Estimates of VOC emissions from refineries and petrochemical are therefore rarely verified by quantitative measurements. Since reported total VOC emissions from a facility are typically a very small fraction (typically in the order of 0.01-0.10 %) of its crude oil capacity, emissions would remain insignificant in any type of mass balance even if they were many times larger than reported.

Measurements during the 2000 TexAQS (Texas Air Quality Study) and the 2006 TexAQS II indicated that current emission inventories significantly underestimate industrial VOC emissions in Houston (Kleinman *et al.* 2002; Ryerson 2003; Wert *et al.* 2003; Jobson 2004; Mellqvist *et al.* 2010; Karl 2003; De Gouw, J. A. de *et al.* 2009; Washenfelder *et al.* 2010; Parrish *et al.* 2009). Similar conclusions have also been drawn from international studies elsewhere such as Sweden (Kihlman 2005; Kihlman *et al.* 2005), The Netherlands (Mellqvist *et al.* 2009), France (INERIS 2010) and Belgium (Samuelsson *et al.* 2011). Several studies have concluded that industrial VOC emissions contribute significantly to ozone formation (Kleinman *et al.* 2002; Ryerson 2003; Jobson 2004; Gilman *et al.* 2009; Kim *et al.* 2011; Wert *et al.* 2003; Kim *et al.* 2011).

In order to improve the understanding of VOC, NO_2 and SO_2 emissions in the South Coast Air Basin (SCAB) and to assess whether they impact the ground level ozone in a significant way, the South Coast Air Quality Management District (SCAQMD) has promoted and sponsored several measurement projects to study these emissions using optical remote sensing methods. The projects include experimental studies of emissions from refineries, oil depots, treatment facilities, oil wells, gas stations, fuel islands, barges and shipping. In addition, a technology demonstration and validation study was carried out to assess the uncertainties of different optical techniques using side-by-side measurements of real sources and controlled source gas releases. This work is an extension of a pilot study that was carried out by FluxSense in Los Angeles area in September/October 2013 (Mellqvist *et al.* 2013a, 2013b).

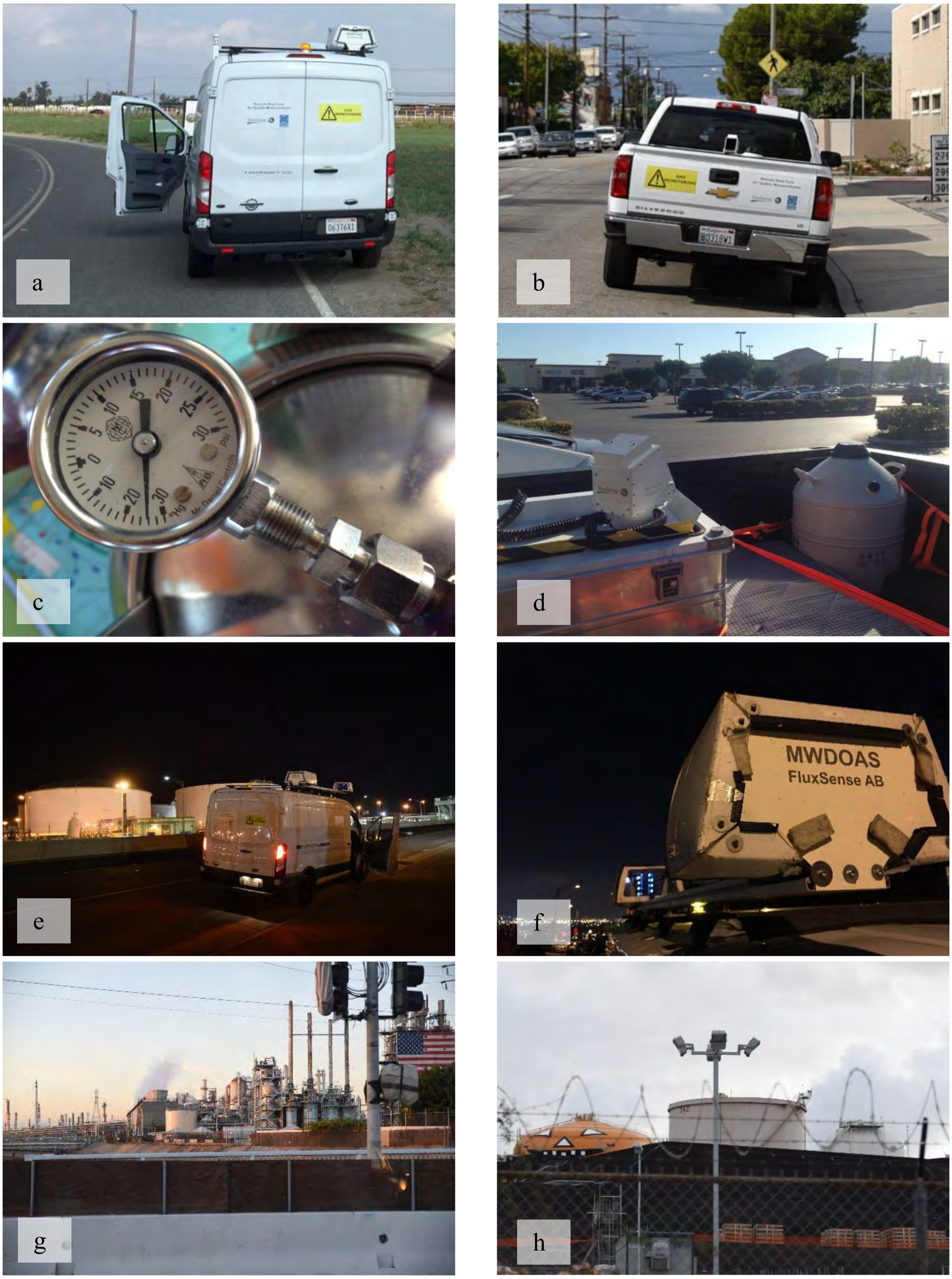

Figure 1. Example images from the 2015 SCAQMD measurement survey. a) FluxSense Mobile lab, b) secondary SOF vehicle, c) Canister sampling, d) Secondary SOF system, e) Night-time MeFTIR measurements, f) MWDOAS measurement, g) Refinery view, h) Tank park view.

This report covers the results from the first of three SCAQMD projects. This project studied emissions of VOCs, CH_4, SO_2 and NO_x from the six main refineries in the SCAB over several months and to compare these to current inventories. This report is one of several other reports describing measurements of smaller emission sources, ship emissions and validation activities. The refineries are denoted Refinery A, Refinery B, Refinery C, Refinery D, Refinery E, and Refinery F respectively. These refineries have a total reported crude oil capacity of more than 900,000 bbl/day (California Energy Commission 2016) and are major contributors of VOC-emissions and, consequently, smog formation in the region.

Two mobile remote gas sensing techniques, SOF (Solar Occultation Flux) and Mobile Sky-DOAS (Differential Optical Absorption Spectroscopy) were operated around the perimeter of the six selected refineries for estimation of facility-wide mass emission fluxes of VOCs, SO_2 and NO_2. The remote gas sensing techniques were complemented by mobile extractive optical methods, i.e. MeFTIR (Mobile extractive FTIR) and MWDOAS (Mobile White cell DOAS) to map ground concentrations of alkanes, methane and aromatic VOCs to calculate inferred fluxes. A mobile wind LIDAR station supplied by SCAQMD allowed for the continuous measurements of vertical wind profiles. Wind data was also obtained from local meteorological stations to complement the LIDAR results. See Figure 1 for example of measurement situations.

SOF is a proven technique employed by FluxSense in over 100 fugitive emission studies around the world. In Europe the SOF technique is Best Available Technology (European Commission 2015) for measurements of fugitive emission of VOCs from refineries and in Sweden it is used together with tracer correlation and optical gas imaging to screen all larger refineries and petrochemical industries annually. The Swedish facilities are visited during at least 10 days per year, spread out over the different seasons, to give a good representation of annual mean conditions. The measurements represent the total emission coming from the entire refinery, divided into sub parts such as process areas, crude oil storage, product storage tanks, water treatment facilities, flares and loading operations. The estimated uncertainty for the emissions is typically 30 % for the total site emissions, and somewhat higher for the individual parts. This has been concluded from several controlled source gas release experiments (blind and non-blind) and side-by-side measurements with other measurement techniques.

The measurements were carried out in the period August 28 to November 11 2015, with up to 15 individual measurements days at the individual sites, and up to 40 individual measurements. Representative statistics of measured emissions (e.g. average, standard deviation, median, etc.) were determined for this time period. Measurements were generally conducted outside the facilities fence-lines along public roads measuring both upwind and downwind the refineries to account for inflow of pollutants from the background. During a week and a half (September 28 to 7 October), measurements were also conducted inside the Refinery A at the main eastern tank farm. The aim was to quantify and to locate leaking tanks and components and to validate the technique by comparative measurements.

In this report, the results from these refinery measurements are compared to the reported annual emission inventories. Discrepancies between reported annual inventories and measured emissions are discussed and further investigated.

In parallel to this project an additional study was carried out in which the SOF method was compared to other optical techniques, DIAL (Differential Absorption LIDAR) and long-path FTIR using side-by-side measurements on various tanks inside a refinery, a treatment plant and an oil well cistern; here the agreement with the other methods was excellent, i.e. 10-20 %. As part of the same study, a blind gas release experiment was carried out, using a controlled source releasing 2-25 kg/h of propane at the parking lot of the Angels of Anaheim baseball stadium, Anaheim, CA. Here the SOF measurements consistently underestimating the true emission by 35% but with a good correlation (R^2 ~98%). This study is compiled in a separate paper.

2 Instrumentation and Methods

The FluxSense mobile laboratory was equipped with four instruments for gas monitoring during the survey; SOF, SkyDOAS, MeFTIR and MWDOAS. Individual measurement methods are described briefly in the subsections below. SOF and SkyDOAS both measure gas columns through the atmosphere by means of light absorption. SOF utilizes infrared light from the direct sun whereas SkyDOAS measure scattered ultraviolet light from the sky. MeFTIR and MWDOAS both measure ground level concentrations of alkanes and BTEX respectively. Accurate wind data is necessary in order to compute emission fluxes. Wind information for the survey was derived from several different sources as described in detail in Section 2.5. A wind LIDAR was used to measure vertical profiles of wind speed and wind direction from 50-1000 m height. The LIDAR data was supported with complimentary data from several wind masts at fixed met network- and mobile stations.

Figure 2 gives a general overview of the measurement setup and the data flow and pictures of the FluxSense mobile lab is found in Figure 3.

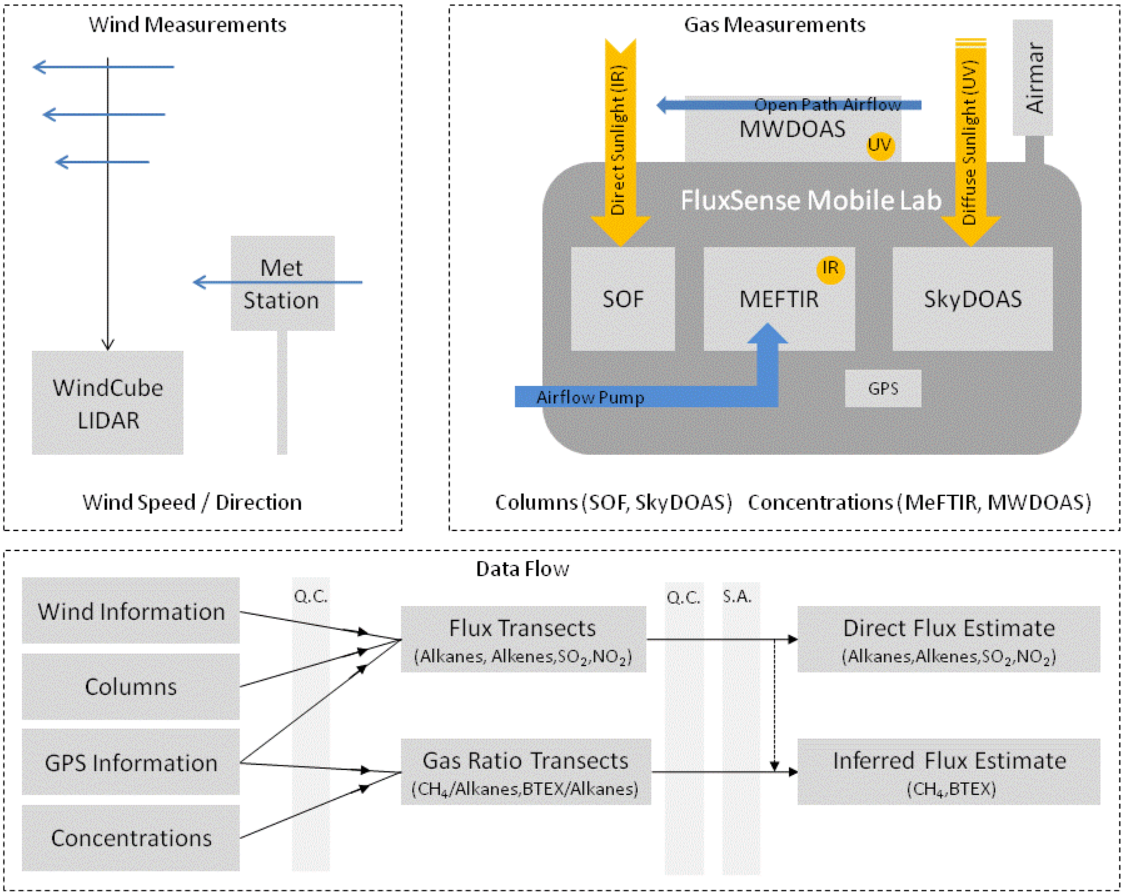

Figure 2. Overview of the FluxSense mobile lab main instruments; SOF, MeFTIR, MWDOAS and SkyDOAS (upper right panel) and wind measurements (upper left panel) and simplified data flow diagram (lower panel). SOF and SkyDOAS are column integrating passive techniques using the Sun as the light source while MeFTIR and SkyDOAS sample local air concentrations using active internal light sources. The data flow describes what information that goes into the flux emission estimates. Direct flux emissions are given from measured columns (SOF and SkyDOAS) of alkanes, SO_2 and NO_2, while inferred fluxes are calculated via gas concentration ratios (MeFTIR and MWDOAS) of BTEX and CH_4. See section 3.2 for principal equations. All emission flux estimates are based on statistical analysis of measured data. Q.C. = Quality Control, S.A.= Statistical Analysis (see Appendix for details).

In order to derive final emission flux estimates, the GPS-tagged gas column measurements by SOF and SkyDOAS are combined with wind data and integrated across plume transects at the various source locations. Gas mass ratio measurements by MeFTIR and MWDOAS are then used to infer emission estimates also for methane and BTEX (which can't be measured directly by SOF and SkyDOAS).

During some of the measurement days at the end of the survey (29 October to 9 November), a second SOF instrument was also used. This additional SOF platform was placed on the bed of a pick-up truck (see Figure 1b) and operated independently of the FluxSense mobile lab, but with a similar optical setup. The second instrument made it possible cover more objects within the survey time frame.

Figure 3. Internal and external view of the FluxSense mobile lab.

A table summarizing the main features and characteristics of all measurement techniques used for this study is found in Table 1.

Table 1. Summary of FluxSense gas measurement techniques. *For typical wind conditions at an optimal distance from the source.

Method	**SOF**	**SkyDOAS**	**MeFTIR**	**MWDOAS**
Compounds	**Alkanes**: (C_nH_{2n+2}) **Alkenes:**C_2H_4, C_3H_6	**SO_2** **NO_2**, **HCHO**	**CH_4** **Alkanes:** (C_nH_{2n+2}) **Alkenes:** C_2H_4, C_3H_6	**BTEX**
Detection limit Column	0.1-5 mg/m^2	0.1-5 mg/m^2	1-10 ppbv	0.5-3 ppbv
Detection limit Flux*	0.2-1 kg/h	1 kg/h	0.2-2 kg/h	1-2 kg/h
Wind Speed Tolerance	1.5-12 m/s	1.5-12 m/s		
Sampling Time Resolution	1-5 s	1-5 s	5-15 s	8-10 s
Measured Quantity [unit]	Integrated vertical column mass [mg/m^2]	Integrated vertical column mass [mg/m^2]	Mass concentration at Vehicle height [mg/m^3]	Concentration at Vehicle height [mg/m^3]
Inferred Quantity [unit]	Mass Flux [kg/h]	Mass Flux [kg/h]	Alkane ratio of ground plume combined with SOF gives mass flux [kg/h] and plume height information [m]	Combined with MeFTIR and SOF gives Mass Flux [kg/h]
Complementary data	Vehicle GPS-coordinates, Plume wind speed and direction	Vehicle GPS-coordinates, Plume wind speed and direction	Vehicle GPS-coordinates, Plume wind direction	Vehicle GPS-coordinates, Plume wind direction

2.1 The SOF method

The SOF method (Mellqvist 1999; Mellqvist *et al.* 2008b; Mellqvist *et al.* 2008a; Mellqvist *et al.* 2009; Mellqvist *et al.* 2010; EPA 2011) is based on the recording of broadband infrared spectra of the sun with a Fourier transform infrared spectrometer (FTIR) that is connected to a solar tracker. The latter is a telescope that tracks the sun and reflects the light into the spectrometer independent of the orientation of the vehicle. From these solar spectra, it is possible to use multivariate optimization to retrieve the path-integrated concentrations (referred to as column concentrations) of various species between the sun and the spectrometer (in the unit mg/m^2). The system used in this project consists of a custom built solar tracker, transfer optics and a Bruker IRCube FTIR spectrometer with a spectral resolution of 0.5 cm^{-1}, equipped with a dual InSb (Indium Antimonide) / MCT (Mercury Cadmium Telluride) detector. A reference spectrum is taken outside the plume so that atmospheric background concentrations can be removed. This means that all measured SOF columns are analyzed relative to the background column concentrations.

The system is installed in a measurement vehicle which allows consecutive column concentration measurements to be performed while driving. The flux of a species in a plume from an industry is measured by collecting spectra while driving the vehicle so that the light path from the sun to the instrument gradually cuts through the whole plume, preferably as orthogonally as possible to the wind direction, see Figure 4.

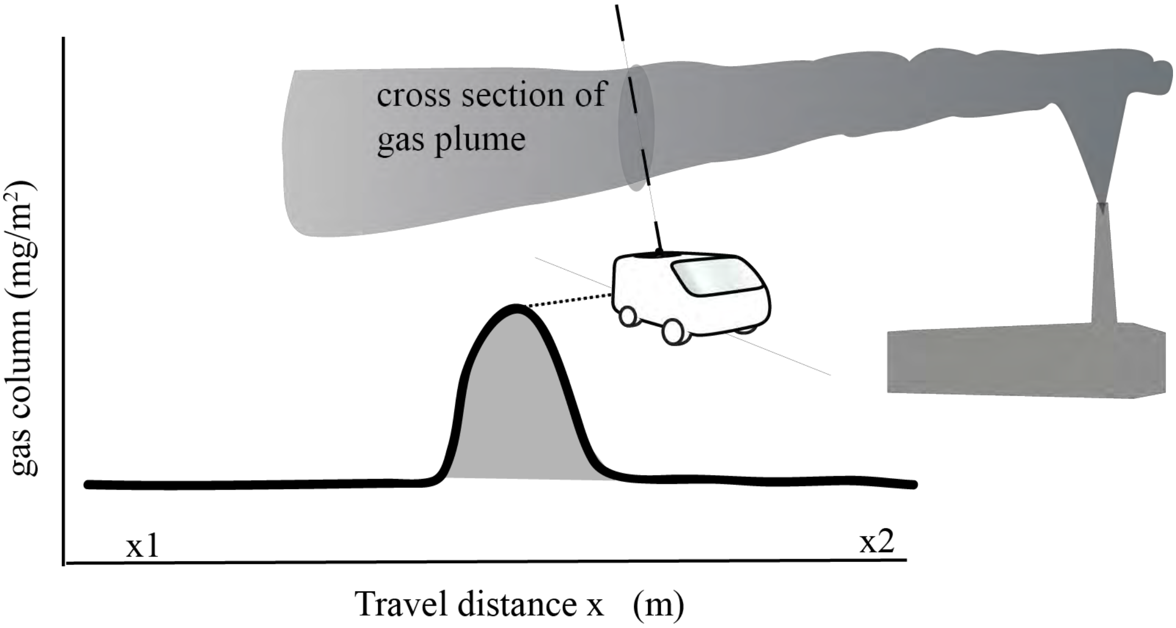

Figure 4. Schematic of the SOF measurement where the vehicle is driven across the prevailing wind so that the solar beam cuts through the emission plume while the sun is locked into the FTIR spectrometer by the solar tracking device on the roof. The VOC mass (or other compound of interest) is integrated through the plume cross section. See section 3.2 for complete equations.

For each spectrum a column concentration of the species is retrieved using custom software (QESOF, i.e. Quantitative evaluation of SOF) (Kihlman *et al.* 2005). These column concentrations, together with positions recorded with a GPS (Global Positioning System) receiver and the solar angle calculated from the time of the measurements, are used to calculate the area integrated column of the species in the intersection area between the plume and the light path. The flux of the species is then obtained by multiplying this area integrated concentration with the orthogonal wind speed vector component.

The IR spectra recorded by the SOF instrument are analyzed in QESOF by fitting a set of spectra from the HITRAN infrared database (Rothman *et al.* 2003) and the PNNL database (Sharpe *et al.* 2004) in a least-squares fitting procedure. Calibration data from the HITRAN database is used to simulate absorption spectra for atmospheric background compounds present in the atmosphere with high enough abundance to have detectable absorption peaks in the wavelength region used by SOF. Spectra, including water vapor, carbon dioxide and methane, are calibrated at the actual pressure and temperature and degraded to the instrumental resolution of the measurements. The same approach is applied for several retrieval codes for high resolution solar spectroscopy developed within Network for the Detection of Atmospheric Composition Change (NDACC) (Rinsland *et al.* 1991; Griffith 1996), and QESOF has been tested against these with good agreement, better than 3%. For the retrievals, high resolution spectra of ethylene, propene, propane, n-butane and n-octane were obtained from the PNNL (Pacific Northwest National Laboratory) database and these are degraded to the spectral resolution of the instrument by convolution with the instrument line shape. The uncertainty in the absorption strength of the calibration spectra is about 3.5% for all five species.

In this project, the SOF method was used to measure VOCs in two different modes. Most VOCs with C-H-bonds absorb strongly in the 3.3-3.7 µm (2700-3005 cm^{-1}) spectral region. This region is mainly used for alkane measurements using a spectral resolution of 8 cm^{-1}. Alkenes (including ethylene and propylene) are instead measured in the spectral region between 910 and 1000 cm^{-1} using a spectral resolution of 0.5 cm^{-1}. In the alkane mode – the IR light absorption is essentially sensitive to the total alkane mass (number of alkane C-H bonds) present in the plume. The absorption structures (cross sections) for the various alkane compounds are rather similar, with the absorption strength scaling to the mass of the alkane species. Hence, the actual mix of alkanes in the plume does not affect the retrieved total alkane mass flux much, although only cross sections from a subset of all alkanes (propane, n-butane and octane) are fitted in the spectral analysis. Typically, the rare event of significant absorption from other species in the plume shows up as elevated residuals and is further investigated in the re-analysis. For the alkene mode the specificity of the measurements is good, since the absorption of different species is rather unique in this so called “fingerprint region” and absorption features are often sharp and well separable from each other at 0.5 cm^{-1} resolution.

2.2 Mobile SkyDOAS

The principle for Mobile SkyDOAS (Mobile Differential Optical Absorption Spectroscopy) measurements is very similar to that of SOF. Instead of measuring direct sun light in the infrared region, scattered light in the UV and visible region is measured in zenith angle with a telescope connected with an optical fiber to a Czerny-Turner spectrometer with a CCD camera. Column concentrations are retrieved from spectra in a similar way as with the SOF, although absorption is generally weaker. The system that was used for this project consists of a quartz telescope (20 mrad field of view, diameter 7.5 cm) connected with an optical fiber (liquid guide, diameter 3 mm) to a 303 mm focal length Czerny-Turner spectrometer with a 1024 by 255 pixels, thermoelectrically cooled CCD camera, see Figure 5.

Figure 5. The mobile Sky-DOAS system: Telescope, optical fibre, spectrometer and control computer.

The system was installed in the same measurement vehicle as the SOF system. Plumes were transected in the same way as with the SOF system and the retrieved column concentrations used to calculate fluxes exactly the same way, except that the SkyDOAS measurement direction is always zenith.

In this project, mobile SkyDOAS was used to measure SO_2, NO_2 and HCHO. NO_2 is retrieved in the wavelength region between 324 and 350 nm and SO_2 in the region 310-325 nm. HCHO is measured in the region 322-350 nm. It was however never found above detection limit in any repeatable measurement during the campaign and is therefore not included in the result section. Apart from SO_2, NO_2 and HCHO the spectral analysis also includes other atmospheric compounds such as O_3 and O_4. The rare event of significant absorption from other species in the plume than those included in the spectral fit shows up as elevated residuals and is further investigated in the re-analysis. The absorption line parameters of the retrieved compounds are well established in published databases, stating an uncertainty of 4% (Vandaele *et al.* 1998) for the UV cross section of NO_2 and less than 2% for the SO_2 cross sections (Bogumil *et al.* 2003).

The DOAS technique was introduced in the 1970's (Platt *et al.* 1979) and has since then become an increasingly important tool in atmospheric research and monitoring both with artificial light sources and in passive mode utilizing the scattered solar light. In recent time the multi axis DOAS technique (scanning passive DOAS) has been applied in tropospheric research for instance measuring formaldehyde (Heckel *et al.* 2005; Pikelnaya *et al.* 2007).

Passive DOAS spectroscopy from mobile platforms has also been quite extensively applied in volcanic gas monitoring (Galle *et al.* 2003) for SO_2 flux measurements and for mapping of formaldehyde flux measurements in megacities (Johansson *et al.* 2009), . Mobile SkyDOAS has been used in several studies for measurements of industries i.e. SO_2, NO_2 and HCHO for several campaigns in Texas including NO_2 measurements at Longview in 2012 (Johansson *et al.* 2014a; Johansson & Mellqvist 2013). (Rivera 2009) did SO_2 measurements on a power plant in Spain for validation purposes. They also made measurements at an industrial conglomerate in Tula in Mexico (Rivera *et al.* 2009a) and measurements of SO_2, NO_2 and HCHO during the TexAQS 2006 campaign (Rivera *et al.* 2009b; Rivera *et al.* 2010). There are also groups in both China and Spain working with mobile mini DOAS.

2.3 Mobile extractive FTIR

Mobile Extractive FTIR (MeFTIR) (Galle *et al.* 2001; Börjesson *et al.* 2009) in combination with tracers has been used to quantify VOC emissions from refinery and petrochemical sources in Europe and in the U.S. Alkanes and alkenes are typically measured, but also methane and other climate gases can be retrieved. MeFTIR is an optical technique capable of monitoring gas concentrations at ppb-sensitivity in mobile field operations. It is used both independently for concentration mapping and flux measurements, but often combined together with simultaneous SOF flux measurements to provide more detailed VOC speciation of plumes and for plume height assessments (Johansson *et al.* 2014b). The plume height can be estimated by dividing measured columns (mg/m^2) with ground concentrations (mg/m^3), assuming that the plume is evenly distributed up to the plume height (and zero above).

The MeFTIR system contains a mid-infrared spectrometer with medium resolution (0.5 cm^{-1}). It utilizes an internal glow bar as an infrared radiation source, and by customized optics this light is transmitted through an optical multi-pass measurement cell with selectable path-length of 9.6-107.2 meters. The system is mounted on a vibration dampening platform to allow for real time plume mapping from a mobile platform, such as a vehicle or boat, see Figure 6.

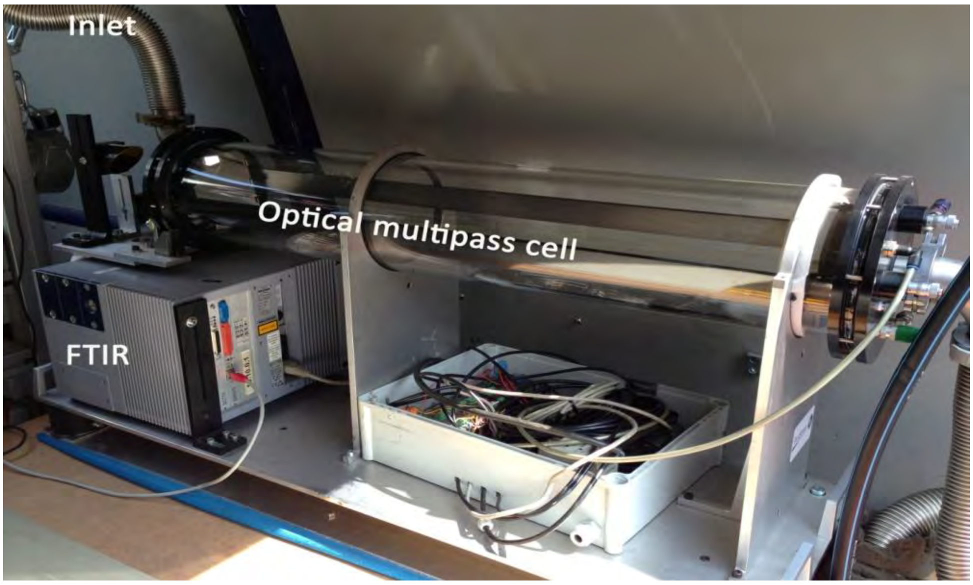

Figure 6. The MeFTIR instrumentation consisting of a Bruker FTIR spectrometer connected to an optical multi-pass cell.

The transmitted light is detected simultaneously with an InSb-detector (Indium Antimonide) in the 2.5–5.5 µm (1800–4000 cm^{-1}) region and a MCT (Mercury Cadmium Telluride) detector in the 8.3–14.3 µm (700–1200 cm^{-1}) region. Temperature and pressure in the cell are averaged over the duration of each measurement. Atmospheric air is continuously pumped at high flow rate through the optical cell from the outside, taking in plume air from the roof of the vehicle (2.5 m height) through a Teflon tube. A high flow pump is used to ensure that the gas volume in the cell is fully replaced within a few seconds. Spectra are typically recorded with an integration time of 10 seconds. A GPS-receiver is used to register the position of the vehicle every second.

The concentration in the spectra is analyzed in real time by fitting a set of calibrated spectra from the Hitran infrared database (Rothman *et al.* 2003) and the PNNL database (Sharpe *et al.* 2004) in a least-squares fitting procedure. Compounds being analyzed include ethylene, propylene, total alkane mass (based on fitting cross sections of ethane, propane, n-butane, i-pentane, n-octane), water, methane, CO, CO_2 and N_2O. The analysis routines are very similar to the ones for SOF, but less complex because strong absorption by atmospheric trace gases (water, methane, CO_2) has less consequence at the shorter path length in the MeFTIR measurement cell.

The MeFTIR tracer approach has been tested in a so called gas release "blind test" together with other techniques in U.S. (Babilotte 2011). In that test, methane was released from an area-distributed source in four different configurations and flow rates ranging from 1.1-3.3 g/s. At a downwind distance of 400 meters MeFTIR retrieved the fluxes within 6% in 3 cases and 19% in the fourth. This is consistent with other validation experiments, showing a flux estimate accuracy of better than 20%. Concentration measurement by FTIR is a widely used procedure, and the main uncertainties are associated with the absorption cross sections (typically < 3.5%) and spectral retrieval, with an aggregate uncertainty better than 10% in the analysis. Concentrations are monitored in real time in order to detect emission plumes and to judge whether any interfering sources are being sampled. Unwanted signals from local traffic exhaust or from the measurement vehicle itself could be filtered out by looking at the carbon monoxide (typical exhaust compound) concentrations. A stationary source is, on the contrary to any local traffic plumes, characterized by recurrent downwind plumes. Transient and non-repeatable observations are therefore excluded from the results. Furthermore, measurements of ambient concentrations of methane and carbon dioxide (with known atmospheric concentrations) are used for consistency check.

2.4 Mobile White Cell DOAS (MWDOAS)

The ground level mass concentration of benzene, toluene, ethylbenzene, *meta*- and *para*- xylene (BTEX) was measured using a mobile real-time system: Mobile White cell DOAS (MWDOAS). The Mobile White cell DOAS system consists of an open, 2.5 m long optical White cell that is mounted on the roof of the measurement vehicle (see Figure 7). By multiple reflections in the White cell mirror system an overall path length of 210 m is obtained, resulting in low detection limits (ppb). The light from the internal lamp is transmitted through the White cell and then analyzed in a DOAS spectrometer, using the UV wavelength region 255 - 285 nm.

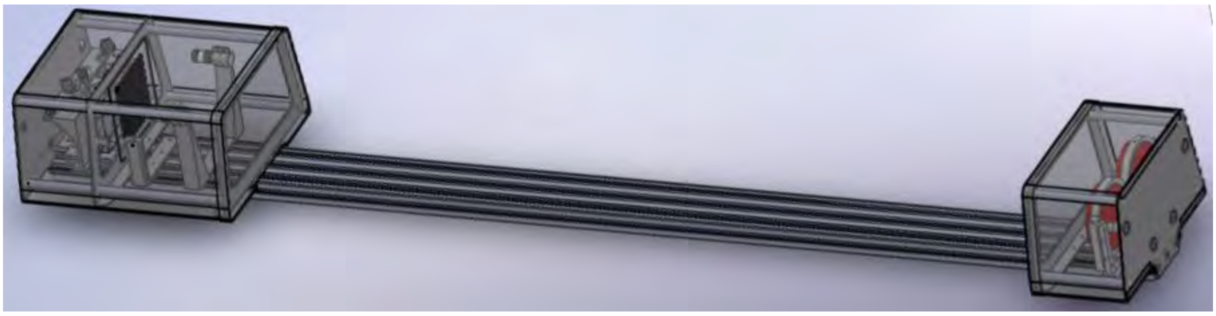

Figure 7. The open path MWDOAS cell having an overall optical path-length of 210 m.

A measurement begins by acquiring a reference spectrum outside the plume, usually upwind of the facility. Spectra are then sampled and averaged continuously while driving through emission plumes. The averaging time is set to around 8 seconds in order to achieve acceptable SNR (see below). This is the lower limit of the temporal sampling between independent measurements, but the spatial sampling is also dependent by the vehicle’s velocity. A typical driving speed for MWDOAS measurements is 10-20 km/h for sufficient plume sampling.

The spectra are geo-tagged and evaluated online using the standard DOAS technique, giving information of plume locations and constituents. Cross-sections included in the evaluation are tabulated in Table 2.

Table 2. The UV-cross-sections used in the evaluation of the MWDOAS spectra.

Chemical compound	**Origin of reference spectrum**
O_3	(Burrows *et al.* 1999)
SO_2	(Bogumil *et al.* 2003)
O_2	(Bogumil *et al.* 2003)
Toluene	(Fally *et al.* 2009)
Benzene	(Etzkorn *et al.* 1999)
1,3,5-Trimethylbenzene	(Etzkorn *et al.* 1999)
1,2,4-Trimethylbenzene	(Etzkorn *et al.* 1999)
Styrene	(Etzkorn *et al.* 1999)
Phenol	(Etzkorn *et al.* 1999)
p-xylene	(Etzkorn *et al.* 1999)
m-xylene	(Etzkorn *et al.* 1999)
Ethylbenzene	(Etzkorn *et al.* 1999)

The MWDOAS data is later post evaluated and merged with the corresponding MeFTIR data to produce a plume specific BTEX/alkane mass ratio. The mass ratio of BTEX/alkanes is then used to calculate the aromatic flux from individual sub areas where alkane fluxes have been measured by SOF, assuming they have the same source. Specific area plumes are ideally probed at several times, and an overall average of all plume transect BTEX/alkane ratios is then made. The method requires in situ access to the plume of the studied source, and as instrumentation typically are mounted on a truck, highly elevated sources with a strong plume lift like hot flares, chimneys and high process towers will not be possible to survey at close distance.

The MWDOAS technique has been validated in various surveys by comparison with canister samples acquired at several different locations and which were subsequently analyzed by gas chromatography (GC-FID). The validation shows that the result from MWDOAS lies well within 10% of the result of the certified canister results for BTEX. Due to an absorption cross-section too weak to be used with reliability in the MWDOAS analysis, the ortho isomer of the xylene has been omitted in this comparison. When total xylene is presented in the present survey, the sum of *m*- and *p*-xylenes from the MWDOAS measurement is multiplied by 1.32. This number comes from a ratio comparison of xylene isomers in 49 canister samples analyzed by GC/FID and taken from eight refineries and tank parks from two countries. The standard deviation in this comparison was 0.07 and adds a 4.5% uncertainty to the total xylene concentration. Hence, the xylene concentration from MWDOAS is defined as the sum of the measured *m*- and *p*-isomers and the inferred *o*-isomer.

The MWDOAS system has been used in previous campaigns in USA during 2013 with good results. During the 2013 DISCOVER-AQ campaign in Houston, Texas, the system was run in parallel to a mobile Proton Transfer Mass spectrometer (PTrMS) lab as a validation check. The results of benzene, toluene and styrene was compared and showed good agreement, with the PTrMS showing slightly elevated benzene concentrations compared to the MWDOAS. The sensitivity of MWDOAS is better than 1 ppb for benzene, better than 3 ppb for toluene, ethylbenzene and *m*-xylene and as good as 0.5 ppb for *p*-xylene.

Since the distribution of the BTEX constituents varies with source we will also present the benzene to alkane ratio to facilitate the calculation of benzene flux and identify specific benzene sources.

Unwanted BTEX signals from local traffic exhausts are generally only significant in congestions (at traffic lights etc.) or in confined spaces, e.g. tunnels. Apart from this, large emitters are also occasionally seen elsewhere. They are generally recognized, partly by their typical gasoline composition signature and partly by their transient nature. A stationary BTEX source is, on the other hand, characterized by recurrent downwind plumes. Transient and non-repeatable BTEX observations are therefore excluded from the result. Note that all concentrations are above the reference/background.

2.5 Wind Measurements and Auxiliary Data

Wind LIDAR

An infrared 3D wind LIDAR provided by the SCAQMD (shown in Figure 8) was used to measure vertical wind profiles of wind speed and wind direction. The unit used for this study (i.e. model WindCube 100S) produced by Leosphere (France) provides wind profiles in the vertical range 50 to around 1000 m above surface level, or even further if atmospheric conditions allow it. Within this range data can be retrieved in 25 m vertical resolution. Stated wind speed accuracy is 0.5 m/s. Applicable radial wind speed range is -30 to 30 m/s. The system records 1s data, but 10 minute averages were used for flux calculations in this study. The principle of detection is based on the Doppler shift of the infrared pulse that the instrument sends out and retrieves. Numerous validation surveys attesting the accuracy of the WindCube LIDARs are publically available through: www.leosphere.com.

Figure 8. The WindCube 100S (Leosphere) LIDAR used for wind profile measurements in this project.

Wind Mast

Meteorological parameters were measured at selected sites using a portable 10 m mast, see Figure 9. This mast was equipped with a calibrated RM Young 05108 “prop and vane” anemometer and a Campbell Scientific CR200 data logger.

The weather mast was installed at an open location near the refinery of interest and with un-obstructed fetch for wind directions that was used for SOF measurements. The sensor was adjusted to point towards magnetic north but compensated to true north in the post-processing. Wind speed information from the 10 m mast or other wind stations in the area is used to fill in the gap of the lowest 40 m of the atmosphere where no LIDAR data exists. Since the plume heights from petrochemical facilities generally are several hundred meters during sunny conditions (some hundred meters downwind where SOF measurements are done), the wind speed information below 40 m does not influence the flux calculations substantially (typically a few percent).

Figure 9. The FluxSense mobile wind mast used in the 2015 SCAQMD survey with an RM Young anemometer mounted on top. The mast could be erected from 3 to 10 m.

Airmar (mobile weather station)

An Airmar WeatherStation (200 WX) sensor was installed on the roof of the measurement vehicle to complement the other wind measurements and give local ground winds at the vehicle. The wind information from the Airmar is not used for flux calculation but acts as a real-time aid to keep track of the plume directions when making the gas emission measurements.

The Airmar provides wind speed and direction relative to true north (compensating for vehicle position), air temperature, pressure and relative humidity. It also provides GPS positions which may be used as back-up to the other GPS-receiver.

GPS

The FluxSense vehicle is equipped with two standard USB GPS-L1 receivers (GlobalSat BU-353S4) hooked up to the SOF and DOAS-computers. They are placed horizontally by the windscreen and on the roof for optimal reception. The receivers give the position at a rate of 1 Hz.

3 Measurement Methodology

Typically the main instruments in the FluxSense mobile lab are operated during favorable meteorological conditions for each individual instrument. SOF and SkyDOAS are mainly used during solar/daytime measurements and MWDOAS and MeFTIR for gas ratio measurements during day or cloudy/nighttime conditions. Plume height calculations are dependent on simultaneous SOF and MeFTIR measurements of alkanes, so MeFTIR was typically running during solar/daytime conditions when feasible. MWDOAS and SkyDOAS were sharing the same spectrometer in this survey. Hence, time sharing between these two different techniques was necessary. In addition to the gas mass ratio measurements by MWDOAS and MeFTIR, some canisters were also sampled in selected plumes for further VOC speciation and complimentary data.

By keeping track of wind directions and avoiding strong upwind sources, the same plumes were essentially sampled during solar/daytime and cloudy/nighttime measurements so that representative gas ratios were collected. Only MeFTIR and MWDOAS measurements with repeated plume signature and high correlation between target and alkane concentrations were accepted. Canister sampling was only performed during cloudy/nighttime measurements when ground plumes are generally present and monitored in real-time.

3.1 Survey Setup

The main objective of this study was to quantify the total gas emissions of non-methane VOCs (alkanes and BTEX), NO_2, SO_2 and methane from six major refineries in the Los Angeles Basin denoted Refinery A, Refinery B, Refinery C, Refinery D, Refinery E and Refinery F respectively (see Figure 10). This was done by conducting fence-line measurements along accessible roads outside the facilities using mobile optical measurements (SOF and mobile DOAS) to obtain total gas emission fluxes from the refineries. Furthermore, ground concentration measurements were carried out with mobile MWDOAS and MeFTIR instruments to infer emission of methane, BTEX and specifically benzene.

Gas measurements were combined with wind data, primarily from SCAQMD's wind LIDAR system, but also from meteorological stations and from a mobile 10 m wind mast, to calculate fluxes and identify sources. Throughout the study the wind LIDAR was moved between four different locations (L1-L4, see Figure 10) depending on the facilities measured. The geographical positions of the refineries are noted as colored areas in Figure 10 along with various meteorological sites and wind LIDAR positions. In general, each measurement day was dedicated to one specific refinery except for Refinery B and Refinery C which were both surveyed within the same time frame.

Emissions from each refinery were calculated by driving around the targeted facility to capture the entire downwind plume and then subtracting potential contributions from emissions deriving from upwind sources. This approach is referred to as “box-measuring” in this report. When complete upwind plume measurement was not possible (e.g. lack of accessible roads), relevant upwind measurement transects were made in close proximity in space and time. The aim was to make multiple measurements during several days over the entire duration of the study (from 28 August to 10 November 2015) in order to map detected plumes at different times, during variable wind conditions, and from different distances from the sites to better understand emission variability, plume dispersion, and the potential for local community exposure.

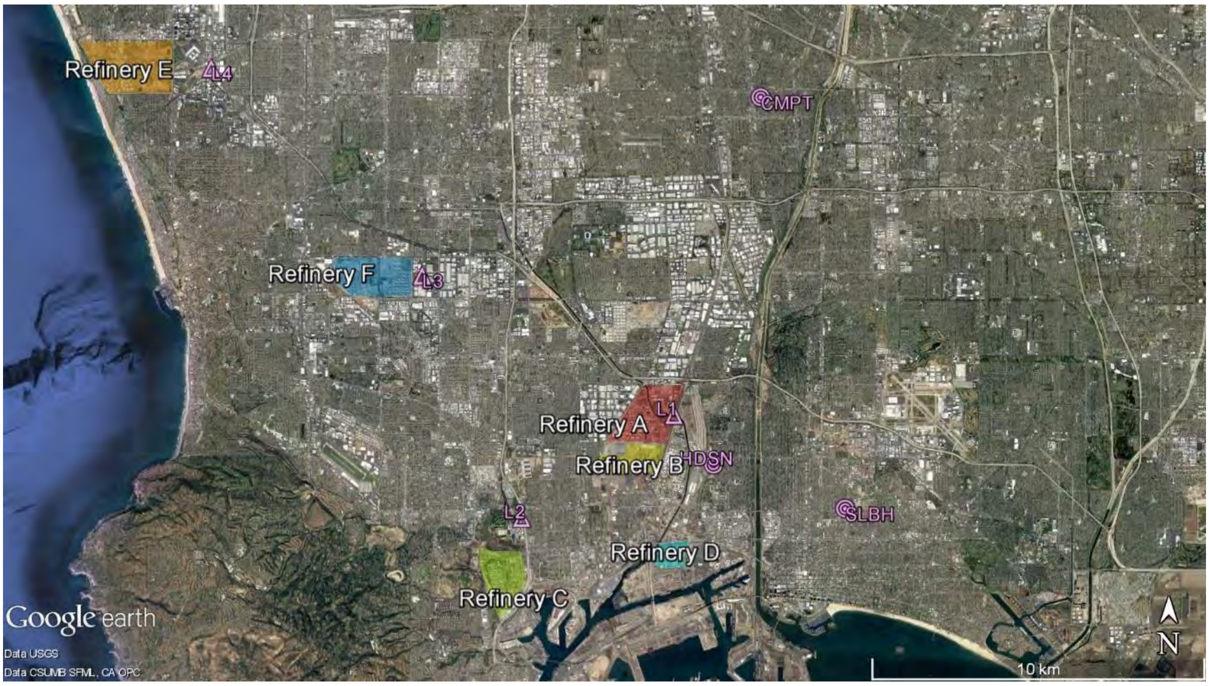

Figure 10. Map showing the locations of the six refineries that were targeted for this study. Also shown are meteorological sites and LIDAR positions. Map from Google Earth © 2016.

Altogether, measurements were carried out during 40 days, however the number of successful and quality assured measurements varied substantially from day to day and from facility to facility depending on weather conditions, local measurement conditions (e.g. road accessibility), and time sharing between different refineries and instruments.

Refinery A is the largest refinery in the Southern California Air Basin (along with Refinery E) and it has been collaborating with SCAQMD to support this campaign and making it possible to carry out 7 days of onsite measurements. In addition, 15 measurement days of total emissions were carried out on refinery fenceline. A statistical estimate of flux emissions (kg/h) was computed for each measurement day at each refinery. Total mean and median values for the entire survey period were calculated in parallel. This data was compared to the reported annual emission inventories. Extreme events (beyond 1.5 times the inter-quartile range) and possible point sources within a refinery were also noted in the report.

3.2 Principal Equations

This report includes two different techniques to measure emission mass fluxes as specified below. The primary method in this project is the direct flux measurements of alkanes from SOF. BTEX and methane fluxes are calculated using inferred fluxes from MWDOAS/MeFTIR gas mass ratios.

DIRECT FLUX MEASUREMENTS:

Direct flux is measured by SOF or SkyDOAS. The emission mass flux (Q) of species (*j*) for a single transect (*T*) across the plume (P) along path (*l*), can be expressed by the following integral (Si-units in gray brackets):

$$Q_T^j[\mathrm{kg/s}] = \bar{v}_T[\mathrm{m/s}] \cdot \int_P C_l^j[\mathrm{kg/m^2}] \cdot \cos(\theta_l) \cdot \sin(\alpha_l)\, dl\ [\mathrm{m}]$$

Where,

$\bar{v}_T$ = the average wind speed at plume height for the transect,
C_l^j = the measured slant column densities for the species j as measured by SOF or SkyDOAS,
θ_l = the angles of the light path from zenith ($\cos(\theta_l)$ gives vertical columns),
α_l = the angles between the wind directions and driving directions
dl = the driving distance across the plume

Note that SOF and SkyDOAS have different light paths, where the SkyDOAS telescope is always looking in the zenith direction while the SOF solar tracker is pointing toward the Sun. Hence, the measured SOF slant column densities will vary with latitude, season and time of day.

To isolate emissions from a specific source, the incoming/upwind background flux must be either insignificant or subtracted. If the source is encircled or "box-measured", the integral along *l* is a closed loop and the flux calculations are done with sign. This is taken care of by the FluxSense software.

INFERRED FLUX MEASUREMENTS:

Inferred flux is computed using a combination of SOF and MeFTIR/MWDOAS measurements. The inferred mass flux ($\hat{Q}^i$) for species (*i*) are calculated from MeFTIR and/or MWDOAS ground level gas ratios integrated over the plume (*P*) along path (*l*) are given by (Si-units in gray brackets):

$$\hat{Q}^i[\mathrm{kg/s}] = \bar{Q}^j[\mathrm{kg/s}] \cdot \frac{1}{k}\sum_k \frac{\int_P N_l^i[\mathrm{kg/m^3}]\, dl[\mathrm{m}]}{\int_P N_l^j[\mathrm{kg/m^3}]\, dl[\mathrm{m}]}$$

Where,
$\bar{Q}^j$ = the average flux of species j from multiple transects as measured by SOF,
N_l^i = the number density concentrations of species i as measured by MWDOAS or MeFTIR,
N_l^j = the number density concentrations of species j as measured by MeFTIR,
k = the number of gas ratio measurements

Note that the inferred flux calculation operates on average values since simultaneous SOF/SkyDOAS, MWDOAS and MeFTIR measurements are generally not performed and because individual gas ratios are more uncertain than the average. Although not necessarily simultaneously measured, SOF and MeFTIR/MWDOAS measurements must represent the same source plume. Note also that gas ratios do not intrinsically depend on complete plume transects (like for direct flux methods) as long as the emission plume is well mixed at the sampling distance.

The uncertainties in the total refinery emissions of BTEX and CH_4 obtained from inferred fluxes are larger than for the direct flux measurements of alkanes. Ideally the gases should be well mixed in the plume for this method to work the best, but in reality there will be a stronger weighting towards low elevated sources (tanks) compared to higher elevated ones (process units) depending on the measurement geometry. In the past we have done canister sampling in several European refineries, and typically the BTEX fraction is higher in the process units (10-15 %) compared to tank farms (5-10 %). The inferred emission flux of BTEX will consequently be a low estimate of the BTEX emission. For smaller, more isolated sources we estimate that the uncertainty of the inferred fluxes is only slightly higher than the direct flux measurement.

PLUME HEIGHT ESTIMATES:

This is a method to calculate approximate plume heights from simultaneous SOF slant columns and MeFTIR ground level concentrations, measured across an emission plume. The plume height, h_T , for a transect, *T*, across a plume, P, along the path, *l*, is given by the following equation (Si-units in gray brackets):

$$h_T^j[\mathrm{m}] = \frac{\int_P \; C_l^j[\mathrm{kg/m^2}] \cdot \cos(\theta_l) \;\, dl[\mathrm{m}]}{\int_P \; N_l^j[\mathrm{kg/m^3}] \;\, dl[\mathrm{m}]}$$

Where,

C_l^j = the slant column density of species j as measured by SOF,
θ_l = the angle of the light path from zenith ($\cos(\theta_l)$ gives vertical columns),
N_l^j = the number density concentrations of species j from MeFTIR,

This method distributes the plume homogeneously from the ground to the plume height (and zero above). In reality, however, emission plumes have a vertical gradient controlled by wind shear, turbulence, atmospheric lapse rate, release altitude etc. Hence, the plume height as calculated using the equation above, is only a first order approximation. In this report, plume heights have consistently been calculated using alkane measurements (i.e. j=*alkane*). Median values of multiple plume height estimates are used to decrease uncertainties.

3.3 Uncertainties and Error Budget

Table 3 summarizes the accuracy, precision, and data completeness for measurements from each instrument employed during this field campaign.

Table 3. Accuracy, precision, and data completeness for measurements from each of FluxSense's measurement methods.* For the optical measurements conducted in this project data completeness is difficult to estimate since the measurements are dependent on external parameters such as weather conditions.

Measurement Parameter	Analysis Method	Accuracy	Precision	Completeness*
SOF column concentrations alkanes, alkenes	QESOF spectral retrieval	±10%	±5%	70-90%
SkyDOAS column concentrations NO_2, SO_2	DOAS spectral retrieval	±10%	±5%	70-90%
MeFTIR concentrations CH_4, VOC,	QESOF spectral retrieval	±10%	±5%	95%
MWDOAS concentrations BTEX, Benzene	MWDOAS spectral retrieval	±10%	±5%	90%
Wind Speed (5m)	R.M. Young Wind monitor	±0.3 m/s or 1%	±0.3 m/s	95%
Wind Direction (5m)	R.M. Young Wind monitor	±5°	±3°	95%
Wind Speed (10m)	Gill WindSonic	±2%	-	95%
Wind Direction (10m)	Gill WindSonic	±3°	-	95%
LIDAR Wind Direction (50-1000m)	Leosphere Windcube 100S	-	-	>90% except in heavy fog
LIDAR Wind Speed (50-1000m)	Leosphere Windcube 100S	±0.5 m/s	-	
GPS position	USB GPS receiver	±2m	±2m	100%
SOF mass flux Alkanes, alkenes	SOF flux calculations	±30%	±10%	80% (in suitable weather conditions)
SkyDOAS mass flux NO_2, SO_2	SkyDOAS flux calculations	±30%	±10%	80% (in suitable weather conditions)

Accuracy of measurement parameters is determined by comparing a measured value to a known standard, assessed in terms of % bias, using the following equation:

$$\left[1-\left(\frac{Measurement}{Standard}\right)\right]\times 100$$

Precision is a measure of the repeatability of the results. The precision for the SOF and mobile SkyDOAS system is difficult to measure when inside the gas plumes. However, it is assumed that the precision of the instrument corresponds to the 1-sigma noise when measuring in clean air background. The precision of each instrument used in this project is listed in Table 3.

Data completeness is calculated on the basis of the number of valid samples collected out of the total possible number of measurements. Data completeness is calculated as follows:

$$\%\,Completeness=\left(\frac{Number\ of\ valid\ measurements}{Total\ possible\ measurements}\right)\times 100$$

3.4 Wind Statistics and Plume Heights

The largest source of error in SOF and SkyDOAS emission flux calculations is typically determined by the quality of the collected wind measurements. The flux is directly proportional to the wind speed (at average plume height) and to the cosine of the wind direction relative to the driving direction. The total wind uncertainty results from a combination of wind measurements errors (see Table 3) and errors due to the assumption that the measured wind velocity measured is representative of the average plume velocity. Wind profile data, as supplied by a LIDAR, has the major advantage of allowing an average wind for an arbitrary height interval to be calculated. Given some approximate information about the mixing height of the plume, a suitable averaging interval can be chosen, and the LIDAR data can also be used to estimate the sensitivity of the wind error to the error in the mixing height. Estimates of the plume mixing height estimates can in turn be retrieved by simultaneous concentration and column measurements with SOF and MeFTIR as described in section 3.2. The method assumes homogeneous plume concentrations from ground level to the plume height. Plume height results for the different refineries in this study are found in Table 4 and Figure 11.

Table 4. Summary of plume height (median values) estimations for all refineries surveyed during this study. Wind information used for flux calculations is also reported (all non-LIDAR winds scaled to LIDAR 0-400m with the given scaling factors). *Measurements at Refinery D were conducted during a flaring event with high elevated plumes.

Refinery	Number of Measurements	Median Plume Height [m]	Primary Wind (0-400m)	Secondary Wind (Scaling factor)
Refinery A	19	475	LIDAR L1	Refinery A Mast (1.34)
Refinery B	3	514	LIDAR L1	Refinery A Mast (1.34)
Refinery C	5	464	LIDAR L2	AQMD-SLBH (1.0)
Refinery D*	2	835	LIDAR L1	ASOS-KLGB (1.17)
Refinery E	11	239	LIDAR L4	ASOS-KLAX (0.83)
Refinery F	6	292	LIDAR L3	LIDAR L1 (1.0)
All Refineries	**46**	**413**		

These results indicate a plume height of 250-500 m with an overall median for all refineries of around 400m. The high values at Refinery D were estimated during a flaring event on November 1, 2015, with non-typical elevated emissions and should be treated cautiously. Based on these estimates, the average wind for the interval 50-400 m, as measured by the wind LIDAR, has been used for flux calculations in this survey. Wind information from Refinery A's 10 m mast during the calibration period (October 2-6, 2015) was used to account for the lowest 50 m of the air column. In this compensation, the 10 m wind data was used from 0 to 20 m and a linear interpolation was applied between the 10 m wind and the LIDAR wind between 20 and 50 m. Although this compensation had a very small effect (~2%) on the total wind speed as provided by the LIDAR between 50 and 400m, it was applied to all flux calculations for consistency.

Note that plumes of different gases may behave differently. Plumes originating from combustion sources (e.g. SO_2 and NO_2), are generally stack releases. As such, they are released at a high altitude and more buoyant (hotter) than fugitive and cold VOC emissions. Hence, SO_2 and NO_2 are expected to be found at a slightly higher altitude than alkanes when measuring refinery emissions at a fence-line distance like in this survey. Plume height estimations are, however, not possible for SO_2 and NO_2 (no simultaneous concentrations measurements). But since the wind gradient with height was weak during the survey and with the emissions confined within in the boundary layer (see discussion below), the effect on the calculated fluxes are small and well within the measurement uncertainty.

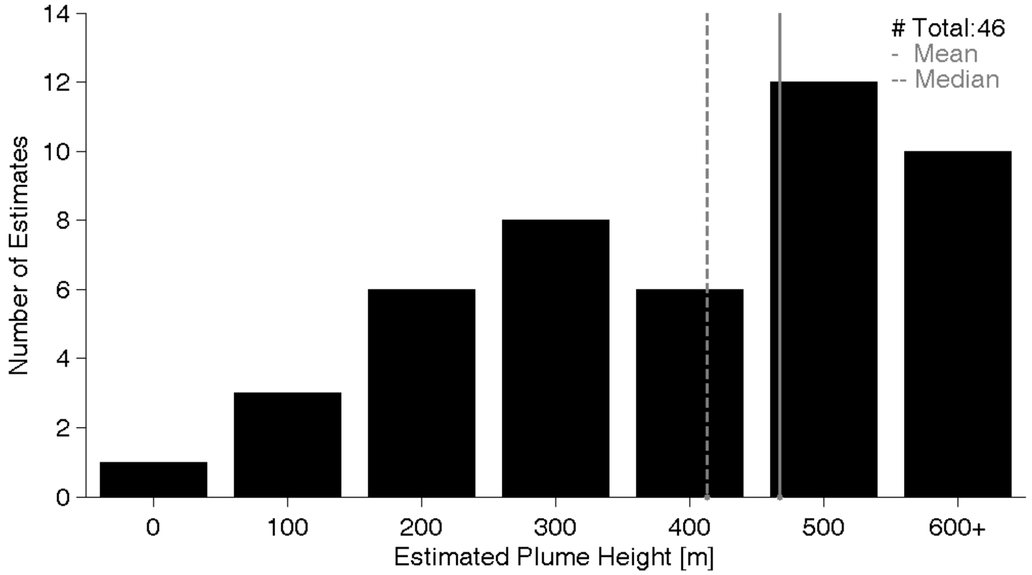

Figure 11. Plume height estimations for all refineries during the 2015 SCAQMD survey. The last bin, denoted ‘600+’, contains all data points above 600 m. The median and average values are indicated as dashed and solid gray lines, respectively.

Wind LIDAR data has always been used as the primary wind information for flux calculations in this survey. The different LIDAR locations/sites are specified in Figure 10. For cases where no LIDAR information was available (e.g. LIDAR malfunction or data collected at non-representative sites) an appropriate secondary wind source was used based on its proximity to the measured refinery. Secondary wind data was scaled to match the 50-400 m LIDAR wind at a location closest to the measurement site using the slope of a linear least-squares-fit, see *Scaling Factors* in Table 4 and plots in Appendix B.

In order to assess the sensitivity of the flux calculations to deviations from the assumed plume mixing height, wind LIDAR data (10 min average) for different altitude ranges (i.e. 50-100 m, 50-200 m, 50-300 m, 50-400 m, and 50-500 m) were compared to the reference LIDAR wind (50-400 m) during the two calibration periods (October 2-6, 2015 at LIDAR site L1 and October 9-16, 2015, at site L3; see Figure 10). For both calibration periods, the wind speed comparisons show that the systematic difference for the alternative height intervals is less 4% compared to the reference interval (50-400 m) and that the vast majority of data points are within 30% of the reference wind (50-400 m) (see example in Figure 12 and the complete data set in Appendix B). For the wind direction, the same comparisons showed a systematic difference of less than 5° to the reference wind and a total spread of the random differences of less than 30° for almost all data points.

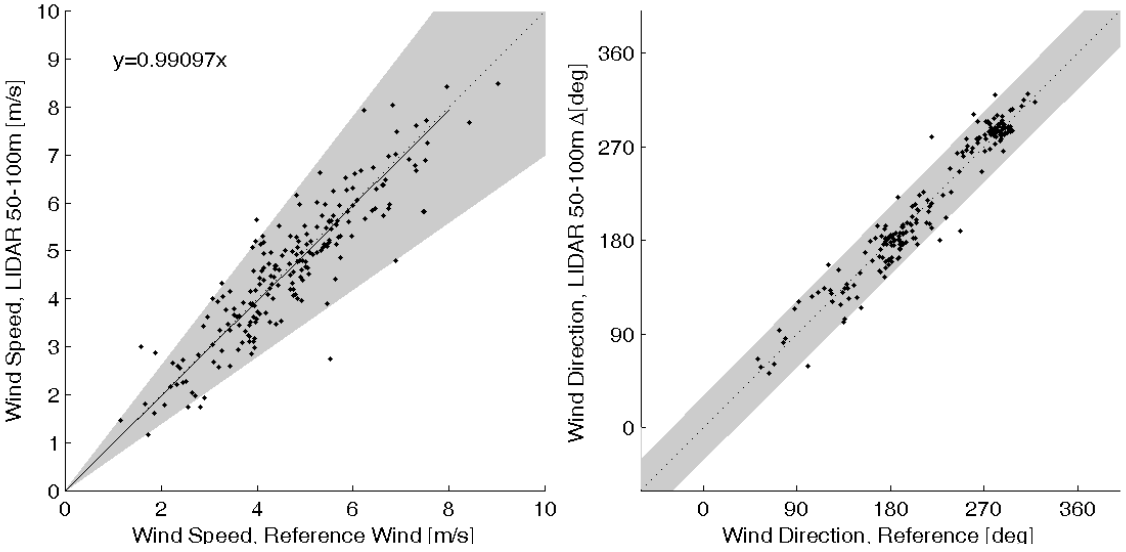

Figure 12. Wind LIDAR data (10 min average from 10AM to 5PM) for 50-100 m versus the reference LIDAR wind (50-400 m) during the calibration period (October 2-6, 2015) at LIDAR site L1. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as a solid line. See Appendix B for the complete data set.

The variability of the wind with height and time is further illustrated in Figure 13. The two upper panels show the average wind (solid lines) at each height level relative to the 50-400 m reference average as well as the average standard deviation (±1σ; dashed lines). These profiles show that the wind does not systematically deviate more than 15% or 5° at any height level and that the standard deviation of the random deviations are generally less than 20% in wind speed and 20° in wind direction, except for the highest levels in the interval. The two lower panels in Figure 13 show the results of comparison between the reference wind and the same reference wind a few minutes earlier. These plots also show the average wind deviation as a function of the time difference (solid lines), as well as the average standard deviation (±1σ; dashed lines). As expected, the random deviations increase with the time difference, while the systematic deviations are close to zero. The reason why the average deviation is not actually zero is that the prevailing wind conditions during the study featured a distinct pattern of winds increasing throughout the day while also shifting direction in a recurring pattern.

Two examples of the evolution of the wind profile over the course of a day are shown in Figure 14. Both of them show clear signs of the prevailing wind pattern throughout the study, with weak winds in the morning that increase in magnitude from approximately 10:00 AM to 12:00 PM and forward while also shifting direction. Since a wind speed of at least 1-2 m/s is typically needed in order to accurately calculate flux, useful data could normally not be collected before 10:00 am. As also seen in these examples, the wind is relatively homogenous within a layer up to 300-500 m, but at higher altitudes the wind direction often varies dramatically. This altitude range coincides very well with the typical plume mixing height estimates in Table 4 indicating that this layer of homogenous wind is the convective boundary layer. The exact height of this layer varies throughout the day and this explains why the wind was on average weaker and more variable in the uppermost levels of the 50-400 m height interval, as seen in Figure 13. The convective boundary layer simply does not always extend above this height level.

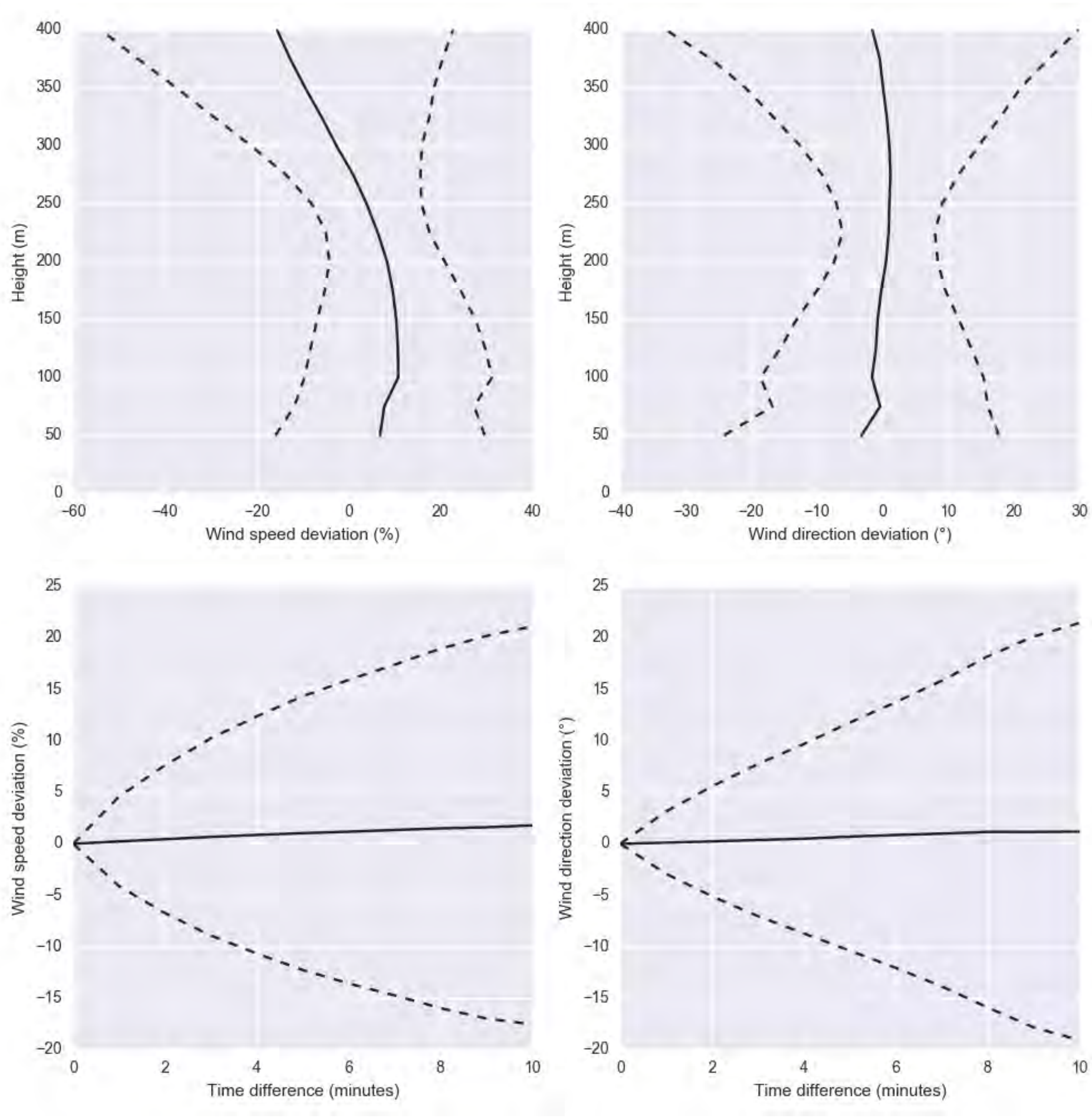

Figure 13. 10-min wind LIDAR data for the entire 2015 SCAQMD survey. Average (solid lines) and standard deviation (±1σ; dashed lines). Top row panels show altitude information and the lower row panels show time dependence (see Appendix B for additional plots).

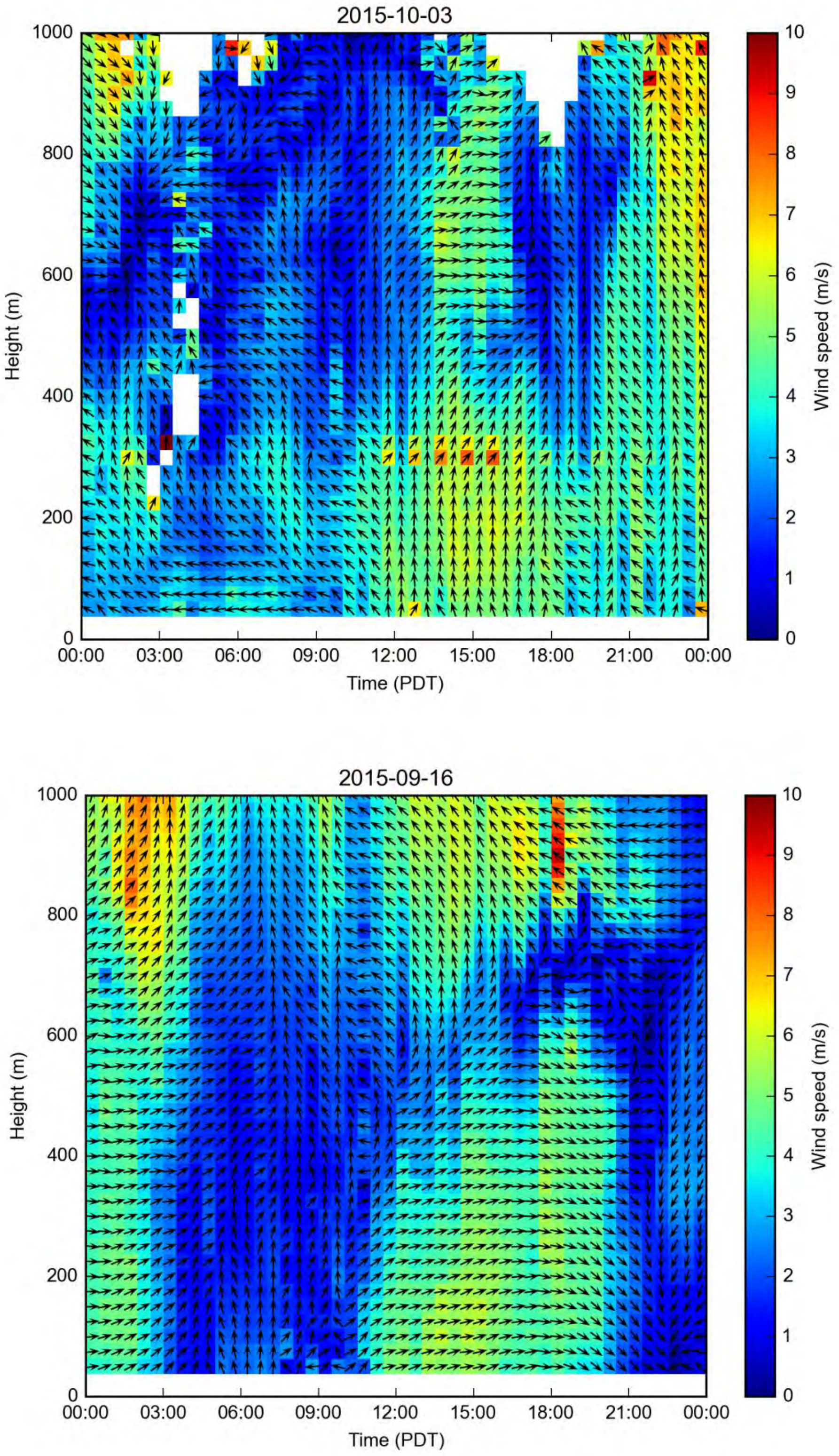

Figure 14. Wind LIDAR raw data at the L1 and L4 site. 30 min averages from 50 to 1000 m measured on October 3, 2015 at the L1 site (upper panel) and on September 16, 2015 at the L4 site (lower panel). The color scale gives the magnitude of the wind speed and the black arrows show the wind direction. Both plots show typical low wind speeds during night-time conditions and stable winds with little altitude variation (wind shear) from 50 to 400m from noon to sunset. See Appendix B for additional data.

4 Results - Total Refinery Measurements

Emission flux measurement results (median values) for the six refineries surveyed during this study are summarized in Table 5. Figure 15 through Figure 17 present graphical representations of measured emissions of alkanes, SO_2, and NO_2. Collectively, refineries in the South Coast Air Basin were found to emit 1130 kg/h of alkanes, 259 kg/h SO_2, 269 kg/h NO_2, 129 kg/h BTEX (of which 18 kg/h is Benzene) and 705 kg/h methane. Section 4.1 through 4.6 below provides detailed description of measured emissions from each studied refinery in the South Coast Air Basin.

Table 5. Summary of emission flux measurements during the 2015 SCAQMD survey. SOF and SkyDOAS results are reported here as median values of all quality assured transects to reduce sensitivity to outliers. *MWDOAS and MeFTIR are inferred values through measured ground level gas mass concentration ratios (See section 2.3 and 2.4). †Excluding eastern tank park that is not owned by Refinery B.

	SOF			*SkyDOAS*				*MWDOAS*		*MeFTIR*
Refinery	**N Days**	**N Meas**	**Alkane Flux** [kg/h]	**N Days**	**N Meas**	**SO_2 Flux** [kg/h]	**NO_2 Flux** [kg/h]	**BTEX Flux*** [kg/h]	**Benzene Flux*** [kg/h]	**CH_4 Flux*** [kg/h]
Refinery A	15	40	269	10	39/34	62	66	24	3.4	167
Refinery B†	5	15	70	10	35	53	31	11	1.1	53
Refinery C	4	15	244	3	9	37	57	37	8.2	142
Refinery D	7	33	164	4	20	17	34	16	1.6	79
Refinery E	7	35	244	7	29/19	53	63	31	2.7	207
Refinery F	4	16	139	2	3	37	18	10	0.8	57
Sum			**1130**			**259**	**269**	**129**	**18**	**705**

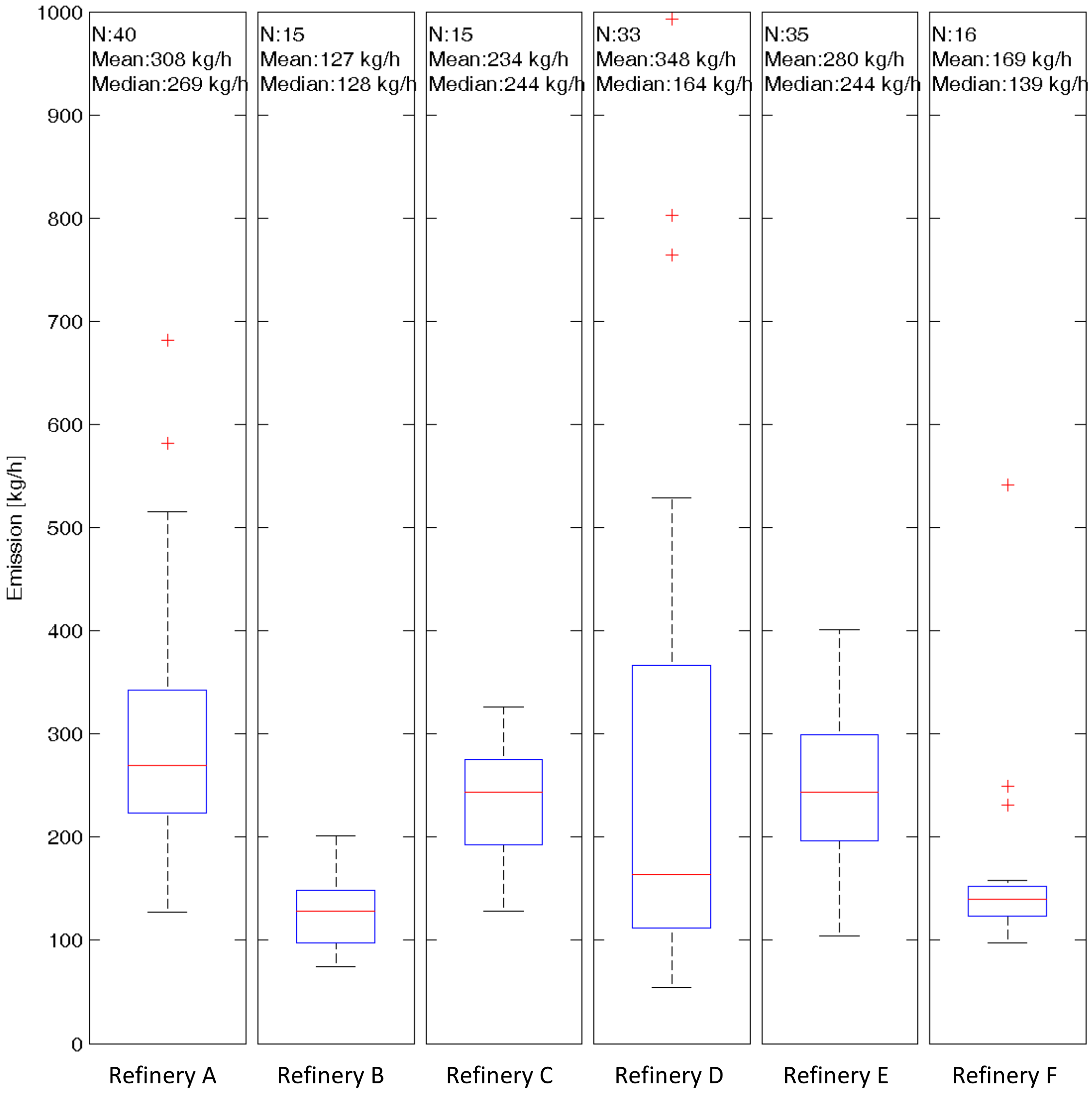

Figure 15. Box-plots of measured alkane emissions (kg/h) from the six refineries surveyed during the 2015 SCAQMD study. Median (50-percentile) values are presented as red bars and upper and lower quartiles as blue boxes with dashed whiskers extending to 1.5 times the inter-quartile range. Outliers beyond the whisker lengths are indicated by red crosses.

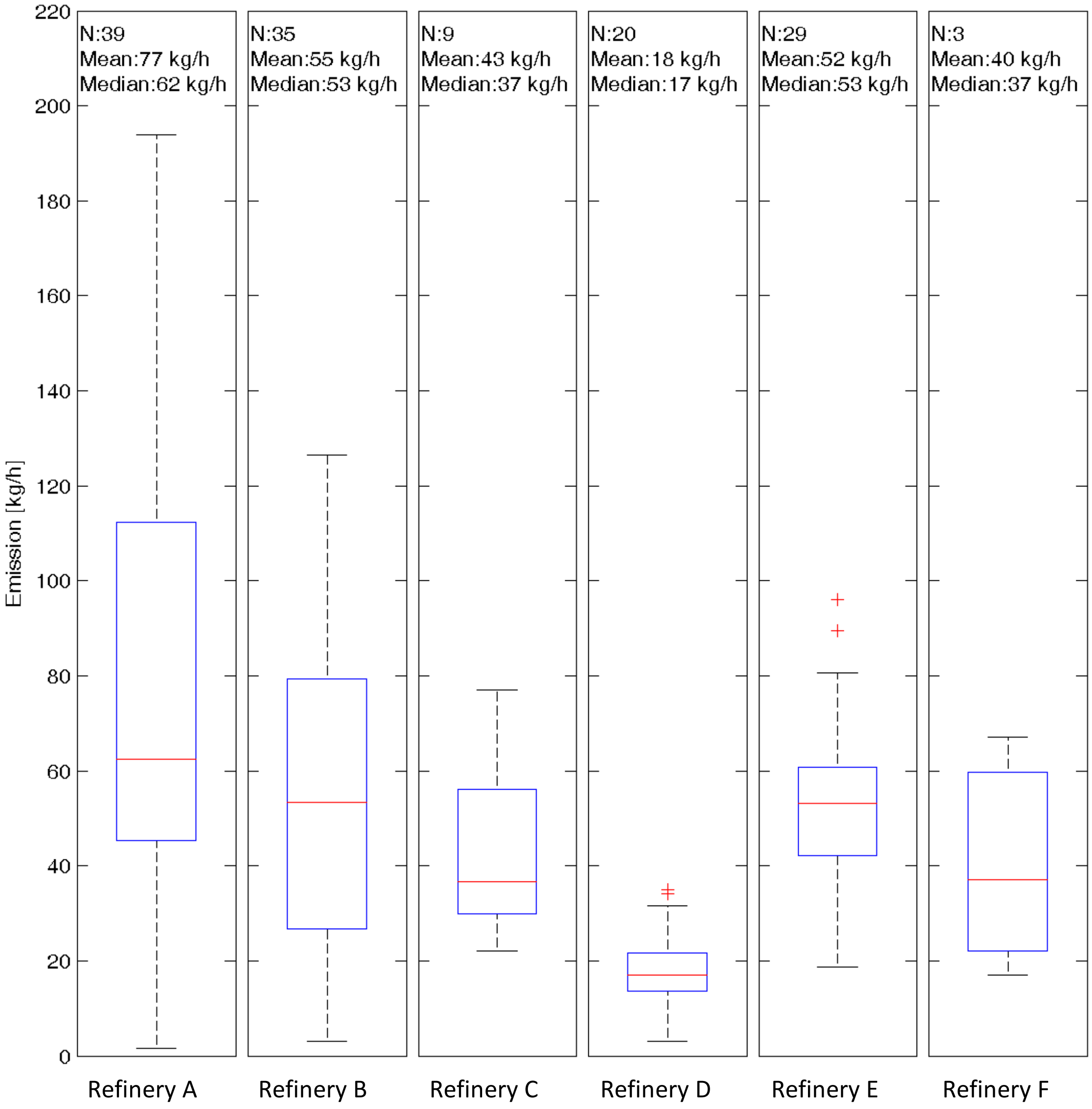

Figure 16. Box-plots of measured SO_2 emissions (kg/h) from the six refineries surveyed during the 2015 SCAQMD study. Median (50-percentile) values are presented as red bars and upper and lower quartiles as blue boxes with dashed whiskers extending to 1.5 times the inter-quartile range. Outliers beyond the whisker lengths are indicated by red crosses.

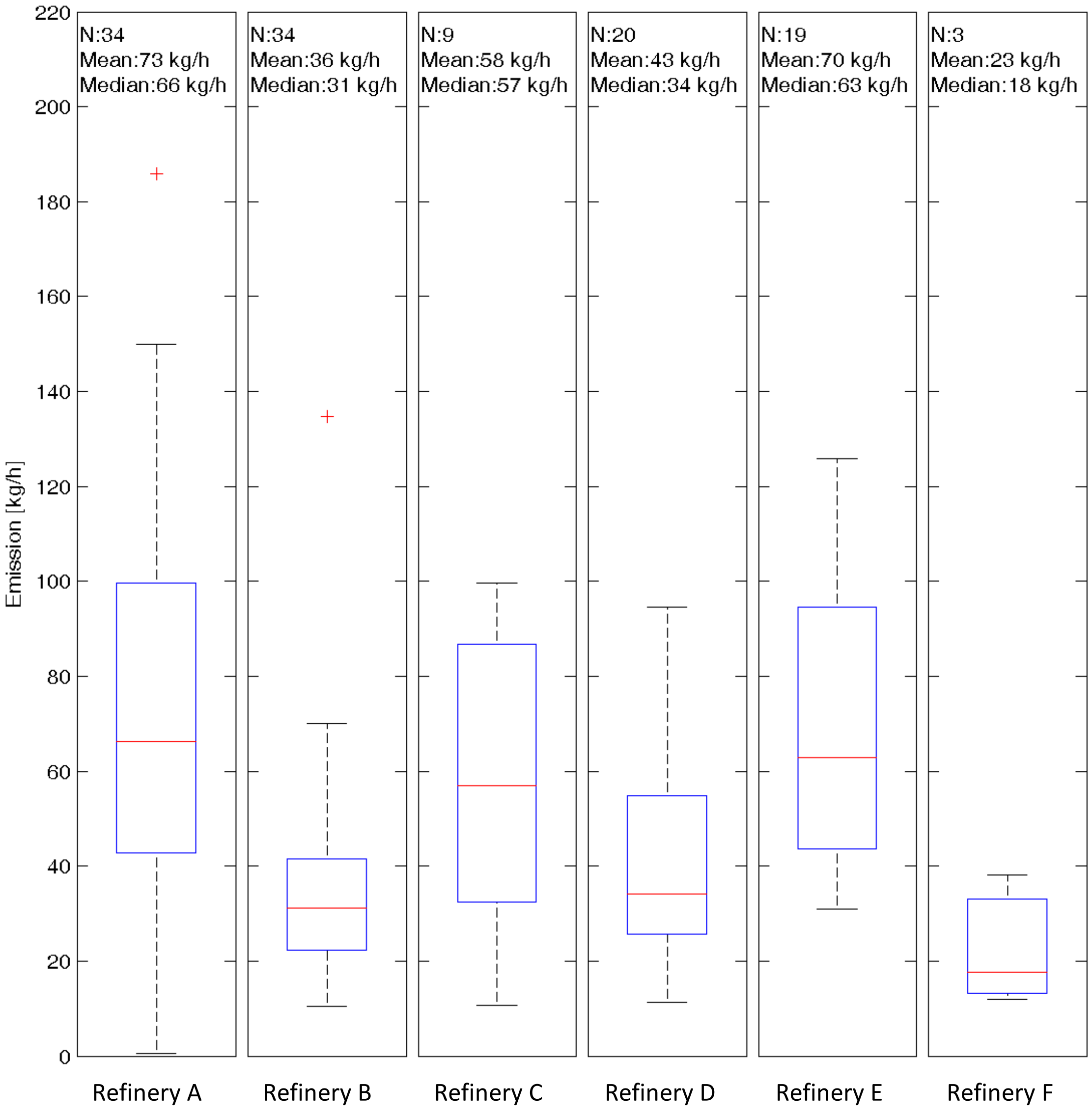

Figure 17. Box-plots of measured NO_2 emissions (kg/h) from the six refineries surveyed during the 2015 SCAQMD study. Median (50-percentile) values are presented as red bars and upper and lower quartiles as blue boxes with dashed whiskers extending to 1.5 times the inter-quartile range. Outliers beyond the whisker lengths are indicated by red crosses.

4.1 Refinery A

At Refinery A (crude oil capacity 257 kBPD (California Energy Commission 2016)) 15 measurement days of total emissions have been carried out and additionally one week of measurements inside the facility (see Section 5) through a collaboration between the refinery and SCAQMD.

The measurements were conducted over a period of eleven weeks, stretching from August 28 to November 10. Note that, typically, the number of successful measurements for each day varies considerably depending on acceptable solar- and wind conditions, interfering background levels and instrument availability. To accurately compensate for incoming background plumes, it was necessary to drive around the targeted facility for multiple times (see example in Figure 18), which is time-consuming.

Wind information for flux calculations were provided by a wind LIDAR (50-400 m average) right across the refinery's fence-line. This wind data was complemented with information collected by a 10 m wind station (scaled to match 50-400 m LIDAR) operated inside Refinery A. Typical wind velocities and direction at these locations were 4-5 m/s and 300°N, respectively (see Figure 19).

4.1.1 Alkanes (non-methane)

Alkane emissions from Refinery A were measured with the SOF during 15 different days from August 29 to November 10, 2015 (see Table 6). Daily means varied from 215 kg/h (September 5) to over 800 kg/h (October 29). The grand total average and standard deviation of all 40 quality assured transects amount to 308±113 kg/h. The median value was 269 kg/h. Histograms of all transects (Figure 20) show a sharp peak at around 250 kg/h and a "tail" of measurements above 500 kg/h. Most transects show a typical column peak directly downwind of the southern tank park (especially downwind of the large reservoir and tank-16) and of the process area (Figure 18).

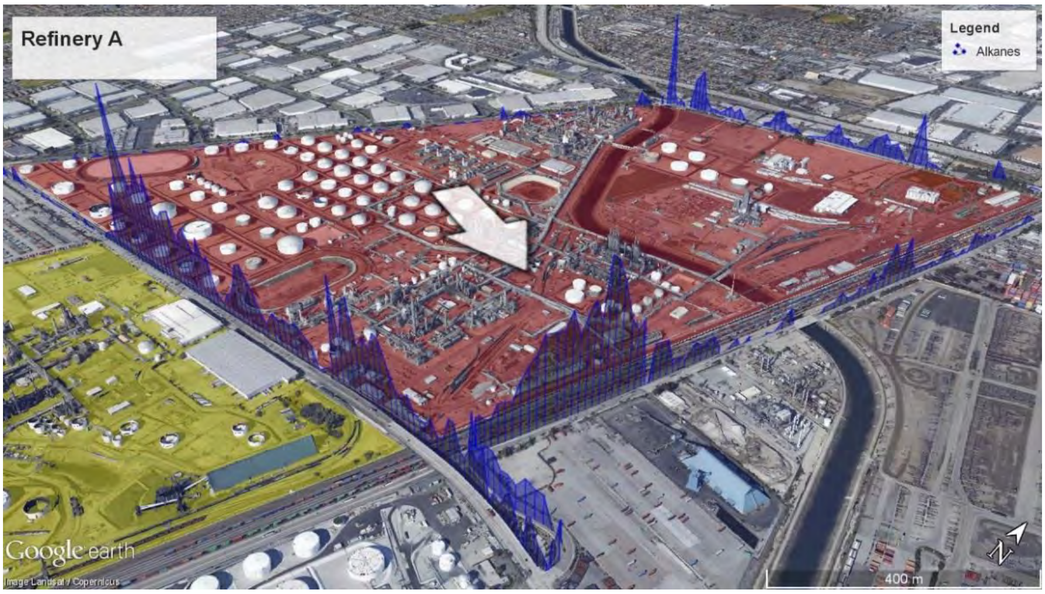

Figure 18. Example of SOF measurements around Refinery A (red area) conducted on September 5, 2015, from 15:20 to 15:37. The height of the blue line is proportional to the amount of alkanes in the gas column (i.e. 10 m is equivalent to 1 mg/m^2; max measured value was 64 mg/m^2). The wind direction is indicated by the white arrow. Average wind speed during this measurement was 6 m/s. Emissions on the upwind side of the facility were subtracted from the downwind side in order to obtain emissions from within the measured area. This particular transect measured 267 kg/h of Alkanes from Refinery A.

Table 6. Summary of SOF alkane measurements for Refinery A. *Single measurement.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150829	144942 -173531	3	413.1±88.6	5.4-7.4	289-295
150902	142535 -154524	3	319.2±74.7	4.7-5.4	305-310
150903*	130746 -131654	1	271.8	3.8	136
150904	134638 -154706	3	226.8±45.2	3.9-5.0	193-199
150905	112732 -165808	7	214.9±84.2	3.1-6.0	181-295
150906	135041 -160653	3	304.7±76.8	2.7-5.5	262-299
150907	142422 -164733	3	223.8±85.7	3.9-7.0	284-285
150908	111515 -123733	2	322.0±223.7	2.6-2.6	272-323
151003	135421 -151958	2	281.8±70.9	4.9-5.2	174-191
151010*	100622 -102546	1	220.8	2.2	65
151018*	143919 -145556	1	281.5	3.7	188
151020	142108 -154446	4	333.5±165.7	4.2-6.0	276-298
151029	110714 -115044	2	866.0±260.3	7.3-7.3	313-316
151107	103907 -114442	3	265.5±38.6	2.7-4.1	17-38
151110	142726 -145648	2	260.6±29.7	9.8-10.1	253-263
Average±SD	**-**	**(total 40)**	**308±113 (37%)**	**-**	**-**
Median	**-**	**(total 40)**	**269**	**-**	**-**

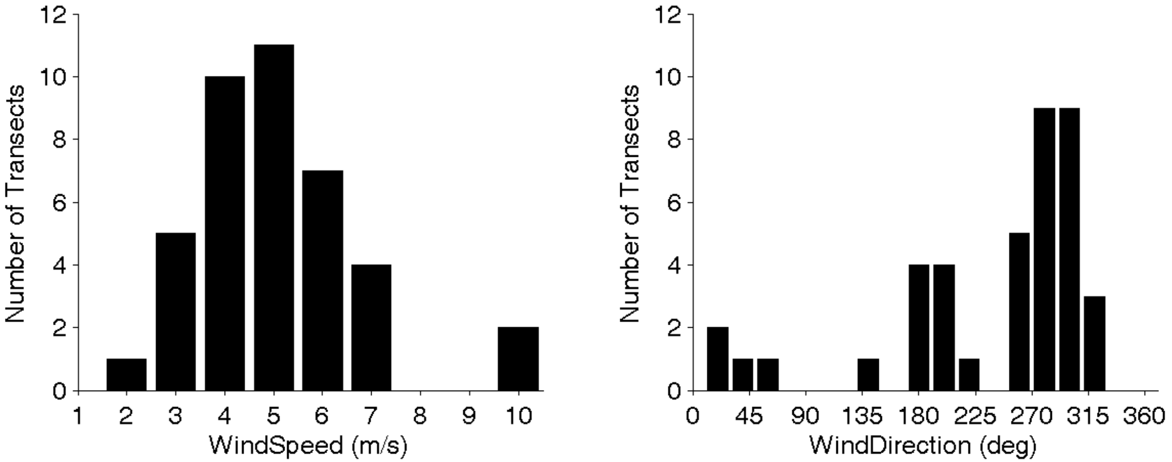

Figure 19. Histograms of wind speed (left) and wind direction (right) for all SOF measurements at Refinery A during the 2015 SCAQMD survey.

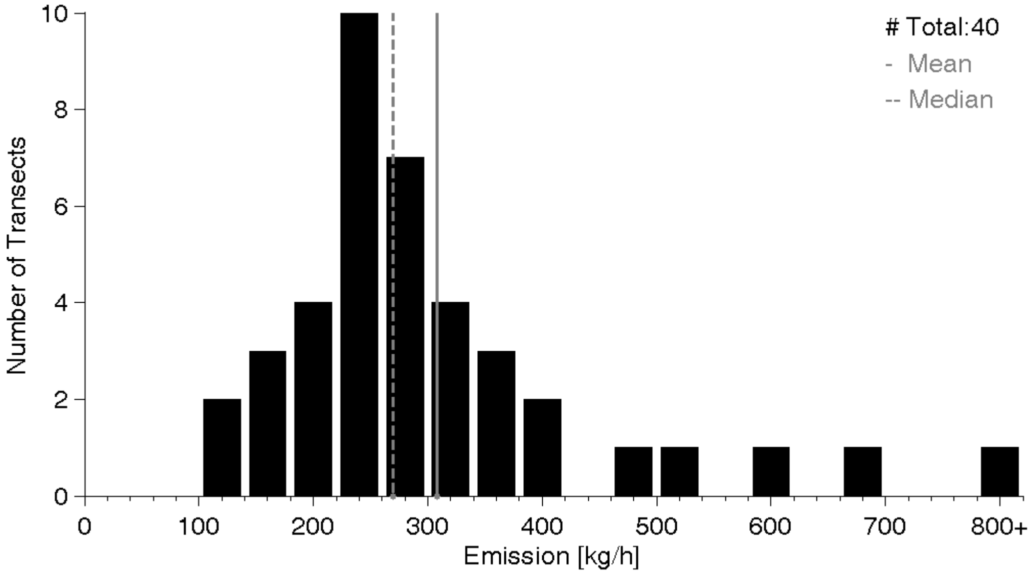

Figure 20. Histogram of all SOF measurements at Refinery A during the 2015 SCAQMD study. The last bin, denoted '800+', contains all data points above 800 kg/h. The median and average values are indicated as dashed and solid gray lines, respectively.

4.1.2 SO_2 and NO_2

SO_2 and NO_2 emissions from Refinery A facility were measured for 10 measurement days during the campaign, from August 29 to November 30 2015 (some of the transects can be seen in Figure 21). Summaries and histograms of SkyDOAS emission measurements are presented in Table 7, Table 8, Figure 22 and Figure 23. Emissions averaged 73 and 77 kg/h for NO_2 and SO_2, respectively. Median values for these two gaseous pollutants were 66 (NO_2) and 62 kg/h (SO_2). The precise origins of the plumes cannot be decided from these measurements, although the Cogen-plant seems to be a matching source for some of the NO_2 plumes.

Figure 21. Transects of plumes originating from Refinery A. NO_2 (pink line) and SO_2 (brown line) were impacted by westerly winds. Conversely, BTEX (blue line) and alkane (yellow line) plumes were measured in the presence of northerly winds. The column thickness for both NO_2 and SO_2 is reported on the same scale (max NO_2 = 3 mg/m^2 flux NO_2 = 114 kg/h, max SO_2 = 11 mg/m^2 flux SO_2 = 46 kg/h). Alkanes and BTEX columns are scaled separately for better visibility (max BTEX = 0.25 mg/m^3, max alkanes = 1.95 mg/m^3). The examples presented here are single transects made on September 2 and on September 19, 2015.

Table 7. Summary of Refinery A NO_2 measurements.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150829	144857 -172703	3	57.0±69.3	5.4-7.6	285-296
150902	140707 -151247	3	59.3±49.8	4.4-6.5	300-314
150903	125302 -134150	2	119.7±42.8	4.1-4.5	115-131
150904	134011 -154225	4	76.2±26.5	4.3-4.9	185-200
150905	113143 -161302	5	67.9±22.9	3.5-6.0	180-295
150906	111801 -165522	5	54.3±18.8	1.8-4.3	266-302
150907*	151830 -152142	1	49.6	5.0	286
150908	113158 -123350	2	26.8±2.1	2.5-2.7	258-323
151029	105412 -150635	7	105.3±49.9	7.0-11.0	275-324
151030	112454 -161144	2	65.7±92.3	2.7-5.0	142-199
Average±SD	**-**	**(total 34)**	**72.8±45.1 (61.9%)**	**-**	**-**
Median	**-**	**(total 34)**	**66.3**	**-**	**-**

Table 8. Summary of Refinery A SO_2 measurements.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150829	144857 -173037	3	114.5±69.1	5.4-7.6	285-296
150902	140726 -154429	4	59.4±40.2	4.4-6.5	298-314
150903	125302 -134150	3	44.2±37.0	2.4-4.5	116-133
150904	134011 -154225	4	66.5±34.2	4.3-4.8	185-200
150905	104604 -161046	7	41.4±28.3	2.1-6.0	103-295
150906	111801 -165332	5	73.2±35.1	1.8-4.4	266-301
150907	134339 -152051	2	54.0±44.8	3.8-5.0	264-286
150908	113244 -123504	2	60.6±11.5	2.6-2.7	259-318
151029	105412 -150635	6	125.5±36.3	6.9-11.0	275-325
151030	112531 -161409	3	129.9±67.3	2.7-5.0	142-202
Average±SD	**-**	**(total 39)**	**77.1±42.0**	**-**	**-**
Median	**-**	**(total 39)**	**62.4**	**-**	**-**

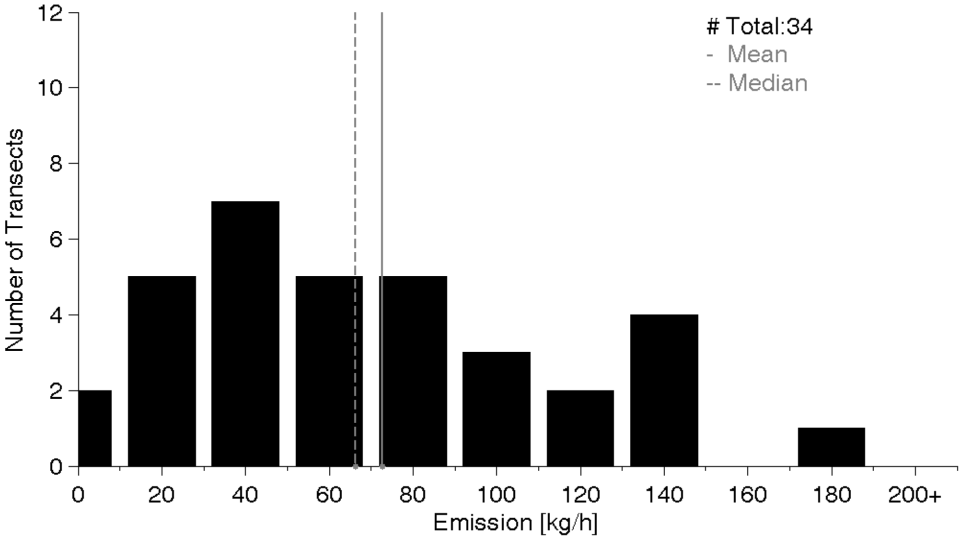

Figure 22. Histogram of all SkyDOAS NO_2 measurements at the Refinery A during the 2015 SCAQMD survey. The last bin, denoted ‘200+’, contains all data points above 200 kg/h. The median and average values are indicated as dashed and solid gray lines, respectively.

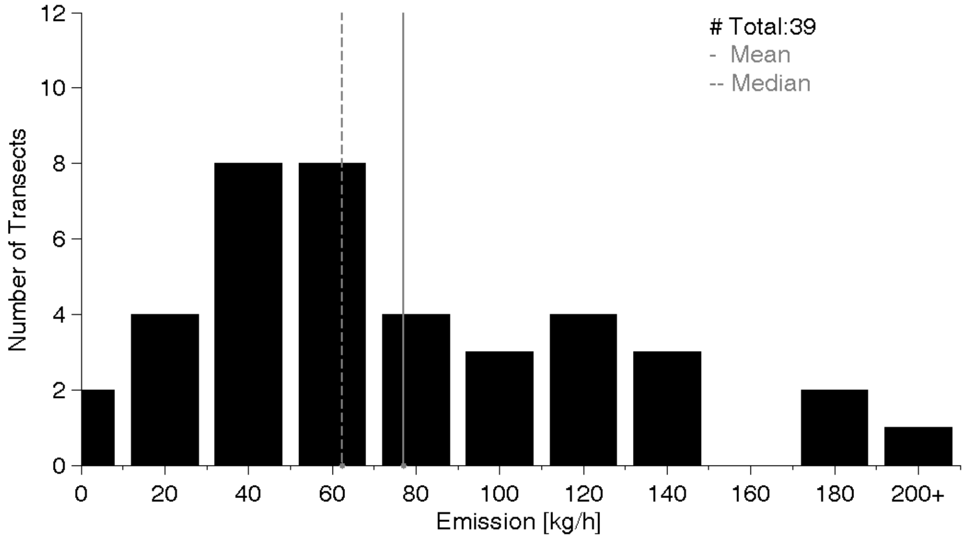

Figure 23. Histogram of all SkyDOAS SO_2 measurements at Refinery A during the 2015 SCAQMD survey. The last bin, denoted ‘200+’, contains all data points above 200 kg/h. The median and average values are indicated as dashed and solid gray lines, respectively.

4.1.3 BTEX

The fraction of BTEX compounds present in the measured alkane plumes emitted from Refinery A was measured either in the late evening or early morning when plumes are closer to the ground. This fraction is calculated by combining BTEX measurements from MWDOAS and alkane measurements from MeFTIR. To determine the source of the plume, wind directions from Refinery A's 10 m mast were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured along two roads depending on wind direction. Results for these measurements are shown in Table 9. The average mass fraction of BTEX to alkanes was 0.087 or 8.7%. The average flux of BTEX can be calculated by multiplying this value by the total alkane flux as measured by the SOF-technique. The average mass fraction of benzene to alkanes was 1.3% and the benzene flux can be calculated in the same way as above.

Table 9. Summary of MWDOAS BTEX measurements at Refinery A. *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	221347-221949	7.8	0.98	2.3	323
150919	231317-231938	5.4	0.92	1.5	329
150921	051934-052525	12.8	1.7	1.8	73
150922	062223-063032	13.4	1.7	2.4	110
150922	073305-074108	6.8	0.65	1.9	81
150922	051356-051759	3.6	0.21	2.1	83
150922	183651-184148	11.2	2.7	2.1	181
Average±SD	-	**8.7±3.8**	**1.3±0.8**	-	-

4.1.4 Methane

The average fraction of methane to total non-methane alkanes in the plume originating from Refinery A was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of correlating alkanes. To determine the source of the plume, wind directions from Refinery A's 10 m mast were used (wind speed is irrelevant for these measurements). Methane measurements were conducted during different times of the day and a summary of these results is shown in Table 10. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux as measured by SOF provides an estimate of the methane flux from the refinery. The average methane-to-alkanes mass fraction for Refinery A was 0.62.

Table 10. Summary of MeFTIR methane measurements at the Refinery A. *Methane/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction* [%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	221206 -231956	2	44	1.6-2.2	332-347
150922	062220 -063024	1	41	1.9	88
151018	144244 -145057	1	64	3.4	177
151020	122426 -154604	6	71	2.4-5.7	135-312
151029	105144 -150803	6	67	4.0-11.3	285-328
151030	113932 -155450	3	57	1.3-4.0	186-289
Average±SD	**-**	**(total 19)**	**62±25**	**-**	**-**

4.2 Refinery B

Refinery B (crude oil capacity (together with Refinery C) 139 kBPD (California Energy Commission 2016)) is located just south of Refinery A, see Figure 24. This site was frequently surveyed in combination with the Refinery A facility. However, due to the proximity to other sources, such as Tank Farm G and Refinery A, there is an increased possibility of interference depending on wind direction and therefore there were fewer valid emissions measurements. Note that the surveyed area also included a crude tank park on the west side that is not owned by Refinery B. Emission contributions from this crude tank park have been accounted for in the data post-processing (see below).

Wind information from the wind LIDAR (L1, 0-400 m average) was mainly used for the flux calculations. This was complemented by Refinery A's 10 m wind station data (scaled to match 0-400 m LIDAR) when needed. Typical wind directions and velocities during the measurements were 4 m/s and 180 or 270°N, see Figure 25.

4.2.1 Alkanes (non-methane)

Alkane emissions from Refinery B were measured with SOF during five non-consecutive days from September 4 to November 10, 2015, see Table 11 and discussion above. Daily means varied from 83 kg/h (September 6) to 173 kg/h (September 7). The grand total average and median for all 15 quality assured transects were 127±23 kg/h and 128 kg/h, respectively. Histogram of all transects shows a "compact" distribution at around 130 kg/h with no outliers, see Figure 26.

Measurement transects typically showed the presence of two peaks, one downwind the western side and another downwind the eastern side, see Figure 24. Based on transects where a complete separation between the two sides/peaks was possible (during S to SW winds), 45% of the emissions were attributed to the western side and 55% to the eastern side. The 55 correction factor has been applied in the survey mean/median calculations (e.g. Table 5), but not for daily means (e.g. Table 11) or individual measurements (e.g. Figure 26). The correction was done in order to exclude the emissions that should not be attributed to Refinery B when inter-comparing the different refineries in this report.

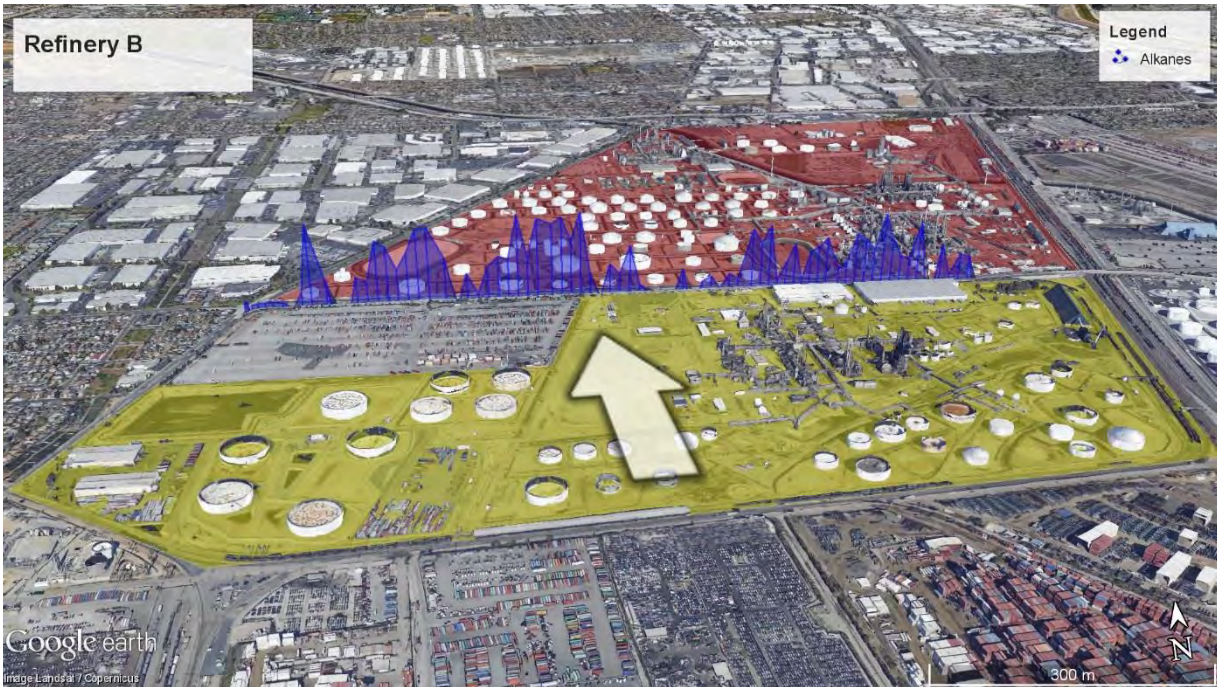

Figure 24. Example of SOF measurements conducted at Refinery B (yellow area) on September 4, 2015, 16:10-16:13. The alkane column is shown as a blue line with apparent height proportional to the gas column (10 m equivalent to 1 mg/m^2, max 32 mg/m^2). Wind direction during the measurements is indicated by the white arrow. The average wind speed during these particular measurements was 3.2 m/s. Emissions on the upwind side are insignificant and not shown in this figure. Emissions resulting from this particular transect were estimated at 107 kg/h.

Table 11. Summary of SOF alkane measurements for Refinery B (including the crude tank park west of the refinery).

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150904	134712 -165939	6	116.3±23.6	3.2-5.5	178-253
150905	153737 -171908	3	121.9±7.4	5.8-6.1	268-279
150906	124744 -163755	2	83.2±13.0	3.4-3.7	165-279
150907	140251 -150726	2	172.8±39.8	3.9-4.3	284-285
151110	143118 -145107	2	161.5±17.6	9.4-10.2	255-255
Average±SD	**-**	**(total 15)**	**127±23 (18%)**	**-**	**-**
Median	**-**	**(total 15)**	**128**	**-**	**-**

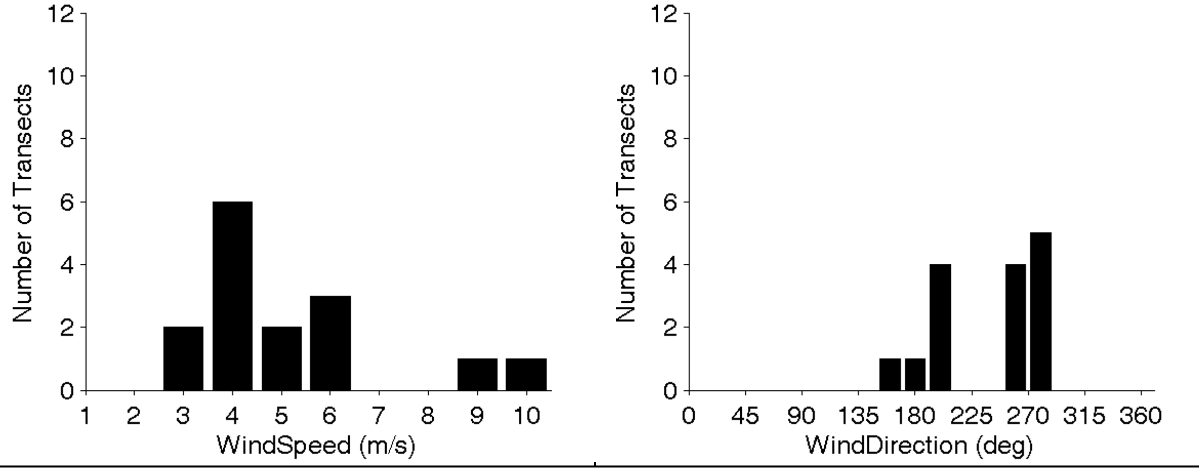

Figure 25. Wind histograms at Refinery B summarizing all wind speed (left) and wind direction (right) measurements conducted during the 2015 SCAQMD study.

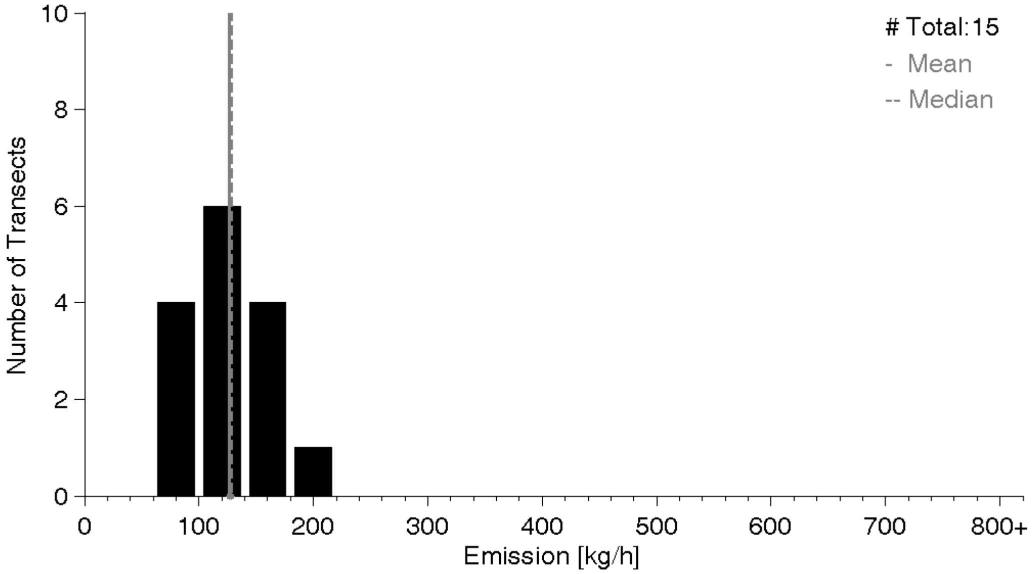

Figure 26. Histogram of all SOF measurements conducted at Refinery B (including crude tank park west of the refinery) during the 2015 SCAQMD study. The median and average values are shown as dashed and solid gray lines, respectively.

4.2.2 SO_2 and NO_2

SO_2 and NO_2 emissions were measured for 10 measurement days during the campaign, from August to October, 2015. Figure 27 shows examples of measurement transects conducted on September 2 and September 19, 2015. Summaries and histograms of SkyDOAS emission measurements are presented in Table 12, Table 13, Figure 28 and Figure 29. In this case NO_2 emissions averaged 36 kg/h and SO_2 55 kg/h. Median values for these two gaseous pollutants were 31 (NO_2) and 53 kg/h (SO_2).

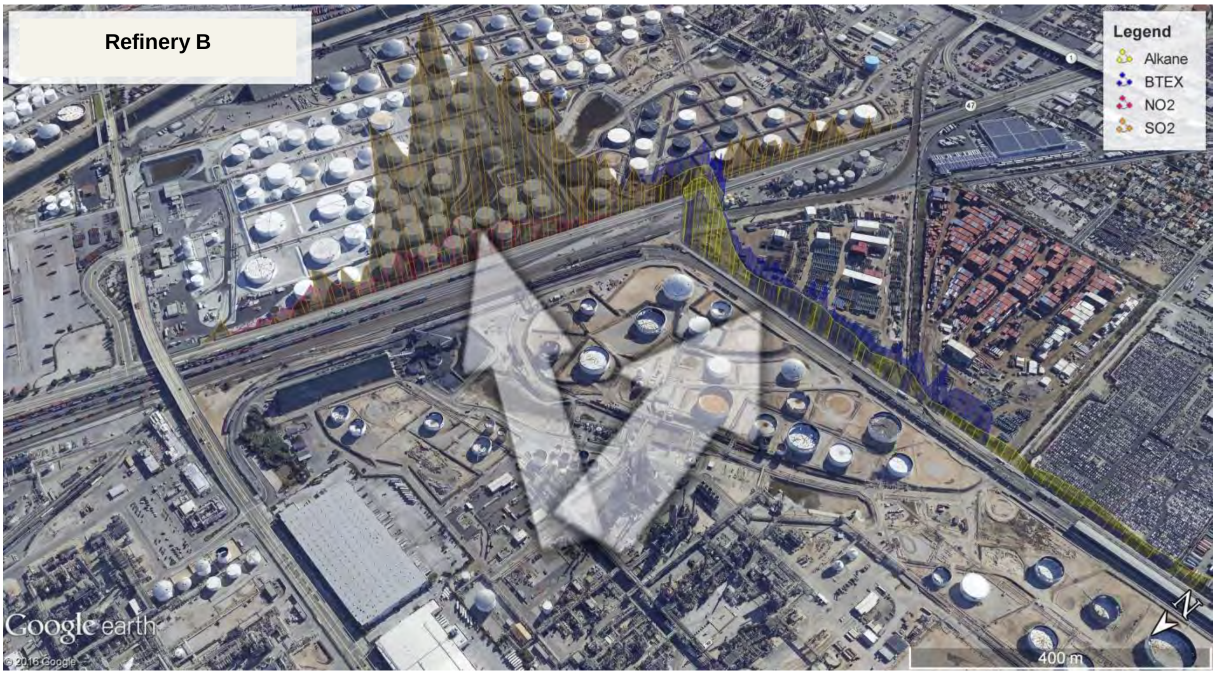

Figure 27. Transects of plumes originating from Refinery B. NO_2 (pink line) and SO_2 (brown line) were impacted by westerly winds (4.3 m/s). Conversely, BTEX (blue line) and alkane (yellow line) plumes were measured in the presence of northerly winds. The column thickness for both NO_2 and SO_2 is reported on the same scale (max NO_2 = 5.6 mg/m^2, flux NO_2 = 11.7 kg/h, max SO_2=25 mg/m^2, flux SO_2 = 68.2 kg/h). Alkanes and BTEX columns are scaled separately for better visibility (max BTEX = 0.03 mg/m^3, max alkanes = 0.36 mg/m^3). The examples shown here were collected on September 8 and on September 19, 2015.

Table 12. Summary of NO_2 measurements at Refinery B.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150829	152225 -152509	1	31.8	7.0	295
150902	132957 -141007	2	21.8±0.7	5.0-6.3	303-315
150903	130123 -133346	2	30.7±15.3	3.9-4.9	106-148
150904	134837 -152937	4	41.2±8.3	3.7-4.9	193-203
150905	103515 -171321	11	27.7±9.2	1.0-6.2	112-286
150906	130316 -163207	4	52.6±12.9	2.6-4.5	162-286
150907	132433 -161506	4	28.5±8.9	3.5-6.1	242-285
150908	110353 -124134	3	57.7±67.2	2.0-8.8	313-327
151029	121217 -121936	1	67.9	7.3	312
151030	114718 -153206	2	19.3±12.6	2.0-4.5	112-193
Average±SD	**-**	**(total 34)**	**35.6±22.4 (62.8%)**	**-**	**-**
Median	**-**	**(total 34)**	**31.2**	**-**	**-**

Table 13. Summary of SO_2 measurements at Refinery B.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150829	152225 -152509	1	126.5	7.0	295
150902	133006 -141007	2	17.9±0.8	5.1-6.3	303-316
150903	130123 -133323	3	34.0±8.6	3.9-4.9	105-150
150904	134828 -152937	4	37.5±20.1	3.7-4.9	193-203
150905	103537 -171321	11	56.1±28.7	1.0-6.2	111-287
150906	130316 -163207	4	78.3±13.5	2.6-4.5	162-286
150907	132433 -161506	4	79.9±18.3	3.5-6.1	242-285
150908	110353 -124134	3	68.9±26.9	2.0-8.8	314-327
151029	121150 -133517	2	14.7±16.5	7.1-7.3	311-313
151030	114718 -115224	1	9.0	2.2	114
Average±SD	**-**	**(total 35)**	**54.5±21.5 (39.3%)**	**-**	**-**
Median	**-**	**(total 35)**	**53.4**	**-**	**-**

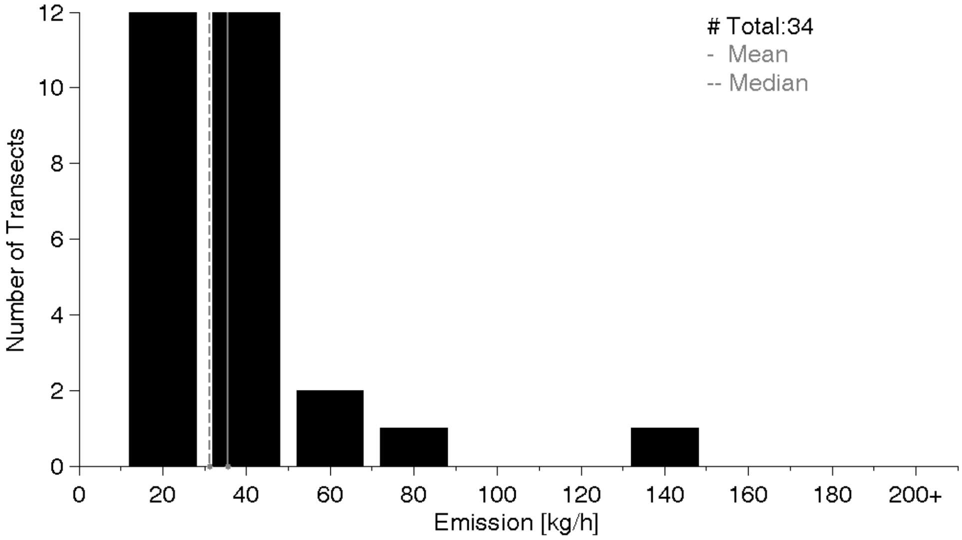

Figure 28. Histogram of all SkyDOAS NO_2 measurements at the Refinery B during the 2015 SCAQMD study. The median and average values are indicated as dashed and solid gray lines, respectively.

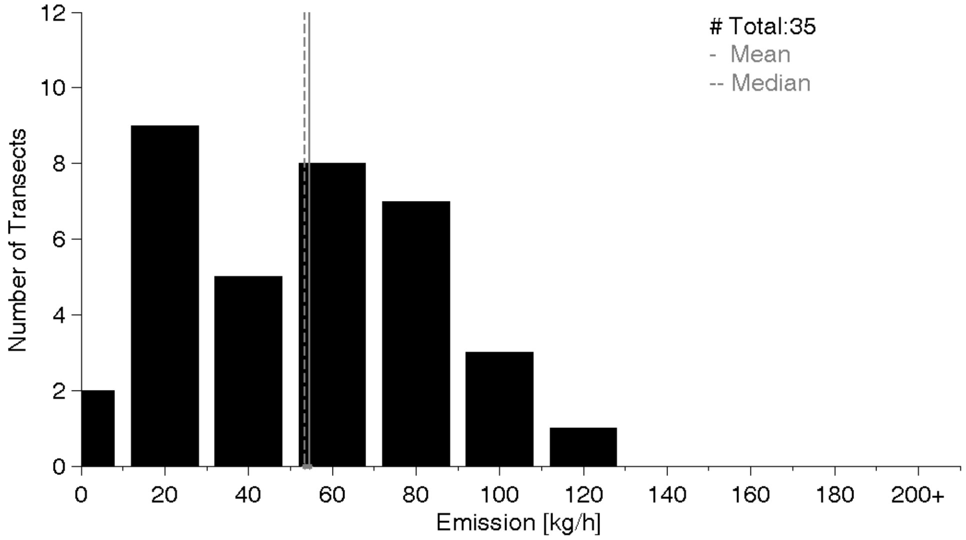

Figure 29. Histogram of all SkyDOAS SO_2 measurements taken at Refinery B during the 2015 SCAQMD study. The median and average values are indicated as dashed and solid gray lines, respectively.

4.2.3 BTEX

The fraction of BTEX compounds present in the measured alkane plumes emitted from Refinery B was measured either in the late evening or early morning when the plume was closer to the ground. This fraction is calculated by combining BTEX level measurements from MWDOAS and alkane measurements from MeFTIR. To determine the source of the plume, wind directions from Refinery A's 10 m mast were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured along two roads depending on wind direction. A summary of these measurements is shown in Table 14 and an example of a plume transect illustrated in Figure 27.

The average mass fraction of BTEX to alkanes was 0.084 or 8.4%. The average flux of BTEX can be calculated by multiplying this value by the total alkane flux as measured by the SOF-technique. The average mass fraction of benzene to alkanes was 0.9% and the benzene flux can be calculated in the same way as above.

Table 14. Summary of MWDOAS BTEX measurements at Refinery B. *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	222903-223809	11.3	0.18	2.5	345
150919	232406-232758	5.5	0.75	2	325
150919	220447-220915	7.3	0.71	2	302
150921	053955-054412	6.5	1.9	0.9	64
150922	070636-071237	11.4	0.9	1.5	64
Average±SD		**8.4±2.8**	**0.9±0.6**		

4.2.4 Methane

The average fraction of methane to total non-methane alkanes in the plume originating from Refinery B was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of correlating alkanes. To determine the source of the plume, wind directions from Refinery A's 10 m mast were used (wind speed is irrelevant for these measurements). Methane measurements were conducted during different times of the day and a summary of these results is shown in Table 15. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux as measured by SOF provides an estimate of the methane flux from the refinery. The average methane-to-alkanes mass fraction for Refinery B was 0.75.

Table 15. Summary of MeFTIR methane measurements at Refinery B. *Methane/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction*** **[%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	222929 -232735	2	73	2.0-2.6	325-346
151018	145106 -145455	1	91	3.1	171
151020	134959 -162614	3	110	1.6-5.4	163-295
151029	121145 -122309	1	23	4.9	317
151030	112324 -155949	3	53	2.1-4.1	121-188
Average±SD	**-**	**(total 10)**	**75±36**	**-**	**-**

4.3 Refinery C

Refinery C, (crude oil capacity together with Refinery B 139 kBPD, (California Energy Commission 2016)) is located north of the Los Angeles port, see Figure 10. Significant upwind background plumes from the port and oil wells on the west side must be compensated for in the flux calculations. This is done by encircling ('box-measuring') the facility when possible (see example in Figure 18).

Wind information for the flux calculations on September 18, 2015 came from the wind LIDAR (0-400 m average) at position L2, located at the golf course parking lot north of the refinery, see Figure 30. For the other days, wind information from the SCAQMD met station at South Long Beach (SLBH) was used (scaled to match 0-400m LIDAR). See section 3.4 for additional wind analysis. Typical wind speeds and wind directions during the measurements are 3 m/s and 130-320°N, see Figure 31. Winds are generally weak at this site due to the hills on the west side.

4.3.1 Alkanes (non-methane)

Alkane emissions from Refinery C was measured with SOF during four days in the period September 7 to November 4, see Table 16. The daily means varied from 128 kg/h (4 November, single measurement) to over 297 kg/h (29 October). The average emission determined from the 15 quality assured transects was 234±36 kg/h and the median emission was 244 kg/h. Histograms of all transects (Figure 32) show a peak at around 230 kg/h and no extreme outliers. Most transects show a typical column peak directly downwind the north-west tank park and the process area, see Figure 30.

Table 16. Summary of SOF alkane measurements for Refinery C. *Single measurement

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150907	104256 -121838	4	296.5±22.4	2.1-2.9	134-163
150918	133231 -165721	5	200.5±47.1	2.6-3.7	301-323
151022	144739 -161143	5	238.4±31.1	2.9-3.9	170-204
151104*	121336 -122731	1	128.2	2.9	239
Average±SD	**-**	**(total 15)**	**234±36 (15%)**	**-**	**-**
Median	**-**	**(total 15)**	**244**	**-**	**-**

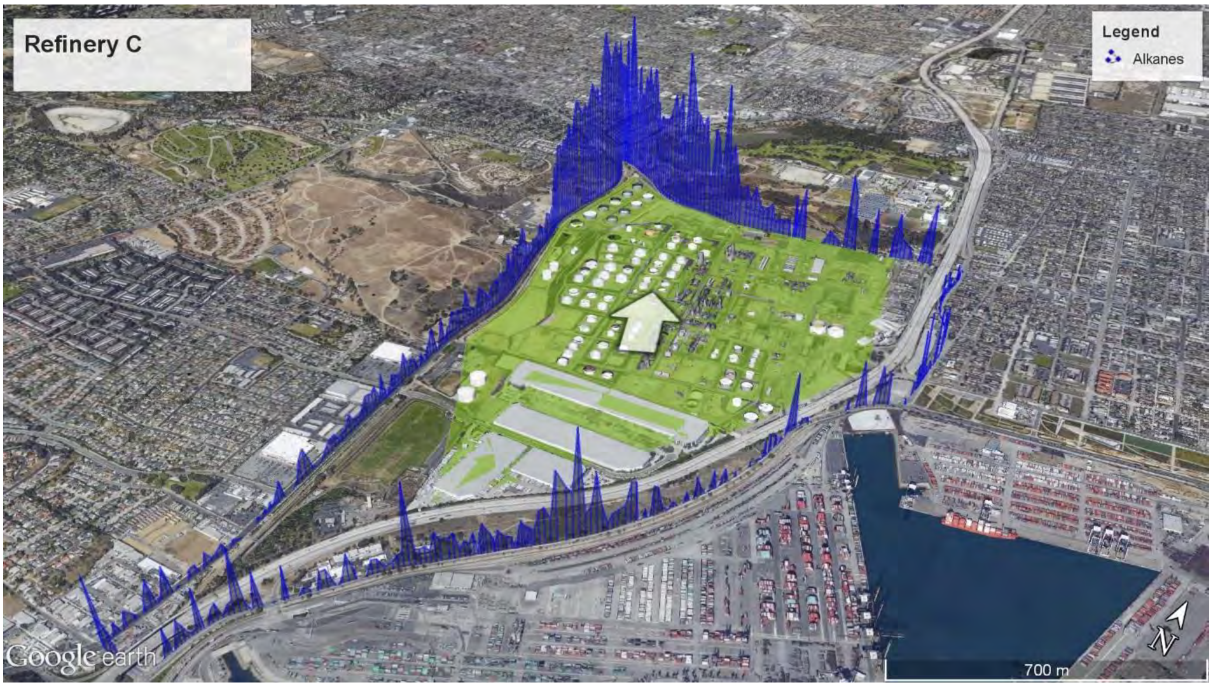

Figure 30. Example of a SOF ‘box’ measurement of the Refinery C (green area) 7 September 2015, 11:57-12:18. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m^2, max 76 mg/m^2). Wind direction during the measurement is indicated by the white arrow. Average wind speed was 2.9 m/s for this particular measurement. Emissions on the upwind side (from LA harbor) are subtracted from the downwind side in order to get emissions from within the box. This particular transect measured 285 kg/h from Refinery C.

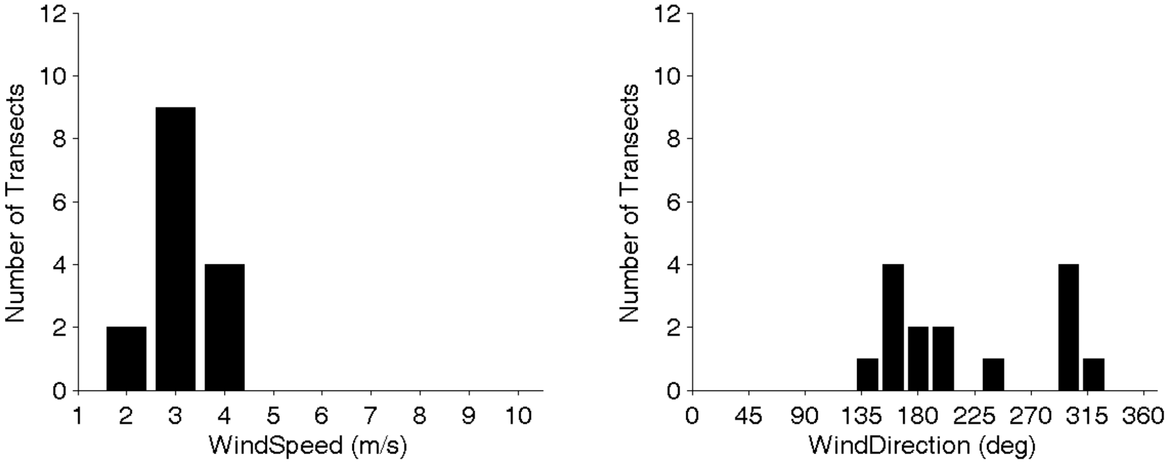

Figure 31. Wind histograms at Refinery C of wind speed (left) and wind direction (right) for the SOF measurements during the SCAQMD survey 2015.

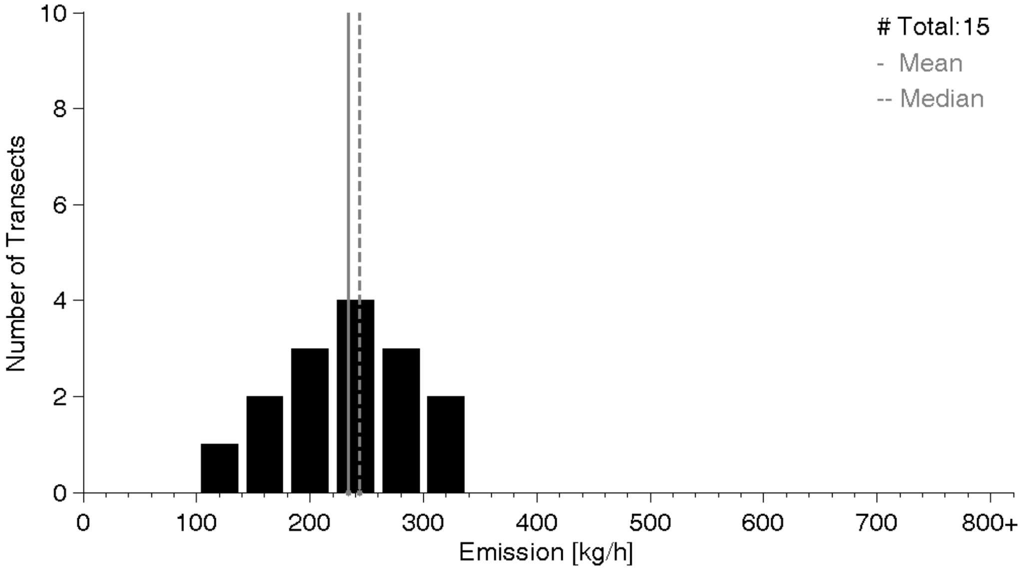

Figure 32. Histogram of all SOF measurements at Refinery C during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.3.2 SO_2 and NO_2

SO_2 and NO_2 emissions from the facilities were measured for three measurement days during the campaign, twice in September and once in November. Summaries and histograms of SkyDOAS emission measurements are presented in Table 17, Table 18, Figure 34 and Figure 35. An example of a measurement is shown in Figure 33. Emissions averaged 58 and 43 kg/h and medians were 57 and 37 kg/h for NO_2 and SO_2 respectively.

Table 17. Summary of NO_2 measurements at Refinery C.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150907	95140 -121752	4	44.7±38.6	1.5-4.0	167-320
150918	134001 -153244	4	78.0±14.4	2.1-3.9	309-329
151104	121533 -122359	1	34.1	4.1	265
Average±SD	**-**	**(total 9)**	**58±29 (50%)**	**-**	**-**
Median	**-**	**(total 9)**	**57**	**-**	**-**

Table 18. Summary of SO_2 measurements at Refinery C.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150907	95122 -121752	4	48.7±21.9	1.4-4.2	166-310
150918	134212 -153244	4	39.5±16.4	1.9-3.9	309-331
151104	121405 -122616	1	30.7	4.1	271
Average±SD	**-**	**(total 9)**	**43±19 (45.4%)**	**-**	**-**
Median	**-**	**(total 9)**	**37**	**-**	**-**

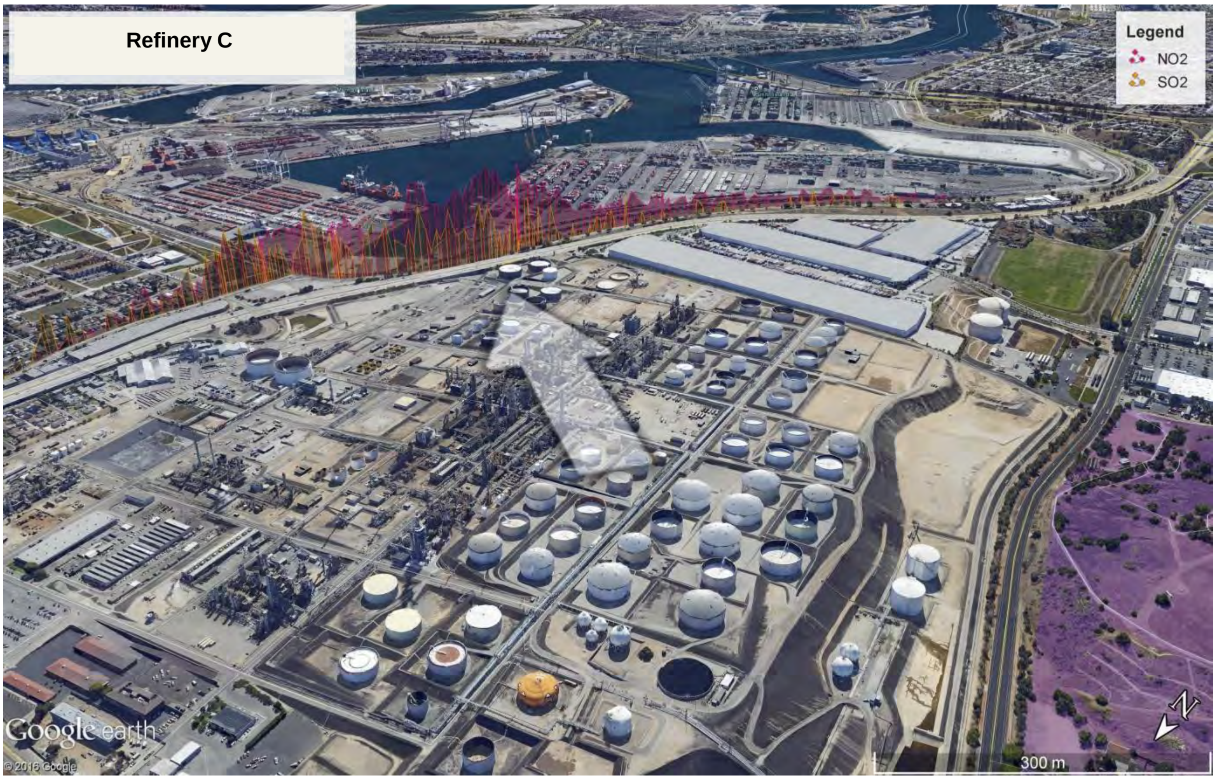

Figure 33. Transects of plumes originating from Refinery C. the NO_2 (pink) and SO_2 (brown) plume from Refinery C in north-westerly wind (3.7 m/s). Max NO_2 = 9.5 mg/m^2, flux NO_2 = 81 kg/h, max SO_2=5.6 mg/m^2, flux SO_2 = 37.5 kg/h Data from September 18 2:59 PM.

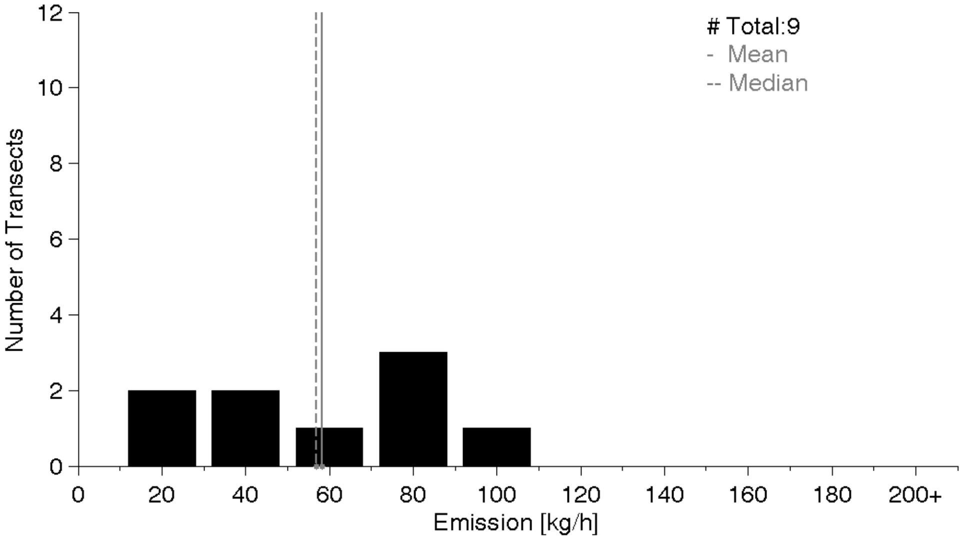

Figure 34. Histogram of all SkyDOAS NO_2 measurements at Refinery C during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

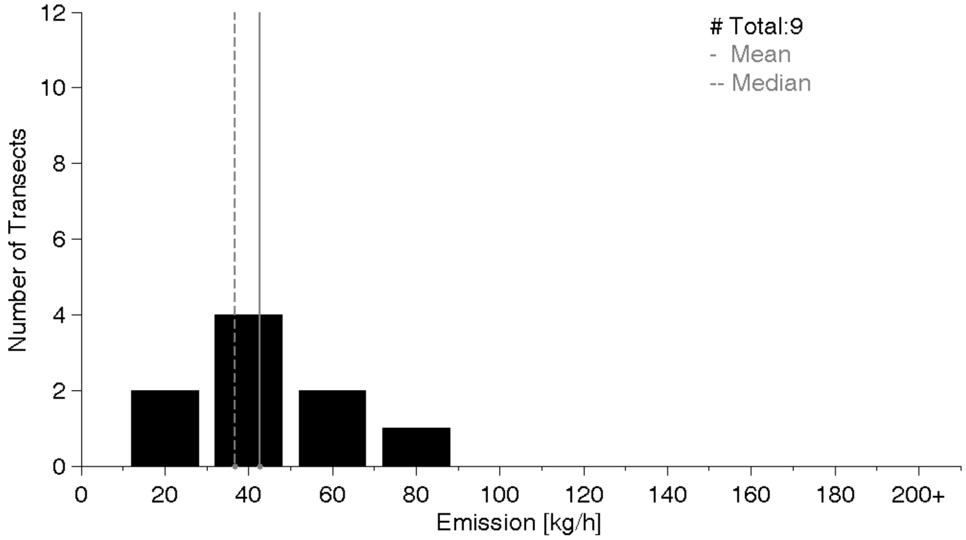

Figure 35. Histogram of all SkyDOAS SO_2 measurements at Refinery C during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.3.3 BTEX

The BTEX mass fraction to alkane in the plumes emitted from Refinery C were measured either in the late evening or early morning when the plumes were closer to ground. The mass fraction is acquired by combining BTEX level measurements from MWDOAS and alkane measurements from MeFTIR. To determine the source of the plume, wind directions from the SCAQMD-SLBH wind station were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured on different public roads surrounding the facility, depending on wind direction. The measurements are shown in Table 19.

The average mass fraction of BTEX to alkanes was 15.1%. The average flux of BTEX can be calculated by multiplying this figure with the total alkane flux as measured by the SOF-technique. The average fraction of benzene to alkanes was 3.4% and the benzene flux can be calculated in the same way as above. The plumes sampled during the measurement at Refinery C were weak and the low levels of both alkanes and BTEX causes a higher degree of uncertainty than usual in the mass ratio determination.

Table 19. Summary of MWDOAS BTEX measurements at Refinery C . *BTEX/alkane fraction.

Day [yymmdd]	Time span [hhmmss-hhmmss]	BTEX Fraction* [%]	Benzene Fraction* [%]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150918	220402-221009	12.6	1.4	2.5	323
151102	155155-155401	8.3	3.2	3.4	235
151102	150946-152855	13.8	2.4	3.5	254
151102	154248-154634	16.1	3.1	3.2	246
151104	160717-162206	24.8	6.7	3.3	275
Average±SD	-	**15.1±6.1**	**3.4±2.0**		

4.3.4 Methane

The average fraction of methane to total non-methane alkanes in the plume originating from Refinery C was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of correlating alkanes measured simultaneously. Wind information from either LIDAR in position L2 or SCAQMD-SLBH was used, only wind direction, not wind speed matters for these measurements. Measurements were made both during the day and in late evenings and are shown in Table 20. Applying the measured fence-line ground level methane-to-alkane mass fraction to the by SOF measured alkane flux, gives an estimate of the methane flux from the refinery. The average methane-to alkane-mass fraction for Refinery C was 0.58.

Table 20. Summary of MeFTIR methane measurements at Refinery C. *Methane/alkane mass fraction.

Day [yymmdd]	**Timespan** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction* [%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150918	213422 -225735	2	61	2.9-3.0	321-327
151022	150050 -161331	5	49	3.1-5.2	182-193
151102	150921 -164835	3	68	2.8-3.8	243-279
151104	144900 -161529	2	62	4.0-12.0	230-262
Average±SD	**-**	**(total 12)**	**58±31**	**-**	**-**

4.4 Refinery D

Refinery D, (crude oil capacity: 105 kBPD (California Energy Commission 2016)) is located north of the Long Beach port, about 4 kilometers south of Refinery A, see Figure 10. To accurately compensate for incoming background plumes, it is necessary to make 'box' measurements (see example in Figure 36) which was easily done using public roads. Some measurements were however excluded since the incoming fluxes were comparable in size to the outgoing fluxes (adding too much uncertainty to the calculated flux). This was especially true for northerly and westerly winds carrying VOC-rich air from Refinery A and Refinery B.

Wind information for the flux calculations comes from the wind LIDAR (0-400 m average) at position L1 - (see Figure 10) or the Long Beach Airport ASOS station (scaled to match 0-400m LIDAR) or SCAQMD South Long Beach (SLBH) (scaled to match 0-400 m LIDAR). See section 3.4 for additional wind analysis. Typical wind directions and velocities during the measurements are 2-5 m/s and around 180°N or 270 degrees, see Figure 37.

4.4.1 Alkanes (non-methane)

Alkane emissions from Refinery D were measured with SOF during 7 days in the period September 3 to November 9, see Table 21. The daily means varied substantially from 90 kg/h (6 September) to an extreme of almost 1000 kg/h (1 November). A flaring event occurred 1 November which explains the large deviation for this day. The grand total average and standard deviation of all the 33 quality assured transects amounts to 348±253 kg/h and the median 164 kg/h. Histogram of all transects, Figure 38, show a gathered distribution at around 120 kg/h and some extreme outliers above 500 kg/h (which exclusively emanate from 1 November). Most transects show a typical column peak directly downwind the process area, see Figure 36. On November 1, significant VOC columns were detected directly downwind the flares in the west corner.

Table 21. Summary of SOF alkane measurements for Refinery D. *Single measurement. †Significantly deviating results due to flaring event.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150903*	140059 -140320	1	191.6	4.3	204
150906	171235 -180214	2	90.3±20.2	3.9-4.2	289-300
150907*	170803 -172210	1	125.6	6.6	269
150908	132545 -173630	9	192.0±66.9	4.0-7.8	274-296
150919	113306 -143232	10	116.7±47.1	2.2-2.6	160-198
151101†	104629 -150057	8	974.7±497.0	2.1-5.3	183-206
151109	135330 -144219	2	141.7±31.2	6.8-7.9	245-256
Average±SD	**-**	**(total 33)**	**348±253 (73%)**	**-**	**-**
Median	**-**	**(total 33)**	**164**	**-**	**-**

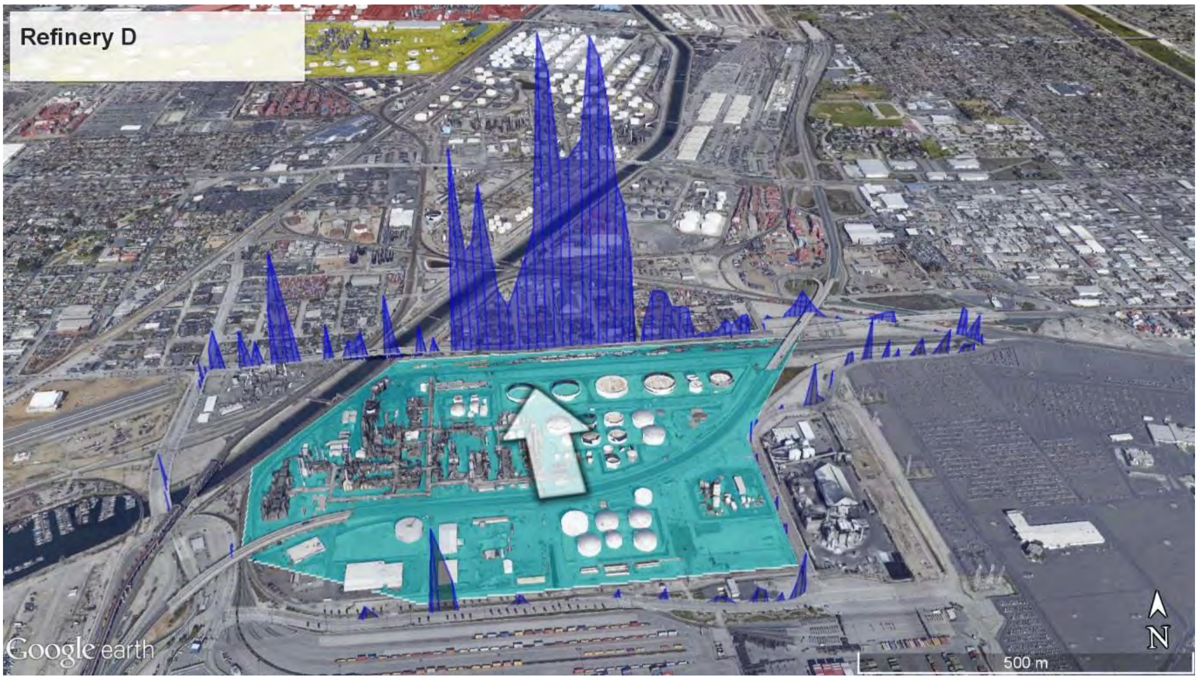

Figure 36. Example of a SOF 'box' measurement of Refinery D (cyan area) 19 September 2015, 13:08-13:20. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m^2, max 80 mg/m^2). Wind direction during the measurement is indicated by the white arrow. Average wind speed during was 2.5 m/s. Emissions on the upwind side are subtracted from the downwind side in order to get emissions from within the box. This particular transect measured 185 kg/h from Refinery D.

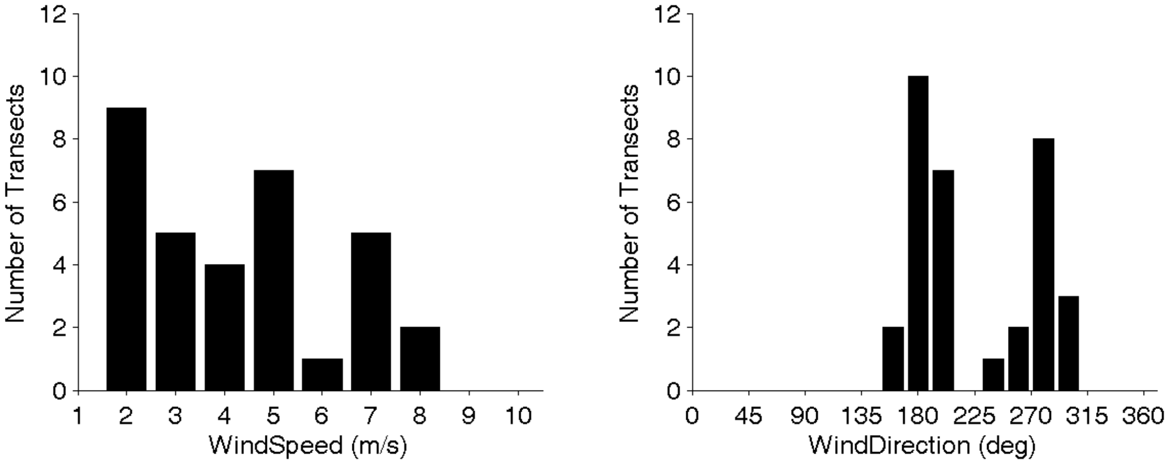

Figure 37. Wind histograms at Refinery D of wind speed (left) and wind direction (right) for the SOF measurements during the SCAQMD survey 2015.

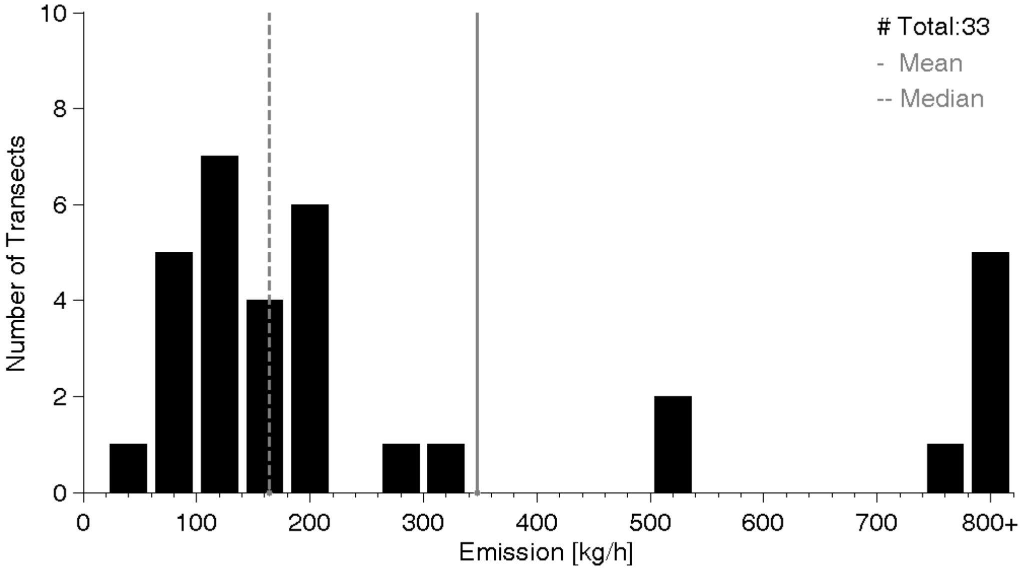

Figure 38. Histogram of all SOF measurements at Refinery D during the SCAQMD survey 2015. The last bin, denoted ‘+’, contains all data points above 800 kg/h. The median and average values are indicated as dashed and solid gray lines.

4.4.2 SO_2 and NO_2

SO_2 and NO_2 emissions from the facilities were measured for four measurement days in September during the campaign, example of a measurement is shown in Figure 39. Summaries and histograms of SkyDOAS emission measurements are presented in Table 22, Table 23, Figure 40 and Figure 41. Emissions averaged 43 and 18 kg/h and medians were 34 and 17 kg/h for NO_2 and SO_2 respectively.

Table 22. Summary of NO_2 measurements at Refinery D. *Single measurement.

Day [yymmdd]	**Timespan** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150902 *	160645 -160817	1	52.0	4.0	229
150906 *	100048 -100200	1	11.4	2.2	322
150908	132935 -152837	6	42.4±25.9	4.0-6.6	290-324
150919	114002 -142810	12	44.4±23.2	3.7-5.6	156-201
Average±SD	**-**	**(total 20)**	**43±24 (55%)**	**-**	**-**
Median	**-**	**(total 20)**	**34**	**-**	**-**

Table 23. Summary of SO_2 measurements at Refinery D . *Single measurement.

Day [yymmdd]	Timespan [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150902*	160645 -160817	1	19.4	4.0	229
150906*	100048 -100205	1	13.6	2.2	322
150908	132935 -152823	6	26.8±8.3	4.0-6.6	289-322
150919	114057 -142758	12	14.0±5.6	3.5-5.7	166-204
Average±SD	**-**	**(total 20)**	**18±6.5 (36%)**	**-**	**-**
Median	**-**	**(total 20)**	**17**	**-**	**-**

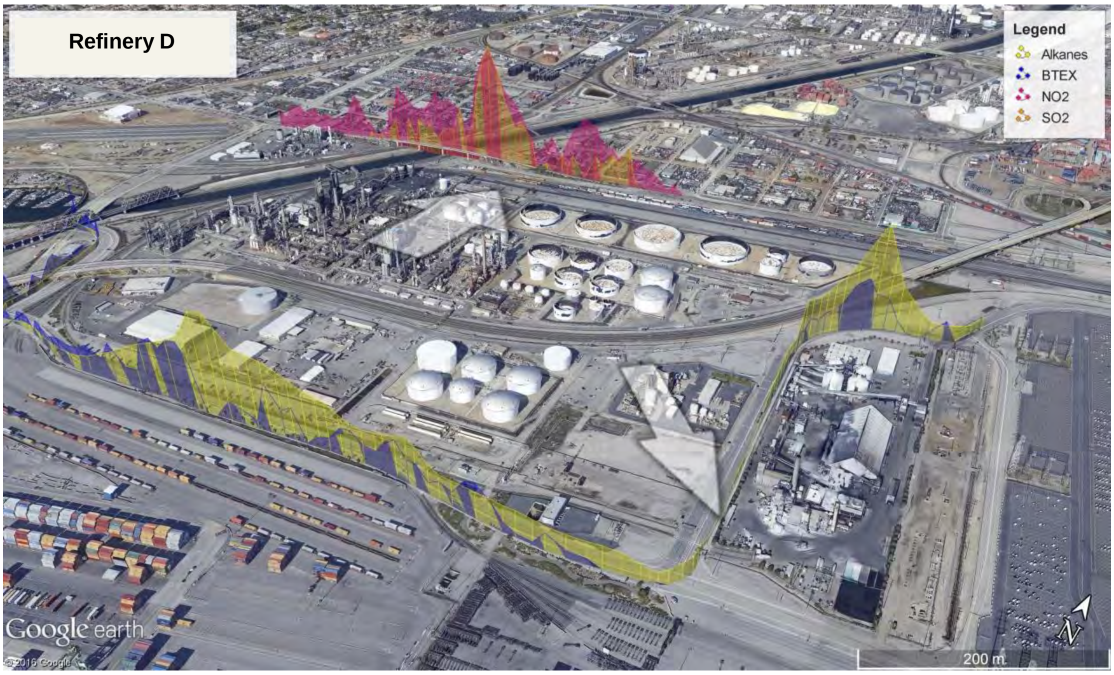

Figure 39. Transects of plumes originating from Refinery D: NO_2 (pink), SO_2 (brown) in south wind and BTEX (blue) and alkane (yellow) in north-westerly winds. NO_2 and SO_2 show column thickness and are both on the same scale (max SO_2 = 10.1 mg/m^2, flux SO_2 = 18.3 kg/h, max NO_2 = 9.8 mg/m^2, flux NO_2 = 39.3 kg/h), alkanes and BTEX show concentrations and are scaled independently for visibility (max BTEX =0.02 mg/m^3, max alkanes = 0.29 mg/m^3). Data from September 19, 12:42 PM and 8:32 PM.

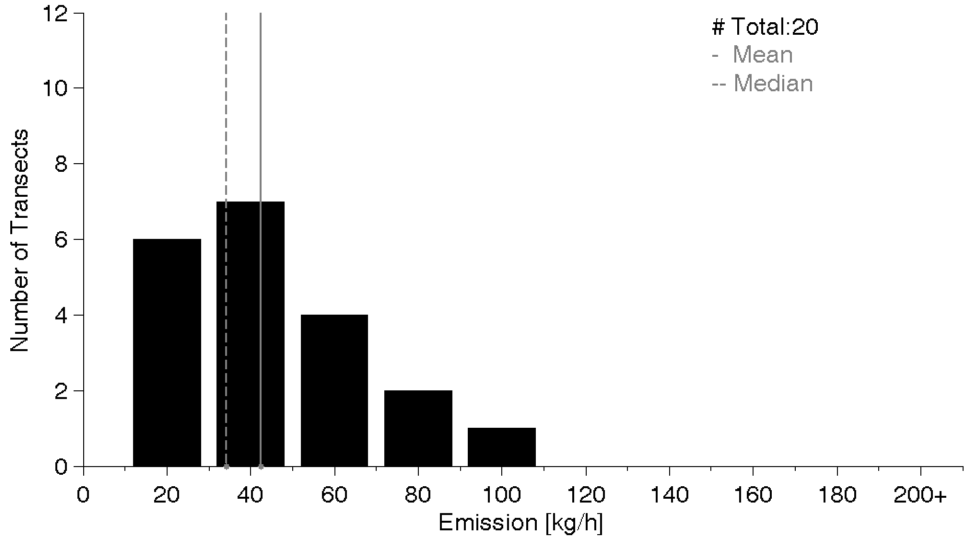

Figure 40. Histogram of all SkyDOAS NO_2 measurements at Refinery D during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

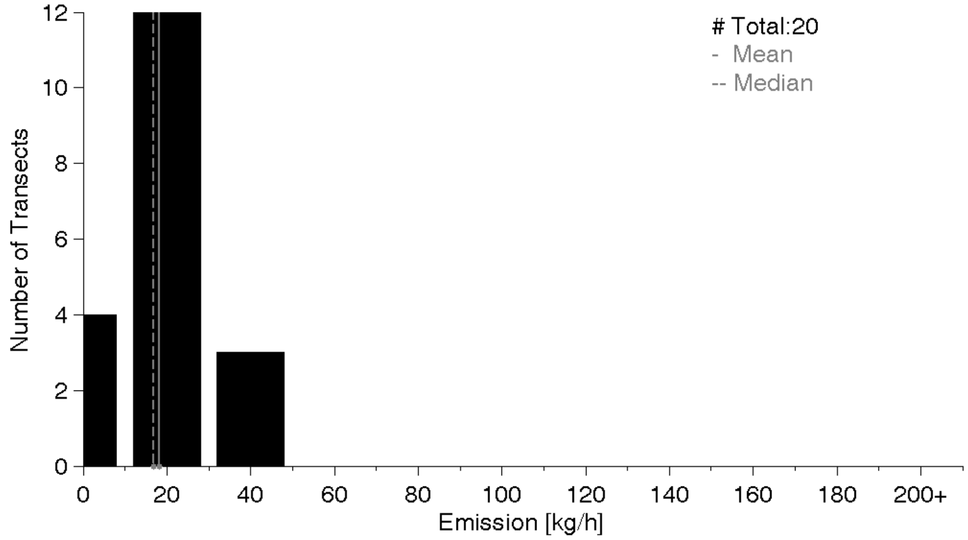

Figure 41. Histogram of all SkyDOAS SO_2 measurements at Refinery D during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.4.3 BTEX

The BTEX mass fraction to alkane in the plumes emitted from Refinery D were measured either in the late evening or early morning when the plumes were closer to ground. The mass fraction is acquired by combining BTEX level measurements from MWDOAS and alkane measurements from MeFTIR. A measurement example is shown in Figure 39. To determine the source of the plume, wind directions from the LIDAR positioned at L1 or the SCAQMD-HDSN wind station were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured on different public roads surrounding the facility, depending on wind direction. The measurements are shown in Table 24.

The average fraction of BTEX to alkanes was 0.099 or 9.9%. The average flux of BTEX can be calculated by multiplying this figure with the total alkane flux as measured by the SOF-technique.

The average fraction of benzene to alkanes was 1.0% and the benzene flux can be calculated in the same way as above.

Table 24. Summary of MWDOAS BTEX measurements at Refinery D. *BTEX/alkane mass fraction.

Day [yymmdd]	Time span [hhmmss-hhmmss]	BTEX Fraction* [%]	Benzene Fraction* [%]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150919	200817-201303	6.3	0.81	3.4	309
150919	205012-205749	16.2	0.93	1.8	330
150919	203234-204133	5.1	1.3	3	331
150919	214233-215112	4.1	0.33	1.2	320
151104	170956-171120	20.7	2.5	2.2	266
151104	171422-171457	11.9	0.7	2.6	273
151104	171504-171546	4.7	0.46	3.8	295
Average±SD		**9.9±6.5**	**1.0±0.7**		

4.4.4 Methane

The average fraction of methane to total non-methane alkanes in the plume from Refinery D was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume were compared to the average concentration of correlating alkanes measured simultaneously. Wind information from ASOS_KLGB was used, though only wind direction, not accurate wind speed matters for these measurements. Measurements were made during daytime and are shown in Table 25. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux measured by SOF, gives an estimate of the methane flux from the refinery. The average methane-to-alkane fraction for Refinery D was 0.48.

Table 25. Summary of MeFTIR methane measurements at Refinery D. *Methane/alkane mass fraction.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Methane fraction* [%]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150919	115502 -234019	10	46	0.5-4.5	41-345
151101	102640 -121744	3	55	0.8-3.9	141-190
Average±SD	**-**	**(total 13)**	**48±20**	**-**	**-**

4.5 Refinery E

Refinery E (crude oil capacity: 269 kBPD, (California Energy Commission 2016)) is located at the Pacific coast, around 20 kilometers northwest of Refinery A (Figure 10). This refinery is totally isolated from the other refineries in this study. There are however, other significant background plumes from the oil wells and power plants along the coast line that must be compensated for in the flux calculations. This is done by encircling ('boxing') the facility when possible (see example in Figure 42). No prevailing night-time VOC-rich air masses during AM were present in this coastal location (as compared to the other refineries in this survey).

Wind information for the flux calculations comes from the wind LIDAR (0-400 m average) at position L4 located around 1 km east of the refinery (see Figure 42) for the period 9-16 September. For the other days, wind information from the Los Angeles International Airport (KLAX) ASOS met station, 3 km north of the refinery, was used (scaled to match 0-400 m LIDAR). See section 3.4 for additional wind analysis. Typical wind directions and velocities during the measurements are 4-7 m/s and 270°N, see Figure 43. Winds were generally steady at this site due the sea breeze.

4.5.1 Alkanes (non-methane)

Alkane emissions from Refinery E were measured with SOF during seven days in the period September 9 to November 6, see Table 26. The daily means varied from 185 kg/h (13 September) to over 700 kg/h (11 September). The increased emissions 11 September points toward the tank park in the northwest corner. The grand total average and standard deviation of all the 35 quality assured transects amounts to 280±223 kg/h and the median 244 kg/h. Histograms of all transects (Figure 44) show a peak at around 240 kg/h and one extreme outlier (from 11 September). Most transects show a broad column peak downwind the core of the facility, see Figure 42.

Figure 42. Example of a SOF 'box' measurement of Refinery E (orange area) 6 November 2015, 10:47-11:22. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m^2, max 55 mg/m^2). Wind direction during the measurement is indicated by the white arrow. Average wind speed during this particular measurement was 1.8 m/s. Emissions on the upwind side are subtracted from the downwind side in order to get emissions from within the box. This particular transect measured 229 kg/h from Refinery E.

Table 26. Summary of SOF alkane measurements at Refinery E. *Single measurement. †Extremely deviating results due to (likely) tank park event.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150909	120735 -152659	5	242.2±83.3	4.6-6.7	266-279
150911†	110544 -133021	3	701.9±718.8	2.3-5.3	240-252
150913	112120 -144848	4	185.0±62.3	1.9-6.4	239-261
150916	145339 -160447	2	206.1±96.9	4.9-5.3	253-254
150920	105011 -143901	7	302.7±75.6	4.2-6.0	265-270
150927	120435 -152615	9	218.9±44.8	3.4-4.9	257-270
151106	104724 -140220	5	249.1±41.5	1.8-4.2	235-255
Average±SD	-	**(total 35)**	**280±223 (80%)**	-	-
Median	-	**(total 35)**	**244**	-	-

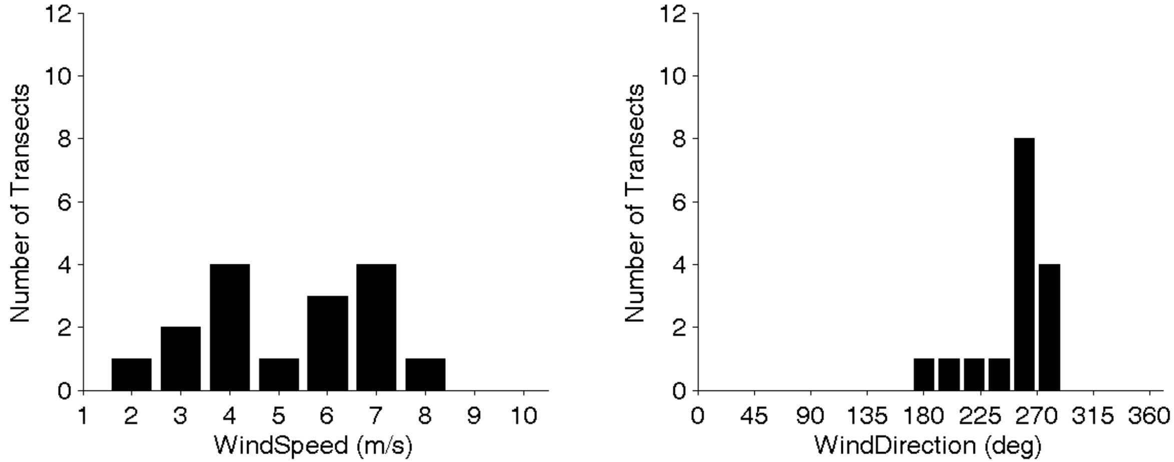

Figure 43. Wind histograms at Refinery E of wind speed (left) and wind direction (right) for the SOF measurements during the SCAQMD survey 2015.

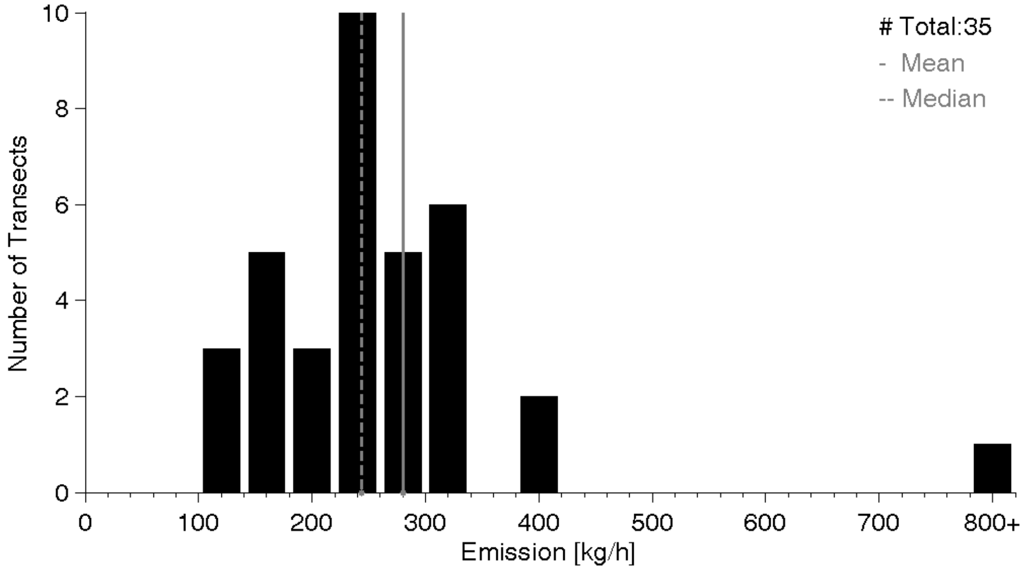

Figure 44. Histogram of all SOF measurements at Refinery E during the SCAQMD survey 2015. The last bin, denoted '+', contains all data points above 800 kg/h. The median and average values are indicated as dashed and solid gray lines.

4.5.2 SO_2 and NO_2

SO_2 and NO_2 emissions from the facilities were measured during 7 measurement days in September and November during the campaign, examples of such measurements can be seen in Figure 45. As these plumes are from combustion sources and presumably stack releases, the plumes are expected to be at a higher altitude than the VOC plume when measuring near the facility, as in nearly all the measurements. Summaries of SkyDOAS emission measurements are presented in Figure 46, Figure 47, Table 27 and Table 28. Emissions were determined using LIDAR-wind, measured at position L4 or scaled KLAX ASOS met station. Typically, baselines were corrected for background (vehicle and other sources for NO_2) thus setting inflow to zero. Emissions averaged 70 and 52 kg/h and medians were 63 and 53 kg/h for NO_2 and SO_2 respectively.

Table 27. Summary of NO_2 measurements at Refinery E. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150909	114049 -145759	5	99.1±19.9	4.6-5.0	260-268
150911	111924 -132450	2	67.2±47.0	3.6-5.0	259-270
150913	112658 -144342	4	60.4±13.9	4.0-5.9	245-258
150916	145850 -163249	3	45.5±16.2	3.7-4.5	249-265
150920	110103 -114007	2	101.3±29.2	4.4-4.8	263-268
150927	140555 -144335	2	44.3±6.3	4.2-4.9	254-264
151106 *	123305 -124620	1	35.9	2.9	251
Average±SD	**-**	**(total 19)**	**70±23 (33%)**	**-**	**-**
Median	**-**	**(total 19)**	**63**	**-**	**-**

Table 28. Summary of SO_2 measurements at Refinery E. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150909	114700 -152537	6	40.5±20.4	4.0-5.2	258-272
150910 *	154026 -155223	1	42.1	4.4	266
150911	103551 -132450	4	49.3±25.7	3.5-5.0	252-270
150913	091458 -144342	7	47.4±11.7	2.3-5.9	242-258
150916	145850 -163249	3	55.6±9.8	3.8-4.7	249-268
150920	105910 -113707	2	76.4±27.7	4.5-4.9	261-271
150927	140555 -151747	4	61.7±9.4	4.2-4.9	254-264
151106	114611 -124623	2	70.7±26.6	2.5-2.8	250-252
Average±SD	**-**	**(total 29)**	**52±19 (35%)**	**-**	**-**
Median	**-**	**(total 29)**	**53**	**-**	**-**

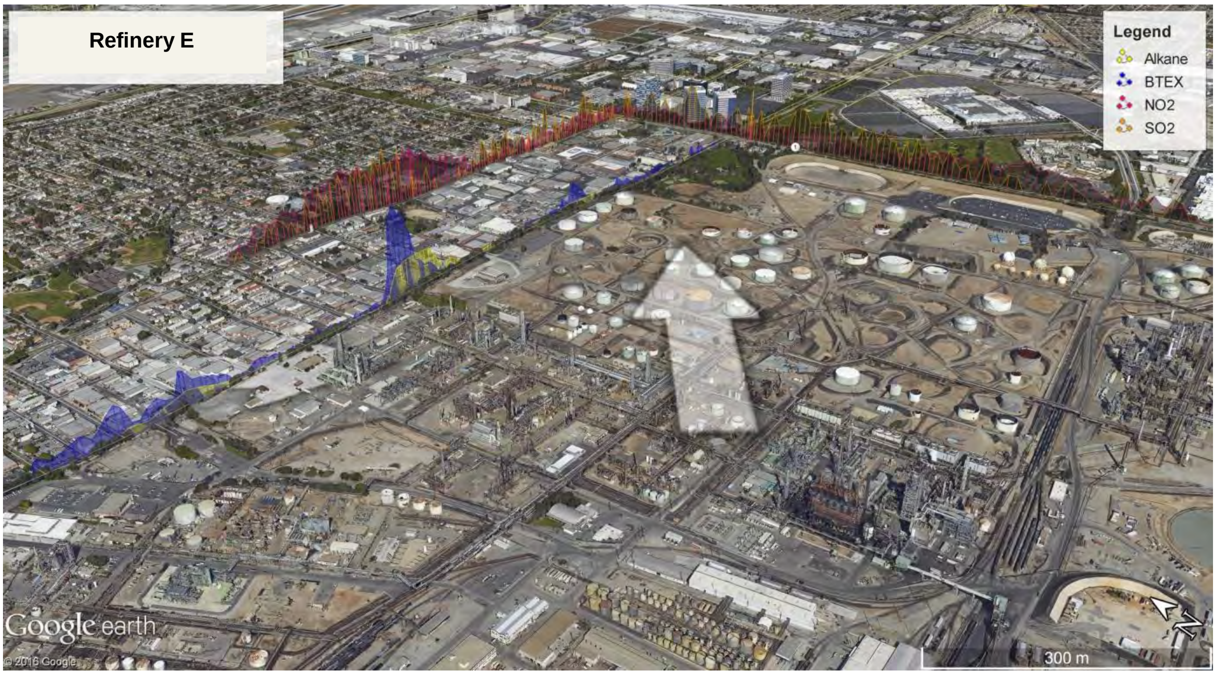

Figure 45. Transects of plumes originating from Refinery E: NO_2 (pink), SO_2 (brown), BTEX (blue) and alkane (yellow). NO_2 and SO_2 show column thickness and are both on the same scale (max NO_2 = 5.9 mg/m^2, flux NO_2 = 42.5 kg/h, max SO_2 = 6.4 mg/m^2, flux SO_2 = 48.9 kg/h), alkanes and BTEX show concentrations and are scaled independently for visibility (max BTEX = 0.04 mg/m^3, max alkanes = 0.13 mg/m^3). Example transects from September 16, 4:23 PM and 9:07 PM.

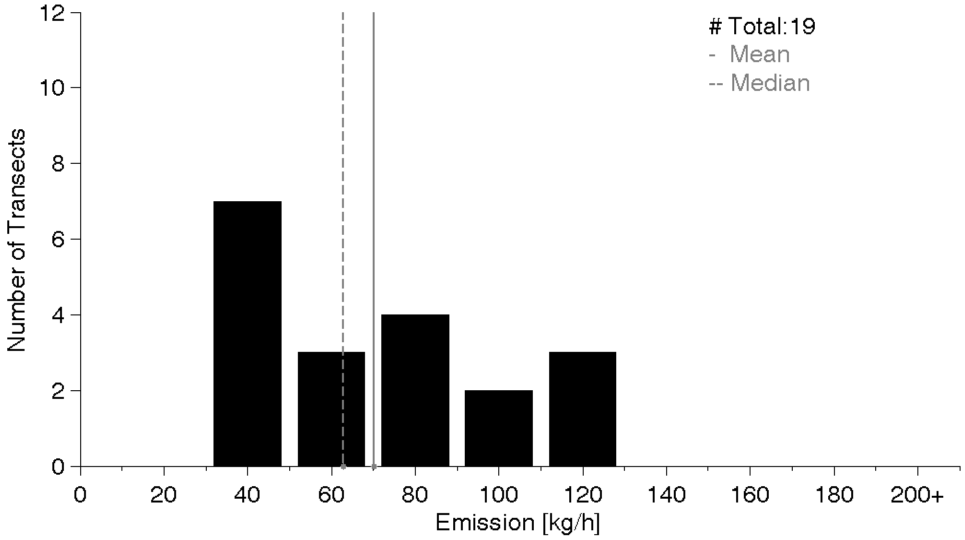

Figure 46. Histogram of all SkyDOAS NO_2 measurements at Refinery E during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

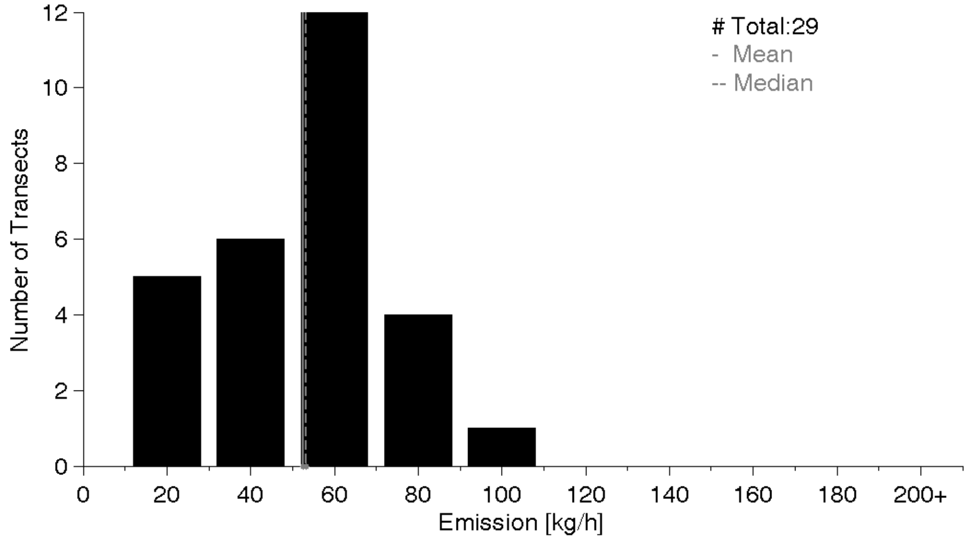

Figure 47. Histogram of all SkyDOAS SO_2 measurements at Refinery E during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.5.3 BTEX

The BTEX mass fraction to alkane in the plumes emitted from Refinery E were measured either in the late evening or early morning when the plumes were closer to ground. The mass fraction is acquired by combining BTEX level measurements from MWDOAS and alkane measurements from MeFTIR. Figure 45 shows an example of a measurement. To determine the source of the plume, wind directions from the LIDAR positioned at L4 or the ASOS-KLAX wind station were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured north of the facility. The measurements are shown in Table 29.

The average mass fraction of BTEX to alkanes was 0.13 or 13.0%. The average flux of BTEX can be calculated by multiplying this figure with the total alkane flux as measured by the SOF-technique. The average mass fraction of benzene to alkanes was 1.1% and the benzene flux can be calculated in the same way as above.

Table 29. Summary of MWDOAS BTEX measurements at Refinery E. *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150916	112732 -165808	12	0.53	0.8	353
150916	130746 -131654	13.5	0.71	1.3	330
150916	134638 -154706	2.1	1	1	331
150916	142535 -154524	20	2	2	320
150916	144942 -173531	17.2	1.4	2.1	317
Average±SD	**-**	**13±6.8**	**1.1±0.6**	**-**	**-**

4.5.4 Methane

The average fraction of methane to total non-methane alkanes in the plume from Refinery E was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of correlating alkanes measured simultaneously.

Wind information from ASOS_KLAX was used, only wind direction, not wind speed matters for these measurements. Measurements were made during daytime and late evening and are shown in Table 30. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux measured by SOF, gives an estimate of the methane flux from the refinery. The average methane-to-alkane fraction for Refinery E was unusually high on the night of September 19 and might have been affected by some temporary release source. Therefore the measurements from September 19 will not be used in the result. When measured on September 27 the fraction was no longer extreme and the average from that day, 0.85 will represent the resulting fraction for Refinery E.

Table 30. Summary of MeFTIR Methane measurements at Refinery E. *Methane/alkane mass fraction. †Extremely deviating results likely due to other non-identified temporal source.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150916†	170318 -224508	5	180	4.0-5.1	230-268
150927	112103 -151358	5	85	4.0-4.0	230-230
Average±SD	**-**	**(total 10)**	**85±7**	**-**	**-**

4.6 Refinery F

Refinery F (crude oil capacity 150 kBPD, (California Energy Commission 2016)) is located around 10 kilometers northwest of Refinery A, see Figure 10. Emission plumes from other refineries in this study or other large emitters do not interfere directly with plumes from Refinery F with the prevailing wind directions. But there are some minor oil wells and storage tanks west of the refinery which must be compensated for in the flux calculations by 'boxing' the facility during westerly winds (see example in Figure 48).

Wind information for the flux calculations comes from the wind LIDAR (0-400 m average) at position L3 located 300 m east of the refinery (see Figure 48) 17 September. For the other days, wind information from the L1 LIDAR site was used. See section 3.4 for additional wind analysis. Typical wind directions and velocities during the measurements are around 4 m/s and around 180 or 270°N, see Figure 49.

4.6.1 Alkanes (non-methane)

Alkane emissions from Refinery F were measured with SOF during four days: 9, 13 and 17 September and 7 November, see Table 31. The daily means varied from 117 kg/h (13 September) to 219 kg/h (17 September). The grand total average and standard deviation of all the 16 quality assured transects amounts to 169±105 kg/h and the median 140 kg/h. Histograms of all transects (Figure 50) show a peak at around 120 kg/h and one extreme outlier (from 17 September). Transects show a column peak downwind the southeast tank park and the process area, see Figure 48.

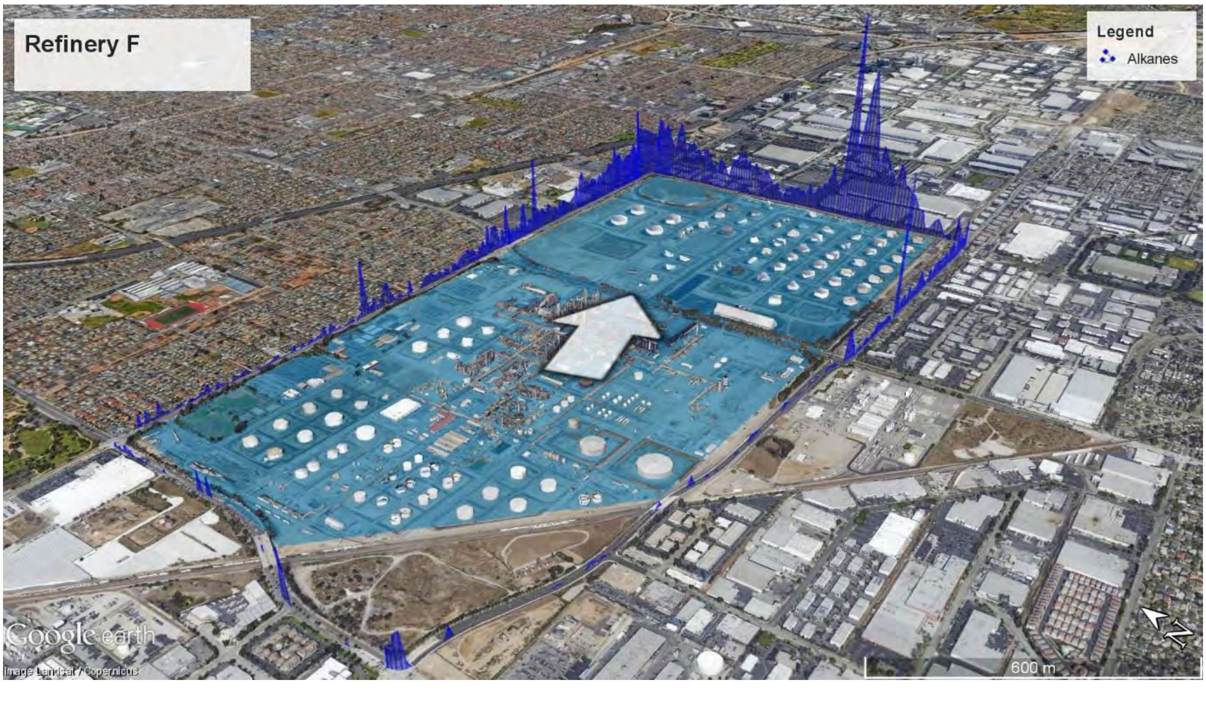

Figure 48. Example of a SOF 'box' measurement of the Refinery F (light blue area) 17 September 2015, 12:39-13:04. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m^2, max 83 mg/m^2). Wind direction during the measurement is indicated by the white arrow. Average wind speed during was 3.1 m/s. Emissions on the upwind side are subtracted from the downwind side in order to get emissions from within the box. This particular transect measured 230 kg/h from Refinery F.

Table 31. Summary of SOF alkane measurements for Refinery F. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150909*	164857 -165755	1	157.7	3.6	226
150913	153509 -170800	4	117.1±18.0	6.2-7.1	270-277
150917	120844 -161940	7	219.4±152.4	3.1-7.6	251-261
151107	133217 -145646	4	135.3±6.5	2.5-4.5	189-277
Average±SD	**-**	**(total 16)**	**169±105 (62%)**	**-**	**-**
Median	**-**	**(total 16)**	**140**	**-**	**-**

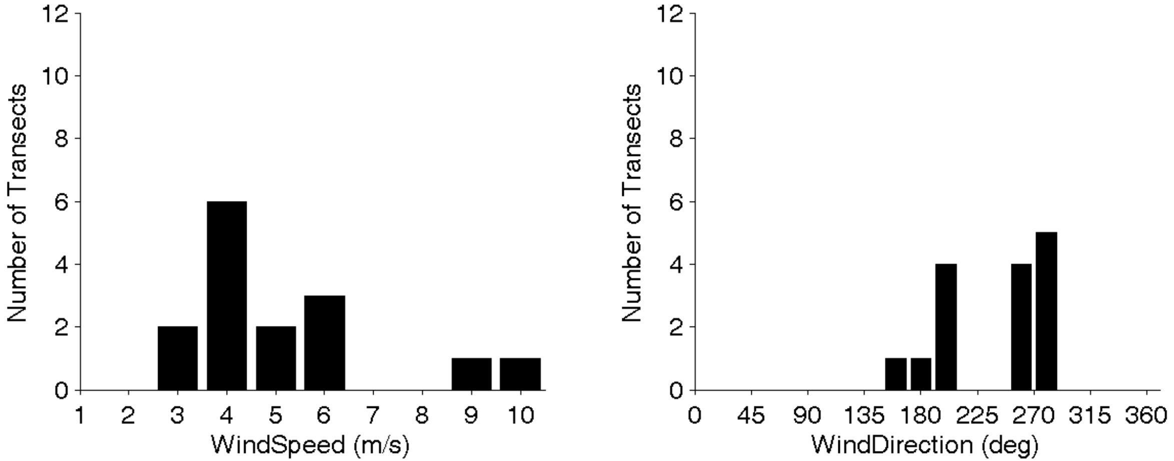

Figure 49. Wind histograms at Refinery F of wind speed (left) and wind direction (right) for the SOF measurements during the SCAQMD survey 2015.

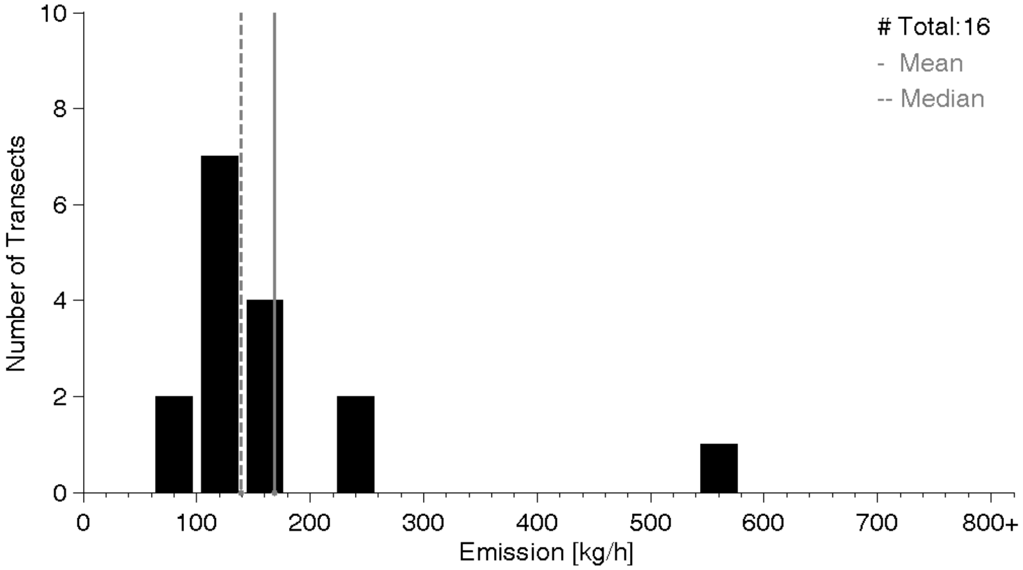

Figure 50. Histogram of all SOF measurements at Refinery F during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.6.2 SO_2 and NO_2

SO_2 and NO_2 emissions from the facilities were measured for 2 measurement days in September. Summaries of SkyDOAS emission measurements are presented in Table 32 and Table 33. An example of a measurement is shown in Figure 51. For Refinery F the number of measurements is very low and the result may therefore be less reliable as a representation of typical emissions. Emissions averaged 23 and 40 kg/h and medians were 18 and 37 kg/h for NO_2 and SO_2 respectively.

Table 32. Summary of NO_2 measurements at Refinery F. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150913	153603 -160753	2	14.8±4.1	6.1-6.1	258-273
150917	132227 -132826	1	38.2	5.0	252
Average±SD	**-**	**(total 3)**	**23±4.1 (18%)**	**-**	**-**
Median	**-**	**(total 3)**	**18**	**-**	**-**

Table 33. Summary of SO_2 measurements at Refinery F. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150913*	153535 -154138	1	67.2	6.2	260
150917	121200 -132803	2	27.0±14.2	3.3-4.9	248-252
Average±SD	**-**	**(total 3)**	**40±14 (35%)**	**-**	**-**
Median	**-**	**(total 3)**	**37**	**-**	**-**

Figure 51. Transects of plumes originating from Refinery F: NO_2 (pink), SO_2 (brown), BTEX (blue) and alkane (yellow). NO_2 and SO_2 show column thickness and are both on the same scale (max NO_2 = 5.0 mg/m^2, flux NO_2 = 38.2 kg/h, max SO_2 = 4.4 mg/m^2, flux SO_2 = 17 kg/h), alkanes and BTEX show concentrations and are scaled independently for visibility (max BTEX = 0.01 mg/m^3, max alkanes = 0.55 mg/m^3). Example transects from September 17, 1:22 PM and 11:36 PM.

4.6.3 BTEX

The BTEX mass fraction to alkane in the plumes emitted from Refinery F were measured either in the late evening or early morning when the plumes were closer to ground. The mass fraction is acquired by combining BTEX ground level measurements from MWDOAS and alkane measurements from MeFTIR. To determine the source of the plume, wind directions from the LIDAR positioned at L3 or the KLAX-ASOS wind station were used (wind speed is irrelevant for these measurements). BTEX mass ratios were measured along one road picking up the plume from the tank park, and along another cutting through the facility and enabling a measurement of the process plume in westerly wind. The measurements are shown in Table 34 and Table 35.

The average mass fraction of BTEX to alkanes was 0.137 or 13.7% and 0.017 or 1.7% for the process and the tank park respectively. The average flux of BTEX can be calculated by multiplying this figure with the alkane flux as measured from these two sources by the SOF-technique. The average mass fraction of benzene to alkanes was 0.9% for the process plume and 0.3% for the tank park plume. Benzene flux can be calculated in the same way as above. Both the total BTEX flux and the benzene flux for Refinery F can be found in Table 5.

Table 34. Summary of MWDOAS BTEX measurements at Refinery F. Tank park plume *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150917	214724-215203	1.9	0.44	1.8	270
150917	232708-232841	1.4	0.19	2.8	251
Average±SD	-	**1.7±0.4**	**0.3±0.2**	-	-

Table 35. Summary of MWDOAS BTEX measurements at Refinery F. Process plume *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150917	221740-221813	12.8	0.87	1.7	244
150917	233614-233641	13.3	1	2.6	252
150917	231920-232007	15.1	0.71	4	45
Average±SD		**13.7±1.2**	**0.9±0.3**		

4.6.4 Methane

The average fraction of methane to total non-methane alkanes in the plume from Refinery F were measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of alkanes measured simultaneously. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux measured by SOF, gives an estimate of the methane flux from the refinery. Wind information from LIDAR in position L3 was used, only wind direction, not wind speed matters for these measurements. Only three measurements were made on one evening September 17 as shown in Table 36. The average methane-to-alkane fraction for the Refinery F was 0.41.

Table 36. Summary of MeFTIR methane measurements at Refinery F. *Methane/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction*** **[%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150917	211536 -233000	3	41	1.9-3.3	251-274
Average±SD	**-**	**(total 3)**	**41±6**	**-**	**-**

5 Results – On-site Measurements in a Refinery Tank Farm

On site measurements in the tank farm of a major refinery in the South Coast Air Basin were carried out for 8 days between 28 September and 7 October 2015 using the mobile optical methods described in the previous sections (i.e. SOF, MWDOAS and MeFTIR). The objective of this activity was to demonstrate the capability of these real time optical techniques to identify and quantify gas leakages inside a refinery and to compare the results with other optical methods used during the same time frame. These include a DIAL (Differential Absorption LIDAR; a laser-based method) operated by NPL (National Physics Laboratory, UK) at different locations within the tank farm, and a stationary long path FTIR system that was operated by Atmosfir in the west part of the tank farm. Here the FTIR coupled to a telescope was automatically pointed towards multiple reflectors put at strategic positions in different parts of the tank farm and at different heights to estimate ground source emissions using the EPA's OTM-10 method (see separate report by Atmosfir). These various methods were used independently but on several occasions side by side measurements were carried out for validation purposes (see report by Pikelnaya et. al. (2016)).

In this study we carried out mobile optical measurements throughout the tank farm on available roads in order to localize potential hot-spot emission areas and quantify emissions from selected tanks and tank groups. The emphasis was to investigate emissions from tank groups and tanks rather than the whole tank farm emissions, although this was also done.

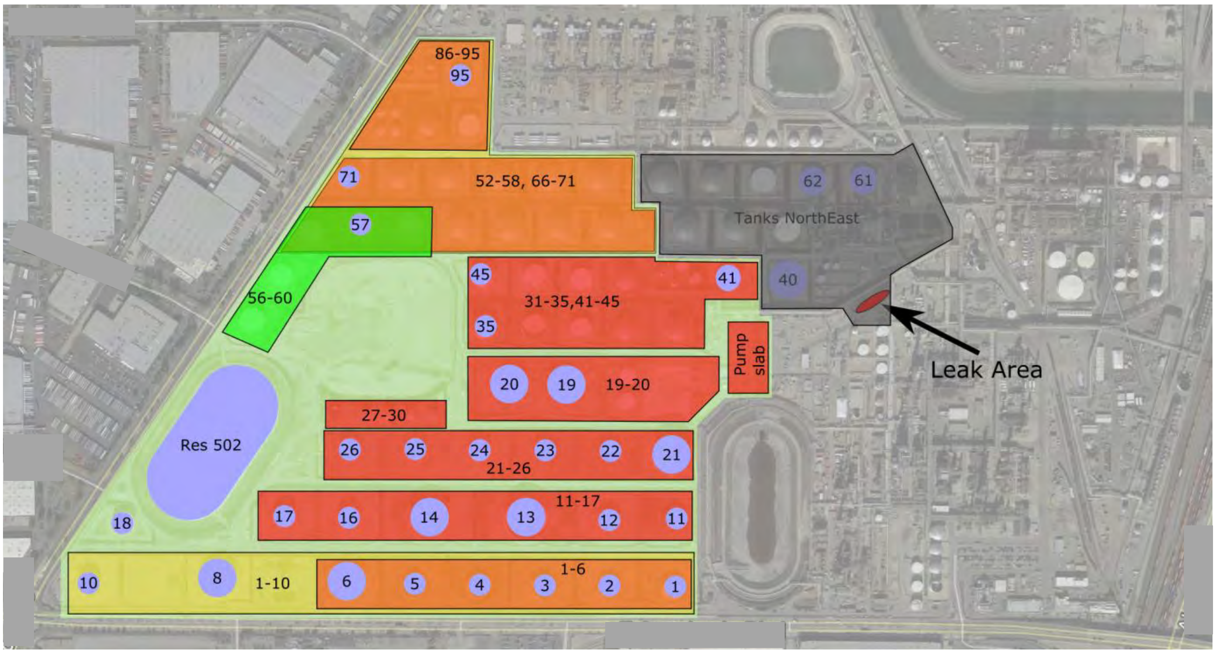

Figure 52. Overview of the tank farm part of the refinery where on site measurements with SOF + MeFTIR + MWDOAS were conducted for about one week in September/October 2015. Tanks, tank groups and specific areas have been given numbers and names respectively for reference to measurement results. North is upwards. Groups of quantified tanks are denoted by coloured rectangles, and individual tanks that have been quantified are indicated by blue shapes/circles. The surveyed part (large light green area) is restricted in the west and south by the site fence-line, and in the east and north by roads going east of tank 1-11-21-Pump slab and then between the "Tanks NorthEast" and tank groups "52-58+66-71" and to the northeast corner of group "86-95".

This limited study included alkane column measurements and ground concentration measurements of alkanes, methane and aromatic VOCs. A wind meter was positioned on an elevated plateau on a big open field inside the tank farm, thus sampling wind at a height comparable to a typical tank roof height.

The real-time capability and sensitivity of the instruments (2 s sampling time resolution for SOF and MWDOAS, 10 s for MeFTIR) was essential to this work as shown in Figure 53. By observing the geo-tagged emissions in real time, any occurring hot-spots can immediately be investigated further to for example conclude if the sources are intermittent or continuous. By driving on the upwind and downwind side of the tanks and unit areas, any incoming emission fluxes or interfering sources can be identified and accounted for.

Figure 53. A picture from the measurement van showing real time data while passing through a source. The column and concentration data is shown together with the measurements position on a map for fast hotspot identification and interpretation.

Validation between SOF (FluxSense) and DIAL (NPL) was done on tank 16 (crude), tank 13 (crude) and on reservoir 502 (vacuum gas oil).

5.1 Tank Park

Table 37 summarizes the plume transects including the whole tank farm in one run. The median emission of all these complete tank farm emission measurements was 145 kg/h based on 9 measurements distributed over four days. This corresponds to approximately half the total measured refinery emission (see section 4.1.1). The overall tank farm single observations ranged from 104-194 kg/h for the daily averages (4 different days).

Figure 54 shows an example of SOF measurements around the tank farm at the selected refinery. In this transect the highest column (165 mg/m^2) of VOC was measured at the elliptically shaped tank (here referred as tank reservoir no 502) in the lower left corner. This is explained by the pass being close to the source before the release was dispersed by convection and turbulence. It’s evident that reservoir 502 is a substantial source of alkanes. However, when following the measurement transect along the perimeter of the tank farm several extended plume sections are observed, and these add up to emission being several times that of reservoir 502 alone. The contribution from different parts of the tank farm is discussed in the next section.

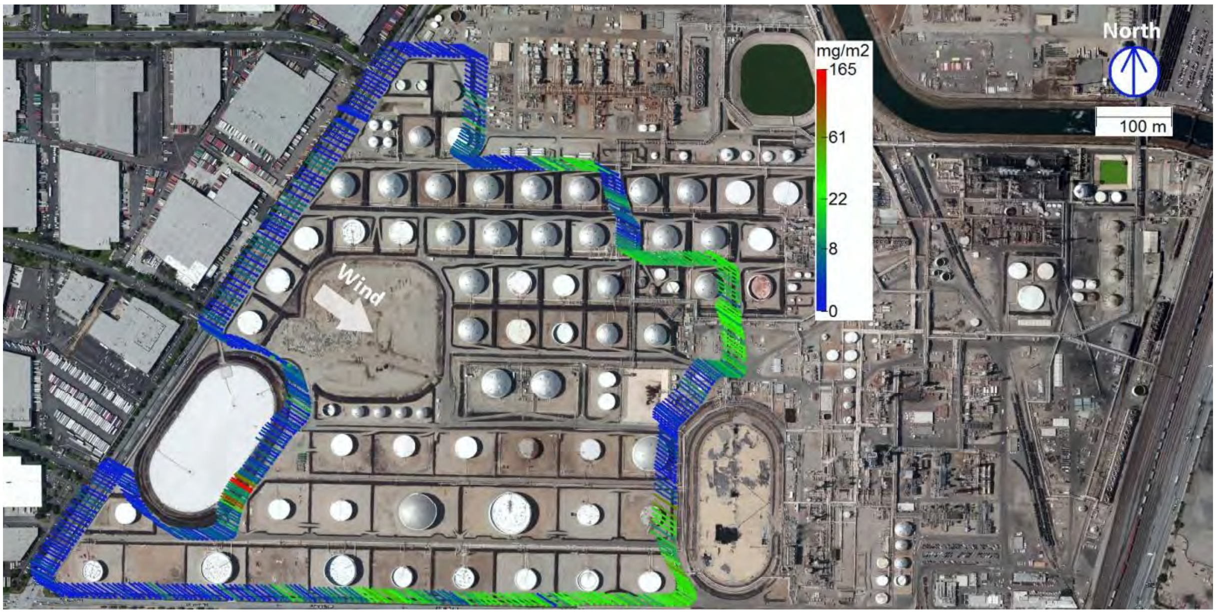

Figure 54. SOF measurement of alkanes around the major body of the tank farm on September 29, 2015 between 2:51 PM and 3:15 PM. Each measured spectrum is represented by a single line, with color indicating the evaluated integrated vertical alkane column. The line orientation indicates the direction from which the wind is blowing. North is upwards and in this case the wind blew from northwest.

Table 37. Summary of SOF alkane measurements for the refinery tank park considered in this study.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150928	143009 -153658	2	187.6±89.2	5.2-5.5	291-299
150929	145455 -150723	2	193.9±33.2	4.7-6.3	302-302
151002	143351 -154352	4	136.5±33.7	4.4-5.5	277-294
151006	140304 -150009	2	104.4±24.7	3.7-5.4	280-285
Average±SD	-	**(total 9)**	**153±53 (35%)**	-	-
Median	-	**(total 9)**	**145**	-	-

5.2 Individual Tanks and Tank groups

Based on 233 measurement transects of different tanks and tank groups, specific tank emissions have been summarized in Table 38. Adding up all the measured tank farm objects give on average 191 kg/h of alkanes. This is in line with the estimate from the SOF measurements for the complete tank farm in one run (153 kg/h, Table 37). Note that these numbers represent two different approaches with varying coverage in time and space. The statistic basis is quite variable among the tank farm objects, ranging from Reservoir 502 having 80 measurements distributed over 8 days to a few objects having only a single observation.

Table 38. Summary of onsite measurements (SOF) of tanks and tank groups. $^{a)}$ For the BTEX emission the average BTEX to alkane mass fraction (6.0 %) has been used for the tanks where the BTEX fraction was not quantified. $^{b)}$ For the benzene emission the average benzene to alkane mass fraction (0.59 %) has been used for the tanks where the benzene fraction was not quantified. *Items in italics and aligned to the right are either subgroups part of other items or not part of the overall Tank farm average.*

Tank_ID	**Average alkane (kg/h)**	**SD (kg/h)**	**No. meas.**	**No. days**	**BTEX to alkane mass fraction (%)**	**BTEX emission a) (kg/h)**	**Benzene to alkane mass fraction (%)**	**Benzene emission b) (kg/h)**
Tank_1	1	0.4	5	3	2	0.02	0.37	0.00
Tank_2	2.8	4.9	3	2	n.m.	0.17	n.m.	0.02
Tank_3	1.3	0.3	4	3	n.m.	0.08	n.m.	0.01
Tank_4	0.6	0.1	4	3	n.m.	0.04	n.m.	0.00
Tank_5	1.7	0.2	4	3	n.m.	0.10	n.m.	0.01
Tank_6	4.2	1.7	8	4	3.3	0.14	0.39	0.02
Tank_8	2.6	1.8	9	3	n.m.	0.16	n.m.	0.02
Tank_11	10.9	5.4	9	4	7.6	0.83	0.65	0.07
Tank_12	2.4	1.7	9	4	5.3	0.13	0.73	0.02
Tank_13	21.6	10.4	32	5	8.9	1.92	0.55	0.12
Tank_14	5.4	4.1	9	4	1.5	0.08	0.48	0.03
Tank_16_all days	*259*	*134*	*55*	*6*	*1.4*	*3.63*	*0.34*	*0.88*
Tank_16_excl. 151005	42	34	13	5	1.4	0.59	0.34	0.14
Tank_17	2.8	1	10	5	0.6	0.02	0.54	0.02
Tank_18	0.7	0.6	2	2	n.m.	0.04	n.m.	0.00
Tanks_19-20	15.8		1	1	n.m.	0.95	n.m.	0.09
Tank_21	6.3	1.4	5	2	12.3	0.77	n.m.	0.04
Tank_22	1.2	0.5	6	2	11.4	0.14	0.25	0.00
Tank_25	2.1		1	1	n.m.	0.13	n.m.	0.01
Tanks_27-30	5.3	0.2	5	4	5.6	0.30	1.5	0.08
Tanks_31-35_42-45	12.6		1	1	n.m.	0.76	n.m.	0.07
Tank_40	*4.5*	*0.1*	*2*	*1*	*n.m.*	*0.27*	*0.48*	*0.02*
Tanks_56-60	*7.6*	*0.6*	*2*	*2*	*n.m.*	*0.46*	*n.m.*	*0.04*
Tank_57	*3.0*		*1*	*1*	*5.6*	*0.17*	*0.24*	*0.01*
Tank_71	*3.7*		*1*	*1*	*5.6*	*0.21*	*0.37*	*0.01*
Tanks_52-58_66-71	13.7		1	1	9.3	1.27	0.88	0.12
Tanks_86-95	8.0	0.7	6	4	4.4	0.35	n.m.	0.05
Reservoir_502	26.1	11.4	80	8	10.7	2.79	1.1	0.29
Total all measured tanks:	**191**		**233**			**12**		**1.2**

As seen in Table 38, Tank 16 had one day (5 October, 2015) where atypical emissions were observed. Including this day would raise the overall average for Tank 16 to 259 kg/h if compared to 42 kg/h if this day is excluded. In the presented grand total average for the tank farm, this atypical event was left out for Tank 16 (42 measurements were conducted on tank 16 this day in a validation experiment with other optical techniques, whereas 13 measurements were done for the other days being included in the average). BTEX to alkane mass fractions were also measured for many of the tanks, and ranged from 1.4 to 12.3 % which is quite normal values for a tank farm containing both crude and refined petroleum product tanks. Last four columns in Table 38 specify measured BTEX fractions, inferred BTEX emissions and corresponding columns for benzene, using the SOF alkane emission and the BTEX and benzene fractions respectively. For tanks where BTEX or benzene were not measured, the average BTEX mass fraction (6.0 %) or benzene average fraction (0.59 %) has been used. Overall a BTEX emission of 12 kg/h is estimated from the tank farm, of which 1.2 kg is estimated to be benzene.

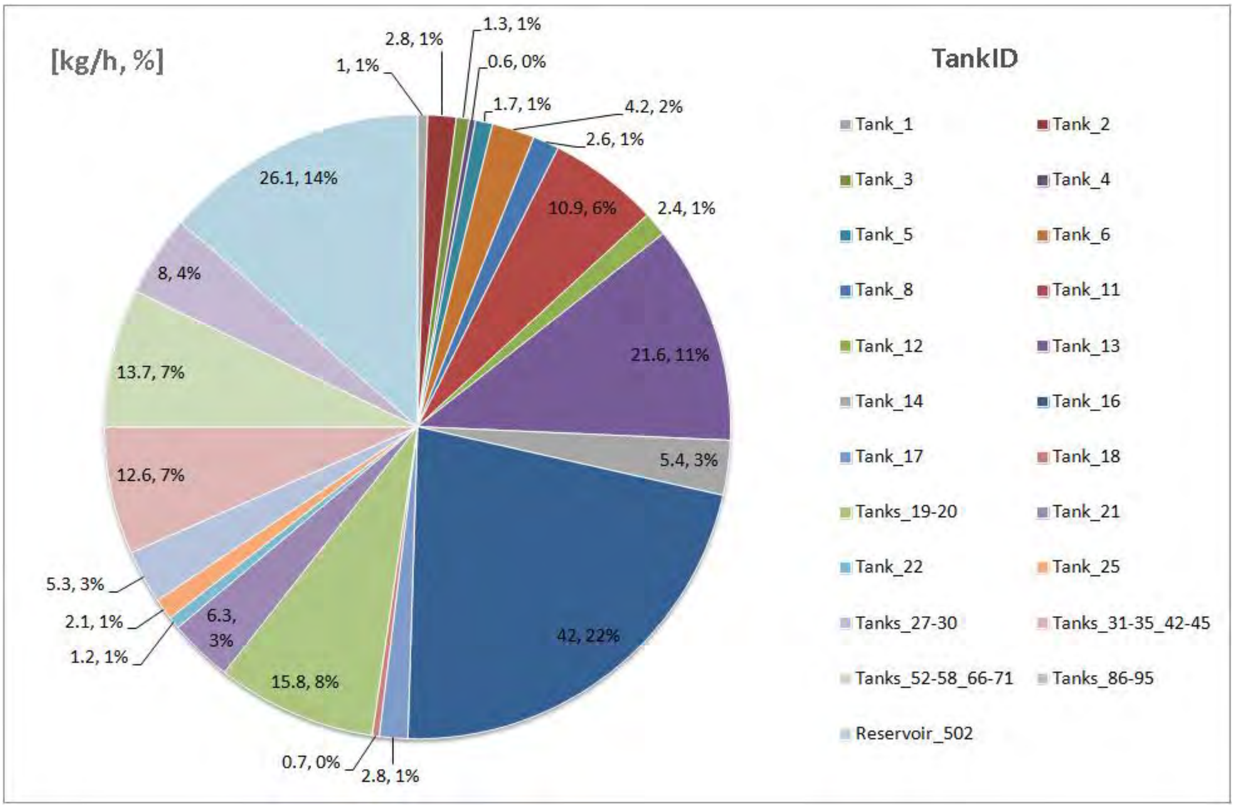

Figure 55. Summary of all measurements on the specified tanks and tank groups and their relative contribution to the total emission of 192 kg/h. The measurements on tank 16 from 5 October were omitted here due an atypical release event.

Figure 55 shows the absolute and relative contribution from all measured tanks and tank groups to the tank farm overall sum of alkanes (191 kg/h). Three tanks stand out with single contributions above 10% each, with Tank_16 being the strongest source (22%, Crude) followed by Reservoir_502 (14%, Vacuum Gas Oil (VGO)) and Tank_13 (11%, Crude). These tanks were also studied in more detail, to obtain better statistics. A validation study between the SOF and DIAL techniques were also done on these tanks with very good agreement of the results (see Pikelnaya et. al. (2016)).

The 502 source is a large covered reservoir which contain vacuum gas oil (VGO). It has two ventilations shafts, one in the north and one in the south. Specific data from tank 502 are found in Table 39 and Figure 56. Histograms of the 80 individual plume transects of this source, from 8 different days, resemble something close to a normal distribution with an average emission of 26 kg/h, very close to the median of 25 kg/h. The observed spread in day to day averages ranged from 20 to 36 kg/h. The emissions from Reservoir 502 were split up on contributions from the north and the south vent respectively, showing that the vast majority of the reservoir emissions originated from the south vent with 90% of the reservoir’s overall emission.

With a BTEX mass fraction of 11%, this was the strongest source of aromatics found in the tank farm, with an estimated emission of 2.8 kg/h BTEX (23% of the overall). Also when considering benzene, Reservoir 502 was the strongest source with 0.3 kg/h. Tank 13 and Tank 16 were found to have a BTEX emission of 1.9 kg/h and 0.6 kg/h respectively. Corresponding benzene emissions were 0.12 kg/h and 0.14 kg/h. The BTEX and benzene results for Tank 13, 16 and Reservoir 502 were based on 8, 57 and 28 observations within each category respectively.

Table 39. Summary of SOF alkane measurements reservoir no 502. *Single measurement.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150928	140807 -155200	4	27.7±7.4	4.2-6.0	287-294
150929	140318 -151343	2	20.2±7.7	3.4-3.8	272-291
150930	133031 -150355	6	26.1±13.4	2.1-3.6	192-303
151001	100906 -152231	9	28.8±11.5	1.5-4.7	276-295
151002	141403 -143033	7	36.3±15.6	3.8-4.9	262-294
151005*	155251 -155806	1	32.3	3.8	173
151006	121009 -160214	16	20.7±8.6	2.6-6.2	256-324
151007	134310 -153441	35	25.9±11.7	3.0-5.5	264-317
Average±SD	**-**	**(total 80)**	**26.1±11.4 (44%)**	**-**	**-**
Median	**-**	**(total 80)**	**24.7**	**-**	**-**

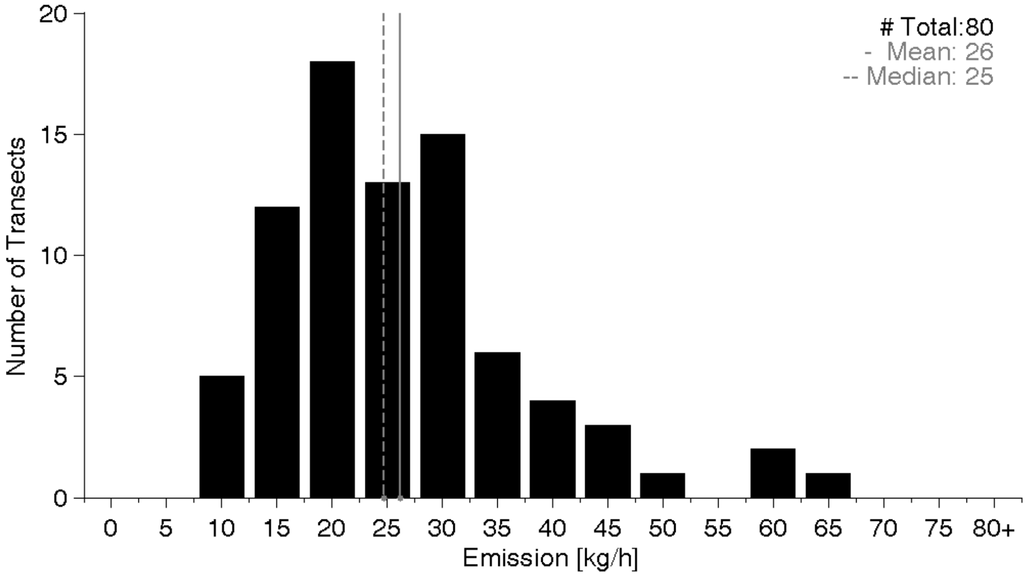

Figure 56. Histogram of all SOF measurements at reservoir 502 during the SCAQMD survey 2015. The median (24.7 kg/h) and average (26.5 kg/h) values are indicated as dashed and solid gray lines.

Figure 57 shows SOF measurements of VOCs in the crude oil part of the tank farm. Here the height of the column corresponds to the measured vertical column of alkanes (non-methane) and the arrow shows the wind direction (south-east in this case). The large columns downwind of the second tank from the left in the middle row (here referred to as tank 16) suggest the presence of a distinct leak at this tank. During the campaign, this tank showed large emissions during several days, see Table 40, and large variability range suggesting a dependence on operations. The refinery personnel and SCAQMD were notified of this finding and service personnel carried out an inspection showing that one of the valves was leaking. When the tank was filled with new product and the floating roof accordingly moved upwards, the displacement of VOC contaminated air between the internal floating roof and the external dome generated the large emissions through the malfunctioning vent gauge. The measurements illustrated in this figure were compared against DIAL measurements with very good agreement (see separate report by Pikelnaya et. al. (2016)).

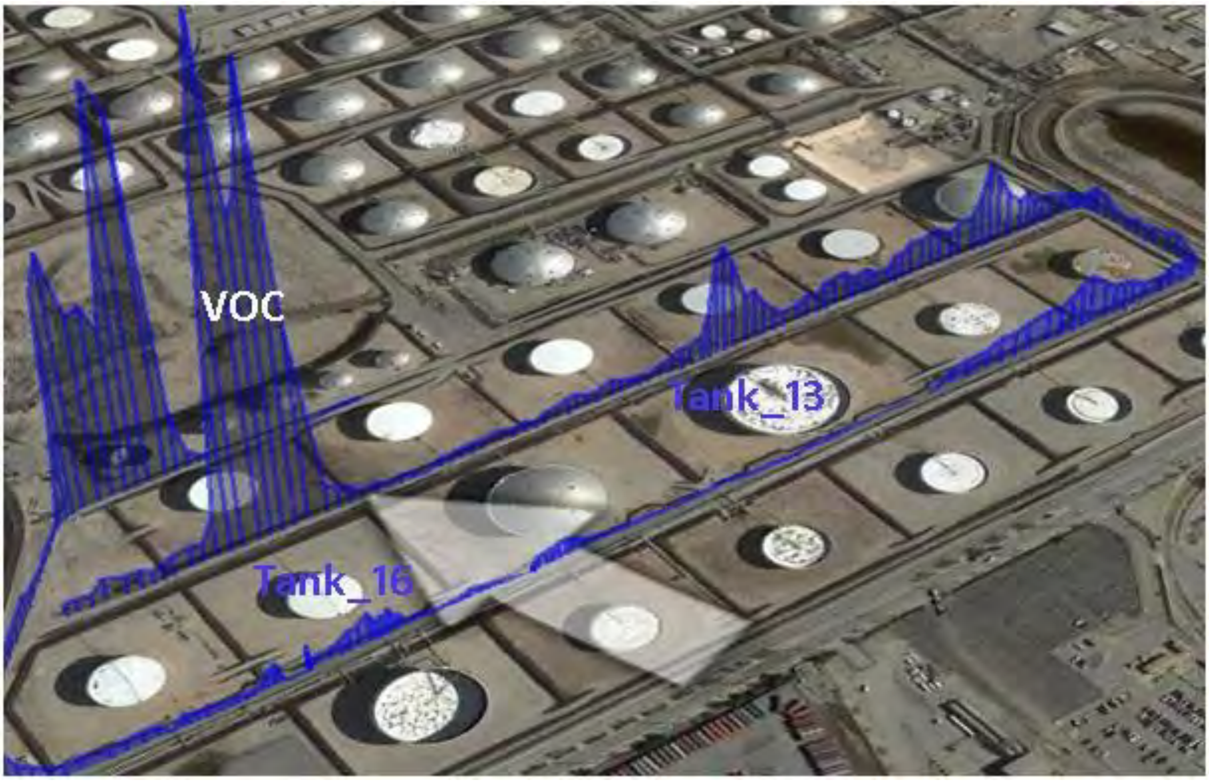

Figure 57. Measurements of VOCs with SOF in the crude oil part of the tank farm. Here the height of the blue columns corresponds to the amount of alkanes present in the column measured by SOF and the white arrow corresponds to the wind direction (south-east in this case).

Figure 57 also shows Tank_13 (two tanks right of tank 16 in the middle row) being a source of emissions – compare the clean upwind columns to the clear VOC plume downwind of tank 13 and 16 respectively. Table 40 and Table 41 include daily average emission data and the total average and median values from SOF measurements at tank 16 and tank 13 respectively.

Table 40. Summary of SOF alkane measurements for tank 16. *Single measurement.† Non-typical event with malfunctioning valve at tank roof on the 5 October 2015.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150928*	141036 -141127	1	28.0	4.9	294
150930*	135622 -135646	1	0.33	2.8	188
151001	133101 -141133	5	73.6±29.9	3.3-4.9	147-194
151002	123616 -133233	5	29.5±12.9	3.1-5.1	147-194
151005†	113438 -155044	42	326.6±151.4	3.1-6.2	144-204
151006*	151220 -151258	1	2.1	4.8	283
Average±SD	All days	(total 55)	259±134 (52%)	-	-
Median	All days	(total 55)	222	-	-
Average±SD	**Excluding 151005**	**(total 13)**	**42.0±33.6 (80%)**	**-**	**-**
Median	**Excluding 151005**	**(total 13)**	**41.5**	**-**	**-**

Table 41. Summary of SOF alkane measurements for tank 13. * Single measurement

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150928*	141153 -141257	1	1.1	4.9	292
150930*	135449 -135542	1	12.9	12.9	194
151001	132928 -141655	5	22.9±10.5	3.4-4.9	154-190
151002	112139 -133118	11	16.1±8.5	2.1-5.1	139-194
151005	123245 -160628	14	27.5±12.0	4.0-7.7	166-205
Average±SD	**-**	**(total 32)**	**21.6±10.4 (48%)**	**-**	**-**
Median	**-**	**(total 32)**	**18.1**	**-**	**-**

Figure 58 and Figure 59 show the frequency distribution of the SOF alkane measurements at tank 13 and tank 16 respectively, for the week of on site measurements. As seen in the distributions, tank 16 emissions show a large spread, almost as two source distributions overlay with a secondary maximum and tail of observations above 250 kg/h corresponding to the atypical event with a malfunctioning valve at the tank roof during filling on October 5 as discussed previously. Tank 13 in Figure 58 showed a more typical tank emission distribution.

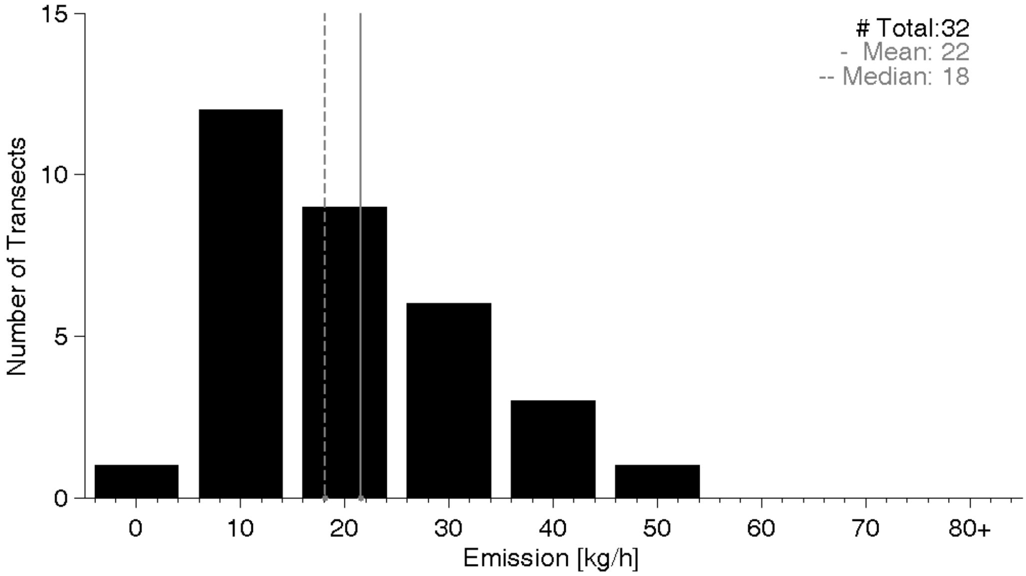

Figure 58. Histogram of all SOF measurements at Tank 13 during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

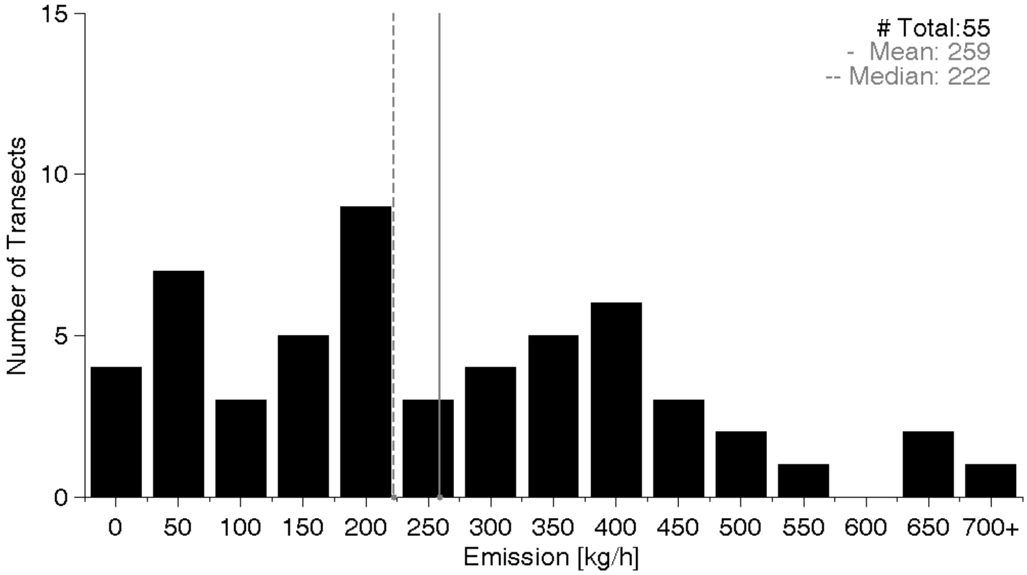

Figure 59. Histogram of all SOF measurements at Tank 16 during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

The ground concentration of aromatic BTEX and alkanes across the refinery tank farm are shown in Figure 60 and Figure 61 respectively. The ratio of aromatics to alkanes was measured using MWDOAS and MeFTIR while driving through the tank park. Measurements were specifically concentrated on tanks 13, 16 and 502.

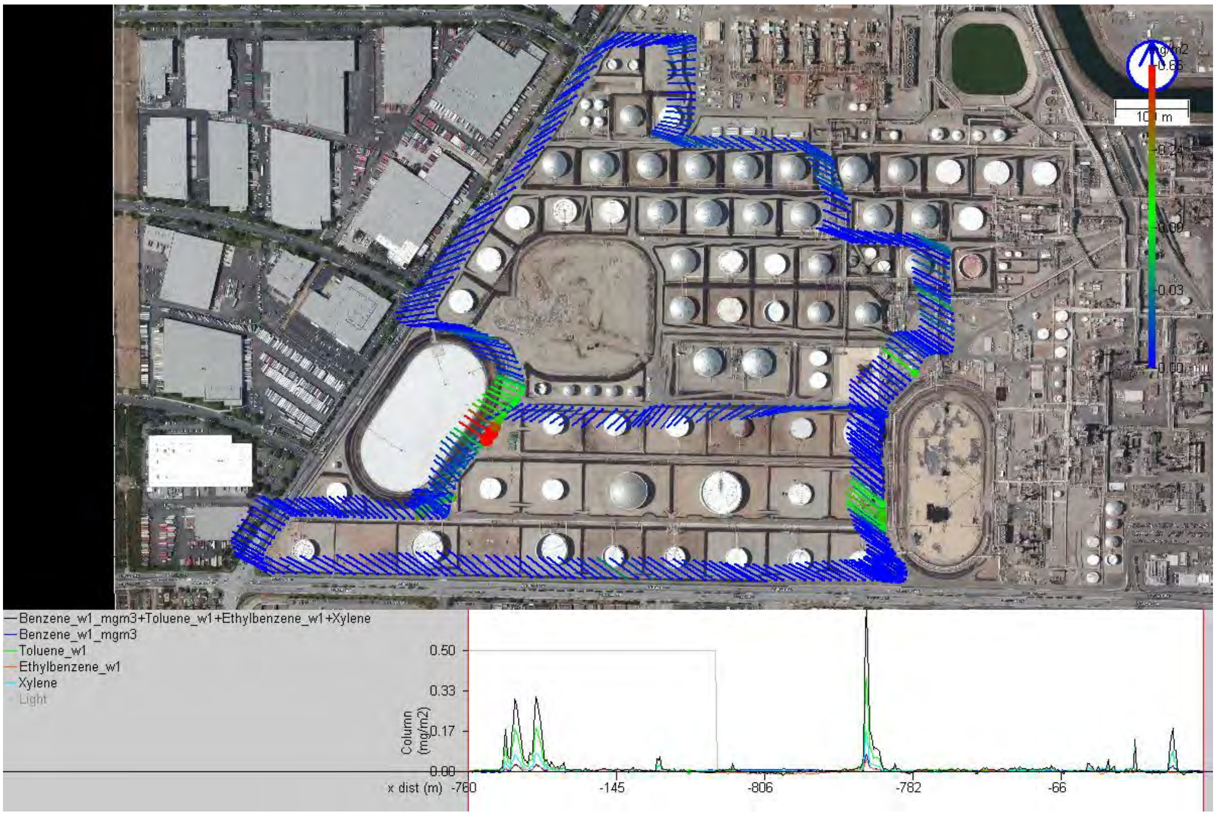

Figure 60. Aromatic VOC concentrations in mg/m^3 across the tank farm measured using MWDOAS. Bars are pointing towards the wind, hence in the direction of the source. North is upwards in the figure.

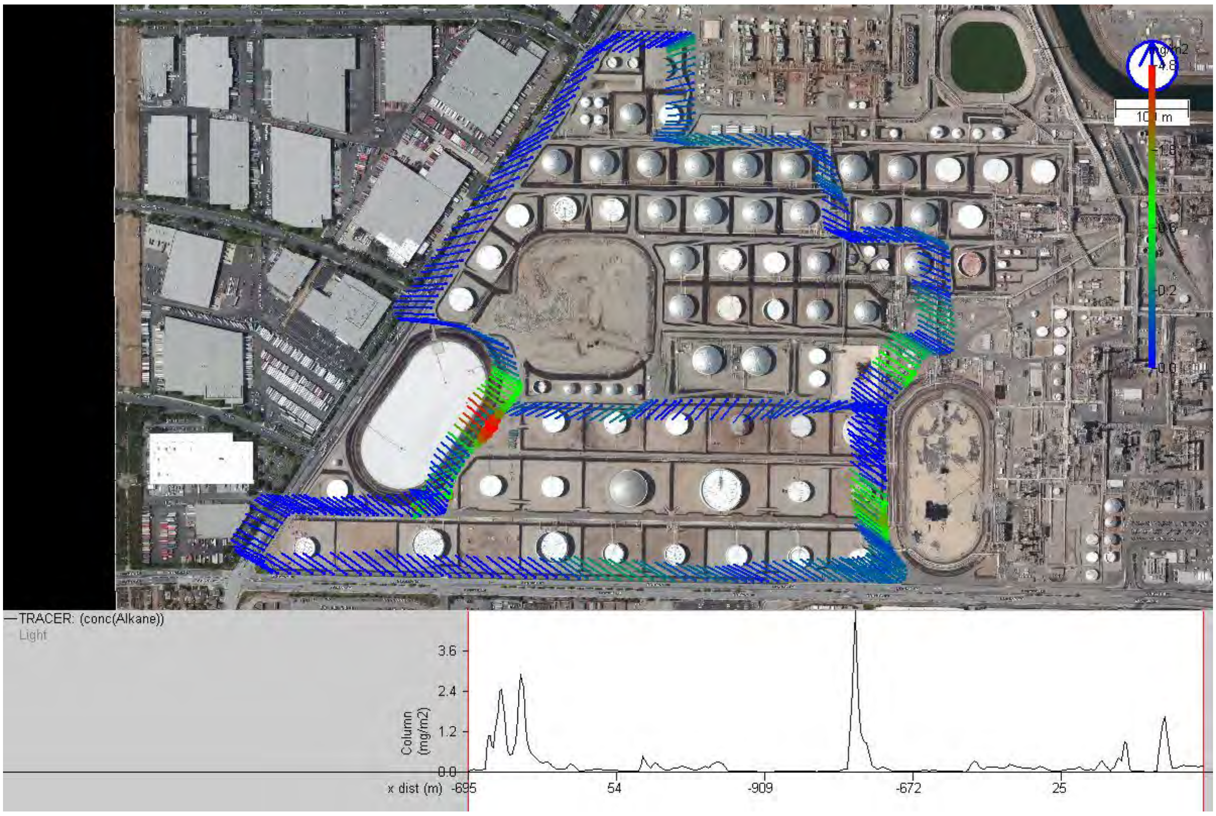

Figure 61. Alkane concentrations in mg/m^3 measured using MeFTIR across the tank farm. Bars are pointing towards the wind, hence in the direction of the source. North is upwards in the figure.

5.3 Further Leak search and Leak Detection

On site measurements with the real time geo-tagged result capabilities of the SOF + MeFTIR + MWDOAS techniques, as described in the previous section, are in a way a continuous leak search task. By driving the mobile lab on accessible roads on the upwind and downwind side of the different sources it’s possible to rather quickly (within hours) build a concentration map of a whole tank farm with located hot spots of elevated concentrations/emissions. Repeating this several times makes it possible to judge whether an observed emission pattern seems recurring or just being an intermittent release (for the time frame of the measurements). Repeated measurements at a site also build confidence in what emission levels that are normally observed, and when an aberration is observed and should be alarmed to the operations department.

During the 8 days of on site measurements between 28 September and 7 October, two major atypical emission events were identified, and reported to the operations and SCAQMD representatives. Tank_16, has already been discussed previously where a malfunctioning vent at the external roof of the crude tank inferred atypical high concentration levels and emission rates downwind of the tank 5 October. This was observed both by the MeFTIR and SOF measurements, and an inspection by operations verified the vent being stuck open.

Another atypical leak was found in the southern part of the so called *Tanks_Northeast* area, see Figure 52. Passing on the road south of the area, elevated alkane concentrations was observed with about 70,000 ppb in contrast to ten to hundred ppb normally observed downwind the various tanks. The leak was discovered late in the day, short before working permits ended as well as the sun setting to low for continued work. SOF and MeFTIR measurements pointed out an area next to the ground in the vicinity of several pipe lines. A gas camera was brought in to visualize that gas was indeed emerging from the soil beneath the pipes. Tubing was also attached to the MeFTIR instrumentation for “walk around” leak search with the tubing sampling air from locations around the pipe lines and at the ground. Figure 62 shows a SOF measurement from the particular site. Six SOF measurements between 4 PM and 5 PM on 30 September estimated the leak to be on average 31 kg/h.

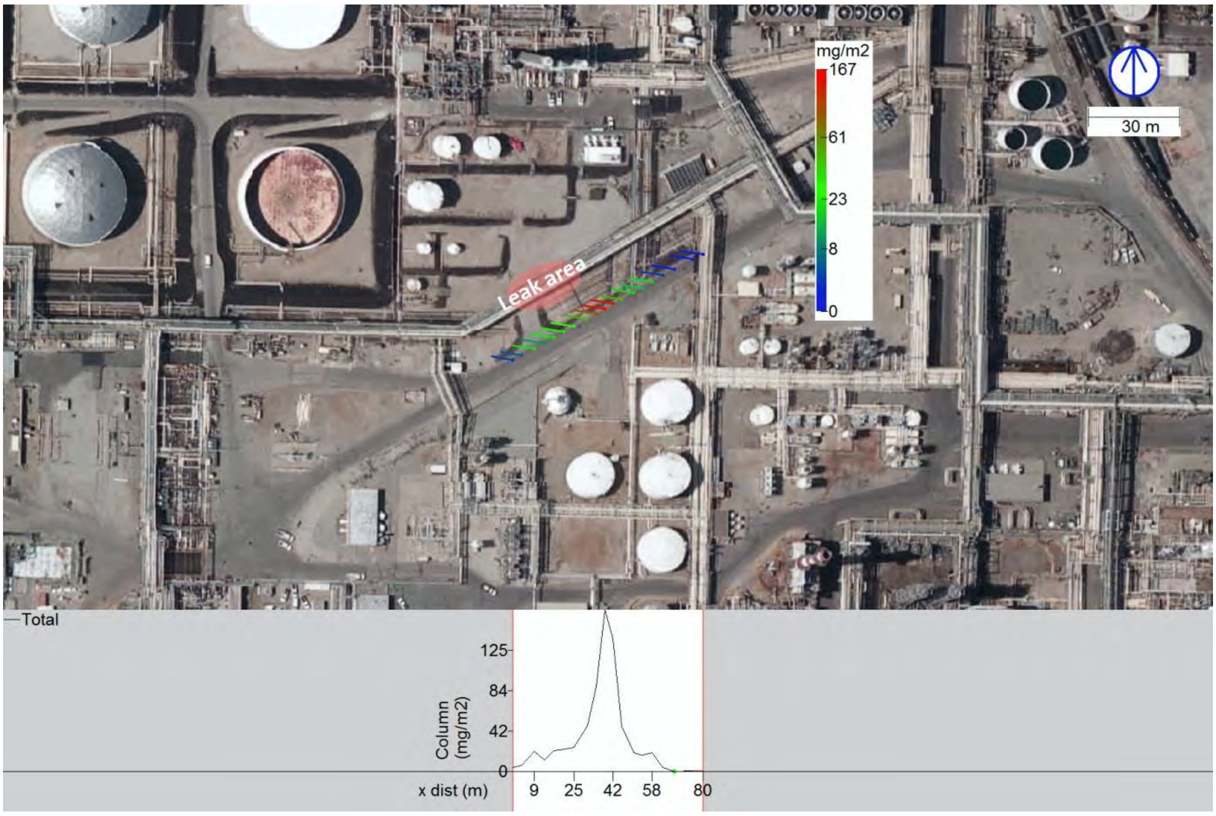

Figure 62. SOF measurement observing an atypical leak from the soil ground near a set of pipe lines. The leak area is indicated by a light-red area. The colored lines show observed alkane column (mg/m^2) with the lines pointing towards the wind and potential source. The graph beneath the picture shows integrated alkane column along the transect through the plume with traversed distance in meters.

Personnel from operations and SCAQMD were notified about the findings at once, and the source of emissions was further investigated by the refinery staff who immediately took appropriate actions. A leak, the size of a pinhole, was found in an alkane pipeline buried 30 cm below the ground. After the leak was repaired additional SOF and MeFTIR measurements were conducted to verify that the issue was resolved.

This case illustrates how mobile optical measurements and gas imaging information can be used to identify unknown leaks, and that immediate call upon and guidance of repair efforts can safely mitigate and suppress the risk of any further, potentially serious, complications. In general during the onsite measurements, working together with the experienced operations staff provided valuable input for interpreting the observed emissions and potential deviations from normal operations.

6 Discussion and Conclusion

Emission measurements of VOCs (alkanes, methane, and BTEX), SO_2 and NO_2 from six major refineries in the SCAB have been carried out by FluxSense Inc. using several state-of-the-art ORS techniques during a two and a half month campaign. The six refineries have a combined capacity of more than 900,000 barrels of crude oil per day and constitute an important stationary source of VOC emissions in Southern California.

For each refinery we compared the measured emission rates to the corresponding emission inventory values obtained by means of the US EPA AP-42 model (US-EPA 2013). The reported annual emissions have been divided by 12 to obtain average monthly emission rates, which were then compared to measured monthly median emissions obtained in this study. Thus, the comparisons are representative for September 2015 (the time-period when most of the measurements were performed).

An analysis of measured monthly emissions from each refinery normalized by the corresponding crude oil capacity is presented in Table 42. The overall alkane emission factor for all refineries in the SCAB (% of total emitted mass of alkanes to total capacity mass of crude oil) is 0.024%, ranging between 0.017 % and 0.045 % for the different facilities. This average emission factor is within 0.03 % and 0.1 %, a range observed from previous measurements conduced at well-run refineries in Europe (Kihlman *et al.* 2005; Mellqvist *et al.* 2009; INERIS 2010; Samuelsson *et al.* 2011). Thus, according to this data, the refineries in the SCAB are characterized by relatively low emissions compared to their capacity.

Table 42. Capacity normalized VOC (Alkanes+BTEX) emission factors * for the 2015 SCAQMD survey.

Measured Refineries 2015 Survey	**Crude Oil Capacity***		**Measured Monthly Emission**	**Emission Factor**
			Alkanes + BTEX	Alkanes + BTEX
	[bbl/day]	Tons¹/mo	Tons¹/mo	[%]
Refinery A	257300	1086215	214	0.020%
Refinery B	139000**	586801**	59	0.045%
Refinery C			205	
Refinery D	104500	441156	132	0.030%
Refinery E	269000	1135608	201	0.018%
Refinery F	149500	631128	109	0.017%
Sum of all	**919300**	**3880908**	**919**	**0.024%**

*Crude capacity data is obtained from the 2016 California Energy Commission report. The overall emission factor is based on the sum of measured emissions for all refineries relative to the total capacity.

**Crude capacity for Refinery B and Refinery C are reported together since Refinery B processes the crude oil and Refinery C upgrades intermediate products to finished products.

[1] Metric Tons

A comparison between the measured monthly emissions and the average monthly emissions from the inventories (i.e., annual inventory emission divided by 12) is presented in Table 43. For all major refineries in the SCAB, the ratio between measured and reported emissions for September 2015 (denoted as D in table 43) is 6.2 for VOCs, 1.5 for SO_2, and 0.83 for NO_x. For benzene this ratio is ~34, although the total measured benzene emissions were relatively small. Note that the inventories report NO_x (NO_2+NO), while only NO_2 is measured by the SkyDOAS. However, previous studies have shown that NO_2 typically constitutes 75 % or more of the NO_x found in the air around refineries (Rivera *et al.* 2010).

Table 43. Reported (*Rep*) average monthly emissions [metric tons per month] from the available inventory for the six SCAB refineries and measured emissions (*Meas*) for the 2015 SCAQMD survey. *D* denotes the ratio between measured and reported emissions (Meas/Rep). The overall discrepancy values (last row) are calculated from the total sum of reported and measured emissions, respectively. The comparisons are representative for September 2015.

Refineries	*Total VOC*			*SOx*			*NOx* [1]			*Benzene*		
2015 Survey	**Rep.**	**Meas.**	**D**	**Rep.**	**Meas.**	**D**	**Rep.**	**Meas.**	**D**	**Rep.**	**Meas.**	**D**
	Tot VOC	*Alk+ BTEX*		*SOx*	*SO_2*		*NOx*	*NO_2*				
	tons /mo	tons /mo	[]	tons /mo	tons /mo	[]	tons /mo	tons /mo	[]	tons /mo	tons /mo	[]
Refinery A	33	214	6.4	38	46	1.2	50	48	1.0	0.06	2.5	43
Refinery B	7	59	8.3	26	39	1.5	30	23	0.8	0.03	0.8	33
Refinery C	17	205	12	10	27	2.7	37	42	1.1	0.03	6.0	202
Refinery D	12	132	11	7	12	1.7	23	25	1.1	0.03	1.2	39
Refinery E	37	201	5.4	23	39	1.7	57	46	0.8	0.05	2.0	38
Refinery F	40	109	2.7	25	27	1.1	39	13	0.3	0.19	0.6	3.2
All refineries	**148**	**919**	**6.2**	**129**	**190**	**1.5**	**237**	**197**	**0.8**	**0.38**	**13**	**34**

[1] Nitrogen oxides (NO_x) are reported in inventories while only the NO_2 fraction was measured by SkyDOAS.

The comparison of measured emissions with annual inventory values presents a number of challenges. Firstly, it is important to know whether the studied refineries operated under typical conditions during the measurement campaign. Since operational data from the facilities is not available for this project, we estimated the average monthly emission rate at each site by dividing the reported annual emission inventory value for each facility by 12.

Secondly, it has to be established that a sufficient number of measurements have been conducted during the measurement period to eliminate the risk of disproportional influence from intermittent emissions due to tank cleaning, maintenance, flaring, etc. To address this point the frequency distributions of the measured emission (as shown in Figure 15) have been analyzed and taken into account in our calculations. As a result median measured emissions were used for comparison with inventories instead of average measured emissions, therefore reducing the sensitivity to outliers.

Thirdly, the effects of differences in meteorological conditions between September 2015 and the entire year need to be considered to establish how representative the emissions measured during the study were to the entire year. In our experience, tank emissions contribute approximately 2/3 of the total refinery emissions (Kihlman 2005). At the same time, emissions from tanks are also more affected by environmental parameters such as wind, temperature and solar insolation, than emissions from process units. Therefore, a sensitivity study for two types of crude oil tanks, external floating roof tank (EFRT) and internal floating roof tank (IFRT), utilizing the formulas in the AP-42 model was conducted. A very similar approach has been previously applied to evaluate seasonal variations of refinery emissions (Johansson *et al.* 2014b). During the measurement campaign, the average maximum daytime temperature was 5.4 °C higher than the 2015 average annual temperature of 19.6 °C (data from weatherunderground.com for Torrance Airport), while the 2015 monthly and annual average wind speeds were both 2.2 m/s (data from weatherunderground.com for Long Beach Airport). In addition, the monthly average solar radiation was 22 W/m^2 higher than the annual average of 226 W/m^2 (data from Torrance airport from the National Solar Radiation Database). According to AP-42 model, these differences in meteorology combined resulted in 11 % and 29 % higher modeled emissions for September 2015 than for the annual average for the IFRT and EFRT, respectively. These values are within the uncertainty of the SOF method.

Additionally, no dependency of measured emissions on temperature and wind speed was observed. Figure 63 illustrates that there was no obvious correlation between measured alkane emissions and wind speed or temperature at Refinery A. Therefore, the observed discrepancies between measured emissions and reported inventories (based on the AP-42 standard (US-EPA 2013)) are considerably higher than what can be explained by measurement uncertainties or short-term sampling alone.

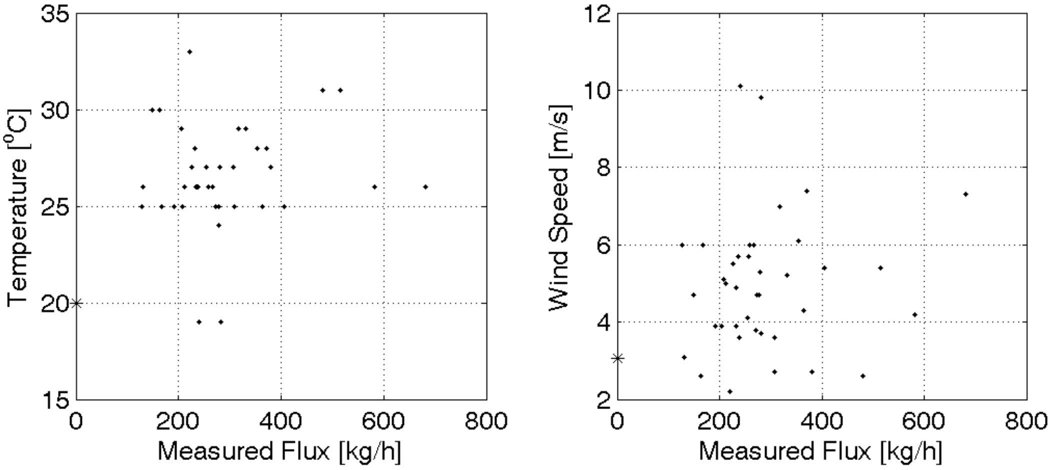

Figure 63. SOF emission data from Refinery A plotted against the corresponding local temperature and wind speed values (left and right plots, respectively). *Annual average values from the meteorological station at Torrance Airport (KTOA) 2015 [www.weatherunderground.com].

Refineries and tank farms are complex environments with a large number of installations and numerous potential emission sources (e.g. tank seals, valves, gauges, flares, vapor recovery units, etc.). Many of these components can show degrading performance over time, and to accurately account for the impact of non-ideal performance in emissions inventory reporting is, we believe, an impossible task. Nevertheless, EPA's AP-42 system provides valuable insights for a specific facility on the production and abatement techniques applied, and on what emission level the site could reach given ideal performance of all installations. Comparing measured emissions to ideal performance levels established by AP-42 could provide a basis for benchmarking of different refineries or sites.

OUTLOOK

Studies conducted in the SCAB, the Bay Area, Texas, and other places worldwide, show that field measurements provide a reliable way to determine actual emissions of VOCs and other pollutants from refineries and various industrial sites. Accurate estimates of VOC and other pollutant emissions from industrial sources are crucial for improving air quality models, to guide air pollution mitigation strategies, promote successful compliance strategies, and reduce exposure for nearby communities.

In our experience, the observed difference in fugitive VOC emissions between measured and inventory estimates is a general issue for the petroleum industry worldwide. We believe that a possible path forward could be to conduct monitoring in parallel with continued AP 42 based reporting, and to use the measurements to guide and verify the efficiency of the emission reduction efforts at the industrial sites.

Longer-term ORS studies spanning over different seasons could be conducted in order to alleviate concerns stemming from comparison of emissions measured over limited-time to annual emissions reported through the inventories. Additionally, future studies could combine ORS measurements and site-specific emission modeling performed for inventory calculations. A better dialog between scientists conducting the measurements and the facility operators could also be crucial to improve our understanding of how site activities may affect measured emissions.

Traditional Leak Detection and Repair (LDAR) is an important practice to control and limit unplanned VOC emissions from refineries and to identify potential leak sources. The ORS techniques used in this study have demonstrated their ability to quickly quantify and map refinery emissions and to identify potential air pollution sources within a facility. Using real time measurements, refinery personnel and air quality regulators can enhance LDAR programs by prioritizing LDAR activities. Addressing the most concerning issues first is important to reduce occupational risks for refinery workers, avoid public hazard exposures, and limit the economic losses due to unplanned evaporation of refinery products.

A continued path towards improved air quality involves a good understanding of current emission levels and sources. Repeated and systematic emission measurements will be an important tool for benchmarking industry's environmental performance as well as for sustaining and verifying efficient emission improvement plans, ultimately resulting in cleaner air and a better environment.

7 References

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8 Acknowledgements

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9 Appendix A: Quality Assessments

Quality checks and measures are performed at several levels in order as indicated in Figure 2 and given below. On arrival, FluxSense personnel will power up the equipment, check operating parameters, and test the instruments. The purpose is to run operational checks to catch problems prior to field deployment and repair all malfunctioning equipment.

Quality Checks and Routines

PRIOR TO MEASUREMENTS:

Vehicle:

1. Checking vehicle status according to safety and performance
2. Mount warning lights and signs
3. Make sure that battery pack is fully charged
4. Make sure any loose items are stowed away securely

Instruments:

1. Turn on instruments and make sure that detectors are properly cooled
2. Optimize signals by optical alignment (SOF, SkyDOAS, MWDOAS, MEFTIR)
3. Cleaning mirrors and optics if necessary (SOF, SkyDOAS, MWDOAS)
4. Rotational alignment (SOF). Tolerance: ±2 mg/m^2 in any direction
5. Checking spectral resolution and response (SOF, SkyDOAS, MWDOAS, MEFTIR)
6. Take calibration spectra (SkyDOAS, MWDOAS)

GPS:

1. Checking that GPS information is available and reasonable
2. Check time synchronization of all instruments and computers

Wind:

1. Checking that the time difference of logger and computer and synchronize if necessary. Tolerance 1s.
2. Select an open flat surface at a representative location for the measurements
3. Erecting the wind mast vertically and secure it firmly
4. Directing sensor correctly (toward magnetic north) using a compass. Tolerance: ±5 deg
5. Put the LIDAR truck on level ground.
6. Check that wind information is available and reasonable.

DURING MEASUREMENTS:

1. Drive slowly and steadily to reduce vibration noise. Around 20-30 km/h for SOF/SkyDOAS and around 10-20 km/h for MWDOAS/MEFTIR (dependent on distance to source and the spatial resolution required)
2. Avoid shadows as far as possible during solar measurements (SOF, SkyDOAS).
3. Try boxing the facilities when possible or make relevant upwind/background measurements continuously.
4. Keep track of wind directions and measured columns/concentrations so that the entire plume from a facility is captured.
5. Always try to start new measurements outside the plume.

6. Aim for 3-5 transects with acceptable quality (See section on data analysis below) per facility and day and at least 1 upwind measurement (if not boxing).
7. Take notes and photos on interesting findings and events
8. Check the wind meter on a regular basis to make sure that it is operational

AFTER MEASUREMENTS:

1. Turn off instruments and download gas measurement data to external hard drive
2. Download data from wind mast logger and save to external hard drive
3. Download data from wind LIDAR and save to external hard drive
4. Dismount wind mast if not in safe location
5. Turn off wind LIDAR and store securely over night
6. Store Airmar data and measurement notes on external hard drive
7. Update survey documents and Google Earth maps accordingly
8. Charge vehicle, LIDAR and data logger batteries over night
9. Make sure that instruments are well protected inside the vehicle from rain/moisture

DATA ANALYSIS:

1. Discard transects with noise levels above the detection limits (see Table 1)
2. Discard transects with significant baseline variations
3. Discard transects with significant data gaps in the plume
4. Discard transects with extended vehicle stops
5. If incoming plumes are of significant magnitude compared to the outgoing plume (SOF and SkyDOAS) treat transects with extra care and require further statistics
6. Discard transects with average wind speeds below 1.5 m/s (SOF and SkyDOAS)
7. Discard transects with highly varying wind directions

Data Analysis, Interpretation, and Management

DATA REPORTING REQUIREMENTS:

A Draft and Final Report will be delivered to SCAQMD electronically (i.e., via file transfer protocol (FTP) or e-mail) in MS-WORD format no later than the established deliverable due date. After post-processing, validation and analysis, the data will be delivered to SCAQMD at the time of the final report.

DATA VALIDATION PROCEDURES:

Project personnel will maintain records that include sufficient information to reconstruct each final reported measurement from the variables originally gathered in the measurement process. This includes, but is not limited to, information (raw data, electronic files, and/or hard copy printouts) related to sampler calibration, sample collection, measurement instrument calibration, quality control checks of sampling or measurement equipment, "as collected" or “raw” measurement values, an audit trail for any modifications made to the "as collected" or “raw” measurement values, and traceability documentation for reference standards.

Difficulties encountered during sampling or analysis, such as interference between adjacent plumes, large upwind fluxes or highly variable wind fields will be documented in narratives that clearly indicate the affected measurements. All electronic versions of data sets should reflect the limitations associated with individual measurement values.

The data collected in the project will be made available in electronic format at the time of the final report. For all data we will produce ASCII tables with the geo-positioning and time. In addition kml files will be produced for the most useful data for Google Earth viewing.

To ensure high quality data an internal audit procedure of the data is carried out. In the project, gas columns obtained from SOF and mobile DOAS measurements are used to calculate gas fluxes through a procedure which includes manual checking of each measurement transect and manual choices of baselines etc (see previous section). In the audit procedure the completed transects will be reviewed by an independent experienced SOF-operator that was not involved in the actual data evaluation. At least one of the persons involved in the data processing must have been in the FluxSense mobile lab while the actual measurements were made

STATISTICAL PROCEDURES:

The final data will be presented as daily means and standard deviations for each facility together with histograms showing all individual measurements. The variability of the result will be a combination of measurement uncertainties, wind variability and actual variability in the emissions from the facility.

Extreme outliers are generally not excluded, unless non-typical conditions/operations at the facility are reported. In this case, the outliers will be reported separately so that these conditions/operations can be followed up.

More samples will provide a closer estimate of the actual emissions. In reality, the number of measurement will be a trade-off between acceptable statistics and available time and conditions for making the measurement and time sharing between other measurements. The aim is 3-5 transects with acceptable quality per facility and day during at least four days. If boxing is not performed, at least 1 representative upwind measurement per facility should be made.

DATA SUMMARY AND ANALYSIS:

The data will be post processed with the spectral retrieval programs QESOF (SOF) and QDOAS (mobile DOAS). This will give time series of column concentrations, positions and solar angles stored in ASCII-files. These files are loaded into custom software, SOF-Report, used to calculate fluxes.

Wind LIDAR data will be processed using the output from Leosphere WindCube system. Data files are saved as ASCII-files.

The weather mast will be connected to a real time data logger and will be periodically downloaded to a computer. The data logger samples the input voltage of each instrument at a set time interval, digitizes it, and stores the data sequentially into a record.

ASCII tables with time stamped geo positioned data will be produced. In addition kml files will be produced for viewing the data in Google Earth. The data will also be retained for a minimum of 5 years at FluxSense.

DATA STORAGE REQUIREMENTS:

The spectra from the spectroscopic measurements (SOF, SkyDOAS, MEFTIR, MWDOAS) are directly saved to the hard drive of the computer used to operate these instruments. At the end of each measurement day, all new such data will be copied to an external hard drive by the operator. Approximately 1 GB of data will be produced per measurements day.

10 Appendix B: Wind Plots

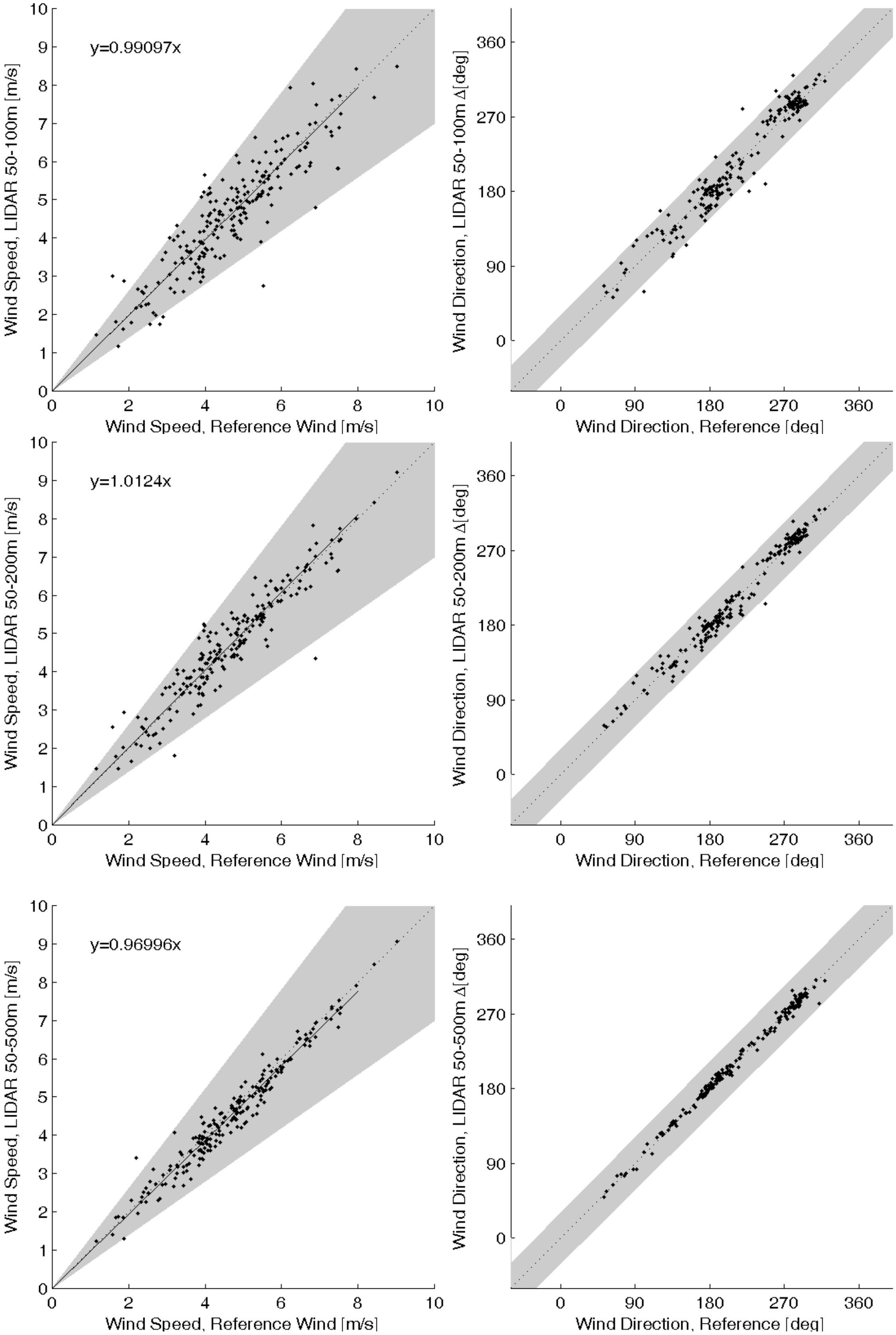


Figure 64. Wind LIDAR data for different altitude ranges versus the reference LIDAR wind (50-400m) during the calibration period 2-6 October 2016 at LIDAR site L1 (10 min average from 10AM to 5PM) . The shaded areas indicate ±30% relative deviation from reference wind speed (left panels) and ±30° deviation from reference wind direction (right panels). Fitted least squares are shown as solid lines.

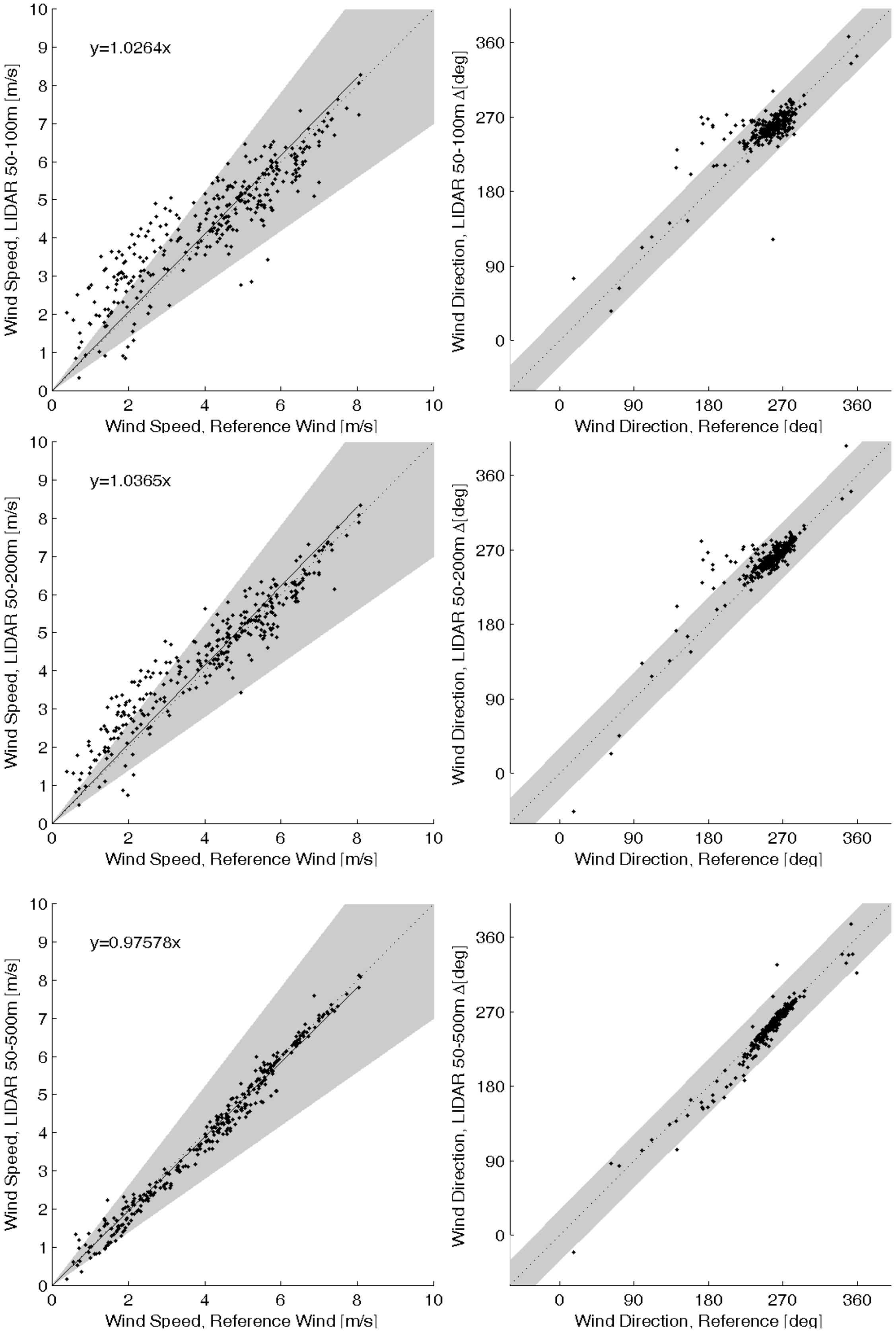


Figure 65. Wind LIDAR data for different altitude ranges versus the reference LIDAR wind (50-400m) during the calibration period 9-16 October 2016 at LIDAR site L4 (10 min average from 10AM to 5PM). The shaded areas indicate ±30% relative deviation from reference wind speed (left panels) and ±30° deviation from reference wind direction (right panels). Fitted least squares are shown as solid lines.

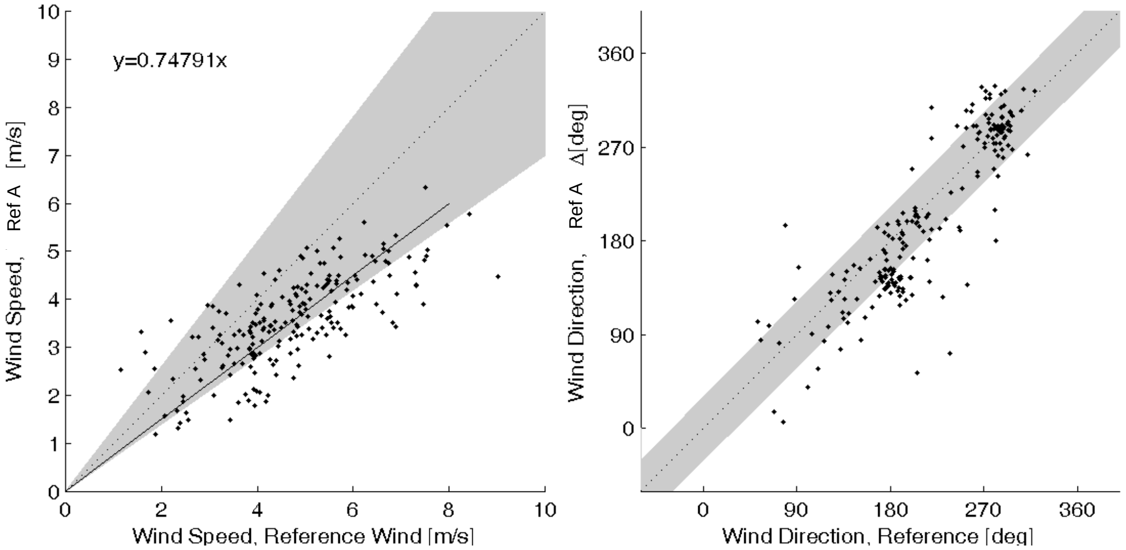


Figure 66. Refinery A´s 10m wind mast data versus the reference LIDAR wind (50-400m) (10 min average from 10AM to 5PM) during the calibration period 2-6 October 2016 at LIDAR site L1. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as solid lines.

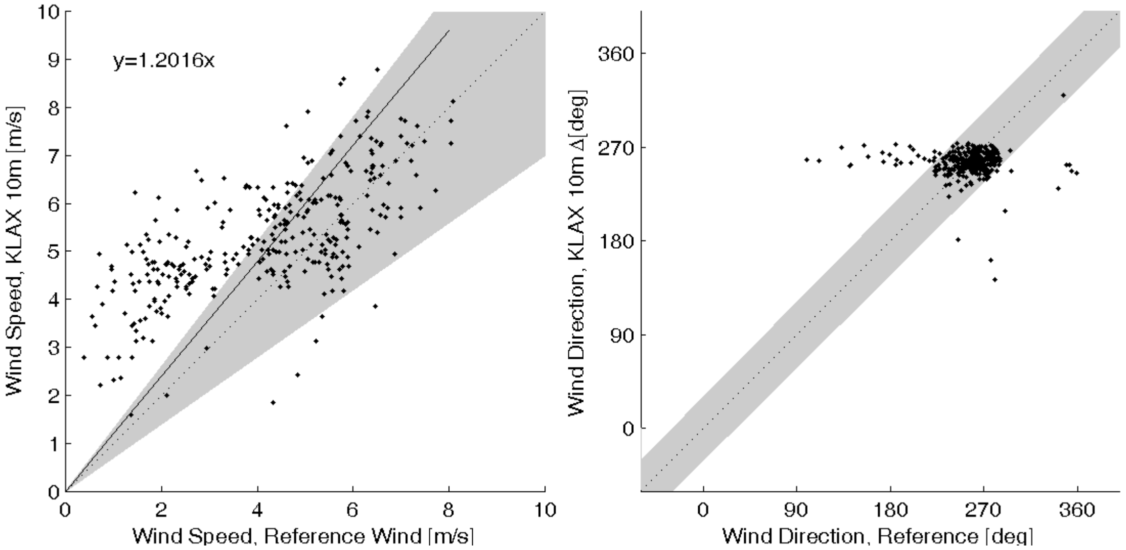


Figure 67. ASOS Met station at Los Angeles International Airport-KLAX versus the reference LIDAR wind (50-400m) (10 min average from 10AM to 5PM)during the calibration period 9-16 October 2016 at LIDAR site L3. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as solid lines.

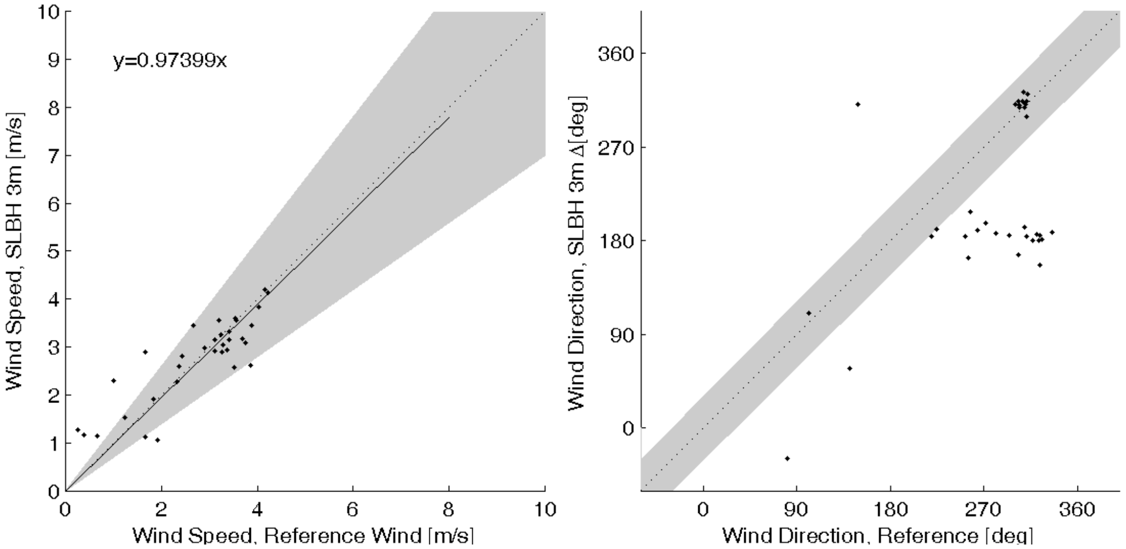


Figure 68. SCAQMD Met station at South Long Beach (SLBH) versus the reference LIDAR wind (50-400m) (10 min average from 10AM to 5PM)during the calibration 18 October 2016 at LIDAR site L2. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as solid lines.

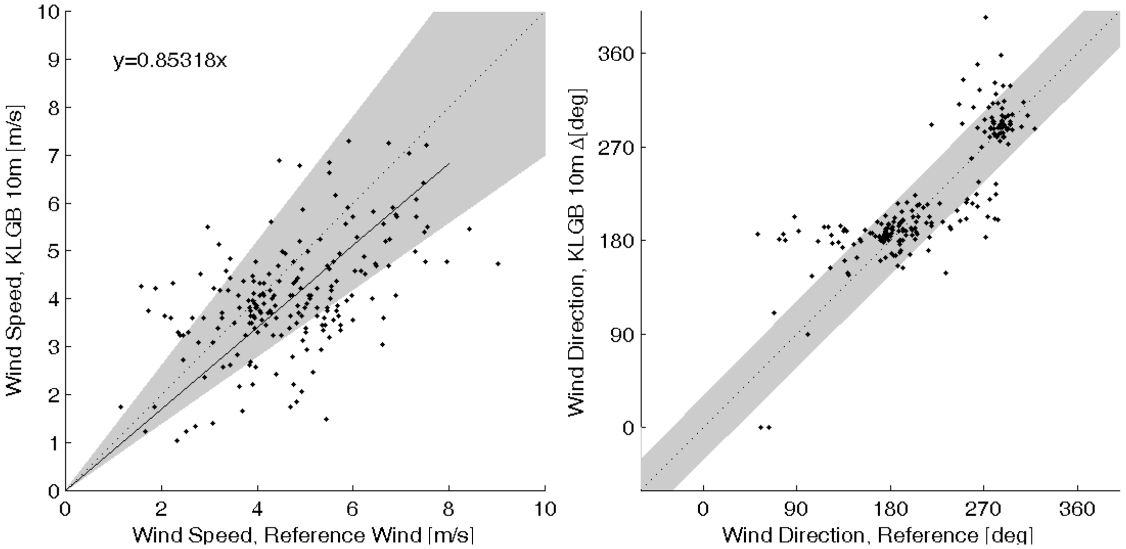


Figure 69. ASOS Met station at Long Beach Airport (KLGB) versus the reference LIDAR wind (50-400m) (10 min average from 10AM to 5PM)during the calibration period 2-6 October 2016 at LIDAR site L1. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as solid lines.

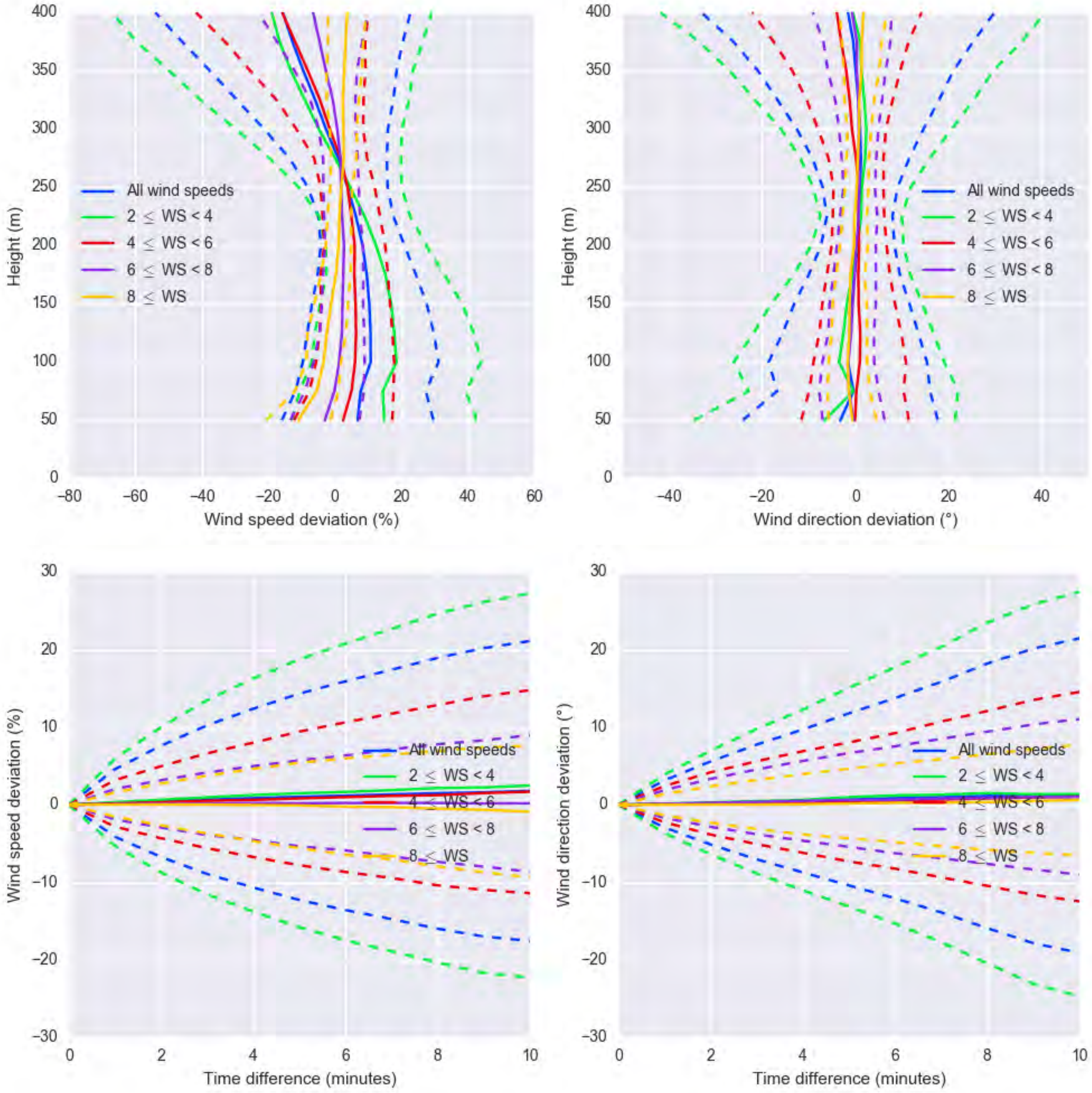


Figure 70. Wind LIDAR 10-min data for the entire SCAQMD survey 2015. Average (solid lines) and 1σ deviations (dashed lines). Top row panels show altitude information and the lower row shows time dependence. Different colors represent different wind speed ranges.

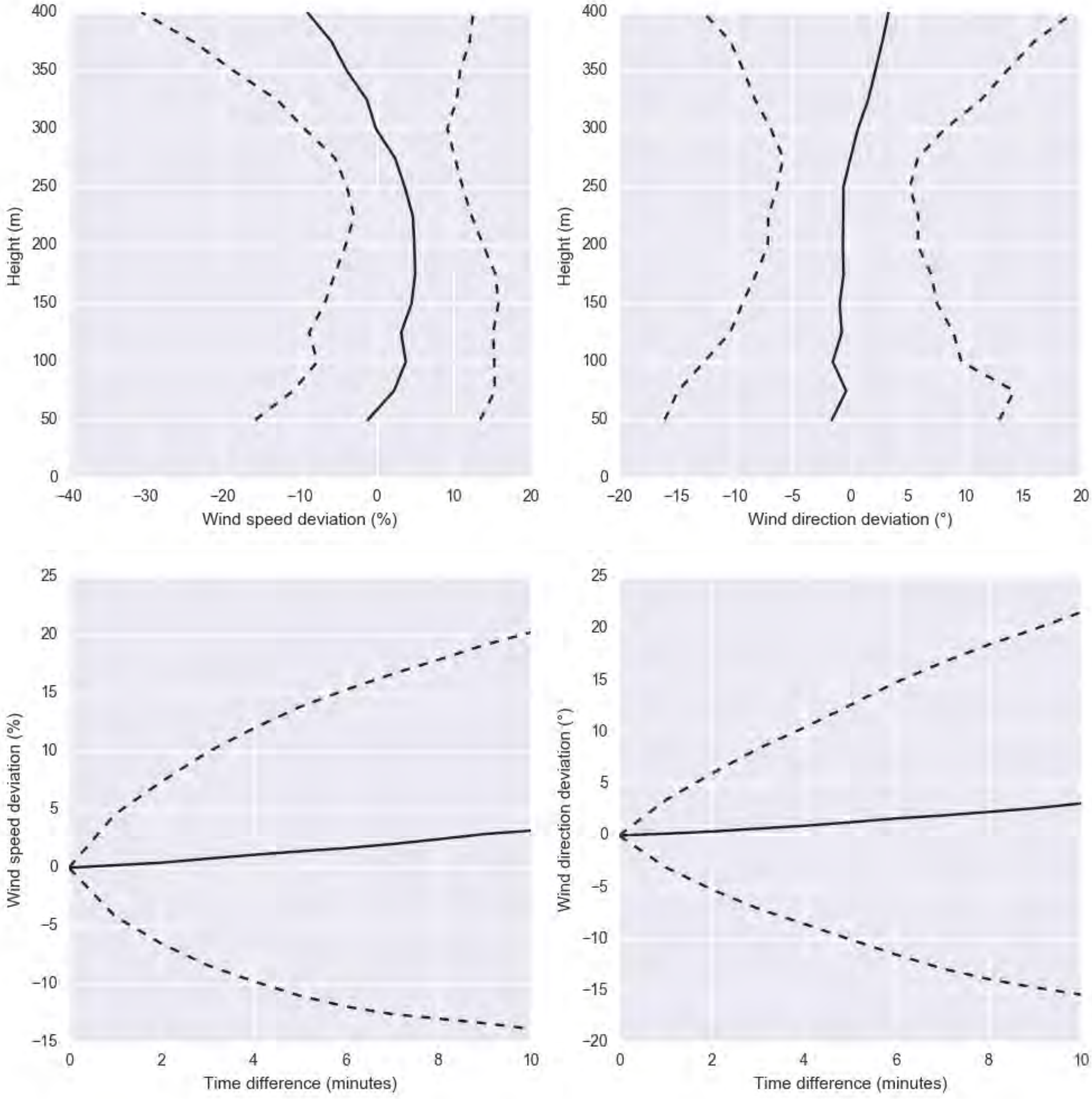


Figure 71. Wind LIDAR 10-min data at L1. Wind data averages (solid lines) and 1σ deviations (dashed lines) for the calibration period (9-16 Oct) during the SCAQMD survey 2015. Top row panels show altitude information and the lower row shows time dependence.

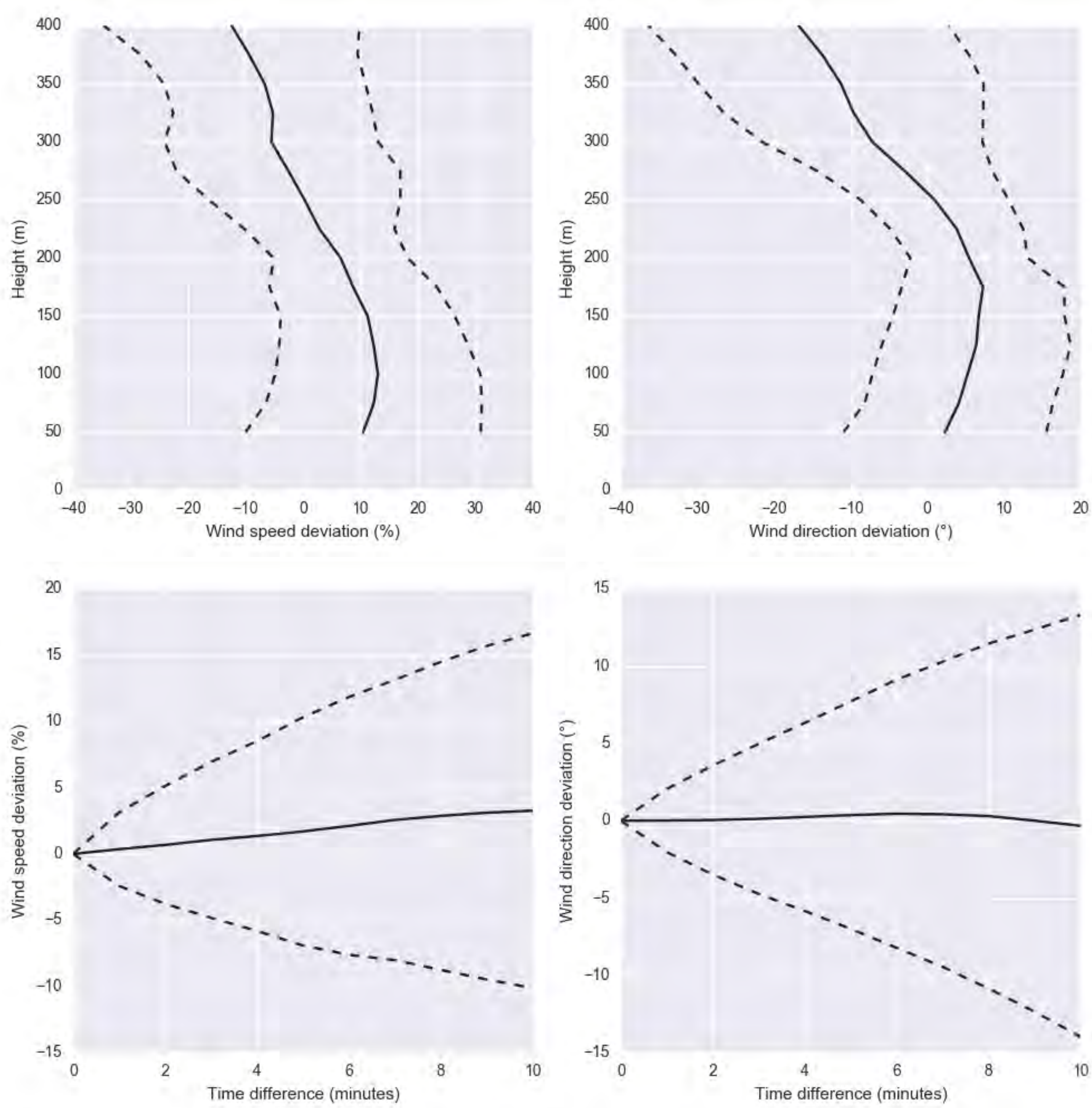
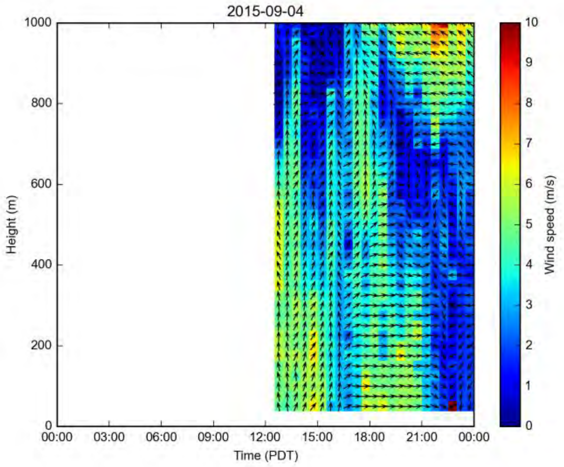


Figure 72. Wind LIDAR 10-min data at L4. Wind data averages (solid lines) and 1σ deviations (dashed lines) for the calibration period (2-6 Oct) during the SCAQMD survey 2015. Top row panels show altitude information and the lower row shows time dependence.

Figure 73. Wind LIDAR data (30 minute averages) from 50 to 1000 m for all measurement daysin this project. Arrows indicate wind direction and color wind speed (0-10 m/s). White gaps when no data available due to limited back scatter signal or other reason. **All panels below**.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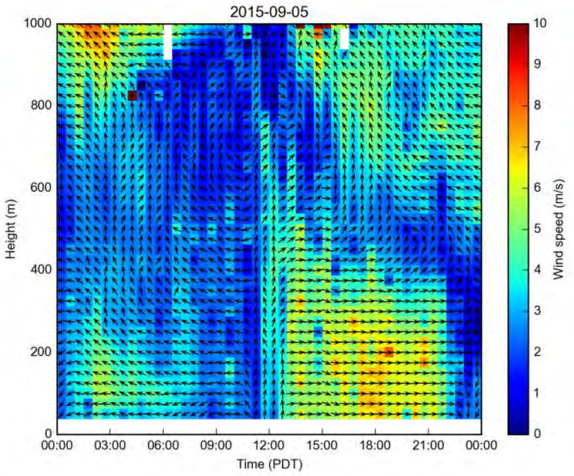
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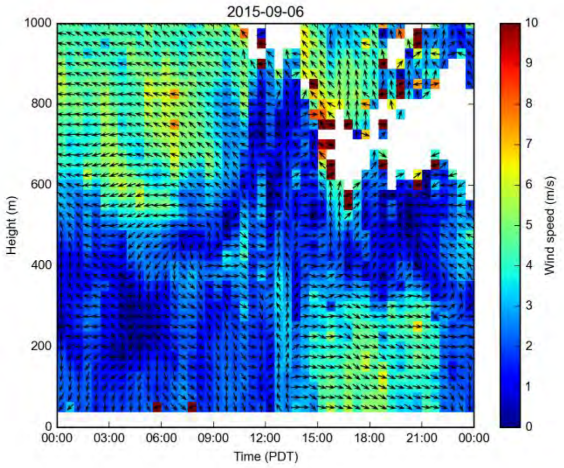
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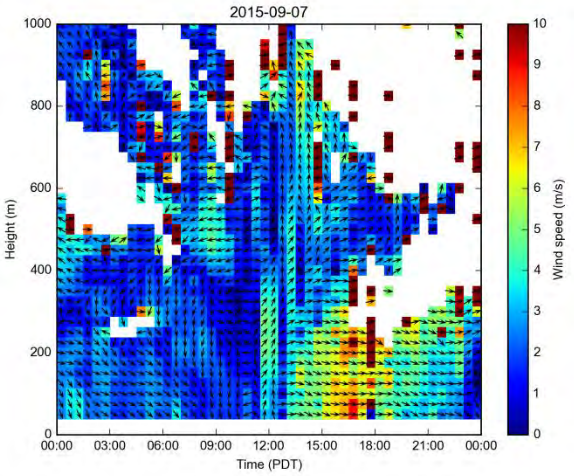
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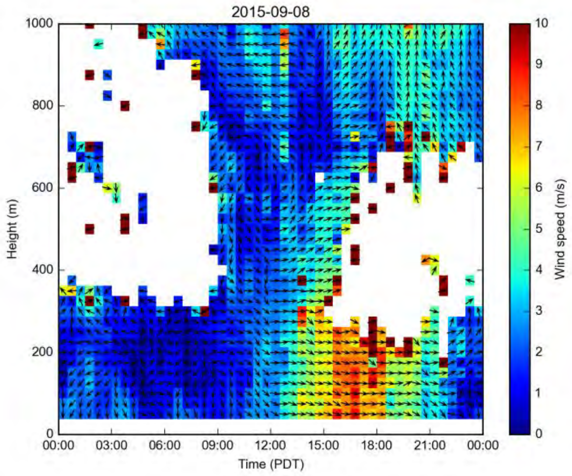
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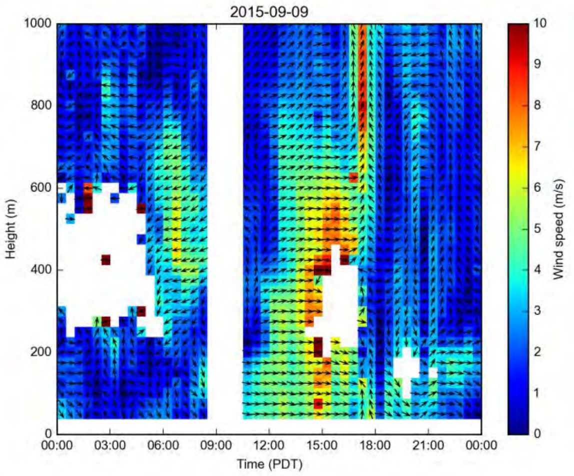
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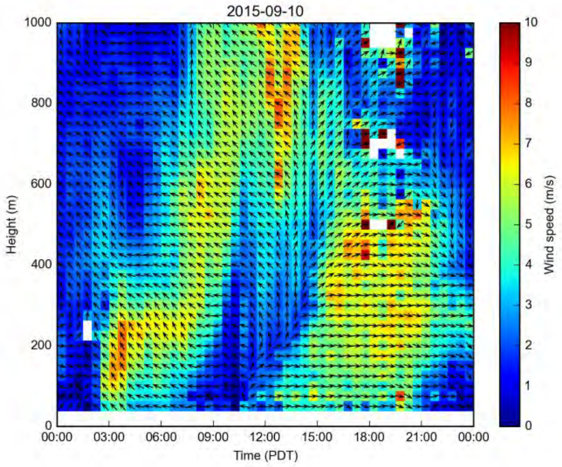
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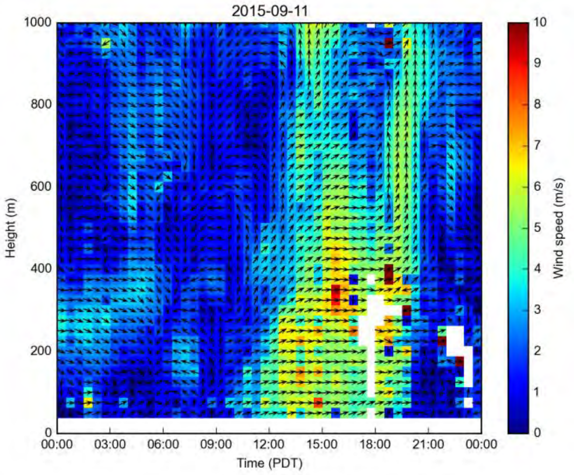
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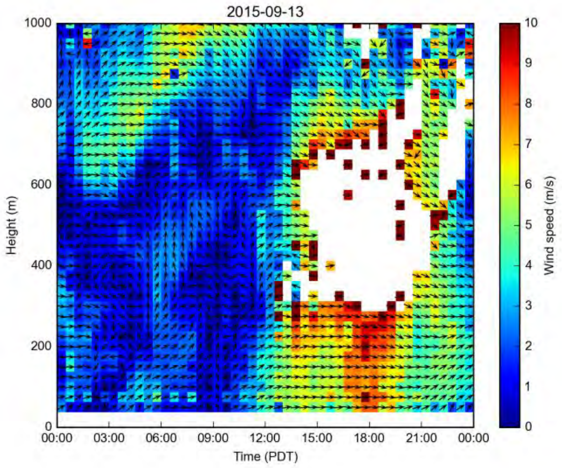
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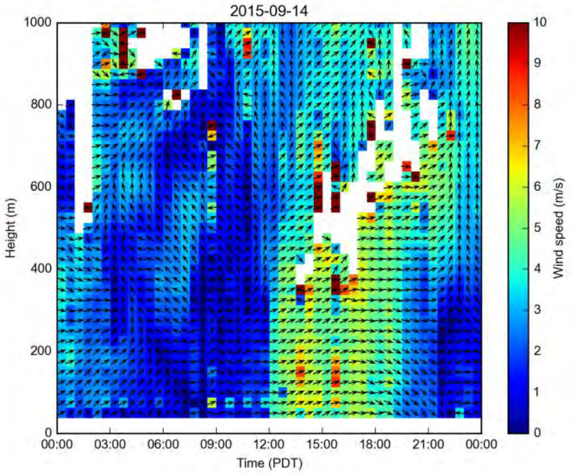
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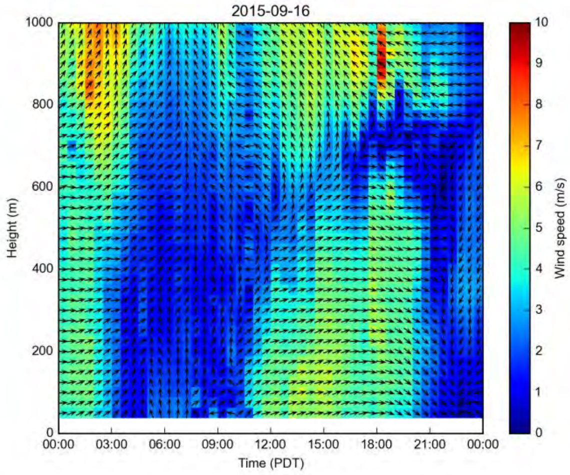
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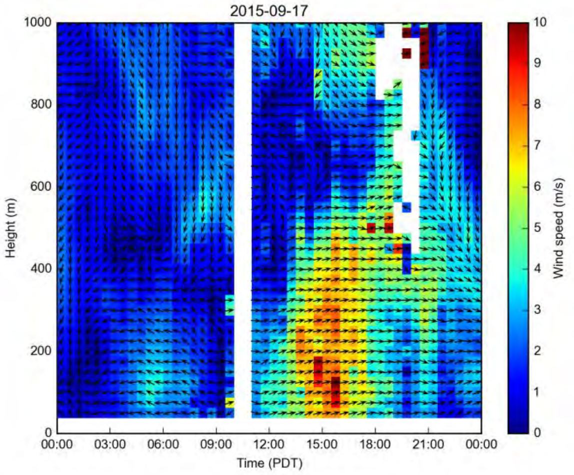
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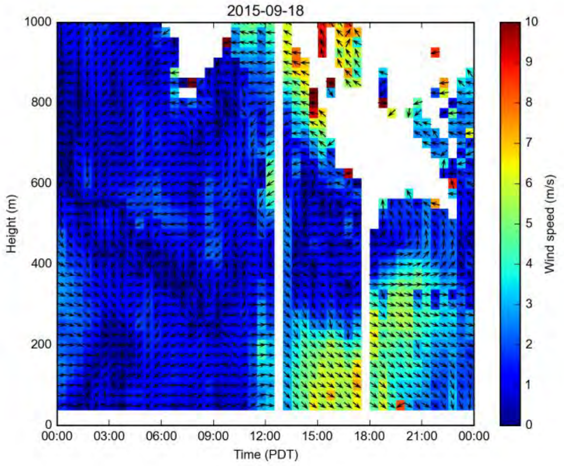
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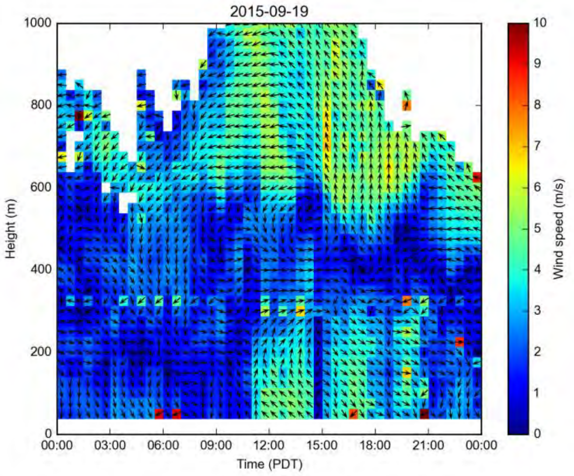
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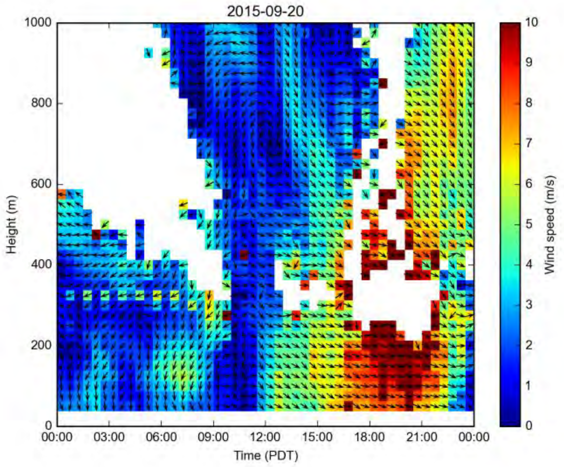
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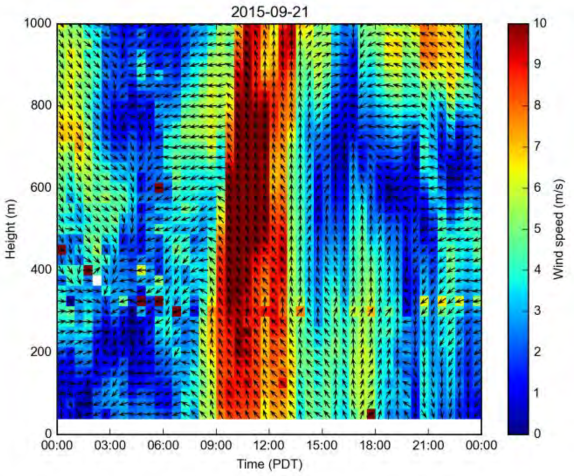
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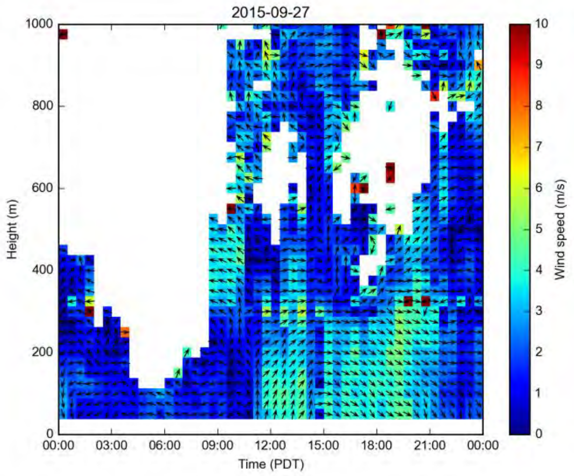
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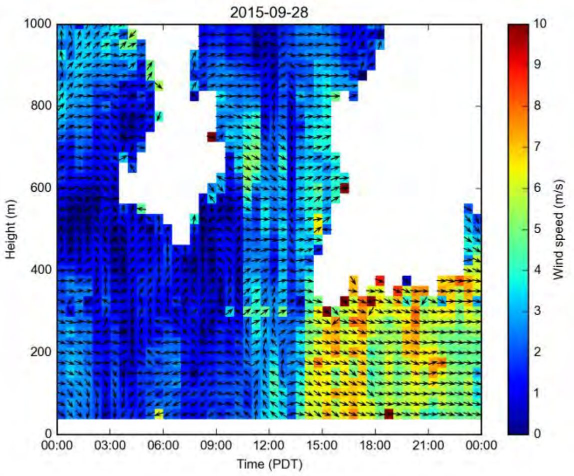
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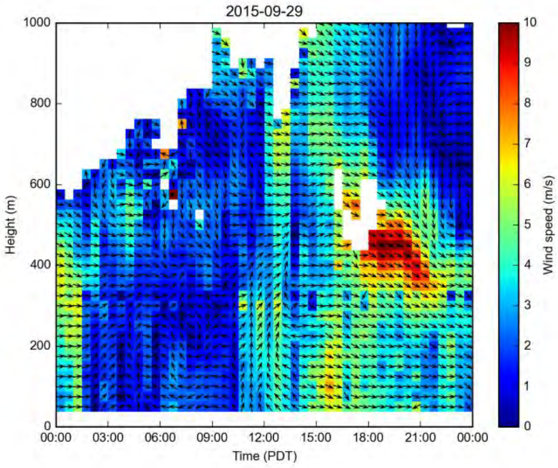
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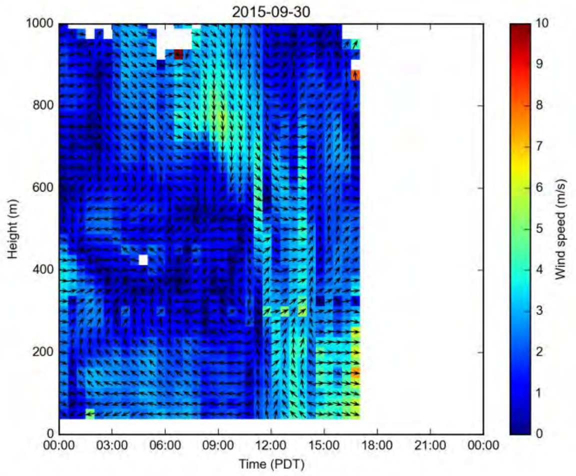
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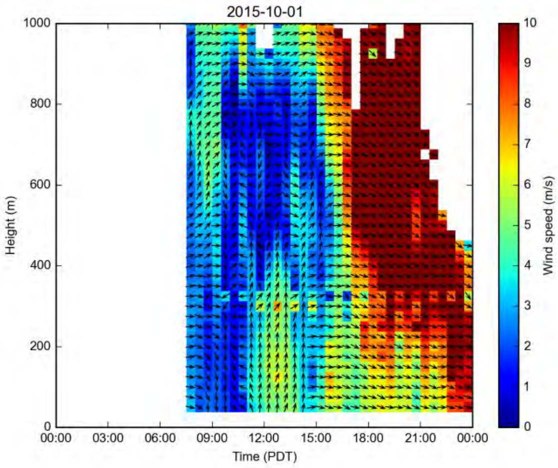
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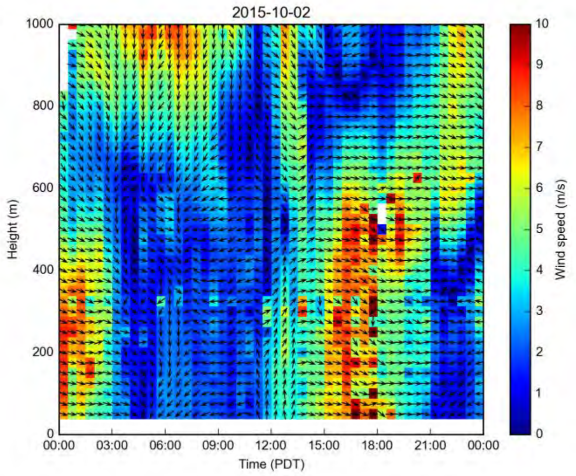
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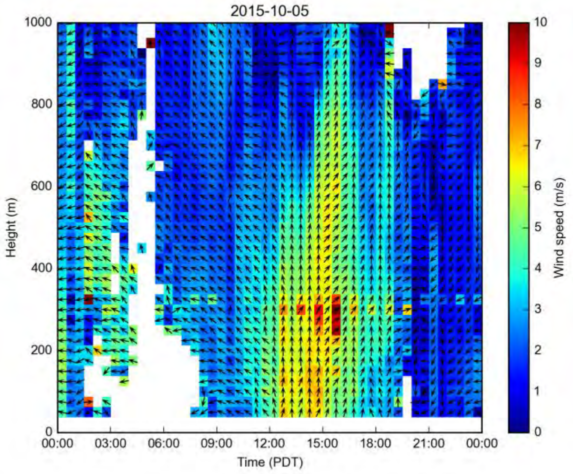
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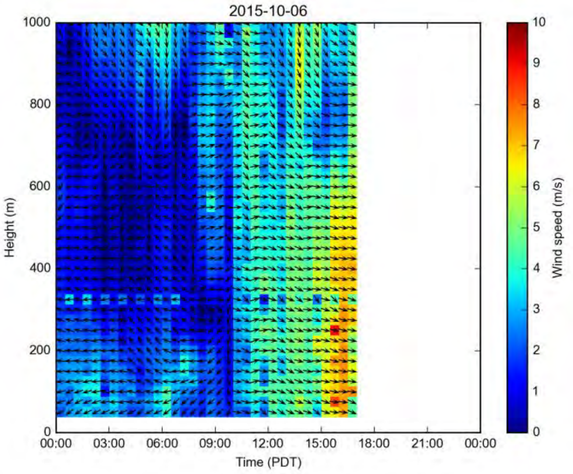
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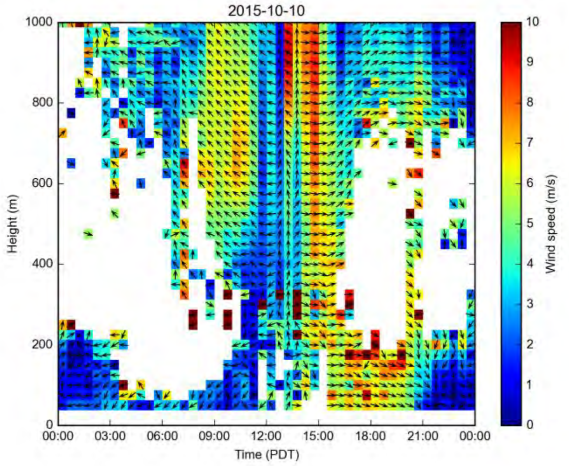
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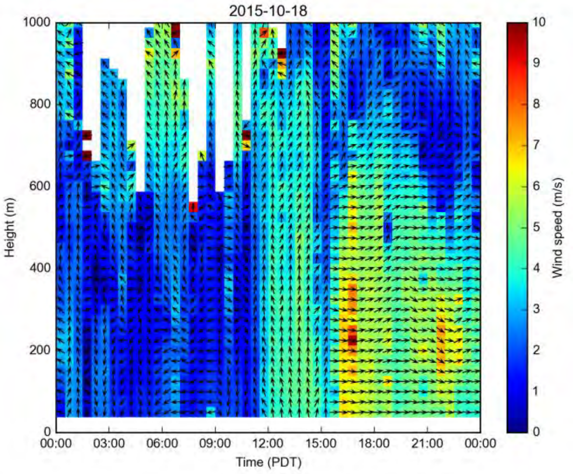
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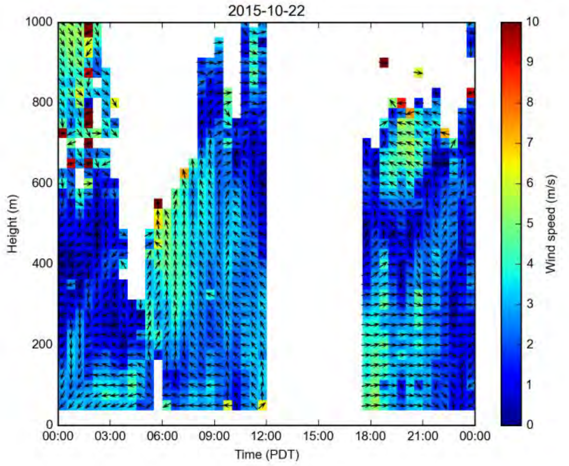
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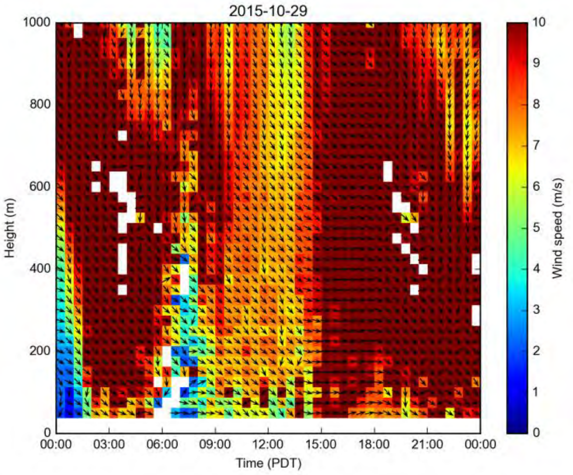
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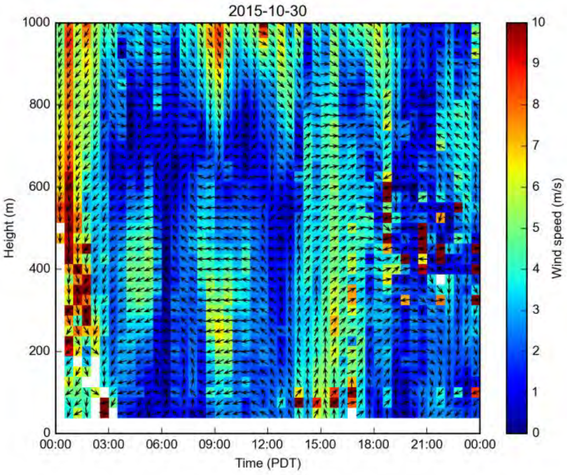
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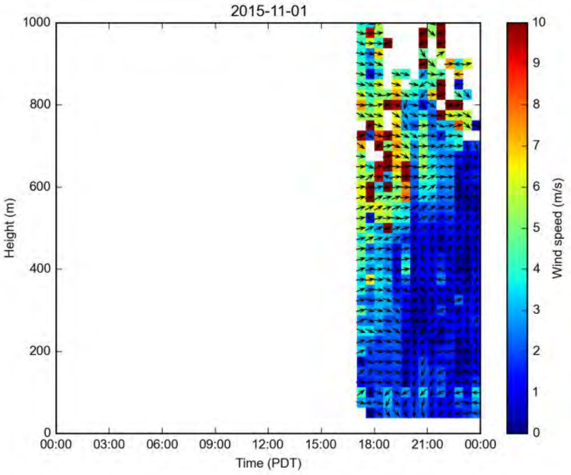
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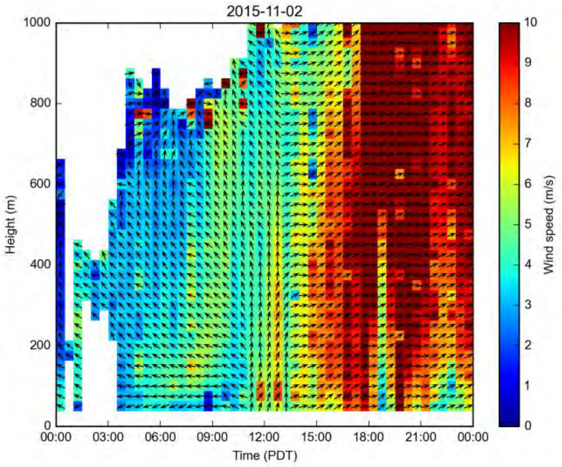
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EXHIBIT 4

Chapter 1

Carbon Adsorbers

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October 2018

DISCLAIMER

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1.1 Introduction

Adsorption is a non-destructive control technology employed to remove volatile organic compounds (VOCs) from low to medium concentration gas streams. Adsorption is generally used when a stringent outlet concentration must be met and/or recovery of the VOC is desired. Carbon adsorbers are used in a wide range of applications from controlling VOC and HAP emissions from storage tanks and process vents at refineries, chemical manufacturing, and pulp and paper plants, to control hydrogen sulfide and VOC emissions from municipal wastewater plants. Carbon adsorber canisters have been used in some smaller applications, such as in portable soil remediation systems. [28] In some industrial applications, adsorbers are used as concentrators to make other air pollution controls (e.g., condensers and thermal oxidizers) more cost-effective. Carbon adsorbers may also be used in conjunction with other less effective technologies (e.g., biofiltration or condensation) as a final polishing process to achieve VOC discharge limits. They are particularly useful for situations where there are relatively dilute VOC concentrations (less than 100 ppmv) and moderate flow rates, which can be difficult or uneconomical to remove using other types of pollution controls. [19] When properly designed, operated and maintained, carbon adsorbers can achieve high VOC removal efficiencies of 95 to 99 percent at input VOC concentrations of between 500 and 2,000 ppm in air. Removal efficiencies greater than 98 percent can be achieved for dilute waste streams. [20, 21]

Adsorption is the term used for the phenomenon where gas molecules passing through a bed of solid particles are selectively held on the surface of the solid by attractive forces which are weaker and less specific than those of chemical bonds. The term chemisorption is used where the gas molecules form actual chemical bonds with the adsorbent surface groups. Energy is released when a molecule from the gas stream adheres to the surface of the solid. This energy is known as the “heat of adsorption” and it typically equals or exceeds the heat of condensation. Adsorptive capacity of the solid for the gas tends to increase with the gas phase concentration, molecular weight, diffusivity, polarity, and boiling point. Most gases (“adsorbates”) can be removed (“desorbed”) from the adsorbent by increasing the temperature, decreasing the pressure or introducing a stronger adsorbed material to displace the VOCs. The methods used to regenerate adsorbent are described in more detail in Section 1.4.

Typical equipment life for carbon adsorbers is between 15 and 25 years. However, systems that handle waste gases that contain corrosive materials, such as hydrogen chloride or other acid gases, have shorter equipment life due to the impact of corrosion on the adsorber components. For example, waste streams that contain corrosive gases can corrode the adsorber vessel walls, carbon bed supports and outlet ducts. Corrosion of the bottom of the adsorber vessel is common where components of the gas stream condense to form corrosive liquids that collect on the bottom of the vessel. Corrosion of the carbon bed supports is also possible and may eventually cause the carbon beds to collapse. Carbon adsorbers used to control gas streams that contain corrosive materials should be constructed of materials that are designed for and resistant to corrosion.

While this chapter focuses primarily on VOC control, carbon adsorption is also used to control hazardous air pollutants (HAP), including inorganic HAPs such as hydrogen sulfide.

1.2 Types of Adsorbers

There are four types of adsorption equipment: (1) fixed regenerable beds; (2) disposable/ rechargeable canisters; (3) moving bed adsorbers; and (4) fluid-bed adsorbers. [2] Of these, the fixed-bed systems and canisters were the first developed and remain the most common systems in use today. [18]

1.2.1 Fixed-bed Units

Fixed-bed units can be sized for controlling continuous, VOC-containing streams over a wide range of flow rates, ranging from several hundred to several hundred thousand cubic feet per minute (cfm). The VOC concentration of streams that can be treated by fixed-bed adsorbers can be as low as several parts per billion by volume (ppbv) in the case of some toxic chemicals or as high as 25% of the VOCs' lower explosive limit (LEL). In some applications, the concentration of VOC in the waste gas stream may exceed the LEL. To reduce the risk of ignition, the waste gas stream is diluted to maintain the waste gas VOC concentration below 25% of LEL. (For most VOCs, the LEL ranges from 2,500 to 10,000 ppmv.[3])

Fixed-bed adsorbers may be operated in either intermittent or continuous modes. In intermittent operation, the adsorber removes VOC for a specified time (the "adsorption time"), which corresponds to the time during which the controlled source is emitting VOC. After the adsorber and the source are shut down (e.g., overnight), the unit begins the desorption cycle during which the captured VOC is removed from the carbon. This cycle, in turn, consists of three steps: (1) regeneration of the carbon by heating, generally by blowing steam through the bed in the direction opposite to the gas flow;[1] (2) drying of the bed, with compressed air or a fan; and (3) cooling the bed to its operating temperature via a fan. In most designs, the same fan is used both for bed drying and cooling. The length of the desorption cycle depends on several factors, including the characteristics of the contaminants in the waste stream, the type of adsorbent, and the regeneration method. The unit sits idle until the emission source starts operating again (for systems controlled by a single adsorber) or another adsorber is taken off-line for regeneration (for systems equipped with two or more adsorbers).

Fixed-bed adsorbers designed to operate continuously consist of two or more carbon beds where at least one regenerated carbon bed is available for adsorption at all times, thereby allowing the emissions source to operate continuously. In a system with two carbon beds, each bed must be large enough to handle the entire gas flow while adsorbing. Hence, twice as much carbon must be provided than an intermittent system handling the same flow. If the desorption cycle is significantly shorter than the adsorption cycle, it may be more economical to have three, four, or even more carbon adsorption beds operating at the same time. This approach reduces the amount of extra carbon capacity needed and can provide some additional benefits, such as maintaining a low VOC content in the effluent. (See Section 1.6 for information on designing a carbon adsorber control system, including how to determine the amount of carbon needed and how to estimate the adsorption and desorption times.)

---

[1] Although steam is the most commonly used regenerant, there are situations where it should not be used. For example, steam regeneration should not be used for operations that emit halogenated VOCs, because the high temperature causes these VOCs to decompose.

A typical two-bed, continuously operated adsorber system is shown in Figure 1.1. One of the two beds is adsorbing at all times, while the other is desorbing or idled. As shown in Figure 1.1, the VOC-laden gas is collected by hoods or by direct pipeline connection and passes through a filter to remove particulates, before passing through the carbon bed in Bed #1 and exiting through the exhaust stack. Meanwhile, Bed #2 is in the desorption cycle in which steam flows through the bed and exits to a condenser. In the condenser, cooling water condenses the steam/VOC mixture. If part of the VOC is immiscible in water, the condensate can be sent to a decanter, where the VOC and water layers are separated and the VOC conveyed to storage. If the VOC collected contains a mixture of compounds, it may receive additional purification by distillation. The water layer is usually discharged to a wastewater treatment facility.

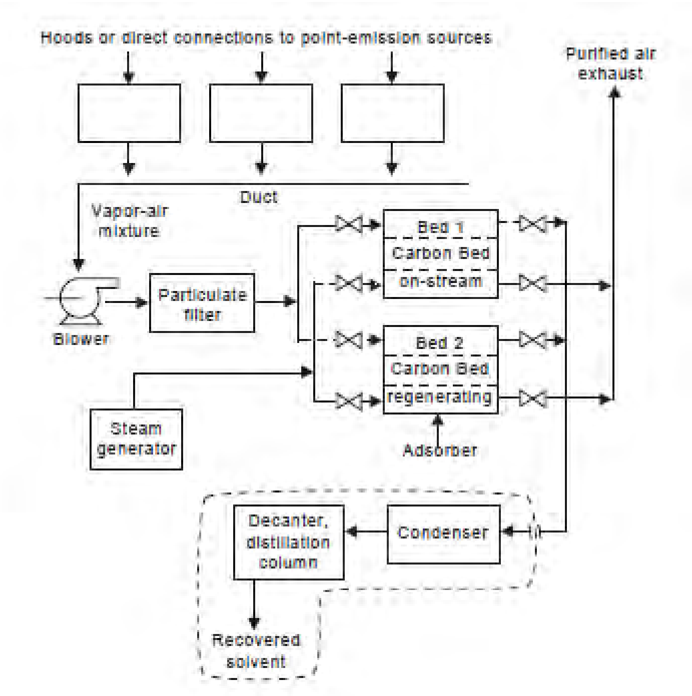

Figure 1.1: Typical-Two-Bed, Continuously Operated Fixed Bed Carbon Adsorber System

1.2.2 Canister Units

Canister-type adsorbers differ from fixed-bed units, in that they are normally limited to controlling lower-volume and intermittent gas streams, such as those emitted by storage tank vents, where process economics dictate that off-site regeneration is appropriate. The carbon canisters are not intended for in-situ desorption as in the fixed-bed units. Instead, they are either returned to the manufacturer or regenerated at a central desorption facility onsite.

Originally, canister adsorbers referred to relatively small returnable containers, such as 55-gallon drums. However, the term canister is becoming something of a misnomer as much of the growth in the industry is in larger vessels without regeneration capabilities. For example, one manufacturer supplies canister systems as large as 18,000 cfm and carbon capacities of 10,000 pounds. [25]

Once the carbon reaches a certain VOC content, the unit is shut down and either the carbon or the canister is replaced. The used carbon or the entire canister is then returned to a reclamation facility or regenerated at a central regeneration facility onsite. Several companies provide carbon replacement services for canisters. These companies analyze the spent carbon returned to them to determine whether it contains hazardous compounds. Fees for testing the spent carbon are typically between $800 and $1,000 based on 2018 prices, but fees may be higher depending on the application (e.g., wood treating and DBCP or PCB treatment).

Each canister unit consists of a vessel, activated carbon, inlet connection connected to distributer leading to the carbon bed, and an outlet connection to connect the unit to an exhaust stack. In one design (Calgon's Ventsorb®), 180 lbs of carbon are installed on an 8- inch gravel bed, in a 55-gallon drum with an internal collector. The type of carbon used depends on the composition of the VOC to be treated [6].

A single carbon canister may be used for emissions sources that operate intermittently or that can be shut down to allow replacement of a saturated carbon canister. However, most systems use two or more canisters, installed either in parallel or in series. Systems with canisters arranged in series are common. This design has two advantages: (1) any breakthrough that occurs in the first canister is controlled by the second canister; and (2) canisters can be replaced without disrupting the production process provided each canister is capable of controlling process emissions. When the first canister becomes saturated with VOC, the second canister becomes the primary carbon adsorber. When the carbon in the primary canister is saturated, the saturated canister is removed and a fresh canister added to the clean end. Periodic sampling for VOC breakthrough between the primary and secondary carbon canisters assures canister replacement occurs frequently enough to avoid VOC being emitted to the atmosphere. This approach also improves cost effectiveness of carbon replacement because the carbon canister is replaced at or near its saturation point. Although safer and more convenient, using two canisters in series is more expensive than systems using a single canister. In theory, a canister unit should remain in service longer than a fixed-bed regenerable unit operates in its adsorption cycle because new carbon adsorbent has a higher theoretical adsorption capacity than carbon regenerated in situ. The operating life of a carbon canister is expressed as the ratio of the theoretical capacity to the working capacity and is used to help ensure the allowable VOC concentration at the outlet is not exceeded. However, canisters sometimes remain connected until the carbon is near or at saturation because there is a cost incentive to operate each canister until the carbon is saturated. Also, unlike fixed-bed units whose outlet VOC concentrations are usually monitored continuously using flame ionization detectors, canisters are generally not monitored continuously. Adequate recordkeeping, periodic monitoring for VOC breakthrough, and bed life modeling provided by vendors are all worthwhile to ensure canister replacement occurs with sufficient frequency that VOC breakthrough does not occur. The primary indicator of the performance is the adsorber outlet VOC concentration. Other indicators of adsorber performance include inlet gas temperature, gas flow rate, inlet VOC concentration, pressure differential, inlet gas moisture content, and leak check monitoring.

1.2.3 Moving-Bed Adsorbers

Similar to fixed-bed adsorbers, moving-bed adsorbers consist of a permanent adsorber vessel in which the waste gases or vapors are brought into contact with the adsorbent. However, in the moving-bed adsorber, the spent adsorbent is continually regenerated. In a typical moving-bed adsorber, the adsorbent is held in two beds sited on coaxial rotating cylinders. VOC is adsorbed as the waste gas flows between the two rotating beds. As the cylinders are rotated, the portion of the adsorbent bed that is outside the waste gas stream is regenerated, thereby, increasing the potential for gas molecules to make contact with freshly regenerated adsorbent. [18]

1.2.4 Fluid-Bed Adsorbers

Fluid-bed adsorbers use a counter-flow design in which waste gas typically enters the adsorber vessel from the bottom and flows up through the vessel, while regenerated adsorbent enters from the top and slowly migrates to the bottom of the vessel. As adsorbent flows down through the vessel it gradually becomes saturated. The spent adsorbent is collected at the bottom of the vessel and transferred to a regeneration chamber, as illustrated in Figure 1.2. Because spent adsorbent is continually removed and fresh adsorbent added, fluid-bed adsorbers operate more efficiently and are less likely to experience the breakthrough issues associated with fixed-bed designs and canisters. [17, 18].

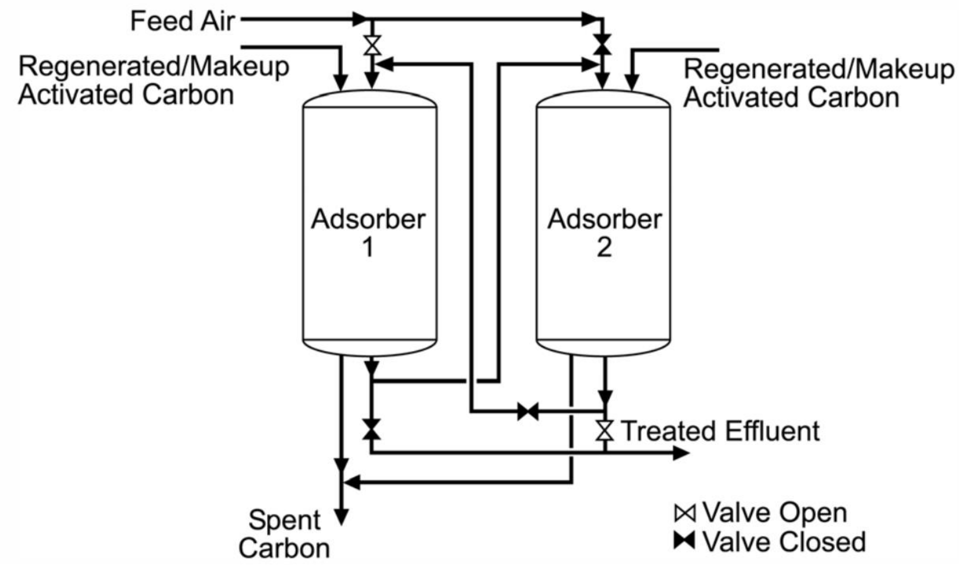

Figure 1.2: Schematic of a Fluid-Bed Adsorber [18]

1.3 Types of Adsorbent

There are three types of adsorbents in large scale use: activated carbon, synthetic zeolites and polymers. Each type of adsorbent has characteristics that make it effective for certain applications and impractical or uneconomic for others. A comparison showing the advantages and disadvantages of the three different types of adsorbents is provided in Table 1.1.

Activated Carbon:

Activated carbon was the first adsorbent used and remains the most commonly used adsorbent today. It is produced by high-temperature steam pyrolysis from a variety of materials, such as coal, wood and coconut husks. The resulting carbon has excellent adsorption characteristics due its high specific surface area (typically 800 to 1,400 square meters per gram) and the presence of small pores of various sizes (typically between 2 and 500 angstroms). The characteristics of the activated carbon produced vary depending on the type of material used. In general, activated carbon made from coconuts performs better at higher humidity than those made from coal. Activated carbon can also be modified to improve adsorption of other pollutants, such as hydrogen sulfide, mercury and ammonia. [18]

Activated carbon can adsorb a wide range of VOCs; however, there are some limitations. First, activated carbon is less effective for compounds that are highly polar, volatile or have small diameters. For example, vinyl chloride, methanol, and formaldehyde are not adsorbed well by activated carbon. Second, activated carbon is less effective in situations where the waste gas has high relative humidity as the water molecules readily adsorb to the activated carbon reducing the number of available absorption sites. [18] Some studies have shown a 30% reduction in removal efficiency when the relative humidity of the waste gas exceeds 75%. [20] Moisture in the bed can also promote biological growth on the carbon surface. [18] Third, carbon bed fires and explosions can occur with activated carbon adsorbers. Wastes with oxygen bearing compounds, such as peroxides, ketones, organic acids, aldehydes and organic sulfur compounds should be avoided as activated carbon can cause exothermic reactions with these compounds. The heat from exothermic reactions can ignite any flammable compounds present in the waste stream. In such cases, fire suppression measures can be used, such as increasing flow rate or using nitrogen or water to reduce the oxygen level. [18] Lastly, some VOCs may undergo chemical reactions to produce contaminants that are difficult to remove during desorption. For example, styrene monomers have been shown to polymerize to polystyrene making desorption possible only at very high temperatures. [18]

Activated carbon is generally regenerated by heating to temperatures of between 250 and 350°F. Steam is often used for this process, followed by a drying cycle to remove moisture. However, some molecules remain after regeneration. The adsorption capacity of regenerated carbon is typically about 50% of that for virgin material. The adsorption capacity declines during subsequent regeneration cycles, until eventually the activated carbon must be replaced. [21]

The typical cost for virgin activated carbon is between \$1.90/lb and \$6.50.[2] Costs for reactivated carbon are slightly lower and range from \$0.95/lb to 1.55/lb.[3]

Zeolites:

Zeolites have a uniform crystalline structure with high specific surface areas and small, uniformly sized pores. Zeolites are sometimes called "molecular sieves" because their pores trap molecules of specific sizes, while allowing other molecules to pass through. For a given application, the zeolite must be carefully selected to match the molecular diameter of the VOCs to be removed.

Zeolites have specific surface areas that are similar to activated carbon. Naturally occurring zeolites include aluminosilicate minerals that are hydrophilic. However, synthetic zeolites are also available with characteristics tailored to a particular application. For example, some synthetic zeolites are hydrophobic with greater affinity for non-polar VOCs and low affinity for water molecules. Unlike activated carbon, zeolites are effective for removing VOC

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[2] Based on 2018 costs for virgin activated carbon provided by Carbtrol and Calgon Carbon Corporation.

[3] Based on 2018 costs for reactivated carbon provided by Calgon Carbon Corporation.

from waste streams with high relative humidity. As shown in the graph in Figure 1.3, the adsorption capacity of a hydrophobic zeolite is impacted only at very high relative humidity, while the adsorption capacity of activated carbon is significantly impacted at levels below 50%. [18]

Zeolites can be used to remove highly polar and volatile VOCs that are difficult to remove with activated carbon, including vinyl chloride, styrene, phenol, methane, acetone, methyl ethyl ketone, formaldehyde and sulfur compounds. Similar to activated carbon, reaction of the contaminants on the adsorbent can complicate removal during desorption. Zeolites are also not suitable for larger molecules as they are not adsorbed effectively. [18]

Zeolites can also be impregnated with other compounds to achieve targeted removal of certain compounds. For example, zeolites impregnated with potassium permanganate have been used to remove vinyl chloride from waste streams.

Zeolite is typically used to treat high-flow, low-concentration waste streams with VOC concentrations less than 150 ppmv and flow rates above 3,000 cfm. They have been used to control waste streams containing petroleum compounds and paint solvents. [18] Zeolites are regenerated by heating or vacuum. Since zeolites are able to withstand much higher temperatures than activated carbon, higher temperatures can be used thereby achieving higher levels of desorption. However, zeolites are more expensive than carbon with one report indicating zeolite costs can be twenty times that of activated carbon. [18]

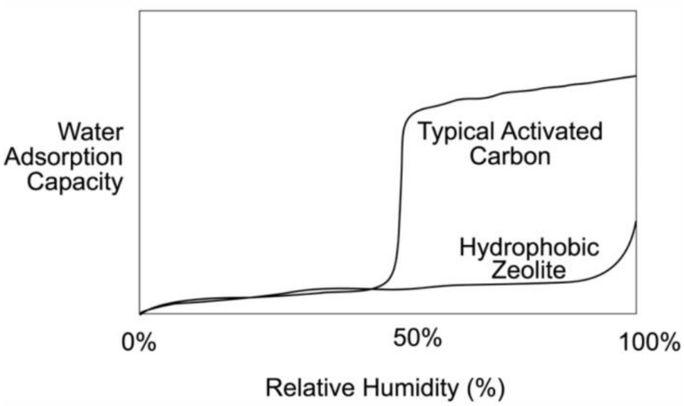

Figure 1.3: Effects of Humidity on Adsorption Capacity of Activated Carbon and Zeolite [18]

Polymers:

Polymer adsorbents are granules or beads made of synthetic polymers that are highly crosslinked to form a matrix of small pores and high surface areas. Polymer adsorbents can be used to control a wide range of VOCs, including styrene, toluene, xylenes, aldehydes, ketones, alcohols and chlorinated VOCs. However, polymers cannot be used with strong oxidizing agents. [18, 22, 23, 24]

The adsorption capacity for polymers is lower than that of zeolites but higher than for activated carbon. Unlike activated carbon adsorbers, they are less prone to fires and are capable of achieving removal efficiencies greater than 95%. [18] Polymers can be designed with a defined pore structure for selective removal of organic molecules. [23]

One advantage of polymeric adsorbents is their hydrophobic surfaces. This gives them a high tolerance for water vapor. Polymeric adsorbents can be used to efficiently treat VOC in waste streams with relative humidity greater than 90%. As a result, polymeric adsorbents have been used to control VOC emissions at soil remediation processes and industrial wastewater facilities, where the waste streams have high relative humidity. [18] Polymer adsorbents have been used to remove VOC/HAPs from soil vapor extraction (SVE) processes. One system demonstrated by Dow Chemical Company achieved 99% removal efficiency on a system with a flow rate of 271 ft^3/min, relative humidity of 98% and ambient temperature. The system consisted of two beds containing 191 lb of Dowex Optipore^{TM} polymeric adsorbent, which was regenerated onsite using conductive heating to 250°F and vacuum with low flow of carrier gas. Capital costs of the system were estimated to be less than \$160,000 with annual costs of \$2,732. [22] Figure 1.4 shows the water adsorption capacity of Dowex Optipore^{TM} compared to activated carbon.

Another advantage of polymers is that they can be used to adsorb reactive solvents without catalyzing their decomposition. Reactive solvents such as acetone, methyl ethyl ketone, cyclohexanone and styrene have been adsorbed and desorbed without measurable decomposition. Uncontrollable exothermic reactions that result in bed fires are also said to be less likely with polymer-based adsorbers than the carbon-based systems. [18, 23, 24]

Polymers are regenerated using heat, pressure and nitrogen purge gas. Desorption temperatures of up to about 250°F may be used with most polymers. Typically, a small quantity of cooling gas (e.g., air or nitrogen) is passed through the adsorber during regeneration. Regenerated polymers typically have lower adsorption capacity than the virgin polymer, but the decrease is typically less than observed with activated carbon. However, the reduction in the working capacity must be considered when designing polymer-based adsorbers as more polymer adsorbent will be needed to offset the decreased adsorption capacity. [18, 23, 24]

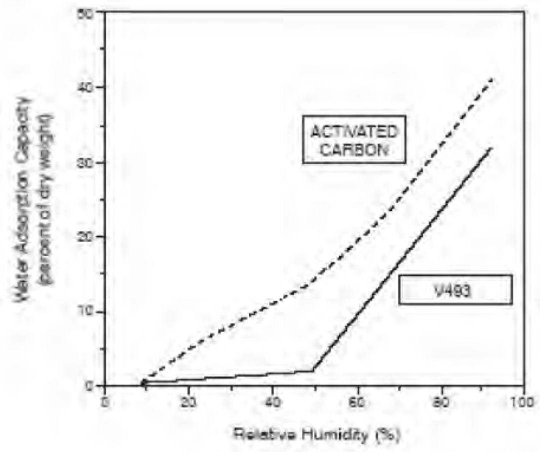

Figure 1.4: Effects of Humidity on Adsorption Capacity of Activated Carbon and Dowex Optipore^{TM} V493 Polymer [24]

Table 1.1: Comparison of Activated Carbon, Zeolite and Polymer Adsorbents

Absorbent Type	Characteristics	Advantages	Disadvantages
Activated Carbon	• Small pores of various sizes (typically between 2 and 500 angstroms). • High specific surface areas of between 800 and 1,400 square meters/gram.	• Lower cost. • Suitable for waste streams containing wide range of VOCs.	• Not effective for VOCs with high polarity (e.g., alcohols, organic acids). • Not effective for highly volatile compounds (e.g., vinyl chloride, MTBE) • Reduced capacity in high moisture applications. • High annual costs for carbon replacement/regeneration when used for concentrated waste streams. • Fire hazard if used with oxygen bearing compounds or VOCs having high heat of adsorption. • Degrades during desorption cycles.
Zeolites	• Uniform Crystalline structures with uniform pores. Pores are typically smaller than those in activated carbon. • Specific surface areas comparable to activated carbon.	• Highly selective VOC removal. • Good at removing small, highly polar and very volatile compounds. • Can be used in high humidity applications. • Longer life. • Less susceptible to fire. • Less susceptible to degradation	• Higher initial costs. • Not suitable for waste streams containing wide ranges of VOC.
Polymers	• Crosslinked polymers with high specific surface areas. Pores are generally larger than found in activated carbon.	• Can be used with reactive solvents without risk of catalyzing their decomposition. • Desorb more quickly than activated carbon. • Less susceptible to fire. • Longer life than activated carbon. • Lower affinity for water than activated carbon.	• Higher initial cost. • Regeneration temperatures cannot exceed 125ºC. • Not suitable for waste streams containing strong oxidizing agents.

The remainder of this chapter focuses primarily on the use of activated carbon, since this is the most commonly used adsorbent for VOCs.

1.4 Adsorbent Regeneration

Regeneration involves removing or desorbing the adsorbed molecules from the adsorbent and can be achieved by changing either the temperature or pressure. If the waste stream flow rate and composition are predictable, regeneration can occur at a preset time. However, if flow rate or the VOC concentration vary unpredictably, a sensor can be used to control when the regeneration cycle occurs. [18, 19]

Three types of regeneration systems are available: thermal swing regeneration, vacuum regeneration and pressure swing adsorption.

Thermal Swing Regeneration:

In systems using thermal swing regeneration, the temperature is increased (swung) from the ambient conditions under which VOC is adsorbed to higher temperatures for the regeneration cycle. Increasing the temperature, increases the kinetic energy of the VOC molecules. The molecules are desorbed when the kinetic energy of the VOC molecules increases sufficiently to overcome the forces holding molecules to the adsorbent. The temperature required depends on the VOC present, but is typically between 250 to 350^{o}F. Once the VOC is desorbed, cooled air is passed through the adsorber vessel to cool and dry the adsorbent before returning the vessel back to the adsorption cycle. Thermal regeneration has historically used steam, which provides the energy to desorb the adsorbate and also carries the desorbed compounds out of the adsorber vessel. The steam is then condensed and the VOC can either be recovered from the wastewater or the wastewater can be sent to wastewater treatment. Hence, steam-based regeneration systems will have additional equipment and operating costs associated with recovering the VOC and/or disposing of the wastewater generated. [19]

In addition to steam, other heat sources have been developed, including using microwaves, embedded heaters, and heated nitrogen. These alternative heat sources make VOC recovery easier and avoid the wastewater treatment costs associated with the steam-based systems. [19]

The physically adsorbed species in the smallest pores of the solid and the chemisorbed species may require rather high temperatures to be removed, and for all practical purposes cannot be desorbed during regeneration. Approximately 3 to 5 percent of organics adsorbed on virgin activated carbon is either chemisorbed or very strongly physically adsorbed and is difficult to desorb during regeneration. [1]

Vacuum Regeneration:

In a vacuum regeneration system, a vacuum pump is used to lower the pressure in the adsorber to below the vapor pressure of the adsorbed VOC. This causes the VOC to boil off from the adsorbent. Some systems use a small flow of purge gas (such as dry nitrogen) to transport of the VOC vapor to the recovery vessel. [19]

Pressure Swing Adsorption:

In a pressure swing adsorption system, the pressure is used to selectively adsorb and desorb individual VOCs based on their molecular characteristics and affinity for the adsorbent used. The method relies on the fact that more VOC is adsorbed at higher pressure. In these systems, the pressure is raised during the adsorption cycle and reduced during the regeneration cycle. When the adsorbent is saturated, the waste stream is stopped and the pressure of the adsorber vessel is reduced. The reduction in pressure results in desorption of the VOC, thereby regenerating the adsorbent. Pressure swing adsorption systems have been used to control gasoline vapors from storage tank vents. [19]

1.5 Adsorption Theory

At equilibrium, the quantity of gas that is adsorbed on activated carbon is a function of the adsorption temperature and pressure, the chemical species being adsorbed, and the carbon characteristics, such as carbon particle size and pore structure. For a given adsorbent-VOC combination at a given temperature, an adsorption isotherm can be constructed that shows the relationship between the mass of adsorbate per unit weight of adsorbent (i.e., the “equilibrium adsorptivity”) to the partial pressure of the VOC in the gas stream.

Figure 1.5 shows a set of typical adsorption isotherms for VOC adsorption on activated carbon. As shown in the graph, the adsorptivity increases with increasing VOC partial pressure and decreases with increasing temperature.

Isotherms with this convex shape are designated as “Type I” isotherms. The Freundlich isotherm in equation 1.1 can be fit to a portion of a Type I curve and is commonly used in the industrial design of adsorbers.[2]

$$w_e = kP^m \tag{1.1}$$

where

w_e = equilibrium adsorptivity (lb adsorbate/lb adsorbent)
P = partial pressure of VOC in gas stream (psia)
k,m = empirical parameters

The treatment of adsorption from gas mixtures is complex and beyond the scope of this chapter. However, where two VOCs in a gas mixture have nearly identical adsorption isotherms, the VOC with the lower vapor pressure will displace the VOC with the higher vapor pressure even when the latter VOC has previously adsorbed to the carbon surface. Thus, during the course of the adsorption cycle the carbon’s capacity for a higher vapor pressure constituent decreases. This phenomenon should be considered when sizing the adsorber. To be conservative, the adsorption cycle requirements should be based on the least adsorbable component in a mixture and the desorption cycle should be based on the most adsorbable component.[1]

The equilibrium adsorptivity is the maximum amount of adsorbate the carbon can hold at a given temperature and VOC partial pressure. In actual control systems where there are not two beds operating in series, however, the entire carbon bed is never allowed to reach equilibrium. Instead, once the outlet concentration reaches a preset limit (the “breakthrough concentration”), the adsorber is shut down for desorption or (in the case of canister units) replacement and disposal. At the point where the carbon adsorber is shut down, the average bed VOC concentration may only be 50% or less of the equilibrium concentration. That is, the carbon bed may be at equilibrium ("saturated") at the gas inlet, but contain only a small quantity of VOC near the outlet.

As Equation 1.1 indicates, the Freundlich isotherm is a power function that plots as a straight line on log-log paper. Conveniently, for the concentrations/partial pressures normally encountered in carbon adsorber operation, most VOC-activated carbon adsorption conforms to Equation 1.1. At the very low concentrations typical of VOC breakthrough, a linear approximation (on arithmetic coordinates) to the Freundlich isotherm is adequate. However, the Freundlich isotherm does not accurately represent the isotherm at high gas concentrations and thus should be used with care as such concentrations are approached.

Adsorptivity data for selected VOCs were obtained from Calgon Corporation, a vendor of activated carbon. The vendor presents adsorptivity data in two forms: a set of graphs displaying equilibrium isotherms [7] and as a modification of the Dubinin-Radushkevich (D-R) equation, a semi-empirical equation that predicts the adsorptivity of a compound based on its adsorption potential and polarizability. [8] In this Manual, the modified D-R equation is referred to as the Calgon fifth-order polynomial. The data displayed in the Calgon graphs [7] has been fit to the Freundlich equation. The resulting Freundlich parameters are shown in Table 1.2 for a limited number of chemicals. The adsorbates listed include aromatics (e.g., benzene, toluene), chlorinated aliphatics (dichloroethane), and one ketone (acetone). However, the list is far from all-inclusive.

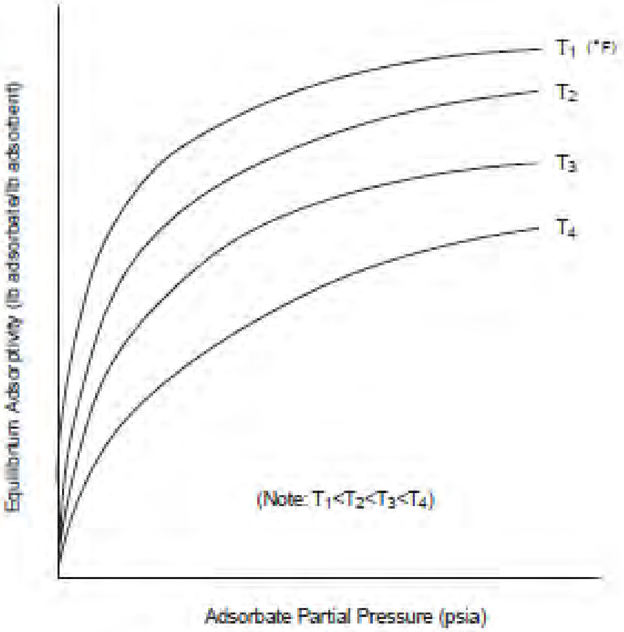

Figure 1.5: Type 1 Adsorption Isotherms for Hypothetical Adsorbate

Notice that a range of partial pressures is listed with each set of parameters, k and m. (Note: In one case (m-xylene) the isotherm was so curvilinear that it had to be split into two parts, each with a different set of parameters.) This is the range to which the parameters apply. Extrapolation beyond this range—especially at the high end—can introduce inaccuracy to the calculated adsorptivity.

But high-end extrapolation may not be necessary, as the following will show. In most air pollution control applications, the system pressure is approximately one atmosphere (14.696 psia). The upper end of the partial pressure ranges in Table 1.2 goes from 0.04 to 0.05 psia. According to Dalton's Law, at a total system pressure of one atmosphere this corresponds to an adsorbate concentration in the waste gas of 2,720 to 3,400 ppmv. As discussed in Section 1.2.1, the adsorbate concentration is usually kept at 25% of the lower explosive limit (LEL).[4] For many VOCs, the LEL ranges from 1 to 1.5 volume %, so that 25% of the LEL would be 0.25 to 0.375% or 2,500 to 3,750 ppmv, which approximates the high end of the partial pressure ranges in Table 1.2.

Finally, each set of parameters applies to a fixed adsorption temperature, ranging from 77°F to 104°F. These temperatures reflect typical operating conditions, although adsorption can take place as low as 32°F and even higher than 104°F. As the adsorption temperature increases to much higher levels, however, the equilibrium adsorptivity decreases to such an extent that VOC recovery by carbon adsorption may become economically impractical.

Table 1.2: Parameters for Selected Adsorption Isotherms [7][a]

Adsorbate	Adsorption Temp (°F)	Isotherm Parameters k	m	Range of Isotherm[b] (psia)
Benzene	77	0.597	0.176	0.0001-0.05
Chlorobenzene	77	1.05	0.188	0.0001-0.01
Cyclohexane	100	0.505	0.210	0.0001-0.05
Dichloroethane	77	0.976	0.281	0.0001-0.04
Phenol	104	0.855	0.153	0.0001-0.03
Trichloroethane	77	1.06	0.161	0.0001-0.04
Vinyl Chloride	100	0.200	0.477	0.0001-0.05
m-Xylene	77	0.708	0.113	0.0001-0.001
	77	0.527	0.0703	0.001-0.05
Acrylonitrile	100	0.935	0.424	0.0001-0.015
Acetone	100	0.412	0.389	0.0001-0.05
Toluene	77	0.551	0.110	0.001-0.05

[a] Each isotherm is of the form $w = kP^m$. (See text for definition of terms.) Data are for adsorption of Calgon type "BPL" carbon.

[b] Equation should not be extrapolated outside these ranges.

The Calgon fifth-order polynomial is somewhat more accurate than the Freundlich parameters from Table 1.2. The polynomial contains a temperature parameter, and it allows one to estimate adsorption isotherms for compounds not shown in Table 1.2 if pure component data are available. The pure component data required are the saturation pressure, liquid molar volume,

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[4] Although, Factory Mutual Insurance will reportedly permit operation at up to 50% of the LEL, if proper VOC monitoring is used.

and the refractive index. It is, however, somewhat more complex to use than the Freundlich equation. The Calgon fifth-order polynomial is as follows:

The mass loading, w_e, is calculated from

$$w_e = \frac{0.01G}{V_m} MW_{ads} \tag{1.2}$$

where

w_e = mass loading, i.e., equilibrium adsorptivity (g adsorbate per g carbon)[5]
G = carbon loading at equilibrium (cm^3 liquid adsorbate per 100 g carbon)
V_m = liquid molar volume of adsorbate (cm^3 per gmole)
MW_{ads} = molecular weight of adsorbate

Note that the terms in Equation 1.2 are given in metric units, not English. This has been done because the carbon loading, G, is calculated from a regression equation in which all the terms are expressed in metric units. This equation for G is the Calgon fifth-order polynomial:

$$\log_{10}(G) = A_0 + A_1 Y + A_2 Y^2 + A_3 Y^3 + A_4 Y^4 + A_5 Y^5 \tag{1.3}$$

where

A_0 = 1.71
A_1 = -1.46×10^{-2}
A_2 = -1.65×10^{-3}
A_3 = -4.11×10^{-4}
A_4 = $+3.14 \times 10^{-5}$
A_5 = -6.75×10^{-7}

and Y is calculated from several equations which follow.

The first step in calculating Y is to calculate the parameter X using Equation 1.4:

$$\chi = \frac{\varepsilon}{(2.303\ RV_m)} \tag{1.4}$$

The adsorption potential, $\mathcal{E}$, is calculated using Equation 1.5:

$$\varepsilon = RT \ln\left(\frac{P_s}{P_i}\right) \tag{1.5}$$

where

R = 1.987 (calories per g-mole-K)
T = absolute temperature (K)
P_s = vapor pressure of adsorbate at the temperature T (kPa)
P_i = partial pressure of adsorbate (kPa)

---

[5] This, of course, is equal to *lb* adsorbate per *lb* carbon.

By substituting for $\mathcal{E}$ in the Equation 1.4, X can alternatively be calculated from[6]:

$$\chi = \left(\frac{T}{V_m}\right) \log 10 \left(\frac{P_s}{P_i}\right) \tag{1.6}$$

The next step in calculating Y is to calculate the relative polarizability, Γ.

$$\Gamma = \frac{\Theta_i}{\Theta_o} \tag{1.7}$$

where

Θ_i = polarizability of component i per unit volume, where component i is the adsorbate

Θ_o = polarizability of component o per unit volume, where component o is the reference component, n-heptane.

$$\Theta = \frac{n^2 - 1}{n^2 + 2} \tag{1.8}$$

Once X and Γ are known, Y can be calculated from:

$$Y = \frac{\chi}{\Gamma} \tag{1.9}$$

Calgon also has a proprietary, seventh-order form in which two additional coefficients are added to the Calgon fifth-order polynomial, but the degree of fit reportedly is improved only modestly. [8] Additional sources of isotherm data include activated carbon vendors, handbooks (such as Perry's Chemical Engineer's Handbook), and the literature.

1.6 Design Procedure

1.6.1 Sizing Parameters

Data received from adsorber vendors indicate that the size and purchase cost of a fixed-bed or canister carbon adsorber system primarily depend on five parameters:

1. The volumetric flow of the VOC laden gas passing through the carbon bed(s);
2. The inlet and outlet *VOC* mass loadings of the gas stream;
3. The adsorption time (i.e., the time a carbon bed remains on-line to adsorb VOC before being taken off-line for desorption of the bed);

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[6] Alternatively, if the available values for T, P_i, P_s, and V_m are in English units, they may be substituted into this equation without conversion. However, to make the result dimensionally consistent with Equation 1.3, it be multiplied by the conversion factor, *34.7.*

4. The working capacity of the activated carbon in regenerative systems or the *equilibrium capacity* in the case of non-regenerative systems,

5. The moisture content of the gas stream.

In addition, the cost could also be affected by other stream conditions, such as the presence/absence of excessive amounts of particulate, moisture, or other substances that require the use of extensive pretreatment and/or corrosive-resistant construction materials. If the inlet concentrations are above 1,000 ppm, the moisture content does not significantly affect the working capacity of activated carbon. However, if the VOC inlet concentration is below 1,000 ppm or the relative humidity is above 50%, then the moisture begins to compete with the adsorbate for the available adsorption sites. If the VOC concentration is below 1,000 ppm or the waste gas has a relative humidity above 50%, then dehumidification equipment can be used to reduce the moisture content of the waste stream before it enters the adsorber vessel. Alternatively, a zeolite or synthetic polymer adsorbent may be used that has lower affinity for water molecules than activated carbon. Zeolite and synthetic polymer adsorbents are effective for waste streams with high moisture contents. Many zeolites and polymers are effective up to a relative humidity of 90%. [18, 21, 22, 23]

The purchased cost depends to a large extent on the volumetric flow (usually measured in actual ft^3/min). The flow, in turn, determines the size of the vessels housing the carbon, the capacities of the fan and motor needed to convey the waste gas through the system, and the diameter of the ducting.

Also important are the VOC inlet and outlet gas stream loadings, the adsorption time, and the working or equilibrium capacity of the carbon. These variables determine the amount and cost of carbon charged to the system initially and, in turn, the cost of replacing that carbon after it is exhausted (typically, five years after startup). Moreover, the amount of the carbon charge affects the size and cost of the auxiliary equipment (condenser, decanter, bed drying/cooling fan), because the sizes of these items are tied to the amount of VOC removed by the bed. The amount of carbon also has a bearing on the size and cost of the vessels.

A carbon adsorber vendor [9] supplied data that illustrate the dependency of the equipment cost on the amount of the carbon charge. Equipment costs were obtained for fixed-bed adsorbers sized to handle three gas flow rates ranging from 4,000 to 100,000 scfm and to treat inlet VOC (toluene) concentrations of 500 and 5,000 ppm. Each adsorber was assumed to have an eight-hour adsorption time. As one might expect, the equipment costs for units handling higher gas flow rates were higher than those handling lower gas flow rates. Likewise, at each of the gas flow rates, the units sized to treat the 5,000 ppm VOC streams had higher equipment costs than those sized to treat the 500 ppm concentration. These cost differences ranged from 23 to 29% and averaged 27%. These higher costs were partly needed to pay for the additional carbon required to treat the higher concentration streams. But some of these higher costs were also needed for enlarging the adsorber vessels to accommodate the additional carbon and for the added structural steel to support the larger vessels. Also, larger condensers, decanters, cooling water pumps, etc., were necessary to treat the more concentrated streams. (See Section 1.7 for procedures to estimate capital costs.)

The VOC inlet loading is set by the source parameters, while the outlet loading is set by the VOC emission limit. (For example, in many states, the average VOC outlet concentration from adsorbers may not exceed 25 ppm.)

1.6.2 Determining Adsorption and Desorption Times

The relative times for adsorption and desorption and the adsorber bed configuration (i.e., whether single or multiple and series or parallel adsorption beds are used) establish the adsorption/ desorption cycle profile. The cycle profile is important in determining carbon and vessel requirements and in establishing desorption auxiliary equipment and utility requirements. An example will illustrate. In the simplest case, an adsorber would be controlling a process which emits a relatively small amount of VOC intermittently—say, during one 8-hour shift per day. During the remaining 16 hours the system would either be desorbing or on standby. Properly sized, such a system would only require a single bed, which would contain enough carbon to treat eight hoursworth of gas flow at the specified inlet concentration, temperature, and pressure. Multiple beds, operating in parallel, would be needed to treat large gas flows (>100,000 actual ft^3/min, generally) [9], as there are practical limits to the sizes to which adsorber vessels can be built. But, regardless of whether a single bed or multiple beds were used, the system would only be on-line for part of the day.

However, if the process operates continuously (24 hours), an extra carbon bed would have to be installed to provide adsorptive capacity during the time the first bed is being regenerated. The amount of this extra capacity depends on the number of carbon beds that would be adsorbing at any one time, the length of the adsorption period relative to the desorption period, and whether the beds were operating in parallel or in series. If only one bed is adsorbing, a second would be needed to come on-line when the first is shut down for desorption. In this case, 100% extra capacity would be needed. Similarly, if five beds in parallel operate in a staggered adsorption cycle, only one extra bed would be needed and the extra capacity would be 20% (i.e., 1/5)—provided, of course, that the adsorption time is at least five times as long as the desorption time. The relationship between adsorption time, desorption time, and the required extra capacity can be generalized.

$$M_c = M_{cI} f \tag{1.10}$$

where

M_c, M_{cI} = amounts of carbon required for continuous or intermittent control of a given source, respectively (lbs)
f = extra capacity factor (dimensionless)

This equation shows the relationship between M_c, and M_{cI}. Section 1.6.3 shows how to calculate these quantities.

The factor, f, is related to the number of beds adsorbing (N_A) and desorbing (N_D) in a continuous system as follows:

$$f = 1 + \frac{N_D}{N_A} \tag{1.11}$$

(Note: N_A is also the number of beds in an intermittent system that would be adsorbing at any given time. The total number of beds in the system would be $N_A + N_D$)

It can be shown that the number of desorbing beds required in a continuous system (N_D) is related to the desorption time (θ_D), adsorption time (θ_A), and the number of adsorbing beds, as follows:

$$\theta_D \leq \theta_A \left(\frac{N_D}{N_A} \right) \tag{1.12}$$

θ_D is the total time needed for bed regeneration, drying, and cooling. For instance, for an eight-hour adsorption time, in a continuously operated system of seven beds (six adsorbing, one desorbing), θ_D would be equal to or less than 8 hours/6 beds or one hour and twenty minutes. If desorption takes longer than one hour and twenty minutes, then additional beds would be needed to provide sufficient extra capacity during desorption.

1.6.3 Estimating Carbon Requirement

1.6.3.1 Overview of Carbon Estimation Procedures

Obtaining the carbon requirement (M_c or M_{cI}) is not as straightforward as determining the other adsorber design parameters. When estimating the carbon charge, the sophistication of the approach used depends on the data and tools available.

For this Manual, we have adopted a rule-of-thumb procedure for estimating the carbon requirement. This procedure, while approximate in nature, appears to have the acceptance of vendors and field personnel. It is sometimes employed by adsorber vendors to make rough estimates of carbon requirement and is relatively simple and easy to use. It normally yields results incorporating a safety margin, the size of which depends on the bed depth (short beds would have less of a safety margin than deep beds), the effectiveness of regeneration, the particular adsorbate and the presence or absence of impurities in the stream being treated.

1.6.3.2 Carbon Estimation Procedure

The rule-of-thumb carbon estimation procedure is based on the “working capacity” (w_c, lb VOC/lb carbon). This is the difference per unit mass of carbon between the amount of VOC on the carbon at the end of the adsorption cycle and the amount remaining on the carbon at the end of the desorption cycle. It should not be confused with the “equilibrium capacity” (w_e,) defined above in Section 1.5. Recall that the equilibrium capacity measures the capacity of virgin activated carbon when the VOC has been in contact with it (at a constant temperature and partial pressure) long enough to reach equilibrium. In adsorber design, it would not be feasible to allow the bed to reach equilibrium. If it were, the outlet concentration would rapidly increase beyond the allowable outlet (or “breakthrough”) concentration until the outlet concentration reached the inlet concentration. During this period the adsorber would be violating the emission limit. With non-regenerable (canister) type systems, placing multiple vessels in a series can substantially decrease concerns of breakthrough.

The working capacity is some fraction of the equilibrium capacity. Like the equilibrium adsorptivity, the working capacity depends upon the temperature, the VOC partial pressure, and the VOC composition. The working capacity also depends on the flow rate and the carbon bed parameters.

The working capacity, along with the adsorption time and VOC inlet loading, is used to compute the carbon requirement for a canister adsorber or for an intermittently operated fixed-bed adsorber as follows:

$$M_{cI} = \frac{m_{voc}}{w_c} \theta_A \tag{1.13}$$

where

m_{VOC} = maximum VOC inlet loading (lb/h)

For waste streams where the VOC concentration is variable, the maximum VOC inlet loading should be used in order to ensure compliance with VOC emission limits at all inlet conditions.

Combining this with Equations 1.10 and 1.11 yields the general equation for estimating the system total carbon charge for a continuously operated system:

$$M_c = \frac{m_{voc}}{w_c} \theta_A \left(1 + \frac{N_D}{N_A} \right) \tag{1.14}$$

Values for w_c may be obtained from knowledge of operating units. If no value for w_c is available for the VOC (or VOC mixture) in question, the working capacity may be estimated at 50% of the equilibrium capacity, as follows:

$$w_c \approx 0.5 w_{e(\max)} \tag{1.15}$$

where

$w_{e(max)}$ = the equilibrium capacity (lb VOC/lb carbon) taken at the adsorber inlet (i.e., the point of maximum VOC concentration).

(Note: To be conservative (that is, to avoid understating working capacity), this 50% figure should be lowered if short desorption cycles, very high vapor pressure constituents, high moisture contents significant amounts of impurities, or difficult- to-desorb VOCs are involved. Furthermore, the presence of strongly adsorbed impurities in the inlet VOC stream may significantly shorten carbon life.)

As Equation 1.14 shows, the carbon requirement is directly proportional to the adsorption time. This would tend to indicate that a system could be designed with a shorter adsorption time to minimize the carbon requirement (and equipment cost). There is a trade-off here not readily apparent from Equation 1.14, however. Certainly, a shorter adsorption time would require less carbon. But, it would also mean that a carbon bed would have to be desorbed more frequently. This would mean that the regeneration steam would have to be supplied to the bed(s) more frequently to remove (in the long run) the same amount of VOC. Further, each time the bed is regenerated the steam supplied must heat the vessel and carbon, as well as drive off the adsorbed

VOC. And the bed must be dried and cooled after each desorption, regardless of the amount of VOC removed. Thus, if the bed is regenerated too frequently, the bed drying/cooling fan must operate more often, increasing its power consumption. Also, more frequent regeneration tends to shorten the carbon life. As a rule-of-thumb, the optimum regeneration frequency for fixed-bed adsorbers treating streams with moderate to high VOC inlet loadings is once every 8 to 12 hours.[1]

1.7 Estimating Total Capital Investment

This section describes the procedures that can be used to estimate the purchased costs for fixed-bed and canister-type carbon adsorbers. Since entirely different procedures should be used to estimate the purchased costs of fixed-bed and canister-type adsorbers, the two systems are discussed separately.

1.7.1 Fixed-Bed Systems

As indicated in the previous section, the purchased cost for fixed-bed carbon adsorbers using steam regeneration is a function of the volumetric flow rate, VOC inlet and outlet loadings, the adsorption time, and the working capacity of the activated carbon. As Figure 1.1 shows, the adsorber system is made up of several different items. Of these, the adsorber vessels and the carbon comprise from one-half to nearly 90% of the total equipment cost. (See Section 1.7.1.3.) There is also auxiliary equipment, such as fans, pumps, condensers, decanters, and internal piping, but because these usually comprise a small part of the total purchased cost, they may be "factored" from the costs of the carbon and vessels without introducing significant error into a cost estimate at a study-level of accuracy, as this one is. The costs of these major items are considered separately.

1.7.1.1 Carbon Cost

Carbon Cost, C_c, in dollars ($) is simply the product of the initial carbon requirement (M_c) and the current price of carbon.

$$C_c = CC \times M_c \tag{1.16}$$

where

C_c = Cost of carbon for the adsorber ($)
CC = Unit cost of carbon ($/lb)
M_c = Amount of carbon required (lbs)

As adsorber vendors buy carbon in very large quantities (million-pound lots or larger), their cost is somewhat lower than the list price. Vendors report typical carbons cost between $1.90 to $6.50 per pound for virgin carbon and $0.95 to $1.55 per pound for reactivated carbon Carbtrol reported costs of $1.90/lb for virgin carbon purchased in 1,100 lb sacks. [25, 29]

1.7.1.2 Vessel Cost

The cost of an adsorber vessel is primarily determined by its dimensions which, in turn, depend upon the amount of carbon it must hold and the superficial gas velocity through the bed that must be maintained for optimum adsorption. The desired superficial velocity is used to calculate the cross-sectional area of the bed perpendicular to the gas flow. An acceptable superficial velocity is established empirically, considering desired removal efficiency, the carbon particle size and bed porosity, and other factors. For example, one adsorber vendor recommends a superficial bed velocity of 85 ft/min[9], while an activated carbon manufacturer cautions against exceeding 60 ft/ min in systems operating at one atmosphere.[7] Another vendor uses a 65 ft/min superficial face velocity in sizing its adsorber vessels.[10] Lastly, there are practical limits to vessel dimensions which also influence their sizing. That is, due to shipping restrictions, vessel diameters rarely exceed 12 feet, while their length is generally limited to 50 feet.[10]

The cost of a vessel is usually correlated with its weight. However, as the weight is often difficult to obtain or calculate, the cost may be estimated from the external surface area. This is true because the vessel material cost—and the cost of fabricating that material—-is directly proportional to its surface area. The surface area (S, ft^2) of a vessel is a function of its length (L, ft) and diameter (D, ft), which in turn, depend upon the superficial bed face velocity, the *L/D* ratio, and other factors.

Most adsorber vessels are cylindrical in shape and may be erected either vertically or horizontally (as in Figure 1.1). For horizontal vessels, the carbon volume occupies no more than 1/3 of the vessel volume [9, 10]. It can be shown that this constraint limits the bed depth to no more than:

$$Maximum\ \ bed\ \ depth\ \approx \frac{\pi D}{12} \tag{1.17}$$

The vessel length, L, and diameter, D, can be estimated by solving two relationships, namely, (1) the equation relating carbon volume, and thus vessel volume, to L and D, and (2) the equation relating volumetric flow rate, superficial velocity, and cross-section normal to flow. If one assumes that the carbon bulk density is 30 lb/ft^3, then one can show that:

$$D = \frac{0.127\, M_c^{'}\, v_b}{Q'} \tag{1.18}$$

$$L = \frac{7.87}{M_c^{'}} \left(\frac{Q'}{v_b} \right)^2 \tag{1.19}$$

where

D = vessel diameter (ft)
L = vessel length (ft)
V_b = bed superficial velocity (ft/min)
M_c' = carbon requirement *per vessel* (lbs)
Q' = volumetric flow rate *per adsorbing vessel* (acfm)

Because the constants in Equations 1.18 and 1.19 are not dimensionless, one must be careful to use the units specified in these equations.

Although other design considerations can result in different values of *L* and *D*, these equations result in *L* and *D* which are acceptable from the standpoint of "study" cost estimation for horizontal, cylindrical vessels which are larger than 2-3 feet in diameter.

The carbon requirement and flow rate for each adsorber vessel can be calculated as follows.

$$M_c^{'} = \frac{M_c}{\left(N_A + N_D\right)} \qquad Q^{'} = \frac{Q}{N_A} \tag{1.20}$$

At gas flow rates (Q') of less than 9,000 scfm, it is usually more feasible to erect the adsorber vessels vertically instead of horizontally.[10] If so, the vessel diameter can be calculated from the volumetric flow rate per adsorbing vessel and the bed superficial velocity as follows:

$$D = \left(\frac{4Q'}{\pi\, v_b}\right)^{1/2} \tag{1.21}$$

The vertical vessel length will depend principally on the carbon bed thickness. Additional space must be included below the carbon bed for bed support and above and below the bed for distribution and disengaging of the gas stream and for physical access to the carbon bed. In smaller diameter vessels, access to both sides of the bed is usually not required. However, 1 to 1½ feet must be provided on each side for gas distribution and disengagement, or 2 to 3 feet overall. For longer vessels, 2 to 3 feet at each end of the vessel is typically provided for access space.

Given the mass of carbon in the bed, the carbon bulk density, and the bed diameter (i.e., the cross-sectional area normal to flow), determining the carbon bed thickness is straight forward using the following equation:

$$t_b = \frac{\text{volume of carbon}}{\text{cross} - \text{sectional area normal to flow}} = \frac{\left(\dfrac{M_c^{'}}{\rho_b}\right)}{\left(\dfrac{Q'}{v_b}\right)} \tag{1.22}$$

where

ρ_b = carbon bulk density (lb/ft^3, assume 30 lb/ft^3)

The vessel length is, therefore,

$$L = t_b + t_{a,g} \tag{1.23}$$

where

$t_{a,g}$ = access/gas distribution allowance
= 2 to 6 feet (depending on vertical vessel diameter)

Finally, use the following equation to calculate the surface area of either a horizontal or vertical vessel:

$$S = \pi D(L + D/2) \tag{1.24}$$

Similar equations can be developed for other vessel shapes, configurations, etc.

Based on vendor data, we developed a correlation between adsorber vessel cost and surface area: [10]

$$C_v = 271 \times F_m \times S^{0.778} \tag{1.25}$$

where

C_v = vessel cost (fall 1999 \$), F.O.B. vender[7]
F_m = adjustment factor for fabrication material (from Table 1.3)
S = surface area of the vessels (ft^2)

Table 1.3: Adjustment Factors to Obtain Costs for Fabricated Material

Material	F_m Factor	Reference(s)
Stainless steel, 304	1.0	[10]
Stainless steel, 316	1.3	[9,10,11]
Carpenter 20 CB-3	1.9	[11]
Monel-400	2.3	[9,11]
Nickel-200	3.2	[11]
Titanium	4.5	[11]

Equation 1.25 is valid for carbon adsorption vessels with surface areas (S) within the following range:

$$97 \le S \le 2110 \; ft^2$$

---

[7] Two vendors provided information for the 1999 updates, neither felt that modifications to the capital costs of adsorber system between 1989 and 1999 were appropriate. The major change for 1999 was a decrease in the price of carbon.[4, 5]

304 stainless steel is the most common material used in fabricating adsorber vessels. [9, 10]

1.7.1.3 Total Purchased Cost

As stated earlier, the costs of such items as the fans, pumps, condenser, decanter, instrumentation, and internal piping can be factored from the sum of the costs for the carbon and vessels. Based on four data points derived from costs supplied by an equipment vendor [10], we found that, depending on the total gas flow rate (Q), the ratio (R_c) of the total adsorber equipment cost to the cost of the vessels and carbon ranged from 1.14 to 2.24. These data points spanned a gas flow rate range of approximately 4,000 to 500,000 acfm. The following regression formula fit these four points:

$$R_c = 5.82\, Q^{-0.133} \tag{1.26}$$

where

Q is in the range of 4,000 to 500,000 acfm
Correlation coefficient (r) = 0.872

The total adsorber equipment cost (C_A) is the product of R_c and the sum of the carbon and vessel costs, as follows:

$$C_A = R_c\left[C_c + C_v\left(N_A + N_D\right)\right] \tag{1.27}$$

1.7.1.4 Total Capital Investment

As discussed in Section 1, in the methodology used in this Manual, the total capital investment (TCI) is estimated from the total purchased cost via an overall direct/indirect installation cost factor. A breakdown of that factor for carbon adsorbers is shown in Table 1.4. As Section 1.2 indicates, the TCI also includes costs for land, working capital, and off-site facilities, which are not included in the direct/indirect installation factor. However, as these items are rarely required with adsorber systems, they will not be considered here. Further, no factors have been provided for site preparation (SP) and buildings (Bldg.), as these site-specific costs depend very little on the purchased equipment cost.

The installation factor is applied to the total purchased equipment cost, which includes the costs of auxiliary equipment (i.e., the stack, external ductwork, etc) and the freight costs and sales taxes (if applicable). The external ductwork consists of the ducting needed to convey the exhaust gas from the emission source to the adsorber system, and then from the adsorber to the stack. (Costs for ductwork and stacks are shown elsewhere in this Manual.) Normally, the adjustment would also cover the instrumentation cost, but this cost is usually included with the adsorber equipment cost. Finally, note that these factors reflect "average" installation conditions and could vary considerably, depending upon the installation circumstances.

Table 1.4: Capital Cost Factors for Carbon Adsorbers [12]

Direct Costs	
Purchased equipment costs	
Adsorber + auxiliary equipment[a]	As estimated, A
Instrumentation[b]	0.10 A
Sales taxes	0.03 A
Freight	0.05 A
Purchased equipment cost, PEC	B = 1.18 A
Direct installation costs	
Foundations & supports	0.08 B
Handling & erection	0.14 B
Electrical	0.04 B
Piping	0.02 B
Insulation	0.01 B
Painting	0.01 B
Direct installation costs	0.30 B
Site preparation	As required, SP
Buildings	As required, Bldg
Total Direct Costs, DC	1.30 B + SP + Bldg.
Indirect Costs (installation)	
Engineering	0.10 B
Construction and field expenses	0.05 B
Start-up	0.02 B
Performance test	0.01 B
Total Indirect Costs, IC	0.18 B
Contractor Fees	0.10(DC + IC)
Contingencies, C	CF(DC + IC)
Total Capital Investment	1.48 B + SP + Bldg + C + Contractor Fees

[a] Ductwork and any other equipment normally not included with unit furnished by adsorber vendor.

[b] Instrumentation and controls often furnished with the adsorber, and thus included in the EC.

[c] Where “CF” is the contingency factor. Typical values for CF for mature technologies such as carbon adsorbers range from 5 to 15 percent.

1.7.2 Canister Systems

Once the carbon requirement is estimated using the procedure in Section 1.6.3, the number of canisters is determined. This is done simply by dividing the total carbon requirement (M_c) by the amount of carbon contained in each canister. This quotient, rounded to the next highest digit, yields the required number of canisters to control the vent in question. Costs for typical canisters of various sizes are listed in Table 1.5. These costs include the vessel, carbon, and connections, but do not include taxes, freight, or installation charges. The cost per canister generally decreases as the quantity of canisters purchased increases. Costs are for canisters containing granular or pelletized activated carbon, commonly used in industrial adsorption applications (e.g., Calgon’s AP4-60). However, to treat certain VOCs, more expensive specialty adsorbents are needed, such as Calgon’s HGR-P - an impregnated pellet activated carbon, which is designed for mercury removal in gas phase applications. These adsorbents can increase the equipment cost by 60% or more.[6] Costs for activated carbon range from $0.95 to $6.50 per pound based on 2018 data. Prices vary depending on mesh, activity and type.

The current trend is toward the use of larger non-regenerable fixed-bed canisters with capacities of 1,000 to 10,000 pounds, where the carbon is typically exchanged in the field. These adsorbers are usually atmospheric designs made of thin steel with an internal coating to inhibit corrosion. Typical prices for these large canisters are provided in Table 1.6. Annual maintenance costs are reported to range from 3% to 10% of the installed capital costs.

Table 1.5: Equipment Costs for Typical Canister Adsorbers [25, 29]

Canister Size (in lb of Activated Carbon)	Maximum Flow Rate (cfm)	Canister Type	Cost with Virgin Carbon ($)*	Cost with Reactivated Carbon ($)*
140	500	Polyethylene	720	-
140	500	Epoxy-Lined Steel	1,105	-
170	300	Epoxy-Lined Steel	1,090	-
180	100	Epoxy-Lined Steel	1,600	980
200	100	Epoxy-Lined Steel	785	-

* Costs are in 2018 dollars and exclude taxes and freight charges.

Table 1.6: Equipment Costs for Typical Large Canister Adsorbers [25, 29]

Adsorber Size (in lb of Activated Carbon)	Maximum Flow Rate (cfm)	Canister Type	Cost with Virgin Carbon ($)*	Cost with Reactivated Carbon ($)*
1,000	600	Epoxy-Lined Steel	6,600	-
1,000	1,000	Epoxy-Lined Steel	11,500	7,000
2,000	2,000	Epoxy-Lined Steel	19,000	10,000
2,000	750	Carbon Steel	22,000	13,200
3,000	2,000	Epoxy-Lined Steel	13,900	-
4,100	8,000	Polypropylene	45,000	-
5,000	2,500	Carbon Steel	42,600	20,100
8,000	4,500	Carbon Steel	66,000	30,000
10,000	18,000	Polypropylene	94,500	-

* Costs are in 2018 dollars and exclude installation, taxes and freight charges.

As fewer installation materials and labor are required to install a canister unit than a fixed-bed system, the composite installation factor is consequently lower. The only costs required are those needed to place the canisters at, and connect them to, the source. This involves a small amount of piping only; little or no electrical work, painting, foundations, or the like would be needed. For typical sites, twenty percent of the sum of the canister(s) cost, freight charges, and applicable sales taxes covers the installation cost. However, installation costs may be higher depending on site-specific conditions. For example, canister units retrofitted at congested sites may require additional duct work, blowers, and valves.

The number and size of canisters can be adjusted to accommodate certain design specifications. For example, the number of canisters calculated using the approach outlined above must be doubled for systems where two canisters are used in series. Similarly, for a system designed to minimize the frequency of canister replacement, canisters with larger capacity than estimated using the approach outlined above should be selected.

1.8 Estimating Total Annual Cost

The total annual cost for a carbon adsorption system is comprised of three components: direct costs, indirect costs, and recovery credits. Each component is considered separately in this section.

1.8.1 Direct Annual Costs

Direct annual costs include the following expenditures: steam, cooling water, electricity, carbon replacement, operating and supervisor labor, and maintenance labor and materials. Of these, only operator/supervisor labor, maintenance and materials labor, electricity and solid waste disposal or carbon replacement/regeneration apply to the canister-type adsorbers.

1.8.1.1 Steam

As explained in Section 1.1, steam is used during the desorption cycle. The quantity of steam required will depend on the amount of carbon in the vessel, the vessel dimensions, the type and amount of VOC adsorbed, and other variables. Experience has shown that the steam requirement ranges from approximately 3 to 4 lbs of steam/lb of adsorbed VOC. [9, 10] Using the midpoint of this range, the annual costs for steam can be estimated by the equation:

$$C_s = 3.50\ m_{voc}\ \theta_s\ p_s \tag{1.28}$$

where

C_s = steam cost (\$/yr)
θ_s = system operating hours (h/yr)
m_{voc} = VOC inlet loading (lbs/hr)
p_s = steam price (\$/thousand lbs)

If steam price data are unavailable, one can estimate its cost at 130% of the fuel cost for oil and natural gas-fired boilers. For example, if the natural gas price for an industrial facility is \$4.00/million BTU[8], then the estimated steam price would be \$5.20/million BTU or approximately \$5.00/thousand lbs of steam. The 1.3 factor covers the costs of producing the steam, including costs for water, water treatment (e.g., clarification, softening, demineralization), feedwater pumping, combustion air fan power, sewer charges for boiler blowdown, air pollution controls for the boiler, maintenance materials and maintenance labor. [26]

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[8] Average price of natural gas in 2017 for industrial facilities, based on data published by the U.S. Department of Energy, Energy Information Administration (see https://www.eia.gov/dnav/ng/ng_pri_sum_dcu_nus_a.htm).

1.8.1.2 Cooling Water

Cooling water is consumed by the condenser in which the steam-VOC mixture leaving the desorbed carbon bed is condensed. Most of the condenser duty is comprised of the latent heat of vaporization (ΔH_v) of the steam and VOC. As the VOC ΔH_v are usually small compared to the steam ΔH_v, (about 1000 BTU/lb), the VOC ΔH_v may be ignored. So may the sensible heat of cooling the water-VOC condensate from the condenser inlet temperature (about 212°F) to the outlet temperature. Therefore, the cooling water requirement is essentially a function of the steam usage and the allowable temperature rise in the coolant, which is typically 30 to 40°F.[9] Using the average temperature rise (35°F), we can write:

$$C_{cw} = 3.43 \frac{C_s}{P_s} p_{cw} \tag{1.29}$$

Where

C_{cw} = cooling water cost (\$/yr)
p_{cw} = cooling water price (\$/thousand gal.)

If the cooling water price is unavailable, use \$1.00 to \$8.25/thousand gallons.[9]

1.8.1.3 Electricity

In fixed-bed adsorbers, electricity is consumed by the system fan, bed drying/cooling fan, cooling water pump, and solvent pump(s). Both the system and bed fans must be sized to overcome the pressure drop through the carbon beds. But, while the system fan must continuously convey the total gas flow through the system, the bed cooling fan is only used during a part of the desorption cycle (one-half hour or less).

For both fans, the horsepower needed depends both on the gas flow and the pressure drop through the carbon bed. The pressure drop through the bed (ΔP_b) depends on several variables, such as the adsorption temperature, bed velocity, bed characteristics (e.g., void fraction), and thickness. But, for a given temperature and carbon, the pressure drop per unit thickness depends solely on the gas velocity. For instance, for Calgon's "PCB" carbon (4 x 10 mesh), the following relationship holds: [7]

$$\frac{\Delta P_b}{t_b} = 0.03679 \ v_b + 1.107 \times 10^{-4} \ v_b^{\ 2} \tag{1.30}$$

where

$\Delta P_b/t_b$ = pressure drop through bed (inches of water/foot of carbon)
v_b = superficial bed velocity (ft/min)

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[9] Based on rates for industrial facilities report in 2013 compiled by Black & Veatch. (see 2012/2013 "50 Largest Cities Water/Wastewater Rate Survey." Available at http://www.saws.org/who_we_are/community/RAC/docs/2014/50-largest-cities-brochure-water-wastewater-rate-survey.pdf.

As Equation 1.22 shows, the bed thickness (t_b, ft) is the quotient of the bed volume (V_b) and the bed cross-sectional area (A_b). For a 30 lb/ft^3 carbon bed density, this becomes

$$t_b = \frac{V_b}{A_b} = \frac{0.0333\,M_c^{'}}{A_b} \tag{1.31}$$

(For vertically erected vessels, $A_b = Q/V_b$, while for horizontally erected cylindrical vessels, $A = LD$.) Once ΔP_b is known, the system fan horsepower requirement (hp_{sf}) can be calculated:

$$hp_{sf} = 2.50 \times 10^{-4} Q\ \Delta P_s \tag{1.32}$$

where

Q = gas volumetric flow through system (acfm)
ΔP_s = total system pressure drop = $\Delta P_b + 1$

(The extra inch accounts for miscellaneous pressure losses through the external ductwork and other parts of the system.[9][10] However, if extra long duct runs and/or preconditioning equipment are needed, the miscellaneous losses could be much higher.)

This equation incorporates a fan efficiency of 70% and a motor efficiency of 90%, or 63% overall.

The horsepower requirement for the bed drying/cooling fan (hp_{cf}) is computed similarly. While the bed fan pressure drop would still be ΔP_b, the gas flow and operating times would be different. For typical adsorber operating conditions, the drying/cooling air requirement would be 50 to 150 ft^3/lb carbon, depending on the bed moisture content, required temperature drop, and other factors. The operating time (θ_{cf}) would be the product of the drying/cooling time per desorption cycle and the number of cycles per year. It can be shown that:

$$\theta_{cf} = 0.4\,\theta_D \left(\frac{N_A \theta_s}{\theta_A} \right) \tag{1.33}$$

(The "0.4" allows for the fact that as a rule-of-thumb, approximately 40% of the desorption cycle is used for bed drying/cooling.)

The cooling water pump horsepower requirement (hp_{cwp}) would be computed as follows:

$$hp_{cwp} = \frac{2.52 \times 10^{-4} q_{cw}\, H\, s}{\eta} \tag{1.34}$$

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[10] To obtain a more precise estimate of ductwork pressure drop, refer to Section 2 of this Manual.

where

q_{cw} = cooling water flow (gal/min)
H = required head (nominally 100 feet of water)
s = specific gravity of fluid relative to water at 60°F
η = combined pump-motor efficiency.

The annual operating hours for the cooling water pump (θ_{cwp}) would be computed using Equation 1.33, after substituting "0.6" for 0.4. The 0.6 factor accounts for the fact that the cooling water pump is only used during the steaming portion of the regeneration, while the condenser is in operation.

Equation 1.34 may also be used to compute the solvent pump horsepower requirement. In the latter case, the flow (q_s) would be different of course, although the same head—100 ft. of water—could be used. The specific gravity would depend on the composition and temperature of the condensed solvent. For example, the specific gravity of toluene at 100°F would be approximately 0.86 at 70°F. (However, the solvent pump horsepower is usually very small—usually < 0.1 hp.— so its electricity consumption can usually be neglected.)

Once the various horsepowers are calculated, the electricity usage (in kWh) is calculated, by multiplying each horsepower value by 0.746 (the factor for converting hp to kilowatts) and the number of hours each fan or pump operates annually. For the system fan, the hours would be the annual operating hours for the system (θ_s). But, as discussed above, the operating times for the bed drying/cooling fan and cooling water pump would be different.

To obtain the annual electricity cost, simply multiply kWh by the electricity price (in $/kWh) that applies to the facility being controlled.

For canister units, use Equation 1.32 to calculate the fan horsepower requirement. However, instead of P_b use the following to compute the total canister pressure drop P_c inches of water:[6]

$$\Delta P_c = 0.0471\ Q_c + 9.29 \times 10^{-4}\ Q_c^2 \tag{1.35}$$

where

Q_c = flow through the canister (acfm).

1.8.1.4 Carbon Replacement

As discussed above, the carbon has a different economic life than the rest of the adsorber system. Therefore, its replacement cost must be calculated separately. Employing the procedure detailed in Section 1, Chapter 2 of this Control Cost Manual, we have:

$$CRC_c = CRF_c\left(1.08\, C_c + C_{cl}\right) \tag{1.36}$$

where

CFR_c = capital recovery factor for the carbon
1.08 = taxes and freight factor
C_c = cost of carbon, $
C_{cl} = labor cost for carbon replacement, $

The replacement labor cost covers the labor cost for removing spent carbon from vessels and replacing it with virgin or regenerated carbon. The cost would vary with the amount of carbon being replaced, the labor rates, and other factors, but can be estimated using equation 1.37. For example, to remove and replace a 50,000 pound carbon charge would require about 16 person-days. [13] Hence, a typical carbon replacement rate is 379 lbs of carbon per hour.

$$C_{cl} = \frac{LR \times M_c}{CRR} \tag{1.37}$$

where

C_{cl} = labor cost for carbon replacement, \$
CRR = carbon replacement rate, lbs of carbon/hour (default value, 379 lbs/hour)
LR = labor rate, \$/hour
M_c = quantity of carbon replaced, lbs

A typical life for the carbon is five years. However, if the inlet contains VOCs that are very difficult to desorb, tend to polymerize, or react with other constituents, a shorter carbon lifetime of one or two years is likely. [1]

The capital recovery factor (CFR_c) is calculated using the following equation:

$$CRF_c = \frac{i\ (1+i)^n}{(1+i)^n - 1} \tag{1.38}$$

Where *i* is the assumed interest rate and *n* is the expected life of the carbon. For a five-year life and 5% interest rate, CRF_c is 0.2310.

1.8.1.5 Solid Waste Disposal

Disposal costs are rarely incurred with fixed-bed adsorbers, because the carbon is almost always regenerated in place, not discarded. The carbon in canister units should also be regenerated in most cases. For larger vessels, common practice is for a carbon vendor to pick up the spent carbon and replace it with fresh carbon. The spent carbon is then returned to a central facility for regeneration. The EPA encourages both solvent recovery and reuse of spent carbon as pollution prevention and waste minimization techniques.

In some cases, the solvent characteristics, such as their toxicity or the difficulty in desorbing them from the carbon, may make landfill disposal the preferred option. In these cases, an entire canister—carbon, drum, connections, etc.— may be shipped to a secure landfill. The cost of landfill disposal could vary considerably, depending on the number of canisters disposed of, the location of the landfill, etc. Based on data obtained from two large landfills, disposal costs range from approximately \$35 to \$65 per canister, excluding transportation costs.[14, 15]

1.8.1.6 Operating and Supervisory Labor

The operating labor for adsorbers is relatively low, as most systems are automated and require little attention. One-half operator hour per shift is typical.[12] The annual labor cost is the product of this labor requirement and the operating labor wage rate ($/h) which, naturally, varies based on the facility location, type of industry, etc. Add to this 15% to cover supervisory labor, as suggested in Section 1, Chapter 2 of the Control Cost Manual.

1.8.1.7 Maintenance Labor and Materials

Use 0.5 hours/shift for maintenance labor [12] and the applicable maintenance wage rate. If the latter data are unavailable, estimate the maintenance wage rate at 110% of the operating labor rate, as Section 1 suggests. Finally, for maintenance materials, add an amount equal to the maintenance labor, also per Section 1, Chapter 2 of the Manual.

1.8.2 Indirect Annual Costs

These include such costs as capital recovery, property taxes, insurance, overhead, and administrative costs ("G&A"). The capital recovery cost is based on the equipment lifetime and the annual interest rate. (See Section 1.2 for a thorough discussion of the capital recovery cost and the variables that determine it.) For adsorbers, the equipment lifetime is typically 15 to 25 years, except for the carbon, which, as stated above, typically needs to be replaced after five years. Therefore, when figuring the system capital recovery cost, one should base it on the installed capital cost less the cost of replacing the carbon (i.e., the carbon cost plus the cost of labor necessary to replace it). Substituting the initial carbon and replacement labor costs from Equation 1.36, we obtain:

$$CRC_s = \left[TCI - \left(1.08C_c + C_{cl}\right)\right]CRF_s \tag{1.39}$$

where

CRC_s = capital recovery cost for adsorber system ($/yr)
TCI = total capital investment ($)
1.08 = taxes and freight factor
C_c, C_{cl} = initial carbon cost (F.O.B. vendor) and carbon replacement labor cost, respectively ($)
CRF_s = capital recovery factor for adsorber system (defined in Section 1.2).

For a 15-year life and a 5% annual interest rate, the CRF_s is 0.0963.

As Section 1.2 indicates, the suggested factor to use for property taxes, insurance, and administrative charges is 4% of the TCI. Finally, the overhead is calculated as 60% of the sum of operating, supervisory, and maintenance labor, and maintenance materials.

The above procedure applies to canister units as well, except in those cases where the entire unit and not just the carbon is replaced. The piping and ducting cost can usually be considered a capital investment with a useful life of ten years. However, whether the canister itself would be treated as a capital or an operating expense would depend on the particular application and would need to be evaluated on a case-by-case basis.

1.8.3 Recovery Credits and Disposal Costs

During the desorption cycle, VOC is desorbed, condensed, and separated from the steam condensate. The recovered VOC can be re-used onsite (e.g., as a solvent or burned as a fuel), sold to recyclers, or sent to a disposal site. If the recovered VOC is sufficiently pure, it can be reused onsite or sold. As the example problem in Section 1.9 illustrates, if the quantity of recovered VOC is large enough, its value can offset the annual costs of the control device, resulting in a net annual credit. However, the current market price of the VOC and its purity impact the size of the credit. The greater the purity, the higher the value. However, if the recovered VOC contains impurities or is a mixture of compounds, further treatment, such as distillation, will be required. Purification and separation costs are beyond the scope of this chapter. Needless to say, the costs of these operations can be significant and should be included in estimates of the capital and operating costs. They may offset the revenues generated by the sale of the VOC. Where the facility is unable to re-use or sell the waste VOC collected, the facility may incur costs associated with its off-site disposal. Costs of disposal for wastes containing hazardous pollutants, such as benzene, can be high and alternative control systems, such as incinerators, may be more cost effective than a carbon adsorber.

Recovery Credits:

The following equation can be used to calculate the recovery credits:

$$RC = m_{voc}\ \theta_s\ p_{voc}\ E \tag{1.40a}$$

where

RC = recovery credit ($/yr)
m_{voc} = VOC inlet loading (lbs/h)
θ_s = system operating hours (h/yr)
p_{voc} = resale value of the recovered VOC ($/lb)
E = adsorber VOC control efficiency

By definition, the efficiency (E) is the difference between the inlet and outlet VOC mass loading, divided by the inlet loading. However, during an adsorption cycle the outlet VOC loading will increase from essentially zero at the start of the cycle to the breakthrough concentration at the end of the cycle. Because the efficiency is a function of time, it should be calculated via integration over the length of the adsorption cycle. However, this approach requires knowledge of the temporal variation of the outlet loading during the adsorption cycle. If this knowledge is not available, a conservative approximation of the efficiency may be made by setting the outlet loading equal to the breakthrough concentration.

Disposal Costs:

In situations where the collected VOC must be sent off-site for disposal, the following equation should be used to calculate the disposal costs:

$$Disposal_{Cost} = m_{voc}\ \theta_s\ D_{voc}\ E \tag{1.40b}$$

where

$Disposal_{Cost}$ = Disposal Cost ($/yr)
m_{voc} = VOC inlet loading (lbs/h)
θ_s = System operating hours (h/yr)
D_{voc} = Disposal costs for the recovered VOC ($/lb)
E = Adsorber VOC control efficiency

1.8.4 Total Annual Cost

Finally, as explained in Section 1, the total annual cost (TAC) is the sum of the direct and indirect annual costs and disposal cost, less any recovery credits, or:

$$TAC = DAC + IAC + Disposal_{cost} - RC \tag{1.41}$$

where

DAC = Direct annual costs,
IAC = Indirect annual costs,
$Disposal_{cost}$ = Costs for disposing or otherwise treating recovered VOC, and
RC = Recovery credit.

1.8.5 Cost Effectiveness

The cost in dollars per ton of VOC removed per year, is calculated using equation 1.42:

$$Cost\ Effectiveness = \frac{TAC}{VOC\ Removed/yr} \tag{1.42}$$

where

Cost Effectiveness = the cost effectiveness, $/ton
VOC Removed/year = annual mass of VOC removed by the carbon adsorber, tons/year

1.9 Example Problem

An example problem that calculates both the design parameters and capital and annual costs for a carbon adsorber applied to a printing plant is presented below. The printing plant will operate continuously for 360 days/year and emit 100 lb/hour of toluene. The waste gas is expected to contain negligible quantities of particulate matter and moisture. The plant proposes to use a carbon adsorber that consists of three beds, with two carbon beds adsorbing VOC, while the third bed is desorbing or on standby. Each carbon bed will be housed in a metal vessel made with 304 stainless steel. No additional site preparation or building modifications are necessary for the installation of the new adsorber. The toluene will be recovered and sold to a solvent recycling company.

The following assumptions are made to perform the calculations:

VOC emitted = Toluene
Required control efficiency = 98%
Emission rate (M_{voc}) = 100 lbs/hour
Toluene concentration at inlet = 710 ppm
Partial pressure of toluene = 0.0104 psia (at atmospheric pressure and 77°F)
Number of operating hours = 8,640 hours/year
Total time for adsorption (Θ_A) = 12 hours
Time available for desorption = 5 hours
Total waste gas flow rate (Q) = 10,000 acfm (at atmospheric pressure and 77°F)

Assume the recovered toluene is recycled at the source.

Superficial bed velocity (v_b) = 75 ft/min
Expected life of the absorber vessels and auxiliary equipment = 15 years
Expected life of carbon = 5 years

In addition to these assumptions, other important inputs to the cost calculations are:

Carbon cost (CC) = \$4.20 per lb[11]
Electricity = \$0.0676 per kWh[12]
Steam = \$5.00 per 1,000 lbs of steam[13]
Cooling water = \$3.55 per 1,000 gallons of water[14]
Operator labor rate = \$27.48 per hour[15]
Re-sale price for recovered toluene = \$0.33 per lb[16]

1.9.1 Design Parameter Example

Carbon Working Capacity: At the stated flow and pollutant loading, the toluene inlet concentration is 710 ppm. This corresponds to a partial pressure of 0.0104 psia. Substituting the partial pressure and the toluene isotherm parameters from Table 1.2 into Equation 1.1, we calculate an equilibrium capacity of 0.333 lb VOC/lb carbon.

$$w_e = k\,P^m = (0.551)(0.0104)^{0.11} = 0.333\,lbVOC\ /\,lbCarbon$$

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[11] Median cost for virgin carbon based on 2018 prices provided by Calgon Carbon Corporation (Moon Township, PA) and Carbtrol Corporation (Bridgeport, CT).

[12] Average electricity price for the industrial sector is based data compiled by the Department of Energy, Energy Information Administration, November 6, 2017. Available at https://www.eia.gov/electricity/sales_revenue_price/.

[13] Price of steam was estimated by multiplying the average price of natural gas for industrial facilities (\$4.00/MMBtu) by 1.3 and converting to \$/1,000 lb of steam. Natural gas price is the 2017 average price for industrial facilities published by the U.S. Department of Energy, Energy Information Administration (see https://www.eia.gov/dnav/ng/ng_pri_sum_dcu_nus_a.htm).

[14] Average water rates for industrial facilities in 2013, compiled by Black & Veatch. (see 2012/2013 "50 Largest Cities Water/Wastewater Rate Survey." Available at http://www.saws.org/who_we_are/community/RAC/docs/2014/50-largest-cities-brochure-water-wastewater-rate-survey.pdf.

[15] Bureau of Labor Statistics, May 2017 National Occupational Employment and Wage Estimates – United States, May 2017 (https://www.bls.gov/oes/current/oes_nat.htm). Hourly rates for operators based on data for plant and System Operators – other (51-8099).

[16] For this example, recovered toluene is valued at one-half the December 2017 market price of \$717.64/metric ton.[16]

By applying the rule-of-thumb discussed in Section 1.6.3.2, the working capacity may be estimated at 50% of the equilibrium capacity, as follows:

$$w_c \approx 0.5 w_{c(\max)} \approx 0.167\, lbVOC \ / \ lbCarbon$$

where

$w_{c(max)}$ = Equilibrium capacity at the adsorber inlet (lb VOC/lb carbon)

Carbon Requirement: When operating, the adsorber will have two beds adsorbing and one bed regenerating/in stand-by at all times. Using equation 1.12 we can estimate the amount of the desorption time (Θ_D):

$$\theta_D \leq \theta_A \left(\frac{N_D}{N_A} \right) = 12\, hours \times \left(\frac{1}{2} \right) = 6\, hours$$

where

N_D = Number of desorbing beds
N_A = Number of adsorbing beds
Θ_A = Total time for adsorption (hours)
Θ_D = Total time needed for bed regeneration, drying, and cooling (hours)

Because the stated design desorption time of 5 hours is less than the 6 hours needed for bed regeneration, the proposed bed configuration is feasible.

Equation 1.14 is used to calculate the amount of carbon required (M_c):

$$M_c = \frac{m_{voc}}{w_e} \theta_A \left(1 + \frac{N_D}{N_A} \right) = \left(\frac{100\, lbVOC \ / \ hour \times 12\, hours}{0.167\, lbVOC \ / \ lbCarbon} \right) \left(1 + \frac{1}{2} \right) = 10{,}800\, lbs$$

Adsorber Vessel Dimensions: Assuming the vessels will be erected horizontally, the vessel diameter (*D*), length (*L*), and surface area (*S*) are calculated using Equations 1.18, 1.19, and 1.24, respectively.

$$D = \frac{0.127\, M_c' v_b}{Q'} = \frac{0.127\,(3{,}600)(75)}{5{,}000} = 6.86\ ft$$

$$L = \frac{7.87}{M_c'} \left(\frac{Q'}{v_b} \right)^2 = \frac{7.87}{3{,}600} \left(\frac{5{,}000}{75} \right)^2 = 9.72\ ft$$

$$S = \pi D \left(L + \frac{D}{2} \right) = \pi (6.86\, ft) \left(9.72\, ft + \frac{6.86\, ft}{2} \right) = 283\ ft$$

Where the volumetric flow rate (*Q'*) and quantity of carbon required (*M_c'*) for each bed are calculated as follows:

$$Q' = \left(\frac{Q}{N_A}\right) = \left(\frac{10{,}000\,acfm}{2}\right) = 5{,}000\,acfm\ /\ bed$$

$$M_c' = \frac{M_c}{(N_A + N_D)} = \frac{10{,}800\,lbs}{(2+1)} = 3{,}600\,lbs\ /\ bed$$

1.9.2 Cost Estimate Example

Once the carbon adsorption system is sized, the total cost of the system can be estimated as the sum of the total capital investment (TCI) and the total annual costs.

Total Capital Investment: The total capital investment (TCI) costs are estimated as

$$TCI = \sum Direct\ Capital\ Costs + \sum Indirect\ Capital\ Costs$$

Table 1.7 shows the direct and indirect capital costs for the carbon adsorption system based on the factors provided in Section 1.8.

Adsorber Equipment Cost (including costs for carbon and instrumentation): The equipment cost is comprised of the adsorber vessels, carbon, and the condenser, decanter, fan, pumps and other equipment usually included in the adsorber price. The costs of the latter items are based on the combined cost of the vessels and carbon. Combining Equations 1.26 and 1.27, we have:

$$C_A = 5.82\ Q^{-0.133}\left[C_c + \left(N_A + N_D\right)C_v\right] \tag{1.43}$$

Because *S* falls between 97 and 2,110 ft^2, equation 1.25 can be used to calculate the cost per vessel, C_v. Additionally, since each vessel will be constructed from 304 stainless steel, the adjustment factor for fabrication material (F_m) in Equation 1.25 is 1, and the cost per vessel is calculated as follows:

$$C_v = 271\,F_m\,S^{0.778} = (271)(1)(283)^{0.778} = \$21{,}900\,/\,vessel$$

The cost per vessel, *Cv*, is then converted to the current year dollars using the Chemical Engineering Plant Cost Index (CEPCI). In this example, the scaling factor for 2017 dollars was 567.5/390.6). Hence, Cv is $31,834 in 2017 dollars.

The total cost of the carbon required for the adsorber (C_c) is calculated using equation 1.16 as follows:

$$C_c = CC \times M_c = \frac{\$4.2}{lb} \times 10{,}800\,lbs = \$45{,}360$$

Substituting the values for C_v and C_c into equation 1.43 yields:

$$C_A = (5.82)(10{,}000)^{-0.133}[45{,}360 + (2+1)(31{,}834)] = \$240{,}800$$

Auxiliary Equipment Costs: Auxiliary equipment includes the costs for the stack and duct work and dampers connecting the coating booth to the carbon adsorber and the carbon adsorber to the stack. The costs for this equipment are estimated using the methods provided in Section 2 of the Manual. For the purposes of this example, assume the costs for the auxiliary equipment have been estimated to be:

Ductwork	$16,500
Dampers	7,200
Stack	8,500
Total	$32,200

Table 1.7: Estimated Total Capital Cost for the Carbon Adsorber

Cost Item	Estimated Cost
Direct Costs	
Purchased equipment costs	
Adsorber vessels and carbon	$240,805
Auxiliary equipment	32,200
Sum = A	$273,005
Instrumentation, 0.1 A[a]	$0
Sales taxes, 0.03 A	$8,190
Freight, 0.05 A	$13,650
Purchased equipment cost (B)	$294,845
Direct installation costs	
Foundations & supports, 0.08 B	$23,588
Handling & erection, 0.14 B	$41,278
Electrical, 0.04 B	$11,794
Piping, 0.02 B	$5,897
Insulation for ductwork, 0.01 B	$2,948
Painting, 0.01 B	$2,948
Direct installation costs	$88,454
Site preparation	$0
Buildings	$0
Total Direct Costs (DC)	**$383,454**
Indirect Costs (installation)	
Engineering, 0.10 B	$29,485
Construction and field expenses, 0.05 B	$14,742
Start-up, 0.02 B	$5,897
Performance test, 0.01 B	$2,948
Total Indirect Cost(IC)	**$53,072**
Contractor Fees, 0.10(DC + IC)	**$43,637**
Contingencies (C), CF(DC + IC + Contractor Fees)[c]	**$48,001**
Total Capital Investment (TCI)[b]	**$528,000**

[a] The costs for instrumentation are included in the adsorber equipment cost.

[b] Value shown has been rounded to three significant figures.

[c] Where “CF” is the contingency factor of 10%, the midpoint of the typical range of 5 to 15% for mature technologies such as this one.

Instrumentation costs are included in the cost of the adsorber. Sales taxes and freight costs are based on the sum of the total equipment costs (i.e., adsorber vessels, carbon, and auxiliary equipment). The sales taxes are assumed for purposes of this cost example to be 3 percent of the equipment costs,[17] while the freight charges are assumed for purposes of this cost example to be 5 percent of the equipment costs. Hence, the purchased equipment cost (B) is given by the following equation:

$$Purchased\ Equipment\ Cost\ (B) = 1.08 \times A = 1.08 \times (\$240{,}805 + \$32{,}200) = \$294{,}845$$

where

A = Sum of adsorber vessels, carbon, and auxiliary equipment costs ($).

Other Direct and Indirect Costs: Table 1.7 shows the calculations for the other direct and indirect costs for the carbon adsorber. These costs are calculated using the factors provided in Section 1.8 and the purchased equipment cost (B) calculated above.

Total Capital Investment: The total capital investment (TCI) is the sum of all the direct and indirect costs and the contingency factor (10% for this example) and is calculated as follows:

$$\text{Total Capital Investment (TCI)} = DC + IC + C + \text{Contractor Fees}$$

$$TCI = 1.48 \text{ x } B + CF(1.48 \text{ x } B) + 0.1(1.48 \text{ x } B) = \$528{,}000$$

1.9.3 Total Annual Costs

Annual Costs, Table 1.8 gives the direct and indirect annual costs for the carbon adsorber system, as calculated from the factors in Section 1.8.

As discussed in Section 1.8.4, the total annual cost (TAC) is comprised of the direct annual costs (DAC), indirect annual costs (IAC), annual disposal costs ($Disposal_{cost}$) and any recovery credits (RC), as described by the equation:

$$TAC = DAC + IAC + Disposal_{Cost} - RC$$

The total direct annual cost (DAC) is the sum of the operator labor, maintenance, carbon replacement, and utility costs.

Operator Labor Costs: The operator costs are the sum of the operator and supervisor costs. As explained in Section 1.8.1.6, the annual operator labor is estimated to be one-half hour per shift. The annual labor cost is calculated as follows:

$$Operator\ \ Labor\ \ Cost = \frac{0.5\ hours}{shift} \times \frac{3\ shifts}{day} \times \frac{360\ \ days}{year} \times \frac{\$27.48}{hour} = \$14{,}839\ /\ year$$

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[17] In some states, pollution control equipment is exempt from sales taxes. This should be accounted for in the TCI estimate if relevant.

The costs for supervisor labor is estimated at 15% of the operator labor cost, as shown below:

$$Supervisor\ \ Labor\ \ Cost\ = 0.15 \times \$14{,}839\ /\ year\ = \$2{,}226\ /\ year$$

Maintenance Costs: The maintenance costs are the sum of the costs of labor and materials. The maintenance labor is estimated to be 0.5 hours/shift. Since the maintenance labor rate is unknown, we estimate the wage rate at 110% of the operating labor rate, as recommended in Section 1 of the Cost Manual. The maintenance labor costs are calculated as follows:

$$Maintenance\ Labor\ Cost = \frac{0.5\ hours}{shift} \times \frac{3\ shifts}{day} \times \frac{360\ days}{year} \times \frac{\$27.48}{hour} \times 1.10 = \$16{,}323$$

Finally, for the maintenance materials, we estimated the materials to be an amount equal to the estimated maintenance labor.

Carbon Replacement Costs: As discussed in Section 1.8.1.4, costs for replacing the carbon are the sum of the labor and the replacement carbon. Because the economic life of the carbon is 5 years, the carbon replacement costs must be calculated separately from the rest of the adsorber system using a capital recovery factor based on 5 years, instead of the 15-year life expected for the absorber vessels and auxiliary equipment. Hence, the costs of replacing the carbon is calculated using equation 1.36.

$$CRC_c = CRF_c\left(1.08\,C_c + C_{cl}\right)$$

Where CRF_c, calculated as follows using a 5% interest rate and 5-year carbon life, is given by:

$$CRF = \frac{\mathrm{i}(1+i)^n}{(1+i)^n-1} = \frac{(0.05)(1+0.05)^5}{(1+0.05)^5} = 0.2310$$

The labor costs for removing the spent carbon from vessels and replacing it with virgin or regenerated carbon is calculated using equation 1.37. For this example, we used the default factor of 379 lbs/hour for the carbon replacement rate (*CRR*) and labor rate of $30.23/hour (110% of the operator rate):

$$C_{cl} = \frac{LR \times M_C}{CRR} = \frac{(\$30.23 \times (10{,}800 lbs)}{379 lbs/hour} = \$861$$

Hence, the total costs for carbon replacement are calculated as follows using the values of CRF_c, C_c and C_{cl} calculated above:

$$CRC_c = CFR_c\left(1.08C_c + C_{cl}\right) = 0.2310\left[(1.08)(\$45{,}360) + \$861\right] = \$11{,}515$$

Utility Costs: Electricity includes the power for the system fan, bed drying/cooling fan, and the cooling water pump. Since the solvent pump motor is normally very small, its power consumption is negligible and may be neglected.

Electricity consumed by the system fan is calculated using Equation 1.32, the operating hours per year and the conversion factor from hp to kW:

$$kWh_{sf} = \frac{0.746\,kW}{hp} \times 2.50 \times 10^{-4} Q\,\Delta P_s\,\theta_S$$

where

$$\Delta P_s(inches\ \ water) = \Delta P_b + 1 = t_b\left(0.03679\ v_b + 1.107 \times 10^{-4} v_b^2\right) + 1$$

(The latter expression was derived from Equation 1.30, assuming that the carbon used in this example system is Calgon's "PCB," 4 x 10 mesh size.)

By assuming a carbon bed density, of 30 lb/ft^3, Equation 1.31 can be used to calculate the bed thickness (t_b):

$$Bed\ Thickness\ = t_b = \frac{0.0333\,M'_c}{A_b} = 1.8\,ft$$

Thus:

$$\Delta P_b = 1 + 1.80\left(0.03679 \times 75 + 1.107 \times 10^{-4} \times 75^2\right) = 7.09\ inches$$

And finally:

$$kWh_{sf} = 0.746\ \times\ 2.5 \times 10^{-4}\ \times\ 7.09 in. \times 10{,}000\ \ acfm\ \times 8{,}640\,h/yr\ = 114{,}200\,kWh/yr$$

Bed drying/cooling fan: During the drying/cooling cycle, the pressure drop through the bed also equals P_b. However, as Section 1.6.1.3 indicates, the flow and operating time are different. For the air flow, take the midpoint of the range (100 ft^3 air/lb carbon) and divide by 2 hours (the bed drying/cooling time), yielding: 100 ft^3/lb x 3,600 lbs x 1/120 min = 3,000 acfm. Substituting this into Equation 1.32 results in:

$$2.50 \times 10^{-4}\ \times\ 7.09\ inches\ \ \times 3{,}000\ \ acfm\ = 5.32\ \ hp$$

From Equation 1.33, we get:

$$\theta_{cf} = 0.4 \times 5h \times 2 \times \frac{8{,}640\,h}{12\,h} = 2{,}880\,h$$

Thus:

$$kWh_{cf} = \frac{0.746\,kW}{hp}\ \times\ 5.32\,hp\ \times\ 2{,}880\,h = 11{,}430\,kWh/yr$$

Cooling water pump: The cooling water pump horsepower is calculated from Equation 1.34. Here, let η = 63% and H = 100 ft. The cooling water flow (q_{cw}) is the quotient of the annual cooling water requirement and the annual pump operating time. From the data in Table 1.8, we obtain the cooling water requirement: 10,400,000 gal/yr. The pump annual operating time is obtained from Equation 1.33 (substituting 0.6 for 0.4), or θ_{cwp} = (0.6)(5 h)(2)(8,640)/12 = 4,320 h/yr.

Thus:

$$hp_{cwp} = \frac{\left(2.52\times 10^{-4}\right)\left(100\,ft\right)}{0.63}\times\frac{10{,}400{,}000\,gal\,/\,yr}{\frac{4{,}320\,h}{yr}\times 60\,\text{min}/\,hr} = 1.60\,hp$$

And:

$$kWh_{cwp} = 0.746\,kW\,/\,hp\times 1.60\,hp\times 4{,}320\,h\,/\,yr = 5{,}160\,kWh\,/\,yr$$

Summing the individual power consumptions, we get the value shown in Table 1.8: 131,000 kWh/yr.

Recovery Credit: In this example, we have included a credit for the recovery and re-sale of toluene. The quantity of toluene recovered is estimated from the toluene emission rate (100 lbs/hour), the number of operating hours (8,640 hours/year), and the control efficiency of the carbon adsorber (98%).

Equation 1.39 is used to calculate the recovery credit:

$$RC = m_{voc}\,\theta_s\,p_{voc}\,E = \left(\frac{100lbs}{hr}\right)(8640hrs)\left(\frac{\$0.33}{lb}\right)(0.98) = \$279{,}000$$

Hence, a recovery credit of \$279,000 can be taken for the recovery and re-sale of 423 tons of recovered toluene. Since all of the recovered toluene can be sold, no disposal costs will be incurred. Hence, for this example the $Disposal_{cost}$ equals zero.

Total Annual Cost: The sum of the direct annual costs, indirect annual costs and annual disposal costs, less the toluene recovery credit, yields a net total annual credit of \$60,400. Clearly, total annual cost is very sensitive to the amount and value of the recovered toluene. For instance, if the market price for toluene was \$0.15/lb, then the recovery credit would be \$127,000 and the total annual cost would be \$92,000. Thus, when incorporating recovery credits, it is imperative to select the value of the recovered product carefully.

Table 1.8: Estimated Annual Costs for the Carbon Adsorber

Cost Item	Factors	Unit Cost	Calculation	Estimated Cost
Direct Annual Costs (DAC)				
Operator Labor Costs:				
Operator	0.5 hours/shift	$27.48/hour[d]	0.5h/shift x 3 shifts/day x 360 days/yr x $27.48/hr	$14,839
Supervisor	15% of operator cost		0.15 x 14,839	$2,226
Operating Materials	—			
Maintenance Costs:				
Labor	0.5h/shift	$27.48/hour[d]	0.5h/shift x 3 shifts/day x 360 days/yr x $27.48/hr x 1.1	$16,323
Material	100% of maintenance labor			$16,323
Carbon Replacement (assuming a 5-year life):				
Labor[b]	CRF	$30.23/hour[d]	0.2310 x $30.23/hour x 10,800 lb/379lbs/hour	$199
Carbon[a,b]	CRF x 1.08	$4.20/lb	0.2310 x $4.20/lb x 10,800 x 1.08	$11,311
Utilities				
Electricity	—	$0.0676/kWh	$0.0676 /kWh x 130,835 kWh/yr	$8,838
Steam	—	$5.00/1,000 lbs	3.5 lb/lb VOC x $5/1000 lb x 100 lb VOC/hr x 8,640 hr/yr	$15,120
Cooling Water	—	$3.55/1,000 gallons[e]	3.43 gal/lb steam x [(3.5 x 100 x 8,640) lb steam x $3.55/1000 gal] / yr	$36,822
Total Direct Annual Cost (DAC)				$122,004
Indirect Annual Costs (IAC)				
Overhead	60% of sum of operating labor, maintenance labor, & maintenance materials		0.6 (14,839 + 2,226 + 16,323 + 16,323)	$29,828
Administrative charges	2% of TCI		0.02 ($445,000)	$10,560
Property tax	1% of TCI		0.01 ($445,000)	$5,280
Insurance	1% of TCI		0.01 ($445,000)	$5,280
Capital recovery[a,b]	CRF[TCI – (1.08Cc + Labor Cost for Carbon Replacement)]		0.0963 [445,000 – (1.08 x 45,360) + 861]	$46,069
Total Indirect Annual Cost (IAC)				$97,017
Recovery Credit for toluene				($279,418)
Total Annual Cost (TAC)[c]				($60,400)

[a] The 1.08 factor applied to the carbon replacement cost is for freight and sales taxes.

[b] The capital recovery cost factor, CRF, is a function of the carbon or equipment life and the opportunity cost of the capital (i.e., interest rate). The CRF is calculated using the following equation: $i(1+i)^n/((1+i)^n-1)$, where n is equipment life and i is the interest rate. For a 5-year carbon life and 5% interest rate, the CFR is 0.2310. For a 15 year equipment life (absorber vessel and auxiliary equipment) and a 5% interest rate, the CRF = 0.0963.

[c] Value shown has been rounded to three significant figures.

[d] Bureau of Labor Statistics, *May 2017 National Occupational Employment and Wage Estimates – United States,* May 2017 (http://www.bls.gov/oes/current/oes_nat.htm).

[e] Based on industrial water rates for users with greater than 15,000 gal monthly usage who purchase water from a municipality. Industrial users that have their own water source or supply with likely have lower water rates [27].

Annual Cost Effectiveness: The total amount of VOC removed can be calculated as follows:

$$VOC\ \mathrm{Re}\,moved\ /\ year\ = \frac{100\,\dfrac{lb}{hour} \times 0.98 \times \dfrac{8640\,hours}{year}}{2{,}000\,\dfrac{lb}{ton}} = 423\,\frac{tons}{year}$$

And the annual cost in terms of VOC removed, or cost effectiveness, is calculated using equation 1.41 and results in a credit of \$170/ton of toluene recovered:

$$Annual\ Cost\ Effectiveness = \frac{TAC}{VOC\ Removed} = \frac{(\$60{,}400)}{423\ tons} = (\$143)/ton$$

1.10 Acknowledgements

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- Carbtrol Corporation (Bridgeport, CT)

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EXHIBIT 5

METHOD 325A—VOLATILE ORGANIC COMPOUNDS FROM FUGITIVE AND AREA SOURCES:

Sampler Deployment and VOC Sample Collection

1.0 SCOPE AND APPLICATION

1.1 This method describes collection of volatile organic compounds (VOCs) at or inside a facility property boundary or from fugitive and area emission sources using passive (diffusive) tube samplers (PS). The concentration of airborne VOCs at or near these potential fugitive- or area-emission sources may be determined using this method in combination with Method 325B. Companion Method 325B (Sampler Preparation and Analysis) describes preparation of sampling tubes, shipment and storage of exposed sampling tubes, and analysis of sampling tubes collected using either this passive sampling procedure or alternative active (pumped) sampling methods.

1.2 This method may be used to determine the average concentration of the select VOCs using the corresponding uptake rates listed in Method 325B, Table 12.1. Additional compounds or alternative sorbents must be evaluated as described in Addendum A of Method 325B or by one of the following national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14), or reported in the peer-reviewed open literature.

1.3 Methods 325A and 325B are valid for the measurement of benzene. Supporting literature (References 1-8) indicates that benzene can be measured by flame ionization detection or mass spectrometry over a concentration range of approximately 0.5 micrograms per cubic meter ($\mu g/m^3$) to at least 500 $\mu g/m^3$ when industry standard (3.5 inch long × 0.25 inch outside diameter (o.d.) × 5 mm inner diameter (i.d.)) inert-coated stainless steel sorbent tubes packed with Carbograph^{TM} 1 TD, Carbopack^{TM} B, or Carbopack^{TM} X or equivalent are used and when samples are accumulated over a period of 14 days.

1.4 This method may be applied to screening average airborne VOC concentrations at facility property boundaries or monitoring perimeters over an extended period of time using multiple sampling periods (*e.g.*, 26 × 14-day sampling periods). The duration of each sampling period is normally 14 days.

1.5 This method requires the collection of local meteorological data (wind speed and direction, temperature, and barometric pressure). Although local meteorology is a component of this method, non-regulatory applications of this method may use regional meteorological data. Such applications risk that the results may not identify the precise source of the emissions.

2.0 SUMMARY OF THE METHOD

2.1 PRINCIPLE OF THE METHOD

The diffusive passive sampler collects VOC from air for a measured time period at a rate that is proportional to the concentration of vapor in the air at that location.

2.1.1 This method describes the deployment of prepared passive samplers, including determination of the number of passive samplers needed for each survey and placement of samplers along or inside the facility property boundary depending on the size and shape of the site or linear length of the boundary.

2.1.2 The rate of sampling is specific to each compound and depends on the diffusion constants of that VOC and the sampler dimensions/characteristics as determined by prior calibration in a standard atmosphere (Reference 1).

2.1.3 The gaseous VOC target compounds migrate through a constant diffusion barrier (*e.g.*, an air gap of fixed dimensions) at the sampling end of the diffusion sampling tube and adsorb onto the sorbent.

2.1.4 Heat and a flow of inert carrier gas are then used to extract (desorb) the retained VOCs back from the sampling end of the tube and transport/transfer them to a gas chromatograph (GC) equipped with a chromatographic column to separate the VOCs and a detector to determine the quantity of target VOCs.

2.1.5 Gaseous or liquid calibration standards loaded onto the sampling ends of clean sorbent tubes must be used to calibrate the analytical equipment.

2.1.6 This method requires the use of field blanks to ensure sample integrity associated with shipment, collection, and storage of the passive samples. It also requires the use of field duplicates to validate the sampling process.

2.1.7 At the end of each sampling period, the passive samples are collected, sealed, and shipped to a laboratory for analysis of target VOCs by thermal desorption gas chromatography, as described in Method 325B.

2.2 APPLICATION OF DIFFUSIVE SAMPLING

2.2.1 This method requires deployment of passive sampling tubes on a monitoring perimeter encompassing all known emission sources at a facility and collection of local meteorological data. It may be used to determine average concentration of VOC at a facility's "fenceline" using time integrated passive sampling (Reference 2).

2.2.2 Collecting samples and meteorological data at progressively higher frequencies may be employed to resolve shorter term concentration fluctuations and wind conditions that could introduce interfering emissions from other sources.

2.2.3 This passive sampling method provides a low cost approach to screening of fugitive or area emissions compared to active sampling methods that are based on pumped sorbent tubes or time weighted average canister sampling.

2.2.3.1 Additional passive sampling tubes may be deployed at different distances from the facility property boundary or from the geometric center of the fugitive emission source.

2.2.3.2 Additional meteorological measurements may also be collected as needed to perform preliminary gradient-based assessment of the extent of the pollution plume at ground level and the effect of "background" sources contributing to airborne VOC concentrations at the location.

2.2.4 Time-resolved concentration measurements coupled with time-resolved meteorological monitoring may be used to generate data needed for source apportionment procedures and mass flux calculations.

3.0 DEFINITIONS (See also Section 3.0 of Method 325B.)

3.1 *Fenceline* means the property boundary of a facility or internal monitoring perimeter established in accordance with the requirements in Section 8.2 of this method.

3.2 *Passive sampler (PS)* means a specific type of sorbent tube (defined in this method) that has a fixed dimension air (diffusion) gap at the sampling end and is sealed at the other end.

3.3 *Passive sampling* refers to the activity of quantitatively collecting VOC on sorbent tubes using the process of diffusion.

3.4 PS_i is the annual average for all PS concentration results from location *i*.

3.5 PS_{i3} is the set of annual average concentration results for PS_i and two sorbent tubes nearest to the PS location *i*.

3.6 PS_{ip} is the concentration from the sorbent tube at location *i* for the test period or episode p.

3.7 *Sampling period* is the length of time each passive sampler is exposed during field monitoring. The sampling period for this method is 14 days.

3.8 *Sorbent tube* (Also referred to as tube, PS tube, adsorbent tube, and sampling tube) is an inert coated stainless steel tube. Standard PS tube dimensions for this method are 3.5-inch (89 mm) long × 0.25-inch (6.4 mm) o.d. with an i.d. of 5 mm, a cross-sectional area of 19.6 mm^2 and an air gap of 15 mm. The central portion of the tube is packed with solid adsorbent material contained between 2 × 100-mesh stainless steel gauzes and terminated with a diffusion cap at the sampling end of the tube. These axial passive samplers are installed under a protective hood during field deployment.

NOTE: Glass and glass- (or fused silica-) lined stainless steel sorbent tubes (typically 4 mm i.d.) are also available in various lengths to suit different makes of thermal desorption equipment, but these are rarely used for passive sampling because it is more difficult to adequately define the diffusive air gap in glass or glass-line tubing. Such tubes are not recommended for this method.

4.0 SAMPLING INTERFERENCES

4.1 GENERAL INTERFERENCES

Passive tube samplers should be sited at a distance beyond the influence of possible obstructions such as trees, walls, or buildings at the monitoring site. Complex topography and physical site obstructions, such as bodies of water, hills, buildings, and other structures that may prevent access to a planned PS location must be taken into consideration. You must document and report siting interference with the results of this method.

4.2 BACKGROUND INTERFERENCE

Nearby or upwind sources of target emissions outside the facility being tested can contribute to background concentrations. Moreover, because passive samplers measure continuously, changes in wind direction can cause variation in the level of background concentrations from interfering sources during the monitoring period. This is why local meteorological information, particularly wind direction and speed, is required to be collected throughout the monitoring period. Interfering sources can include neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, and nearby highways or roads. As PS data are evaluated, the location of potential interferences with respect to PS locations and local wind conditions should be considered, especially when high PS concentration values are observed.

4.3 TUBE HANDLING

You must protect the PS tubes from gross external contamination during field sampling. Analytical thermal desorption equipment used to analyze PS tubes must desorb organic compounds from the interior of PS tubes and exclude contamination from external sampler surfaces in the analytical/sample flow path. If the analytical equipment does not comply with this requirement, you must wear clean, white, cotton or powder-free nitrile gloves to handle sampling tubes to prevent contamination of the external sampler surfaces. Sampling tubes must be capped with two-piece, brass, 0.25 inch, long-term storage caps fitted with combined polytetrafluoroethylene ferrules (see Section 6.1 and Method 325B) to prevent ingress of airborne contaminants outside the sampling period. When not being used for field monitoring, the capped tubes must be stored in a clean, air-tight, shipping container to prevent the collection of VOCs (see Section 6.4.2 of Method 325B).

4.4 LOCAL WEATHER CONDITIONS AND AIRBORNE PARTICULATES

Although air speeds are a constraint for many forms of passive samplers, axial tube PS devices have such a slow inherent uptake rate that they are largely immune to these effects (References 4,5). Passive samplers must nevertheless be deployed under non-emitting weatherproof hoods to moderate the effect of local weather conditions such as solar heating and rain. The cover must not impede the ingress of ambient air. Sampling tubes should also be orientated vertically and pointing downwards, to minimize accumulation of particulates.

4.5 TEMPERATURE

The normal working range for field sampling for sorbent packing is 0-40 °C (References 6,7). Note that most published passive uptake rate data for sorbent tubes is quoted at 20 °C. Note also that, as a rough guide, an increase in temperature of 10 °C will reduce the collection capacity for a given analyte on a given sorbent packing by a factor of 2, but the uptake rate will not change significantly (Reference 4).

5.0 SAFETY

This method does not purport to include all safety issues or procedures needed when deploying or collecting passive sampling tubes. Precautions typical of field air sampling projects are required. Tripping, falling, electrical, and weather safety considerations must all be included in plans to deploy and collect passive sampling tubes.

6.0 SAMPLING EQUIPMENT AND SUPPLIES, AND PRE-DEPLOYMENT PLANNING

This section describes the equipment and supplies needed to deploy passive sampling monitoring equipment at a facility property boundary. Details of the passive sampling tubes themselves and equipment required for subsequent analysis are described in Method 325B.

6.1 PASSIVE SAMPLING TUBES

The industry standard PS tubes used in this method must meet the specific configuration and preparation requirements described in Section 3.0 of this method and Section 6.1 of Method 325B.

NOTE: The use of PS tubes packed with various sorbent materials for monitoring a wide variety of organic compounds in ambient air has been documented in the literature (References 4-10). Other sorbents may be used in standard passive sampling tubes for monitoring additional target compound(s) once their uptake rate and performance has been demonstrated following procedures in Addendum A to Method 325B. Guidance on sorbent selection can also be obtained from relevant national and international standard methods such as ASTM D6196-03 (Reapproved 2009) (Reference 14) and ISO 16017-2:2003(E) (Reference 13) (both incorporated by reference—see §63.14).

6.2 PASSIVE OR DIFFUSIVE SAMPLING CAP

One diffusive sampling cap is required per PS tube. The cap fits onto the sampling end of the tube during air monitoring. The other end of the tube remains sealed with the long-term storage cap. Each diffusive sampling cap is fitted with a stainless steel gauze, which defines the outer limit of the diffusion air gap.

6.3 SORBENT TUBE PROTECTION COVER

A simple weatherproof hood, suitable for protecting passive sampling tubes from the worst of the weather (see Section 4.4) consists of an inverted cone/funnel constructed of an inert, non-outgassing material that fits over the diffusive tube, with the open (sampling) end of the tube projecting just below the cone opening. An example is shown in Figure 6.1 (Adapted from Reference 13).

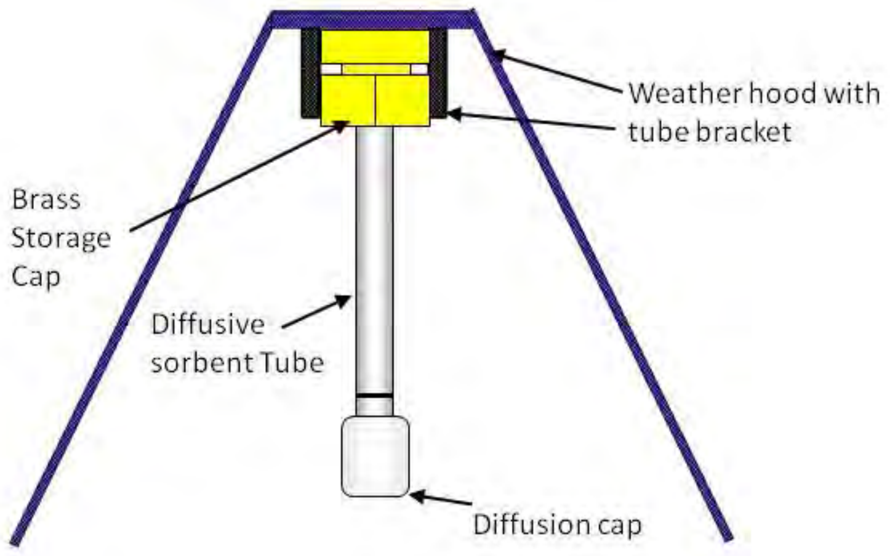


Figure 6.1. PS Tube with Weather Protector

6.4 THERMAL DESORPTION APPARATUS

If the analytical thermal desorber that will subsequently be used to analyze the passive sampling tubes does not meet the requirement to exclude outer surface contaminants from the sample flow path (see Section 6.6 of Method 325B), then clean, white, cotton or powder-free nitrile gloves must be used for handling the passive sampling tubes during field deployment.

6.5 SORBENT SELECTION

Sorbent tube configurations, sorbents or other VOC not listed in this method must be evaluated according to Method 325B, Addendum A or ISO 16017-2:2003(E) (Reference 13) (incorporated by reference—see §63.14). The supporting evaluation and verification data described in Method 325B, Addendum A for configurations or compounds different from the ones described in this method must meet the performance requirements of Method 325A/B and must be submitted with the test plan for your measurement program.

7.0 REAGENTS AND STANDARDS

No reagents or standards are needed for the field deployment and collection of passive sampling tubes. Specifications for sorbents, gas and liquid phase standards, preloaded standard tubes, and carrier gases are covered in Section 7 of Method 325B.

8.0 SAMPLE DEPLOYMENT, RECOVERY, AND STORAGE

Pre-deployment and planning steps are required before field deployment of passive sampling tubes. These activities include but are not limited to conducting a site visit, determining suitable and required monitoring locations, and determining the monitoring frequency to be used.

8.1 CONDUCTING THE SITE VISIT

8.1.1 Determine the size and shape of the facility footprint in order to determine the required number of monitoring locations.

8.1.2 Identify obstacles or obstructions (buildings, roads, fences), hills and other terrain issues (*e.g.,* bodies of water or swamp land) that could interfere with air parcel flow to the sampler or that prevent reasonable access to the location. You may use the general guidance in Section 4.1 of this method during the site visit to identify sampling locations. You must evaluate the placement of each passive sampler to determine if the conditions in this section are met.

8.1.3 Identify to the extent possible and record potential off-site source interferences (*e.g.,* neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, nearby highways).

8.1.4 Identify the closest available meteorological station. Identify potential locations for one or more on-site or near-site meteorological station(s) following the guidance in EPA-454/B-08-002 (Reference 11) (incorporated by reference—see §63.14).

8.2 DETERMINING SAMPLING LOCATIONS (REFERENCES 2, 3)

8.2.1 The number and placement of the passive samplers depends on the size, the shape of the facility footprint or the linear distance around the facility, and the proximity of emission sources near the property boundaries. Aerial photographs or site maps may be used to determine the size (acreage) and shape of the facility or the length of the monitoring perimeter. Place passive samplers on an internal monitoring perimeter on or inside the facility boundary encompassing all emission sources at the facility at different angles circling the geometric center of the facility or at different distances based on the monitoring perimeter length of the facility.

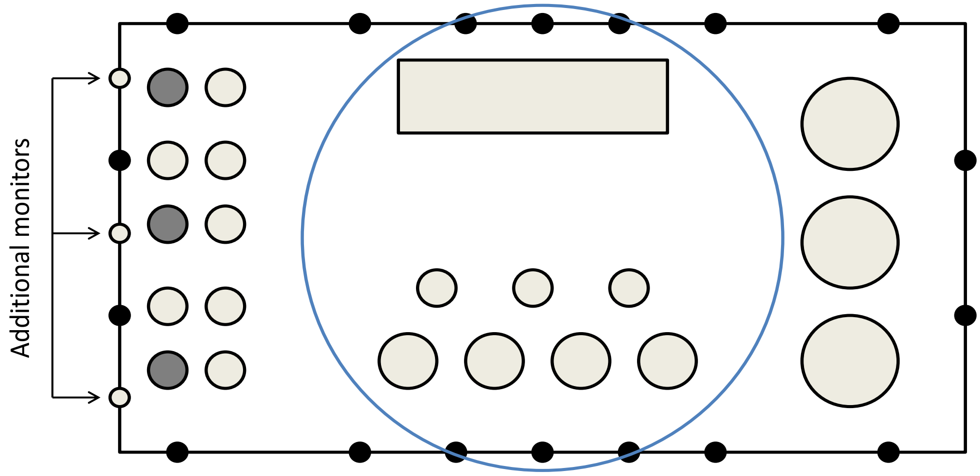
NOTE: In some instances, permanent air monitoring stations may already be located in close proximity to the facility. These stations may be operated and maintained by the site, or local or state regulatory agencies. If access to the station is possible, a PS may be deployed adjacent to other air monitoring instrumentation. A comparison of the pollutant concentrations measured with the PS to concentrations measured by site instrumentation may be used as an optional data quality indicator to assess the accuracy of PS results.

8.2.1.1 The monitoring perimeter may be located between the property boundary and any potential emission source near the property boundary, as long as the distance from the source to the monitoring perimeter is at least 50 meters (162 feet). If a potential emissions source is within

50 meters (162 feet) of the property boundary, the property boundary shall be used as the monitoring perimeter near that source.

8.2.1.2 Samplers need only be placed around the monitoring perimeter and not along internal roads or other right of ways that may bisect the facility.

8.2.1.3 An extra sampler must be placed near known sources of VOCs if potential emission sources are within 50 meters (162 feet) of the boundary and the source or sources are located between two monitors. Measure the distance (x) between the two monitors and place another monitor approximately halfway between (x/2 ±10 percent) the two monitors. Only one extra sampler is required between two monitors to account for known sources of VOCs. For example, in Figure 8.1, the facility added three additional monitors (*i.e.*, light shaded sampler locations), and in Figure 8.2, the facility added two additional monitors to provide sufficient coverage of all area sources.



Refinery (20% Angle)

Note: Shaded sources are within 50 meters of the property boundary and are located between two monitors. Additional coverage required by this method was accomplished by placing the monitors halfway between two existing monitors.

Figure 8.1. Facility with a Regular Shape Between 750 and 1,500 Acres in Area

8.2.2 Option 1 for Determining Sampling Locations.

8.2.2.1 For facilities with a regular (circular, triangular, rectangular, or square) shape, determine the geographic center of the facility.

8.2.2.1.1 For facilities with an area of less than or equal to 750 acres, measure angles of 30 degrees from the center point for a total of twelve 30 degree measurements evenly spaced (±1 degree).

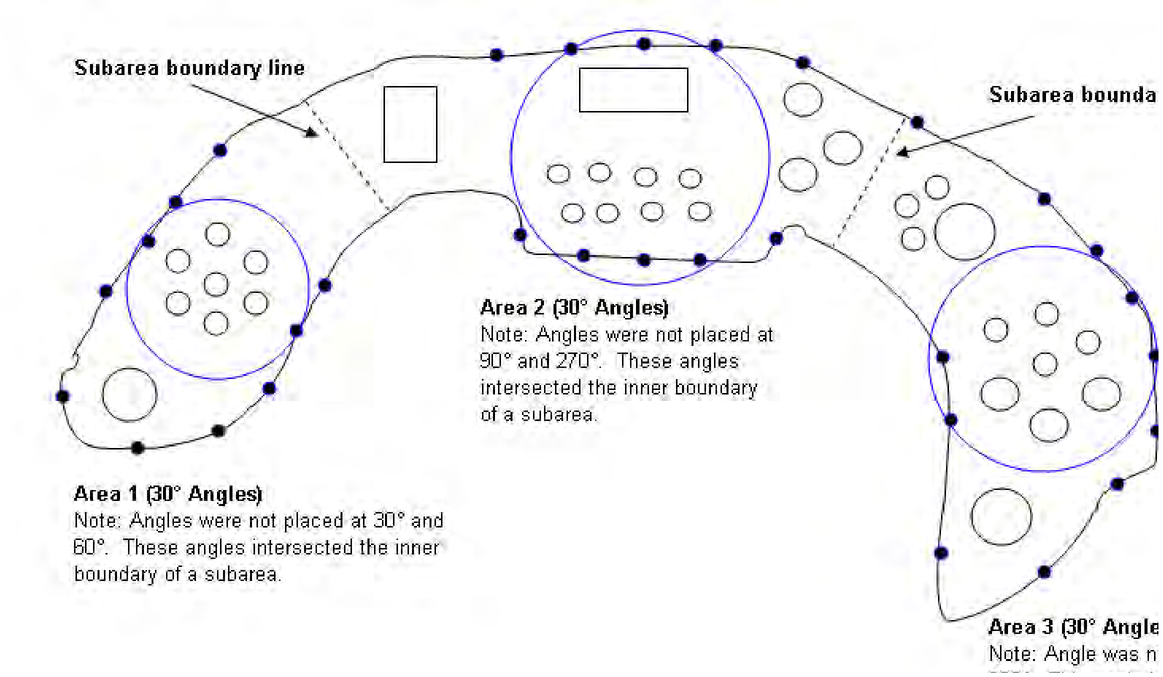
8.2.2.1.2 For facilities covering an area greater than 750 acres but less than or equal to 1,500 acres, measure angles of 20 degrees from the center point for a total of eighteen 20 degree measurements evenly spaced (±1 degree). Figure 8.1 shows the monitor placement around the property boundary of a facility with an area between 750 and 1,500 acres. Monitor placements are represented with black dots along the property boundary.

8.2.2.1.3 For facilities covering an area greater than 1,500 acres, measure angles of 15 degrees from the center point for a total of twenty-four 15 degree measurements evenly spaced (±1 degree).

8.2.2.1.4 Locate each sampling point where the measured angle intersects the outer monitoring perimeter.

8.2.2.2 For irregularly shaped facilities, divide the area into a set of connecting subarea circles, triangles or rectangles to determine sampling locations. The subareas must be defined such that a circle can reasonably encompass the subarea. Then determine the geometric center point of each of the subareas.

8.2.2.2.1 If a subarea is less than or equal to 750 acres (*e.g.,* Figure 8.3), measure angles of 30 degrees from the center point for a total of twelve 30 degree measurements (±1 degree).



Area 2 (30° Angles)
Note: Angles were not placed at 90° and 270°. These angles intersected the inner boundary of a subarea.

Area 1 (30° Angles)
Note: Angles were not placed at 30° and 60°. These angles intersected the inner boundary of a subarea.

Area 3 (30° Angle
Note: Angle was n

Figure 8.3. Facility Divided into Three Subareas

8.2.2.2.2 If a subarea is greater than 750 acres but less than or equal to 1,500 acres (*e.g.,* Figure 8.4), measure angles of 20 degrees from the center point for a total of eighteen 20 degree measurements (±1 degree).

8.2.2.2.3 If a subarea is greater than 1,500 acres, measure angles of 15 degrees from the center for a total of twenty-four 15 degree measurements (±1 degree).

8.2.2.2.4 Locate each sampling point where the measured angle intersects the outer monitoring perimeter. Sampling points need not be placed closer than 152 meters (500 feet) apart (or 76 meters (250 feet) if known sources are within 50 meters (162 feet) of the monitoring perimeter), as long as a minimum of 3 monitoring locations are used for each subarea.

8.2.2.2.5 Sampling sites are not needed at the intersection of an inner boundary with an adjacent subarea. The sampling location must be sited where the measured angle intersects the subarea's outer monitoring perimeter.

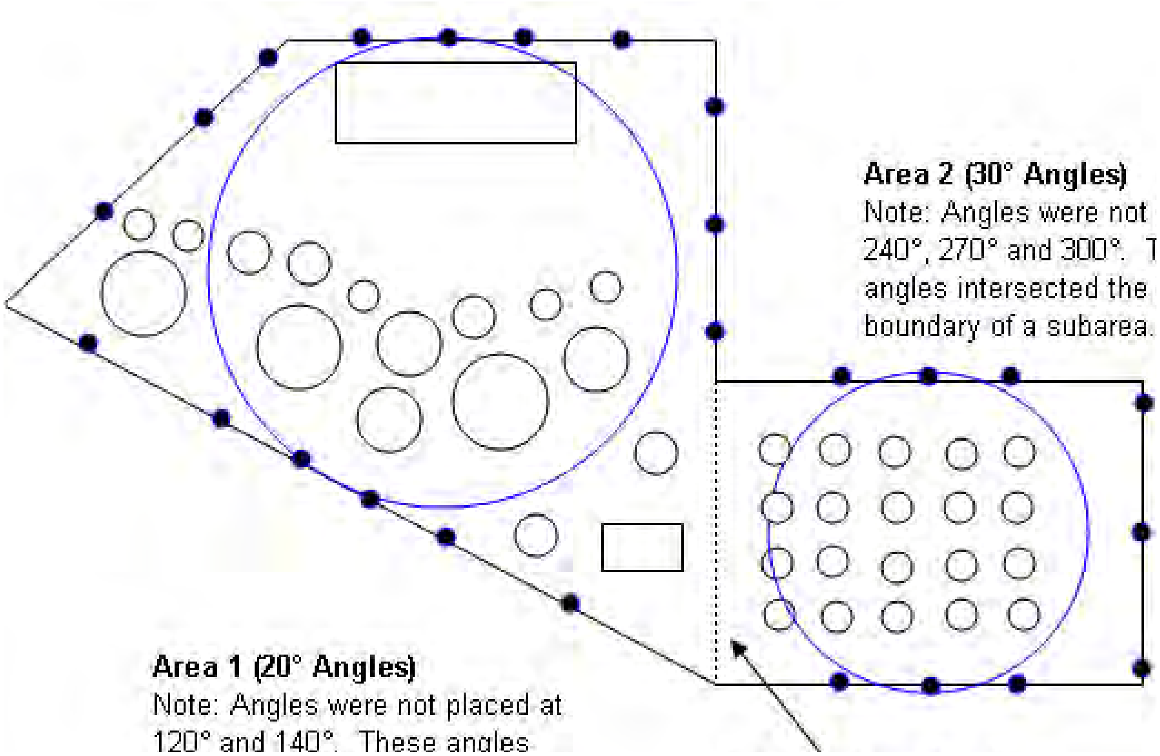


Figure 8.4. Facility Divided into Two Subareas

8.2.3 Option 2 for Determining Sampling Locations.

8.2.3.1 For facilities with a monitoring perimeter length of less than 7,315 meters (24,000 feet), a minimum of twelve sampling locations evenly spaced ±10 percent of the location interval is required.

8.2.3.2 For facilities with a monitoring perimeter length greater than or equal to 7,315 meters (24,000 feet), sampling locations are spaced 610 ± 76 meters (2,000 ± 250 feet) apart.

8.2.3.3 Unless otherwise specified in an applicable regulation, permit or other requirement, for small disconnected subareas with known sources within 50 meters (162 feet) of the monitoring perimeter, sampling points need not be placed closer than 152 meters (500 feet) apart as long as a minimum of 3 monitoring locations are used for each subarea.

8.3 SITING A METEOROLOGICAL STATION

A meteorological station is required at or near the facility you are monitoring. A number of commercially available meteorological stations can be used. Information on meteorological instruments can be found in EPA-454/R-99-005 (Reference 11) (incorporated by reference—see §63.14). Some important considerations for siting of meteorological stations are detailed below.

8.3.1 Place meteorological stations in locations that represent conditions affecting the transport and dispersion of pollutants in the area of interest. Complex terrain may require the use of more than one meteorological station.

8.3.2 Deploy wind instruments over level, open terrain at a height of 10 meters (33 feet). If possible, locate wind instruments at a distance away from nearby structures that is equal to at least 10 times the height of the structure.

8.3.3 Protect meteorological instruments from thermal radiation and adequately ventilate them using aspirated shields. The temperature sensor must be located at a distance away from any nearby structures that is equal to at least four times the height of the structure. Temperature sensors must be located at least 30 meters (98 feet) from large paved areas.

8.3.4 Collect and record meteorological data, including wind speed, wind direction, temperature and barometric pressure on an hourly basis. Calculate average unit vector wind direction, sigma theta, temperature and barometric pressure per sampling period to enable calculation of concentrations at standard conditions. Supply this information to the laboratory.

8.3.5 Identify and record the location of the meteorological station by its GPS coordinate.

8.4 MONITORING FREQUENCY

8.4.1 Sample collection may be performed for periods up to 14 days.

8.4.2 A site screening protocol that meets method requirements may be performed by collecting samples for a year where each PS accumulates VOC for a 14-day sampling period. Study results are accumulated for the sampling periods (typically 26) over the course of one calendar year. To the extent practical, sampling tubes should be changed at approximately the same time of day at each of the monitoring sites.

8.4.3 When extenuating circumstances do not permit safe deployment or retrieval of passive samplers (*e.g.,*extreme weather, power failure), sampler placement or retrieval earlier or later than the prescribed schedule is allowed but must occur as soon as safe access to sampling sites is possible.

8.5 PASSIVE SAMPLER DEPLOYMENT

8.5.1 Clean (conditioned) sorbent tubes must be prepared and packaged by the laboratory as described in Method 325B and must be deployed for sampling within 30 days of conditioning.

8.5.2 Allow the tubes to equilibrate with ambient temperature (approximately 30 minutes to 1 hour) at the monitoring location before removing them from their storage/shipping container for sample collection.

8.5.3 If there is any risk that the analytical equipment will not meet the requirement to exclude contamination on outer tube surfaces from the sample flow path (see Section 6.6 of Method 325B), sample handlers must wear clean, white, cotton or powder-free nitrile gloves during PS deployment and collection and throughout any other tube handling operations.

8.5.4 Inspect the sampling tubes immediately prior to deployment. Ensure that they are intact, securely capped, and in good condition. Any suspect tubes (*e.g.*, tubes that appear to have leaked sorbent) should be removed from the sampling set.

8.5.5 Secure passive samplers so the bottom of the diffusive sampling cap is 1.5 to 3 meters (4.9 to 9.8 feet) above ground using a pole or other secure structure at each sampling location. Orient the PS vertically and with the sampling end pointing downward to avoid ingress of particulates.

NOTE: Duplicate sampling assemblies must be deployed in at least one monitoring location for every 10 monitoring locations during each field monitoring period.

8.5.6 Protect the PS from rain and excessive wind velocity by placing them under the type of protective hood described in Section 6.1.3 or equivalent.

8.5.7 Remove the storage cap on the sampling end of the tube and replace it with a diffusive sampling cap at the start of the sampling period. Make sure the diffusion cap is properly seated and store the removed storage caps in the empty tube shipping container.

8.5.8 Record the start time and location details for each sampler on the field sample data sheet (see example in Section 17.0.).

8.5.9 Expose the sampling tubes for the required sampling period-normally 14-days.

8.5.10 Field blank tubes (see Section 9.3 of Method 325B) are stored outside the shipping container at representative sampling locations around the site, but with both long-term storage caps kept in place throughout the monitoring exercise. Collect at least two field blanks sorbent samples per sampling period to ensure sample integrity associated with shipment, collection, and storage.

8.6 SORBENT TUBE RECOVERY AND METEOROLOGICAL DATA COLLECTION

Recover deployed sampling tubes and field blanks as follows:

8.6.1 After the sampling period is complete, immediately replace the diffusion end cap on each sampled tube with a long-term storage end cap. Tighten the seal securely by hand and then tighten an additional quarter turn with an appropriate tool. Record the stop date and time and any additional relevant information on the sample data sheet.

8.6.2 Place the sampled tubes, together with the field blanks, in the storage/shipping container. Label the storage container, but do not use paints, markers, or adhesive labels to identify the tubes. TD-compatible electronic (radio frequency identification (RFID)) tube labels are available commercially and are compatible with some brands of thermal desorber. If used, these may be programmed with relevant tube and sample information, which can be read and automatically transcribed into the sequence report by the TD system.

NOTE: Sampled tubes must not be placed in the same shipping container as clean conditioned sampling tubes.

8.6.3 Sampled tubes may be shipped at ambient temperature to a laboratory for sample analysis.

8.6.4 Specify whether the tubes are field blanks or were used for sampling and document relevant information for each tube using a Chain of Custody form (see example in Section 17.0) that accompanies the samples from preparation of the tubes through receipt for analysis, including the following information: Unique tube identification numbers for each sampled tube; the date, time, and location code for each PS placement; the date, time, and location code for each PS recovery; the GPS reference for each sampling location; the unique identification number of the duplicate sample (if applicable); and problems or anomalies encountered.

8.6.5 If the sorbent tubes are supplied with electronic (*e.g.,* RFID) tags, it is also possible to allocate a sample identifier to each PS tube. In this case, the recommended format for the identification number of each sampled tube is AA-BB-CC-DD-VOC, where:

AA = Sequence number of placement on route (01, 02, 03 . . .)

BB = Sampling location code (01, 02, 03 . . .)

CC = 14-day sample period number (01 to 26)

DD = Sample code (SA = sample, DU = duplicate, FB = field blank)

VOC = 3-letter code for target compound(s) (*e.g.,* BNZ for benzene or BTX for benzene, toluene, and xylenes)

NOTE: Sampling start and end times/dates can also be logged using RFID tube tags.

9.0 QUALITY CONTROL

9.1 Most quality control checks are carried out by the laboratory and associated requirements are in Section 9.0 of Method 325B, including requirements for laboratory blanks, field blanks, and duplicate samples.

9.2 Evaluate for potential outliers the laboratory results for neighboring sampling tubes collected over the same time period. A potential outlier is a result for which one or more PS tube does not agree with the trend in results shown by neighboring PS tubes—particularly when data from those locations have been more consistent during previous sampling periods. Accidental contamination by the sample handler must be documented before any result can be eliminated as an outlier. Rare but possible examples of contamination include loose or missing storage caps or contaminated storage/shipping containers. Review data from the same and neighboring monitoring locations for the subsequent sampling periods. If the anomalous result is not repeated for that monitoring location, the episode can be ascribed to transient contamination and the data in question must be flagged for potential elimination from the dataset.

9.3 DUPLICATES AND FIELD BLANKS

9.3.1 Collect at least one co-located/duplicate sample for every 10 field samples to determine precision of the measurements.

9.3.2 Collect at least two field blanks sorbent samples per sampling period to ensure sample integrity associated with shipment, collection, and storage. You must use the entire sampling apparatus for field blanks including unopened sorbent tubes mounted in protective sampling hoods. The tube closures must not be removed. Field blanks must be placed in two different quadrants (*e.g.,* 90° and 270°) and remain at the sampling location for the sampling period.

10.0 CALIBRATION AND STANDARDIZATION

Follow the calibration and standardization procedures for meteorological measurements in EPA-454/B-08-002 March 2008 (Reference 11) (incorporated by reference—see §63.14). Refer to Method 325B for calibration and standardization procedures for analysis of the passive sampling tubes.

11.0 ANALYTICAL PROCEDURES

Refer to Method 325B, which provides details for the preparation and analysis of sampled passive monitoring tubes (preparation of sampling tubes, shipment and storage of exposed sampling tubes, and analysis of sampling tubes).

12.0 DATA ANALYSIS, CALCULATIONS AND DOCUMENTATION

12.1 CALCULATE ANNUAL AVERAGE FENCELINE CONCENTRATION.

After a year's worth of sampling at the facility fenceline (for example, 26 14-day samples), the average (PS_i) may be calculated for any specified period at each PS location using Equation 12.1.

$$PS_i = \frac{\sum PS_{ip}}{N} \qquad \text{Eq. 12.1}$$

Where:

PS_i = Annual average for location *i.*

PS_{ip} = Sampling period specific concentration from Method 325B.

i = Location of passive sampler (0 to 360°).

p = The sampling period.

N = The number of sampling periods in the year (*e.g.,* for 14-day sampling periods, from 1 to 26).

NOTE: PS_{ip} is a function of sampling location-specific factors such as the contribution from facility sources, unusual localized meteorological conditions, contribution from nearby interfering sources, the background caused by integrated far-field sources and measurement error due to deployment, handling, siting, or analytical errors.

12.2 IDENTIFY SAMPLING LOCATIONS OF INTEREST

If data from neighboring sampling locations are significantly different, then you may add extra sampling points to isolate background contributions or identify facility-specific "hot spots."

12.3 EVALUATE TRENDS

You may evaluate trends and patterns in the PS data over multiple sampling periods to determine if elevated concentrations of target compounds are due to operations on the facility or if contributions from background sources are significant.

12.3.1 Obtain meteorological data including wind speed and wind direction or unit vector wind data from the on-site meteorological station. Use this meteorological data to determine the prevailing wind direction and speed during the periods of elevated concentrations.

12.3.2 As an option you may perform preliminary back trajectory calculations (*http://ready.arl.noaa.gov/HYSPLIT.php*) to aid in identifying the source of the background contribution to elevated target compound concentrations.

12.3.3 Information on published or documented events on- and off-site may also be included in the associated sampling period report to explain elevated concentrations if relevant. For example, you would describe if there was a chemical spill on site, or an accident on an adjacent road.

12.3.4 Additional monitoring for shorter periods (See section 8.4) may be necessary to allow better discrimination/resolution of contributing emission sources if the measured trends and associated meteorology do not provide a clear assessment of facility contribution to the measured fenceline concentration.

12.3.5 Additional records necessary to calculate sampling period average target compound concentration can be found in Section 12.1 of Method 325B.

13.0 METHOD PERFORMANCE

Method performance requirements are described in Method 325B.

14.0 POLLUTION PREVENTION

[Reserved]

15.0 WASTE MANAGEMENT

[Reserved]

16.0 REFERENCES

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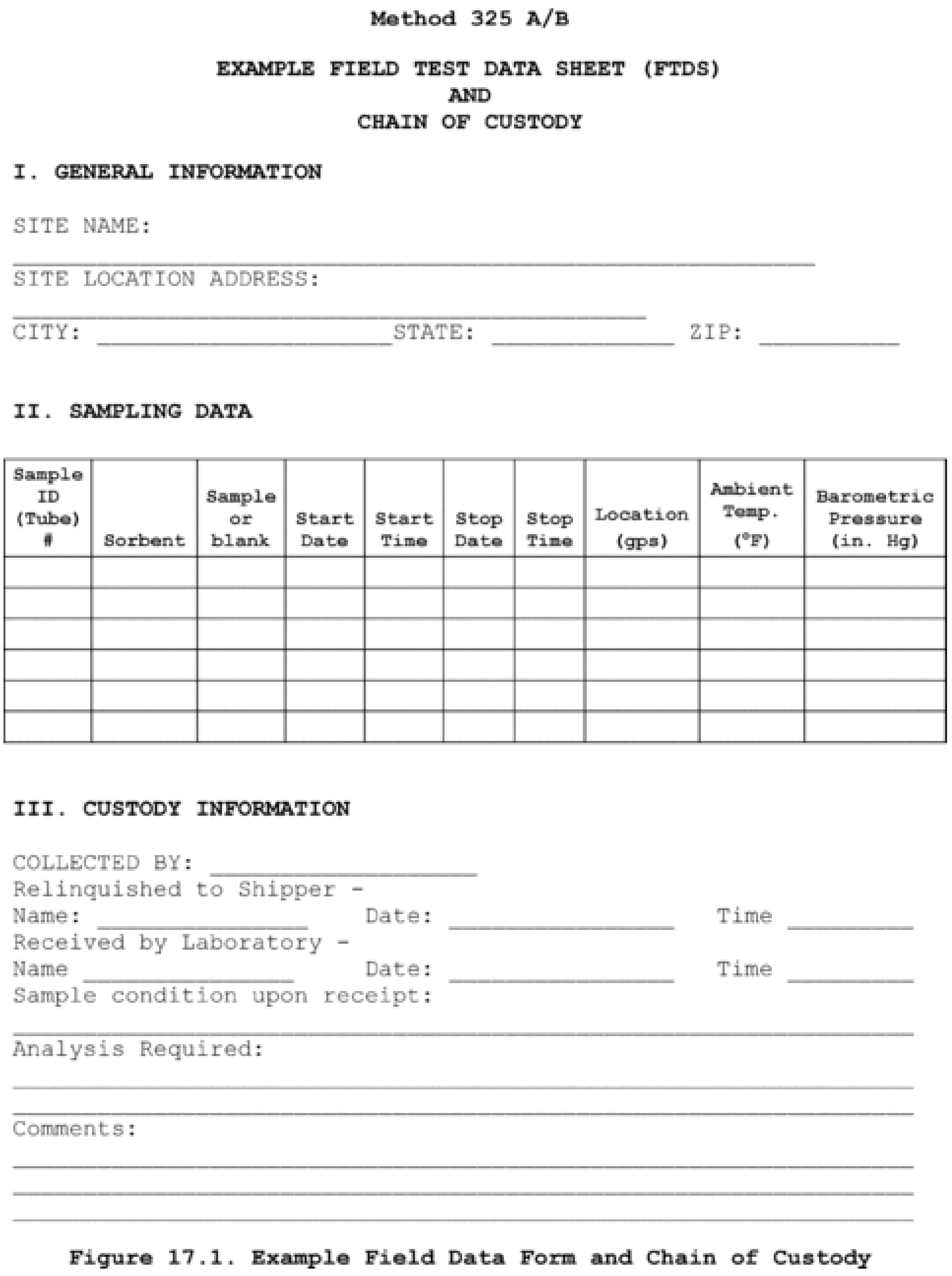
12. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume IV: Meteorological Measurements Version 2.0 Final, EPA-454/B-08-002 March 2008. Available at *http://www.epa.gov/ttnamti1/files/ambient/met/Volume%20IV_Meteorological_Measurements.pdf*.

13. ISO 16017-2:2003(E), Indoor, ambient and workplace air—Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Part 2: Diffusive sampling.

14. ASTM D6196-03 (Reapproved 2009): Standard practice for selection of sorbents, sampling, and thermal desorption analysis procedures for volatile organic compounds in air.

17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA



Method 325 A/B

EXAMPLE FIELD TEST DATA SHEET (FTDS)
AND
CHAIN OF CUSTODY

I. GENERAL INFORMATION

SITE NAME:
____
SITE LOCATION ADDRESS:
____
CITY: ____________________STATE: ____________ ZIP: _________

II. SAMPLING DATA

Sample ID (Tube) #	Sorbent	Sample or blank	Start Date	Start Time	Stop Date	Stop Time	Location (gps)	Ambient Temp. (°F)	Barometric Pressure (in. Hg)

III. CUSTODY INFORMATION

COLLECTED BY: __________________
Relinquished to Shipper -
Name: _______________ Date: ________________ Time _________
Received by Laboratory -
Name _______________ Date: ________________ Time _________
Sample condition upon receipt:
____
Analysis Required:
____
____
Comments:
____
____
____

Figure 17.1. Example Field Data Form and Chain of Custody

EXHIBIT 6

METHOD 325B—VOLATILE ORGANIC COMPOUNDS FROM FUGITIVE AND AREA SOURCES:

SAMPLER PREPARATION AND ANALYSIS

1.0 SCOPE AND APPLICATION

1.1 This method describes thermal desorption/gas chromatography (TD/GC) analysis of volatile organic compounds (VOCs) from fugitive and area emission sources collected onto sorbent tubes using passive sampling. It could also be applied to the TD/GC analysis of VOCs collected using active (pumped) sampling onto sorbent tubes. The concentration of airborne VOCs at or near potential fugitive- or area-emission sources may be determined using this method in combination with Method 325A. Companion Method 325A (Sampler Deployment and VOC Sample Collection) describes procedures for deploying the sorbent tubes and passively collecting VOCs.

1.2 The preferred GC detector for this method is a mass spectrometer (MS), but flame ionization detectors (FID) may also be used. Other conventional GC detectors such as electron capture (ECD), photoionization (PID), or flame photometric (FPD) may also be used if they are selective and sensitive to the target compound(s) and if they meet the method performance criteria provided in this method.

1.3 There are 97 VOCs listed as hazardous air pollutants in Title III of the Clean Air Act Amendments of 1990. Many of these VOC are candidate compounds for this method. Compounds with known uptake rates for Carbograph^{TM} 1 TD, Carbopack^{TM} B, or Carbopack^{TM} X are listed in Table 12.1. This method provides performance criteria to demonstrate acceptable performance of the method (or modifications of the method) for monitoring one or more of the compounds listed Table 12.1. If standard passive sampling tubes are packed with other sorbents or used for other analytes than those listed in Table 12.1, then method performance and relevant uptake rates should be verified according to Addendum A to this method or by one of the following national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14), or reported in the peer-reviewed open literature.

1.4 The analytical approach using TD/GC/MS is based on previously published EPA guidance in Compendium Method TO-17 (*http://www.epa.gov/ttnamti1/airtox.html#compendium*) (Reference 1), which describes active (pumped) sampling of VOCs from ambient air onto tubes packed with thermally stable adsorbents.

1.5 Inorganic gases not suitable for analysis by this method include oxides of carbon, nitrogen and sulfur, ozone (O_3), and other diatomic permanent gases. Other pollutants not suitable for this analysis method include particulate pollutants, (*i.e.*, fumes, aerosols, and dusts), compounds too labile (reactive) for conventional GC analysis, and VOCs that are more volatile than propane.

2.0 SUMMARY OF METHOD

2.1 This method provides procedures for the preparation, conditioning, blanking, and shipping of sorbent tubes prior to sample collection.

2.2 Laboratory and field personnel must have experience of sampling trace-level VOCs using sorbent tubes (References 2,5) and must have experience operating thermal desorption/GC/multi-detector instrumentation.

2.3 Key steps of this method as implemented for each sample tube include: Stringent leak testing under stop flow, recording ambient temperature conditions, adding internal standards, purging the tube, thermally desorbing the sampling tube, refocusing on a focusing trap, desorbing and transferring/injecting the VOCs from the secondary trap into the capillary GC column for separation and analysis.

2.4 Water management steps incorporated into this method include: (a) Selection of hydrophobic sorbents in the sampling tube; (b) optional dry purging of sample tubes prior to analysis; and (c) additional selective elimination of water during primary (tube) desorption (if required) by selecting trapping sorbents and temperatures such that target compounds are quantitatively retained while water is purged to vent.

3.0 DEFINITIONS

(See also Section 3.0 of Method 325A).

3.1 Blanking is the desorption and confirmatory analysis of conditioned sorbent tubes before they are sent for field sampling.

3.2 *Breakthrough volume and associated relation to passive sampling.* Breakthrough volumes, as applied to active sorbent tube sampling, equate to the volume of air containing a constant concentration of analyte that may be passed through a sorbent tube at a given temperature before a detectable level (5 percent) of the input analyte concentration elutes from the tube. Although breakthrough volumes are directly related to active rather than passive sampling, they provide a measure of the strength of the sorbent-sorbate interaction and therefore also relate to the efficiency of the passive sampling process. The best direct measure of passive sampling efficiency is the stability of the uptake rate. Quantitative passive sampling is compromised when the sorbent no longer acts as a perfect sink—*i.e.*, when the concentration of a target analyte immediately above the sorbent sampling surface no longer approximates to zero. This causes a reduction in the uptake rate over time. If the uptake rate for a given analyte on a given sorbent tube remains relatively constant —*i.e.*, if the uptake rate determined for 48 hours is similar to that determined for 7 or 14 days—the user can be confident that passive sampling is occurring at a constant rate. As a general rule of thumb, such ideal passive sampling conditions typically exist for analyte:sorbent combinations where the breakthrough volume exceeds 100 L (Reference 4).

3.3 *Continuing calibration verification sample (CCV).* Single level calibration samples run periodically to confirm that the analytical system continues to generate sample results within acceptable agreement to the current calibration curve.

3.4 *Focusing trap* is a cooled, secondary sorbent trap integrated into the analytical thermal desorber. It typically has a smaller i.d. and lower thermal mass than the original sample tube allowing it to effectively refocus desorbed analytes and then heat rapidly to ensure efficient transfer/injection into the capillary GC analytical column.

3.5 *High Resolution Capillary Column Chromatography* uses fused silica capillary columns with an inner diameter of 320 µm or less and with a stationary phase film thickness of 5 µm or less.

3.6 *h* is time in hours.

3.7 *i.d.* is inner diameter.

3.8 *min* is time in minutes.

3.9 *Method Detection Limit* is the lowest level of analyte that can be detected in the sample matrix with 99% confidence.

3.10 *MS-SCAN* is the mode of operation of a GC quadrupole mass spectrometer detector that measures all ions over a given mass range over a given period of time.

3.11 *MS-SIM* is the mode of operation of a GC quadrupole mass spectrometer detector that measures only a single ion or a selected number of discrete ions for each analyte.

3.12 *o.d.* is outer diameter.

3.13 *ppbv* is parts per billion by volume.

3.14 *Thermal desorption* is the use of heat and a flow of inert (carrier) gas to extract volatiles from a solid matrix. No solvent is required.

3.15 *Total ion chromatogram* is the chromatogram produced from a mass spectrometer detector collecting full spectral information.

3.16 *Two-stage thermal desorption* is the process of thermally desorbing analytes from a sorbent tube, reconcentrating them on a focusing trap (see Section 3.4), which is then itself rapidly heated to "inject" the concentrated compounds into the GC analyzer.

3.17 *VOC* is volatile organic compound.

4.0 ANALYTICAL INTERFERENCES

4.1 *Interference from Sorbent Artifacts.* Artifacts may include target analytes as well as other VOC that co-elute chromatographically with the compounds of interest or otherwise interfere with the identification or quantitation of target analytes.

4.1.1 Sorbent decomposition artifacts are VOCs that form when sorbents degenerate, *e.g.,* when exposed to reactive species during sampling. For example, benzaldehyde, phenol, and acetophenone artifacts are reported to be formed via oxidation of the polymeric sorbent Tenax® when sampling high concentration (100-500 ppb) ozone atmospheres (Reference 5).

4.1.2 Preparation and storage artifacts are VOCs that were not completely cleaned from the sorbent tube during conditioning or that are an inherent feature of that sorbent at a given temperature.

4.2 *Humidity.* Moisture captured during sampling can interfere with VOC analysis. Passive sampling using tubes packed with hydrophobic sorbents, like those described in this method, minimizes water retention. However, if water interference is found to be an issue under extreme conditions, one or more of the water management steps described in Section 2.4 can be applied.

4.3 *Contamination from Sample Handling.* The type of analytical thermal desorption equipment selected should exclude the possibility of outer tube surface contamination entering the sample flow path (see Section 6.6). If the available system does not meet this requirement, sampling tubes and caps must be handled only while wearing clean, white cotton or powder free nitrile gloves to prevent contamination with body oils, hand lotions, perfumes, etc.

5.0 SAFETY

5.1 This method does not address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate field and laboratory safety and health practices prior to use.

5.2 Laboratory analysts must exercise extreme care in working with high-pressure gas cylinders.

5.3 Due to the high temperatures involved, operators must use caution when conditioning and analyzing tubes.

6.0 EQUIPMENT AND SUPPLIES

6.1 *Tube Dimensions and Materials.* The sampling tubes for this method are 3.5-inches (89 mm) long, ¼ inch (6.4 mm) o.d., and 5 mm i.d. passive sampling tubes (see Figure 6.1). The tubes are made of inert-coated stainless steel with the central section (up to 60 mm) packed with sorbent, typically supported between two 100 mesh stainless steel gauze. The tubes have a cross sectional area of 19.6 square mm (5 mm i.d.). When used for passive sampling, these tubes have an internal diffusion (air) gap (DG) of 1.5 cm between the sorbent retaining gauze at the sampling end of the tube, and the gauze in the diffusion cap.

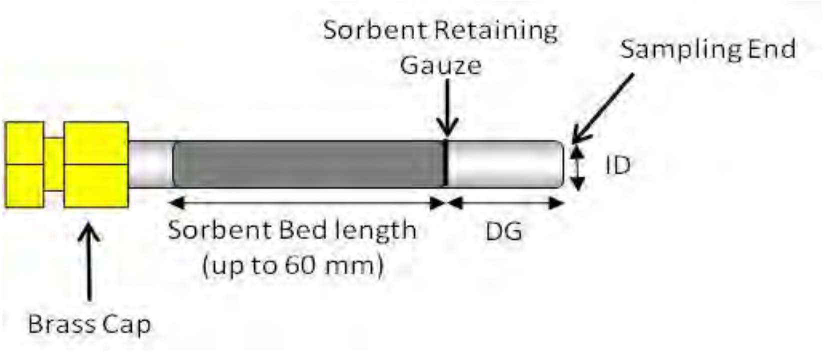


Figure 6.1. Cross Section View of Passive Sorbent Tube

6.2 TUBE CONDITIONING APPARATUS

6.2.1 Freshly packed or newly purchased tubes must be conditioned as described in Section 9 using an appropriate dedicated tube conditioning unit or the thermal desorber. Note that the analytical TD system should be used for tube conditioning if it supports a dedicated tube conditioning mode in which effluent from contaminated tubes is directed to vent without passing through key parts of the sample flow path such as the focusing trap.

6.2.2 Dedicated tube conditioning units must be leak-tight to prevent air ingress, allow precise and reproducible temperature selection (±5 °C), offer a temperature range at least as great as that of the thermal desorber, and support inert gas flows in the range up to 100 mL/min.

NOTE: For safety and to avoid laboratory contamination, effluent gases from freshly packed or highly contaminated tubes should be passed through a charcoal filter during the conditioning process to prevent desorbed VOCs from polluting the laboratory atmosphere.

6.3 TUBE LABELING

6.3.1 Label the sample tubes with a unique permanent identification number and an indication of the sampling end of the tube. Labeling options include etching and TD-compatible electronic (radio frequency identification (RFID)) tube labels.

6.3.2 To avoid contamination, do not make ink markings of any kind on clean sorbent tubes or apply adhesive labels.

NOTE: TD-compatible electronic (RFID) tube labels are available commercially and are compatible with some brands of thermal desorber. If used, these may be programmed with relevant tube and sample information, which can be read and automatically transcribed into the sequence report by the TD system (see Section 8.6 of Method 325A).

6.4 BLANK AND SAMPLED TUBE STORAGE APPARATUS

6.4.1 Long-term storage caps. Seal clean, blank and sampled sorbent tubes using inert, long-term tube storage caps comprising non-greased, 2-piece, 0.25-inch, metal SwageLok®-type screw caps fitted with combined polytetrafluoroethylene ferrules.

6.4.2 Storage and transportation containers. Use clean glass jars, metal cans or rigid, non-emitting polymer boxes.

NOTE: You may add a small packet of new activated charcoal or charcoal/silica gel to the shipping container for storage and transportation of batches of conditioned sorbent tubes prior to use. Coolers without ice packs make suitable shipping boxes for containers of tubes because the coolers help to insulate the samples from extreme temperatures (*e.g.*, if left in a parked vehicle).

6.5 UNHEATED GC INJECTION UNIT FOR LOADING STANDARDS ONTO BLANK TUBES

A suitable device has a simple push fit or finger-tightening connector for attaching the sampling end of blank sorbent tubes without damaging the tube. It also has a means of controlling carrier gas flow through the injector and attached sorbent tube at 50-100 mL/min and includes a low emission septum cap that allows the introduction of gas or liquid standards via appropriate syringes. Reproducible and quantitative transfer of higher boiling compounds in liquid standards is facilitated if the injection unit allows the tip of the syringe to just touch the sorbent retaining gauze inside the tube.

6.6 THERMAL DESORPTION APPARATUS

The manual or automated thermal desorption system must heat sorbent tubes while a controlled flow of inert (carrier) gas passes through the tube and out of the sampling end. The apparatus must also incorporate a focusing trap to quantitatively refocus compounds desorbed from the tube. Secondary desorption of the focusing trap should be fast/efficient enough to transfer the compounds into the high resolution capillary GC column without band broadening and without any need for further pre- or on-column focusing. Typical TD focusing traps comprise small sorbent traps (Reference 16) that are electrically-cooled using multistage Peltier cells (References 17, 18). The direction of gas flow during trap desorption should be the reverse of that used for focusing to extend the compatible analyte volatility range. Closed cycle coolers offer another cryogen-free trap cooling option. Other TD system requirements and operational stages are described in Section 11 and in Figures 17-2 through 17-4.

6.7 THERMAL DESORBER—GC INTERFACE

6.7.1 The interface between the thermal desorber and the GC must be heated uniformly and the connection between the transfer line insert and the capillary GC analytical column itself must be leak tight.

6.7.2 A portion of capillary column can alternatively be threaded through the heated transfer line/TD interface and connected directly to the thermal desorber.

NOTE: Use of a metal syringe-type needle or unheated length of fused silica pushed through the septum of a conventional GC injector is not permitted as a means of interfacing the thermal desorber to the chromatograph. Such connections result in cold spots, cause band broadening and are prone to leaks.

6.8 GC/MS ANALYTICAL COMPONENTS

6.8.1 The GC system must be capable of temperature programming and operation of a high resolution capillary column. Depending on the choice of column (*e.g.*, film thickness) and the volatility of the target compounds, it may be necessary to cool the GC oven to subambient temperatures (*e.g.*, −50 °C) at the start of the run to allow resolution of very volatile organic compounds.

6.8.2 All carrier gas lines supplying the GC must be constructed from clean stainless steel or copper tubing. Non-polytetrafluoroethylene thread sealants. Flow controllers, cylinder regulators, or other pneumatic components fitted with rubber components are not suitable.

6.9 CHROMATOGRAPHIC COLUMNS

High-resolution, fused silica or equivalent capillary columns that provide adequate separation of sample components to permit identification and quantitation of target compounds must be used.

NOTE: 100-percent methyl silicone or 5-percent phenyl, 95-percent methyl silicone fused silica capillary columns of 0.25- to 0.32-mm i.d. of varying lengths and with varying thicknesses of stationary phase have been used successfully for non-polar and moderately polar compounds. However, given the diversity of potential target lists, GC column choice is left to the operator, subject to the performance criteria of this method.

6.10 MASS SPECTROMETER

Linear quadrupole, magnetic sector, ion trap or time-of-flight mass spectrometers may be used provided they meet specified performance criteria. The mass detector must be capable of collecting data from 35 to 300 atomic mass units (amu) every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode, and producing a mass spectrum that meets all the instrument performance acceptance criteria in Section 9 when 50 ηg or less of p-bromofluorobenzene is analyzed.

7.0 REAGENTS AND STANDARDS

7.1 SORBENT SELECTION

7.1.1 Use commercially packed tubes meeting the requirements of this method or prepare tubes in the laboratory using sieved sorbents of particle size in the range 20 to 80 mesh that meet the retention and quality control requirements of this method.

7.1.2 This passive air monitoring method can be used without the evaluation specified in Addendum A if the type of tubes described in Section 6.1 are packed with 4-6 cm (typically 400-650 mg) of the sorbents listed in Table 12.1 and used for the respective target analytes.

NOTE: Although Carbopack^{TM} X is the optimum sorbent choice for passive sampling of 1,3-butadiene, recovery of compounds with vapor pressure lower than benzene may be difficult to achieve without exceeding sorbent maximum temperature limitations (see Table 8.1). See ISO 16017-2:2003(E) or ASTM D6196-03 (Reapproved 2009) (both incorporated by reference—see §63.14) for more details on sorbent choice for air monitoring using passive sampling tubes.

7.1.3 If standard passive sampling tubes are packed with other sorbents or used for analytes other than those tabulated in Section 12.0, method performance and relevant uptake rates should be verified according to Addendum A to this method or by following the techniques described in one of the following national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14)—or reported in the peer-reviewed open literature. A summary table and the supporting evaluation data demonstrating the selected sorbent meets the requirements in Addendum A to this method must be submitted to the regulatory authority as part of a request to use an alternative sorbent.

7.1.4 Passive (diffusive) sampling and thermal desorption methods that have been evaluated at relatively high atmospheric concentrations (*i.e.,* mid-ppb to ppm) and published for use in workplace air and industrial/mobile source emissions testing (References 9-20) may be applied to this procedure. However, the validity of any shorter term uptake rates must be verified and adjusted if necessary for the longer monitoring periods required by this method by following procedures described in Addendum A to this method or those presented in national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference-see §63.14).

7.1.5 Suitable sorbents for passive sampling must have breakthrough volumes of at least 20 L (preferably >100 L) for the compounds of interest and must quantitatively release the analytes during desorption without exceeding maximum temperatures for the sorbent or instrumentation.

7.1.6 Repack/replace the sorbent tubes or demonstrate tube performance following the requirements in Addendum A to this method at least every 2 years or every 50 uses, whichever occurs first.

7.2 GAS PHASE STANDARDS

7.2.1 Static or dynamic standard atmospheres may be used to prepare calibration tubes and/or to validate passive sampling uptake rates and can be generated from pure chemicals or by diluting concentrated gas standards. The standard atmosphere must be stable at ambient pressure and accurate to ±10 percent of the target gas concentration. It must be possible to maintain standard atmosphere concentrations at the same or lower levels than the target compound concentration objectives of the test. Test atmospheres used for validation of uptake rates must also contain at least 35 percent relative humidity.

NOTE: Accurate, low-(ppb-) level gas-phase VOC standards are difficult to generate from pure materials and may be unstable depending on analyte polarity and volatility. Parallel monitoring of vapor concentrations with alternative methods, such as pumped sorbent tubes or sensitive/selective on-line detectors, may be necessary to minimize uncertainty. For these reasons, standard atmospheres are rarely used for routine calibration.

7.2.2 Concentrated, pressurized gas phase standards. Accurate (±5 percent or better), concentrated gas phase standards supplied in pressurized cylinders may also be used for calibration. The concentration of the standard should be such that a 0.5-5.0 mL volume contains approximately the same mass of analytes as will be collected from a typical air sample.

7.2.3 Follow manufacturer's guidelines concerning storage conditions and recertification of the concentrated gas phase standard. Gas standards must be recertified a minimum of once every 12 months.

7.3 LIQUID STANDARDS

Target analytes can also be introduced to the sampling end of sorbent tubes in the form of liquid calibration standards.

7.3.1 The concentration of liquid standards must be such that an injection of 0.5-2 µl of the solution introduces the same mass of target analyte that is expected to be collected during the passive air sampling period.

7.3.2 Solvent Selection. The solvent selected for the liquid standard must be pure (contaminants <10 percent of minimum analyte levels) and must not interfere chromatographically with the compounds of interest.

7.3.3 If liquid standards are sourced commercially, follow manufacturer's guidelines concerning storage conditions and shelf life of unopened and opened liquid stock standards.

NOTE: Commercial VOC standards are typically supplied in volatile or non-interfering solvents such as methanol.

7.3.4 Working standards must be stored at 6 °C or less and used or discarded within two weeks of preparation.

7.4 GAS PHASE INTERNAL STANDARDS

7.4.1 Gas-phase deuterated or fluorinated organic compounds may be used as internal standards for MS-based systems.

7.4.2 Typical compounds include deuterated toluene, perfluorobenzene and perfluorotoluene.

7.4.3 Use multiple internal standards to cover the volatility range of the target analytes.

7.4.4 Gas-phase standards must be obtained in pressurized cylinders and containing vendor certified gas concentrations accurate to ±5 percent. The concentration should be such that the mass of internal standard components introduced is similar to those of the target analytes collected during field monitoring.

7.5 PRELOADED STANDARD TUBES

Certified, preloaded standard tubes, accurate within ±5 percent for each analyte at the microgram level and ±10 percent at the nanogram level, are available commercially and may be used for auditing and quality control purposes. (See Section 9.5 for audit accuracy evaluation criteria.) Certified preloaded tubes may also be used for routine calibration.

NOTE: Proficiency testing schemes are also available for TD/GC/MS analysis of sorbent tubes preloaded with common analytes such as benzene, toluene, and xylene.

7.6 CARRIER GASES

Use inert, 99.999-percent or higher purity helium as carrier gas. Oxygen and organic filters must be installed in the carrier gas lines supplying the analytical system according to the manufacturer's instructions. Keep records of filter and oxygen scrubber replacement.

8.0 SORBENT TUBE HANDLING (BEFORE AND AFTER SAMPLING)

8.1 SAMPLE TUBE CONDITIONING

8.1.1 Sampling tubes must be conditioned using the apparatus described in Section 6.2.

8.1.2 New tubes should be conditioned for 2 hours to supplement the vendor's conditioning procedure. Recommended temperatures for tube conditioning are given in Table 8.1.

8.1.3 After conditioning, the blank must be verified on each new sorbent tube and on 10 percent of each batch of reconditioned tubes. See Section 9.0 for acceptance criteria.

TABLE 8.1—EXAMPLE SORBENT TUBE CONDITIONING PARAMETERS

Sampling sorbent	**Maximum temperature (°C)**	**Conditioning temperature (°C)**	**Carrier gas flow rate**
Carbotrap® C	>400	350	100 mL/min
Carbopack™ C			
Anasorb® GCB2			
Carbograph™ 1 TD			
Carbotrap®			

Carbopack™ B			
Anasorb® GCB1			
Tenax® TA Carbopack™ X	350	330	100 mL/min

8.2 Capping, Storage and Shipment of Conditioned Tubes

8.2.1 Conditioned tubes must be sealed using long-term storage caps (see Section 6.4) pushed fully down onto both ends of the PS sorbent tube, tightened by hand and then tighten an additional quarter turn using an appropriate tool.

8.2.2 The capped tubes must be kept in appropriate containers for storage and transportation (see Section 6.4.2). Containers of sorbent tubes may be stored and shipped at ambient temperature and must be kept in a clean environment.

8.2.3 You must keep batches of capped tubes in their shipping boxes or wrap them in uncoated aluminum foil before placing them in their storage container, especially before air freight, because the packaging helps hold caps in position if the tubes get very cold.

8.3 Calculating the Number of Tubes Required for a Monitoring Exercise

8.3.1 Follow guidance given in Method 325A to determine the number of tubes required for site monitoring.

8.3.2 The following additional samples will also be required: Laboratory blanks as specified in Section 9.1.2 (one per analytical sequence minimum), field blanks as specified in Section 9.3.2 (two per sampling period minimum), CCV tubes as specified in Section 10.9.4. (at least one per analysis sequence or every 24 hours), and duplicate samples as specified in Section 9.4 (at least one duplicate sample is required for every 10 sampling locations during each monitoring period).

8.4 Sample Collection

8.4.1 Allow the tubes to equilibrate with ambient temperature (approximately 30 minutes to 1 hour) at the monitoring location before removing them from their storage/shipping container for sample collection.

8.4.2 Tubes must be used for sampling within 30 days of conditioning (Reference 4).

8.4.3 During field monitoring, the long-term storage cap at the sampling end of the tube is replaced with a diffusion cap and the whole assembly is arranged vertically, with the sampling end pointing downward, under a protective hood or shield—See Section 6.1 of Method 325A for more details.

8.5 Sample Storage

8.5.1 After sampling, tubes must be immediately resealed with long-term storage caps and placed back inside the type of storage container described in Section 6.4.2.

8.5.2 Exposed tubes may not be placed in the same container as clean tubes. They should not be taken back out of the container until ready for analysis and after they have had time to equilibrate with ambient temperature in the laboratory.

8.5.3 Sampled tubes must be inspected before analysis to identify problems such as loose or missing caps, damaged tubes, tubes that appear to be leaking sorbent or container contamination. Any and all such problems must be documented together with the unique identification number of the tube or tubes concerned. Affected tubes must not be analyzed but must be set aside.

8.5.4 Intact tubes must be analyzed within 30 days of the end of sample collection (within one week for limonene, carene, bis-chloromethyl ether, labile sulfur or nitrogen-containing compounds, and other reactive VOCs).

NOTE: Ensure ambient temperatures stay below 23 °C during transportation and storage. Refrigeration is not normally required unless the samples contain reactive compounds or cannot be analyzed within 30 days. If refrigeration is used, the atmosphere inside the refrigerator must be clean and free of organic solvents.

9.0 QUALITY CONTROL

9.1 LABORATORY BLANK

The analytical system must be demonstrated to be contaminant free by performing a blank analysis at the beginning of each analytical sequence to demonstrate that the secondary trap and TD/GC/MS analytical equipment are free of any significant interferents.

9.1.1 Laboratory blank tubes must be prepared from tubes that are identical to those used for field sampling.

9.1.2 Analysis of at least one laboratory blank is required per analytical sequence. The laboratory blank must be stored in the laboratory under clean, controlled ambient temperature conditions.

9.1.3 Laboratory blank/artifact levels must meet the requirements of Section 9.2.2 (see also Table 17.1). If the laboratory blank does not meet requirements, stop and perform corrective actions and then re-analyze laboratory blank to ensure it meets requirements.

9.2 TUBE CONDITIONING

9.2.1 Conditioned tubes must be demonstrated to be free of contaminants and interference by running 10 percent of the blank tubes selected at random from each conditioned batch under standard sample analysis conditions (see Section 8.1).

9.2.2 Confirm that artifacts and background contamination are ≤ 0.2 ppbv or less than three times the detection limit of the procedure or less than 10 percent of the target compound(s) mass that would be collected if airborne concentrations were at the regulated limit value, whichever is larger. Only tubes that meet these criteria can be used for field monitoring, field or laboratory blanks, or for system calibration.

9.2.3 If unacceptable levels of VOCs are observed in the tube blanks, then the processes of tube conditioning and checking the blanks must be repeated.

9.3 FIELD BLANKS

9.3.1 Field blank tubes must be prepared from tubes that are identical to those used for field sampling—*i.e.,* they should be from the same batch, have a similar history, and be conditioned at the same time.

9.3.2 Field blanks must be shipped to the monitoring site with the sampling tubes and must be stored at the sampling location throughout the monitoring exercise. The field blanks must be installed under a protective hood/cover at the sampling location, but the long-term storage caps must remain in place throughout the monitoring period (see Method 325A). The field blanks are then shipped back to the laboratory in the same container as the sampled tubes. Collect at least two field blank samples per sampling period to ensure sample integrity associated with shipment, collection, and storage.

9.3.3 Field blanks must contain no greater than one-third of the measured target analyte or compliance limit for field samples (see Table 17.1). If either field blank fails, flag all data that do not meet this criterion with a note that the associated results are estimated and likely to be biased high due to field blank background.

9.4 DUPLICATE SAMPLES

Duplicate (co-located) samples collected must be analyzed and reported as part of method quality control. They are used to evaluate sampling and analysis precision. Relevant performance criteria are given in Section 9.9.

9.5 METHOD PERFORMANCE CRITERIA

Unless otherwise noted, monitoring method performance specifications must be demonstrated for the target compounds using the procedures described in Addendum A to this method and the statistical approach presented in Method 301.

9.6 METHOD DETECTION LIMIT

Determine the method detection limit under the analytical conditions selected (see Section 11.3) using the procedure in Section 15 of Method 301. The method detection limit is defined for each system by making seven replicate measurements of a concentration of the compound of interest within a factor of five of the detection limit. Compute the standard deviation for the seven replicate concentrations, and multiply this value by three. The results should demonstrate that the method is able to detect analytes such as benzene at concentrations as low as 50 ppt or 1/3rd (preferably 1/10th) of the lowest concentration of interest, whichever is larger.

NOTE: Determining the detection limit may be an iterative process as described in 40 CFR part 136, Appendix B.

9.7 ANALYTICAL BIAS

Analytical bias must be demonstrated to be within ±30 percent using Equation 9.1. Analytical bias must be demonstrated during initial setup of this method and as part of the CCV carried out with every sequence of 10 samples or less (see Section 9.14). Calibration standard tubes (see Section 10.0) may be used for this purpose.

$$Analytical\ Bias = \frac{(Spiked\ Value - Measured\ Value)}{Spiked\ Value} \times 100 \qquad \text{Eq. 9.1}$$

Where:

Spiked Value = A known mass of VOCs added to the tube.

Measured Value = Mass determined from analysis of the tube.

9.8 ANALYTICAL PRECISION

Demonstrate an analytical precision within ±20 percent using Equation 9.2. Analytical precision must be demonstrated during initial setup of this method and at least once per year. Calibration standard tubes may be used (see Section 10.0) and data from CCV may also be applied for this purpose.

$$Analytical\ Precision = \frac{(|A1 - A2|)}{\bar{A}} \times 100 \qquad \text{Eq. 9.2}$$

Where:

A1 = A measurement value taken from one spiked tube.

A2 = A measurement value taken from a second spiked tube.

A = The average of A1 and A2.

9.9 FIELD REPLICATE PRECISION

Use Equation 9.3 to determine and report replicate precision for duplicate field samples (see Section 9.4). The level of agreement between duplicate field samples is a measure of the precision achievable for the entire sampling and analysis procedure. Flag data sets for which the duplicate samples do not agree within 30 percent.

$$Field\ Precision = \frac{(|F1-F2|)}{\bar{F}} \times 100 \qquad \text{Eq. 9.3}$$

Where:

F1 = A measurement value (mass) taken from one of the two field replicate tubes used in sampling.

F2 = A measurement value (mass) taken from the second of two field replicate tubes used in sampling.

F = The average of F1 and F2.

9.10 DESORPTION EFFICIENCY AND COMPOUND RECOVERY

The efficiency of the thermal desorption method must be determined.

9.10.1 Quantitative (>95 percent) compound recovery must be demonstrated by repeat analyses on a same standard tube.

9.10.2 Compound recovery through the TD system can also be demonstrated by comparing the calibration check sample response factor obtained from direct GC injection of liquid standards with that obtained from thermal desorption analysis response factor using the same column under identical conditions.

9.10.3 If the relative response factors obtained for one or more target compounds introduced to the column via thermal desorption fail to meet the criteria in Section 9.10.1, you must adjust the TD parameters to meet the criteria and repeat the experiment. Once the thermal desorption conditions have been optimized, you must repeat this test each time the analytical system is recalibrated to demonstrate continued method performance.

9.11 AUDIT SAMPLES

Certified reference standard samples must be used to audit this procedure (if available). Accuracy within 30 percent must be demonstrated for relevant ambient air concentrations (0.5 to 25 ppb).

9.12 MASS SPECTROMETER TUNING CRITERIA

Tune the mass spectrometer (if used) according to manufacturer's specifications. Verify the instrument performance by analyzing a 50 ηg injection of bromofluorobenzene. Prior to the beginning of each analytical sequence or every 24 hours during continuous GC/MS operation for this method demonstrate that the bromofluorobenzene tuning performance criteria in Table 9.1 have been met.

TABLE 9.1—GC/MS TUNING CRITERIA[1]

Target mass	Rel. to mass	Lower limit %	Upper limit %
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5	9
173	174	0	2
174	95	50	120
175	174	4	9
176	174	93	101
177	176	5	9

[1] All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

9.13 ROUTINE CCV AT THE START OF A SEQUENCE

Run CCV before each sequence of analyses and after every tenth sample to ensure that the previous multi-level calibration (see section 10.0) is still valid.

9.13.1 The sample concentration used for the CCV should be near the mid-point of the multi-level calibration range.

9.13.2 Quantitation software must be updated with response factors determined from the CCV standard. The percent deviation between the initial calibration and the CCV for all compounds must be within 30 percent.

9.14 CCV AT THE END OF A SEQUENCE

Run another CCV after running each sequence of samples. The initial CCV for a subsequent set of samples may be used as the final CCV for a previous analytical sequence, provided the same analytical method is used and the subsequent set of samples is analyzed immediately (within 4 hours) after the last CCV.

9.15 ADDITIONAL VERIFICATION

Use a calibration check standard from a second, separate source to verify the original calibration at least once every three months.

9.16 INTEGRATION METHOD

Document the procedure used for integration of analytical data including field samples, calibration standards and blanks.

9.17 QC RECORDS

Maintain all QC reports/records for each TD/GC/MS analytical system used for application of this method. Routine quality control requirements for this method are listed below and summarized in Table 17.1.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibrate the analytical system using standards covering the range of analyte masses expected from field samples.

10.2 Analytical results for field samples must fall within the calibrated range of the analytical system to be valid.

10.3 Calibration standard preparation must be fully traceable to primary standards of mass and/or volume, and/or be confirmed using an independent certified reference method.

10.3.1 Preparation of calibration standard tubes from standard atmospheres.

10.3.1.1 Subject to the requirements in Section 7.2.1, low-level standard atmospheres may be introduced to clean, conditioned sorbent tubes in order to produce calibration standards.

10.3.1.2 The standard atmosphere generator or system must be capable of producing sufficient flow at a constant rate to allow the required analyte mass to be introduced within a reasonable time frame and without affecting the concentration of the standard atmosphere itself.

10.3.1.3 The sampling manifold may be heated to minimize risk of condensation but the temperature of the gas delivered to the sorbent tubes may not exceed 100 °F.

10.3.1.4 The flow rates passed through the tube should be in the order of 50-100 mL/min and the volume of standard atmosphere sampled from the manifold or chamber must not exceed the breakthrough volume of the sorbent at the given temperature.

10.4 Preparation of calibration standard tubes from concentrated gas standards.

10.4.1 If a suitable concentrated gas standard (see Section 7.2.2) can be obtained, follow the manufacturer's recommendations relating to suitable storage conditions and product lifetime.

10.4.2 Introduce precise 0.5 to 500.0 mL aliquots of the standard to the sampling end of conditioned sorbent tubes in a 50-100 mL/min flow of pure carrier gas.

NOTE: This can be achieved by connecting the sampling end of the tube to an unheated GC injector (see Section 6.6) and introducing the aliquot of gas using a suitable gas syringe. Gas sample valves could alternatively be used to meter the standard gas volume.

10.4.3 Each sorbent tube should be left connected to the flow of gas for 2 minutes after standard introduction. As soon as each spiked tube is removed from the injection unit, seal it with long-term storage caps and place it in an appropriate tube storage/transportation container if it is not to be analyzed within 24 hours.

10.5 Preparation of calibration standard tubes from liquid standards.

10.5.1 Suitable standards are described in Section 7.3.

10.5.2 Introduce precise 0.5 to 2 µl aliquots of liquid standards to the sampling end of sorbent tubes in a flow (50-100 mL/min) of carrier gas using a precision syringe and an unheated injector (Section 6.5). The flow of gas should be sufficient to completely vaporize the liquid standard.

NOTE: If the analytes of interest are higher boiling than n-decane, reproducible analyte transfer to the sorbent bed is optimized by allowing the tip of the syringe to gently touch the sorbent retaining gauze at the sampling end of the tube.

10.5.3 Each sorbent tube is left connected to the flow of gas for 5 minutes after liquid standard introduction.

10.5.3.1 As soon as each spiked tube is removed from the injection unit, seal it with long-term storage caps and place it in an appropriate tube storage container if it is not to be analyzed within 24 hours.

NOTE: In cases where it is possible to selectively purge the solvent from the tube while all target analytes are quantitatively retained, a larger 2 µL injection may be made for optimum accuracy. However, if the solvent cannot be selectively purged and will be present during analysis, the injection volume should be as small as possible (*e.g.*, 0.5 µL) to minimize solvent interference.

NOTE: This standard preparation technique requires the entire liquid plug including the tip volume be brought into the syringe barrel. The volume in the barrel is recorded, the syringe is inserted into the septum of the spiking apparatus. The liquid is then quickly injected. Any remaining liquid in the syringe tip is brought back into the syringe barrel. The volume in the barrel is recorded and the amount spiked onto the tube is the difference between the before spiking volume and the after spiking volume. A bias occurs with this method when sample is drawn continuously up into the syringe to the specified volume and the calibration solution in the syringe tip is ignored.

10.6 Preparation of calibration standard tubes from multiple standards.

10.6.1 If it is not possible to prepare one standard containing all the compounds of interest (*e.g.*, because of chemical reactivity or the breadth of the volatility range), standard tubes can be prepared from multiple gas or liquid standards.

10.6.2 Follow the procedures described in Sections 10.4 and 10.5, respectively, for introducing each gas and/or liquid standard to the tube and load those containing the highest boiling compounds of interest first and the lightest species last.

10.7 Additional requirements for preparation of calibration tubes.

10.7.1 Storage of Calibration Standard Tubes

10.7.1.1 Seal tubes with long-term storage caps immediately after they have been disconnected from the standard loading manifold or injection apparatus.

10.7.1.2 Calibration standard tubes may be stored for no longer than 30 days and should be refrigerated if there is any risk of chemical interaction or degradation. Audit standards (see section 9.11) are exempt from this criteria and may be stored for the shelf-life specified on their certificates.

10.8 Keep records for calibration standard tubes to include the following:

10.8.1 The stock number of any commercial liquid or gas standards used.

10.8.2 A chromatogram of the most recent blank for each tube used as a calibration standard together with the associated analytical conditions and date of cleaning.

10.8.3 Date of standard loading.

10.8.4 List of standard components, approximate masses and associated confidence levels.

10.8.5 Example analysis of an identical standard with associated analytical conditions.

10.8.6 A brief description of the method used for standard preparation.

10.8.7 The standard's expiration date.

10.9 TD/GC/MS using standard tubes to calibrate system response.

10.9.1 Verify that the TD/GC/MS analytical system meets the instrument performance criteria given in Section 9.1.

10.9.2 The prepared calibration standard tubes must be analyzed using the analytical conditions applied to field samples (see Section 11.0) and must be selected to ensure quantitative transfer and adequate chromatographic resolution of target compounds, surrogates, and internal standards in order to enable reliable identification and quantitation of compounds of interest. The analytical conditions should also be sufficiently stringent to prevent buildup of higher boiling, non-target contaminants that may be collected on the tubes during field monitoring.

10.9.3 Calibration range. Each TD/GC/MS system must be calibrated at five concentrations that span the monitoring range of interest before being used for sample analysis. This initial multi-level calibration determines instrument sensitivity under the analytical conditions selected and the linearity of GC/MS response for the target compounds. One of the calibration points must be within a factor of five of the detection limit for the compounds of interest.

10.9.4 One of the calibration points from the initial calibration curve must be at the same concentration as the daily CCV standard (*e.g.*, the mass collected when sampling air at typical concentrations).

10.9.5 Calibration frequency. Each GC/MS system must be recalibrated with a full 5-point calibration curve following corrective action (*e.g.*, ion source cleaning or repair, column replacement) or if the instrument fails the daily calibration acceptance criteria.

10.9.5.1 CCV checks must be carried out on a regular routine basis as described in Section 9.14.

10.9.5.2 Quantitation ions for the target compounds are shown in Table 10.1. Use the primary ion unless interferences are present, in which case you should use a secondary ion.

TABLE 10.1—CLEAN AIR ACT VOLATILE ORGANIC COMPOUNDS FOR PASSIVE SORBENT SAMPLING

Compound	**CAS No.**	**BP (°C)**	**Vapor pressure (mmHg)**[a]	**MW**[b]	**Characteristic ion(s)**	
					Primary	**Secondary**
1,1-Dichloroethene	75-35-4	32	500	96.9	61	96
3-Chloropropene	107-05-1	44.5	340	76.5	76	41, 39, 78
1,1,2-Trichloro-1,2,2-trifluoroethane-1,1-Dichloroethane	75-34-3	57.0	230	99	63	65, 83, 85, 98, 100
1,2-Dichloroethane	107-06-2	83.5	61.5	99	62	98
1,1,1-Trichloroethane	71-55-6	74.1	100	133.4	97	99, 61
Benzene	71-43-2	80.1	76.0	78	78	
Carbon tetrachloride	56-23-5	76.7	90.0	153.8	117	119
1,2-Dichloropropane	78-87-5	97.0	42.0	113	63	112
Trichloroethene	79-01-6	87.0	20.0	131.4	95	97, 130, 132
1,1,2-Trichloroethane	79-00-5	114	19.0	133.4	83	97, 85

Toluene	108-88-3	111	22.0	92	92	91
Tetrachloroethene	127-18-4	121	14.0	165.8	164	129, 131, 166
Chlorobenzene	108-90-7	132	8.8	112.6	112	77, 114
Ethylbenzene	100-41-4	136	7.0	106	91	106
m,p-Xylene	108-38-3, 106-42-3	138	6.5	106.2	106	91
Styrene	100-42-5	145	6.6	104	104	78
o-Xylene	95-47-6	144	5.0	106.2	106	91
p-Dichlorobenzene	106-46-7	173	0.60	147	146	111, 148

[a] Pressure in millimeters of mercury.

[b] Molecular weight.

11.0 ANALYTICAL PROCEDURE

11.1 PREPARATION FOR SAMPLE ANALYSIS

11.1.1 Each sequence of analyses must be ordered as follows:

11.1.1.1 CCV.

11.1.1.2 A laboratory blank.

11.1.1.3 Field blank.

11.1.1.4 Sample(s).

11.1.1.5 Field blank.

11.1.1.6 CCV after 10 field samples.

11.1.1.7 CCV at the end of the sample batch.

11.2 PRE-DESORPTION SYSTEM CHECKS AND PROCEDURES

11.2.1 Ensure all sample tubes and field blanks are at ambient temperature before removing them from the storage container.

11.2.2 If using an automated TD/GC/MS analyzer, remove the long-term storage caps from the tubes, replace them with appropriate analytical caps, and load them into the system in the sequence described in Section 11.1. Alternatively, if using a manual system, uncap and analyze each tube, one at a time, in the sequence described in Section 11.1.

11.2.3 The following thermal desorption system integrity checks and procedures are required before each tube is analyzed.

NOTE: Commercial thermal desorbers should implement these steps automatically.

11.2.3.1 Tube leak test: Each tube must be leak tested as soon as it is loaded into the carrier gas flow path before analysis to ensure data integrity.

11.2.3.2 Conduct the leak test at the GC carrier gas pressure, without heat or gas flow applied. Tubes that fail the leak test should not be analyzed, but should be resealed and stored intact. On automated systems, the instrument should continue to leak test and analyze subsequent tubes after a given tube has failed. Automated systems must also store and record which tubes in a sequence have failed the leak test. Information on failed tubes should be downloaded with the batch of sequence information from the analytical system.

11.2.3.3 Leak test the sample flow path. Leak check the sample flow path of the thermal desorber before each analysis without heat or gas flow applied to the sample tube. Stop the automatic sequence of tube desorption and GC analysis if any leak is detected in the main sample flow path. This process may be carried out as a separate step or as part of Section 11.2.3.2.

11.2.4 OPTIONAL DRY PURGE

11.2.4.1 Tubes may be dry purged with a flow of pure dry gas passing into the tube from the sampling end, to remove water vapor and other very volatile interferents if required.

11.2.5 INTERNAL STANDARD (IS) ADDITION

11.2.5.1 Use the internal standard addition function of the automated thermal desorber (if available) to introduce a precise aliquot of the internal standard to the sampling end of each tube after the leak test and shortly before primary (tube) desorption).

NOTE: This step can be combined with dry purging the tube (Section 11.2.4) if required.

11.2.5.2 If the analyzer does not have a facility for automatic IS addition, gas or liquid internal standard can be manually introduced to the sampling end of tubes in a flow of carrier gas using the types of procedure described in Sections 10.3 and 10.4, respectively.

11.2.6 Pre-purge. Each tube should be purged to vent with carrier gas flowing in the desorption direction (*i.e.,*flowing into the tube from the non-sampling end) to remove oxygen before heat is applied. This is to prevent analyte and sorbent oxidation and to prevent deterioration of key analyzer components such as the GC column and mass spectrometer (if applicable). A series of schematics illustrating these steps is presented in Figures 17.2 and 17.3.

11.3 ANALYTICAL PROCEDURE

11.3.1 STEPS REQUIRED FOR THERMAL DESORPTION

11.3.1.1 Ensure that the pressure and purity of purge and carrier gases supplying the TD/GC/MS system, meet manufacturer specifications and the requirements of this method.

11.3.1.2 Ensure also that the analytical method selected meets the QC requirements of this method (Section 9) and that all the analytical parameters are at set point.

11.3.1.3 Conduct predesorption system checks (see Section 11.2).

11.3.1.4 Desorb the sorbent tube under conditions demonstrated to achieve >95 percent recovery of target compounds (see Section 9.5.2).

NOTE: Typical tube desorption conditions range from 280-350 °C for 5-15 minutes with a carrier gas flow of 30-100 mL/min passing through the tube from the non-sampling end such that analytes are flushed out of the tube from the sampling end. Desorbed VOCs are concentrated (refocused) on a secondary, cooled sorbent trap integrated into the analytical equipment (see Figure 17.4). The focusing trap is typically maintained at a temperature between −30 and +30 °C during focusing. Selection of hydrophobic sorbents for focusing and setting a trapping temperature of +25 to 27 °C aid analysis of humid samples because these settings allow selective elimination of any residual water from the system, prior to GC/MS analysis.

NOTE: The transfer of analytes from the tube to the focusing trap during primary (tube) desorption can be carried out splitless or under controlled split conditions (see Figure 17.4) depending on the masses of target compounds sampled and the requirements of the system—sensitivity, required calibration range, column overload limitations, etc. Instrument controlled sample splits must be demonstrated by showing the reproducibility using calibration standards. Field and laboratory blank samples must be analyzed at the same split as the lowest calibration standard. During secondary (trap) desorption the focusing trap is heated rapidly (typically at rates >40 °C/s) with inert (carrier) gas flowing through the trap (3-100 mL/min) in the reverse direction to that used during focusing.

11.3.1.5 The split conditions selected for optimum field sample analysis must also be demonstrated on representative standards.

NOTE: Typical trap desorption temperatures are in the range 250-360 °C, with a “hold” time of 1-3 minutes at the highest temperature. Trap desorption automatically triggers the start of GC analysis. The trap desorption can also be carried out under splitless conditions (*i.e.*, with everything desorbed from the trap being transferred to the analytical column and GC detector) or, more commonly, under controlled split conditions (see Figure 17.4). The selected split ratio depends on the masses of target compounds sampled and the requirements of the system—sensitivity, required calibration range, column overload limitations, etc. If a split is selected during both primary (trap) desorption and secondary (trap) desorption, the overall split ratio is the product of the two. Such `double' split capability gives optimum flexibility for accommodating concentrated samples as well as trace-level samples on the TD/GC/MS analytical system. High resolution capillary columns and most GC/MS detectors tend to work best with approximately 20-200 ng per compound per tube to avoid saturation. The overall split ratio must be adjusted such that, when it is applied to the sample mass that is expected to be collected during field monitoring, the amount reaching the column will be attenuated to fall within this range. As a rule of thumb this means that ~20 ng samples will require splitless or very low split analysis, ~2 µg samples will require a split ratio in the order of ~50:1 and 200 µg samples will require a double split method with an overall split ratio in the order of 2,000:1.

11.3.1.6 Analyzed tubes must be resealed with long-term storage caps immediately after analysis (manual systems) or after completion of a sequence (automated systems). This prevents contamination, minimizing the extent of tube reconditioning required before subsequent reuse.

11.3.2 GC/MS ANALYTICAL PROCEDURE

11.3.2.1 Heat/cool the GC oven to its starting set point.

11.3.2.2 If using a GC/MS system, it can be operated in either MS-Scan or MS-SIM mode (depending on required sensitivity levels and the type of mass spectrometer selected). As soon as trap desorption and transfer of analytes into the GC column triggers the start of the GC/MS analysis, collect mass spectral data over a range of masses from 35 to 300 amu. Collect at least 10 data points per eluting chromatographic peak in order to adequately integrate and quantify target compounds.

11.3.2.3 Use secondary ion quantitation only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, flag the data and document the reasons for the alternative quantitation procedure.

11.3.2.4 Data reduction is performed by the instruments post processing program that is automatically accessed after data acquisition is completed at the end of the GC run. The concentration of each target compound is calculated using the previously established response factors for the CCV analyzed in Section 11.1.1.6.

11.3.2.5 Whenever the thermal desorption—GC/MS analytical method is changed or major equipment maintenance is performed, you must conduct a new five-level calibration (see section 10.0). System calibration remains valid as long as results from subsequent CCV are within 30 percent of the most recent 5-point calibration (see section 9.13). Include relevant CCV data in the supporting information in the data report for each set of samples.

11.3.2.6 Document, flag and explain all sample results that exceed the calibration range. Report flags and provide documentation in the analytical results for the affected sample(s).

12.0 DATA ANALYSIS, CALCULATIONS, AND REPORTING

12.1 RECORDKEEPING PROCEDURES FOR SORBENT TUBES

12.1.1 Label sample tubes with a unique identification number as described in Section 6.3.

12.1.2 Keep records of the tube numbers and sorbent lots used for each sampling period.

12.1.3 Keep records of sorbent tube packing if tubes are manually prepared in the laboratory and not supplied commercially. These records must include the masses and/or bed lengths of sorbent(s) contained in each tube, the maximum allowable temperature for that tube and the date each tube was packed. If a tube is repacked at any stage, record the date of tube repacking and any other relevant information required in Section 12.1.

12.1.4 Keep records of the conditioning and blanking of tubes. These records must include, but are not limited to, the unique identification number and measured background resulting from the tube conditioning.

12.1.5 Record the location, dates, tube identification and times associated with each sample collection. Record this information on a Chain of Custody form that is sent to the analytical laboratory.

12.1.6 Field sampling personnel must complete and send a Chain of Custody to the analysis laboratory (see Section 8.6.4 of Method 325A for what information to include and Section 17.0 of this method for an example form). Duplicate copies of the Chain of Custody must be included with the sample report and stored with the field test data archive.

12.1.7 Field sampling personnel must also keep records of the unit vector wind direction, sigma theta, temperature and barometric pressure averages for the sampling period. See Section 8.3.4 of Method 325A.

12.1.8 Laboratory personnel must record the sample receipt date, and analysis date.

12.1.9 Laboratory personnel must maintain records of the analytical method and sample results in electronic or hardcopy in sufficient detail to reconstruct the calibration, sample, and quality control results from each sampling period.

12.2 CALCULATIONS

12.2.1 Complete the calculations in this section to determine compliance with calibration quality control criteria (see also Table 17.1).

12.2.1.1 Response factor (RF). Calculate the RF using Equation 12.1:

$$RF = \frac{[A_s \times M_{is}]}{[A_{is} \times M_s]} \qquad \text{Eq. 12.1}$$

Where:

A_s = Peak area for the characteristic ion of the analyte.

A_{is} = Peak area for the characteristic ion of the internal standard.

M_s = Mass of the analyte.

M_{is} = Mass of the internal standard.

12.2.1.2 Standard deviation of the response factors (SD_{RF}). Calculate the SDRF using Equation 12.2:

$$SD_{RF} = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{(n-1)}} \qquad \text{Eq. 12.2}$$

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Where:

RF_i = RF for each of the calibration compounds.

RF = Mean RF for each compound from the initial calibration.

n = Number of calibration standards.

12.2.1.3 Percent deviation (%DEV). Calculate the %DEV using Equation 12.3:

$$\%DEV = SD_{RF} \div \overline{RF} \times 100 \qquad \text{Eq. 12.3}$$

Where:

SD_{RF} = Standard deviation.

RF = Mean RF for each compound from the initial calibration.

12.2.1.4 Relative percent difference (RPD). Calculate the RPD using Equation 12.4:

$$RPD = \frac{R1 - R2}{[(R1+R2)/2]} \times 100 \qquad \text{Eq. 12.4}$$

Where:

R1, R2 = Values that are being compared (*i.e.*, response factors in CCV).

12.2.2 Determine the equivalent concentrations of compounds in atmospheres as follows. Correct target compound concentrations determined at the sampling site temperature and atmospheric pressure to standard conditions (25 °C and 760 mm mercury) using Equation 12.5.

$$C_c = \frac{(m_{meas}) * 10^6}{U_{NTP} * \left[\frac{t_{SS}}{298.15}\right]^{1/2} * t} \qquad \text{Eq. 12.5}$$

Where:

m_{meas} = The mass of the compound as measured in the sorbent tube (µg).

t = The exposure time (minutes).

t_{ss} = The average temperature during the collection period at the sampling site (K).

U_{NTP} = The method defined diffusive uptake rate (sampling rate) (mL/min).

NOTE: Diffusive uptake rates (U_{NTP}) for common VOCs, using carbon sorbents packed into sorbent tubes of the dimensions specified in section 6.1, are listed in Table 12.1. Adjust analytical conditions to keep expected sampled masses within range (see sections 11.3.1.3 to 11.3.1.5). Best possible method detection limits are typically in the order of 0.1 ppb for 1,3-butadiene and 0.05 ppb for volatile aromatics such as benzene for 14-day monitoring. However, actual detection limits will depend upon the analytical conditions selected.

TABLE 12.1—VALIDATED SORBENTS AND UPTAKE RATES (ML/MIN) FOR SELECTED CLEAN AIR ACT COMPOUNDS

Compound	**Carbopack™ X**[a]	**Carbograph™1 TD**	**Carbopack™ B**
1,1-Dichloroethene	0.57 ±0.14	not available	not available.
3-Chloropropene	0.51 ±0.3	not available	not available.
1,1-Dichloroethane	0.57 ±0.1	not available	not available.
1,2-Dichloroethane	0.57 ±0.08	not available	not available.
1,1,1-Trichloroethane	0.51 ±0.1	not available	not available.
Benzene	0.67 ±0.06	0.63 ±0.07[b]	0.63 ±0.07[b].
Carbon tetrachloride	0.51 ±0.06	not available	not available.
1,2-Dichloropropane	0.52 ±0.1	not available	not available.
Trichloroethene	0.5 ±0.05	not available	not available.
1,1,2-Trichloroethane	0.49 ±0.13	not available	not available.
Toluene	0.52 ±0.14	0.56 ±0.06[c]	0.56 ±0.06[c].
Tetrachloroethene	0.48 ±0.05	not available	not available.
Chlorobenzene	0.51 ±0.06	not available	not available.
Ethylbenzene	0.46 ±0.07	not available	0.50[c].
m,p-Xylene	0.46 ±0.09	0.47 ±0.04[c]	0.47 ±0.04[c].
Styrene	0.5 ±0.14	not available	not available.

o-Xylene	0.46 ±0.12	0.47 ±0.04[c]	0.47 ±0.04[c].
p-Dichlorobenzene	0.45 ±0.05	not available	not available.

[a] Reference 3, McClenny, J. Environ. Monit. 7:248-256. Based on 24-hour duration.

[b] Reference 24, BS EN 14662-4:2005 (incorporated by reference—see §63.14). Based on 14-day duration.

[c] Reference 25, ISO 16017-2:2003(E) (incorporated by reference—see §63.14). Based on 14-day duration.

13.0 METHOD PERFORMANCE

The performance of this procedure for VOC not listed in Table 12.1 is determined using the procedure in Addendum A of this Method or by one of the following national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14).

13.1 The valid range for measurement of VOC is approximately 0.5 $\mu g/m^3$ to 5 mg/m^3 in air, collected over a 14-day sampling period. The upper limit of the useful range depends on the split ratio selected (Section 11.3.1) and the dynamic range of the analytical system. The lower limit of the useful range depends on the noise from the analytical instrument detector and on the blank level of target compounds or interfering compounds on the sorbent tube (see Section 13.3).

13.2 Diffusive sorbent tubes compatible with passive sampling and thermal desorption methods have been evaluated at relatively high atmospheric concentrations (*i.e.*, mid-ppb to ppm) and published for use in workplace air and industrial/mobile source emissions (References 15-16, 21-22).

13.3 Best possible detection limits and maximum quantifiable concentrations of air pollutants range from sub-part-per-trillion (sub-ppt) for halogenated species such as CCl4 and the freons using an electron capture detector (ECD), SIM Mode GC/MS, triple quad MS or GC/TOF MS to sub-ppb for volatile hydrocarbons collected over 72 hours followed by analysis using GC with quadrupole MS operated in the full SCAN mode.

13.3.1 Actual detection limits for atmospheric monitoring vary depending on several key factors. These factors are:

- Minimum artifact levels.
- GC detector selection.
- Time of exposure for passive sorbent tubes.
- Selected analytical conditions, particularly column resolution and split ratio.

14.0 POLLUTION PREVENTION

This method involves the use of ambient concentrations of gaseous compounds that post little or no danger of pollution to the environment.

15.0 WASTE MANAGEMENT

Dispose of expired calibration solutions as hazardous materials. Exercise standard laboratory environmental practices to minimize the use and disposal of laboratory solvents.

16.0 REFERENCES

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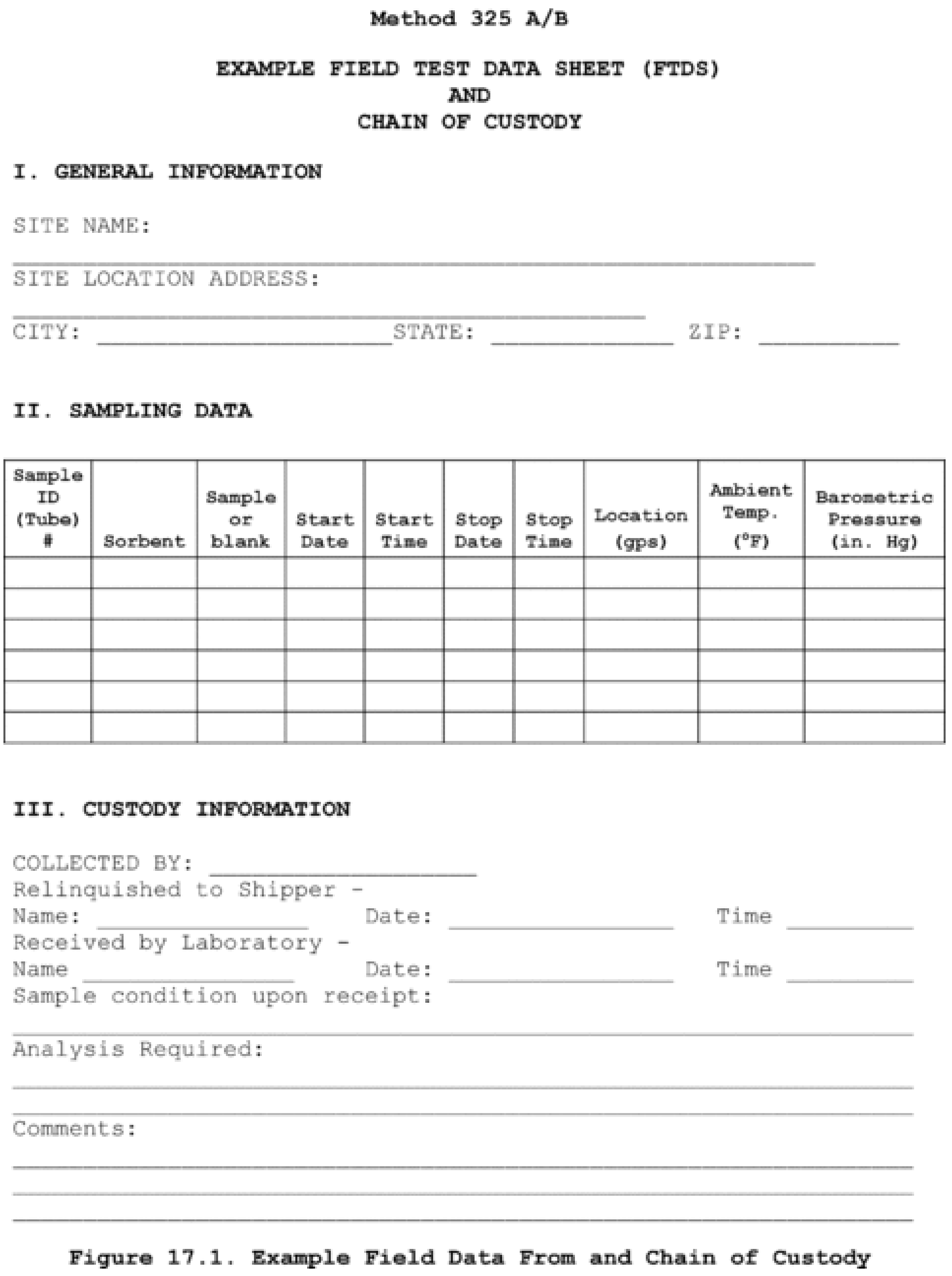
17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA>

TABLE 17.1—SUMMARY OF GC/MS ANALYSIS QUALITY CONTROL PROCEDURES

Parameter	**Frequency**	**Acceptance criteria**	**Corrective action**
Bromofluorobenzene Instrument Tune Performance Check	Daily[a] prior to sample analysis	Evaluation criteria presented in Section 9.5 and Table 9.2	(1) Retune and or (2) Perform Maintenance.
Five point calibration bracketing the expected sample concentration	Following any major change, repair or maintenance or if daily CCV does not meet method requirements. Recalibration not to exceed three months	(1) Percent Deviation (%DEV) of response factors ±30% (2) Relative Retention Times (RRTs) for target peaks ±0.06 units from mean RRT	(1) Repeat calibration sample analysis. (2) Repeat linearity check. (3) Prepare new calibration standards as necessary and repeat analysis.
Calibration Verification (CCV Second source calibration verification check)	Following the calibration curve	The response factor ±30% DEV from calibration curve average response factor	(1) Repeat calibration check. (2) Repeat calibration curve.
Laboratory Blank Analysis	Daily[a] following bromofluoro benzene and calibration check; prior to sample analysis	(1) ≤0.2 ppbv per analyte or ≤3 times the LOD, whichever is greater (2) Internal Standard (IS) area response ±40% and IS Retention Time (RT) ±0.33 min. of most recent calibration check	(1) Repeat analysis with new blank tube. (2) Check system for leaks, contamination. (3) Analyze additional blank.

Blank Sorbent Tube Certification	One tube analyzed for each batch of tubes cleaned or 10 percent of tubes whichever is greater	<0.2 ppbv per VOC targeted compound or 3 times the LOD, whichever is greater	Re-clean all tubes in batch and reanalyze.
Samples—Internal Standards	All samples	IS area response ±40% and IS RT ±0.33 min. of most recent calibration validation	Flag Data for possible invalidation.
Field Blanks	Two per sampling period	No greater than one-third of the measured target analyte or compliance limit	Flag Data for possible invalidation due to high blank bias.

[a] Every 24 hours.



Method 325 A/B

EXAMPLE FIELD TEST DATA SHEET (FTDS)
AND
CHAIN OF CUSTODY

I. GENERAL INFORMATION

SITE NAME: ____

SITE LOCATION ADDRESS: ____

CITY: _____________________STATE: _____________ ZIP: __________

II. SAMPLING DATA

Sample ID (Tube) #	Sorbent	Sample or blank	Start Date	Start Time	Stop Date	Stop Time	Location (gps)	Ambient Temp. (°F)	Barometric Pressure (in. Hg)

III. CUSTODY INFORMATION

COLLECTED BY: ___________________
Relinquished to Shipper -
Name: ________________ Date: ________________ Time _________
Received by Laboratory -
Name ________________ Date: ________________ Time _________
Sample condition upon receipt: ____

Analysis Required: ____
____

Comments: ____
____
____

Figure 17.1. Example Field Data From and Chain of Custody

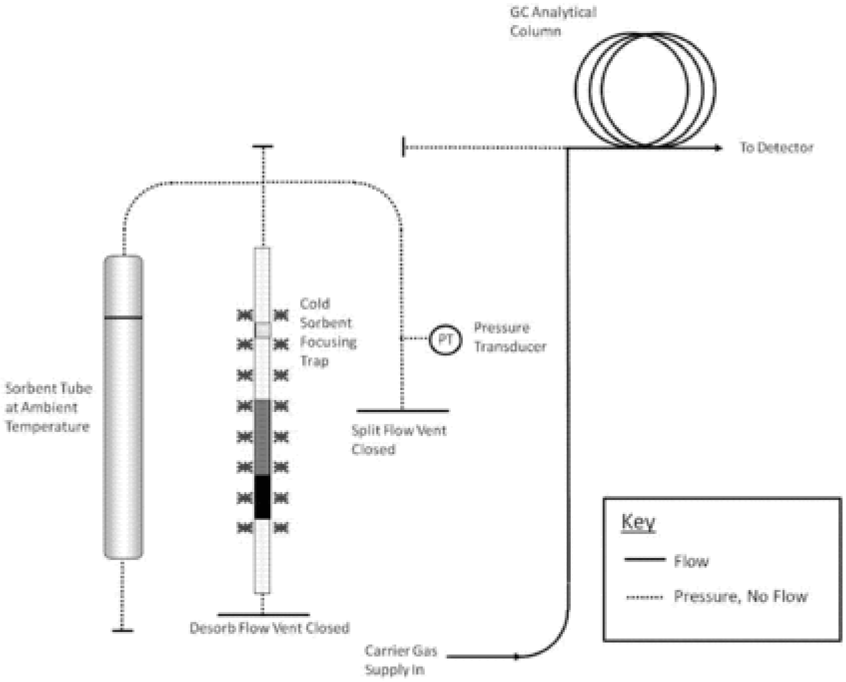


Figure 17.2. Schematic of Thermal Desorption Flow Path During Leak Testing

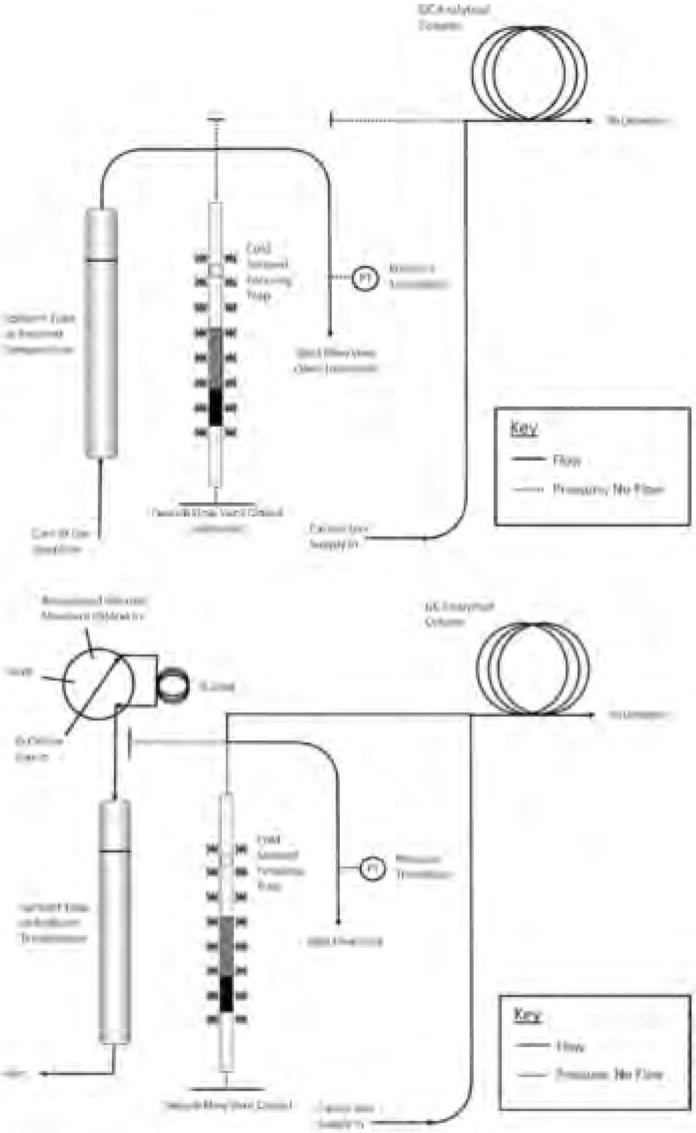


Figure 17.3. Schematic of Thermal Desorption Flow During Purge of Air (Top) and Addition of IS Gas to the Sorbent Tube (Bottom)

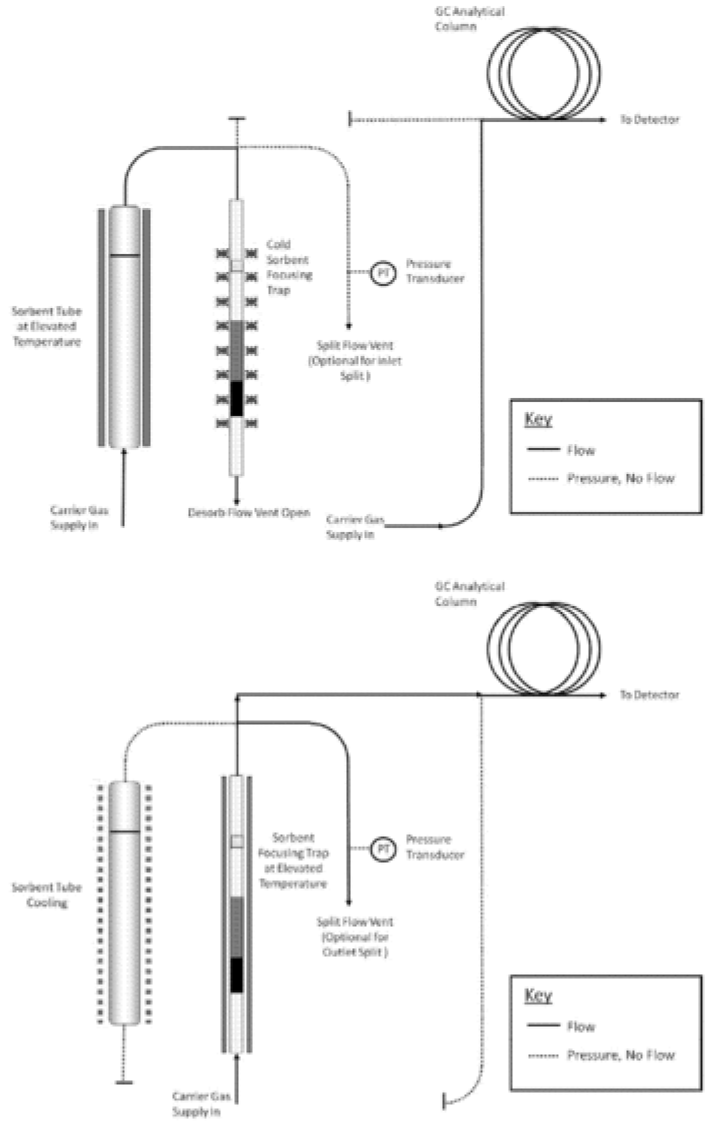


Figure 17.4. Schematic of Thermal Desorption Flow Path During Primary (Tube) Desorption (Top) and Secondary (Trap) Desorption and Transfer to the GC (Bottom)

ADDENDUM A to Method 325B—Method 325 Performance Evaluation

A.1 SCOPE AND APPLICATION

A.1.1 To be measured by Methods 325A and 325B, each new target volatile organic compound (VOC) or sorbent that is not listed in Table 12.1 must be evaluated by exposing the selected sorbent tube to a known concentration of the target compound(s) in an exposure chamber following the procedure in this Addendum or by following the procedures in the national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14), or reported in peer-reviewed open literature.

A.1.2 You must determine the uptake rate and the relative standard deviation compared to the theoretical concentration of volatile material in the exposure chamber for each of the tests required in this method. If data that meet the requirement of this Addendum are available in the peer reviewed open literature for VOCs of interest collected on your passive sorbent tube configuration, then such data may be submitted in lieu of the testing required in this Addendum.

A.1.3 You must expose sorbent tubes in a test chamber to parts per trillion by volume (pptv) and low parts per billion by volume (ppbv) concentrations of VOCs in humid atmospheres to determine the sorbent tube uptake rate and to confirm compound capture and recovery.

A.2 SUMMARY OF METHOD

NOTE: The technique described here is one approach for determining uptake rates for new sorbent/sorbate pairs. It is equally valid to follow the techniques described in any one of the following national/international standards methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14).

A.2.1 Known concentrations of VOC are metered into an exposure chamber containing sorbent tubes filled with media selected to capture the volatile organic compounds of interest (see Figure A.1 and A.2 for an example of the exposure chamber and sorbent tube retaining rack). VOC are diluted with humid air and the chamber is allowed to equilibrate for 6 hours. Clean passive sampling devices are placed into the chamber and exposed for a measured period of time. The passive uptake rate of the passive sampling devices is determined using the standard and dilution gas flow rates. Chamber concentrations are confirmed with whole gas sample collection and analysis or direct interface volatile organic compound measurement methods.

A.2.2 An exposure chamber and known gas concentrations must be used to challenge and evaluate the collection and recovery of target compounds from the sorbent and tube selected to perform passive measurements of VOC in atmospheres.

A.3 DEFINITIONS

A.3.1 *cc* is cubic centimeter.

A.3.2 *ECD* is electron capture detector.

A.3.3 *FID* is flame ionization detector.

A.3.4 *LED* is light-emitting diode.

A.3.5 *MFC* is mass flow controller.

A.3.6 *MFM* is mass flow meter.

A.3.7 *min* is minute.

A.3.8 *ppbv* is parts per billion by volume.

A.3.9 *ppmv* is parts per million by volume.

A.3.10 *PSD* is passive sampling device.

A.3.11 *psig* is pounds per square inch gauge.

A.3.12 *RH* is relative humidity.

A.3.13 *VOC* is volatile organic compound.

A.4 INTERFERENCES

A.4.1 VOC contaminants in water can contribute interference or bias results high. Use only distilled, organic-free water for dilution gas humidification.

A.4.2 Solvents and other VOC-containing liquids can contaminate the exposure chamber. Store and use solvents and other VOC-containing liquids in the exhaust hood when exposure experiments are in progress to prevent the possibility of contamination of VOCs into the chamber through the chamber's exhaust vent.

NOTE: Whenever possible, passive sorbent evaluation should be performed in a VOC free laboratory.

A.4.3 PSDs should be handled by personnel wearing only clean, white cotton or powder free nitrile gloves to prevent contamination of the PSDs with oils from the hands.

A.4.4 This performance evaluation procedure is applicable to only volatile materials that can be measured accurately with direct interface gas chromatography or whole gas sample collection, concentration and analysis. Alternative methods to confirm the concentration of volatile materials in exposure chambers are subject to Administrator approval.

A.5 SAFETY

A.5.1 This procedure does not address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate field and laboratory safety and health practices and determine the applicability of regulatory limitations prior to use.

A.5.2 Laboratory analysts must exercise appropriate care in working with high-pressure gas cylinders.

A.6 EQUIPMENT AND SUPPLIES

A.6.1 You must use an exposure chamber of sufficient size to simultaneously expose a minimum of eight sorbent tubes.

A.6.2 Your exposure chamber must not contain VOC that interfere with the compound under evaluation. Chambers made of glass and/or stainless steel have been used successfully for measurement of known concentration of selected VOC compounds.

A.6.3 The following equipment and supplies are needed:

- Clean, white cotton or nitrile gloves;
- Conditioned passive sampling device tubes and diffusion caps; and
- NIST traceable high resolution digital gas mass flow meters (MFMs) or flow controllers (MFCs).

A.7 REAGENTS AND STANDARDS

A.7.1 You must generate an exposure gas that contains between 35 and 75 percent relative humidity and a concentration of target compound(s) within 2 to 5 times the concentration to be measured in the field.

A.7.2 Target gas concentrations must be generated with certified gas standards and diluted with humid clean air. Dilution to reach the desired concentration must be done with zero grade air or better.

A.7.3 The following reagents and standards are needed:

- Distilled water for the humidification;
- VOC standards mixtures in high-pressure cylinder certified by the supplier (NOTE: The accuracy of the certified standards has a direct bearing on the accuracy of the measurement results. Typical vendor accuracy is ±5 percent accuracy but some VOC may only be available at lower accuracy (*e.g.*, acrolein at 10 percent)); and
- Purified dilution air containing less than 0.2 ppbv of the target VOC.

A.8 SAMPLE COLLECTION, PRESERVATION AND STORAGE

A.8.1 You must use certified gas standards diluted with humid air. Generate humidified air by adding distilled organic free water to purified or zero grade air. Humidification may be accomplished by quantitative addition of water to the air dilution gas stream in a heated chamber or by passing purified air through a humidifying bubbler. You must control the relative humidity in the test gas throughout the period of passive sampler exposure.

NOTE: The RH in the exposure chamber is directly proportional to the fraction of the purified air that passes through the water in the bubbler before entering the exposure chamber. Achieving uniform humidification in the proper range is a trial-and-error process with a humidifying bubbler. You may need to heat the bubbler to achieve sufficient humidity. An equilibration period of approximately 15 minutes is required following each adjustment of the air flow through the humidifier. Several adjustments or equilibration cycles may be required to achieve the desired RH level.

NOTE: You will need to determine both the dilution rate and the humidification rate for your design of the exposure chamber by trial and error before performing method evaluation tests.

A.8.2 Prepare and condition sorbent tubes following the procedures in Method 325B Section 7.0.

A.8.3 You must verify that the exposure chamber does not leak.

A.8.4 You must complete two evaluation tests using a minimum of eight passive sampling tubes in each test with less than 5-percent depletion of test analyte by the samplers.

A.8.4.1 Perform at least one evaluation at two to five times the estimated analytical detection limit or less.

A.8.4.2 Perform second evaluation at a concentration equivalent to the middle of the analysis calibration range.

A.8.5 You must evaluate the samplers in the test chamber operating between 35 percent and 75 percent RH, and at 25 ±5 °C. Allow the exposure chamber to equilibrate for 6 hours before starting an evaluation.

A.8.6 The flow rate through the chamber must be ≤0.5 meter per second face velocity across the sampler face.

A.8.7 Place clean, ready to use sorbent tubes into the exposure chamber for predetermined amounts of time to evaluate collection and recovery from the tubes. The exposure time depends on the concentration of volatile test material in the chamber and the detection limit required for the sorbent tube sampling application. Exposure time should match sample collection time. The sorbent tube exposure chamber time may not be less than 24 hours and should not be longer than 2 weeks.

A.8.7.1 To start the exposure, place the clean PSDs equipped with diffusion caps on the tube inlet into a retaining rack.

A.8.7.2 Place the entire retaining rack inside the exposure chamber with the diffusive sampling end of the tubes facing into the chamber flow. Seal the chamber and record the exposure start time, chamber RH, chamber temperature, PSD types and numbers, orientation of PSDs, and volatile material mixture composition (see Figure A.2).

A.8.7.3 Diluted, humidified target gas must be continuously fed into the exposure chamber during cartridge exposure. Measure the flow rate of target compound standard gas and dilution air to an accuracy of 5 percent.

A.8.7.4 Record the time, temperature, and RH at the beginning, middle, and end of the exposure time.

A.8.7.5 At the end of the exposure time, remove the PSDs from the exposure chamber. Record the exposure end time, chamber RH, and temperature.

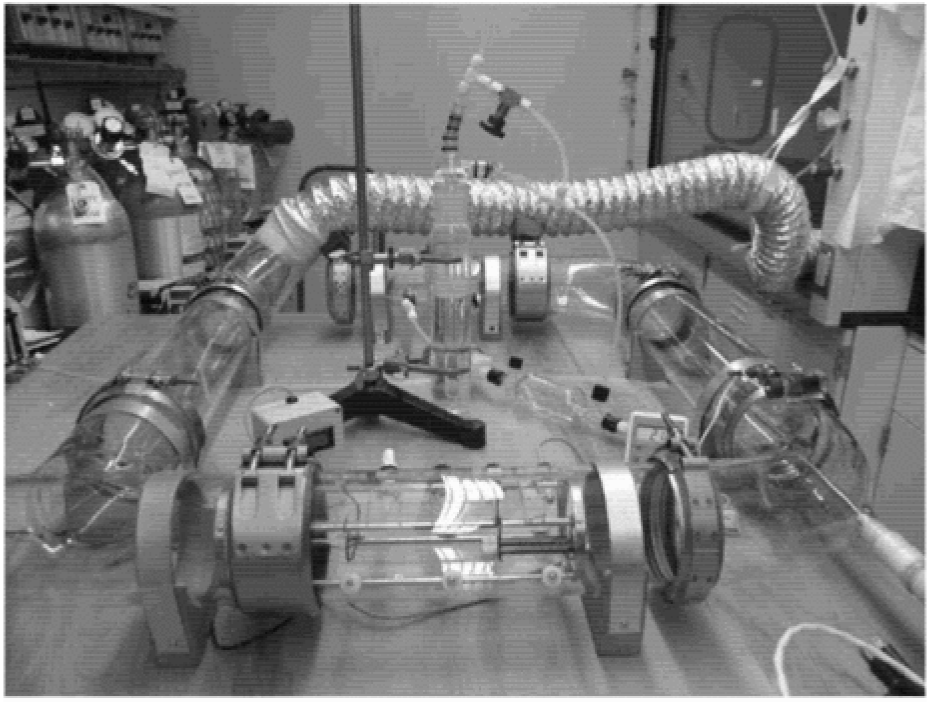
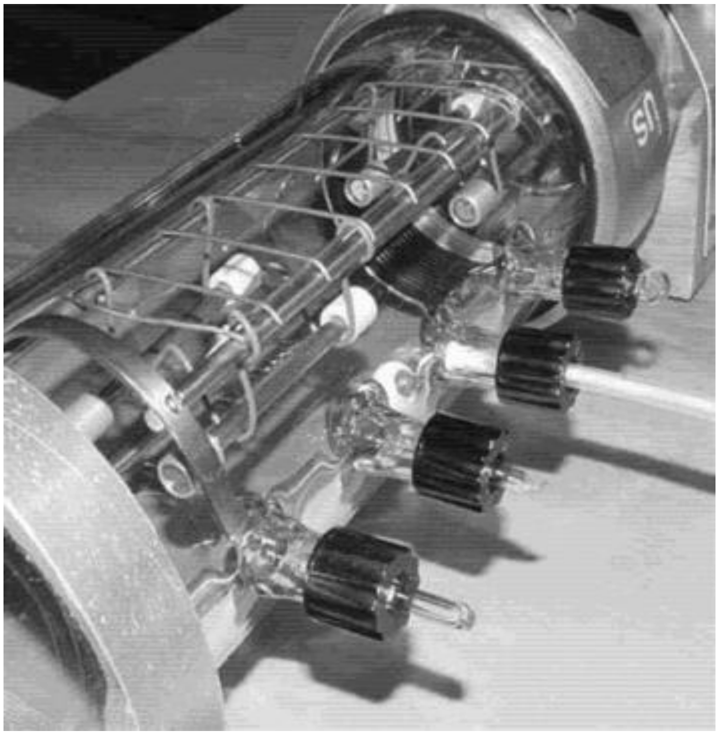


Figure A.1. Example Sorbent Tube Exposure Chamber



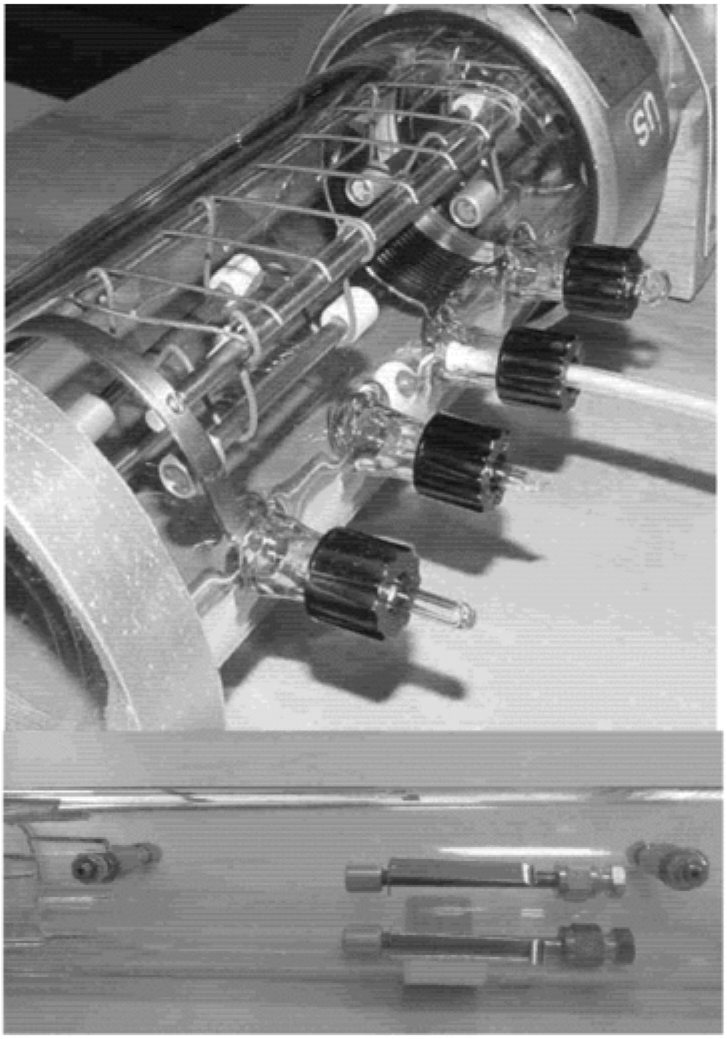


Figure A.2. Example Tube Retaining Rack in Exposure Chamber

A.9 QUALITY CONTROL

A.9.1 Monitor and record the exposure chamber temperature and RH during PSD exposures.

A.9.2 Measure the flow rates of standards and purified humified air immediately following PSD exposures.

A.10 CALIBRATION AND STANDARDIZATION

A.10.1 Follow the procedures described in Method 325B Section 10.0 for calibration.

A.10.2 Verify chamber concentration by direct injection into a gas chromatograph calibrated for the target compound(s) or by collection of an integrated SUMMA canister followed by analysis using a preconcentration gas chromatographic method such as EPA Compendium Method TO-15, Determination of VOCs in Air Collected in Specially-Prepared Canisters and Analyzed By GC/MS.

A.10.2.1 To use direct injection gas chromatography to verify the exposure chamber concentration, follow the procedures in Method 18 of 40 CFR part 60, Appendix A-6. The method ASTM D6420-99 (Reapproved 2010) (incorporated by reference—see §63.14) is an acceptable alternative to EPA Method 18 of 40 CFR part 60).

NOTE: Direct injection gas chromatography may not be sufficiently sensitive for all compounds. Therefore, the whole gas preconcentration sample and analysis method may be required to measure at low concentrations.

A.10.2.2 To verify exposure chamber concentrations using SUMMA canisters, prepare clean canister(s) and measure the concentration of VOC collected in an integrated SUMMA canister over the period used for the evaluation (minimum 24 hours). Analyze the TO-15 canister sample following EPA Compendium Method TO-15.

A.10.2.3 Compare the theoretical concentration of volatile material added to the test chamber to the measured concentration to confirm the chamber operation. Theoretical concentration must agree with the measured concentration within 30 percent.

A.11 ANALYSIS PROCEDURE

Analyze the sorbent tubes following the procedures described in Section 11.0 of Method 325B.

A.12 RECORDKEEPING PROCEDURES FOR SORBENT TUBE EVALUATION

Keep records for the sorbent tube evaluation to include at a minimum the following information:

A.12.1 Sorbent tube description and specifications.

A.12.2 Sorbent material description and specifications.

A.12.3 Volatile analytes used in the sampler test.

A.12.4 Chamber conditions including flow rate, temperature, and relative humidity.

A.12.5 Relative standard deviation of the sampler results at the conditions tested.

A.12.6 95 percent confidence limit on the sampler overall accuracy.

A.12.7 The relative accuracy of the sorbent tube results compared to the direct chamber measurement by direct gas chromatography or SUMMA canister analysis.

A.13 METHOD PERFORMANCE

A.13.1 Sorbent tube performance is acceptable if the relative accuracy of the passive sorbent sampler agrees with the active measurement method by ±10 percent at the 95 percent confidence limit and the uptake ratio is equal to greater than 0.5 mL/min (1 ng/ppm-min).

NOTE: For example, there is a maximum deviation comparing Perkin-Elmer passive type sorbent tubes packed with Carbopack^{TM} X of 1.3 to 10 percent compared to active sampling using the following uptake rates.

	1,3-butadiene uptake rate mL/min	**Estimated detection limit (2 week)**	**Benzene uptake rates mL/min**	**Estimated detection limit (2 week)**
Carbopack^{TM} X (2 week)	0.61 ±0.11[a]	0.1 ppbv	0.67[a]	0.05 ppbv

[a] McClenny, W.A., K.D. Oliver, H.H. Jacumin, Jr., E.H. Daughtrey, Jr., D.A. Whitaker. 2005. 24 h diffusive sampling of toxic VOCs in air onto Carbopack^{TM} X solid adsorbent followed by thermal desorption/GC/MS analysis—laboratory studies. J. Environ. Monit. 7:248-256.

A13.2 Data Analysis and Calculations for Method Evaluation

A.13.2.1 Calculate the theoretical concentration of VOC standards using Equation A.1.

$$C_f = \left[\frac{FR_i}{FR_t + FR_a}\right] \times C_s \qquad \text{Eq. A.1}$$

Where:

C_f = The final concentration of standard in the exposure chamber (ppbv).

FR_i = The flow rate of the target compound I (mL/min).

FR_t = The flow rate of all target compounds from separate if multiple cylinders are used (mL/min).

FR_a = The flow rate of dilution air plus moisture (mL/min).

C_s = The concentration of target compound in the standard cylinder (parts per million by volume).

A.13.2.3 Determine the uptake rate of the target gas being evaluated using Equation A.2.

$$U = \frac{M_x}{C_e \times T_t} \qquad \text{Eq. A.2}$$

Where:

M_X = The mass of analyte measured on the sampling tube (ηg).

C_e = The theoretical exposure chamber concentration (ηg/mL).

T_t = The exposure time (minutes).

A.13.2.4 Estimate the variance (relative standard deviation (RSD)) of the inter-sampler results at each condition tested using Equation A.3. RSD for the sampler is estimated by pooling the variance estimates from each test run.

$$S^2 = \sum_i^n \frac{\left(X_i - \overline{X}\right)^2}{n-1} \qquad \text{Eq. A.3}$$

Where:

X_i = The measured mass of analyte found on sorbent tube *i*.

X_i = The mean value of all X_i.

n = The number of measurements of the analyte.

A.13.2.4 Determine the percent relative standard deviation of the inter-sampler results using Equation A.4.

$$\%RSD_x = 100 \times \frac{\sqrt{S^2}}{\overline{X}} \qquad \text{Eq. A.4}$$

A.13.2.5 Determine the 95 percent confidence interval for the sampler results using Equation A.5. The confidence interval is determined based on the number of test runs performed to evaluate the sorbent tube and sorbent combination. For the minimum test requirement of eight samplers tested at two concentrations, the number of tests is 16 and the degrees of freedom are 15.

$$\varDelta_{95\%} = \frac{\%RSD \times t_{0.95} \times f}{\sqrt{n}} \qquad \text{Eq. A.5}$$

Where:

$\Delta_{95\%}$ = 95 percent confidence interval.

%RSD = percent relative standard deviation.

$t_{0.95}$ = The Students t statistic for f degrees of freedom at 95 percent confidence.

f = The number of degrees of freedom.

n = Number of samples.

A.13.2.6 Determine the relative accuracy of the sorbent tube combination compared to the active sampling results using Equation A.6.

$$RA = \overline{X_i} - \overline{X_A} \pm \varDelta_{95\%} \qquad \text{Eq. A.6}$$

Where:

RA = Relative accuracy.

X_i = The mean value of all X_i.

X_i = The average concentration of analyte measured by the active measurement method.

$\Delta_{95\%}$ = 95 percent confidence interval.

A.14 POLLUTION PREVENTION

This method involves the use of ambient concentrations of gaseous compounds that post little or no pollution to the environment.

A.15 WASTE MANAGEMENT

Expired calibration solutions should be disposed of as hazardous materials.

A.16 REFERENCES

1. ISO TC 146/SC 02 N 361 Workplace atmospheres—Protocol for evaluating the performance of diffusive samplers.

EXHIBIT 7

Analysis of Refinery Chemical Emissions and Health Effects

March 2019

Office of Environmental Health
Hazard Assessment

California Environmental Protection Agency

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[1] The authors would like to acknowledge the contributions of Ms. Lilian Polsky in editing this document.

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PREFACE

The Office of Environmental Health Hazard Assessment (OEHHA) has collaborated with the California Air Resources Board (CARB) and the Interagency Refinery Task Force to develop information on chemicals emitted from refineries and their health effects. This information can support CARB and other groups in developing plans for air monitoring in the vicinity of refineries in California. In the event of a refinery emergency, knowledge of health guidance values and emissions of chemicals can also help emergency responders characterize potential health effects that may occur following a chemical release.

In August 2012, there was a serious fire at the Chevron Refinery in Richmond, CA. During that event, an estimated 15,000 people from the nearby community sought care at local emergency departments and clinics. Follow-up investigations of the incident revealed a number of refinery safety issues. In July 2013, CARB released a report entitled “Air Monitoring for Accidental Refinery Releases: Assessment of Capabilities and Potential Improvements Project Plan.” This report laid out a stepwise plan to improve California’s refinery air monitoring and emergency response system.

In February 2014, Governor Brown issued a report titled “Improving Public and Worker Safety at Oil Refineries,” which echoed the importance of monitoring air quality near refineries and resulted in the establishment of the Interagency Refinery Task Force coordinated by the California Environmental Protection Agency (CalEPA). In public meetings following the release of the governor’s report, community members asked if a complete list of chemicals that could be released from refineries existed, and if those chemicals had been prioritized for monitoring to ensure that monitoring systems would be tailored—insofar as feasible—to measure the most important chemicals.

As a result of these questions from the public, OEHHA compiled the information in this report. The report presents as comprehensive a list of chemicals as possible using existing data sources, and then prioritizes the chemicals according to their emissions and toxicity. This report does not attempt to estimate exposure or risk in communities.

OEHHA released a draft of this report in September 2017, while CARB concurrently released a draft report titled *Refinery Emergency Air Monitoring Assessment Report. Objective 2: Evaluation of Air Monitoring Capabilities, Gaps and Potential Enhancements.* OEHHA, CARB, and CalEPA participated in a series of workshops throughout California in 2018 to receive feedback on the reports. During the workshops, OEHHA did not receive any comments on its report that necessitated any changes or additions. The final OEHHA report is now being released. This report offers a useful compendium of information to assist local air districts and communities as they make decisions about air monitoring, emergency response, and other efforts related to refinery chemicals and public health.

EXECUTIVE SUMMARY

Introduction

The Office of Environmental Health Hazard Assessment (OEHHA), in collaboration with the California Air Resources Board (CARB) and the California Environmental Protection Agency's (CalEPA) Interagency Refinery Task Force, has developed information on chemicals emitted from refineries, and their health effects. This information may assist CARB, local air districts, and communities in developing plans for air monitoring at refineries in California. In the event of a refinery emergency, this information may also help emergency responders characterize the potential health effects that may occur following a chemical release.

OEHHA has compiled a list of 188 chemicals that have been reported to be emitted from California refineries. This list can assist the CARB in identifying candidate chemicals for potential air monitoring near refineries.

OEHHA created this list of chemicals based on:

- Data on routine releases of toxic air contaminants from California refineries reported to CARB during the years 2009-2012 and 2014.
- Data on routine and non-routine emissions from California refineries reported to the US Environmental Protection Agency (US EPA) as part of a data call-in in 2010.
- Publicly available data in government reports, internet databases, and peer-reviewed journal articles.

The presence of a chemical on this list does not necessarily mean it is released from all refineries, at all times, or in significant quantities. Nor does it indicate the chemical's degree of toxicity.

For these reasons, OEHHA took steps to screen the list of 188 chemicals, based on exposure and toxicity potential.

Comparisons between high routine emissions of chemicals and health guidance values or emergency exposure levels that measure the toxicity of those chemicals may help determine which chemicals are appropriate for air monitoring, and may ultimately help protect communities surrounding these refineries by limiting exposures to those chemicals. To that end, OEHHA has performed some preliminary analyses of the compiled data. Measures of toxicity of individual chemicals included OEHHA's Reference Exposure Levels (RELs), Cancer Potency Factors (CPFs) and Unit Risk Values, No Significant Risk Levels and Maximum Allowable Dose Levels for chemicals on California's Proposition 65 list, and the US Environmental Protection Agency's (US EPA) Reference Concentrations (RfCs). In addition, OEHHA looked at US EPA's Acute Emergency Exposure Guidelines (AEGLs) and the National Institute for Occupational Safety and Health's (NIOSH) Immediately Dangerous to Life and Health (IDLH) values.

These health guidance values and toxicity designations were compared to routine and non-routine (including accidental) emissions from refineries, chemicals involved in previous incidents, and chemicals with involvement in the most refinery equipment or processes. Finally, US EPA toxicity-weighting factors were used in conjunction with routine emissions data to calculate toxicity-weighted emissions scores. The report also provides health and safety information for select candidate chemicals known to be emitted in high quantities from refineries in California, with the understanding that potential health effects are dependent on the extent and duration of exposure.

Toxicity: Health Guidance Values and Toxicity Designations for the General Population

OEHHA and other agencies develop health guidance values for cancer and noncancer endpoints, to guide regulatory agencies like CARB in taking actions that protect the general public from the effects of possible toxic chemical exposures. In general, the health guidance value for an airborne pollutant is the air concentration of the chemical that is not likely to cause adverse health outcomes in humans, including sensitive subgroups, for the specified exposure duration.

After compiling the list of chemicals emitted from California refineries, OEHHA determined which chemicals had health guidance values. Specific types of health guidance values included in our analysis are described below. Any one chemical may have multiple types of health guidance values.

OEHHA determines Reference Exposure Levels (RELs) for airborne chemicals as required by California's Air Toxics 'Hot Spots' Program. The REL assessments identify human systems (e.g. the respiratory system) or organs that could be affected by the noncancer effects of the chemicals. These RELs can cover three types of exposure durations: acute (for infrequent 1-hour exposure), 8-hour (for repeated 8-hour exposures), and chronic (for continuous long-term exposure). OEHHA determined which refinery chemicals from the list of 188 had each of these RELs. OEHHA found that 67 chemicals have at least one REL and some of these have more than one REL. Forty chemicals have an acute REL, 10 have an 8-hour REL, and 62 have a chronic REL. OEHHA found that there are RELs for all the listed chemicals with combined releases of greater than 10,000 pounds per year across all refineries in California.

US EPA also establishes noncancer health guidance values referred to as Reference Concentrations (RfCs) for air contaminants. US EPA RfCs are developed using a different risk assessment methodology, and therefore may be different from OEHHA's RELs. OEHHA identified 48 chemicals found in refinery emissions with RfC values, of which nine do not have RELs. Overall, 109 of the 188 chemicals reported to be released from California refineries were determined to have at least one REL or RfC.

OEHHA develops Cancer Potency Factors (CPF) and Unit Risk Factors (URF) for the Air Toxics 'Hot Spots' program to address the carcinogenic effects of chemicals. These values are applied to measured or modeled airborne chemical concentrations to estimate the cancer risks to an exposed population. Of the 188 refinery chemicals on the list, OEHHA identified 70 chemicals that have CPFs, and 57 that have URFs.

For each chemical in the refinery chemical list, OEHHA noted whether it was also on the Proposition 65 list for cancer or reproductive toxicity. Of the 188 chemicals on the list, 54 are listed under Proposition 65 as carcinogens with No Significant Risk Levels, 21 are listed for developmental effects, and 13 are listed for effects on the male or female reproductive system with a Maximum Allowable Dose Level.

Overall, 46 of the listed chemicals have none of the types of health guidance values described here; however, the absence of health guidance values does not necessarily mean that the chemicals are not hazardous.

Refinery accidents, if they occur, may release high concentrations of chemicals into the air. Therefore, in accident scenarios where high concentrations of chemicals are measured or estimated in the air, it can be appropriate to reference *emergency exposure levels*. These levels are designed to evaluate risks during emergencies related to emergency-response worker exposure. They are *not* applicable in evaluating exposures for the general public or sensitive populations such as children and the elderly.

Emergency exposure levels can help emergency responders evaluate the immediate dangers from such chemical releases. OEHHA identified which chemicals from the list have emergency exposure levels using Acute Exposure Guideline Levels (AEGL) and Immediately Dangerous to Life and Health (IDLH) values. AEGLs are developed by US EPA, and IDLH values are developed by the National Institute for Occupational Safety and Health. Of the 188 chemicals on the list, 94 chemicals have at least one of these two emergency exposure levels. The absence of emergency exposure levels does not necessarily mean that these chemicals are not hazardous.

Most Highly Emitted Chemicals and Other Supporting Information

OEHHA investigated publicly available data on California’s refinery incident history and the process units or equipment associated with such incidents. For the years 2001-2012, OEHHA found reports on 127 incidents. Flares were the most common category/source of incidents that resulted in emissions to outdoor air. The term “smoke” (from explosion, fire, or flares) was associated with the highest number of incidents (63) reported during that period. The most frequently cited chemicals are included on the candidate list for air monitoring provided below: benzene, 1,3-butadiene, hydrogen fluoride, hydrogen sulfide, particulate matter (PM), sulfur dioxide, sulfuric acid, toluene, and hydrocarbons (not otherwise specified).

All California refineries active during the year 2010 were required to measure air emissions from each of their process or emission points for a certain amount of time, and to submit this data to US EPA. OEHHA used these emissions inventories to identify the most commonly occurring processes along with their associated chemical emissions. A total of 20 processes were examined and chemicals involved in the most processes or equipment were considered for the candidate chemical list. The candidate chemicals released in the majority of processes were benzene, naphthalene, and toluene.

OEHHA collected information on routine and non-routine emissions from California refineries. One source of data on routine emissions came from the Assembly Bill 2588 Air Toxics 'Hot Spots' Program reported in the California Emission Inventory Development and Reporting System database (CEIDARS) for 2009-2012 and 2014.

The ten most frequently reported routine toxic air contaminant emissions from California refineries from 2009-2012 (starting with the highest) were:

- ammonia
- formaldehyde
- methanol
- sulfuric acid
- hydrogen sulfide
- toluene
- xylene
- benzene
- hexane
- hydrogen chloride

The average routine emissions for all chemicals reported in CEIDARS for California refineries for 2009-2012 in pounds per year are compiled in this report.

OEHHA also used additional data for routine and non-routine emissions of all pollutants (not just TACs) that California refineries reported to the US EPA for the year 2010 only. Using these data, OEHHA determined the most frequently emitted chemicals (starting with the highest) were:

- sulfur dioxide
- carbon monoxide
- nitrogen oxides
- PM_{10} and $PM_{2.5}$
- butane
- nitrogen dioxide
- propylene
- hexane

OEHHA totaled the amount of routine and non-routine emissions for all chemicals reported in this data set in the report.

Conclusions

Of the 188 chemicals identified as emitted from California refineries, the chemicals listed below are the top candidates for air monitoring, based on their toxicity, average levels of emissions from refineries statewide, and involvement in multiple refinery processes and incidences. OEHHA also derived a “toxicity-weighted” emissions score for each chemical for which emissions data were available for all refineries across California. OEHHA calculated the toxicity-weighted emissions scores using emissions data (pounds emitted per year) obtained from the Air Toxics ‘Hot Spots’ Emissions Inventory database (CEIDARS) for 2014, and a toxicity weight derived from US EPA’s Inhalation Toxicity Scores for individual chemicals. The candidate chemicals that had high calculated toxicity-weighted emissions are noted in the candidate list below with an asterisk (in alphabetical order).

These candidates for air monitoring were not further ranked or prioritized.

- acetaldehyde*
- ammonia*
- benzene*
- 1,3-butadiene*
- cadmium*
- diethanolamine*
- formaldehyde*
- hydrogen fluoride
- hydrogen sulfide*
- manganese*
- naphthalene*
- nickel*
- nitrogen oxide
- polycyclic aromatic hydrocarbons (PAH)*
- particulate matter (PM)
- sulfur dioxide
- sulfuric acid
- toluene

An important consideration for air monitoring at individual refineries is that the candidate chemicals will differ based on location as well as year. Some top-candidate chemicals are only released in small amounts from individual refineries.

Finally, the release of these chemicals from refineries does not necessarily mean that local communities face substantial exposures or significant health risks. However, it does increase their likelihood of exposure. Air monitoring of these chemicals may inform decisions that could reduce exposure.

I. INTRODUCTION

This report may assist the California Air Resources Board (CARB) in making decisions for the air monitoring of communities near refineries, and assist local air districts in selecting the most appropriate monitoring methods and tools when responding to future emergency releases. This report may inform statewide guidance and recommendations being developed by CARB and the California Air Pollution Control Officers Association (CAPCOA) as part of their joint effort to improve air monitoring near California's refineries.

CARB and CAPCOA initiated a statewide assessment of emergency air monitoring capabilities at California oil refineries in an effort to improve employee and public safety. CARB is collaborating with other members of the California Environmental Protection Agency's (CalEPA) Interagency Refinery Task Force (IRTF) to develop findings, recommendations, and proposed implementation measures for improving emergency air monitoring at refineries.

As part of this interagency collaboration, the Interagency Refinery Task Force asked the Office of Environmental Health Hazard Assessment (OEHHA) to assess the potential health effects of chemicals commonly emitted from California refineries and to provide specific regulatory and advisory health values for these chemicals. To this end, OEHHA first compiled an initial list of chemicals emitted from California refineries based on data for Toxic Air Contaminants (TACs)[1] reported in the California Emission Inventory Development and Reporting System (CEIDARS) database for all California refineries active from 2009 to 2012. Further data on California refinery chemicals, not limited to TACs, were provided by internet databases, publicly available data, government reports, and peer-reviewed journal articles. Upon completion of the refinery chemicals list, OEHHA researched chemical-specific information regarding health effects and advisory health standards. Information on chemical health effects was obtained from the OEHHA Reference Exposure Level (REL) web page, the US Environmental Protection Agency (US EPA) Integrated Risk Information System (IRIS) web page, and the Agency for Toxic Substances and Disease Registry (ATSDR) Toxic Substances Portal. Additional sources include the web pages for the National Institutes of Health (NIH) Hazardous Substances Data Bank (HSDB) and Toxicology Data Network (TOXNET), the Centers for Disease Control and Prevention (CDC) Emergency Preparedness and Response web page, the NIOSH Pocket Guide to Chemical Hazards, and the National Oceanic and Atmospheric Administration's (NOAA) Computer-Aided Management of Emergency Operations (CAMEO) Chemicals.

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[1] "Toxic air contaminants" are defined in California law as air pollutants which may cause or contribute to an increase in mortality or in serious illness, or which may pose a present or potential hazard to human health (Health and Safety Code section 39655)
URL to current list: https://www.arb.ca.gov/toxics/quickref.htm#TAC

II. LIST OF CHEMICALS EMITTED FROM CALIFORNIA REFINERIES

To create an initial list of chemicals that have been reported as emitted from California oil refineries, OEHHA obtained a list of TACs reported in the CEIDARS database from CARB for all California refineries active at any point during 2009 to 2012. These emissions data were reported in accordance with the Air Toxics Hot Spots Information and Assessment Act (AB 2588) and served as the foundation of OEHHA's list of refinery-emitted chemicals. Chemicals other than TACs were added to the list based on California refinery emissions data provided by US EPA. To identify other chemicals not included in the CEIDARS or US EPA datasets, OEHHA also performed a literature search and compiled information on refinery air monitoring and incidents in California. This search resulted in additional sources such as peer-reviewed journal articles, government reports such as Bay Area Air Quality Management District (BAAQMD) incident reports, and online databases such as the US Chemical Safety Board (CSB) Industrial Chemical Incident Screening Database and the list of major accidents at refineries reported by Contra Costa Health Services (CCHS). After the later release of CEIDARs data for 2014, OEHHA also examined and analyzed this dataset

The name and Chemical Abstracts Service Registry Number (CAS RN) of each chemical included in the initial list of California refinery chemicals are shown in Table 1 below. Some chemicals on this list are routinely emitted from refineries, others may be emitted only during incidents, and others may rarely be emitted.

Table 1. List of Chemicals Emitted from California Refineries

Chemical	CAS RN	Source[1]	Chemical	CAS RN	Source
Acenaphthene	83329	[1]	Carbon monoxide	630080	[2]
Acenaphthylene	208968	[1]	Carbon tetrachloride	56235	[1]
Acetaldehyde	75070	[1]	Carbonyl sulfide	463581	[2]
Acetone	67641	[2]	Chlorine	7782505	[1]
Acetylene	74862	[2]	Chlorobenzene	108907	[2]
Acrolein	107028	[1]	Chlorodifluoromethane	75456	[2]
Aluminum	7429905	[1]	Chloroform	67663	[1]
Ammonia	7664417	[1]	2-Chloronaphthalene	91587	[2]
Aniline	62533	[2]	Chromium	7440473	[2]
Anthracene	120127	[1]	Chromium (hexavalent & compounds)	18540299	[1]
Antimony	7440360	[2]	Chromium III (& compounds)	16065831	[2]
Arsenic	7440382	[2]	Chrysene	218019	[2]
Asbestos	1332214	[1]	Cobalt	7440484	[2]
Barium	7440393	[2]	Copper	7440508	[1]
Benz[a]anthracene	56553	[1]	Cresols (mixtures of)	1319773	[2]
Benzene	71432	[1]	m-Cresol	108394	[2]
Benzo[b]fluoranthene	205992	[1]	o-Cresol	95487	[2]
Benzo[j]fluoranthene	205823	[1]	p-Cresol	106445	[2]
Benzo[k]fluoranthene	207089	[1]	Cumene	98828	[2]
Benzo[g,h,i]perylene	191242	[1]	Cyclohexane	110827	[2]
Benzo[a]pyrene	50328	[1]	Cyclopentadiene	542927	[2]
Benzo[e]pyrene	192972	[1]	Cyclopentane	287923	[2]
Beryllium	7440417	[1]	Dibenz[a,h]anthracene	53703	[1]
Biphenyl	92524	[2]	Dibenzo-p-dioxins (chlorinated)	—	[1]
1,2-Butadiene	590192	[2]	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	35822469	[2]
1,3-Butadiene	106990	[2]	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	39227286	[2]
Butane	106978	[2]	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	57653857	[2]
1-Butene	106989	[2]	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	19408743	[2]
2-Butene	107017	[2]	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	3268879	[1]
Cadmium	7440439	[1]	1,2,3,7,8-Pentachlorodibenzo-p-dioxin	40321764	[2]

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[1] Sources: 1 Air Resources Board; 2 US EPA, 2012a; US EPA, 2012b; 3 Chemical Safety Board (CSB)

Chemical	CAS RN	Source[1]	Chemical	CAS RN	Source
Carbon disulfide	75150	[2]	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746016	[2]
Dibenzofuran	132649	[2]	Ethylene glycol monoethyl ether acetate	111159	[2]
Dibenzofurans (chlorinated)	1080	[1]	Fluoranthene	206440	[2]
1,2,3,4,6,7,8-Heptachlorodibenzofuran	67562394	[2]	Fluorene	86737	[2]
1,2,3,4,7,8,9-Heptachlorodibenzofuran	55673897	[2]	Formaldehyde	50000	[1]
1,2,3,4,7,8-Hexachlorodibenzofuran	70648269	[2]	Glutaraldehyde	111308	[2]
1,2,3,6,7,8-Hexachlorodibenzofuran	57117449	[2]	Glycol ethers (& acetates)	1115	[1]
1,2,3,7,8,9-Hexachlorodibenzofuran	72918219	[2]	Heptane	142825	[2]
2,3,4,6,7,8-Hexachlorodibenzofuran	60851345	[2]	Hexachloroethane	67721	[2]
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	39001020	[2]	Hexane	110543	[2]
1,2,3,7,8-Pentachlorodibenzofuran	57117416	[2]	Hydrogen	1333740	[3]
2,3,4,7,8-Pentachlorodibenzofuran	57117314	[2]	Hydrogen chloride	7647010	[1]
2,3,7,8-Tetrachlorodibenzofuran	51207319	[2]	Hydrogen cyanide	74908	[2]
Dibutyl phthalate	84742	[2]	Hydrogen fluoride	7664393	[1]
1,4-Dichlorobenzene	106467	[2]	Hydrogen sulfide	7783064	[1]
1,1-Dichloroethane	75343	[2]	Indeno[1,2,3-c,d]pyrene	193395	[2]
1,1-Dichloroethylene	75354	[2]	Isobutane	75285	[3]
1,2-Dichloropropane	78875	[1]	Isobutene	115117	[2]
1,3-Dichloropropene	542756	[1]	Isopentane	78784	[2]
Diesel engine exhaust	9901	[1]	Isoprene	78795	[2]
Diethanolamine	111422	[2]	Isopropanol	67630	[1]
Diethyl phthalate	84662	[2]	Lead	7439921	[2]
Di(2-ethylhexyl)phthalate	117817	[2]	Manganese	7439965	[2]
1,1-Dimethylallene	598254	[2]	Mercury	7439976	[2]
7,12-Dimethylbenz[a]anthracene	57976	[1]	Methane	74828	[2]
1,4-Dioxane	123911	[1]	Methanol	67561	[1]
Ethane	74840	[2]	Methyl bromide	74839	[2]
Ethyl chloride	75003	[2]	Methyl chloride	74873	[2]
Ethylbenzene	100414	[2]	Methyl chloroform	71556	[1]
Ethylene	74851	[1]	Methyl ethyl ketone	78933	[2]
Ethylene dibromide	106934	[2]	Methyl isobutyl ketone	108101	[2]
Ethylene dichloride	107062	[2]	Methyl tert-butyl ether	1634044	[2]
Ethylene glycol monoethyl ether	110805	[2]	3-Methylcholanthrene	56495	[2]

Chemical	CAS RN	Source[1]	Chemical	CAS RN	Source
Methylcyclohexane	108872	[2]	Propane	74986	[2]
Methylene chloride	75092	[2]	Propylene	115071	[2]
2-Methylnaphthalene	91576	[1]	Propylene glycol monomethyl ether	107982	[2]
Molybdenum	7439987	[2]	Propylene glycol monomethyl ether acetate	108656	[2]
Naphthalene	91203	[2]	Propylene glycol mono-t-butyl ether	57018527	[2]
Nickel	7440020	[2]	Propylene oxide	75569	[2]
Nitrogen dioxide	10102440	[2]	Pyrene	129000	[2]
Nitrogen oxides	—	[2]	Selenium (& compounds)	7782492	[1]
Nitrous oxide	10024972	[1]	Selenium sulfide	7488564	[2]
Octane	111659	[2]	Styrene	100425	[2]
PAHs, total, w/ individ. components reported	1150	[1]	Sulfur dioxide	7446095	[2]
PAHs, total, w/o individ. components reported	1151	[1]	Sulfur monoxide	13827322	[3]
1,2-Pentadiene	591957	[2]	Sulfur trioxide	744619	[3]
cis-1,3-Pentadiene	1574410	[2]	Sulfuric acid	766439	[1]
trans-1,3-Pentadiene	2004708	[2]	1,1,2,2-Tetrachloroethane	79345	[1]
1,4-Pentadiene	591935	[2]	Toluene	108883	[2]
2,3-Pentadiene	591968	[2]	1,1,2-Trichloroethane	79005	[1]
Pentane	109660	[2]	Trichloroethylene	79016	[2]
Perchloroethylene	127184	[2]	Trichlorofluoromethane	75694	[2]
Perylene	198550	[2]	1,1,2-Trichloro-1,2,2-trifluoroethane	76131	[2]
Phenanthrene	85018	[2]	Triethylamine	121448	[2]
Phenol	108952	[2]	Trimethylbenzene	25551137	[2]
Phosphoric acid	7664382	[1]	1,2,4-Trimethylbenzene	95636	[1]
Phosphorus	7723140	[1]	2,2,4-Trimethylpentane	540841	[2]
PM (condensable)	—	[2]	Vanadium	7440622	[1]
PM_{10}	—	[2]	Vinyl chloride	75014	[2]
PM_{10} (filterable)	—	[2]	Xylenes (mixed)	1330207	[2]
$PM_{2.5}$	—	[2]	m-Xylene	108383	[2]
$PM_{2.5}$ (filterable)	—	[2]	o-Xylene	95476	[2]
Polychlorinated biphenyls	1336363	[2]	p-Xylene	106423	[2]
Propadiene	463490	[2]	Zinc	7440666	[1]

~~[1] Air Resources Board; [2] US EPA, 2012a; US EPA, 2012b; [3] Chemical Safety Board (CSB)~~

III. HEALTH GUIDANCE AND EMERGENCY EXPOSURE VALUES

A. OEHHA and US EPA Health Guidance Values

The release of chemicals from refineries may potentially result in exposure to workers, bystanders (persons proximate to the refinery), and nearby communities. In the event of a refinery emergency, health guidance values can help responders characterize potential health effects that may result following a chemical release. OEHHA determines Reference Exposure Levels (RELs) associated with physiological systems that are could be affected (for example, respiratory system) for the noncancer effects of airborne chemicals as part of the Air Toxics Hot Spots program. US EPA also establishes noncancer health guidance values referred to as Reference Concentrations (RfCs) for air contaminants. It can be reasonably anticipated that no adverse health effects will occur in exposed populations, including sensitive subpopulations for exposures to concentrations at or below the OEHHA RELs, including the acute REL for short-term exposures (one-hour), the eight-hour REL for repeated eight-hour exposures, and the chronic REL for continuous long-term exposures. The US EPA RfCs are similar to OEHHA's chronic RELs for long-term exposures, but are developed using a different risk assessment methodology than OEHHA employs and therefore may be different.

Cancer Potency Factors (CPF), also referred to as Cancer Slope Factors (CSF), and unit risk values are calculated for chemicals known to be carcinogenic. These values are developed under several OEHHA's programs: the Air Toxics Hot Spots Program; Public Health Goals (PHG) for drinking water; Toxic Air Contaminant Program; and Proposition 65. In addition, CPFs are obtained from US EPA's Integrated Risk Information System (IRIS). These factors are used in combination with measured or modeled airborne concentrations to estimate lifetime cancer risks to an exposed population.

The health guidance values shown in Table 2 below have been developed to protect the general public from the cancer and noncancer endpoints that may result from toxic chemical exposures.

Table 2. OEHHA and US EPA Health Guidance Values and Descriptions

Guidance Value[1]	Source	Description
Reference Exposure Level (**REL**) (µg/m^3 inhalation, µg/kg-day oral)	OEHHA	Airborne concentration level at or below which no adverse health effects are anticipated for a specified exposure duration. OEHHA has acute RELs for an exposure lasting one hour[2], eight-hour RELs for long-term, repeated (up to daily) exposures of eight hours, and chronic RELs for continuous exposures lasting ≥12% of a lifetime. A few RELs are based on an oral exposure.
Reference Concentration (**RfC**) (mg/m^3)	US EPA (IRIS)	Estimate of continuous inhalation exposure to the human population (including sensitive subgroups) lasting ≥12% of an individual's lifetime that is likely to be without an appreciable risk of deleterious effects during a lifetime.
Cancer Slope Factor (**CSF**) (mg/kg-day)$^{-1}$	OEHHA (Air Toxics Hot Spots, TAC, Proposition 65), US EPA (IRIS)	Upper 95% confidence limit of the slope of the extrapolated dose-response curve; this is equivalent to the probability of developing cancer from continuous lifetime exposure to a substance (in units of milligram per kilogram of body weight per day).
Unit Risk (µg/m^3)$^{-1}$	OEHHA (Air Toxics Hot Spots, TAC, Proposition 65), US EPA (IRIS)	Upper 95% confidence limit of the slope of the extrapolated dose-response curve; this is equivalent to the probability of developing cancer from continuous lifetime exposure to a substance (in units of microgram per cubic meter of air).

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[1] micrograms per meter cubed, micrograms per kilogram-day

[2] A few acute RELs are for slightly longer durations – see OEHHA (2008).

This section does not include all potential health guidance values. Regional Screening Levels (RSLs), for instance, are developed by US EPA and can be used to determine chemical-specific concentrations for contaminants found in air, drinking water, and soil that warrant hazardous waste site cleanup. Additionally, OEHHA develops California Human Health Screening Levels (CHHSLs) to enable property owners and government officials to determine the degree of effort that may be required to remediate contaminated soil. CHHSLs include Soil-Screening Numbers for nonvolatile chemicals based on total exposure to contaminated soil (inhalation, ingestion, and dermal absorption), and Soil-Gas Screening Numbers for volatile chemicals below buildings constructed with and without engineered fill below sub-slab gravel. For further information on RSLs and CHHSLs, see the US EPA regional screening levels web page or the OEHHA soil and soil gas risk assessment web page (URLs in References section).

Table 3 lists the refinery-emitted chemicals from Table 1 that have one or more of the health guidance values described above, or that are included on the Proposition 65 list of carcinogens and reproductive or developmental toxicants.

Table 3. Health Guidance Values for Chemicals Emitted from California Refineries

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
Acetaldehyde	—	A	470	—	Eyes; respiratory system (sensory irritation)	C	0.01[a]	$2.7x10^{-6}$
	—	8	300	—	Respiratory system	—	—	—
	9	C	140	—	Respiratory system	—	—	—
Acrolein	—	A	2.5	—	Eyes, respiratory system (sensory irritation)	—	—	—
	—	8	0.7	—	Respiratory system	—	—	—
	0.02	C	0.35	—	Respiratory system	—	—	—
Ammonia	—	A	3,200	—	Respiratory system; eyes	—	—	—
	100	C	200	—	Respiratory system	—	—	—
Aniline	1	—	—	—	—	C	$5.7x10^{-3}$ [b]	$1.6x10^{-6}$
Arsenic	—	A	0.2	—	Development; cardiovascular system; nervous system	C	12[a]	$3.0x10^{-3}$
	—	8	0.015	—	Development; cardiovascular system; nervous system; respiratory system; skin	—	1.5[b] (oral)	—
	—	C	0.015	$3.5x10^{-3}$	Inhalation and Oral: Development; cardiovascular system; nervous system; respiratory system; skin	—	—	—
Asbestos	—	—	—	—	—	C	220[a]	0.063

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[1] US EPA Inhalation Reference Concentrations (RfC). http://www2.epa.gov/iris.

[2] OEHHA acute, eight-hour, and chronic Reference Exposure Levels (REL) with corresponding hazard index target organs. https://oehha.ca.gov/air/general-info/oehha-acute-8-hour-and-chronic-reference-exposure-level-rel-summary

[3] Proposition 65 status, Chemicals denoted with a *C* are classified as carcinogens; those with a *D* are classified as developmental toxicants; those with R_m, R_f, or $R_{m/f}$ are reproductive toxicants in males, females or both.

[4] OEHHA Cancer Potency Factors (CPF), also known as Cancer Slope Factors (CSF) and Unit Risk Factors, from *Appendix A* (updated 2011) of the *Technical Support Document for Cancer Potency Factors*. http://oehha.ca.gov/media/downloads/crnr/appendixa.pdf. Sources of values: (a) Toxic Air Contaminant (TAC); (b) Integrated Risk Information System (IRIS); (c) Proposition 65; (d) Public Health Goal (PHG) document.

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
Benz[a]anthracene	—	—	—	—	—	C	0.39[a]	$1.1x10^{-4}$
	—	—	—	—	—	—	1.2 (oral)	—
Benzene	—	A	27	—	Development; immune system; hematologic system	C	0.1[a]	$2.9x10^{-5}$
	—	8	3	—	Hematologic system	D, R_m	—	—
	30	C	3	—	Hematologic system	—	—	—
Benzo[a]pyrene	—	—	—	—	—	C	3.9[a]	$1.1x10^{-3}$
	—	—	—	—	—	—	12 (oral)	—
Benzo[b]fluoranthene	—	—	—	—	—	C	0.39[a]	$1.1x10^{-4}$
	—	—	—	—	—	—	1.2 (oral)	—
Benzo[j]fluoranthene	—	—	—	—	—	C	0.39[a]	$1.1x10^{-4}$
	—	—	—	—	—	—	1.2 (oral)	—
Benzo[k]fluoranthene	—	—	—	—	—	C	0.39[a]	$1.1x10^{-4}$
	—	—	—	—	—	—	1.2 (oral)	—
Beryllium	0.02	C	$7.0x10^{-3}$	2	Inhalation: Respiratory system, immune system; Oral: Alimentary system (gastrointestinal tract)	C	8.4[b]	$2.4x10^{-3}$
1,3-Butadiene	—	A	660	—	Development	C	0.6[a]	$1.7x10^{-4}$
	—	8	9	—	Reproductive system	D, $R_{m/f}$	—	—
	2	C	2	—	Reproductive system	—	—	—
Cadmium	—	C	0.02	0.5	Inhalation: Kidney, respiratory system; Oral: Kidney	C	15[a]	$4.2x10^{-3}$
	—	—	—	—	—	D, R_m	—	—
Carbon disulfide	—	A	6,200	—	Reproductive/development; nervous system	D, $R_{m/f}$	—	—
	700	C	800	—	Nervous system; reproductive system	—	—	—
Carbon monoxide	—	A	$2.3x10^{4}$	—	Cardiovascular system	D	—	—
Carbon tetrachloride	—	A	1,900	—	Alimentary system (liver); reproductive/development; nervous system	C	0.15[a]	$4.2x10^{-5}$
	100	C	40	—	Alimentary and nervous systems; development	—	—	—

Chemical	US EPA RfC[1] (μg/m^{3})	OEHHA Inhalation REL[2] (μg/m^{3})		OEHHA Oral REL[2] (μg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (μg/m^{3})$^{-1}$
Carbonyl sulfide		A	660		Nervous system	—	—	—
		8	10		Nervous system	—	—	—
		C	10		Nervous system	—	—	—
Chlorine	—	A	210	—	Respiratory system; eyes	—	—	—
	—	C	0.2	—	Respiratory system	—	—	—
Chlorobenzene	—	C	1,000	—	Alimentary system (liver); kidney; reproductive system	—	—	—
Chlorodifluoromethane	5.0x10^{4}	—	—	—	—	—	—	—
Chloroform	—	A	150	—	Reproductive/development; respiratory system; nervous system	C	0.019[a]	5.3x10^{-6}
	—	C	300	—	Alimentary system; kidney; development	D	—	—
Chromium (hexavalent)& compounds)	8.0x10^{-3} (aerosols)	C	0.2	20	Inhalation: Respiratory system; Oral: Hematologic system	C	510[a]	0.15
	0.1 (particulates)	—	—	—	—	D, R$_{m/f}$	0.42[c] (oral)	—
Chrysene	—	—	—	—	—	C	0.039[a]	1.1x10^{-5}
	—	—	—	—	—	—	0.12 (oral)	—
Cobalt	—	—	—	—	—	C	—	—
Copper	—	A	100	—	Respiratory system	—	—	—
Cresols (mixtures of)	—	C	600	—	Nervous system	—	—	—
Cumene	400	—	—	—	—	C	—	—
Cyclohexane	6,000	—	—	—	—	—	—	—
Dibenz[a,h]anthracene	—	—	—	—	—	C	4.1[c]	1.2x10^{-3}
Dibenzo-p-dioxins[5] (chlorinated)	—	C	4.0x10^{-5}	1.0x10^{-5}	Inhalation and Oral: Alimentary (liver), reproductive, endocrine, respiratory, hematologic systems; development	C	—	—
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1,300[a]	0.38
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1.3x10^{4} [a]	3.8

Chemical	US EPA RfC[1] (μg/m^3)	OEHHA Inhalation REL[2] (μg/m^3)		OEHHA Oral REL[2] (μg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (μg/m^3)$^{-1}$
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,7,8-Pentachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1.3x10^{5} [a]	38
2,3,7,8-Tetrachlorodibenzo-p-dioxin[5]	—	C	4.0x10^{-5}	1.0x10^{-5}	Inhalation and Oral: Alimentary (liver), reproductive, endocrine, respiratory, hematologic systems; development	C	1.3x10^{5} [a]	38
1,2,3,4,6,7,8-Heptachlorodibenzofuran	—	—	—	—	—	—	1,300[a]	0.38
1,2,3,4,7,8,9-Heptachlorodibenzofuran	—	—	—	—	—	—	1,300[a]	0.38
1,2,3,4,7,8-Hexachlorodibenzofuran	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,6,7,8-Hexachlorodibenzofuran	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,7,8,9-Hexachlorodibenzofuran	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
2,3,4,6,7,8-Hexachlorodibenzofuran	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,7,8-Pentachlorodibenzofuran	—	—	—	—	—	—	6,500[a]	1.9
2,3,4,7,8-Pentachlorodibenzofuran	—	—	—	—	—	—	6.5x10^{4} [a]	19
2,3,7,8-Tetrachlorodibenzofuran	—	—	—	—	—	C	1.3x10^{4} [a]	3.8

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[5] Polychlorinated biphenyls individual congeners evaluated using toxic equivalent factor (TEF) methodology, relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin. No specific value

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
1,4-Dichlorobenzene	800	C	800	—	Nervous and respiratory; alimentary system (liver); kidney	C	0.04[c]	1.1x10^{-5}
1,1-Dichloroethane	—	—	—	—	—	C	5.7x10^{-3} [c]	1.6x10^{-6}
1,1-Dichloroethylene	200	C	70	—	Alimentary system (liver)	—	—	—
1,2-Dichloropropane	4	—	—	—	—	C	—	—
1,3-Dichloropropene	20	—	—	—	—	C	—	—
Mercury	—	A	0.6	—	Nervous system; development	D		
	—	8	0.06	—	Nervous system; development; kidney	—	—	—
	0.3	C	0.03	0.16	Inhalation & Oral: Nervous system; development; kidney	—	—	—
Methanol	—	A	2.8x10^{4}	—	Nervous system	D	—	—
	2.0x10^{4}	C	4,000	—	Development	—	—	—
Methyl bromide	—	A	3,900	—	Nervous system; respiratory system; reproductive/ development	D	—	—
	5	C	5	—	Respiratory system; nervous system; development	—	—	—
Methyl chloride	90	—	—	—	—	D, R$_m$	—	—
Methyl chloroform	—	A	6.8x10^{4}	—	Nervous system	—	—	—
	5,000	C	1,000	—	Nervous system	—	—	—
Methyl ethyl ketone	5,000	A	1.3x10^{4}	—	Respiratory system; eyes	—	—	—
Methyl isobutyl ketone	3,000	—	—	—	—	C	—	—
	—	—	—	—	—	D	—	—
Methyl tert-butyl ether	3,000	C	8,000	—	Kidney; eyes; alimentary system (liver)	—	1.8x10^{-3} [a]	2.6x10^{-7}
3-Methylcholanthrene	—	—	—	—	—	C	22[c]	6.3x10^{-3}
Methylene chloride	—	A	1.4x10^{4}	—	Cardiovascular system; nervous system	C	3.5x10^{-3} [a]	1.0x10^{-6}
	600	C	400	—	Cardiovascular system; nervous system	—	—	—
Naphthalene	3	C	9	—	Respiratory system	C	0.12[a]	3.4x10^{-5}

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
Nickel	—	A	0.2	—	Immune system	C	0.91[a]	2.6x10^{-4}
	—	8	0.06	—	Respiratory, immune systems	—	—	—
	—	C	0.014	11	Inhalation: Respiratory system; hematologic system; Oral: Development	—	—	—
Nitrogen dioxide	—	A	470	—	Respiratory system	—	—	—
Nitrous oxide	—	—	—	—	—	D, R$_f$	—	—
Perchloroethylene	—	A	2.0x10^4	—	Nervous system; respiratory system; eyes	C	0.21[a]	5.9x10^{-6}
	40	C	35	—	Kidney; alimentary system (liver)	—	0.051[c] (oral)	—
Phenol	—	A	5,800	—	Respiratory system; eyes	—	—	—
	—	C	200	—	Alimentary system; cardiovascular system; kidney; nervous system	—	—	—
Phosphoric acid	10	C	7	—	Respiratory system	—	—	—
Polychlorinated biphenyls	—	C[5]	—	—	Inhalation and Oral: Alimentary (liver), reproductive, endocrine, respiratory, hematologic systems; development	C	2[b]	5.7x10^{-4}
	—	—	—	—	—	D	—	—
Propylene	—	C	3,000	—	Respiratory system	—	—	—
Propylene glycol monomethyl ether	2,000	C	7,000	—	Alimentary system (liver)	—	—	—
Propylene glycol mono-t-butyl ether	—	—	—	—	—	C	—	—
Propylene oxide	—	A	3,100	—	Respiratory system; eyes; reproductive/development	C	0.013[b]	3.7x10^{-6}
	30	C	30	—	Respiratory system	—	0.24 (oral)	—
Selenium (& compounds)	—	C	20	5	Inhalation and Oral: Alimentary system (liver); cardiovascular system; nervous system	—	—	—

Chemical	US EPA RfC[1] (μg/m^3)	OEHHA Inhalation REL[2] (μg/m^3)		OEHHA Oral REL[2] (μg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (μg/m^3)$^{-1}$
Selenium sulfide	—	C	20	5	Inhalation and Oral: Alimentary system (liver); cardiovascular system; nervous system	C	—	—
Styrene	—	A	2.1x10^{4}	—	Respiratory system; eyes; reproductive/development	—	—	—
	1,000	C	900	—	Nervous system	—	—	—
Sulfur dioxide	—	A	660	—	Respiratory system	D	—	—
Sulfuric acid	—	A	120	—	Respiratory system	C (mist)	—	—
	—	C	1	—	Respiratory system	—	—	—
1,1,2,2-Tetrachloroethane	—	—	—	—	—	C	0.2[b]	5.8x10^{-5}
Toluene	—	A	3.7x10^{4}	—	Respiratory, nervous systems; eyes; reproductive/development	D	—	—
	5,000	C	300	—	Nervous system; respiratory system; development	—	—	—
1,1,2-Trichloroethane	—	—	—	—	—	C	0.057[b]	1.6x10^{-5}
Trichloroethylene	2	C	600	—	Nervous system; eyes	C	7.0x10^{-3} [a]	2.0x10^{-6}
	—	—	—	—	—	D, R_m	0.015[c] (oral)	—
Triethylamine	—	A	2,800	—	Nervous system; eyes	—	—	—
	7	C	200	—	Eyes	—	—	—
Vinyl chloride	100	A	1.8x10^{5}	—	Nervous system; respiratory system; eyes	C	0.27[a]	7.8x10^{-5}
Xylenes (mixed and m-xylene, o-xylene, and p-xylene isomers)	—	A	2.2x10^{4}	—	Nervous and respiratory systems; eyes	—	—	—
	100	C	700	—	Nervous and respiratory systems; eyes	—	—	—

For information on the development of Reference Exposure Levels, see OEHHA (2008), and to access the complete list of existing OEHHA RELs, see OEHHA's Acute, 8-hour and Chronic Reference Exposure Level (REL) Summary. For US EPA RfCs, see the US EPA IRIS website. Additional information regarding chemical-specific cancer studies and the development of CSFs can be found in OEHHA (2009) and on OEHHA's Proposition 65 web page. The International Agency for Research on Cancer (IARC) Monographs on Evaluation of Carcinogenic Risks to Humans provides information on studies related to carcinogenicity in animals and humans. These Monographs can be accessed on the IARC web page (URLs in References section).

B. US EPA and NIOSH Emergency Exposure Levels

Refinery accidents are unpredictable and may release high concentrations of chemicals into the air. Emergency exposure levels can help emergency responders evaluate the immediate dangers from such chemical releases. While health guidance values can be used to anticipate the health risks associated with exposure to low chemical concentrations, emergency exposure levels may be applied in scenarios in which high concentrations of chemicals are measured or estimated in the air. For this reason, OEHHA has compiled information on the emergency exposure levels for chemicals in Table 1 including: US EPA's Acute Exposure Guideline Levels (AEGL), and the National Institute for Occupational Safety and Health's (NIOSH) Immediately Dangerous to Life and Health (IDLH) values In addition, OEHHA notes which chemicals have Lower Explosive Limits (LEL).

AEGLs and IDLHs are used to protect workers and emergency responders. Based on the severity of toxic effects resulting from exposure, chemicals can have up to three AEGLs and an IDLH. AEGLs are used to make informed decisions on shelter-in-place orders or emergency evacuations. The US EPA Office of Pollution Prevention and Toxics' (OPPT) National Advisory Committee for the Development of Acute Exposure Guideline Levels for Hazardous Substances (NAC/AEGL Committee) and NIOSH, respectively develop AEGLs and IDLHs for chemical exposures.

LELs and Upper Explosive Limits (UEL) establish a range of concentrations in which a flash will occur or a flame will travel if flammable vapor or gas in air is ignited. Thus, LELs are calculated for flammable chemicals and may be used as guidelines to avoid accidental chemical explosions.

AEGLs are established for varying durations of exposure. The 10-minute AEGLs listed can be used in acute exposure scenarios such as those which may occur in a refinery emergency. There are additional emergency exposure levels which are also used to plan for and respond to uncontrolled chemical releases. Chemicals can have up to three AEGLs, Emergency Response Planning Guidelines (ERPG), Temporary Emergency Exposure Limits (TEEL), and Protective Action Criteria (PAC) depending on the severity of toxic effects resulting from inhalation exposure. The American Industrial Hygiene Association (AIHA) Emergency Response Planning Committee develops

ERPGs to assist emergency responders in evaluating the potential spread and airborne concentration in the event of a release, particularly for chemicals that have high potential for uncontrolled releases and those that may pose hazards due to their volatility and toxicity. Because AEGLs and ERPGs exist only for a limited number of chemicals, the US Department of Energy Subcommittee on Consequence Assessment and Protective Actions (SCAPA) also develops Temporary Emergency Exposure Levels (TEELs), which serve as temporary limits for chemicals until AEGLs or ERPGs are developed. TEELs are used in similar situations as one-hour AEGLs and ERPGs. TEELs estimate the concentrations at which most people will begin to experience health effects from exposure in air. In combination, AEGLs, ERPGs, and TEELs are referred to as PACs. During an emergency, these criteria may be used to assess the severity of the event and its health consequences, identify potential outcomes, and determine what protective actions should be taken.

Further information about the development, application, and current list of ERPGs can be found on the AIHA web page. For additional information on the PAC dataset and TEEL development, visit the SCAPA PAC/TEEL web page.

The definitions of AEGLs, IDLHs, and LELs are shown in Table 4 below.

Table 4. US EPA and NIOSH Emergency Exposure Levels and Descriptions

Exposure Level	Source	Description
Acute Exposure Guideline Level (**AEGL**) (mg/m^3)	US EPA (NAC/AEGL Committee)	1: Airborne concentration above which the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects after an exposure duration of 10 minutes, 30 minutes, 1 hour, 4 hours, or 8 hours. Effects are not disabling and are transient and reversible upon cessation of exposure. 2: Airborne concentration above which the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or impaired ability to escape after an exposure duration of 10 minutes, 30 minutes, 1 hour, 4 hours, or 8 hours.
Immediately Dangerous to Life and Health (**IDLH**) (mg/m^3)	NIOSH	Airborne concentration likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment as a consequence of a 30-minute exposure.

Table 5 displays the chemicals from OEHHA’s list of refinery chemical emissions (Table 1) that have 10-minute AEGLs, IDLHs, or LELs.

Table 5. Emergency Exposure Levels for Chemicals Emitted from California Refineries

Chemical	AEGL-1[1] ($\mu g/m^3$)	AEGL-2[1] ($\mu g/m^3$)	IDLH[2] ($\mu g/m^3$)	LEL[3] (%)
Acenaphthene	—	—	—	0.6
Acetaldehyde	8.11×10^4	6.13×10^5	3.60×10^6	4
Acetone	4.75×10^5	2.21×10^7	5.95×10^6	2.5
Acetylene	—	—	—	2.5
Acrolein	69	1,009	4,580	2.8
Ammonia	2.09×10^4	1.53×10^5	2.09×10^5	15
Aniline	1.83×10^5	2.74×10^5	3.81×10^5	1.3
Anthracene	—	—	—	0.6
Antimony	—	—	5.00×10^4	—
Arsenic	—	—	5,000	—
Barium	—	—	5.00×10^4	—
Benzene	4.15×10^5	6.39×10^6	1.60×10^6	1.2
Beryllium	—	—	4,000	—
Biphenyl	—	7.57×10^4	1.00×10^5	0.6 (232°F)
1,3-Butadiene	1.48×10^6	1.48×10^7	4.43×10^6	2
Butane	2.38×10^7	5.71×10^7	—	1.6
1-Butene	—	—	—	1.6
Cadmium	130	1,400	9,000	—
Carbon disulfide	5.30×10^4	6.23×10^5	1.56×10^6	1.3
Carbon monoxide	—	4.81×10^5	1.37×10^6	12.5
Carbon tetrachloride	—	1.70×10^5	1.26×10^6	—
Carbonyl sulfide	—	1.70×10^5	—	—
Chlorine	1,450	8,120	2.90×10^4	—
Chlorobenzene	4.60×10^4	1.98×10^6	4.60×10^6	1.3
Chloroform	—	5.86×10^5	2.44×10^6	—
Chromium (hexavalent & compounds)	—	—	2.50×10^5	—
Chromium III	—	—	2.50×10^4	—
Cobalt	—	—	2.00×10^4	—
Copper	—	—	1.00×10^5	—
m-Cresol	—	—	1.11×10^6	1.1 (300°F)
o-Cresol	—	—	1.11×10^6	1.4 (300°F)
p-Cresol	—	—	1.11×10^6	1.1 (300°F)
Cumene	2.46×10^5	2.70×10^6	4.42×10^6	0.9

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[1] US EPA 10-minute Acute Exposure Guideline Levels (AEGL) from OPPT.

[2] NIOSH Immediately Dangerous to Life and Health (IDLH) values.

[3] Lower Explosive Limits (LEL) for flammable chemicals, expressed as percent in air from NIOSH.

Chemical	AEGL-1[1] ($\mu g/m^3$)	AEGL-2[1] ($\mu g/m^3$)	IDLH[2] ($\mu g/m^3$)	LEL[3] (%)
Cyclohexane	—	—	4.47×10^6	1.3
Cyclopentadiene	—	—	2.03×10^6	—
Cyclopentane	—	—	—	1.1
Dibutyl phthalate	—	—	4.00×10^6	0.5
1,4-Dichlorobenzene	—	—	9.02×10^5	2.5
1,1-Dichloroethane	—	—	1.22×10^7	5.4
1,1-Dichloroethylene	—	—	—	6.5
1,2-Dichloropropane	—	—	1.85×10^6	3.4
1,3-Dichloropropene	—	—	—	5.3
Diethanolamine	—	—	—	1.6
Diethyl phthalate	—	—	—	0.7 (368˚F)
Di(2-ethylhexyl)phthalate	—	—	5.00×10^6	0.3 (473˚F)
1,4-Dioxane	6.13×10^4	2.09×10^6	1.80×10^6	2
Ethane	—	—	—	2.9
Ethyl chloride	—	—	1.00×10^7	3.8
Ethylbenzene	1.43×10^5	1.26×10^7	3.47×10^6	0.8
Ethylene	—	—	—	2.75
Ethylene dibromide	4.00×10^5	5.61×10^5	7.68×10^5	—
Ethylene dichloride	—	—	2.02×10^5	6.2
Ethylene glycol monoethyl ether	—	—	1.85×10^6	1.8
Ethylene glycol monoethyl ether acetate	—	—	2.71×10^6	1.7
Formaldehyde	1,105	1.72×10^4	2.46×10^4	7
Heptane	—	—	3.07×10^6	1.05
Hexachloroethane	—	—	2.90×10^6	—
Hexane	—	1.41×10^7	3.88×10^6	1.1
Hydrogen	—	—	—	4
Hydrogen chloride	2,687	1.49×10^5	7.46×10^4	—
Hydrogen cyanide	2,761	1.88×10^4	5.52×10^4	5.6
Hydrogen fluoride	818	7.77×10^4	2.45×10^4	—
Hydrogen sulfide	1,045	5.71×10^4	1.39×10^5	4
Isobutane	—	—	—	1.6
Isopropanol	—	—	4.92×10^6	2
Lead	—	—	1.00×10^5	—
Manganese	—	—	5.00×10^5	—
Mercury	—	3,100	1.00×10^4	—
Methane	—	—	—	5
Methanol	8.78×10^5	1.44×10^7	7.86×10^6	6
Methyl bromide	—	3.65×10^6	9.73×10^5	10

Chemical	AEGL-1[1] ($\mu g/m^3$)	AEGL-2[1] ($\mu g/m^3$)	IDLH[2] ($\mu g/m^3$)	LEL[3] (%)
Methyl chloride	—	2.27×10^6	4.13×10^6	8.1
Methyl chloroform	1.25×10^6	5.08×10^6	3.82×10^6	7.5
Methyl ethyl ketone	5.90×10^5	1.45×10^7	8.85×10^6	1.8
Methyl isobutyl ketone	—	—	2.05×10^6	1.4
Methyl tert-butyl ether	1.80×10^5	5.05×10^6	—	—
Methylcyclohexane	—	—	4.82×10^6	1.2
Methylene chloride	1.01×10^6	5.91×10^6	7.99×10^6	13
Molybdenum	—	—	5.00×10^6	—
Naphthalene	—	—	1.31×10^6	0.9
Nickel	—	—	1.00×10^4	—
Nitrogen dioxide	941	3.76×10^4	3.76×10^4	—
Octane	—	—	4.67×10^6	1
Pentane	—	—	4.43×10^6	1.5
Perchloroethylene	2.37×10^5	1.56×10^6	1.02×10^6	—
Phenol	7.31×10^4	1.12×10^5	9.62×10^5	1.8
Phosphoric acid	—	—	1.00×10^6	—
Phosphorus	—	—	5,000	—
Propane	—	—	3.79×10^6	2.1
Propylene	—	—	—	2
Propylene glycol monomethyl ether	—	—	—	1.6
Propylene oxide	1.73×10^5	1.06×10^6	9.50×10^5	2.3
Selenium (& compounds)	—	—	1,000	—
Styrene	8.52×10^4	9.80×10^5	2.98×10^6	0.9
Sulfur dioxide	524	1,965	2.62×10^5	—
Sulfur trioxide	200	8,700	—	—
Sulfuric acid	200	8,700	1.50×10^4	—
1,1,2,2-Tetrachloroethane	—	—	6.87×10^5	—
Toluene	2.52×10^5	5.28×10^6	1.88×10^6	1.1
1,1,2-Trichloroethane	—	—	5.46×10^5	6
Trichloroethylene	1.40×10^6	5.16×10^6	5.37×10^6	12.5
1,1,2-Trichloro-1,2,2-trifluoroethane	—	—	1.53×10^7	—
Triethylamine	—	—	8.28×10^5	1.2
1,2,4-Trimethylbenzene	8.85×10^5	2.26×10^6	—	0.9
Vanadium (fume or dust)	—	—	3.50×10^4	—
Vinyl chloride	1.16×10^6	7.17×10^6	—	3.6
Xylenes (mixed)	5.64×10^5	1.09×10^7	—	—
m-Xylene	—	—	3.91×10^6	1.1
o-Xylene	—	—	3.91×10^6	0.9
p-Xylene	—	—	3.97×10^6	1.1

To learn more about the AEGLs, IDLHs, and LELs described in this section, visit the US EPA AEGL web page or the NIOSH Pocket Guide to Chemical Hazards web page (URLs in References section).

IV. HEALTH EFFECTS OF SELECT CALIFORNIA REFINERY CHEMICALS

This section provides further information for select California refinery chemicals on various health and safety risks to exposed populations. These include noncancer health effects, carcinogenic effects, and effects on development or reproduction. Appendix A provides an expanded description of the acute and chronic health effects for a number of refinery chemicals. The chemicals described below are only a few of many chemicals that may have adverse effects on human health. OEHHA selected these chemicals based on their high emissions, low health guidance values, emissions from multiple processes and equipment, involvement in incident history, or level of toxicity-weighted emissions.

Table 6 presents health effects for select California refinery chemicals including information on the physical/chemical properties, acute health effects, and chronic health effects of each chemical. These effects are dependent on level and duration of exposure. Web sources for the health summaries are also included below.

Table 6. Health Effects of Select California Refinery Chemicals

Chemical	Health Effects
Acetaldehyde	Physical/Chemical Properties: Colorless liquid with distinct, pungent odor. Flammable. Acute Health Effects: bronchoconstriction; irritation of the eye, upper respiratory tract, nose, throat, and lung; decreased pulmonary function Chronic Health Effects: degeneration, inflammation, and hyperplasia of nasal airways; in animals: changes in nasal mucosa, respiratory distress, growth retardation, early mortality
Ammonia	Physical/Chemical Properties: Colorless gas with pungent and irritating odor. Corrosive at high concentrations. Slight fire hazard. Acute Health Effects: irritation of the eyes, nose, throat, and skin; corrosive injury to the skin and mucus membranes of the eyes, lungs, and gastrointestinal tract; eye redness and lacrimation; cough, choking sensation; dyspnea; death from pulmonary edema Chronic Health Effects: decreased pulmonary function; irritation of the eyes, skin, and respiratory tract; chronic cough; asthma; lung fibrosis; chronic irritation of the eye membranes and skin
Arsenic	Physical/Chemical Properties: Grey metallic solid with no characteristic taste or smell. Noncombustible in large amounts, but a slight fire hazard if dust is exposed to flame. Acute Health Effects: decreased fetal weight (mice); respiratory tract irritation, cough, dyspnea, chest pain, sore throat, dermatitis, laryngitis, mild bronchitis, conjunctivitis, death if ingested
	Chronic Health Effects: impairment of intellectual function and neurobehavioral development; malaise; peripheral sensorimotor neuropathy; anemia; jaundice; gastrointestinal discomfort; darkened skin with warts on the palms, soles, and torso; irritation of the throat and respiratory tract; perforation of the nasal septum
Benzene	Physical/Chemical Properties: Colorless liquid with a petroleum-like smell. Highly flammable.
	Acute Health Effects: developmental damage in blood cells (mice); irritation of the eyes, nose, and throat; central nervous system depression; drowsiness; dizziness; rapid heart rate; headache; tremor; confusion; unconsciousness; death from respiratory failure
	Chronic Health Effects: increases and decreases in blood cell count, aplastic anemia, excessive bleeding, damage to the immune system

Chemical	Health Effects
Benzo[a]pyrene	Physical/Chemical Properties: Pale yellow solid with a faint aromatic odor. Nonflammable.
	Acute Health Effects: irritation and burning sensation of the eyes and skin
1,3-Butadiene	Physical/Chemical Properties: Colorless gas with a mild gasoline-like odor. Highly flammable.
	Acute Health Effects: decreased male fetal weight (mice); irritation of the eyes, nose, throat, and lungs; blurred vision; nausea; paresthesia; dryness of the mouth, throat, and nose; fatigue; headache; vertigo; hypotension; unconsciousness; central nervous system depression
	Chronic Health Effects: ovarian atrophy (mice); exacerbation of asthmatic symptoms, increased incidence of respiratory tract infections, cardiovascular diseases, effects on the blood and female reproductive organs
Dibenzofurans (PCDF), Dibenzo-p-dioxins (PCDD)	Physical/Chemical Properties: Colorless crystals. Nonflammable.
	Acute Health Effects: chloracne, gastrointestinal upsets, increased levels of serum enzymes and triglycerides, numbness of the extremities
	Chronic Health Effects: increased mortality; decreased weight gain; changes in the liver, lungs, and lymphoid and vascular tissues (rats)
Diethanolamine	Physical/Chemical Properties: Colorless powder or liquid with ammonia-like odor. Combustible.
	Acute Health Effects: cough, nausea, headache, lacrimation, sneezing, smothering sensation, eye and skin burns, corneal necrosis
	Chronic Health Effects: asthmatic airway obstruction

Chemical	Health Effects
Ethylbenzene	Physical/Chemical Properties: Colorless liquid with a gasoline-like odor. Highly flammable.
	Acute Health Effects: chest constriction, irritation of the eyes and throat, dizziness, vertigo; in animals: eye irritation, central nervous system toxicity, effects on the liver and kidney, pulmonary effects
	Chronic Health Effects: cellular alterations and necrosis in the liver, nephrotoxicity, pituitary gland hyperplasia (mice, rats); developmental toxicity (rats, rabbits); other effects in animals: effects on the blood, irreversible damage to the inner ear and hearing
Formaldehyde	Physical/Chemical Properties: Colorless gas with distinct, pungent odor. Flammable.
	Acute Health Effects: mild and moderate eye irritation, headache, rhinitis, dyspnea, lacrimation, mucous membrane irritation, burning, difficulty breathing, bronchitis, pulmonary edema, pneumonia
	Chronic Health Effects: nasal obstruction and discomfort, lower airway discomfort, allergic sensitization, cough, running nose, lacrimation, cellular changes in airway membranes, decreased lung function, headache, depression, mood changes, insomnia, attention deficit, impairment of dexterity and memory
Hydrogen Fluoride	Physical/Chemical Properties: Colorless fuming liquid or gas with a strong, pungent odor. Emits highly irritating and poisonous fumes that are corrosive to metals and body tissues when heated. Nonflammable.
	Acute Health Effects: eye, nose, and throat irritation; lacrimation; sore throat; cough; chest tightness; wheezing; pulmonary edema
	Chronic Health Effects: dental fluorosis; congestion and irritation of the nose, throat, and bronchi; liver and kidney damage

Chemical	Health Effects
Hydrogen Sulfide	Physical/Chemical Properties: Colorless gas with a pungent rotten egg odor. Corrosive and highly flammable.
	Acute Health Effects: headache; nausea; irritation of the skin, eyes, mucus membranes, and respiratory tract; conjunctivitis with ocular pain, lacrimation, and photophobia; death from respiratory arrest
	Chronic Health Effects: nasal inflammation (mice); low blood pressure, headache, nausea, loss of appetite, weight loss, ataxia, eye membrane inflammation, chronic cough
Manganese	Physical/Chemical Properties: Silver solid. Combustible.
	Acute Health Effects: impaired function, nonspecific pulmonary edema, brain damage
	Chronic Health Effects: impaired visual reaction time, hand-eye coordination, and hand steadiness; manganism; changes in neurobehavioral and cognitive abilities; increased incidence of cough, bronchitis, and dyspnea during exercise; increased susceptibility to infectious lung disease
Naphthalene	Physical/Chemical Properties: Volatile white crystalline volatile solid. Flammable in the presence of an ignition source.
	Acute Health Effects: headache, nausea, vomiting, diarrhea, malaise, confusion, anemia, jaundice, convulsions, neurological damage in infants, hemolytic anemia, liver damage, coma
	Chronic Health Effects: nasal inflammation, olfactory epithelia metaplasia, respiratory epithelial hyperplasia (mice); hemolytic anemia, cataracts, retinal hemorrhage; in animals: chronic inflammation of the lung, chronic nasal inflammation, hyperplasia of nasal respiratory epithelium, metaplasia of the olfactory epithelium

Chemical	Health Effects
Nitrogen Oxides (Nitrogen Dioxide)	Physical/Chemical Properties: Yellow-brown liquid or reddish brown gas with a strong odor. Corrosive. Noncombustible, but will accelerate burning of combustible materials.
	Acute Health Effects: increased airway reactivity in asthmatics, cough, fatigue, nausea, choking, headache, abdominal pain, strained breathing, anxiety, mental confusion, lethargy, loss of consciousness, pneumonitis, bronchitis, death from pulmonary edema and inflammatory changes
	Chronic Health Effects: permanent and obstructive lung disease, increased risk of respiratory infections in children
Particulate Matter (PM10, PM2.5)	Physical/Chemical Properties: Mixture of liquid droplets and solids such as dust, dirt, soot, and smoke. Nonflammable.
	Acute Health Effects: irritation of the eyes, nose, and throat; reduced lung function; asthma attacks; irregular heartbeat; cough; wheezing; increased risk of heart attack, stroke, cardiac arrest, and/or congestive heart failure; premature death
	Chronic Health Effects: increased incidence of heart and lung problems
Sulfur Dioxide	Physical/Chemical Properties: Colorless, irritating gas with a choking or suffocating odor. Nonflammable.
	Acute Health Effects: impairment of airway function; irritation of the eyes, mucous membrane, skin, and respiratory tract; airway obstruction from reflex laryngeal spasm and edema, bronchospasm, pneumonitis, pulmonary edema; death
	Chronic Health Effects: altered sense of smell, increased susceptibility to respiratory infections, symptoms of chronic bronchitis, accelerated decline in pulmonary function

Chemical	Health Effects
Sulfuric Acid	Physical/Chemical Properties: Colorless, oily liquid. Corrosive to metals and all body tissues. Noncombustible, but may be explosive or incompatible with other substances.
	Acute Health Effects: small changes in airway function, dental erosion, respiratory tract irritation, bronchoconstriction, altered lung function
	Chronic Health Effects: hyperplasia of bronchial cells in lungs (monkeys); decreased lung function, tracheobronchitis, stomatitis, conjunctivitis, gastritis
Toluene	Physical/Chemical Properties: Clear, volatile liquid with an aromatic odor. Flammable.
	Acute Health Effects: irritation of the eyes, skin, and respiratory tract; impaired reaction time; headache; dizziness; feeling of intoxication; fatigue; sleepiness; nausea; central nervous system depression; ataxia; euphoria; hallucinations; tremors; seizures; coma; death
	Chronic Health Effects: decreased brain weight and altered dopamine receptor binding (rats); nausea, fatigue, eye and upper respiratory tract irritation, dizziness, headache, difficulty with sleep, disorders of the optic nerve, central nervous system depression, permanent neuropsychiatric effects, muscle disorders, cardiovascular effects, renal tube damage, death
Xylene	Physical/Chemical Properties: Colorless, volatile liquid with an aromatic odor. Flammable.
	Acute Health Effects: irritation of the eyes, skin, and respiratory tract; headache; decreased muscle coordination; dizziness; confusion; lung function, liver, and memory impairment; delayed response to visual stimuli; stomach discomfort; ventricular arrhythmias; acute pulmonary edema; death
	Chronic Health Effects: eye irritation; sore throat; floating sensation; lack of appetite; headache; fatigue; dizziness; tremors; loss of coordination; anxiety; impairment of short-term memory; inability to concentrate; cardiovascular, renal, and gastrointestinal effects; permanent neuropsychiatric manifestations; chronic toxic encephalopathy

Health effects described should not be considered a complete profile of the toxicity of the listed chemicals. For more information about the health effects of specific chemicals, see the OEHHA REL web page, the US EPA IRIS web page, or the Agency for Toxic Substances and Disease Registry (ATSDR) Toxic Substances Portal. Additional information can be obtained from sources such as the web pages for the National Institutes of Health (NIH) Hazardous Substances Data Bank (HSDB) and Toxicology Data Network (TOXNET), the Centers for Disease Control and Prevention (CDC) Emergency Preparedness and Response web page, the NIOSH Pocket Guide to Chemical Hazards, or the National Oceanic and Atmospheric Administration's (NOAA) Computer-Aided Management of Emergency Operations (CAMEO) Chemicals.

V. MOST HIGHLY EMITTED CHEMICALS AND OTHER SUPPORTING INFORMATION

High emissions increase a person's risk of exposure. Refinery incident history, common processes, chemical emission rates, and knowledge of health guidance values and emergency exposure levels can help to judge whether air monitoring is needed and guide decisions that may reduce adverse health effects caused by chemical exposures. Refinery incident history and knowledge of common refinery processes can provide responders with information about which processes have had non-routine emissions in the past, and chemicals that may be released in the event of a refinery emergency. Chemical emissions can be useful in assessing the acute and chronic health effects that are anticipated based on the degree of chemical exposure. OEHHA has collected further information on these factors and summarized the findings below.

A. California Refinery Incident History

Refinery incidents are unanticipated conditions at facilities that allow chemicals to be released into the ambient air. These events can include situations in which chemical emissions exceed typical emissions in an accidental release, normal controls are bypassed, or the effectiveness of the normal controls is reduced. During refinery emergencies, large amounts of chemical-rich emissions may be carried to populated areas and cause exposure to a number of compounds. The extent of exposure depends on factors such as the quantity released, chemical properties, and meteorological conditions. In addition to these factors, understanding the chemicals present in a release, the amount emitted, the acute and chronic health effects of exposure, and the air monitoring capabilities for chemicals can help responders characterize the risk associated with a refinery incident or emergency event. Furthermore, members of nearby communities may experience cumulative exposure from multiple events over time and may be more susceptible to pollution-related health problems.

To compile data on recent refinery incidents in California, OEHHA performed searches using the Google search engine. Searches on individual web pages included: CalEPA IRTF, the Chemical Safety Board (CSB), the Bay Area Air Quality Management District's (BAAQMD), various other California Air Quality Management District (AQMD) and Air Pollution Control District (APCD) web pages, and the Contra Costa Health Services web page. OEHHA performed these searches between August and December of 2015.

Based on this research, sulfur dioxide, hydrogen sulfide, and hydrocarbons were the most commonly reported chemicals emitted during refinery incidents. In many instances, adverse health effects were reported following the release of sulfur compounds. Symptoms were consistent with those associated with acute sulfur dioxide and/or hydrogen sulfide exposure: nausea; dizziness; irritation of the eyes, nose, throat, and skin; and unconsciousness.

OEHHA also looked for information on the process units, emission points, and equipment linked to refinery incidents since knowledge of individual refinery processes involved in incidents can provide information on which chemicals are likely to be released into the air. Of the process units, emission points, and equipment identified, flares were the most common sources involved in incidents resulting in emissions to outdoor air. Flares are used at refineries for the combustion and disposal of combustible gases and hydrocarbons to prevent release directly into the atmosphere. Flare events can be planned or unplanned, and usually occur due to emergency relief, overpressure, process upsets, startups, shutdowns, power outages, and other operational safety reasons. Certain chemicals such as sulfur dioxide, hydrogen sulfide, and carbon monoxide are commonly associated with such events. Because they involve the release of smoke, flaring events also result in the release of particulate matter.

Other process units, emission points, and equipment associated with emissions commonly identified in the literature include heaters, storage tanks, cokers, sulfur recovery units, boilers, gas compressors, fluid catalytic cracking units (FCCU), and crude units. Table 7 below displays the process units, emission points, and equipment reported to be associated with refinery incidents based on data for 2001-2012 for California.

Table 7. Process Units, Emission Points, and Equipment Reported to be Associated with California Refinery Incidents[3]

- Ammonia recovery unit
- Boiler
- Cogeneration unit
- Coker
- Cooling unit
- Crude unit
- Diesel unit
- FCCU[4]
- Flares
- Gas compressor
- Heater/furnace
- Hydrogen plant
- Hydrotreater
- Jet fuel unit
- Oxidizer
- Sonic meter system
- Storage tank
- Sulfur recovery unit
- Vacuum distillation unit
- Vapor recovery unit

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[3] Process units reported to be associated with refinery incidents are listed in alphabetical order based on California data for 2001-2012 reported by Chemical Safety Board, Bay Area Air Quality Management District, and Contra Costa Health Services web pages. Note that the process units listed above may not constitute all equipment or processes involved in refinery incidents in the state.

[4] Fluid catalytic cracking unit (FCCU)

Findings discussed in this section refer to the frequency of refinery incidents with identified chemical releases in California from 2001-2012. They are based on limited data and do not represent all of the refinery incidents during this period. The majority of incidents included in this search was self-reported by personnel from California refineries and community residents and were not the result of air monitoring efforts. The occurrence of refinery incidents varies from refinery to refinery and may reflect site-specific equipment failure and equipment maintenance and upkeep.

B. California Refinery Process Units, Emission Points, and Equipment

To expand OEHHA's list of refinery chemical emissions, chemicals associated with specific refinery areas, equipment, or processes were identified using data provided by US EPA (2012a, 2012b). In response to a request from US EPA, all refineries active during the year 2010 were asked to measure air emissions from each process, emission point, or piece of equipment for a specified period and submit the data to that agency. This request resulted in a list of chemicals routinely emitted and measured for each process unit, emission point, or equipment. OEHHA used these emissions inventories to identify the most commonly occurring processes and their associated chemical emissions.

Appendix B displays a list of chemical emissions associated with each process unit or emission point based on these 2010 California data. The process data and chemicals shown in Appendix B are those most commonly found based on OEHHA's research and do not represent a complete list of all refinery processes or chemicals emitted from each process.

Table 8 shows a sample of process units and release types (fugitive and point emissions) selected based on comparison of data obtained from California refineries active during the year 2010.

Table 8. California Refinery Process Units, Emission Points, and Equipment Sorted by Release Type

Fugitive Emissions	Point Emissions	Fugitive and Point Emissions
Hydrogen plant	Boiler	Alkylation unit
Product loading	Flare	Cogeneration unit
Wastewater treatment	Heater	Coker
	Hydrotreater	Cooling tower
	Sulfur recovery unit	Crude unit
	Thermal oxidizer	Fluid catalytic cracking unit
	Vent	Hydrocracker
		Incinerator
		Stack
		Storage tank

C. Chemical Analysis Categories for Air Monitoring

Upon completion of OEHHA's compilation of California refinery chemicals (Table 1), chemicals were sorted by CARB (Appendix C) into chemical analysis categories based upon air monitoring capabilities and methodology for collecting air samples. This classification scheme allowed for the consideration of emissions, health effects, and health guidance values of chemicals that require similar procedures for air monitoring. Table 9 is an overview of the chemical analysis categories provided by CARB.

Table 9. Chemical Analysis Categories for Air Monitoring

Acid
Aldehyde
Dioxin/Dibenzofuran
Extractable
Gas
Glycol
Metal
Microscopy (for asbestos)
Mass/Particulate Matter (PM)
Polycyclic Aromatic Hydrocarbons (PAH)
Volatile Organic Compounds (VOC)

D. Most Highly Emitted Routine Emissions of Toxic Air Contaminants from California Refineries

Since high emissions increase a person’s risk of exposure, consideration of chemical emission rates can help CARB make judgements about air monitoring. Routine emissions data from California refineries for 2009-2012 were obtained from the CEIDARS database facility search tool. The emissions data were submitted to CARB under the AB 2588 Air Toxics Hot Spots Program requirements and reflect TAC releases that occurred during routine facility operations. The Hot Spots program requires facilities to report emission inventory updates every four years. Therefore, not all facilities update emission inventories in the same year. As a result, some chemicals may not be reported each year. Based on this quadrennial method of updating emission inventories in the Hot Spots Program, the information that the CEIDARS database provides on the TACs emitted from refineries may underestimate total routine emissions across refineries in any given year.

US EPA’s Toxics Release Inventory (TRI) Program is an additional resource for learning about toxic chemical releases into the air, as well as into land and water. The TRI Program requires certain industrial facilities in the US to report annual release data in accordance to the Emergency Planning and Community Right-to-Know Act (EPCRA). The TRI database contains data by facility and by year. The focus of this report is the potential health effects of chemicals emitted from refineries. This is not an assessment of the potential health effects of all emissions. However, OEHHA found it useful to understand the relative routine and non-routine emissions to compare with the health effects of those chemicals to assist CARB in prioritizing chemicals for air monitoring.

Appendix D provides the complete list of average routine TAC emissions obtained from CEIDARS from 2009-2012. A four-year average was calculated for each chemical. The 10 pollutants routinely released from refineries in California in the greatest quantities per year based on 2009-2012 data are displayed in Table 10.

In evaluating the emissions, the toxic potency of the chemical emitted can also be taken into account. Summing emissions of a chemical for all California refineries and weighting it by a value related to its toxic potency results in a “toxicity-weighted” emissions score. The toxicity-weighted emissions score was calculated using emissions data (pounds emitted per year) obtained from the Air Toxics “Hot Spots’ Emissions Inventory” (2014) multiplied by a toxicity-weight derived from US EPA’s Inhalation Toxicity Scores for individual chemicals. (https://www.epa.gov/rsei/rsei-toxicity-data-and-calculations).

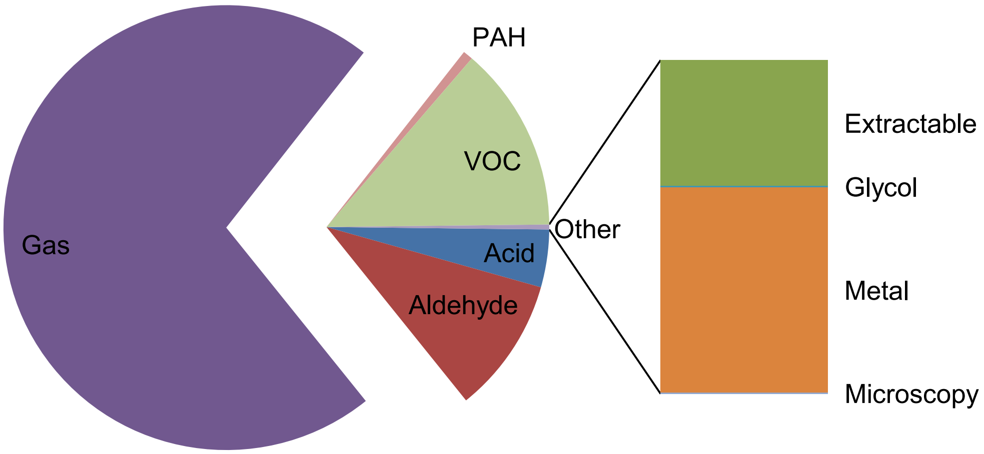
In terms of toxicity, by applying toxicity weights to the total pounds released, the top toxicity-weighted releases, starting with the highest are: formaldehyde, nickel, arsenic, cadmium, and benzene followed by polycyclic aromatic hydrocarbons (PAHs) (total), hexavalent chromium, benzo(a)pyrene, phenanthrene, beryllium, ammonia, 1,3-butadiene, naphthalene, hydrogen sulfide, acetaldehyde, manganese, and diethanolamine. However, it should be noted that the amount released of hexavalent chromium, arsenic, and beryllium are minimal, all less than 100 lbs annually. Appendix H provides more information on TAC emissions for the 2014 CEIDARs data and the toxicity-weighted emissions scores.

Table 10. Toxic Air Contaminants with the Ten Highest Routine Emissions from California Refineries

Chemical	Emissions (lb/year)[5]
Ammonia	2,085,824
Formaldehyde	288,412
Methanol	122,611
Sulfuric acid	104,573
Hydrogen sulfide	103,385
Toluene	87,945
Xylenes	79,177
Benzene	43,308
Hexane	39,646
Hydrogen chloride	21,450

Routine TAC emissions from California refineries during 2009-2012 were examined based on the chemical analysis categories provided by CARB. Gases made up the majority of the routine TAC emissions. The VOC, aldehyde, and acid categories also had notable amounts. Figure 1 below displays the relative occurrence of CARB's chemical analysis categories for air monitoring (Table 9) among the routine TAC emissions from the refineries during this period.

Figure 1. Relative Occurrence of Chemical Analysis Categories in Routine Toxic Air Contaminant Emissions from California Refineries



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[5] Average annual routine TAC emissions from 28 California refineries based on data from the Air Resources Board CEIDARS database for 2009-2012.

E. Routine and Non-routine Chemical Emissions by California Refineries

OEHHA compiled data on routine and non-routine chemical emissions, not limited to TACs, from the California refineries active during 2010 using data provided by US EPA (2012a, 2012b). Routine emissions represent chemical releases that occur during normal facility operations, while non-routine releases reflect emissions during any non-routine refinery operation. Non-routine operations include startups, shutdowns, and malfunction operations such as refinery-wide power loss, maintenance, and flaring events.

The refinery emissions shown in this section were measured or calculated at various process units, emission points, and equipment and reported by refineries to US EPA; however, these data were limited to a single reporting year of 2010, and therefore may not be representative of all non-routine emissions from California refineries. Appendix E includes the complete list of routine and non-routine emissions data reported by California refineries for 2010. In some instances, non-routine emissions exceeded routine emissions during this period. The 10 pollutants routinely released from refineries in California in the greatest quantities in 2010 based on data from US EPA are displayed in Table 11 below.

Table 11: Ten Highest Routine Chemical Emissions by California Refineries[1]

Chemical	Emissions (lb)
Sulfur dioxide	21,158,748
Carbon monoxide	16,972,733
Nitrogen oxides	16,415,674
Volatile organic compounds (VOC)	13,562,963
PM_{10}	6,617,952
Butane	5,881,551
PM_{10} (filterable)	2,805,076
$PM_{2.5}$	2,004,663
Nitrogen dioxide	1,971,085
PM (condensable)	1,677,433

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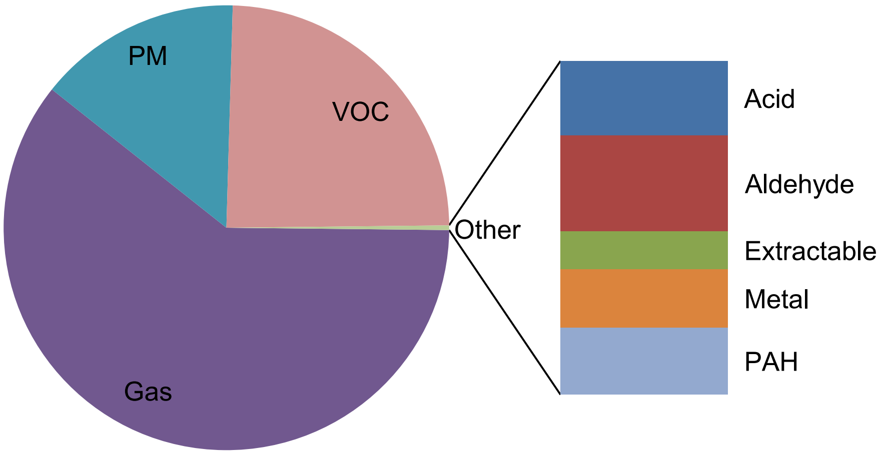
[1] Annual routine chemical emissions from California refineries based on data for 2010 (US EPA, 2012a; US EPA, 2012b).

Routine emissions from California refineries were composed primarily of chemicals in the gas, VOCs, and particulate matter categories. Although data for routine emissions is limited to 2010, OEHHA included this dataset because it provides information about the chemicals other than TACs that are present in refinery emissions. Figure 2 shows the relative occurrence of CARB's categories for air monitoring (Table 9) found in routine refinery emissions during 2010.

Figure 2. Relative Occurrence of Chemical Analysis Categories in Routine Toxic Air Contaminant Emissions from California Refineries[1]



[1] PM is Particulate Matter and includes PM10 and PM2.5. The chemical analysis category is also referred to as “mass”.

Table 12 displays the ten highest non-routine chemical emissions from refineries in California in the greatest quantities in 2010 based on data from US EPA.

Table 12. Ten Highest Non-routine Chemical Emissions by California Refineries[1]

Chemical	Emissions (lb)
Volatile organic compounds (VOC)	1,123,158
Sulfur dioxide	553,834
Carbon monoxide	418,331
Nitrogen oxides	223,792
PM_{10}	89,572
$PM_{2.5}$	26,306
PM_{10} (filterable)	22,802
Nitrogen dioxide	12,397
Propylene	7,799
Hexane	7,625

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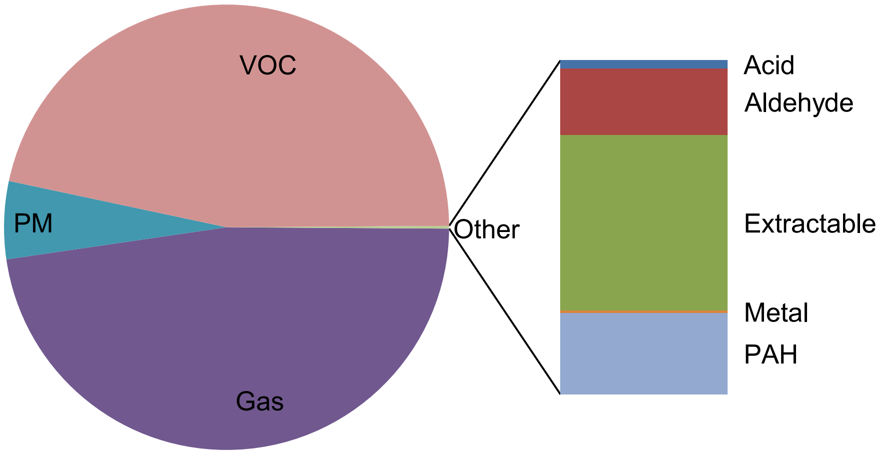
[1] Annual non-routine emissions from California refineries based on data for 2010 (US EPA, 2012a; US EPA, 2012b).

While these emissions appeared to have a similar profile of chemical analysis categories to that of routine emissions, non-routine emissions from California refineries were composed of a greater fraction of VOC releases than releases of gases and particulate matter. The relative occurrence of CARB's chemical analysis categories for air monitoring (Table 9) found in non-routine refinery emissions during 2010 are shown in Figure 3 below.

Figure 3. Relative Occurrence of Chemical Analysis Categories in Non-routine Chemical Emissions by California Refineries



F. Refinery Emissions in the US and Fuel-Burning Experiments

Because refineries are only required to report emissions of regulated chemicals, knowledge of unregulated chemicals also released can provide information on chemical speciation or characteristics that can ultimately be used by officials for air monitoring or risk assessment purposes. To this end, OEHHA conducted a literature search in peer-reviewed journal articles to find additional chemicals associated with refinery emissions in the US. Appendix F lists the chemicals and CAS RNs found in literature describing refinery air monitoring in the US or controlled burning experiments during 1979-2007.

VI. CONCLUSIONS

OEHHA has compiled a list of chemicals emitted from petroleum refineries in California. This list identifies possible acute and chronic health effects resulting from exposure to these chemicals, including cancer and effects on development or reproduction. OEHHA has compiled a list of health guidance values and emergency exposure levels for refinery chemicals that can be referenced during or after emergencies to evaluate the potential for health risks associated with unanticipated chemical releases into the air. Health effects were summarized for a selection of chemicals based on the availability of health guidance values and emergency exposure levels, the quantities emitted in routine and non-routine emissions, and the frequency of occurrence of these chemical emissions in refinery processes and emissions. The refinery chemicals were sorted by chemical analysis categories based on current air monitoring capabilities.

The list of California refinery chemicals, processes, and routine and non-routine emissions included in this report represent data obtained from sources that represent different periods and durations of time in different levels of detail. The data does not encompass all of the refinery chemicals, processes, and emissions points occurring in California. OEHHA has compiled this information to assist CARB and local air districts in making decisions and recommendations for air monitoring of chemicals in communities near refineries, especially during emergencies.

The top candidates for air monitoring based on amounts of emission and toxicity considerations include acetaldehyde, ammonia, benzene, 1,3-butadiene, cadmium, diethanolamine, formaldehyde, hydrogen sulfide, manganese, naphthalene, nickel, PAHs, PM, sulfur dioxide, sulfuric acid, and toluene. The release of these chemicals from refineries does not necessarily mean that local communities face a significant health risk or substantial exposures, but it does increase the likelihood of exposure for nearby communities. Air monitoring of these chemicals may inform decisions that could reduce exposure.

The top toxicity-weighted releases, starting with the highest, are: formaldehyde, nickel, arsenic, cadmium, and benzene followed by polycyclic aromatic hydrocarbons (PAHs) (total), hexavalent chromium, the individual PAHs benzo(a)pyrene and phenanthrene, beryllium, ammonia, 1,3-butadiene, naphthalene, hydrogen sulfide, acetaldehyde, manganese, and diethanolamine. However, it should be noted that the total amount released of hexavalent chromium, arsenic, and beryllium from all California refineries is minimal, less than 100 lbs annually, so these would be unlikely candidates for air monitoring. This data was obtained from CEIDARS for 2014.

The top candidates for air monitoring are not ranked or prioritized further, as this report identifies the top candidates based on their average emissions across all California refineries. An important consideration for air monitoring at individual refineries is that the candidate chemicals will differ based on location as well as year. Some top-candidate chemicals are only released in small amounts from individual refineries.

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APPENDIX A: SUPPLEMENTARY INFORMATION ON HEALTH EFFECTS OF SELECT REFINERY CHEMICALS

Appendix A provides further information on select California refinery chemicals based on various factors that may pose health and safety risks to exposed populations, such as noncancer health effects, carcinogenic effects, effects on development or reproduction, and flammability. OEHHA selected these specific chemicals for inclusion here based on their high emissions, low health guidance values, emissions from multiple processes and equipment, involvement in incident history, or based on their toxicity-weighted emissions.

The health summaries included in Appendix A expand upon the basic acute and chronic health effects of the refinery-associated chemicals in California shown in Table 6, but should not be considered a complete list of health effects of the chemicals. The health and exposure summaries described in this section are derived primarily from the OEHHA web page for REL documents, the US EPA IRIS and Technology Transfer Network web pages, the ATSDR Medical Management Guidelines for Acute Chemical Exposures, or the NIOSH Pocket Guide to Chemical Hazards. Additional information on chemical toxicity profiles can be obtained from sources such as the web pages for NIH's Hazardous Substances Database (HSDB) and Toxicology Data Network (TOXNET), CDC's Emergency Preparedness and Response, or CAMEO Chemicals (URLs in References section).

Information regarding CPFs and the Proposition 65 status of carcinogens and developmental or reproductive toxicants was obtained from publically available OEHHA documents. To learn more about chemical-specific cancer studies, the development of CSFs, and Proposition 65 status, see OEHHA (2009) and visit the OEHHA air toxics and Proposition 65 web pages, or the IARC web page (URLs in References section).

Descriptions of California refinery incidents occurring in 2001-2012 were derived from data provided by CSB, BAAQMD, and CCHS. In addition, California refinery process and air emissions data were provided by US EPA (2012a, 2012b) and CARB unless otherwise noted.

The following chemicals are discussed in Appendix A:

i. Acetaldehyde
ii. Ammonia
iii. Arsenic
iv. Benzo[a]pyrene
v. Benzene, Toluene, Ethylbenzene, and Xylene (BTEX)
vi. 1,3-Butadiene
vii. Dibenzofurans/Dibenzo-p-dioxins
viii. Diethanolamine
ix. Formaldehyde
x. Hydrogen Fluoride

xi. Hydrogen Sulfide
xii. Manganese
xiii. Naphthalene
xiv. Nitrogen Oxides
xv. Particulate Matter (PM_{10} and $PM_{2.5}$)
xvi. Sulfur Dioxide
xvii. Sulfuric Acid

i. Acetaldehyde

At room temperature, acetaldehyde is a colorless liquid with a distinct, pungent odor detectable even at low concentrations. Acetaldehyde is found in air in the vapor, water vapor, and particulate phases. It is flammable with an LEL of 4%, and combustion may generate carbon monoxide. Emissions of acetaldehyde into the environment commonly occur during combustion processes, making inhalation the primary route of exposure.

Acetaldehyde has been detected in both ambient air emissions and at several refinery process units such as boilers, cokers, crude units, FCCUs, heaters, and incinerators (Lucas, 2002). Vapors of acetaldehyde are heavier than air and can cause asphyxiation in low-lying, enclosed, or poorly ventilated areas. In addition, it has been shown that this respiratory irritant has a more severe impact on infants and children.

In acute and chronic inhalation studies, the respiratory system has been the hazard index target tissue for acetaldehyde. Acute exposure to acetaldehyde has been linked to eye redness and swelling, sensory (eye, nose, throat) irritation, and bronchoconstriction in asthmatics. Asthmatics are more sensitive to the adverse effects of acetaldehyde and may be more likely to show symptoms such as shortness of breath, bronchoconstriction, wheezing, and decreased pulmonary function. Because children are more likely to be diagnosed with asthma than adults and their asthma episodes can be more severe, they are particularly vulnerable to the effects of acetaldehyde exposure. In a study conducted on adult human volunteers, asthmatics exhibited bronchoconstriction after inhalation of 142 mg/m^3 acetaldehyde for two to four minutes. In a supporting study, eye irritation, followed by upper respiratory tract, nose, throat, and lung irritation, was observed following whole-body exposure to 45 mg/m^3 for 15 minutes. At high concentrations, the temporary onset of transient conjunctivitis (inflammation or infection of the eye) was also noted. The OEHHA acute REL for acetaldehyde was determined to be 470 µg/m^3 after time and dose adjustments and consideration of uncertainties in these studies.

Inflammation and injury to the respiratory tract occurs following prolonged exposure to acetaldehyde. In animals, acetaldehyde exposure targets the nasal cavity and has been shown to lead to effects such as changes in the nasal mucosa, respiratory distress, growth retardation, and early mortality in rats. OEHHA used an inhalation study on rats exposed to various concentrations of acetaldehyde as the basis for the OEHHA chronic REL. The degenerative, inflammatory, and hyperplastic (increased cell proliferation) effects on the nasal airways observed in this study at 270 mg/m^3 were used as the point of departure to derive the OEHHA chronic REL and US EPA RfC for acetaldehyde of 140 µg/m^3 and 9 µg/m^3, respectively.

Acetaldehyde is a carcinogenic TAC with CPFs derived by OEHHA based on the nasal tumors observed in rats following exposure. In hamsters, laryngeal tumors have also been reported. Acetaldehyde has a CSF of 1.0×10^{-2} (mg/kg-day)$^{-1}$ and a unit risk value of 2.7×10^{-6} (µg/m^3)$^{-1}$. In addition, this chemical has been shown to cause developmental and teratogenic effects in rats and mice and may have a role in the manifestation of fetal alcohol syndrome. It has also been shown to cross the placenta in animals.

ii. Ammonia

At room temperature, ammonia is a colorless gas that is typically found in air in the form of water vapor or particulates. Ammonia is corrosive at high concentrations. Although the odor of ammonia is pungent and irritating, it provides precautionary warning of its presence in most cases. However, after prolonged exposure to this chemical, it is more difficult to detect due to olfactory fatigue or adaptation. Ammonia has been categorized as a slight fire hazard by the National Fire Protection Association (LEL = 15%), but this hazard is increased in the presence of oil or other combustible materials. The majority of exposures occur by way of inhalation, and accidental releases of ammonia can form toxic, dense vapor clouds that travel downwind and put nearby residents at risk.

In California refineries, ammonia emissions have been detected at several process units. Major emissions are primarily from the FCCU process. Ammonia is the most commonly released routine facility emission of all the chemicals examined in this report. In addition, two nonfire incidents during 2001-2012 have been reported in the CSB Chemical Incident Screening Database. Ammonia is listed as the worst-case-scenario toxic release in the Risk Management Plans (RMP) of multiple California refineries evaluated in the 2015 Refinery Emergency Air Monitoring Assessment Report prepared by CARB OER and CAPCOA (CARB and CAPCOA, 2015). It is also listed in the RMPs of many refineries as an alternative release scenario, indicating that it is considered to be more likely than the worst-case-scenario.

Acute inhalation of ammonia may lead to corrosive injury to the skin and mucus membranes of the eyes, lungs, and gastrointestinal tract. Exposure to very high concentrations may result in eye redness and lacrimation (tearing), nose and throat irritation, cough, choking sensation, dyspnea (labored breathing or shortness of breath), lung damage, or death. Fatalities from ammonia exposure are most commonly caused by pulmonary edema (fluid accumulation in the lung). People with asthma and other respiratory conditions such as cardiopulmonary disease or with no tolerance developed from recent exposure may be more sensitive to the toxic effects of ammonia. In addition, blood ammonia levels are increased by chronic high dose aspirin therapy and therapy with valproic acid. Several studies, including one in which human volunteers were exposed to ammonia for 10 minutes, have demonstrated effects of exposure such as the urge to cough and irritation of the eyes, nose, and throat beginning at concentrations around 36 mg/m^3. These critical effects were used as the point of departure for the ammonia OEHHA acute REL of 3.2 mg/m^3.

Chronic exposure to ammonia may impact pulmonary function tests or lead to subjective symptomatology in workers. Chronic cough, asthma, lung fibrosis, and chronic irritation of the eye membranes and skin have also been reported. The most sensitive endpoints of chronic ammonia exposure are decreased pulmonary function, and eye, skin, and respiratory irritation, which were reported in an occupational inhalation study at a concentration of 6.5 mg/m^3. After time and dose adjustments and consideration of uncertainties, a chronic OEHHA REL of 200 µg/m^3 and US EPA RfC of 100 µg/m^3 for ammonia have been developed.

iii. Arsenic

In its elemental form, arsenic is a grey metallic solid with no characteristic taste or smell. Inorganic arsenic compounds are respiratory irritants and may vary in relative toxicity. Arsenic exists in air in the particulate phase. Contact with acid or acid vapors produces arsine, the most dangerous form of arsenic. While ingestion is the most important route of exposure for arsenic trioxide, exposure to other arsenic compounds sufficient to cause toxicity may be more likely to occur via inhalation.

Arsenic likely originates as an impurity in crude oil (Stigter et al., 2000), and it has been detected at many of the process units such as boilers, crude units, heaters, storage tanks, cokers, FCCUs, and incinerators. Arsenic has also been detected in routine and non-routine refinery emissions.

Acute exposure to arsenic has been associated with severe irritation of the mucus membranes of the respiratory tract and symptoms of cough, dyspnea (labored breathing or shortness of breath), and chest pain. Breathing high levels of arsenic may lead to a sore throat and lung irritation. Ingestion may result in symptoms characteristic of severe gastritis or gastroenteritis (inflammation, irritation, or erosion of the stomach) and even death due to severe inflammation of the mucus membranes and increased capillary permeability. Signs of acute arsenic poisoning include dermatitis, nasal mucosal irritation, laryngitis, mild bronchitis, and conjunctivitis (inflammation or infection of the eye). In an inhalation study of pregnant mice, decreased fetal weight was reported at concentrations starting at 0.2 mg/m^3. After time and dose adjustments and consideration of uncertainties, OEHHA derived an acute REL for arsenic of 0.2 µg/m^3.

Chronic exposure to arsenic has been associated with symptoms such as malaise (general feeling of discomfort), peripheral sensorimotor neuropathy (nerve damage), anemia, jaundice, and gastrointestinal discomfort. Prolonged exposure to arsenic also targets the lungs and skin and can cause darkened skin and the appearance of small “corns” or “warts” on the palms, soles, and torso. Conjunctivitis (inflammation or infection of the eye), irritation of the throat and respiratory tract, and perforation of the nasal septum have also been reported. Additionally, literature suggests that arsenic exposure during childhood may impart greater toxicity than adult exposure. In a study conducted on 10-year-old children exposed to 0.23 μg/m^3 of arsenic by drinking water, the impairment of intellectual function and neurobehavioral development was observed. After time and dose adjustments and consideration of uncertainties, OEHHA developed a chronic inhalation REL of 0.015 μg/m^3 and a chronic oral REL of 0.035 μg/kg-day.

Arsenic is listed by IARC as a known human carcinogen of the lung, urinary bladder, and skin. Some studies have also observed carcinogenesis in several other organs. Arsenic is on the Proposition 65 list for both cancer and developmental toxicity. Arsenic has an inhalation and oral CSF of 12 (mg/kg-day)$^{-1}$ and 1.5 (mg/kg-day)$^{-1}$, respectively, based on the incidence of lung tumors in workers occupationally exposed via inhalation and the incidence of skin cancer in individuals exposed via drinking water. The unit risk for arsenic is 0.003 (μg/m^3)$^{-1}$. Arsenic ions originating from arsenic trioxide have been shown to cross the placenta and can also be excreted in breast milk. In animals exposed to arsenic compounds, embryonic lethality, fetal malformations, decreased fetal weight, delayed bone maturation, skeletal malformations, and increased risk of chromosome aberrations in liver cells have been reported. A decrease in spermatozoa motility has also been observed following exposure.

iv. Benzo[a]pyrene

In pure form, benzo[a]pyrene is a pale yellow solid with a faint aromatic odor. Most benzo[a]pyrene in air is bound to particulates and is formed as a by-product of incomplete combustion from sources like volcanoes, automobile exhaust, cigarette smoke, and burning coal. Although it is considered to be nonflammable, benzo[a]pyrene emits acrid smoke and toxic carbon monoxide and carbon dioxide fumes or vapors when it is heated to decomposition. Due to its consistent association with the presence of smoke, benzo[a]pyrene may serve as an air monitoring surrogate for other polycyclic aromatic hydrocarbons (PAH) and smoke itself in addition to particulate matter in the event of a refinery emergency.

The general population is exposed to benzo[a]pyrene primarily by breathing air containing PAHs attached to particles and by consumption of PAHs in food. Once in the environment, PAHs are of concern due to their ability to travel long distances in the air, persist in the environment for extended periods of time, and bioaccumulate up the food chain. Benzo[a]pyrene has been detected in routine refinery emissions and around many areas of petroleum refineries such as separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents.

Benzo[a]pyrene generally occurs in conjunction with other PAHs, therefore most available information on its relevant health effects is in reference to the chemical as part of a mixture containing benzo[a]pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, dibenz[a,h]anthracene, and other carcinogenic or potentially carcinogenic compounds. Acute exposure can cause irritation and a burning sensation of the eyes and skin.

Benzo[a]pyrene is currently classified as a known carcinogen by OEHHA and US EPA, and has additionally been classified as a human carcinogen by IARC, based on the increased incidence of tumors observed in animals on the skin, in lymphoid and hematopoietic tissues, and in various organs such as the lung, forestomach, liver, oesophagus, and tongue. Benzo[a]pyrene has an inhalation CSF of 3.9 $(mg/kg\text{-}day)^{-1}$ based on the occurrence of respiratory tract tumors in male hamsters exposed via inhalation and an oral CSF of 12 $(mg/kg\text{-}day)^{-1}$ based on the occurrence of gastric tumors in male and female mice exposed via diet. The unit risk for benzo[a]pyrene is 0.0011 $(\mu g/m^3)^{-1}$.

Benzo[a]pyrene has also been shown to cause reproductive effects in humans such as decreased sperm quality and fertility in males. In animals, decrements in sperm quality, changes in testicular histology, and hormone alterations in males and decreased fertility and ovotoxic effects in females have been reported. In addition, adverse effects on fetal survival, postnatal growth, and development have been associated with human exposure during gestation. Changes in fetal survival, pup weight, blood pressure, fertility, reproductive organ weight and histology, and neurological function have also been observed in animals exposed during gestation and/or early life.

v. Benzene, Toluene, Ethylbenzene, and Xylene (BTEX)

Benzene, toluene, ethylene, and xylene, collectively called BTEX, are volatile and well-absorbed chemicals that are found in petroleum products such as gasoline, jet fuels, and kerosene. BTEX chemicals often occur simultaneously at hazardous waste sites and emissions of each have been widely detected in similar areas within California refineries. BTEX is both an environmental and health concern because it can contaminate all media (air, water, and soil) and cause neurological impairment with exposure.

Benzene

Benzene is an aromatic hydrocarbon emitted into the air during the production and combustion of diesel and petroleum fuels. It is highly volatile and primarily found in the vapor phase. At room temperature, benzene is a colorless and highly flammable liquid (LEL = 1.2%) with a petroleum-like smell. Benzene vapor is heavier than air and can cause asphyxiation in enclosed, poorly ventilated, or low-lying areas. Benzene is of concern because it is emitted from numerous routine refinery operations (sulfuric acid loading, separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents) and is commonly found in refinery emissions.

In humans, acute inhalation of benzene may lead to eye, nose, and throat irritation, and central nervous system depression. Acute hazard index targets include developmental effects and potential damage to the immune and hematologic systems. Drowsiness, dizziness, rapid heart rate, headaches, tremors, confusion, and unconsciousness may result from breathing high levels of benzene. Acute exposure can also increase cardiac sensitivity to epinephrine-induced arrhythmias. Brief exposure to very high levels in air can lead to death through respiratory failure. People with existing hematologic disorders and cellular anemias or heart conditions may be at increased risk for bone marrow toxicity and cardiac arrhythmias, respectively. In addition, intake of epinephrine and ethanol has been shown to increase the cardiac toxicity of benzene in humans and the bone marrow toxicity of benzene in mice, respectively. In mice, acute benzene exposure has been shown to cause developmental damage in the blood cells of fetal and neonatal mice. This is the basis of OEHHA's acute benzene REL of 27 $\mu g/m^3$.

The hematologic system is the main hazard index target for chronic benzene exposure. Long-term or repeated benzene exposure may cause noncancer detrimental health effects, including decreases in blood cell count, as well as leukemia. Chronic exposure to benzene can also lead to aplastic anemia, excessive bleeding, and damage to the immune system. Metabolic breakdown products of benzene have been shown to cause chromosomal changes that are consistent with those occurring in cases of hematopoietic cancer. Both the OEHHA chronic REL (3 $\mu g/m^3$) and the US EPA RfC (30 $\mu g/m^3$) for benzene are derived from human occupational inhalation studies finding decreased blood cells counts in workers exposed to an average concentration of 0.61 mg/m^3 for durations lasting 1 to 21 years.

Any benzene exposure is a concern regardless of exposure length. Benzene is currently listed under Proposition 65 as a carcinogen, a developmental toxicant, and a male reproductive toxicant. It has also been classified as a known human carcinogen of the hematopoietic system, primarily leukemia, by IARC. At benzene exposures between 0.13 – 0.45 $\mu g/m^3$, US EPA estimates that 1 in 1,000,000 individuals will be at risk of benzene-induced cancer. Children are at particular risk to the carcinogenic effects of benzene due to the high level of cell growth and turnover in their developing systems. Based on both animal and human data, the benzene CSF is 0.1 $(mg/kg\text{-}day)^{-1}$. The unit risk for benzene is 2.9×10^{-5} $(\mu g/m^3)^{-1}$.

Benzene has been shown to cross the placenta and, in animals exposed to benzene via inhalation, developmental effects such as low birth weight, bone marrow toxicity, and delayed bone formation have been observed. At very high levels of exposure, benzene has also been associated with adverse effects on the reproductive organs of animals.

Ethylbenzene

Ethylbenzene is a colorless, highly flammable liquid (LEL = 0.8%) with an odor similar to that of gasoline. Ethylbenzene vapor is formed in air during the combustion of oil, gas, and coal, and breaks down within a few days by reaction with sunlight. The general population is exposed to ethylbenzene by breathing air, especially in cities with multiple factories or busy highways. Residential drinking water wells near landfills, waste sites, or leaking underground storage tanks can also lead to high levels of exposure. Because it occurs naturally in oil, ethylbenzene vapors can additionally be released into the environment during the production, transport, and refining of petroleum. Ethylbenzene emissions have been detected at many refinery process units including: separators, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents, and in routine and non-routine refinery emissions.

Acute exposure to ethylbenzene can cause chest constriction, irritation of the eyes and throat, and neurological effects such as dizziness and vertigo in humans. In animals acutely exposed to ethylbenzene by inhalation, eye irritation, central nervous system toxicity, effects on the liver and kidney, and pulmonary effects have been observed.

Studies on long-term occupational exposure to ethylbenzene have provided limited information regarding its effects on the blood, likely due to the presence of other chemicals such as xylenes in the same environment. In animals chronically exposed to ethylbenzene, effects on the blood, liver, and kidneys have been reported. Irreversible damage to the inner ear and hearing has also been noted. Based on the adverse effects on the liver (cellular alterations and necrosis), kidney (nephrotoxicity), and pituitary gland (hyperplasia) appearing in mice and rats discontinuously exposed to 1.1 μg/m^3 ethylbenzene via inhalation, OEHHA developed a chronic REL of 2 mg/m^3. A US EPA RfC for ethylbenzene of 1 mg/m^3 has also been established due to the developmental toxicity observed in rats and rabbits following chronic exposure.

Because inhalation exposure has been associated with an increase in tumors of the kidney in rats and of the lung and liver in mice, ethylbenzene was classified by IARC in 2010 as a possible human carcinogen. In 2004, it was also listed as a carcinogen by OEHHA under Proposition 65. The inhalation and oral CSFs for ethylbenzene are 8.7×10^{-3} (mg/kg-day)$^{-1}$ and 1.1×10^{-2} (mg/kg-day)$^{-1}$, respectively, and are based on the incidence of kidney cancer in male rats. Ethylbenzene also has a unit risk value of 2.5×10^{-6} (μg/m^3)$^{-1}$.

Toluene

Toluene is a clear, volatile liquid with an aromatic odor that generally serves as an adequate warning of acutely toxic concentrations. It can be ignited under almost all ambient temperature conditions (LEL = 1.1%). While toluene may give rise to toxic effects by inhalation, ingestion, or dermal contact, the general population is primarily exposed to toluene by way of inhalation. Because its vapors are heavier than air, caution should be taken to avoid possible asphyxiation in enclosed, poorly ventilated, or low-lying areas. Toluene is a natural constituent in crude oil and is produced in large quantities by distillation during petroleum refining, serving as a sentinel chemical for benzene exposure. As with the rest of the BTEX chemicals, toluene vapors have been widely detected at various refinery emission points (sulfuric acid loading, separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents) and in outdoor refinery emissions.

Both acute and chronic exposures to toluene are a serious concern because they target the nervous system. Symptoms such as fatigue, sleepiness, headaches, nausea, and irritation of the eyes, skin, and respiratory tract may be experienced in people acutely exposed to low or moderate levels in air. Central nervous system depression, ataxia (lack of muscle control during voluntary movements), euphoria, hallucinations, tremors, seizures, coma, and death may occur at higher levels of exposure. Some people with liver, neurological, or heart disease may be at increased risk for adverse effects resulting from exposure. Concurrent use of salicylates, alcohol, or over-the-counter bronchial dilators containing epinephrine may also increase an individual's susceptibility to toluene. A human acute inhalation study demonstrated eye and nose irritation, impaired reaction time, headache, dizziness, and a feeling of intoxication. This study of toluene exposure was used in OEHHA's development of the acute REL (37 mg/m^3).

Most studies regarding the effects of chronic toluene exposure involve deliberate sniffing of toluene-containing solvents or workplace exposures and have reported a range of neurotoxic effects such as brain damage and decreased performance on psychometric tests. Prolonged exposure has also been associated with nausea, fatigue, eye and upper respiratory tract irritation, sore throat, dizziness, headache, and difficulty with sleep. In cases of occupational exposure, disorders of the optic nerve and neurobehavioral effects such as loss of coordination, memory loss, and loss of appetite have been reported. Chronic toluene abuse can lead to symptoms indicative of central nervous system depression including: drowsiness, ataxia (lack of muscle control during voluntary movements), tremors, cerebral atrophy (loss of neurons), involuntary eye movements, and impairment of speech, hearing, and vision. Permanent neuropsychiatric effects, muscle disorders, cardiovascular effects, renal tube damage, and sudden death can also occur. OEHHA derived the chronic REL (300 μg/m^3) for toluene based on an inhalation study on rats that began showing neurotoxic effects (decreased brain weight and altered dopamine receptor binding) at a concentration of 300 μg/m^3 following exposure to an average of 26.3 mg/m^3. Neurological effects in occupationally-exposed workers were also observed in multiple studies, serving as the basis for the US EPA inhalation RfC of 5 mg/m^3.

Toluene is listed under Proposition 65 as a developmental toxicant and has been shown to cross the placenta and be excreted in breast milk. Children whose mothers were toluene abusers during pregnancy were born with small heads and have head, face, and limb abnormalities, attention deficits, hyperactivity, and developmental delay with language impairment. Preterm delivery, perinatal death, and growth retardation have also been reported.

Xylene

Xylene exists in three forms (m-xylene, o-xylene, and p-xylene) that are commonly combined to form what is known as mixed or technical xylene. An entry for each constituent of technical xylene, as well as the mixture itself, is included in Table 1. For the purposes of this section, the term “xylene” will refer to technical xylene, which is richest in m-xylene and usually also contains ethylbenzene and traces of toluene.

Xylene is a colorless, volatile, flammable liquid (LEL = 1.1%) with an aromatic odor. In air, xylene exists as vapor and may be an explosion hazard. Combustion of this chemical will produce irritating gases that are corrosive and/or toxic. Xylene can be found in drinking water, but because it easily evaporates into the air, exposure typically occurs via inhalation. Exposure to high concentrations of xylene vapors can result in asphyxiation in low-lying or poorly ventilated areas. Xylenes occur naturally in petroleum and coal and are additionally used as solvents and gasoline additives in the petroleum industry. Data from US EPA show that xylene vapors have been detected in refinery emissions and around separation, conversion, product handling, and auxiliary processes carried out in refineries.

Both short-term and long-term exposure to high levels of xylene may cause eye, skin, and respiratory tract irritation, but the central nervous system is the primary target of such encounters. Headaches, decreased muscle coordination, dizziness, confusion, and altered sense of balance may be experienced following acute exposure. Short-term exposure to elevated levels in air have also been associated with symptoms such as strained breathing, lung function impairment, delayed response to visual stimuli, impaired memory, stomach discomfort, ventricular arrhythmias, acute pulmonary edema (fluid accumulation in the lung), and hepatic impairment. Very high levels may be fatal. In addition, studies have shown that xylene may increase the rate of metabolism of other chemicals; however, the presence of other solvents inhibits the breakdown of xylene itself and may thus lead to increased toxicity. OEHHA used acute exposure studies demonstrating eye, nose, and throat irritation in humans exposed to xylene to develop the acute REL of 22 mg/m^3.

Chronic exposure to xylene in occupational settings has led to neurological effects such as headache, fatigue, dizziness, tremors, loss of coordination, anxiety, impairment of short-term memory, and inability to concentrate. Cardiovascular effects (labored breathing, impairment of pulmonary function, heart palpitations, chest pain, and abnormal electrocardiogram) and effects on the gastrointestinal system (nausea, vomiting, and gastric discomfort) have also been associated with prolonged exposure. Some studies also report effects on the kidneys. Xylene exposure from solvent abuse has also been shown to lead to permanent neuropsychiatric manifestations, which can progress to become chronic toxic encephalopathy (malfunction or degradation of brain function). In workers occupationally exposed to xylene, eye irritation, sore throat, floating sensation, and lack of appetite were observed at a concentration of 61.6 ng/m^3 and used as the basis for the OEHHA chronic REL of 700 µg/m^3. A US EPA RfC of

100 μg/m^3 was also established for this chemical based on the impaired motor coordination seen in rats following subchronic inhalation exposure.

Xylene has been reported to cross the placenta in humans and high doses may be fetotoxic in animals. Animal inhalation studies have shown developmental effects such as skeletal variations in fetuses, delayed bone formation, fetal resorptions, decreased body weight, and decreased motor performance during adolescence. Maternal toxicity has also been observed. The isomers with the greatest fetotoxicity and maternal toxicity are p-xylene and m-xylene, respectively.

vi. 1,3-Butadiene

1,3-Butadiene is a colorless gas with a mild gasoline-like odor that is usually an adequate warning to protect individuals against acutely hazardous levels. Although this gas is noncorrosive, it is highly flammable (LEL = 2%) and forms explosive peroxides upon prolonged exposure to air. The primary route of exposure to 1,3-butadiene is inhalation. While motor vehicle exhaust contributes to ambient levels of 1,3-butadiene, exposure to higher levels of the chemical primarily occurs in occupational settings since it is produced through the processing of petroleum, and used in making other products. 1,3-Butadiene is heavier than air and at high concentrations can cause asphyxiation in enclosed, poorly ventilated, or low-lying areas.

In refineries 1,3-butadiene emissions have been detected in many different areas: sulfuric acid loading, separators, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, and wastewater treatment. Boilers, internal combustion engines, and turbines may be additional sources of release. 1,3-Butadiene has been detected in routine and non-routine refinery emissions and has been identified in a refinery fire incident linked to the coking unit.

At low concentrations, acute inhalation of 1,3-butadiene vapors may be irritating to the eyes, nose, throat, and lungs. OEHHA reports that blurred vision, nausea, paresthesia (tingling or pricking sensation), and mouth, throat, and nose dryness are the initial signs of acute exposure to high concentrations, and may be followed by fatigue, headache, vertigo, hypotension, decreased heart rate, and unconsciousness. At very high concentrations, central nervous system depression can occur. A whole-body inhalation study of pregnant mice leading to decreased male fetal weight was the basis of the OEHHA acute REL (660 μg/m^3) for 1,3-butadiene chemical because it addressed the most sensitive endpoint of 1,3-butadiene exposure, developmental effects.

Chronic exposure to 1,3-butadiene, in the presence of other pollutants, has been found to exacerbate symptoms of asthma and increase incidence of respiratory tract infections. While long-term exposure to the gas has been linked to cardiovascular diseases and effects on the blood, female reproductive organs are considered the critical target of chronic exposure for noncancer effects. In addition, animal studies have shown that chronic exposure to 1,3-butadiene can lead to bone marrow depression and DNA repair deficiencies. The chronic OEHHA REL and US EPA RfC of 2 µg/m^3 are the same for 1,3-butadiene and were derived based on the increased occurrence of ovarian atrophy (degeneration of cells) observed during an inhalation study conducted on mice exposed daily for 6 hours, 5 days per week, for a duration of 9 to 24 months.

1,3-Butadiene is a carcinogen and a male and female developmental toxicant under Proposition 65. It has also been classified as a human carcinogen by IARC based on evidence that it causes cancer of the hematolymphatic organs. The CSF and unit risk for 1,3-butadiene are 0.6 (mg/kg-day)$^{-1}$ and 1.7×10^{-4} (µg/m^3)$^{-1}$, respectively, and were derived by OEHHA based on the incidence of lung tumors reported in inhalation studies of female mice. Although information regarding the developmental or reproductive effects of 1,3-butadiene is limited, animal studies have reported developmental effects such as skeletal malformations and decreased fetal weights, and reproductive effects such as damage to the ovaries and testes following inhalation exposure.

vii. Dibenzo-p-dioxins/Dibenzofurans

Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) make up a group of 210 closely related halogenated aromatic compounds collectively referred to as “dioxins.” In pure form, many dioxins are colorless crystals. Polyhalogenated compounds like dioxins are one of eight major categories of polycyclic organic matter, a broad class of compounds that is present in the atmosphere. Dioxins released into the air are deposited on land or water, where they persist for long periods of time and can build up in the fatty tissues of animals that ingest it (bioaccumulation). In refineries, dioxins are formed during catalyst regeneration and during the combustion of organic materials in the presence of chlorine and have been detected at process units such as heaters, incinerators, and wastewater (Thompson et al., 1990; Shaw et al., 2013).

Dioxins are a major concern due to the wide range of severe health effects induced by chronic exposure to low doses. In humans, exposure to dioxins has been shown to lead to the development of a skin condition resembling severe acne (chloracne), gastrointestinal upset, increased levels of serum enzymes and triglycerides, and numbness of the extremities. Although the toxic responses observed in animals treated with various members of this group are generally similar, those chlorinated at the 2, 3, 7, and 8 positions are particularly toxic. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) is considered the most potent congener of the dioxin family and is thus the most widely studied of the group. The most sensitive targets of chronic dioxin exposure include the alimentary system (liver), reproductive system, development, endocrine system (pineal, pituitary, thyroid, parathyroid, and adrenal glands, pancreas, ovaries, testes, hypothalamus, and gastrointestinal tract), respiratory system, and hematopoietic system (bone marrow, spleen, tonsils, and lymph nodes). In a study on rats continuously exposed to TCDD for two years via diet, effects such as increased mortality, decreased weight gain, and changes in the liver, lungs, and lymphoid and vascular tissues were noted at a dose of 0.001 µg/kg/day, which served as the point of departure for the chronic REL for dioxins (4×10^{-5} µg/m^3). Because of the ability of dioxins to bioaccumulate, a chronic oral REL of 1×10^{-5} µg/kg-day has also been developed. There is no acute REL or RfC for this group of chemicals. US EPA developed a Reference Dose (RfD) for 2,3,7,8-tetrachlorodibenzo-p-dioxin of 7×10^{-10} mg/kg-d based on decreased sperm count in men exposed as boys and decreased thyroid stimulating hormone (TSH) in neonates.

Both PCDDs and PCDFs are carcinogenic TACs with CPFs derived by OEHHA based on the occurrence of liver tumors in male mice after exposure. Dioxin-related cancer mortality following an accidental release of TCDD from a 1,2,3-trichloropropane-producing plant in Seveso, Italy included conditions such as digestive cancer, stomach cancer, lymphatic and hemopoietic cancer, multiple myeloma, rectal cancer, leukemia, ovarian cancer, and thyroid cancer. TCDD has a CSF and a unit risk value of 1.3×10^5 (mg/kg-day)$^{-1}$ and 38 (µg/m^3)$^{-1}$, respectively. PCDDs and PCDFs have been classified as carcinogens by OEHHA under Proposition 65 and by US EPA. PCDDs including TCDD have also been classified as multi-site carcinogens in animals by IARC. Immunotoxicity, particularly from perinatal exposure, and developmental toxicity are key endpoints of concern for infants and children. In addition, dioxins have been shown to cross the placenta and can be transferred from mother to infant during breastfeeding. Effects on thyroid development and infant neurodevelopment and an increased risk of diabetes and endometriosis from dietary intake have also been reported (Arisawa et al., 2005).

viii. Diethanolamine

Diethanolamine is a hydrocarbon found in air in the water vapor and particulate phases. It is a colorless powder or liquid in pure form and has an odor resembling that of ammonia. Diethanolamine produces acrid vapors when heated that are slightly heavier than air. It has been classified as a slight fire hazard by the National Fire Protection Association, but must be preheated prior to ignition. In petroleum refineries, diethanolamine is used in desulfurization processes and may contaminate wastewater (Bord et al., 2004). This chemical has been detected at multiple refinery process units included in this report (crude units, storage tanks, cokers, and wastewater treatment) and may also be found in amine scrubbers used for natural gas purification (Nelson, 2013).

In humans, acute inhalation exposure to diethanolamine may cause nose and throat irritation. Coughing, nausea, headache, and a smothering sensation may result from breathing its vapors. Other effects of acute exposure may include eye burns, corneal necrosis (death of corneal cells), skin burns, lacrimation (tearing), and sneezing.

Currently, there is inadequate information on the chronic effects of diethanolamine in humans. The respiratory and cardiovascular systems are the targets for chronic exposure. In one occupational case report, the handling of diethanolamine-containing cutting fluid caused asthmatic airway obstruction. Diethanolamine may exacerbate asthma; thus, children may be more vulnerable to its irritant effects. The chronic REL of 3 µg/m^3 was derived based on an inhalation study in rats that showed chronic inflammation and abnormal cellular changes (squamous hyperplasia, metaplasia) of the larynx at a concentration of 15 mg/m^3. Diethanolamine has been shown to cause liver tumors in rats by IARC and has been classified as a carcinogen by OEHHA under Proposition 65.

ix. Formaldehyde

At room temperature, formaldehyde is a colorless gas with a distinct, pungent odor detectable even at low concentrations. Formaldehyde is found in air in the vapor, water vapor, and particulate phases. Formaldehyde is flammable with an LEL of 7%, and its combustion may generate carbon monoxide. Emissions of this chemical into the environment commonly occurs during combustion processes; thus, inhalation is the primary route of exposure. Formaldehyde has been detected in both ambient air emissions and at several refinery process units such as boilers, cokers, crude units, FCCUs, heaters, and incinerators (Lucas, 2002). Vapors of formaldehyde are heavier than air and high concentrations can cause asphyxiation in low-lying, enclosed, or poorly ventilated areas. In addition, this respiratory irritant may have a more severe impact on infants and children.

Acute exposure to low concentrations of formaldehyde can result in eye irritation, headache, rhinitis (irritation or inflammation of mucous membrane in the nose), and dyspnea (labored breathing or shortness of breath). Some people may be more sensitive to the effects of formaldehyde exposure and experience exacerbation of asthma and dermatitis at low doses. Higher doses may cause lacrimation (tearing), severe mucous membrane irritation, burning, difficulty breathing, and effects on the lower respiratory system such as bronchitis, pulmonary edema (fluid accumulation in the lung), or pneumonia. Asthmatics and individuals previously sensitized to formaldehyde may be more vulnerable to the adverse respiratory effects resulting from exposure. Because studies have shown that asthma is more common and may be more severe in children than adults, formaldehyde exposure is also a concern for infants and children. An acute REL was derived for formaldehyde based on a study in which non-asthmatic, nonsmoking individuals were exposed to the chemical for three hours and began experiencing mild and moderate eye irritation at an airborne concentration of 0.9 mg/m^3. The OEHHA acute REL is 55 µg/m^3 after adjustments for dose, time, and uncertainties.

Long-term exposure to formaldehyde primarily targets the respiratory system and may lead to allergic sensitization, respiratory symptoms such as coughing and wheezing, nasal symptoms such as running nose and crusting, lacrimation (tearing), cellular changes in airway membranes, and decreased lung function. Effects on the nervous system such as headaches, depression, mood changes, insomnia, attention deficit, and dexterity and memory impairment have also been reported. OEHHA used an occupational study in which workers experienced nasal obstruction and discomfort and lower airway discomfort at an average concentration of 0.09 mg/m^3 to derive the chronic REL of 9 µg/m^3 for formaldehyde.

Formaldehyde is a carcinogenic TAC with CPFs derived by OEHHA based on the incidence of nasal tumors in male and female rats and male mice resulting from exposure. In humans, formaldehyde exposure has additionally been associated with cancers of the upper respiratory tract, specifically buccal cancer, pharyngeal cancer, and nasopharyngeal cancer. Formaldehyde has also been associated with an elevated risk of leukemia and sinonasal cancer. The CSF for formaldehyde is 2.1×10^{-2} (mg/kg-day)$^{-1}$ and the unit risk value is 6.0×10^{-6} (µg/m^3)$^{-1}$. Formaldehyde has been classified as a carcinogen by OEHHA, US EPA, and IARC.

x. Hydrogen Fluoride

Hydrogen fluoride is a colorless fuming liquid or gas with a strong, pungent odor. Dissolution in water forms corrosive hydrofluoric acid, a systemic poison. Although it will not burn under typical fire conditions, this acid emits highly irritating and poisonous vapors that are corrosive to metals and body tissues when heated. Because it is corrosive to metals, hydrogen fluoride may yield hydrogen and may thus indirectly create a fire hazard. Hydrogen fluoride in air is normally found in the water vapor and particulate phases. The general population may be exposed to hydrogen fluoride in the ambient environment from industrial process emissions and coal combustion. In refineries, this chemical is used as a catalyst during alkylation or cracking and has been detected in refinery emissions and around crude units and cokers.

Short-term inhalation of hydrogen fluoride can lead to severe respiratory damage (irritation and fluid accumulation in the lung), lacrimation (tearing), sore throat, cough, chest tightness, and wheezing. Due to the ability of the fluoride ion to penetrate tissues, some health effects may be delayed for one to two days after exposure. Breathing high levels of the gas or in combination with dermal exposure may be fatal due to pulmonary edema (fluid accumulation in the lung) and bronchial pneumonia. People with cardiopulmonary disease may be particularly vulnerable to lower airway irritation at high concentrations. The most sensitive endpoint for short-term inhalation exposure to hydrogen fluoride is eye, nose, and throat irritation, which was observed in an inhalation study of healthy, male volunteers after one hour of exposure to concentrations of 0.2-0.6 mg/m^3. After time and dose adjustments and consideration of uncertainties, OEHHA established an acute REL of 240 µg/m^3 to protect individuals from these effects.

Long-term exposure to low levels of hydrogen fluoride has been linked to congestion and irritation of the nose, throat, and bronchi. Liver and kidney damage has also been noted. Exposure to higher levels has been associated with increased bone density (skeletal fluorosis). This was observed in a study on fertilizer plant workers chronically exposed to an average of 0.14 mg/m^3 hydrogen fluoride. In this study, OEHHA determined the point of departure for increased bone density to be 1.13 mg/m^3, which served as the basis of the chronic REL of 14 µg/m^3. Because fluorides may contaminate food and drinking water, OEHHA has also developed a chronic oral REL for hydrogen fluoride, based on the dental fluorosis observed in the inhabitants of several US cities exposed via drinking water. A point of departure of 0.82 mg/m^3 at which the incidence of moderate to severe dental fluorosis was considered to be rare among the population was used to calculate the chronic oral REL of 40 µg/kg-day. Dental fluorosis has additionally been noted in children after maternal exposure to high levels during pregnancy.

xi. Hydrogen Sulfide

Found in air in the water vapor and particulate phases, hydrogen sulfide is a corrosive gas with a pungent rotten egg odor. For this chemical, odor is not a reliable indicator of its presence due to the olfactory fatigue that occurs at both high concentrations and continuous low concentrations. Hydrogen sulfide is highly flammable (LEL = 4%) and may produce an explosion at levels above 4.5% in air. When heated, highly toxic sulfur oxide fumes or vapors are emitted. Hydrogen sulfide is slightly heavier than air and may be present at higher levels in enclosed, poorly ventilated, and low-lying areas. Because it is released naturally as a product of decaying organic matter, hydrogen sulfide is a natural component and the predominant impurity of crude oil and natural gas (Skrtic, 2006).

In oil refineries, hydrogen sulfide is formed during the removal of sulfur compounds from petroleum products and has been detected at various process units such as boilers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, and incinerators. Hydrogen sulfide is one of the most routinely emitted refinery pollutants included in this report and its distinct smell made it one of the most frequently mentioned chemicals in refinery incident reports during 2001-2012. As with ammonia, it appears in many refineries' RMPs as the worst-case-scenario toxic release and alternate release scenario (CARB and CAPCOA, 2015).

Hydrogen sulfide is very toxic by inhalation. Because exposure to this chemical affects most organ systems, hydrogen sulfide is considered to be a broad spectrum toxicant and may pose a significant health risk to those exposed. Acute exposure to hydrogen sulfide targets the central nervous system and leads to symptoms such as headache, nausea, and irritation of the skin, eyes, mucus membranes, and respiratory tract. Acute exposure to higher levels of hydrogen sulfide can cause conjunctivitis (inflammation or infection of the eye) with ocular pain, lacrimation (tearing), and photophobia. Concentrations in air high enough to exceed the body's detoxification threshold lead to cellular respiratory poisoning and asphyxiation (Skrtic, 2006). Death due to hydrogen sulfide exposure is typically caused by respiratory arrest. In addition, ethanol has been shown to decrease the average time-to-unconsciousness in mice exposed to the gas and may thus potentiate its effects.

The most sensitive endpoints for acute hydrogen sulfide exposure are headache and nausea in human volunteers, which were reported at levels below the odor threshold after exposure to doses ranging from 16.8 to 96.6 µg/m^3. After time and dose adjustments and consideration of uncertainties, an acute REL of 42 µg/m^3 was developed by OEHHA.

Chronic effects of hydrogen sulfide include: low blood pressure, headache, nausea, loss of appetite, weight loss, ataxia (lack of muscle control during voluntary movements), eye membrane inflammation, and chronic cough. In mice, prolonged exposure to hydrogen sulfide targets the respiratory system and causes nasal inflammation (chronic REL = 10 µg/m^3). The inhalation RfC of 2 µg/m^3 was derived based on a study showing olfactory loss and nasal lesions in rats following subchronic exposure to 42.5 mg/m^3 of the chemical. Individuals living in close proximity to oil refineries may be at risk of chronic exposure to hydrogen sulfide. Hydrogen sulfide is not listed as a carcinogen under Proposition 65, but the literature indicates that this chemical may be a reproductive toxicant that increases risk of spontaneous abortion.

xii. Manganese

Naturally-occurring manganese compounds are often associated with organic materials or metals. The general public is exposed to manganese through inhalation, particularly in areas where it is used in manufacturing and through consumption of food and water. Manganese is of concern because of the amount of routine refinery emissions and the many process units with which it is associated (boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, and incinerators). Manganese may be ignited by friction, heat, sparks, or flames. It may also react violently or explosively with water, and dusts or vapors may yield explosive mixtures in air.

Both short-term and long-term inhalation exposures to manganese have the potential to cause adverse health effects and appear to target the nervous system. While small amounts of manganese are beneficial to human health, exposure to higher levels may cause brain damage. Acute manganese exposure may lead to impaired function and nonspecific pulmonary edema (fluid accumulation in the lung).

Chronic manganese exposure may lead to more serious health effects, including “manganism” neurotoxicity. The symptoms of “manganism” appear similar to those of Parkinson’s disease, with affected individuals suffering from dystonia (involuntary muscle contractions), altered gait, generalized rigidity, and fine tremor. Some individuals may also suffer from psychiatric disturbances. Lower levels of prolonged manganese exposure can lead to changes in neurobehavioral and cognitive abilities such as slower visual reaction time, poorer hand steadiness, and impaired hand-eye coordination in both adults and children. Chronic exposure may also cause respiratory effects such as increased incidence of cough, bronchitis, dyspnea (labored breathing or shortness of breath) during exercise, and increased susceptibility to infectious lung disease. Manganese exposure in early life may affect behavioral and intellectual capabilities. The manganese OEHHA chronic REL of 0.09 µg/m^3 was derived based on the impaired human neurobehavioral functioning (impaired visual reaction time, hand-eye coordination, and hand steadiness) reported in a study of battery plant workers occupationally exposed to 0.04 to 4.43 mg manganese/m^3 per year via inhalation of respirable dust. US EPA's RfC for manganese is 0.05 µg/m^3, and is similarly based on impairment of neurobehavioral functioning seen in individuals occupationally exposed to manganese.

Animal studies have shown decreased dopamine in the striatum and poorer performance on behavioral tests in rats orally exposed to manganese. Decreased activity levels and average pup weights have been noted in mice exposed via inhalation. High levels of exposure may also lead to accumulation of the metal in brain regions such as the striatum and the midbrain.

xiii. Naphthalene

Naphthalene is a volatile white crystalline solid that exists in air in the form of vapor or adsorbed to particulates. It is released into the atmosphere from coal and oil combustion and from the use of mothballs. The primary route of human exposure to naphthalene is inhalation. Naphthalene emissions have been detected at several refinery process units (separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents) and naphthalene has been detected in both routine and non-routine emissions. Naphthalene is of particular concern due to its flammability in the presence of an ignition source (LEL = 0.9%). Fire may yield irritating or toxic gases, and powders, dusts, and shavings may be explosive.

People who are acutely exposed to naphthalene may experience headache, nausea, vomiting, diarrhea, malaise (general feeling of discomfort), confusion, anemia, jaundice, convulsions, and coma. Short-term exposure has also been associated with neurological damage in infants, hemolytic anemia, and liver damage.

Prolonged exposure to large amounts of naphthalene may damage or destroy red blood cells, leading to hemolytic anemia, and has been reported to cause cataracts and retinal hemorrhage in humans. In mice chronically exposed to naphthalene via inhalation, chronic inflammation of the lung, chronic nasal inflammation, hyperplasia of nasal respiratory epithelium, and metaplasia of the olfactory epithelium has been noted. The OEHHA chronic REL of 9 µg/m^3 for naphthalene was derived (after time and dose adjustments and consideration of uncertainties) on the noncancer respiratory effects observed in mice chronically exposed to a concentration of 52.6 ng/m^3 including: nasal inflammation, olfactory epithelia metaplasia, and respiratory epithelial hyperplasia (Abdo et al., 2001). Such symptoms are indicative of the carcinogenic potential of naphthalene. An RfC of 3,000 µg/m^3 has also been developed by US EPA based on this study.

Naphthalene is listed as a carcinogen on the Proposition 65 list and has been classified as a possible human carcinogen by IARC based on the nasal tumors seen in rats and the lung tumors seen in female mice exposed by inhalation. Naphthalene has a CSF of 0.12 (mg/kg-day)$^{-1}$, which is based on data for incidence of nasal tumors, specifically nasal respiratory epithelial adenoma and nasal olfactory epithelial neuroblastoma, in male rats. In mice, inhalation exposure to naphthalene has also been shown to increase the incidence of lung tumors. The unit risk for naphthalene is 3.4×10^{-5} (µg/m^3)$^{-1}$.

Because their bodies have not fully developed detoxification mechanisms, newborns and infants are thought to be especially vulnerable to the effects to naphthalene exposure. In infants born to mothers who were exposed by inhalation and ingestion during pregnancy, hemolytic anemia has been reported. Oral exposure in mice has also been shown to cause maternal toxicity (increased mortality and decreased weight gain) and fetotoxicity.

xiv. Nitrogen Oxides (NOx)

Nitrogen oxides (NOx) represent a group of highly reactive gasses including nitric oxide, nitrogen dioxide, nitrogen trioxide, nitrogen tetroxide, and nitrogen pentoxide that are released into the air from combustion sources. Because nitrogen dioxide is considered to be one of the most toxicologically significant of the nitrogen oxides and is used by both the US EPA and CalEPA as the indicator for the group, it will be the focus of this subsection. Nitrogen dioxide is a yellow-brown liquid at room temperature that takes the form of a reddish brown gas at temperatures above 70^{o}F. It is a corrosive gas with a strong odor that generally provides adequate warning of acute exposure to high levels. Although it is nonflammable, nitrogen dioxide will accelerate the burning of combustible materials and may react violently with cyclohexane, fluorine, formaldehyde and alcohol, nitrobenzene, petroleum, and toluene. In the environment, nitrogen dioxide can form nitric acid, a major constituent of acid rain, and contributes to the formation of ozone and fine particle pollution. Gaseous nitrogen dioxide is also heavier than air and at high concentrations can lead to asphyxiation in poorly ventilated, enclosed, or low-lying areas.

NOx has been detected in non-routine refinery emissions and around many refinery process units such as boilers, crude units, heaters, storage tanks, cokers, FCCUs, incinerators, and flares. It has also been associated with multiple fire incidents reported during 2001-2012.

Coughing, fatigue, nausea, choking, headache, abdominal pain, and strained breathing may be experienced immediately following acute exposure to nitrogen dioxide. Short-term exposure to nitrogen dioxide may also have delayed health effects such as pulmonary edema (fluid accumulation in the lung) with anxiety, mental confusion, lethargy, loss of consciousness, pneumonitis (inflammation of lung tissue), and bronchitis. Exposure to high concentrations of nitrogen dioxide may lead to pulmonary edema (fluid accumulation in the lung) and delayed inflammatory changes, which can be life-threatening. Burns, spasms, swelling of tissues in the throat, and upper airway obstruction may also occur. In addition to children and the elderly, individuals with asthma and other preexisting pulmonary diseases, especially RADS, may be more sensitive to the toxic effects of nitrogen dioxide. OEHHA developed an acute REL of 470 $\mu g/m^3$ for nitrogen dioxide based on the increased airway reactivity observed in asthmatics following a one-hour exposure at this concentration. Since that time, the CARB has promulgated a one-hour AAQS of 340 $\mu g/m^3$ based on OEHHA's health-based recommendation.

Chronic exposure to nitrogen oxides can cause permanent and obstructive lung disease from bronchiolar damage. Increased risk of respiratory infections in children has also been associated with long-term exposure. While NOx has not been classified as carcinogens or developmental or reproductive toxicants under Proposition 65, they have mutagenic, clastogenic (inducing disruption or breakage of chromosomes), and fetotoxic effects in rats. In one study exposing pregnant rats to nitrogen dioxide, an increased occurrence of intrauterine deaths, stillbirths, developmental abnormalities, and low birth weights was observed.

xv. Particulate Matter (PM_{10} and $PM_{2.5}$)

Particulate matter (PM) is a mixture of liquid droplets and solids such as dust, dirt, soot, and smoke in the air. These particles exist in a large variety of shapes, sizes, and chemical compositions. In addition to the well-characterized health effects of PM, particle pollution reduces visibility and damages welfare such as crops and buildings. Two size categories of PM are regulated at the state and federal levels. Respirable particles (PM_{10}) are those with a mass mean aerodynamic diameter of 10 micrometers or less, and pose a health concern due to their ability to pass through the nose and throat and into the deeper portions of the respiratory system. Fine particles ($PM_{2.5}$) are those with a diameter of 2.5 micrometers or smaller and are considered to be a significant health risk due to their ability to travel into deep areas of the lungs and smaller ultrafine particles (generally less than 100 nanometers) may even enter the bloodstream.

The composition of PM largely depends on particle size and origin. Fine particles commonly contain ionic species (e.g. sulfate, nitrate, and ammonium), acid (e.g., hydrogen ion, H+), organic and elemental carbon, and trace elements (e.g. aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, nickel, copper, zinc, selenium, bromine, arsenic, cadmium, and lead). $PM_{2.5}$ can also contain larger amounts of PAHs such as naphthalene, chrysene, phenanthrene, and anthracene than PM_{10} (Catoggio et al., 1989).

Particulates have been detected at many emissions points in petroleum refineries (abrasive blasting, asbestos abatement, boilers, cooling towers, crude units, heaters, cokers, FCCUs, incinerators, and flares) and in non-routine emissions outdoors. Because of the ubiquitous nature of particulates in smoke, all fire events reported in the 2001-2012 data also involved the unintentional release of particulate matter.

Short-term exposure to $PM_{2.5}$ has been linked to increased hospitalizations and emergency room visits for heart and lung-related illnesses and premature death. Inhalation of fine particles can be harmful to the heart and blood vessels, and may increase risk of heart attack, stroke, cardiac arrest, and/or congestive heart failure. Other symptoms of exposure include eye, nose, and throat irritation, reduced lung function, asthma attacks, irregular heartbeat, and increased respiratory symptoms such as coughing, wheezing, and shortness of breath.

Chronic exposure to fine particle pollution also leads to increased incidence of heart and lung problems, and some studies further suggest its possible association with cancer and reproductive and developmental toxicity. Population-based epidemiological studies have found associations between ambient particulate pollution and lung cancer. While healthy individuals may experience temporary symptoms, the elderly, children, people with heart or lung conditions, and people exposed to unusually high levels of pollution are considered to be more susceptible to the adverse health effects of particulate matter exposure. Pregnant women, newborns, and individuals with certain health conditions such as obesity and diabetes may also be at increased risk. For further information on the health effects of PM, see CARB and OEHHA (2002).

xvi. Sulfur Dioxide

At room temperature, the criteria air pollutant sulfur dioxide is a colorless, irritating gas with a choking or suffocating odor that generally provides adequate warning of exposure at high levels of exposure. Found in the vapor and particulate phases, sulfur dioxide in the atmosphere is formed both endogenously from volcanic eruptions and marine and terrestrial biogenic emissions and exogenously from the combustion of coal and oil. It may be converted to sulfuric acid, sulfur trioxide, and sulfates in air, and its dissolution in water can yield corrosive sulfurous acid. Gaseous sulfur dioxide will not burn under typical fire conditions. Exposure to sulfur dioxide occurs mainly via inhalation. Sulfur dioxide is heavier than air and asphyxiation may result from exposure to high concentrations in poorly ventilated, enclosed, or low-lying areas.

Sulfur dioxide and its vapors have been detected at various refinery emission points including boilers, crude units, heaters, cokers, FCCUs, and incinerators. Sulfur dioxide has been detected in non-routine refinery emissions and was noted in incident reports more frequently than any other chemical included in this report, often during or after flaring events.

Acute inhalation exposure to sulfur dioxide has been associated with eye, mucous membrane, skin, and respiratory tract irritation. Symptoms of respiratory irritation include sneezing, sore throat, wheezing, shortness of breath, chest tightness, and a feeling of suffocation. Breathing very high levels can be life-threatening. Airway obstruction from reflex laryngeal spasm and edema, bronchospasm, pneumonitis (inflammation of lung tissue), and pulmonary edema (fluid accumulation in the lung) after exposure has been reported. Asthmatics, especially when exercising or when in cold, dry air, and some individuals that are atopic (predisposed toward developing certain allergic hypersensitivity reactions) or have RADS are more sensitive to the irritant properties of sulfur dioxide. Since the occurrence of asthma is most common in African Americans, children ages 8-11 years, and people living in cities, African American children in urban areas are also expected to have increased vulnerability to this chemical. Further, adverse effects on pulmonary function may be more severe in asthmatics and those with cardiopulmonary disease dually exposed to sulfur dioxide and other irritants such as sulfuric acid, nitrogen dioxide, and ozone. OEHHA used multiple inhalation studies of healthy, asthmatic, and atopic (predisposed toward developing certain allergic hypersensitivity reactions) volunteers for the derivation of the acute REL for sulfur dioxide (660 $\mu g/m^3$). This value is identical to the California AAQS for one-hour exposure. The most sensitive endpoint observed at this concentration was impairment of airway function, particularly in asthmatics.

Chronic exposure to sulfur dioxide may lead to an altered sense of smell, increased susceptibility to respiratory infections, symptoms of chronic bronchitis, and accelerated decline in pulmonary function. The California AAQS for 24-hour averaging is 0.04 ppm (105 $\mu g/m^3$) for sulfur dioxide. In 2011, sulfur dioxide was added to the Proposition 65 list as a developmental toxicant based on studies showing increased incidence of preterm birth and indicators of fetal growth retardation such as low birth weight. Evidence that air pollution containing sulfur dioxide induces DNA damage in human sperm has also been reported.

xvii. Sulfuric Acid

Sulfuric acid is a colorless, oily liquid that exists in air in water vapor and particulates. It is corrosive to metals and organic materials and emits toxic sulfur trioxide-containing fumes or vapors when heated. While it will not burn under typical fire conditions, sulfuric acid in high concentrations is explosive or incompatible with a variety of substances including organic materials, chlorates, carbides, fulminates, water, and powdered metals. The general population is exposed to this chemical by breathing ambient air where oil, gas, or coal is burned. In petroleum refineries, sulfuric acid is used as a catalyst during alkylation and in various treatment processes (Lewis, 2012). This chemical has also been detected in large amounts in refinery air emissions and reported in multiple fire and non-fire incidents.

Both acute and chronic exposures to sulfuric acid target the respiratory system. Breathing sulfuric acid mists for short periods of time in occupational settings has been associated with dental erosion and respiratory tract irritation, which leads to bronchoconstriction and altered lung function. Multiple exposures to other pollutants also common to industrial areas may increase the irritant effects of sulfuric acid, particularly for individuals with asthma. In addition, animal studies suggest that the young may be more sensitive to adverse effects than adults. The most sensitive endpoint of acute exposure was observed in a human study that showed small changes in airway function, particularly in asthmatics, following a 16-minute exposure to 450 $\mu g/m^3$ of sulfuric acid. After time and dose adjustments and consideration of uncertainties, an OEHHA acute REL of 120 $\mu g/m^3$ was established.

Long-term exposure to sulfuric acid has been associated with decreased lung function. Chronic exposure may also lead to tracheobronchitis (inflammation of the windpipe and bronchioles), stomatitis (inflamed or sore mouth), conjunctivitis (inflammation or infection of the eye), and gastritis (inflammation, irritation, or erosion of the stomach). The chronic REL for sulfuric acid was derived from a continuous inhalation study that led to abnormal changes in bronchial cells in the lungs of monkeys (increased cell reproduction and organ/tissue enlargement) at a concentration of 380 $\mu g/m^3$. OEHHA determined the chronic REL for sulfuric acid to be 1 $\mu g/m^3$.

APPENDIX B: CALIFORNIA REFINERY PROCESS UNITS AND EMISSION POINTS WITH ASSOCIATED CHEMICAL EMISSIONS

In response to a request by US EPA, all refineries active during 2010 measured air emissions from each process and emission point for a specified time period and submitted the data to US EPA. This request resulted in a list of chemicals measured to be routinely emitted in each process, and OEHHA used these emissions inventories to identify the most commonly occurring processes in California refineries (Table 8) and their reported chemical emissions. Since some refinery processes are associated with a particular chemical profile, such information can be used to help anticipate the types of chemicals that may be released during a refinery accident and characterize the potential health effects of chemical exposure. Thus, consideration of common processes and characteristic emissions, in addition to knowledge of health guidance values and emergency exposure levels, can be used to help CARB make judgements about air monitoring.

Appendix B displays a list of chemical emissions associated with each process based on California data for 2010. The processes and chemicals shown in Appendix B reflect a sample of those most commonly found in our research based on California data for 2010 provided by US EPA but are not intended to be a complete list of all refinery processes or chemicals emitted from each process.

Table B1. California Refinery Process Units and Emissions Points Associated with Chemical Emissions

	Process[1]														
Chemical [2]	Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
Acenaphthene	X	X	X	X	X			X	X	X	X	X	X	X	X
Acenaphthylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Acetaldehyde	X	X	X	X	X	X	X	X	X	X			X	X	X
Acetylene				X			X	X	X					X	
Acrolein		X	X	X	X	X	X	X	X				X	X	
Ammonia	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Analine	X	X	X	X	X	X	X	X	X	X		X	X	X	
Anthracene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Antimony		X	X	X	X	X	X	X	X	X			X	X	
Arsenic		X	X	X	X	X	X	X	X	X	X		X	X	
Barium		X	X	X	X	X	X	X	X	X			X	X	
Benz[a]anthracene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[b]fluoranthene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[k]fluoranthene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[g,h,i]perylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[a]pyrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[e]pyrene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Beryllium		X	X	X	X	X	X	X	X	X	X		X	X	
Biphenyl	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
1,2-Butadiene				X	X		X	X	X					X	

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[1] Abbreviations for the fluid catalytic cracking unit (FCCU), the sulfur recovery unit (SRU), and wastewater treatment (WWT) have been used.

[2] Chemical emissions detected at California refinery process units and emission points in 2010 (US EPA, 2012a; US EPA, 2012b).

	Process[1]														
Chemical [2]	Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
1,3-Butadiene	X		X	X	X	X	X	X	X	X	X	X		X	X
Butane	X		X	X	X	X	X	X	X	X		X	X	X	X
1-Butene	X		X	X			X	X	X	X		X		X	
2-Butene	X		X	X			X		X	X		X		X	
Cadmium		X	X	X	X	X	X	X	X	X	X		X	X	
Carbon disulfide	X		X	X	X	X	X		X	X	X	X	X	X	X
Carbon monoxide		X	X	X	X	X	X	X	X		X		X	X	
Carbonyl sulfide	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Chlorine					X					X			X	X	
Chloroform	X		X		X	X				X		X	X	X	X
Chloromethane	X			X		X				X		X	X		
2-Chloronaphthalene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Chromium (hexavalent)		X	X	X	X	X	X	X	X		X		X	X	
Chromium (total)		X	X	X	X	X	X	X	X	X	X		X	X	
Chrysene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Cobalt		X	X	X	X	X	X	X	X	X			X	X	
Copper		X	X	X	X	X	X	X	X	X	X		X	X	
Cresols (total)	X		X	X	X	X	X	X	X	X	X	X	X	X	X
m-Cresol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
o-Cresol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
p-Cresol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Cumene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Cyclohexane	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Cyclopentadiene				X			X	X	X					X	
Cyclopentane				X			X		X					X	

Chemical [2]	**Process**[1] Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
Dibenz[a,h]anthracene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin														X	
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin														X	
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin														X	
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin														X	
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin														X	
1,2,3,7,8-Pentachlorodibenzo-p-dioxin														X	
2,3,7,8-Tetrachlorodibenzo-p-dioxin			X						X				X	X	
Dibenzofuran(s)	X		X	X	X	X			X	X		X		X	
1,2,3,4,6,7,8-Heptachlorodibenzofuran														X	
1,2,3,4,7,8,9-Heptachlorodibenzofuran														X	
1,2,3,6,7,8-Hexachlorodibenzofuran														X	
1,2,3,7,8,9-Hexachlorodibenzofuran														X	
2,3,4,6,7,8-Hexachlorodibenzofuran														X	
1,2,3,4,6,7,8,9-Octachlorodibenzofuran														X	
1,2,3,7,8-Pentachlorodibenzofuran			X											X	
2,3,4,7,8-Pentachlorodibenzofuran														X	
2,3,7,8-Tetrachlorodibenzofuran					X									X	
Dibutyl phthalate														X	
1,4-Dichlorobenzene	X		X		X			X	X	X		X	X		X
1,1-Dichloroethane													X		
Di(2-ethylhexyl)phthalate								X						X	

	Process[1]														
Chemical [2]	Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
1,1-Dichloroethylene											X		X	X	
1,2-Dichloropropane													X		
1,3-Dichloropropene													X		
Diethanolamine	X		X	X	X	X				X	X	X	X	X	X
Diethyl phthalate														X	
7,12-Dimethylbenz[a]anthracene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Ethane	X		X	X			X	X	X	X		X	X	X	
Ethylbenzene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Ethylene	X		X	X	X	X	X	X	X	X		X		X	X
Ethylene dibromide	X		X							X		X	X		
Ethylene dichloride	X		X							X	X	X	X		X
Fluoranthene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Fluorene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Formaldehyde		X	X	X	X	X	X	X	X	X			X	X	
Heptane (& isomers)				X			X		X					X	
Hexachloroethane													X		
Hexane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Hydrogen chloride				X	X	X	X	X	X		X		X	X	
Hydrogen cyanide (& compounds)	X		X	X	X	X	X	X	X				X	X	
Hydrogen fluoride	X			X		X				X		X			X
Hydrogen sulfide	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Indeno[1,2,3-cd]pyrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Isobutane	X		X					X		X		X		X	
Isobutene	X		X	X			X	X	X	X		X		X	X
Isopentane			X	X			X		X					X	

Chemical [2]	Process[1] Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
Isoprene				X			X		X					X	
Lead		X	X	X	X	X	X	X	X	X	X		X	X	X
Manganese		X	X	X	X	X	X	X	X	X	X		X	X	
Mercury		X	X	X	X	X	X	X	X	X	X		X	X	
Methanol	X		X		X	X		X	X	X	X	X	X	X	X
Methyl bromide													X		
3-Methyl-1,2-butadiene				X			X							X	
Methyl ethyl ketone	X		X	X	X	X	X	X	X	X	X	X		X	X
Methyl isobutyl ketone	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Methyl tert-butyl ether	X		X	X	X	X	X	X	X	X	X	X	X	X	X
3-Methylchloranthrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Methylcylcohexane				X			X		X					X	
2-Methylnaphthalene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Molybdenum			X	X		X	X	X	X	X			X		
Naphthalene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Nickel		X	X	X	X	X	X	X	X	X	X		X	X	
Nitrogen dioxide		X	X	X	X		X	X	X				X	X	
Nitrogen oxides		X	X	X	X	X	X	X	X		X	X	X	X	
Octane (& isomers)				X			X		X	X				X	
1,2-Pentadiene				X			X		X					X	
cis-1,3-Pentadiene				X			X		X					X	
trans-1,3-Pentadiene				X			X		X					X	
1,4-Pentadiene				X			X		X					X	
2,3-Pentadiene				X			X		X					X	
Pentane	X		X	X		X	X	X	X			X	X	X	X

	Process[1]														
Chemical [2]	Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
Perchloroethylene			X		X					X			X	X	X
Perylene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Phenanthrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Phenol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Phosphorus			X	X			X	X	X				X		
PM (condensable)		X	X	X	X	X	X	X	X	X			X	X	
PM_{10}		X	X	X	X	X	X	X	X	X			X	X	
PM_{10} (filterable)		X	X	X	X	X	X		X	X			X	X	
$PM_{2.5}$		X	X	X	X	X	X	X	X	X			X	X	
$PM_{2.5}$ (filterable)		X	X	X	X	X	X		X	X			X	X	
Polychlorinated biphenyls		X	X		X				X				X	X	
Propadiene				X			X	X	X					X	
Propane	X		X	X		X	X	X	X	X		X	X	X	
Propylene	X	X	X	X	X	X	X	X	X	X		X	X	X	X
Pyrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Selenium		X	X	X	X	X	X	X	X	X	X		X	X	
Styrene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Sulfur dioxide		X	X	X	X	X	X	X	X	X		X	X	X	
1,1,2,2-Tetrachloroethane													X	X	
Tetrachloroethylene				X	X	X								X	
Toluene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
1,1,2-Trichloroethane	X									X		X		X	X
Trichloroethylene	X											X	X	X	
Triethylamine	X		X	X		X				X	X	X	X	X	X
Trimethylbenzene(s)	X		X	X	X	X	X	X	X	X	X	X	X	X	X

Chemical [2]	**Process[1]**														
	Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
2,2,4-Trimethylpentane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Vanadium		X	X	X	X	X	X	X	X	X			X	X	
Vinyl chloride												X		X	
Volatile organic compounds	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Xylenes (total)	X		X	X	X	X	X	X	X	X	X	X	X	X	X
m-Xylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
o-Xylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
p-Xylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Zinc			X	X	X	X	X	X	X	X	X		X	X	

APPENDIX C: CALIFORNIA REFINERY CHEMICALS SORTED BY CHEMICAL ANALYSIS CATEGORY

OEHHA used a classification scheme provided by CARB by assigning specific chemical analysis categories, shown in Table 9, to chemicals included in OEHHA's list of California refinery chemicals (Table 1). The classification of chemicals by air monitoring capability allowed for the consideration of emissions, health effects, and health guidance values of chemicals with similar properties. Appendix C displays the chemicals included in each chemical analysis category. The analysis categories and chemicals within them are sorted in alphabetical order.

Table C1. California Refinery Chemicals Sorted by Chemical Analysis Category

Chemical Analysis Category	Chemical
Acid	Hydrogen chloride
Acid	Hydrogen cyanide
Acid	Hydrogen fluoride
Acid	Phosphoric acid
Acid	Sulfuric acid
Aldehyde	Acetaldehyde
Aldehyde	Formaldehyde
Aldehyde	Glutaraldehyde
Dioxins, Dibenzofurans	Dibenzo-p-dioxins (chlorinated)
Dioxins, Dibenzofurans	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,7,8-Pentachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	2,3,7,8-Tetrachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	Dibenzofurans (chlorinated)
Dioxins, Dibenzofurans	1,2,3,4,6,7,8-Heptachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,4,7,8,9-Heptachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,4,7,8-Hexachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,6,7,8-Hexachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,7,8,9-Hexachlorodibenzofuran
Dioxins, Dibenzofurans	2,3,4,6,7,8-Hexachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,4,6,7,8,9-Octachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,7,8-Pentachlorodibenzofuran
Dioxins, Dibenzofurans	2,3,7,8-Tetrachlorodibenzofuran
Extractable	Phenol
Extractable Aromatic	Biphenyl

Chemical Analysis Category	Chemical
Extractable Aromatic	Cresols (mixtures of)
Extractable Aromatic	Dibutyl phthalate
Extractable Aromatic	Di(2-ethylhexyl)phthalate
Extractable Hetero Aromatic	Aniline
Extractable Hetero Aromatic	Polychlorinated biphenyls
Extractable Hetero Hydrocarbon	Diethanolamine
Gas	Ammonia
Gas	Methane
Gas	Nitrous oxide
Gas	Propylene oxide
Gas, CEM	Nitrogen oxides
Gas, CEM	Sulfur dioxide
Gas, Colorimetric, CEM	Carbonyl sulfide
Gas, Colorimetric, CEM	Chlorine
Gas, Colorimetric, CEM	Hydrogen sulfide
Gas, Colorimetric, VOC, CEM	Carbon monoxide
Glycol	Ethylene glycol monoethyl ether
Glycol	Propylene glycol monomethyl ether
Glycol Acid	Ethylene glycol monoethyl ether acetate
Glycol Acid	Propylene glycol monomethyl ether acetate
Glycol Ether	Propylene glycol mono-t-butyl ether
Glycol, Glycol Acid	Glycol ethers (& acetates)
Mass	PM_{10}
Mass	$PM_{2.5}$
Metal	Aluminum
Metal	Antimony
Metal	Arsenic
Metal	Barium
Metal	Beryllium
Metal	Cadmium
Metal	Chromium III
Metal	Chromium (hexavalent & compounds)
Metal	Cobalt
Metal	Copper
Metal	Lead
Metal	Manganese
Metal	Mercury
Metal	Nickel
Metal	Particulate divalent mercury

Chemical Analysis Category	Chemical
Metal	Selenium (& compounds)
Metal	Selenium sulfide
Metal	Vanadium (fume or dust)
Metal	Zinc
Metal Spectrophotometric	Elemental gaseous mercury
Metal Spectrophotometric	Gaseous divalent mercury
Metal, Acid	Phosphorus
Microscopy	Asbestos
PAH	Acenaphthene
PAH	Acenaphthylene
PAH	Anthracene
PAH	Benz[a]anthracene
PAH	Benzo[b]fluoranthene
PAH	Benzo[j]fluoranthene
PAH	Benzo[k]fluoranthene
PAH	Benzo[g,h,i]perylene
PAH	Benzo[a]pyrene
PAH	Benzo[e]pyrene
PAH	2-Chloronaphthalene
PAH	Chrysene
PAH	Dibenz[a,h]anthracene
PAH	7,12-Dimethylbenz[a]anthracene
PAH	Fluoranthene
PAH	Fluorene
PAH	Indeno[1,2,3-c,d]pyrene
PAH	3-Methylcholanthrene
PAH	2-Methylnaphthalene
PAH	Naphthalene
PAH	PAHs, total, w/ individ. components reported
PAH	PAHs, total, w/o individ. components reported
PAH	Perylene
PAH	Phenanthrene
PAH	Pyrene
VOC Canister	Acetylene
VOC Canister	Acrolein
VOC Canister	1,3-Butadiene
VOC Canister	Butane
VOC Canister	1-Butene
VOC Canister	2-Butene

Chemical Analysis Category	Chemical
VOC Canister	Carbon disulfide
VOC Canister	Chlorodifluoromethane
VOC Canister	Ethylene
VOC Canister	Isopropanol
VOC Canister	Methyl bromide
VOC Canister	Methyl chloride
VOC Canister	Methylene chloride
VOC Canister	cis-1,3-Pentadiene
VOC Canister	Propylene
VOC Canister	Trichlorofluoromethane
VOC Canister	1,1,2-Trichloro-1,2,2-trifluoroethane
VOC Canister	Vinyl chloride
VOC Canister, Sorbent	Benzene
VOC Canister, Sorbent	Carbon tetrachloride
VOC Canister, Sorbent	Chlorobenzene
VOC Canister, Sorbent	Chloroform
VOC Canister, Sorbent	Cumene
VOC Canister, Sorbent	Cyclohexane
VOC Canister, Sorbent	Cyclopentadiene
VOC Canister, Sorbent	Cyclopentane
VOC Canister, Sorbent	1,4-Dichlorobenzene
VOC Canister, Sorbent	1,2-Dichloropropane
VOC Canister, Sorbent	1,3-Dichloropropene
VOC Canister, Sorbent	Ethylbenzene
VOC Canister, Sorbent	Ethylene dibromide
VOC Canister, Sorbent	Ethylene dichloride
VOC Canister, Sorbent	Hexane
VOC Canister, Sorbent	Methyl chloroform
VOC Canister, Sorbent	Methyl ethyl ketone
VOC Canister, Sorbent	Methyl isobutyl ketone
VOC Canister, Sorbent	Methyl tert-butyl ether
VOC Canister, Sorbent	Perchloroethylene
VOC Canister, Sorbent	Propylene dichloride
VOC Canister, Sorbent	Styrene
VOC Canister, Sorbent	1,1,2,2-Tetrachloroethane
VOC Canister, Sorbent	Toluene
VOC Canister, Sorbent	1,1,2-Trichloroethane
VOC Canister, Sorbent	Trichloroethylene
VOC Canister, Sorbent	1,2,4-Trimethylbenzene
VOC Canister, Sorbent	2,2,4-Trimethylpentane

Chemical Analysis Category	Chemical
VOC Canister, Sorbent	Xylenes (mixed)
VOC Canister, Sorbent	m-Xylene
VOC Canister, Sorbent	o-Xylene
VOC Canister, Sorbent	p-Xylene
VOC Sorbent	Methanol

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APPENDIX D: ROUTINE TOXIC AIR CONTAMINANT EMISSIONS FROM CALIFORNIA REFINERIES

OEHHA obtained a list of TACs reported in the California Emission Inventory Development and Reporting System (CEIDARS) database for all California refineries active during 2009-2012. The emissions data obtained from CEIDARS were submitted to CalEPA in accordance with the AB 2588 Air Toxics Hot Spots Program requirements, and reflect TAC releases that occurred during routine facility operations. The Hot Spots program requires facilities to report emission inventory updates every four years. Therefore, not all facilities update emission inventories in the same year. As a result, some chemicals may not be reported each year. Based on this quadrennial method of updating emission inventories in the Hot Spots Program, the information that the CEIDARS database provides on the TACs emitted from refineries are likely underestimates of total routine emissions across refineries in any given year.

Appendix D is an expanded version of Table 10 and displays the average annual routine TAC emissions for California refineries during 2009-2012 based on data provided by CARB. Emissions data are reported in pounds per year and listed in descending order.

Table D1. Average Annual Routine Toxic Air Contaminant Emissions for California Refineries

Chemical	Routine Emissions (lb/year)[1]
Ammonia	2,085,824
Formaldehyde	288,412
Methanol	122,611
Sulfuric acid	104,573
Hydrogen sulfide	103,385
Toluene	87,945
Xylenes (mixed)	79,177
Benzene	43,308
Hexane	39,646
Hydrochloric acid	21,450
Naphthalene	17,836
Acetaldehyde	16,136
Carbonyl sulfide	15,111
Ethyl benzene	11,960
1,2,4-Trimethylbenzene	9,815
Propylene	6,022
Diethanolamine	3,511

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[1] Average annual routine Toxic Air Contaminant (TAC) emissions for California refineries during 2009-2012, listed in descending order.

Chemical	Routine Emissions (lb/year)[1]
Hydrogen fluoride	3,463
1,3-Butadiene	3,156
Acrolein	2,804
Perchloroethylene	2,742
PAHs, total, w/o individ. components reported	2,666
o-Xylene	2,662
Manganese	2,587
Chloroform	2,048
Nickel	1,720
Copper	1,145
m-Xylene	1,000
Selenium	826
Phenanthrene	817
Methane	790
Benzo[a]pyrene	735
Methyl chloroform	720
p-Xylene	677
Chlorodifluoromethane	621
Phenol	598
Lead	431
Mercury	415
Cadmium	283
Phosphorus	275
Styrene	249
Chlorine	228
Glutaraldehyde	168
Fluorene	156
Arsenic	145
Diesel engine exhaust	123
Methyl ethyl ketone	111
PAHs, total, w/ individ. components reported	103
Trichloroethylene	86
Methyl tert-butyl ether	74
1,1,2-Trichloro-1,2,2-trifluoroethane	65
Glycol ethers (& acetates)	50
Asbestos	45
Isopropanol	45
Trichlorofluoromethane	36
Nitrous oxide	31

Chemical	Routine Emissions (lb/year)[1]
Chromium (hexavalent & compounds)	24
Beryllium	23
Methylene chloride	21
Chrysene	14
Propylene oxide	13
Cresols (mixtures of)	11
Phosphoric acid	10
Ethylene dichloride	7
Ethylene dibromide	6
Propylene glycol monomethyl ether	3
Fluoranthene	3
Pyrene	3
Vanadium (fume or dust)	2
Indeno[1,2,3-cd]pyrene	2
Methyl isobutyl ketone	2
Acenaphthylene	2
Benzo[b]fluoranthene	2
Anthracene	1
2-Methyl naphthalene	1
Benz[a]anthracene	1
Carbon tetrachloride	1
Carbon disulfide	1
Benzo[k]fluoranthene	1
Acenaphthene	1
Zinc	1
Benzo[e]pyrene	0.4
Vinyl chloride	0.3
1,1,2,2-Tetrachloroethane	0.3
Dibenz[a,h]anthracene	0.2
1,1,2-Trichloroethane	0.2
1,2-Dichloropropane	0.2
1,3-Dichloropropene	0.2
Benzo[g,h,i]perylene	0.2
Methyl chloride	0.1
Aluminum	0.1
Propylene glycol monomethyl ether acetate	0.06
Perylene	0.03
7,12-Dimethylbenz[a]anthracene	0.01
Benzo[j]fluoranthene	0.006

Chemical	Routine Emissions (lb/year)[1]
Chlorobenzene	0.005
1,4-Dioxane	0.004
Dibenzofurans (chlorinated)	0.002
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	9×10^{-6}

APPENDIX E: NON-ROUTINE AND ROUTINE EMISSIONS

OEHHA has compiled data on routine and non-routine emissions, not limited to TACs, from the California refineries active during 2010 using data provided by US EPA (Tables 11 and 12). While routine emissions represent chemical releases that occur during normal facility operations, non-routine releases reflect emissions during any non-routine refinery operation, including startups, shutdowns, and malfunction operations such as refinery-wide power loss, maintenance, and flaring events.

The refinery emissions shown in Appendix E were measured or calculated at various processes and emission points and self-reported by refineries to US EPA; however, these data were limited to 2010, and therefore may not be representative of all chemical emissions based on reporting requirements.

Table E1. Annual Routine and Non-routine Chemical Emissions by California Refineries

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
Acenaphthene	855	0.03
Acenaphthylene	129	0.02
Acetaldehyde	14,613	60
Acrolein	85,112	22
Ammonia	1,457,960	1,735
Aniline	462	—
Anthracene	959	1
Antimony	348	0.5
Arsenic	129	0.2
Barium	1,248	4
Benz[a]anthracene	242	0.02
Benzene	91,584	6,755
Benzo[b]fluoranthene	118	0.02
Benzo[k]fluoranthene	78	0.01
Benzo[g,h,i]perylene	146	0.002
Benzo[a]pyrene	225	0.04
Benzo[e]pyrene	41	—
Beryllium	62	0.09
Biphenyl	22,021	681
1,2-Butadiene	16	—
1,3-Butadiene	7,781	5,374

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[1] Routine and non-routine emissions as reported by California refineries for 2010, listed in alphabetical order (US EPA, 2012a; US EPA, 2012b).

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
Butane	5,881,551	4,446
1-Butene	179	155
2-Butene	165	—
Cadmium	5,781	1
Carbon disulfide	21,240	27
Carbon monoxide	16,972,733	418,331
Carbonyl sulfide	68,329	90
Chlorine	3,040	—
Chloroform	690	0.02
2-Chloronaphthalene	3	—
Chromium	1,291	2
Chromium (hexavalent & compounds)	226	0.2
Chrysene	285	0.01
Cobalt	167	0.07
Copper	1,062	1
Cresols (mixtures of)	3,265	417
m-Cresol	351	1
o-Cresol	364	—
p-Cresol	364	—
Cumene	21,988	237
Cyclohexane	22,567	204
Cyclopentadiene	—	3,190
Cyclopentane	23	—
Dibenz[a,h]anthracene	134	0.001
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	0.03	—
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	6×10^{-6}	—
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	8×10^{-6}	—
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	8×10^{-6}	—
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	0.001	—
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	5×10^{-6}	—
2,3,7,8-Tetrachlorodibenzo-p-dioxin	5×10^{-4}	—
Dibenzofuran	0.03	—
1,2,3,4,6,7,8-Heptachlorodibenzofuran	7×10^{-4}	—
1,2,3,4,7,8,9-Heptachlorodibenzofuran	1×10^{-5}	—
1,2,3,4,7,8-Hexachlorodibenzofuran	2×10^{-4}	—

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
1,2,3,6,7,8-Hexachlorodibenzofuran	0.04	—
1,2,3,7,8,9-Hexachlorodibenzofuran	5x10^{-6}	—
2,3,4,6,7,8-Hexachlorodibenzofuran	2x10^{-4}	—
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	3x10^{-4}	—
1,2,3,7,8-Pentachlorodibenzofuran	2x10^{-5}	—
2,3,4,7,8-Pentachlorodibenzofuran	0.02	—
2,3,7,8-Tetrachlorodibenzofuran	5x10^{-5}	—
Dibutyl phthalate	0.03	—
1,4-Dichlorobenzene	129	0.03
1,1-Dichloroethane	2	—
1,2-Dichloropropane	2	—
1,3-Dichloropropene	2	—
Diethanolamine	3,496	321
Diethyl phthalate	0.3	—
Di(2-ethylhexyl)phthalate	5	—
7,12-Dimethylbenz[a]anthracene	8	0.01
Ethane	502,829	3,029
Ethyl chloride	0.2	—
Ethylbenzene	75,917	1,317
Ethylene	15,450	2,184
Ethylene dibromide	5	—
Ethylene dichloride	3	—
Fluoranthene	181	0.02
Fluorene	1,228	0.2
Formaldehyde	78,370	923
Heptane	243	—
Hexane	809,803	7,625
Hydrogen chloride	37,893	121
Hydrogen cyanide	34,445	3
Hydrogen fluoride	62	—
Hydrogen sulfide	79,310	2,981
Indeno[1,2,3-c,d]pyrene	124	0.05
Isobutane	794	2,437
Isobutene	168	167
Isopentane	803	—
Lead	1,084	1
Manganese	3,238	0.4

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
Mercury	519	0.2
Methanol	308,640	0.02
Methyl bromide	51	—
Methyl chloride	1	—
Methyl ethyl ketone	157	—
Methyl isobutyl ketone	123	—
Methyl tert-butyl ether	23,558	1,980
3-Methylcholanthrene	3	0.002
Methylcyclohexane	111	—
2-Methylnaphthalene	23,387	0.02
Molybdenum	6,629	1
Naphthalene	33,216	1,192
Nickel	3,509	2
Nitrogen dioxide	1,971,085	12,397
Nitrogen oxides	16,415,674	223,792
Octane	35	—
Pentane	433,457	2,457
Perchloroethylene	1,354	4×10^{-6}
Perylene	41	—
Phenanthrene	2,979	3
Phenol	6,509	1,171
Phosphorus	602	0.1
PM (condensable)	1,677,433	3,855
PM_{10} (filterable)	2,805,076	22,802
PM_{10} (primary)	6,617,951	89,572
$PM_{2.5}$ (filterable)	1,088,791	1,303
$PM_{2.5}$ (primary)	2,004,663	26,306
Polychlorinated biphenyls	0.1	—
Propadiene	—	0.1
Propane	332,004	5,012
Propylene	71,931	7,799
Pyrene	465	0.01
Selenium (& compounds)	1,583	1
Styrene	58,849	1
Sulfur dioxide	21,158,748	553,834
1,1,2,2-Tetrachloroethane	6×10^{-5}	—
Toluene	273,000	4,530
1,1,2-Trichloroethane	2	—

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
Triethylamine	111	—
Trimethylbenzene	31,177	21
2,2,4-Trimethylpentane	501,931	84
Vanadium (fume or dust)	8,455	2
Volatile organic compounds	13,562,963	1,123,158
Xylenes (mixed)	274,547	4,700
m-Xylene	1,209	—
o-Xylene	1,096	—
p-Xylene	1,151	—
Zinc	20,726	26

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APPENDIX F: REFINERY EMISSIONS IN THE US AND FUEL-BURNING EXPERIMENTS

Based on research in peer-reviewed journal articles, OEHHA has provided a list of additional chemicals measured in US refinery emissions or oil-burning experiments during 1979-2007. Because refineries are only required to report emissions of regulated chemicals, knowledge of unregulated chemicals also released can provide information on chemical speciation or characteristics that may ultimately be used by officials for air monitoring or risk assessment purposes. The chemicals found in the literature describing controlled burning experiments or refinery air monitoring in the US are listed in Appendix F.

Table F1. Additional Chemicals Found in the Literature on Refinery Emissions in the US and Fuel-Burning Experiments

Chemical	CAS RN	Source
Benzaldehyde	100527	[2]
Benzo[a]fluorine	238846	[3]
Benzo[b]fluorine	30777196	[2]
Benzo[b]thiophene	55712602	[3]
Benzo[def]fluorine	203645	[3]
Benzoic acid	65850	[3]
2-Benzylnaphthalene	613592	[3]
Biphenylene	259790	[3]
Butyraldehyde	123728	[4]
Cerium	7440451	[5]
cis-1,3-Dimethyl cyclohexane	638040	[3]
Crotonaldehyde	123739	[2]
Cymene	99876	[3]
Decane	124185	[2]
1,3-Diethyl-5-methylbenzene	2050240	[3]
Diethylbenzene	25340174	[3]
2,2-Dimethyl-1-hexene	6975924	[3]
2,5-Dimethylbenzaldehyde	93027	[2]
1,2-Dimethylcyclopentane	2452995	[3]
4,4’-Dimethyldiphenylmethane	4957146	[3]
2,3-Dimethylfluorene	4612639	[3]
3,4-Dimethylheptane	922281	[3]
1,2-Dimethylindane	17057828	[3]
1,4-Dimethylnaphthalene	571584	[3]
1,5-Dimethylnaphthalene	571619	[3]
1,7-Dimethylnaphthalene	575371	[3]
2,3-Dimethylnaphthalene	581408	[3]
2,6-Dimethylnaphthalene	1123564	[4]
4,5-Dimethylnonane	17302237	[3]
2,6-Dimethyloctane	2051301	[3]

Chemical	CAS RN	Source
3,3-Dimethylpentane	562492	[3]
2,3-Dimethylphenanthrene	3674655	[3]
2,5-Dimethylphenanthrene	3674666	[3]
3,6-Dimethylphenanthrene	1576676	[3]
2,5-Dimethylphenol	95874	[3]
3,4-Dimethylphenol	95658	[3]
3,5-Dimethylphenol	108689	[3]
1,1-Dimethylpropylbenzene	2049958	[3]
1,2-Diphenoxybenzene	3379371	[3]
1,4-Diphenoxybenzene	3061367	[3]
2,5-Diphenyl-1,4-benzoquinone	844519	[3]
Diphenylbutadiyne	886668	[3]
Dodecane	112403	[2]
Dysprosium	7429916	[5]
1-Ethenyl-2-methylbenzene	611154	[3]
1-Ethenyl-3-methylenecyclopentene	61142072	[3]
1-Ethyl-2,3-dimethylbenzene	933982	[3]
1-Ethyl-2-methylbenzene	611143	[3]
2-Ethyl-1,1’-biphenyl	1812517	[3]
2-Ethyl-4-methylphenol	3855263	[3]
Ethylcyclohexane	1678917	[3]
3-Ethylhexane	619998	[3]
2-Ethylnaphthalene	939275	[3]
2-Ethylphenol	90006	[3]
1-Ethylpropylbenzene	1196583	[3]
m-Ethyltoluene	620144	[3]
o-Ethyltoluene	611143	[3]
p-Ethyltoluene	622968	[3]
Ethynylbenzene	536743	[3]
Europium	7440531	[5]
Gadolinium	744542	[5]
Hexadecane	544763	[2]
Hexanal	66251	[2]
Iron	7439896	[6]
1-Isobutyl-3-methylcyclopentane	29053041	[3]
Isohexane	107835	[1]
Isopentane	78784	[2]
Isovaleraldehyde	590863	[2]
Lanthanum	7439910	[5]
1-Methyl-2-[2-phenylethenylbenzene]	74685420	[3]
1-Methyl-2-[3-methylphenyl-methylbenzene]	21895136	[3]

Chemical	CAS RN	Source
1-Methyl-3-[4-methylphenyl-methylbenzene]	21895169	[3]
1-Methyl-3-[2-phenylethenylbenzene]	14064483	[3]
1-Methyl-2-phenylmethylbenzene	713360	[3]
1-Methyl-4-phenylmethylbenzene	620837	[3]
1-Methyl-2-propylbenzene	1074175	[3]
3-Methyl-1,1’-biphenyl	643936	[3]
3-Methyl-2-butenylbenzene	4489843	[3]
2-Methylanthracene	613127	[3]
4-Methylbenzaldehyde	104870	[3]
3-Methyldecane	13151343	[3]
9-Methylenefluorene	4425825	[3]
9-Methylene-fluorene	4425825	[3]
1-Methylethenyl-1,1’-biphenyl	—	[3]
1-Methylfluorene	730376	[2]
1-Methylfluorene	1730376	[3]
2-Methylfluorene	1430973	[3]
5-Methylhexan-5-olide	2610959	[3]
3-Methylhexane	589344	[3]
1-Methylnaphthalene	90120	[4]
3-Methylnonane	5911046	[3]
2-Methylpentane	107835	[3]
3-Methylpentane	96140	[1]
1-Methylphenanthrene	832699	[4]
2-Methylphenanthrene	2531842	[3]
3-Methylphenanthrene	832713	[3]
2-Methylpropylcyclohexane	1678984	[3]
2-Methylpyrene	3442782	[3]
Naphtho[2,1-b]furan	232951	[3]
Neodymium	7440008	[5]
Nonane	111842	[2]
Pentamethylbenzene	700129	[3]
Propyne	74997	[2]
3-Penten-1-yne	2206237	[3]
1-Pentene	109671	[1]
Platinum	7440064	[6]
Praseodymium	7440100	[5]
Propionaldehyde	123386	[2]
Propylbenzene	103651	[3]
Samarium	7440199	[5]
Silicon	7440213	[6]
Silver	7440224	[6]

Chemical	CAS RN	Source
Tetradecane	629594	[2]
1,2,3,4-Tetramethylbenzene	488233	[3]
1,2,3,5-Tetramethylbenzene	527537	[3]
1,2,4,5-Tetramethylbenzene	95932	[3]
p-Tolualdehyde	104870	[2]
1,3,5-Trimethylbenzene	108678	[3]
1,2,4-Trimethylcyclohexane	2234755	[3]
1,3,5-Trimethylcyclohexane	1839630	[3]
1,4,5-Trimethylnaphthalene	2131411	[3]
1,4,6-Trimethylnaphthalene	2131422	[3]
2,3,5-Trimethylnaphthalene	2245387	[4]
2,3,5-Trimethylphenanthrene	3674735	[3]
Triphenylene	217594	[3]
Undecane	1120214	[2]
Valeraldehyde	110623	[2]

[1] Sexton and Westberg, 1979.
[2] Booher and Janke, 1997.
[3] Strosher, 2000.
[4] Fingas et al., 2001.
[5] Kulkarni et al., 2007.
[6] Lewis et al., 2012.

APPENDIX G: DATA ANALYSIS OF REFINERY CHEMICALS ACROSS CATEGORIES

Comparisons between high routine emissions and health guidance values or emergency exposure levels may help determine chemicals for air monitoring and may help protect the community surrounding these refineries by limiting exposure. To that end, OEHHA has performed some preliminary analysis of the compiled data to offer comparisons between various categories of information and to note which chemicals are most common in the comparisons. Table G-1 uses information already in the report to make these assessments.

The analysis in Table G-1 compares chemicals with health guidance values with chemicals that have high routine emissions. The footnotes to the table explain each comparison in detail.

Table G1. Comparison of Chemicals with High Routine Emissions and Other Health Guidance Values

High Routine Emissions and OEHHA Noncancer REL[1]	High Routine Emissions and US EPA RfC[2]	High Routine Emissions and OEHHA Proposition 65 (D or R)[3]	High Routine Emissions and OEHHA Proposition 65 (C)[4]	High Routine Emissions and OEHHA CPF[5]	High Routine Emissions and Noncancer and Cancer Effects[6]	High Routine Emissions and Emergency Exposure Levels[7]	Incident History[8]	High Routine Emissions and Processes[9]
Ammonia (A, C)	Ammonia					Ammonia		Ammonia
Benzene (A,8,C)	Benzene	Benzene (D, Rm)	Benzene	Benzene	Benzene	Benzene		Benzene
						Butane		
Carbon Monoxide (A)		Carbon Monoxide (D)				Carbon Monoxide		
Formaldehyde (A,8,C)			Formaldehyde	Formaldehyde	Formaldehyde	Formaldehyde		Formaldehyde
Hexane (C)						Hexane		Hexane
							Hydrocarbons	
Hydrogen Chloride (A,C)	Hydrogen Chloride					Hydrogen Chloride		
Hydrogen Sulfide (A,C)	Hydrogen Sulfide					Hydrogen Sulfide	Hydrogen Sulfide	Hydrogen Sulfide
Methanol (A,C)	Methanol	Methanol (D)				Methanol		
Nitrogen Dioxide (A)	Nitrogen Dioxide					Nitrogen Dioxide		
Sulfur Dioxide (A)	Sulfur Dioxide	Sulfur Dioxide (D)				Sulfur Dioxide	Sulfur Dioxide	
Sulfuric Acid (A,C)	Sulfuric Acid		Sulfuric Acid		Sulfuric Acid	Sulfuric Acid		
Toluene (A,C)	Toluene	Toluene (D)				Toluene		Toluene
Xylenes (mixed) (A,C)	Xylenes (mixed)					Xylenes (mixed)		Xylenes (mixed)

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[1] Have Acute (A), 8-hour (8), or Chronic (C) OEHHA noncancer RELs (Table 3) and high routine emissions (Table 10, 11)
[2] Have US EPA RfC (Table 3) and high routine emissions (Table 10, 11)
[3] Have Proposition 65 status for Reproductive (R) or Developmental (D) harm (Table 3) and high routine emissions (Table 10, 11)
[4] Have Proposition 65 status as Carcinogenic (C) (Table 3) and high routine emissions (Table 10, 11)
[5] Have OEHHA CPF (Table 3) and high routine emissions (Table 10, 11)
[6] Have OEHHA RELs and/or US EPA RfCs and Proposition 65 status as carcinogenic and/or CPFs (Table 3) and high routine emissions (Table 10, 11)
[7] Have US EPA AEGL 1 or AEGL 2, NIOSH IDLH, or LEL (Table 5) and high routine emissions (Table 10, 11)
[8] Involved in incidents mentioned in Section V-4: California Refinery Incident History
[9] Involved in the most processes (15 of 15 total processes) (Table D-1)

To complement Table G-1, OEHHA expanded on the analysis in column 1 of Table I-1 comparing chemicals with high routine emissions to specific values of OEHHA noncancer RELs for acute, 8-hour, and chronic exposure in Table 1-2.

Table G2. OEHHA REL Values for Chemicals with High Routine Emissions

Chemical	Acute (µg/m^3)	8-Hour (µg/m^3)	Chronic (µg/m^3)
Ammonia	3,200		200
Benzene	27	3	3
Carbon Monoxide	2.3×10^4		
Formaldehyde	55	9	9
Hexane			7×10^3
Hydrogen Chloride	2,100		9
Hydrogen Sulfide	42		10
Methanol	2.8×10^4		4,000
Nitrogen Dioxide	470		
Sulfur Dioxide	660		
Sulfuric Acid	120		1
Toluene	3.7×10^4		300

In Table G3, OEHHA prioritized chemicals by chemical analysis category based on presence in all the tables in the report. In addition to total number of categories, some chemicals were prioritized based on considerations of toxicity, volatility, and highest or lowest values in particular categories (highest routine or non-routine emissions or lowest RELs/RfCs). The top chemicals for each chemical analysis category are noted.

Table G3. Chemicals Sorted by Chemical Analysis Category

Chemical Analysis Category	Avg Routine emissions	Non-routine 2010	REL	RfC	Prop 65	Processes	Incident History 2001-12	AEGLs	IDLH	TOTAL
ACIDS										
Sulfuric acid	X		X				X	X	X	**5**
Hydrogen fluoride		X	X				X	X	X	**5**
Hydrogen Cyanide		X	X	X	X	X				**5**
ALDEHYDES										
Acetaldehyde*	X		X	X	X	X		X	X	**7**
Formaldehyde*	X		X		X	X		X	X	**6**
DIOXINS, DIBENZOFURANS										
Dibenzofurans (chlorinated) {PCDFs}	X		X		X	X				**4**
Tetrachlorodibenzo-p-Dioxin (2,3,7,8) **			X		X	X				**3**
Hexachlorodibenzofuran (1,2,3,7,8,9)			X		X					**2**
Hexachlorodibenzofuran (2,3,4,6,7,8)			X		X					**2**
EXTRACTABLES (PHENOLS, AROMATICS, HYDROCARBONS)										
Phenol	X	X	X			X		X		**5**
Aniline				X	X			X	X	**4**
Cresols (mixtures of) {Cresylic acid}		X	X						X	**3**
GASES										

Chemical Analysis Category	**Avg Routine emissions**	**Non-routine 2010**	**REL**	**RfC**	**Prop 65**	**Processes**	**Incident History 2001-12**	**AEGLs**	**IDLH**	**TOTAL**
Hydrogen sulfide {H2S}			X	X			X	X	X	**5**
Chlorine	X		X					X	X	**4**
Carbon monoxide		X	X		X	X				**4**
Propylene oxide			X	X	X					**3**
Sulfur dioxide		X	X		X		X			**3**
Ammonia {NH3}	X		X			X				**3**
Carbonyl sulfide	X	X	X							
GLYCOLS										
Propylene glycol monomethyl ether	X		X	X						**3**
ethylene glycol monoethyl ether			X	X	X					**3**
Glycol ethers (and their acetates)	X		X							**2**
MASS										
Diesel engine exhaust, particulate matter (Diesel PM)	X		X	X	X					**4**
PM10						X				**1**
PM2.5						X				**1**
METALS										
Cadmium			X		X	X		X		**4**
Beryllium			X	X	X	X				**4**
Manganese	X		X	X		X				**4**
Arsenic			X		X	X			X	**4**
Mercury					X	X		X		**3**
Lead			X		X	X				**3**

Chemical Analysis Category	**Avg Routine emissions**	**Non-routine 2010**	**REL**	**RfC**	**Prop 65**	**Processes**	**Incident History 2001-12**	**AEGLs**	**IDLH**	**TOTAL**
PAH										
Naphthalene	X	X	X	X	X	X			X	**7**
Anthracene		X				X				**2**
Benz[a]Anthracene					X	X				**2**
Benzo[a]pyrene					X	X				**2**
Benzo[k]fluoranthene					X	X				**2**
Dibenz[a,h]anthracene					X	X				**2**
PAHs, total, w/o individ. components reported [Treated as B(a)P for HRA]	X				X					**2**
VOC CANISTER										
Butadiene (1,3) **	X		X		X	X	X			**5**
Methyl Bromide			X	X	X			X	X	**5**
Acrolein			X	X				X	X	**4**
Carbon disulfide			X		X	X		X		**4**
Propylene	X	X	X			X				**4**
Methylene chloride {Dichloromethane} **			X		X					**2**
Vinyl chloride			X		X					**2**
VOC CANISTER, SORBENT										
Benzene	X		X		X	X	X			**5**
Styrene			X		X			X		**3**
Carbon tetrachloride **	X		X		X					**3**
Ethylene dichloride {EDC}			X		X				X	**3**
Hexane (listed as n-Hexane in CA refinery)		X	X			X				**3**
Ethyl benzene **			X		X	X				**3**
Toluene			X			X	X			**3**
Xylenes (mixed)			X		X	X				**3**
Chlorobenzene			X					X		**2**

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APPENDIX H: TOXICITY WEIGHTED TOTALS FOR CHEMICALS RELEASED FROM CALIFORNIA REFINERIES

OEHHA reviewed recent data from CEIDARs on Toxic Air Contaminants (TACs) routinely released from California refineries in 2014. OEHHA used the average annual routine TAC emissions for California refineries during 2014 to derive a "toxicity-weighted" emission score for each chemical across all refineries in California for which emissions data were available. The toxicity-weighted emissions score was calculated using emissions data (pounds emitted per year) obtained from the Air Toxics "Hot Spots' Emissions Inventory and a toxicity-weight derived from US EPA's Inhalation Toxicity Scores for individual chemicals. For more information on toxicity weights see: https://www.epa.gov/rsei/rsei-toxicity-data-and-calculations.

Chemicals listed in Table H1 have the highest calculated overall toxicity-weighted pounds emitted. Table H1 shows the sum of emissions by chemical for all California refineries included in this analysis. The calculated toxicity-weighted pounds emitted for each chemical across all California refineries are the product of total pounds released and their corresponding chemical specific toxicity-weights.

Table 1. Toxicity Weighted Totals for Chemicals Released From California Refineries (2014)

Chemical	Total lbs. released[1]	Toxicity weights[2]	Toxicity-weighted lbs. released[3]
Formaldehyde	91682	46,000	4,217,368,613
Nickel	1338	930,000	1,244,140,036
Arsenic	65	17,000,000	1,101,338,814
Cadmium	155	6,400,000	992,557,509
Benzene	20313	28,000	568,775,348
PAHs	711	710,000	504,822,625
Hexavalent chromium	10	43,000,000	426,073,431
Benzo[a]pyrene	500	710,000	355,219,396
Phenanthrene	280	710,000	198,694,330
Beryllium	12	8,600,000	106,826,366
Ammonia	2,517,005	35	88,095,180
1,3-Butadiene	740	110,000	81,404,664
Naphthalene	6,313	12,000	75,756,270
Hydrogen Sulfide	12,321	1,800	22,178,439
Acetaldehyde	1,392	7,900	10,997,059
Manganese	474	12,000	5,691,981
Diethanolamine	1,778	1,200	2,133,390

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[1] Total amount of chemical released across California refineries

[2] Proportional numerical weight given to each chemical based on chronic adverse health outcomes

[3] Total chemical release multiplied by the toxicity weight

APPENDIX I: LIST OF ABBREVIATIONS

AAQS	Ambient Air Quality Standards
AEGL	Acute Exposure Guideline Levels
AIHA	American Industrial Hygiene Association
APCD	Air Pollution Control District
AQMD	Air Quality Management District
ATSDR	Agency for Toxic Substances and Disease Registry
BAAQMD	Bay Area Air Quality Management District
BTEX	Benzene, toluene, ethylene, and xylene
CAD	Coronary Artery Disease
CalEPA	California Environmental Protection Agency
CAMEO	Computer-Aided Management of Emergency Operations
CAPCOA	California Air Pollution Control Officers Association
CARB	California Air Resources Board
CAS RN	Chemical Abstracts Service Registry Number
CCHS	Contra Costa Health Services
CDC	Centers for Disease Control and Prevention
CEIDARS	California Emission Inventory Development and Reporting System
CHHSL	California Human Health Screening Level
COPD	Chronic Obstructive Pulmonary Disease
CPF	Cancer Potency Factor
CSB	Chemical Safety Board
CSF	Cancer Slope Factor
EPCRA	Emergency Planning and Community Right-to-Know Act
ERPG	Emergency Response Planning Guidelines
FCCU	Fluid Catalytic Cracking Unit
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
ICR	Information Collection Request
IDLH	Immediately Dangerous to Life and Health
IRIS	Integrated Risk Information System
IRTF	Interagency Refinery Task Force
LEL	Lower Explosive Limit
NAAQS	National Ambient Air Quality Standard
NAC/AEGL	National Advisory Committee for the Development of Acute Exposure Guideline Levels for Hazardous Substances
NIH	National Institutes of Health
NIOSH	National Institute for Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NOx	Nitrogen oxides
OEHHA	Office of Environmental Health Hazard Assessment
OER	Office of Emergency Response
OPPT	Office of Pollution Prevention and Toxics
PAC	Protective Action Criteria
PAH	Polycyclic Aromatic Hydrocarbon

PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PHG	Public Health Goal
PM	Particulate matter
PM_{10}	Particulate matter ≤10 µm in diameter
$PM_{2.5}$	Particulate matter ≤2.5 µm in diameter
RADS	Reactive Airway Dysfunction Syndrome
REL	Reference Exposure Level
RfC	Reference Concentration
RfD	Reference Dose
RMP	Risk Management Plan
RSL	Regional Screening Level
SCAPA	Subcommittee on Consequence Assessment and Protective Actions
SCAQMD	South Coast Air Quality Management District
SRU	Sulfur Recovery Unit
TAC	Toxic Air Contaminant
TCDD	2,3,7,8-Tetrachlorodibenzo-p-dioxin
TEEL	Temporary Emergency Exposure Limit
TOXNET	Toxicology Data Network
TRI	Toxics Release Inventory
TSH	Thyroid stimulating hormone
US EPA	United States Environmental Protection Agency
UEL	Upper Explosive Limit
VOC	Volatile Organic Compound
WWT	Wastewater treatment

EXHIBIT 8

Managing your aluminum dome asset

April 20, 2020 in Features 7 min read

Photo courtesy of DIORCA

In today's world of uncertainty, it becomes very important to maintain and manage current assets. Geodesic aluminum domes are an investment within our oil and gas industry that protects the product in the storage tank and has a service life of 50 plus years with some maintenance along the way.

What is a geodesic dome? A geodesic dome is a site specific, structurally engineered dome roof composed from an integrated aluminum system of interlocking panels, extruded struts, gusset plates, batten bars and hubs.

Why do I want a geodesic dome? One major reason is to seal the tank from the elements of nature such as rainfall and snow. Many open top tanks with carbon steel floating roofs have drainage issues with their roof drain systems in severe rain seasons, hurricanes and in severe snow seasons. Not having to worry about your roof drain system keeping up with the elements keeps your floating roof from sinking into the product. Other reasons are for the strength-to-span-ratio. This allows for a dome to span a large area without structural support columns, unlike a fixed cone roof. In today's world where storage for your oil & gas products has led to larger and larger storage tanks, a clear-span aluminum dome allows for the columns that would be required on a typical cone style roof to be eliminated. These columns are called out as emission points. By removing them your tank system gains emission credits. Emission loss is also prevented by covering an open-top EFR style tank. The dome prevents this loss by deflection of the wind over the top of the dome, eliminating the vortex effect of wind passing over the top of a floating roof.

The dome's ability to handle additional loads, such as cable suspending an aluminum internal floater from the dome roof, makes it possible to increase product capacity in a storage tank and provide tank maintenance benefits. This additional load of a suspended internal floating roof is considered during the design phase of the dome, just like live, snow, wind and other loads would be evaluated. The removal of the internal floating roof legs enables the floating roof to be set at the lowest possible point inside a tank. By not having legs, you can set a maintenance roof level of 10-ft above the floor so that you can drive equipment in/out of the tank during out-of-service work. Also, by having an aluminum internal floating roof suspended with the dome, you gain greater storage capacity versus a typical carbon steel pontoon style floater due to the thickness of the internal floating roof and the requirements for the seal system height.

Geodesic domes typically require less maintenance than a steel cone roof. Have you ever gone into a tank with a floater during inspection time and seen all the rusted material on your floater? This is from the rafter system and the underside of the steel cone roof plates. This corroded material accumulates on the secondary seal system and can create holes, ultimately causing emission leaks. One solution is the expensive and time-consuming task of sandblasting and coating the underside of the steel cone roof After taking the tank out of service. In addition, the top side of the steel roof must be sandblasted, repaired and coated to prevent corrosion-based breaching of the surface. Clear-span aluminum domes do not need to be painted for corrosion protection. Aluminum has a natural oxidation process that occurs, creating a thin layer of protection over time that will last the lifetime of the dome and most likely the tank. This is a major cost savings over the life of the storage tank, and it protects the stored product from UV and weather exposure.

How do I maintain a dome? An above-ground storage tank requires regularly scheduled preventative maintenance that will prolong your asset and keep it working correctly for your team. With a dome, we suggest an annual visual inspection from the platform. What is an inspector looking for during this visual?

- Look at the flashing connections where the dome meets the top of the tank, to make sure they are secured properly, and all fasteners are present.
- Look at the strut caps (batten bars) to see if there are any missing or loose screws. Is the gasket material fully compressed or wedged, is the gasket flexible/deteriorated? Is the gasket material missing?
- Visually inspect the sealant. Is the sealant adhering properly to the material? Is the sealant properly and neatly tooled? Is there sealant at all joints/splices around the interfaces of appurtenances?

- Visually inspect the hub covers to ensure they are present, sufficiently sealed, are there any dents or penetrations in them.
- Note if any of the appurtenances are missing or damaged – circulation vents, hatches, skylights, etc.
- Look at the mounting supports of the dome (dome shoes) and verify they are attached correctly.
- Note any customizations or modifications that have been done to the dome after it was originally installed.
- Unattended damage or defects to the existing dome should be noted. If there is a leak pattern on the floating roof, it should be documented to help facilitate future repairs.

Once all issues have been documented, a skilled contractor familiar with domes can suggest the proper repairs required to restore the dome as close as possible to its original condition. Beware of temporary fixes such as applying more sealant over the existing areas of sealant or covering with “flash band” style tape. These may temporarily remedy a leaking dome, but they do not offer a full cycle of protection and often require extensive cleaning or replacing of parts to properly get the dome back to a water-tight condition. If your dome has developed a leak, it is important to have an experienced dome contractor inspect and evaluate what is required to address the cause of the leaks and restore it to original condition.

For more information: Call +1 844-44-TANKS, or contact inspectionservices@cstindustries.com

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EXHIBIT 9

Report to the Joint Standing Committee on the Environment and Natural Resources

Measurement and Control of Emissions from Aboveground Petroleum Storage Tanks

January 1, 2021

MAINE DEPARTMENT OF ENVIRONMENTAL PROTECTION
17 State House Station | Augusta, Maine 04333-0017
www.maine.gov/dep

Contents

I. Introduction

In the second regular session of 2020, the 129th Maine Legislature passed L.D. 1915: "Resolve, Directing the Department of Environmental Protection To Evaluate Emissions from Aboveground Petroleum Storage Tanks." The resolve directs the Department of Environmental Protection (Department) to study methods to measure and estimate air emissions from aboveground petroleum storage tanks, to study methods to control odor and other air emissions from emission sources at oil terminal facilities including emissions from aboveground petroleum storage tanks, loading racks, and vessel offloading, to identify methods or programs for assisting municipalities in the use and application of mobile air quality monitoring devices, and to report its findings to the joint standing committee of the Legislature having jurisdiction over environment and natural resources matters (Committee) by January 1, 2021.

Several Bureau of Air Quality staff were involved in conducting the requested studies over the past several months and in completing this report. Bureau of Air Quality staff consulted various resources, including reaching out to other state environmental agencies to conduct these studies. In accordance with the resolve, this report contains the Department's findings. The report also contains the Department's recommendations for consideration by the Committee. The Department is available to present a summary of this report to the Committee and answer any questions.

II. Description of Sources

A. Facilities Included in Study

This study focused on facilities which store and distribute petroleum products on a large scale, referred to throughout this document as petroleum storage facilities[1]. In general, a petroleum storage facility consists of storage tanks and a system for receiving and distributing the stored product. The storage tanks may be of various sizes and configurations. The stored products may be received and/or distributed by pipeline, ship, rail, or truck.

Maine has 11 existing petroleum storage facilities with air emission licenses (Appendix A). Three of these licensed facilities are categorized as major sources[2] of criteria pollutants including volatile organic compounds (VOC). The remaining facilities operate with license constraints that limit emissions to 50 tons/year of VOC or less, classifying these facilities as synthetic minor sources[3]. In some cases, facilities have accepted license restrictions significantly less than the 50 tons/year major source threshold. Maine has no petroleum storage facilities classified as major sources of hazardous air pollutants[4] (HAP), defined as having the potential to emit greater than 10 tons/year of any one HAP or 25 tons/year for all HAP combined[5].

Eight of Maine's licensed facilities are considered bulk gasoline terminals, since their gasoline throughput is potentially greater than 20,000 gallons per day[6]. These facilities may store and distribute other petroleum products in addition to gasoline. Maine has no licensed bulk gasoline plants, which are petroleum storage facilities with gasoline throughputs less than 20,000 gallons per day. The three remaining facilities store and distribute petroleum products other than gasoline (e.g., distillate fuel, asphalt, etc.).

In addition to the petroleum storage facilities addressed in this study, there are smaller bulk storage facilities located throughout the state. These include local storage and distribution tanks associated with home heating oil providers; fuel oil tanks located at industrial and electrical generating facilities; and asphalt tanks associated with hot-mix asphalt plants. These storage tanks were determined to be outside the scope of this study.

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[1] See Section III.A for regulatory references.

[2] 06-096 C.M.R. ch. 100, §125(C)

[3] "Synthetic minor source" means a source that otherwise has the potential to emit pollutants in amounts that are at or above the thresholds for major sources but has taken an enforceable license restriction so that its potential to emit is less than those major source thresholds.

[4] Compounds which are considered a hazardous air pollutant are defined by Section 112(b) of the Clean Air Act.

[5] 06-096 C.M.R. ch. 100, §125(A)

[6] 06-096 C.M.R. ch. 100, §24

B. Pollutants Studied

Air emissions from petroleum storage facilities occur when the product being stored evaporates, either directly into the atmosphere or into a vapor space inside a tank that is later released to the atmosphere.

The main pollutant of concern from petroleum storage facilities is VOC. VOC comprise a large class of carbon-containing compounds which participate in atmospheric photochemical reactions. A few compounds are specifically excluded from this definition, including carbon monoxide and carbon dioxide. VOC typically have high volatility, high vapor pressure[7], and low water solubility. This study focused on methods to estimate and control VOC emissions from petroleum storage facilities.

HAP, also known as toxic air pollutants or air toxics, are those pollutants that are known or suspected to cause cancer or to have other serious health effects, such as reproductive system effects or birth defects, or that are known or suspected to have adverse environmental effects[8]. Like emissions of VOC, emissions of HAP from petroleum storage facilities come from evaporative losses of the product being stored or transferred. Although not all HAP are VOC, the vast majority of HAP emissions from petroleum storage facilities are also VOC, and any control equipment that reduces emissions of VOC also reduces HAP from those facilities. Therefore, throughout this document, VOC has been used as a surrogate for all regulated air pollutants from petroleum storage facilities, including HAP.

Emissions from petroleum storage facilities may or may not result in a detectable odor. Available methods for controlling odor from these facilities were also addressed in this study.

C. Products Stored

The products stored in the petroleum storage facilities studied included products of various classifications and properties, primarily gasoline, distillate fuel, residual fuel, liquid asphalt, and crude oil.

1. Crude Oil

Crude oil is a naturally occurring, unprocessed petroleum product comprised of a mixture of liquid hydrocarbons and includes small amounts of nitrogen, sulfur, and

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[7] Vapor pressure is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its liquid phase at a given temperature. It relates to the tendency of particles to escape from the liquid. A substance with a higher vapor pressure is considered more volatile.

[8] https://www.epa.gov/haps/what-are-hazardous-air-pollutants

oxygen. Gasoline, distillate fuels, residual fuels, and liquid asphalt are produced from the fractional distillation of crude oil.

2. Gasoline

Gasoline is a spark-ignition engine fuel which may or may not be blended with oxygenates, such as alcohols and ethers. The characteristics and requirements of gasoline are described in *Standard Specification for Automotive Spark-Ignition Engine Fuel*, ASTM[9] D4814-20. Gasoline typically has a true vapor pressure of greater than 3.5 pounds per square inch absolute (psia) and less than 11.0 psia[10] at 60 °F. For the purposes of this study, aviation gasoline is included in this category of product.

3. Distillate Fuels

The term "distillate fuels" refers to a group of petroleum products including kerosene, diesel fuel, #2 fuel oil, and home heating oil. This term encompasses all of the following:

- Fuel oil that complies with the specifications for fuel oil number 1 or 2, as defined by *Standard Specification for Fuel Oils*, ASTM D396-19a;
- Diesel fuel oil number 1 or 2, as defined in *Standard Specification for Diesel Fuel*, ASTM D975-19c;
- Kerosene, as defined in *Standard Specification for Kerosene*, ASTM D3699-19;
- Biodiesel, as defined in *Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels,* ASTM D6751-20; and
- Biodiesel blends, as defined in *Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)*, ASTM D7467-20.

Distillate fuels are used in compression-ignition reciprocating internal combustion engines (i.e., diesel engines); combustion turbines; and residential, commercial, and industrial furnaces and boilers. Distillate fuel has a true vapor pressure of approximately 0.006 psia[11] at 60 °F. For the purposes of this report, jet fuel is considered a type of distillate fuel.

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[9] ASTM International, formerly known as American Society for Testing and Materials, is an international standards organization that develops and publishes technical standards for a wide range of materials, products, systems, and services.

[10] EPA's *Fifth Edition Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources* (AP-42), Table 7.1-2

[11] AP-42, Table 7.1-2

4. Residual Fuels

The term “residual fuels” refers to a group of dense petroleum products commonly referred to as “#6 fuel oil” or by the Navy specification “Bunker C.” Residual fuels are the products that remain after distillation of crude oil. They include fuel oil that complies with the specifications for fuel oil number 4, 5, or 6 in *Standard Specification for Fuel Oils*, ASTM D396-19a. Viscosity, an important quality specification for residual fuel oil, is a measure of a liquid's resistance to flow. High-viscosity fuel oil is more difficult to pump and is therefore less desirable as a product. Oil refiners manage fuel oil viscosity either through processing or through blending in a material of lower viscosity. Material added to reduce the viscosity of residual fuel is called cutter stock. Common cutter stocks for fuel oil blending are light cycle oil (from the diesel-range product of crude oil refinement) and kerosene. These cutter stocks are significantly more valuable than the resulting fuel oil blend, so refiners work to minimize the amount of cutter stock in a finished blend while still producing on-specification fuel oil.[12] Such fuel blending usually is done by the refiner prior to transportation to petroleum storage facilities such as those in Maine.

Due to its physical properties, i.e., being a thick, black, sticky liquid, the true vapor pressure of #6 fuel oil is difficult to measure. Previous estimates assumed a true vapor pressure of 0.00004 psia at 60 °F. However, the #6 fuel oil currently on the market is typically blended with light cutter stock to improve characteristics such as viscosity and heat content. The true vapor pressure of #6 fuel oil is now estimated to be approximately 0.002 psia[13] at 60 °F.

Residual fuels have a high viscosity and must be stored at greater than 100 °F and heated to 200 °F – 300 °F before they can be effectively pumped through pipes. At cooler temperatures, they congeal into a semi-solid. True vapor pressure is an exponential function of temperature. The true vapor pressure of #6 fuel oil is 0.06 psia[14] at 200 °F and 0.38 psia at 300 °F.

Fuels referred to as #4 fuel oil or #5 fuel oil are typically a blend of #6 fuel oil with distillate fuel. Very little #4 fuel oil or #5 fuel oil is currently used in Maine, and the blending typically takes place just prior to delivery to the customer. As such, there are no #4 fuel oil or #5 fuel oil storage tanks of significant size in this state.

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[12] https://www.mckinseyenergyinsights.com/resources/refinery-reference-desk/cutter-stock/#:~:text=Cutter%20stock%20is%20any%20stream%20that%20is%20blended,stock%20is%20commonly%20used%20in%20fuel%20oil%20blending.

[13] AP-42, Table 7.1-2

[14] AP-42, Table 7.1-2 and Equation 1-25

Residual fuels are typically used by large industrial or electrical generating boilers or to fuel engines on large ships.

5. Asphalt

Asphalt is a dense petroleum product which may occur naturally or be produced in the crude oil refining process. Similar to residual fuel, asphalt is comprised of the heavy remains left over from the distillation process and may have been blended with cutter stock to reduce the viscosity to meet product specifications. The vast majority of asphalt stored in Maine is used in road construction to bind aggregate particles to create asphalt concrete. It is extremely viscous and will not flow at ambient temperatures. Asphalt is stored at temperatures above 300 °F because it solidifies at temperatures below 250 °F.

Due to its physical properties, i.e., being a thick, black, sticky semi-solid, the true vapor pressure of asphalt is nearly impossible to measure. However, it is generally assumed to be lower than that of #6 fuel oil based on its position in the refinery process.

D. Emission Units

Petroleum storage facilities generally consist of a system for receiving product, tanks for storing product, and a system for distributing product. These facilities also include other equipment and processes which emit air pollutants, including but not limited to maintenance activities and combustion units for facility heating. There is potential to release VOC and/or odor at each point in the system. Following is a discussion of the different processes and pieces of equipment where emissions may occur.

1. Receiving Product

Petroleum product may be received at the petroleum storage facility by pipeline, ship (oil tanker), rail, or truck. In the case of ship, rail, or truck delivery, the product is pumped from the delivery vessel to a petroleum storage tank.

2. Product Storage

Petroleum storage tanks may be found in many configurations based primarily on volume, product stored, and age. The tanks included in this study ranged in capacity from 180 thousand gallons to over seven million gallons. All tanks included in this study were cylindrical, above-ground petroleum storage tanks with various roof configurations as appropriate for the stored material. Types of tank roofs will be discussed in more detail in Section III of this report. Depending on the product being stored, the tank may be heated or unheated; and uninsulated, partially insulated, or fully insulated.

3. Product Distribution

   Product distribution involves movement of the petroleum product out of the petroleum storage facility to the end user or to facilities where the product is marketed (e.g., gas stations). This study is limited to emissions that take place at bulk petroleum storage facilities and does not include emissions from on-road transportation, pipelines, marketing of petroleum products (e.g., gas stations, home heating oil vendors), or end-users (e.g., asphalt batch plants).

4. Miscellaneous Emissions

   Piping, Tank Landings, Tank Cleaning, Control Equipment

   In addition to the operations described above, emissions at petroleum storage facilities can also occur from facility piping, floating roof landings, tank cleaning, heating equipment, and control equipment.

   a. Facility Piping

      The pipes, fittings, and valves that transport liquid product and vapors throughout a petroleum storage facility can be a source of emissions, especially if this equipment is not kept in good repair.

   b. Floating Roof Landings

      Emissions from petroleum storage tanks vary depending on the product stored and the tank roof configurations. When using floating roof tanks (as described in Section III) the roof floats on the surface of the liquid product inside the tank and reduces evaporative losses during routine operations. However, floating roofs cannot be lowered all the way to the floor of the tank without preventing access to the inside of the tank for maintenance and inspection activities. Therefore, floating roof tanks have deck legs or hangers that prevent them from lowering beyond a certain point.

      When a floating roof tank is emptied beyond the point where the roof lands on its deck legs or hangers, the tank behaves as if it were a fixed roof tank with corresponding differences in emissions mechanisms. Therefore, the petroleum storage facility must keep records of every time the roof is “landed” in order to accurately estimate emissions from those periods.

c. Tank Cleaning

As part of routine or non-routine maintenance, a tank may occasionally need to be fully emptied and “degassed” or ventilated to allow personnel to enter the tank to perform repairs or maintenance. Tank cleaning includes the following phases:

(1) Pumpout

The tank roof will be landed (if a floating roof) and as much product as possible will be pumped out of the tank in the normal manner. Emissions from the pumpout are equivalent to regular product transfers. As the product is pumped out of the tank, fresh (ambient) air is drawn in to replace the volume.

(2) Standing Idle

After pumpout, the tank may remain in an idle condition for a period of time until the next steps occur. A pumpout does not remove all product from the bottom of the tank. Some amount of product, called liquid heel, will remain in the bottom of the tank. The amount of product depends on location of the pipe used to empty the tank. Emissions that occur during this period are accounted for the same as routine breathing losses from a fixed roof tank. (Breathing losses are discussed in Section III(B)(2)(a)(2).)

(3) Vapor Space Purge and Forced Ventilation

In order to provide a safe environment for repair and maintenance activities, the vapor space within the tank must be purged by fans or blowers either at the top of the tank or at a manhole or other fitting in the side of the tank.

The first exchange of air from the vapor space results in the highest emissions because the evacuated air is saturated with VOC from the product. This initial exchange is called the vapor space purge. A vapor space purge will occur each time the fans/blowers are started up after the tank has sat idle for a period of time without forced ventilation (e.g., sitting idle overnight).

After a vapor space purge, subsequent exchanges of air within the vapor space are referred to as forced ventilation. As long as some product remains in the tank, some portion of the volatile material will evaporate into the air being moved through the tank by forced ventilation. However, the concentration of VOC in the exhausted air stream will be less than in a vapor space purge since the evacuated air is not completely saturated with VOC.

(4) Remain Clean

Once the tank has been rendered clean and vapor-free, it may remain in the clean condition for some period of time. While forced ventilation may continue, if the liquid heel at the bottom of the tank has been completely removed, there are no further emissions.

(5) Refilling

As the tank is refilled, vapors are generated by the incoming product. This VOC-laden air is then expelled from the tank as it is displaced by the rising liquid level. For a fixed roof tank, the emissions are similar to normal working losses. For a floating roof tank, emissions are similar to working losses from a fixed roof tank until the level of the product reaches the roof and the roof is re-floated.

d. Heating Equipment

Tanks that store residual fuels or asphalt need to be heated to keep the product in a liquid, flowable form. Heat is provided to the tanks typically by boilers or furnaces that heat an intermediate liquid, usually a thermal oil, that is circulated through pipes that surround the tank. The boilers or furnaces used to provide this heat emit combustion byproducts, such as particulate matter, sulfur dioxide, nitrogen oxides, and carbon monoxide.

e. Control Equipment

Equipment used to control emissions from petroleum storage facilities may itself result in emissions of VOC or other pollutants depending on the type of control. For example, control equipment which destroys VOC by burning the vapors will result in emissions of combustion byproducts, such as particulate matter, sulfur dioxide, nitrogen oxides, and carbon monoxide.

III. Methods for Controlling Emissions

A. Resources Consulted

The following resources were consulted in researching the control options available for petroleum storage facilities.

1. State Regulations

Petroleum Liquid Storage Vapor Control, 06-096 C.M.R. ch. 111, addresses state requirements for fixed roof petroleum storage tanks larger than 39,000 gallons.

Bulk Terminal Petroleum Liquid Transfer Requirements, 06-096 C.M.R. ch. 112, addresses state requirements for bulk gasoline terminals with a daily gasoline throughput of 20,000 gallons or more. Maine has eight petroleum storage facilities in this category.

Major and Minor Source Air Emission License Regulation, 06-096 C.M.R. ch. 115, specifies who must obtain an air emission license, the information that must be submitted to apply for an air emission license, and the criteria for license approval. In order to receive a license, the applicant must control emissions from each unit to a level considered by the Department to represent Best Practical Treatment (BPT). BPT for existing emissions equipment means that method which controls or reduces emissions to the lowest possible level considering the existing state of technology, the effectiveness of available alternatives for reducing emissions, and the economic feasibility for the type of establishment involved. BPT for new sources and modifications requires a demonstration that emissions are receiving Best Available Control Technology (BACT). BACT is a top-down approach to selecting air emission controls considering economic, environmental, and energy impacts.

Reasonably Available Control Technology for Facilities That Emit Volatile Organic Compound (VOC-RACT), 06-096 C.M.R. ch. 134, establishes requirements for facilities that emit or have the potential to emit forty tons or more per year of VOC. Maine has nine petroleum storage facilities in this category.

2. Federal Regulations

The following federal regulations address requirements for specific categories of petroleum storage tanks:

- *Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After June 11, 1973, and Prior to May 19, 1978*, 40 C.F.R. Part 60, Subpart K.

- *Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After May 18, 1978, and Prior to July 23, 1984*, 40 C.F.R. Part 60, Subpart Ka.
- *Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984*, 40 C.F.R. Part 60, Subpart Kb.
- *Standards of Performance for Bulk Gasoline Terminals*, 40 C.F.R. Part 60, Subpart XX, addresses requirements for loading racks constructed or modified after December 17, 1980.
- *National Emission Standards for Gasoline Distribution Facilities (Bulk Gasoline Terminals and Pipeline Breakout Stations)*, 40 C.F.R. Part 63, Subpart R, addresses requirements for loading racks, storage vessels, and equipment leaks at bulk gasoline terminals. However, this regulation only applies to facilities categorized as major sources of HAP, i.e., facilities with the potential to emit greater than 10 tons/year of any single HAP or 25 tons/year of all HAP combined. Maine has no petroleum storage facilities in this category.
- *National Emission Standards for Hazardous Air Pollutants for Source Category: Gasoline Distribution Bulk Terminals, Bulk Plants, and Pipeline Facilities*, 40 C.F.R. Part 63, Subpart BBBBBB, addresses requirements for area sources of HAP (i.e., facilities with potential HAP emissions less than major source levels).
- *National Emission Standards for Marine Tank Vessel Loading Operations*, 40 C.F.R. Part 63, Subpart Y, addresses requirements for the transferring of petroleum products to ships.

3. EPA’s Compilation of Air Pollutant Emission Factors (AP-42)

The Department considered EPA’s *Fifth Edition Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources* (AP-42). Since 1972, AP-42 has been considered EPA’s primary compilation of emission factor information. It contains emissions factors and process information for more than 200 air pollution source categories. A source category is a specific industry sector or group of similar emitting sources. Specifically, the Department considered information contained in AP-42, Chapter 5.2, *Transportation and Marketing of Petroleum Liquids* (July 2008) and Chapter 7.1, *Organic Liquid Storage Tanks* (March 2020). AP-42 provides a significant amount of information on control equipment and strategies in common use throughout the industry.

4. EPA Control Cost Manual

The Department referred to EPA’s *Air Pollution Control Cost Manual (Sixth Edition),* *Section 3: VOC Controls* for descriptions and design considerations for various control devices.

5. RACT/BACT/LAER[15] Clearinghouse

   The RACT/BACT/LAER Clearinghouse (RBLC) is an EPA database containing case-specific information on the “Best Available” air pollution technologies that have been required to reduce the emission of air pollutants from stationary sources (e.g., power plants, chemical plants, etc.). The information contained in the RBLC is provided to EPA by state and local permitting agencies.

   The terms “RACT,” “BACT,” and “LAER” are acronyms for different program requirements under the new source review (NSR) permitting program. They represent different types of determinations regarding appropriate emission limits and control equipment for a particular facility or emissions unit. BACT and LAER are determined on a case-by-case basis, usually by state or local permitting agencies. EPA established the RBLC to provide a central database of air pollution technology information, including previous BACT and LAER determinations, to promote the sharing of information among permitting agencies and to aid in future case-by-case determinations.

   The information in the RBLC is not limited to RACT, BACT, or LAER decisions. Noteworthy prevention and control technology decisions and information may be included even if they are not related to past RACT, BACT, or LAER decisions.

   Control technologies included in the RBLC for petroleum storage facilities were considered as part of this report.

6. California South Coast Air Quality Management District Determinations

   Similar to the RBLC, California’s South Coast Air Quality Management District (South Coast AQMD) has a database[16] of BACT determinations searchable by equipment type. Control technologies included in South Coast AQMD’s database for petroleum storage facilities were considered as part of this report.

7. Texas Best Available Control Technology Guidelines

   The Texas Commission on Environmental Quality (Texas CEQ) posts on its website[17]

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[15] RACT stands for Reasonably Available Control Technology; BACT stands for Best Available Control Technology; and LAER stands for Lowest Achievable Emission Rate. These represent different program requirements defined in federal regulations.

[16] http://www.aqmd.gov/home/permits/bact/guidelines/i---scaqmd-laer-bact

[17] https://www.tceq.texas.gov/permitting/air/nav/bact_index.html

guidelines for performing a BACT analysis for projects in that state. Their guidance document titled *Air Permit Reviewer Reference Guide, APDG 6110, Air Pollution Control, How to Conduct a Pollution Control Evaluation*, provides permit reviewers with a process to evaluate and determine air pollution control requirements.

Texas uses a three-tiered approach to evaluate BACT proposals in NSR permit applications. In Tier I, an applicant's BACT proposal is compared to the emission reduction performance levels accepted as BACT in recent NSR permit reviews for the same process and/or industry. The analysis only moves on to Tier II or Tier III if BACT requirements have not already been established for a particular process/industry or if there are compelling technical differences between the applicant's facility and others in the same industry. Therefore, if a Tier I BACT determination exists for a given process, that Tier I BACT is, by default, considered to be the most appropriate control.

There are Tier I BACT determinations[18] available for the following categories:

- Fixed roof tanks with capacities < 25 thousand gallons (Mgal) and true vapor pressure (TVP) < 0.5 pounds per square inch absolute (psia);
- Fixed roof tanks with capacities ≥ 25 Mgal and TVP < 11.0 psia;
- Fixed roof tanks with TVP ≥ 11.0 psia; and
- Floating roof tanks with TVP < 11.0 psia.

Requirements of these Tier I BACT determinations were considered as part of this report.

8. Other States

In developing this report, the Department attempted to survey all other state environmental agencies across the country. A total of 34 state and local agencies responded to our request for information and provided insight on their requirements for controlling emissions from petroleum storage facilities.

B. Available Control Strategies for VOC

Petroleum storage facilities generally consist of a system for receiving product, storage tanks for storing product, and a system for distributing product. These facilities also include miscellaneous equipment and processes which release air emissions, including maintenance activities. There is potential to release VOC at each point in the system.

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[18] https://www.tceq.texas.gov/assets/public/permitting/air/Guidance/NewSourceReview/bact/bact-chemical.xlsx

Following is a description of the available options and strategies for control of VOC emissions from petroleum storage facilities.

1. Receiving Product

   When product is delivered to the petroleum storage facility via ship, rail, or tank truck, fresh air is drawn into the delivery vessel as product is transferred to the petroleum storage tank. Emissions from the delivery vessel are typically minimal since the product is being pumped out of the vessel and air is pulled into the vessel to replace the missing volume. However, once the product transfer is complete, there is the potential for the delivery vessel to off-gas any product remaining in its hold if it remains open to the atmosphere. Of the resources consulted, none specifically addressed sealing the delivery vessel once transfer is complete. However, this is a common practice for safety reasons as leaving the emptied delivery vessel open to the air could create a potentially explosive environment inside the delivery vessel.

   VOC may be released when product is added to a petroleum storage tank, displacing vapors from within the tank that may be saturated with product. Emissions from petroleum storage tanks, including during filling operations, are addressed in the next section.

2. Product Storage

   There are various emission control options available for petroleum storage tanks including those add-on controls for existing tanks and inherently low-emitting storage tank designs.

   Five basic types of tanks are used to store petroleum liquids: fixed roof, external floating roof, internal floating roof, domed external floating roof, and variable vapor space.

   a. Fixed Roof Tanks

      (1) Description

      A fixed roof tank is the most basic type of petroleum storage tank. Fixed roof tanks are used to store products with lower vapor pressures, such as distillate fuels, residual fuels, and asphalt.

      A typical vertical fixed roof tank is shown in Figure 1. This type of tank consists of a cylindrical steel shell with a permanently affixed roof, which may be conical, domed, or flat. The tank may be heated or unheated. Heated tanks are usually insulated whereas unheated tanks often are not.

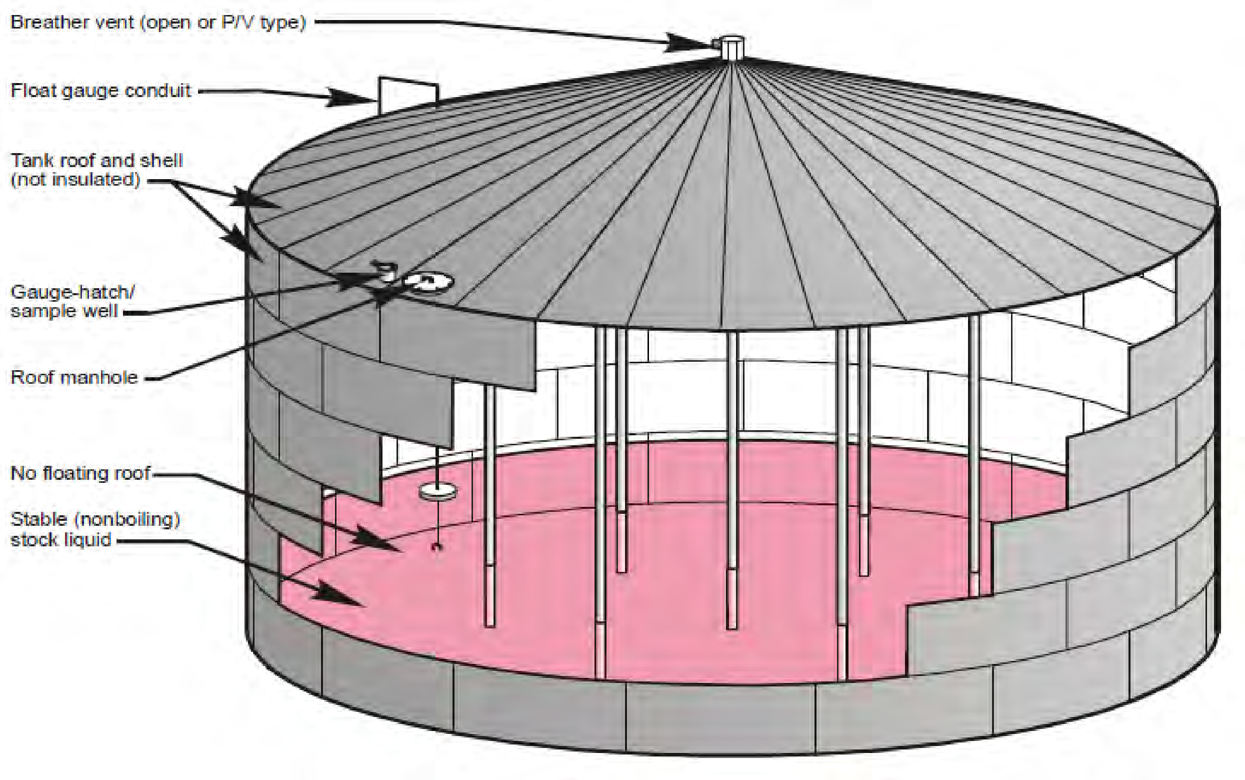

Figure 1: Typical fixed roof tank.[19]

(2) Emissions

Emissions from fixed roof tanks are caused by changes in temperature, pressure, and liquid level. When the tank is filled, the VOC-laden air above the liquid is forced out of the tank as the space is taken up by the liquid product. Emissions from actively filling the tank are known as “working losses,” and occur relatively infrequently. However, working losses may result in a large volume of VOC-laden air being exhausted from the tank over a relatively short period of time.

Fixed roof tanks can also have emissions when no product is being added or removed. These emissions, known as “breathing losses,” occur when there is an increase in temperature inside the tank. Both the liquid product and gases in the vapor space expand, forcing VOC-laden air out of the tank. When the interior of the tank cools, the opposite occurs, and fresh air is drawn into the tank as the product and gases inside the tank contract. Breathing losses result in a much smaller flow rate of vapor from the tank, but the emissions occur more frequently (daily).

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[19] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

Unheated fixed roof tanks experience breathing losses as the tanks are naturally heated by the sun during the day and then cool at night. To help limit breathing losses, fixed roof tanks are often painted white or another light color to minimize solar heating.

Heated fixed roof tanks with uninsulated roofs experience breathing losses similar to unheated tanks because diurnal solar heating and cooling through the roof affects the gases in the vapor space inside the tank.

Fixed roof tanks that are fully insulated are less likely to have breathing losses driven by diurnal ambient temperature cycles. Instead, expansion and contraction of the product and vapors inside the tank may be driven by cyclic heating of the tank. Tanks are heated by furnaces or boilers that heat an intermediate fluid, usually a type of thermal oil. The heated thermal oil is circulated through pipes that heat the product being stored. If this heating process is intermittent, i.e., the product is heated to 350° F and then allowed to cool to 300° F before being heated again, then the heating and cooling cycles will cause the product and vapor inside the tank to expand and contract, causing breathing losses. However, if the product in a fully insulated tank is maintained at a constant temperature, the product and vapor in the tank stay at a constant volume, and breathing losses are essentially eliminated.

(3) Potential Control Strategies

Following are potential control strategies for fixed roof petroleum storage tanks:

(i) Low Vapor Pressure Products

Low vapor pressure products result in a vapor space within the tank that contains a lower concentration of VOC than results from higher vapor pressure products. Therefore, working and breathing losses are less when the product stored has a lower vapor pressure. Fixed roof tanks are typically only appropriate for products with vapor pressures less than 0.50 psia at 60° F such as distillate fuel, residual fuel, or asphalt.

(ii) Annual Throughput Limits

Limiting a tank’s annual throughput can limit working losses. However, it has no effect on breathing losses.

(iii) Paint Color

Many entries in the RBLC required the tank to be painted white or another reflective color. Uninsulated, fixed roof tanks experience breathing losses as the tanks are naturally heated by the sun during the day and cool at night. Painting the tank a light color minimizes solar heating.

(iv) Submerged Fill

Submerged fill describes the filling of a storage tank in a way that causes product to enter the vessel below the liquid level. For example, use of a drop tube allows the product to flow through the tube and emerge at a point near the bottom of the tank. When the tank is filled, the product level quickly rises above this point. As a consequence, most of the product entering the tank does not splash and instead flows beneath the liquid surface. Using submerged fill greatly reduces turbulence and therefore reduces vapor generation.

(v) Insulation

Breathing losses from fixed roof tanks can be nearly eliminated by keeping the vapor space inside the tank at a constant temperature. Breathing losses occur as the vapor inside the tank expands when heated. This can be due to natural heating from changes in ambient temperature and solar radiation, or tank heaters can be used to increase the product temperature.

If the tank is fully insulated, including the roof, breathing losses due to natural heating cycles are minimized. Similarly, heated tanks that are fully insulated and held at a constant temperature also have minimal emissions due to breathing losses.

(vi) Vapor Recovery Units

Vapor recovery units (VRUs) route VOC-laden vapors to a device which separates the VOC from the exhaust stream. Depending on the design, the VRU may either trap/bind the VOC to a solid to be disposed of or recover the VOC back as a liquid that can either be disposed of or piped back to the petroleum storage tank. VRUs can achieve control efficiencies for VOC greater than 98%. VRUs recover the product in the displaced vapors through adsorption or condensation.

1. Carbon Adsorption

   Carbon adsorption is the process of passing the VOC-laden air stream through a bed of adsorbent material, typically activated carbon, although other media may be suitable for certain applications. Hydrocarbons attach to the surfaces of the activated carbon particles. Carbon adsorbers are also referred to as "carbon beds."

   Carbon adsorbers can be either regenerative or non-regenerative. With non-regenerative carbon adsorption, the adsorbent eventually becomes saturated with adsorbed VOC and loses its effectiveness. The adsorbent needs to be periodically replaced and the spent material disposed of. Due to the cost to replace the spent media and the creation of an additional waste stream, non-regenerative carbon adsorption is best suited to low volume and/or low concentration streams.

   With regenerative carbon adsorption, hydrocarbons are desorbed and collected, typically by drawing a vacuum on the sorbent bed or by using heated air, steam, or nitrogen. The recovered hydrocarbons can be returned to the petroleum storage tank. A drawback of this control approach is that the adsorbent typically binds strongly to heavy hydrocarbons and is less effective at capturing lighter organics such as propane. Therefore, it may be difficult to desorb some materials, which can foul the adsorbent over time. Additionally, lighter materials are even more likely to pass through without being adequately collected if heavy hydrocarbons have already bound to the adsorbent. Therefore, regenerative carbon adsorption is typically used for VRUs associated with exhaust streams carrying gasoline or distillate fuel vapors and not used with heavier hydrocarbon products such as crude oil, residual fuels, and asphalt.

   Carbon adsorbers may be designed to reduce VOC and/or odors. However, they require an active system where fans or blowers draw a flow across the tank vents to capture emissions. If the carbon bed is not carefully monitored and maintained, the carbon media may become spent or fouled such that it no longer removes pollutants from the exhaust stream. This could have the unintended consequence of increasing emissions since the blower system will pull more vapors out of the tank than if the tank were left uncontrolled.

2. Condensers

VOC can be removed from an exhaust stream by condensing the product to a liquid. Condensation occurs when an exhaust stream that is saturated with product vapors undergoes a phase change from gas to liquid. The phase change can be achieved in two ways: The system pressure can be increased at a given temperature (i.e., compression), or the temperature may be lowered at a constant pressure (i.e., refrigeration).

For a more volatile product (i.e., a product with a low boiling point and high vapor pressure), larger amounts can remain in the vapor phase at a given temperature. To induce condensation, the exhaust stream must be cooled, compressed, or both. Therefore, it is more energy-intensive to operate a condenser to control a more volatile product (e.g., gasoline) than a less volatile product (e.g. distillate fuels). However, the less volatile products also often contain heavy, sticky compounds that can stick to the inside of a condenser, reducing its efficiency and effectiveness over time.

(vii) Vapor Combustion Units

A vapor combustion unit (VCU) raises the temperature of the exhaust stream to oxidize (burn) the VOC components. VCUs can be designed to achieve control efficiencies for VOC greater than 98%. Types of VCUs include open flares, enclosed thermal oxidizers, and regenerative thermal oxidizers.

1. Flares

Flaring is a type of thermal oxidizer that directs the VOC-laden exhaust stream through a vertical pipe to a burner assembly located well above ground level. VOC are burned in the open air using a specially designed burner tip, auxiliary fuel, and steam or air to promote mixing. Completeness of combustion in a flare is governed by flame temperature, residence time in the combustion zone, turbulent mixing of the components to complete the oxidation reaction, and available oxygen for free radical formation. Combustion is complete if all VOC are converted to carbon dioxide and water. Incomplete combustion results in some of the VOC being unaltered or converted to other organic compounds such as aldehydes or acids.

The flaring process can produce some undesirable byproducts including noise, smoke, heat radiation, light, sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO), and an additional source of ignition introducing additional fire hazard at a petroleum facility.

A major drawback to using an open flare is the inability to conduct performance testing. Due to its open nature, it is impossible to measure actual emissions of VOC after the control device, i.e., after the flame. Therefore, facilities which utilize a VCU for control of VOC emissions typically use an enclosed thermal oxidizer instead of an open flare where a precise measurement of actual emissions is required.

2. Enclosed Thermal Oxidizers

Enclosed thermal oxidizers (enclosed TOs), also known as ground flares, have burner heads which are inside an insulated shell. This equipment is located at ground level. The shell reduces noise, light, and heat radiation, and provides wind protection.

Enclosed TOs have a defined exhaust point which can be tested for control efficiency and compliance with emission limit regulations.

Enclosed TOs are most often used with exhaust streams with high concentrations of VOC, such as emissions from loading of gasoline. They are less cost-effective when used to control exhaust streams with lower concentrations of VOC. A recent analysis performed for a Maine facility indicated the cost of using a thermal oxidizing system for control of distillate vapors was approximately $600,000 per ton of pollutant controlled.

3. Regenerative Thermal Oxidizers

Regenerative thermal oxidizers (RTOs) preheat the inlet emissions stream with heat recovered from the exhaust gases generated by their operation. The inlet gas stream is passed through preheated ceramic media, and an auxiliary gas burner is used to heat it to between 1,450 ºF and 1,600º F at a specific residence time. The combusted gas exhaust then passes through a cooled ceramic bed where heat is extracted.

RTOs can very efficiently meet high destruction efficiencies of exhaust streams with a continuous, consistent VOC loading. However, the amount of exhaust experienced from fixed roof tanks varies widely between those experienced during daily breathing losses and intermittent working losses. Additionally, short-term batch processes, such as working losses from a fixed roof tank, are not well suited for control by an RTO. The intermittent nature of emissions in the exhaust stream means there could be significant periods of time between high VOC loads, allowing the ceramic media to cool and fail to effectively or efficiently pre-heat the incoming gases. This would result in less efficient operation and the use of more auxiliary fuel.

(viii) Mist Eliminators

Mist eliminators, also known as “demisters” or “entrainment separators,” are designed to remove mist droplets from an air stream. Unlike condensers (described below in the section on Product Distribution), mist eliminators do not involve a phase change. The product entrained in the air stream is already in a liquid form, but the droplets are small enough to become airborne.

Mist eliminators are relatively simple devices that involve passing the exhaust stream past or through some type of filter system such as wire mesh, filters, or baffles. The filter system removes liquid droplets from the air stream by three methods: initial impaction (forcing gases around a tight bend), direct interception (impacting the filter surface), and Brownian diffusion (causing chaotic and irregular movement of the particle such that it impacts other particles).

Mist eliminators have almost no control efficiency for more volatile products (e.g., gasoline) as they do not reduce emissions of product already in the gaseous phase. They do reduce emissions of aerosols or droplets of less volatile products (e.g., asphalt) at temperatures below the product’s boiling point. However, since the product is already in the liquid phase, this is considered a control method for fine particulate matter and not for VOC.

(4) Summary of Control Strategies in Use

Maine DEP regulation *Petroleum Liquid Storage Vapor Control*, 06-096 C.M.R. ch. 111, applies to fixed roof petroleum storage tanks larger than 39,000 gallons. Such tanks storing a petroleum product with a vapor pressure greater than 1.0 psia but less than 1.52 psia are required to maintain records of the average monthly storage temperatures, the type of petroleum product stored, and the maximum true vapor pressure of the product stored. Further requirements of this regulation are described in the section on floating roof tanks.

Throughout all of the resources consulted, the use of low vapor pressure products, throughput limits, white/light tank color, and submerged fill were common strategies for minimization of emissions of VOC from fixed roof petroleum storage tanks. The use of insulation was not called out specifically as a required control strategy, except that insulated portions of tanks were often exempted from the requirement to be painted a white/light color.

Tanks which store petroleum products with a true vapor pressure greater than 0.50 psia at 60 °F (e.g., gasoline) are commonly required to use some type of floating roof as a control strategy, although the Texas CEQ's Tier I BACT does provide for fixed roof tanks to be used with these higher vapor pressure products provided the tank is vented to a control device. The specific type of control device is not specified but is likely some form of VRU or VCU.

The South Coast AQMD BACT database had one entry for fixed roof tanks. This determination applied to products with a vapor pressure greater than 0.10 psia at 70 °F but less than the vapor pressure of hexane (1.9 psia) or methanol (1.5 psia) depending upon the tank. The facility was required to install a thermal oxidizer (VCU) with an assumed overall control efficiency of 95%.

Regarding products with a true vapor pressure less than 0.10 psia (e.g., distillate fuels, residual fuels, asphalt), there were no examples requiring floating roofs or add-on controls found in the Texas CEQ's Tier I BACT or the South Coast AQMD BACT database.

In their response to our survey, the State of Illinois stated that asphalt vent packages consisting of a pre-filter and mist eliminator have been permitted for control of asphalt storage tanks. While the installation of these controls for asphalt tanks is not required by state or federal rule, they are nevertheless expected to reduce emissions and potential odors.

The State of Ohio indicated that they have required the use of a carbon bed or thermal oxidizer to control emissions from some fixed roof asphalt tanks.

The State of New York is considering for a future regulatory proposal a passive vent control system such as a tank vent condenser or activated carbon filter as a requirement during the filling of asphalt tanks.

There was one entry in the RBLC where an RTO (i.e., VCU) was installed to control emissions from heated residual fuel storage tanks. This entry is from 2008 for a petroleum storage facility located in Chelsea, Massachusetts. The control system was designed to capture 95% of the vapor-laden air from the tank vent system and route it to an RTO with a 99% destruction efficiency for an overall control effectiveness of 94%. This control system was installed voluntarily by the facility owner as a strategy intended to limit emissions at the facility to minor source levels.

b. Floating Roof Tanks

(1) Description

There are three types of floating roof tanks; external floating roof tanks (EFRT), internal floating roof tanks (IFRT), and domed external floating roof tanks (domed EFRT).

(i) External Floating Roof Tanks

A typical EFRT consists of an open-top cylindrical steel shell equipped with a roof that floats on the surface of the stored liquid. The floating roof consists of a deck, deck fittings, and a rim seal system. Floating decks are constructed of welded steel plates with built-in buoyancy, allowing them to sit/float on top of the liquid. They are most commonly of two general types: pontoon or double-deck. A pontoon-type EFRT is shown in Figure 2.

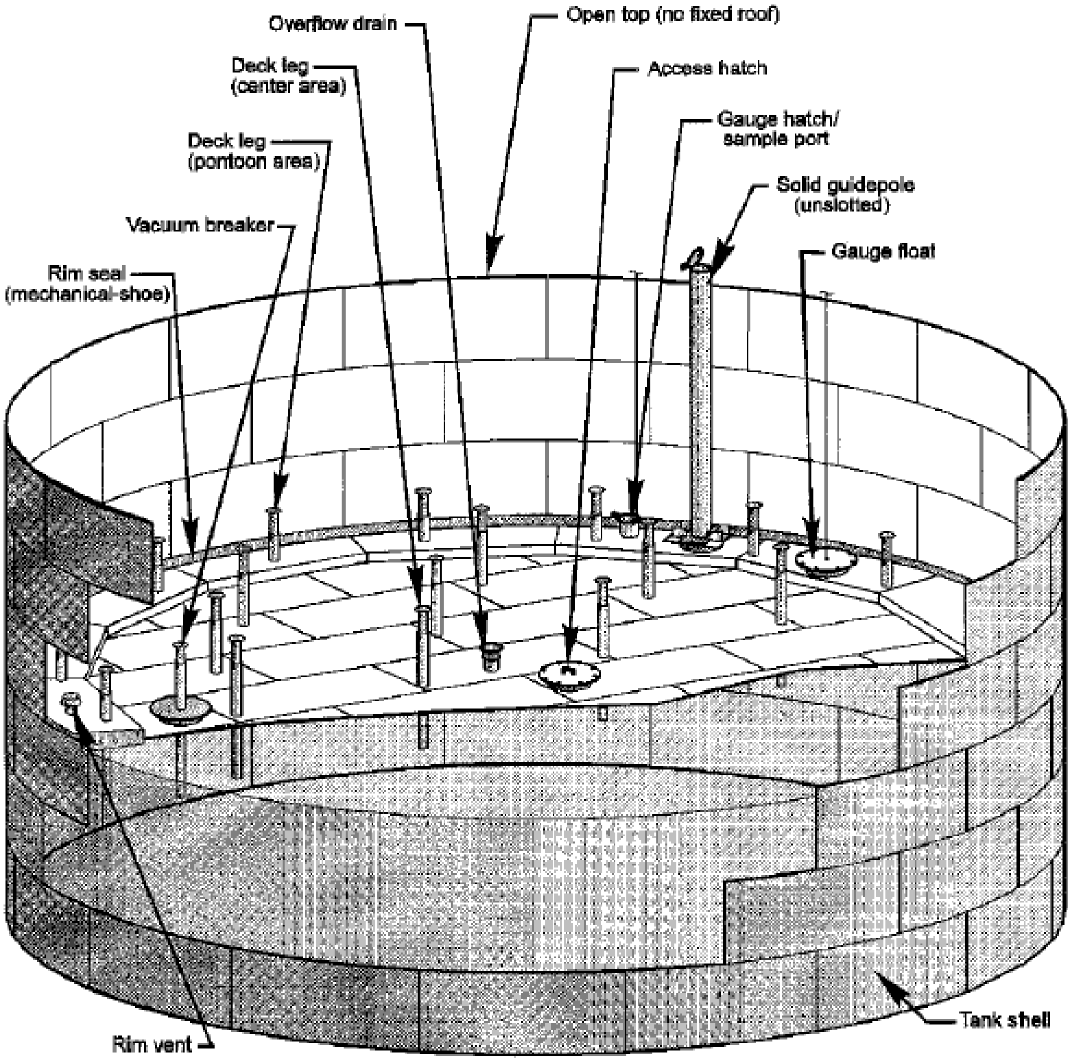

Figure 2: External floating roof tank (pontoon type)[20]

(ii) Internal Floating Roof Tanks

IFRTs have a permanent fixed roof with a floating roof inside. A typical IFRT is shown in Figure 3.

An IFRT can be designed and installed as an IFRT or can be initially designed and installed as a fixed roof tank and later retrofitted with a floating roof. The floating roofs for IFRTs tend to be thinner and do not typically have surface drains or other design elements for snow, rain, and wind considerations since the floating roof was designed for use with a fixed roof.

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[20] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

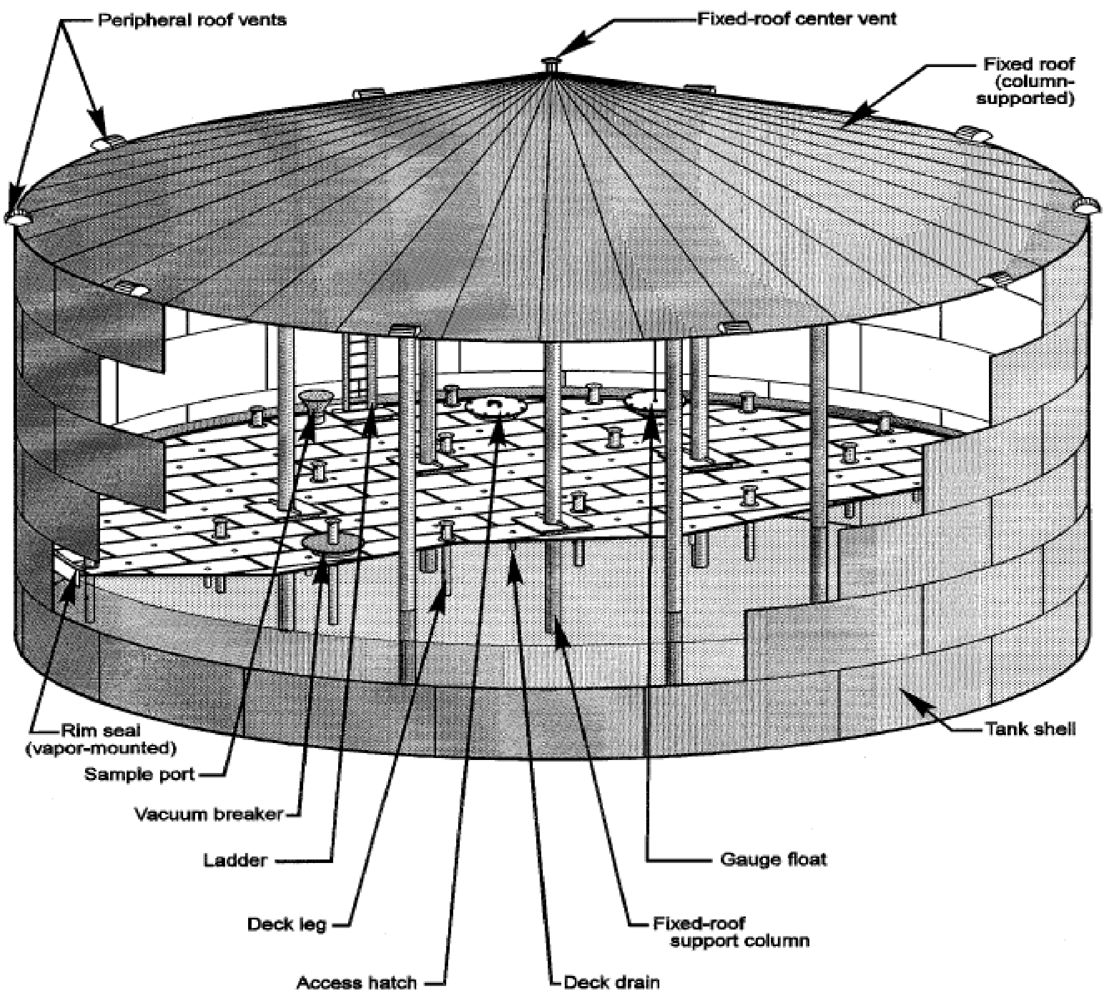

Figure 3: Internal floating roof tank[21]

There are two basic types of IFRTs: tanks in which the fixed roof is supported by vertical columns within the tank and tanks with a self-supporting fixed roof and no internal support columns. Fixed roof tanks that have been retrofitted to use a floating roof are typically of the first type. EFRTs that have been converted to IFRTs typically have a self-supporting roof. Newly constructed IFRTs may be of either type. The deck in IFRTs rises and falls with the liquid level and either floats directly on the liquid surface (contact deck) or rests on pontoons several inches above the liquid surface (noncontact deck). The majority of aluminum IFRTs currently in service have noncontact decks.

Installing a floating roof minimizes evaporative losses of the stored liquid. Both contact and noncontact decks incorporate rim seals and deck fittings with purpose and function similar to those seen in EFRTs. Evaporative losses from floating roofs may come from deck fittings,

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[21] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

nonwelded deck seams, and the annular space between the deck and tank wall. However, the additional fixed roof minimizes the effect of wind on evaporative losses from the floating roof.

IFRTs are usually freely vented by circulation vents at the top of the fixed roof. The vents minimize the possibility of organic vapor building up in the space between the floating roof and the fixed roof and approaching flammable and/or explosive limits.

(iii) Domed External Floating Roof Tanks

As with IFRTs, domed EFRTs have a permanent fixed roof with a floating roof inside. A typical domed EFRT is shown in Figure 4.

Domed EFRTs tend to be initially designed and installed as EFRTs with a more robust floating roof than IFRTs designed to accommodate snow, rain, and wind. The external fixed roof is usually added later to prevent water getting into the product.

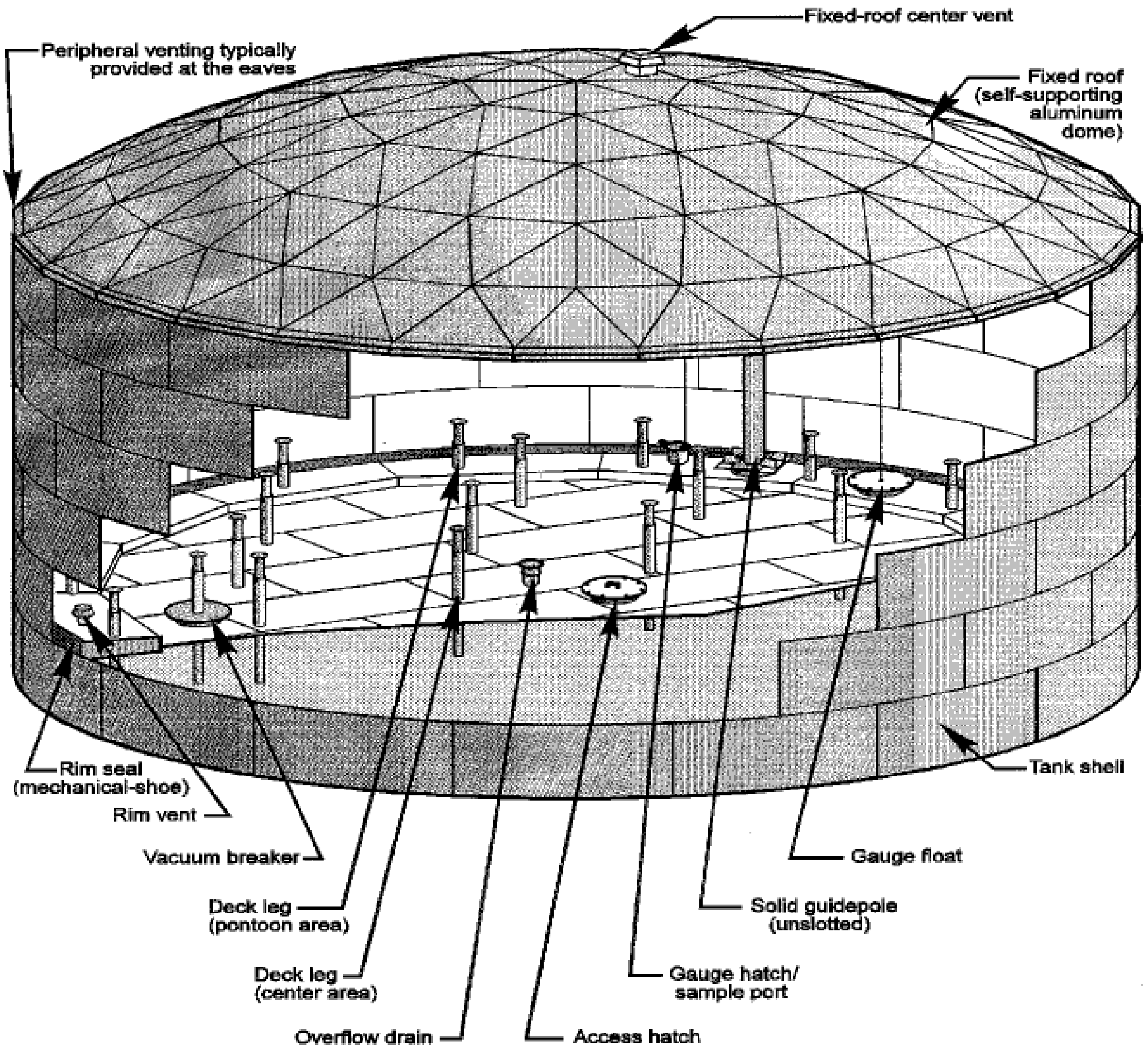

Figure 4: Domed external floating roof tank[22]

As with IFRTs, the fixed roof is not intended to act as a vapor barrier but instead to block the wind and minimize its evaporative effect.

The type of fixed roof most commonly used is a self-supporting aluminum dome roof, which is of bolted construction. Like the IFRTs, these tanks are freely vented by circulation vents at the top and around the perimeter of the fixed roof. The deck fittings and rim seals, however, are identical to those on EFRTs. In the event that the floating deck is replaced with a lighter IFRT-type deck, the tank would be reclassified as an IFRT.

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[22] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

The distinction between a domed EFRT and an IFRT is primarily for purposes of recognizing differences in the deck fittings when estimating emissions. In particular, the domed EFRT deck typically has significantly taller leg sleeves than are found on an IFRT deck. The longer leg sleeves have lower associated emissions than the shorter leg sleeves of the IFRT deck. While a domed EFRT is distinct from an IFRT for purposes of estimating emissions, a domed EFRT can be considered a type of IFRT.

(2) Emissions

In all types of floating roof tanks, the roof rises and falls with the liquid level in the tank. They are equipped with a flexible rim seal system, which is attached to the deck perimeter and contacts the tank wall. The purpose of the floating roof and rim seal system is to reduce evaporative loss of the stored liquid. Some annular space remains between the seal system and the tank wall. The seal system slides against the tank wall as the roof level changes. The floating deck is also equipped with deck fittings that penetrate the deck and serve operational functions.

Unlike fixed roof tanks which have “working losses” and “breathing losses,” emissions from floating roof tanks are the sum of “working losses” and “standing losses.” Working losses (also known as withdrawal losses) from a floating roof tank occur when product is transferred out of the tank. Some product is left behind on the tank walls, and emissions occur when this product evaporates when the walls are exposed as the roof level drops. For IFRTs that have a column supported fixed roof, some product also clings to the columns and evaporates.

Standing losses from floating roof tanks include rim seal and deck fitting losses for floating roof tanks with welded decks and include deck seam losses for constructions other than welded decks.

Rim seal losses can occur through many complex mechanisms, but for EFRTs, the majority of rim seal vapor losses have been found to be wind induced. No dominant wind loss mechanism has been identified for IFRTs or domed EFRT rim seal losses. Losses can also occur due to permeation of the rim seal material by the vapor or via a wicking effect of the liquid, but permeation of the rim seal material generally does not occur if the correct seal fabric is used. Testing has indicated that breathing, solubility, and wicking loss mechanisms are small in comparison to the wind-induced loss.

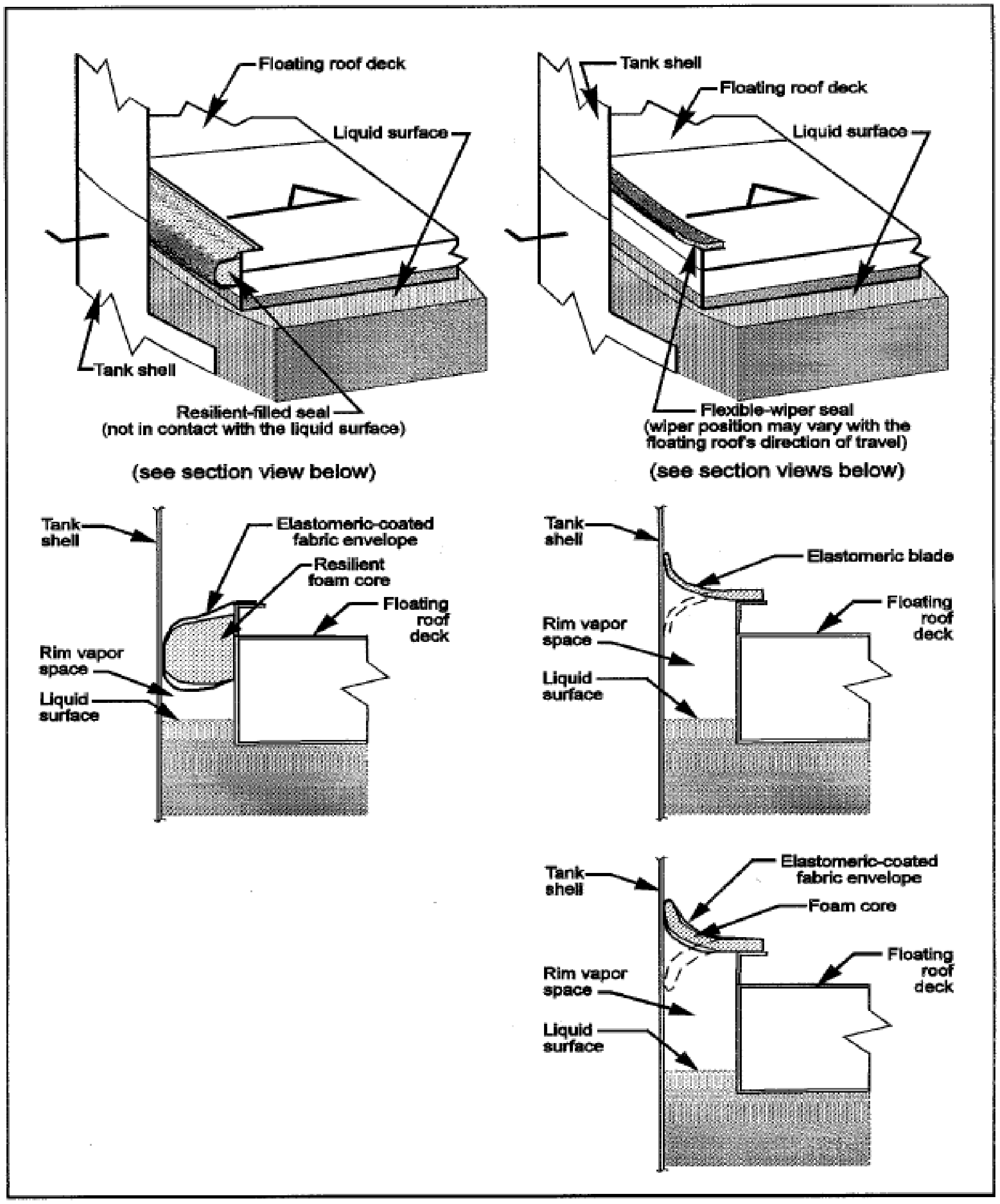

Figure 5: Vapor-mounted primary seals[23]

The rim seal system is used to allow the floating roof to rise and fall within the tank as the liquid level changes. The rim seal system also helps to fill the annular space between the rim and the tank shell and therefore minimize evaporative losses from this area. A rim seal system may consist of just a primary seal or a primary and a secondary seal, which is mounted above the

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[23] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

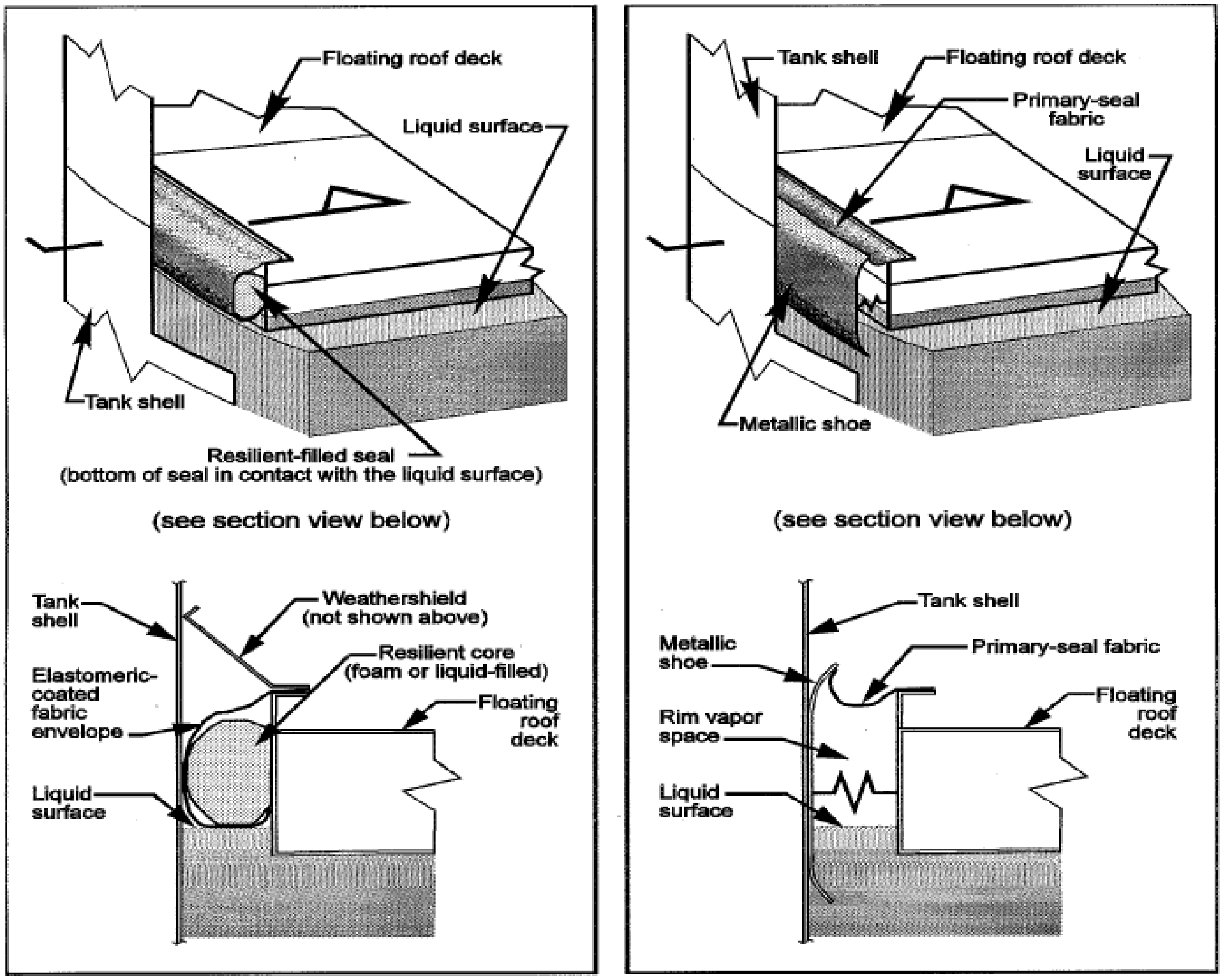

Figure 6: Liquid-mounted and mechanical shoe primary seals[24]

primary seal. Examples of primary and secondary seal configurations are shown in Figure 5, Figure 6, and Figure 7.

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[24] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

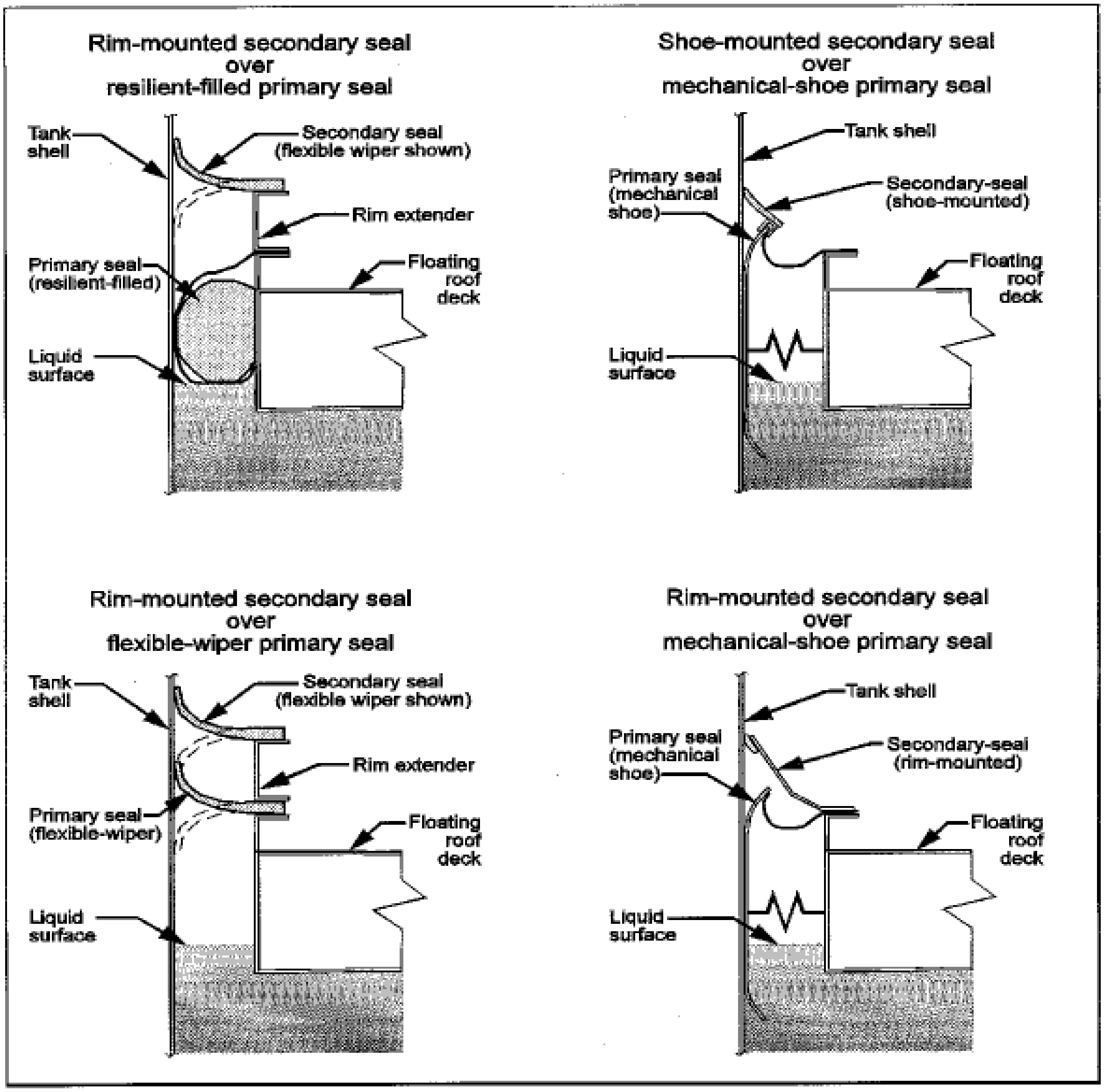

Figure 7: Secondary rim seals[25]

The primary seal serves as a vapor conservation device by closing the annular space between the edge of the floating deck and the tank wall. Three basic types of primary seals are used on floating roofs: mechanical (metallic) shoe, resilient filled (nonmetallic), and flexible wiper seals. Some primary seals on external floating roof tanks are protected by a weather shield. Weather shields may be of metallic, elastomeric, or composite materials and provide the primary seal with longer life by protecting the primary seal fabric from deterioration due to exposure to weather, debris, and sunlight. Mechanical shoe seals, resilient filled seals, and wiper seals are discussed below.

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[25] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

A mechanical shoe seal uses a light-gauge metallic band as the sliding contact with the shell of the tank, as shown in Figure 6. The band is formed as a series of sheets (shoes) which are joined together to form a ring and are held against the tank shell by a mechanical device. The shoes are normally 3 to 5 feet deep when used on an EFRT and are often shorter when used on an IFRT.

Expansion and contraction of the ring can be provided for as the ring passes over shell irregularities or rivets by jointing narrow pieces of fabric into the ring or by crimping the shoes at intervals. The bottoms of the shoes extend below the liquid surface to confine the rim vapor space between the shoe and the floating deck.

The rim vapor space, which is bounded by the shoe, the rim of the floating deck, and the liquid surface, is sealed from the atmosphere by bolting or clamping a coated fabric to the shoe. This “primary seal fabric” extends from the shoe to the rim to form an "envelope". Two locations are used for attaching the primary seal fabric; most commonly the top of the shoe and the rim of the floating deck. To reduce the rim vapor space, the fabric can be attached to the shoe and the floating deck rim near the liquid surface. Rim vents can be used to relieve any excess pressure or vacuum in the vapor space.

A resilient filled seal can be configured to allow a vapor space between the rim seal and the liquid surface (vapor mounted), or to eliminate the vapor space between the rim seal and liquid surface (liquid mounted). These configurations are shown in Figure 5 and Figure 6 respectively. Resilient filled seals work as the expansion and contraction of a resilient material maintains contact with the tank shell while accommodating variations in the width of the annular rim space. These rim seals allow the roof to move up and down freely, without binding.

Resilient filled seals typically consist of a core of open-cell foam encapsulated in a coated fabric. The seals are mounted on the deck perimeter and extend around the deck circumference. Polyurethane-coated nylon fabric and polyurethane foam are commonly used materials. For emission control, it is important that the attachment of the seal to the deck and the radial seal joints be vapor-tight and that the seal be in substantial contact with the tank shell.

Wiper seals generally consist of a continuous annular blade of flexible material fastened to a mounting bracket on the deck perimeter that spans the annular rim space and contacts the tank shell. This type of seal is depicted in Figure 5. New tanks with wiper seals may have dual wipers, one mounted above the other. The mounting is such that the blade is flexed, and its elasticity provides a sealing pressure against the tank shell.

Wiper seals are vapor mounted; a vapor space exists between the liquid stock and the bottom of the seal. For emission control, it is important that the mounting be vapor-tight, that the seal extend around the circumference of the deck, and that the blade be in substantial contact with the tank shell. Two types of materials are commonly used to make the wipers. One type consists of a cellular, elastomeric material tapered in cross section with the thicker portion at the mounting. Rubber is a commonly used material; urethane and cellular plastic are also available. All radial joints in the blade are joined. The second type of material that can be used is a foam core wrapped with a coated fabric. Polyurethane on nylon fabric and polyurethane foam are common materials. The core provides the flexibility and support, while the fabric provides the vapor barrier and wear surface.

A secondary seal may be used to further reduce evaporative loss beyond that achieved by the primary seal. Secondary seals can be either flexible wiper seals or resilient filled seals. For mechanical shoe primary seals, two configurations of secondary seals are available: shoe mounted and rim mounted, as shown in Figure 7. Rim mounted secondary seals are more effective in reducing losses than shoe mounted secondary seals because they cover the entire rim vapor space. For IFRTs, the secondary seal is mounted to an extended vertical rim plate, above the primary seal, as shown in Figure 7. However, for some floating roof tanks, using a secondary seal further limits the tank's operating capacity due to the need to keep the seal from interfering with fixed roof rafters or to keep the secondary seal in contact with the tank shell when the tank is filled.

The deck fitting losses from floating roof tanks can be explained by the same mechanisms as the rim seal losses. While the relative contribution of each mechanism to the total emissions from a given deck fitting is not known, emission factors have been developed for individual deck fittings by testing, thereby accounting for the combined effect of all of the mechanisms.

Numerous fittings pass through or are attached to floating roof decks to accommodate structural support components or allow for operational functions. Internal floating roof deck fittings are typically of different configuration than those for external floating roof decks. Rather than having tall housings to avoid rainwater entry, internal floating roof deck fittings tend to have lower profile housings to minimize the potential for the fitting to contact the fixed roof when the tank is filled. Deck fittings can be a source of evaporative loss when they require openings in the deck. The most common components that require openings in the deck are described below.

Access hatches

An access hatch is an opening in the deck with a peripheral vertical well that is large enough to provide passage for workers and materials through the deck for construction or servicing. Attached to the opening is a removable cover that may be bolted and/or gasketed to reduce evaporative loss. On IFRTs with noncontact decks, the well should extend down into the liquid to seal off the vapor space below the noncontact deck. A typical access hatch is shown in Figure 8.

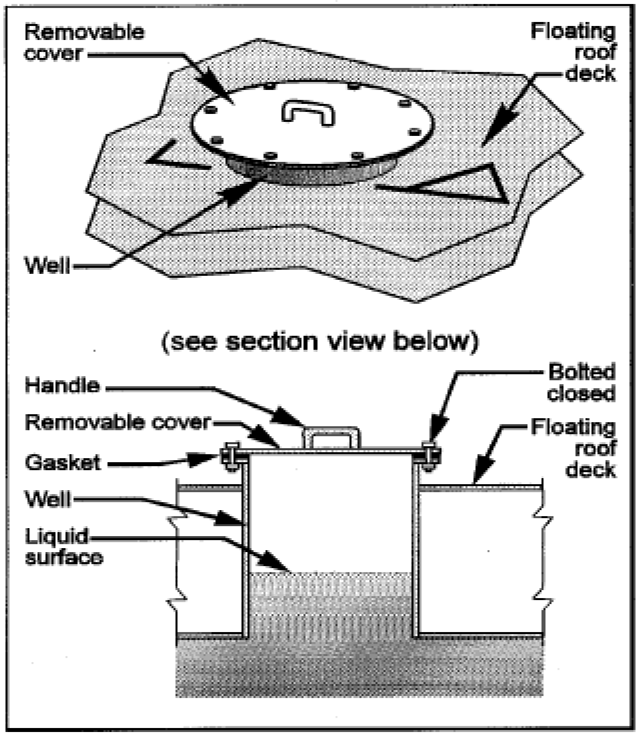

Figure 8: Access Hatch[26]

Gauge-floats

A gauge-float is used to indicate the level of liquid within the tank. The float rests on the liquid surface and is housed inside a well that is closed by a cover. The cover may be bolted and/or gasketed to reduce evaporation loss. As with other similar deck penetrations, the well extends down into the liquid on noncontact decks in internal floating roof tanks. A typical gauge-float and well are shown in Figure 9.

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[26] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

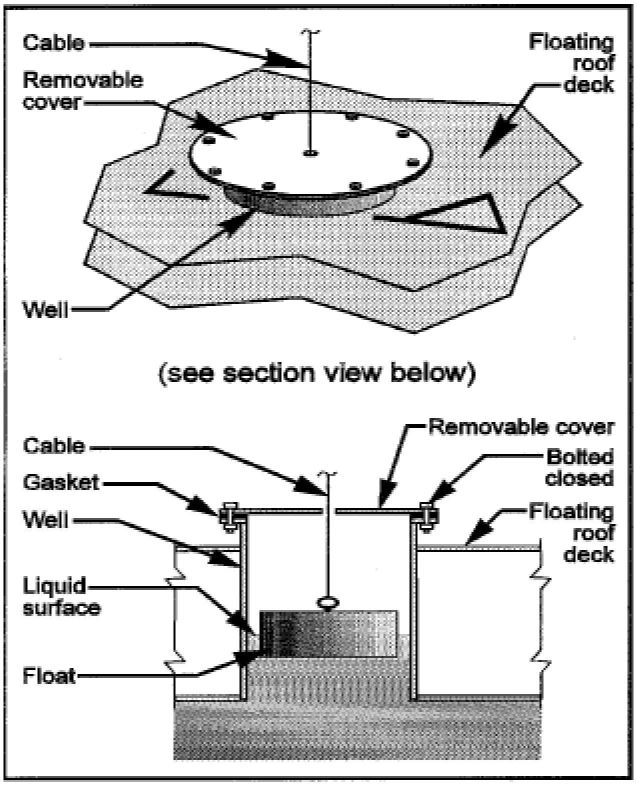

Figure 9: Gauge Float[27]

<u>Gauge-hatch/sample ports</u>

A gauge-hatch/sample port consists of a pipe sleeve through the deck for hand-gauging or sampling of the stored liquid. The gauge-hatch/sample port is usually located beneath a gauger's platform, which is mounted on top of the tank shell. A cover may be attached to the top of the opening, and the cover may be equipped with a gasket to reduce evaporative losses. A cord may be attached to the cover so that the cover can be opened from the platform. Alternatively, the opening may be covered with a slit-fabric seal. A funnel may be mounted above the opening to guide a sampling device or gauge stick through the opening. A typical gauge-hatch/sample port is shown in Figure 10.

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[27] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

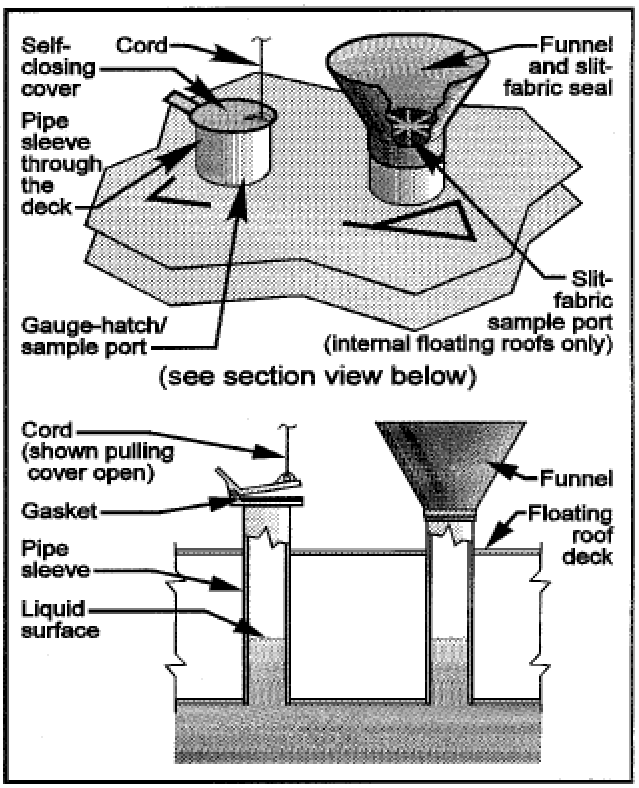

Figure 10: Gauge-hatch / Sample Port[28]

Rim vents

Rim vents are used on tanks equipped with a seal design that creates a vapor pocket in the seal and rim area, such as a mechanical shoe seal. A typical rim vent is shown in Figure 11. The vent is used to release any excess pressure that is present in the vapor space bounded by the primary-seal shoe and the floating roof rim and the primary seal fabric and the liquid level. Rim vents usually consist of weighted pallets that rest over the vent opening.

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[28] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

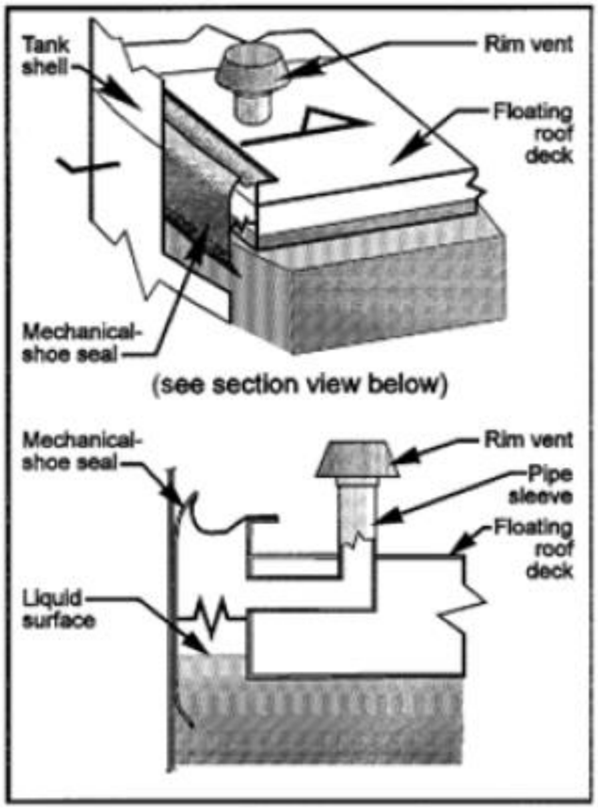

Figure 11: Rim Vent[29]

Deck drains

Currently two types of deck drains (closed and open deck drains) are in use to remove rainwater from a floating deck. Open deck drains can be either flush or overflow drains. Both types of open deck drains consist of a pipe that extends below the deck to allow the rainwater to drain into the stored liquid. Only open deck drains are subject to evaporative loss. Flush drains are flush with the deck surface. Overflow drains are elevated above the deck surface. Typical overflow and flush deck drains are shown in Figure 12. Overflow drains are used to limit the maximum amount of rainwater that can accumulate on the floating deck, providing emergency drainage of rainwater if necessary. Closed deck drains carry rainwater from the surface of the deck though a flexible hose or some other type of piping system that runs through the stored liquid prior to exiting the tank. The rainwater does not come in contact with the liquid, so no evaporative losses result. Overflow drains are usually used in conjunction with a closed drain system to carry rainwater outside the tank.

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[29] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

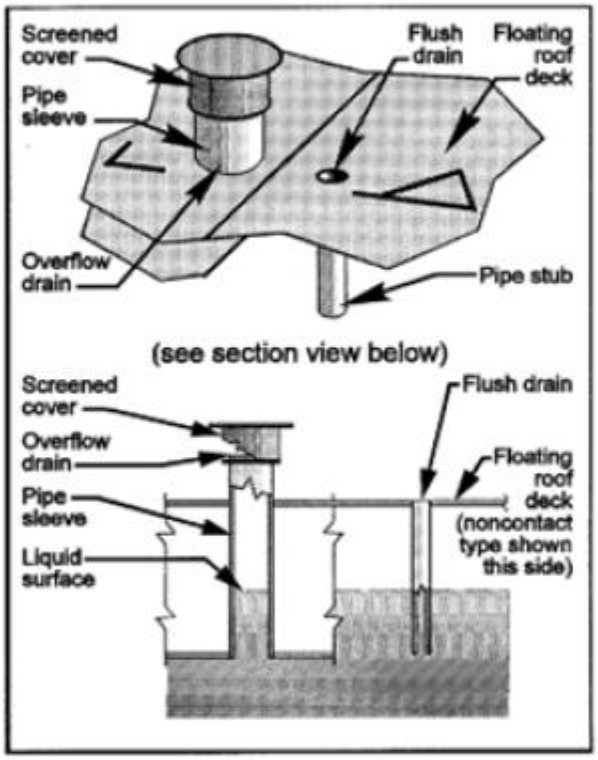

Figure 12: Deck Drains[30]

Deck legs

Deck legs are used to prevent damage to fittings underneath the deck and to allow for tank cleaning or repair, by holding the deck at a predetermined distance off the tank bottom. These supports consist of adjustable or fixed legs attached to the floating deck or hangers suspended from the fixed roof. For adjustable legs or hangers, the load-carrying element may pass through a well or sleeve into the deck. With noncontact decks, the well should extend into the liquid. Evaporative losses may occur in the annulus between the deck leg and its sleeve. A typical deck leg is shown in Figure 13.

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[30] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

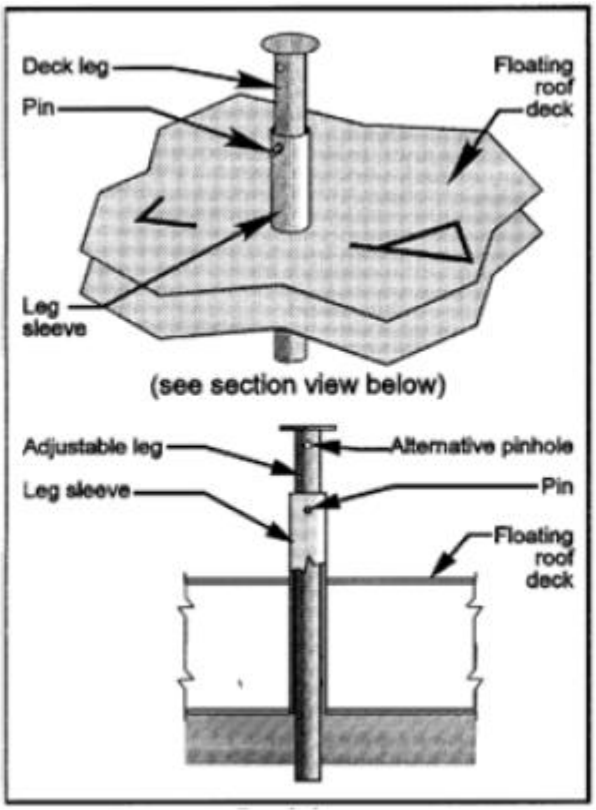

Figure 13: Deck Leg[31]

Unslotted guidepoles and wells

A guidepole is an anti-rotational device that is fixed to the top and bottom of the tank, passing through a well in the floating roof. The guidepole is used to prevent adverse movement of the roof (e.g., spinning) and thus damage to deck fittings and the rim seal system. In some cases, an unslotted guidepole is used for gauging purposes, but there is a potential for differences in the pressure, level, and composition of the liquid inside and outside of the guidepole. A typical unslotted guidepole and well are shown in Figure 14.

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[31] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

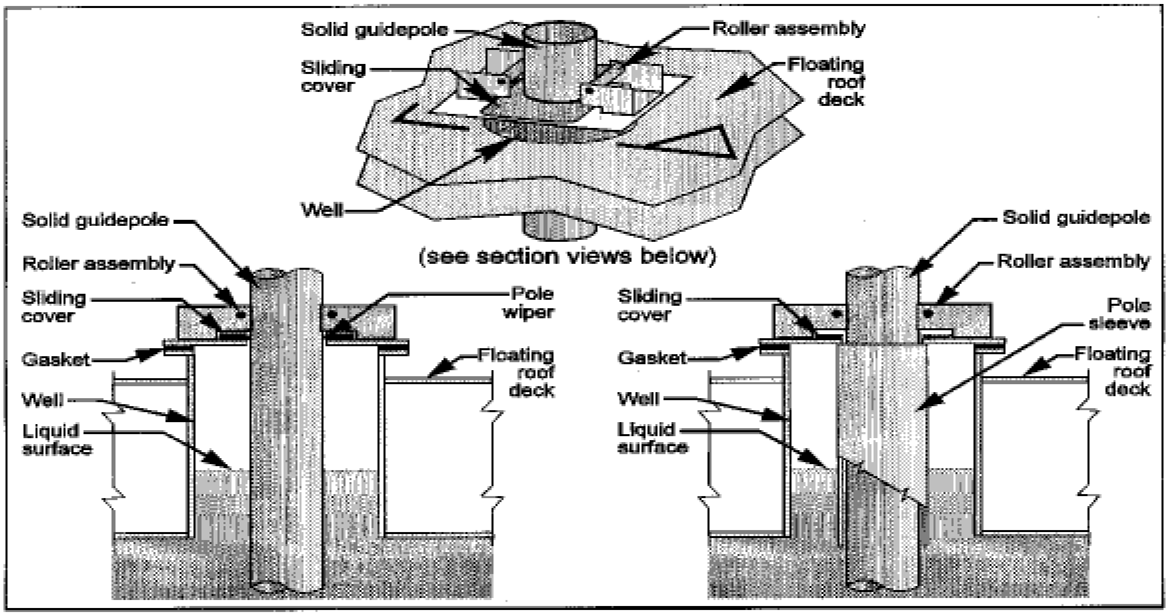

Figure 14: Unslotted (solid) Guidepole[32]

Slotted (perforated) guidepoles and wells

The function of the slotted guidepole is similar to the unslotted guidepole but with additional features. Perforated guidepoles can be either slotted or drilled hole guidepoles. A typical slotted guidepole and well are shown in Figure 15. As shown in this figure, the guide pole is slotted to allow stored liquid to enter. The same can be accomplished with drilled holes. The liquid entering the guidepole has the same composition as the remainder of the stored liquid and is at the same liquid level as the liquid in the tank. Representative samples can therefore be collected from the slotted or drilled hole guidepole. Evaporative loss from the guidepole can be reduced by a combination of modifying the guidepole or well with the addition of gaskets, sleeves, or enclosures or placing a float inside the guidepole, as shown in Figure 15 and Figure 16. Guidepoles are also referred to as gauge poles, gauge pipes, or stilling wells.

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[32] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

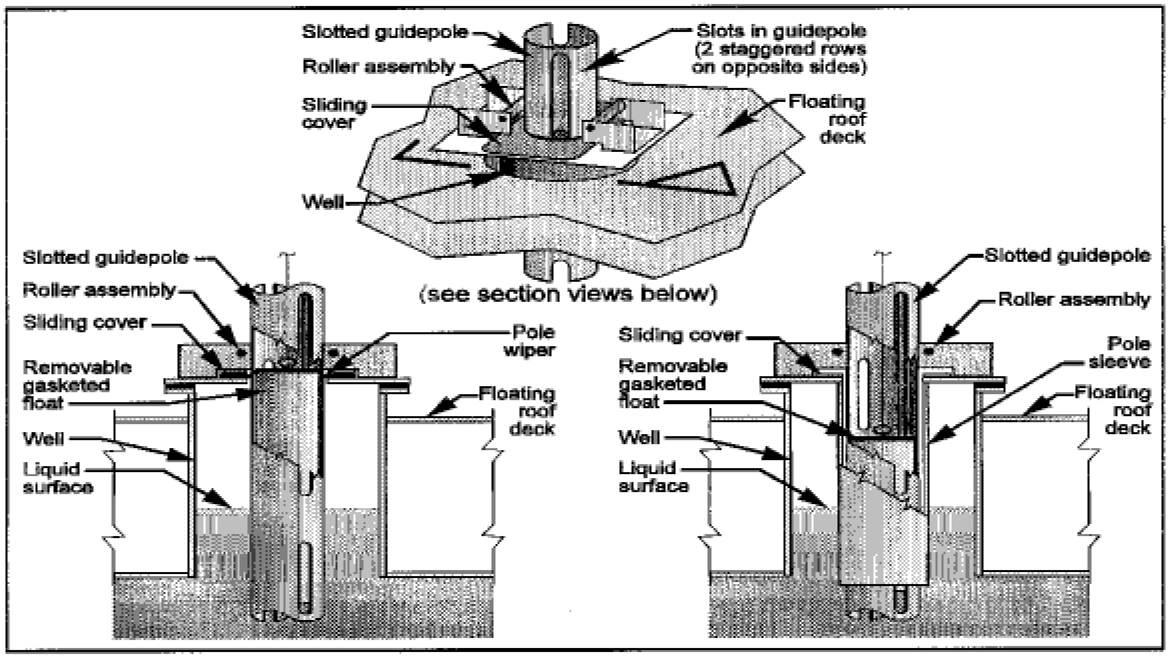

Figure 15: Slotted (perforated) Guidepole[33]

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[33] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

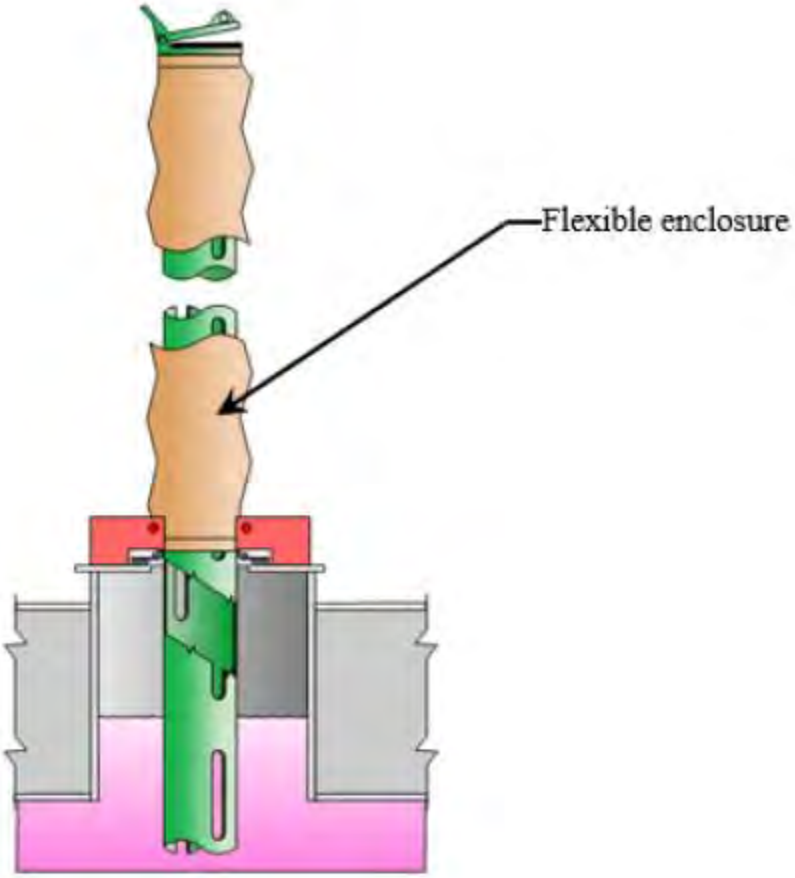

Figure 16: Slotted-guidepole with flexible enclosure[34]

Vacuum breakers

A vacuum breaker equalizes the pressure of the vapor space across the deck as the deck is either being landed on or floated off its legs. A typical vacuum breaker is shown in Figure 17. As depicted in this figure, the vacuum breaker consists of a well with a cover. Attached to the underside of the cover is a guided leg long enough to contact the tank bottom as the floating deck approaches. When in contact with the tank bottom, the guided leg mechanically opens the breaker by lifting the cover off the well; otherwise, the cover closes the well. The closure may be gasketed or ungasketed. Because the purpose of the vacuum breaker is to allow the free exchange of air and/or vapor, the well does not extend appreciably below the deck. While vacuum breakers have historically tended to be of the leg-actuated design described above, they may also be vacuum actuated similar to the pressure/vacuum vent on a fixed roof tank such that they do not begin to open until the floating roof has actually landed. In some cases, this is achieved by replacing the rim vent described above with a pressure/vacuum vent.

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[34] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

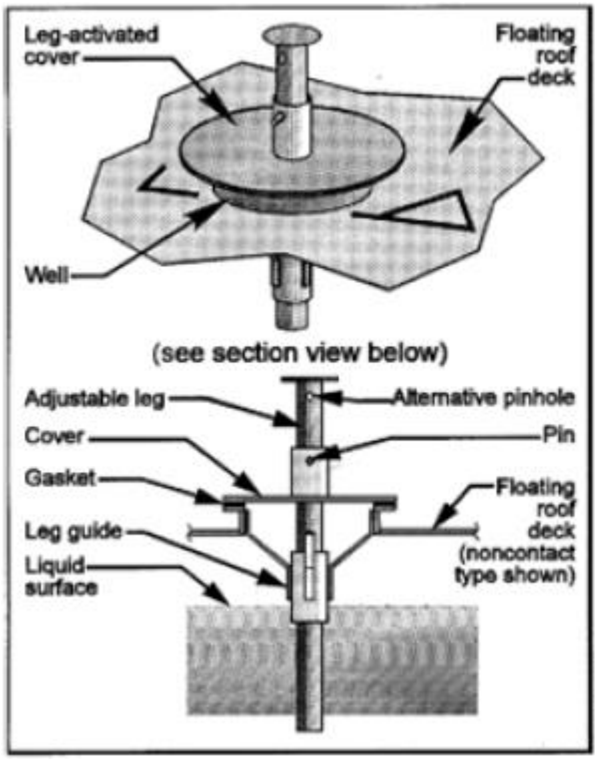

Figure 17: Vacuum Breaker[35]

The following are fittings typically used only on internal floating roof tanks:

<u>Columns and wells</u>

Some fixed-roof designs are normally supported from inside the tank by means of vertical columns, which necessarily penetrate an internal floating deck. (Some fixed roofs are entirely self-supporting from the perimeter of the roof, and therefore have no interior support columns.) Column wells resemble unslotted guide pole wells on external floating roofs. Columns are made of pipe with circular cross sections or of structural shapes with irregular cross sections (built-up). The number of columns varies with tank diameter, from a minimum of 1 to over 50 for very large diameter tanks. A typical fixed roof support column and well are shown in Figure 18.

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[35] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

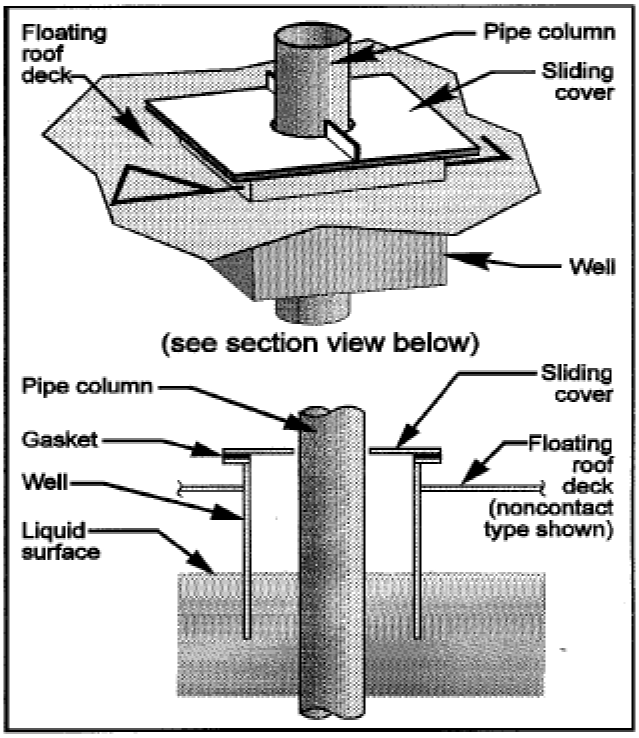

Figure 18: Fixed-Roof Support Column[36]

The columns pass through deck openings via peripheral vertical wells. With noncontact decks, the well should extend down into the liquid. Generally, a closure device exists between the top of the well and the column. Several proprietary designs exist for this closure, including sliding covers and fabric sleeves, which must accommodate the movements of the deck relative to the column as the liquid level changes. A sliding cover rests on the upper rim of the column well (which is normally fixed to the deck) and bridges the gap or space between the column well and the column. The cover, which has a cutout, or opening, around the column slides vertically relative to the column as the deck raises and lowers. At the same time, the cover may slide horizontally relative to the rim of the well to accommodate a column that is out of plumb. A gasket around the rim of the well reduces emissions from this fitting. A flexible fabric sleeve seal between the rim of the well and the column (with a cutout or opening to allow vertical motion of the seal relative to the columns) similarly accommodates any limited horizontal motion of the deck relative to the column.

Ladders and wells

Some tanks are equipped with internal ladders that extend from a manhole in the fixed roof to the tank bottom. The deck opening through which the ladder passes is constructed with design details and considerations similar to those

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[36] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

for deck openings for column wells, as previously discussed. A typical ladder well is shown in Figure 19.

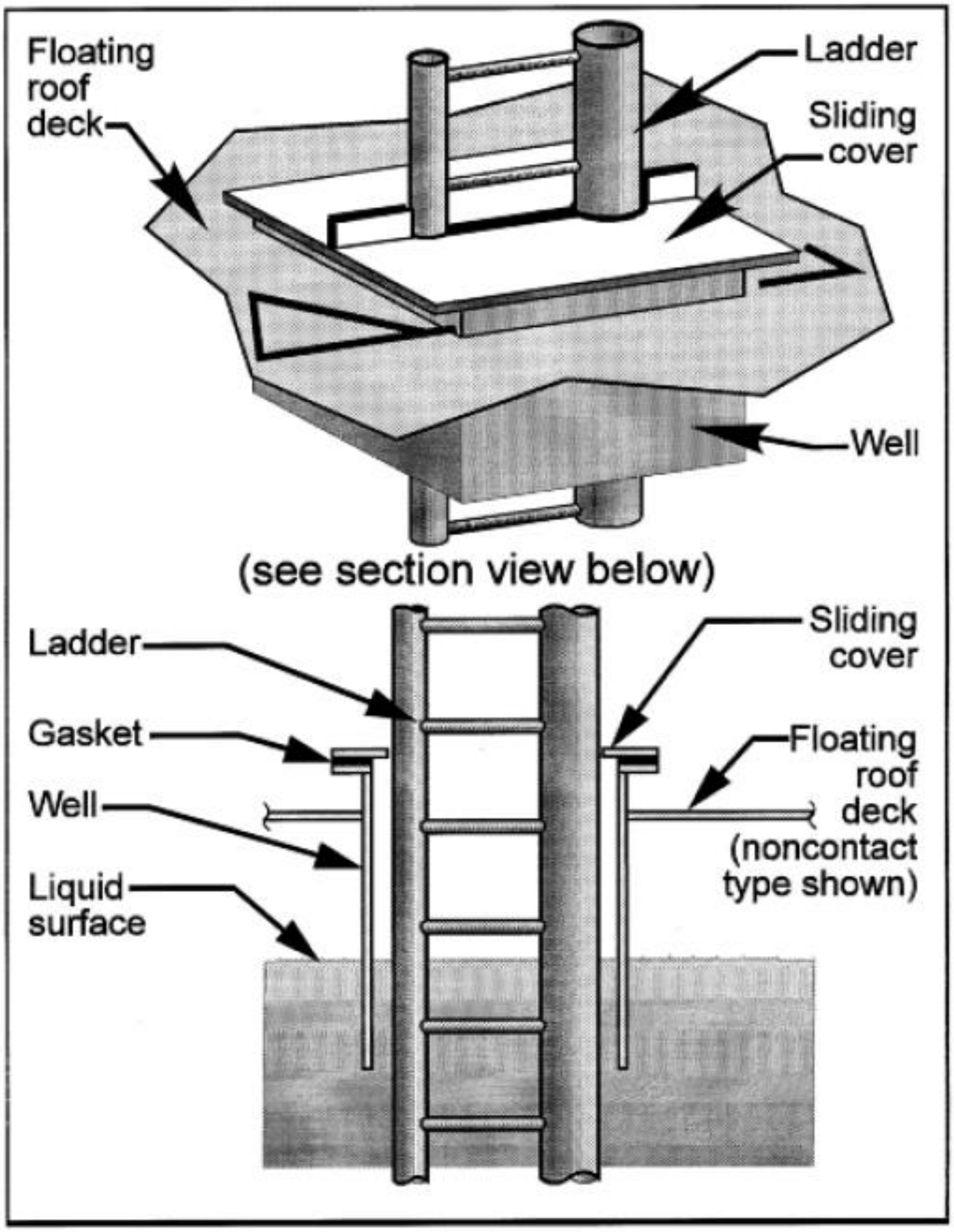

Figure 19: Ladder Well[37]

Tanks are sometimes equipped with a ladder-slotted guidepole combination, in which one or both legs of the ladder is a slotted pipe that serves as a guidepole for purposes such as level gauging and sampling. A ladder-slotted guidepole combination is shown in Figure 20 with a ladder sleeve to reduce emissions.

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[37] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

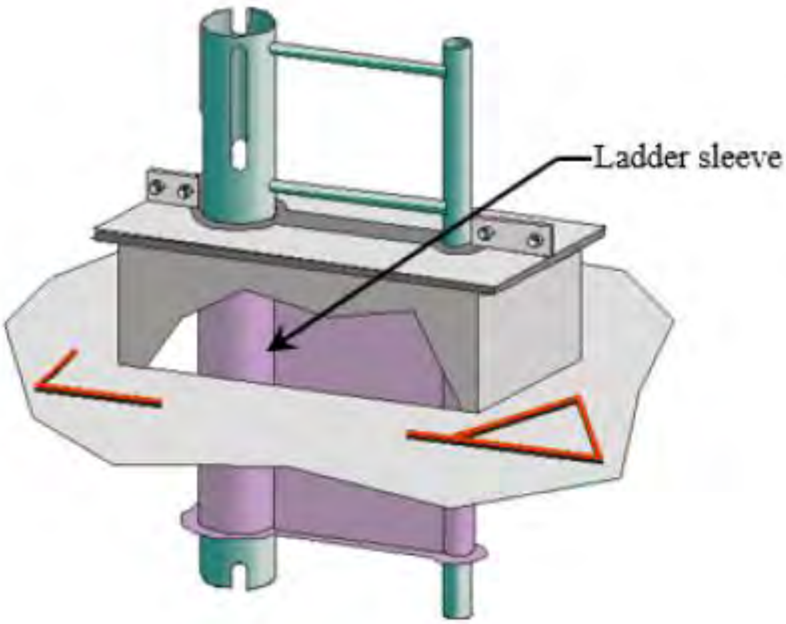

Figure 20: Ladder-slotted guidepole combination with ladder sleeve[38]

Stub drains

Bolted internal floating roof decks are typically equipped with stub drains to allow any product that may be on the deck surface to drain back to the underside of the deck. The drains are attached so that they are flush with the upper deck. Stub drains are approximately 1 inch in diameter and extend down into the product on noncontact decks. A typical flush stub drain is shown in Figure 12. Stub drains may be equipped with floating balls to reduce emissions. The floating ball acts as a check valve, in that it remains covering the stub drain unless liquid is present to lift it.

Deck seams

Deck seams in IFRTs are a source of emissions to the extent that these seams may not be completely vapor tight if they are not welded. A weld sealing a deck seam does not have to be structural (i.e., may be a seal weld) to constitute a welded deck seam for purposes of estimating emissions, but a deck seam that is bolted or otherwise mechanically fastened and sealed with elastomeric materials or chemical adhesives is not a welded seam. Generally, the same loss mechanisms for deck fittings apply to deck seams.

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[38] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

(3) Potential Control Strategies

The use of a floating roof is itself a strategy to control emissions of VOC from petroleum storage tanks. The floating roof design is such that routine evaporative losses from the stored liquid are limited to the standing and working losses described above. Since the vapor space between the product surface and the tank roof is minimized, there are no breathing losses as would occur in a fixed roof tank. Although there are working losses, they are substantially different from the working losses of a fixed roof tank. Again, there is no vapor space to purge when the tank is filled. Instead, working losses occur when the tank is emptied based on the amount of product that clings to the walls as the roof descends.

Following are additional potential control considerations for floating roof petroleum storage tanks:

(i) Secondary Rim Seals

Secondary seals provide additional control of VOC losses through evaporation over that achieved by the primary seal.

(ii) Gasketed Sliding Covers

The use of gaskets or sleeves minimizes VOC losses through evaporation.

(iii) Welded Deck Seams

Welded deck seams are more vapor-tight than bolted seams.

(iv) Fixed Roofs

Both IFRTs and domed EFRTs have a permanent fixed roof with a floating roof inside. The fixed roof does not act as a vapor barrier but does work to block the wind. Emissions from rim seals and deck fittings are partly dependent on wind speed. When a tank is equipped with a fixed roof over the floating roof, the wind-dependent component is reduced to zero leaving only wind-independent losses.

(4) Summary of Control Strategies in Use

As explained above, the use of a floating roof is itself a strategy to control emissions of VOC from a petroleum storage tank.

Maine DEP's regulation *Petroleum Liquid Storage Vapor Control*, 06-096 C.M.R. ch. 111, applies to fixed roof petroleum storage tanks larger than 39,000 gallons. Such a tank storing a petroleum product with a vapor pressure greater than 1.52 psia is required to be equipped with an internal floating roof or an equally effective alternative control approved by the DEP Commissioner and the US EPA.

The following federal regulations address emissions from petroleum storage tanks.

(i) *Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After June 11, 1973, and Prior to May 19, 1978*, 40 C.F.R. Part 60, Subpart K, applies to petroleum storage tanks with a capacity between 40,000 and 65,000 gallons that were constructed, reconstructed, or modified between March 8, 1974, and May 9, 1978 as well as to petroleum storage tanks greater than 65,000 gallons constructed, reconstructed, or modified between June 11, 1973, and May 19, 1978. Subpart K requires a tank storing a product with a vapor pressure greater than 1.5 psia (e.g., gasoline) to be equipped with a floating roof or vapor recovery system. This regulation contains no requirements for products with vapor pressures less than 1.5 psia.

(ii) *Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After May 18, 1978, and Prior to July 23, 1984*, 40 C.F.R. Part 60, Subpart Ka, applies to petroleum storage tanks constructed, reconstructed or modified in the time period listed that have a capacity greater than 40,000 gallons. Subpart Ka requires a tank which stores a product with a vapor pressure between than 1.5 and 11.1 psia (e.g., gasoline) to be equipped with one of the following: an external floating roof with both primary and secondary seals, an internal floating roof, or a vapor collection/reduction system designed to achieve 95% reduction of emissions. If the external floating roof option is chosen, the primary seal must be a mechanical shoe seal, a liquid-mounted seal, or a vapor-mounted seal. If either floating roof option is chosen, openings in the roof must be equipped with covers, lids, or seals. This regulation contains no requirements for products with vapor pressures less than 1.5 psia.

(iii) *Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984*, 40 C.F.R. Part 60, Subpart Kb applies to storage vessels (including petroleum storage tanks) constructed, reconstructed, or modified after July 23, 1984, which have a capacity between 20,000 and 40,000 gallons and store products with a vapor pressure greater than 0.5 psia or which have a capacity greater than 40,000 gallons and store products with a vapor pressure greater than 2.2 psia.

Subpart Kb requires storage tanks between 20,000 and 40,000 gallons which store products with vapor pressures between 3.9 and 1.1 psia and storage tanks greater than 40,000 gallons which store products with vapor pressures between 0.75 and 11.1 psia to use one of the following control strategies:

1. Use of a fixed roof with an internal floating roof. The internal floating roof must use either a mechanical shoe seal, a liquid-mounted seal, or two seals (i.e., primary and secondary seals) mounted one above the other. Openings in the roof must be equipped with covers, lids, sleeves, gaskets, or similar seals.
2. Use of an external floating roof with both primary and secondary seals. The primary seal must be a mechanical shoe seal or liquid-mounted seal. Openings in the roof must be equipped with covers, lids, or seals.
3. Use of a closed vent system and control device designed to achieve 95% reduction of emissions.

(iv) *National Emission Standards for Hazardous Air Pollutants for Source Category: Gasoline Distribution Bulk Terminals, Bulk Plants, and Pipeline Facilities*, 40 C.F.R. Part 63, Subpart BBBBBB contains requirements for petroleum storage tanks at bulk gasoline plants and bulk gasoline terminals.

Bulk gasoline plants are facilities with a maximum gasoline throughput of less than 20,000 gallons per day. (Maine has no facilities in this category.) Gasoline storage tanks at bulk gasoline plants must use submerged fill, and the facility must perform a monthly leak inspection of all equipment in gasoline service.

Bulk gasoline terminals have a maximum gasoline throughput of 20,000 gallons per day or more. (Maine has eight licensed bulk gasoline terminals.) Subpart BBBBBB requires gasoline storage tanks at bulk gasoline terminals that have a capacity of less than 20,000 gallons or a capacity of less than 40,000 gallons and a throughput of less than

480 gallons per day to be equipped with fixed roofs provided all openings are in the closed position at all times when not in use. Subpart BBBBBB does not require floating roofs for these tanks.

Subpart BBBBBB requires gasoline storage tanks at bulk terminals not meeting the exemption above to use one of the following control strategies:

1. Use of a fixed roof with an internal floating roof. The internal floating roof must use either a mechanical shoe seal, a liquid-mounted seal, or two seals (i.e., primary and secondary seals) mounted one above the other. Openings in the roof must be equipped with covers, lids, sleeves, gaskets, or similar seals.
2. Use of an external floating roof with both primary and secondary seals. The primary seal must be a mechanical shoe seal or liquid-mounted seal. Openings in the roof must be equipped with covers, lids, or seals.
3. Use of a closed vent system and control device designed to achieve 95% reduction of emissions.

(v) *National Emission Standards for Gasoline Distribution Facilities (Bulk Gasoline Terminals and Pipeline Breakout Stations)*, 40 C.F.R. Part 63, Subpart R contains requirements for petroleum storage tanks at bulk gasoline terminals which are major sources of HAP. (Note, no applicable facility exists in Maine.) Subpart R refers back to 40 C.F.R. Part 60, Subpart Kb (discussed earlier in this section) for requirements for petroleum storage tanks.

The Texas CEQ’s Tier I BACT requires both IFRT and EFRT to have all uninsulated exterior surfaces exposed to the sun be aluminum in color or painted white. IFRTs must have a mechanical or liquid mounted primary seal or have a vapor mounted primary seal with a rim mounted secondary seal. EFRTs must have a mechanical or liquid mounted primary seal and a rim mounted secondary seal.

The South Coast AQMD BACT database has one entry for floating roof tanks. This determination applies to products similar to crude oil and other mixed petroleum products. The facility was required to utilize external floating roofs with geodesic dome covers. The tanks have metallic shoe primary seals, rim mounted secondary seals, and guide pole gasketed sliding covers with wipers.

The RBLC contains numerous entries for floating roof tanks (both internal and external) for products with vapor pressures above 0.5 psia. Floating roofs, both internal and external, are a common and expected tank design for storage of these products. There are a few instances where floating roofs appear to be indicated for tanks storing distillate fuel, but these are usually dual-purpose tanks, meaning they can store either distillate fuel or gasoline.

Almost all states that responded to our survey have some requirement to control emissions from tanks with capacities greater than 40,000 gallons that store products with a vapor pressure greater than 1.5 psia. Most states give facilities the option of utilizing a floating roof or installing a vapor capture and control system. None of the states surveyed have regulations requiring floating roofs for tanks which store products with vapor pressures below 0.5 psia.

Summary

Floating roofs, both internal and external, are a common and expected design for tanks that store gasoline and crude oil. Floating roofs are also sometimes required for tanks storing distillate fuel.

The use of floating roofs for tanks storing residual oil or asphalt was not addressed in any of the resources consulted. It is very likely that the viscous nature of these products and the need to keep the tanks heated and fully insulated result in technical problems in designing and operating floating roofs for these products.

In the references consulted, preference was given to floating roofs with a rim seal system with both primary and secondary seals, the use of gasketed sliding covers for all deck fittings, and welded deck seams.

It was unclear if any of the resources required a fixed roof in addition to a floating roof as IFRTs and EFRTs were equally represented. In most cases it appeared that the petroleum storage facility owner/operator was given the option of using either type of tank.

c. Variable Vapor Space Tanks

(1) Description

Variable vapor space tanks are equipped with expandable vapor reservoirs to accommodate vapor volume fluctuations attributable to changes in temperature and barometric pressure. Although variable vapor space tanks are sometimes used independently, they are normally connected to the vapor spaces of one or more fixed roof tanks. The two most common types of variable vapor space tanks are lifter roof tanks and flexible diaphragm tanks.

Lifter roof tanks have a telescoping roof that fits loosely around the outside of the main tank wall. The space between the roof and the wall is closed by either a wet seal, which is a trough filled with liquid, or a dry seal, which uses a flexible coated fabric.

Flexible diaphragm tanks use flexible membranes to provide expandable volume. They may be either separate gasholder units or integral units mounted atop fixed roof tanks.

(2) Emissions

Variable vapor space filling losses result when vapor is displaced by liquid during filling operations. Since the variable vapor space tank has an expandable vapor storage capacity, this loss is not as large as the filling loss associated with fixed roof tanks but is more than that associated with a floating roof tank. Loss of vapor occurs when the tank's vapor storage capacity is exceeded.

Variable vapor space tanks that rely on either a flexible diaphragm or a flexible coated fabric seal will have additional losses to the extent that vapors leak through or past the membrane used for the diaphragm or seal. The leakage rate through the membrane is a function of the permeability of the fabric material from which the membrane is manufactured, and a leakage rate past the membrane is a function of the leak tightness of the seam or seams where the membrane is attached to the tank wall. These leakage rates depend upon the type of fabric used for the membrane and the manner in which the membrane is attached to the tank wall.

(3) Potential Control Strategies

The use of a variable vapor space roof is itself a strategy for control of VOC emissions from the storage tank. The roof design is such that routine evaporative losses from the stored liquid are limited to the losses described above. No additional control strategies for this type of tank were found in the resources consulted for this report.

(4) Summary of Control Strategies in Use

As explained above, the use of variable vapor space roof is itself a strategy to control emissions of VOC from a petroleum storage tank.

The use of variable vapor space tanks is not common. They are for use with higher vapor pressure products but are less effective at controlling emissions than floating roof tanks. Therefore, new tank installations tend to require floating roofs over variable vapor space tanks. None of the resources consulted for this report contained information on variable vapor space tanks.

3. Product Distribution

a. Description

The transportation and marketing of petroleum products involves many distinct operations, each of which represents a potential source of VOC emissions. Petroleum storage facilities in Maine distribute their products to market primarily by loading them into tank trucks. However, products may also be distributed by loading railcars and ships and through pipelines. For simplicity, railcars, tank trucks, and marine vessels will be referred to collectively as cargo tanks.

Cargo tanks are loaded with product at the petroleum storage facility at a loading rack. At the loading rack, pipes are connected to or lowered into the cargo tank and used to fill the cargo tank with product.

b. Emissions

Loading losses are the primary source of VOC emissions from operations at cargo tank loading racks.

Loading losses occur as VOC in "empty" cargo tanks are displaced to the atmosphere by the liquid being loaded into the tanks. These VOC are a composite of (1) vapors formed in the empty cargo tank by evaporation of left-over product from previous loads, (2) vapors transferred to the cargo tank in vapor balance systems as product is being unloaded (e.g., gas station vapor balance systems), and (3) vapors generated in the cargo tank as the new product is being loaded.

The recent loading history of the cargo tank is an important factor in loading losses. The air inside the empty cargo tank is expelled when the tank is loaded. Cargo tanks are sometimes designated to transport only one product, known as “dedicated service.” However, cargo tanks may also be “switch-loaded” such that a less volatile liquid may be loaded and expel vapors remaining from a previous load of volatile product. If the cargo tank’s last load was a product with low volatility (e.g., distillate fuel), the VOC contained in the empty cargo tank’s vapor space will be significantly less than if the cargo tank’s last load was a product with high volatility (e.g., gasoline). Therefore, an understanding of the most recent previous load carried by the cargo tank is often as important as the product being loaded.

The quantity of evaporative losses from loading operations is, therefore, a function of the following parameters:

- Physical and chemical characteristics of the previous cargo;
- Method of unloading the previous cargo;

- Method of loading the new cargo; and
- Physical and chemical characteristics of the new cargo.

c. Potential Control Strategies

Following are control strategies for distribution of product at petroleum storage facilities:

(1) Submerged Fill

The principal methods used to load product into cargo tanks are splash loading and submerged fill.

In splash loading, the fill pipe dispensing the petroleum product is lowered only part way into the cargo tank. Significant turbulence and vapor/liquid contact occur during the splash loading operation, resulting in high levels of vapor generation and loss. If the turbulence is great enough, liquid droplets can be entrained in the vented vapors.

In submerged filling, the fill pipe opening is below the liquid surface level for most, if not all, of the time the cargo tank is being loaded. This is accomplished either by the submerged fill pipe method, where the fill pipe extends almost to the bottom of the cargo tank, or the bottom loading method, where a permanent fill pipe is attached to the cargo tank bottom. With submerged fill, liquid turbulence is significantly reduced, resulting in much lower vapor generation than splash loading.

(2) Vapor Balance

At gasoline stations, a delivery truck retrieves the vapors displaced in the underground storage tank when the truck is emptied. A similar operation can sometimes be performed at petroleum storage facilities. Vapors can be returned to the storage tank when the vapors inside the cargo tank are displaced during the filling operation.

Vapor balance alone has limitations. If the petroleum storage tank dispensing the product has a floating roof, there is no vapor space in the tank for the cargo tank vapors to be returned to. Returning vapors to a fixed roof tank may cause turbulence, which would increase emissions from the tank’s vents. Therefore, vapor balance systems used at petroleum storage facility loading racks typically do not return the vapor to a storage tank, but instead deliver it to a control device such as those described below.

Residual fuel and asphalt are transported at high temperatures (150 - 300 °F). To ensure that the product stays hot during transport, special double-walled trailers or railcars are used. Due to the design of the cargo tanks, these products are "top-loaded." Top-loading involves lowering a fill pipe through a hatch in the roof of the cargo tank. These cargo tanks are not equipped to accommodate vapor balancing equipment.

(3) Vapor Recovery Units

Vapor recovery units (VRUs) route VOC-laden vapors to a device which separates the VOC from the exhaust stream. Depending on the design, the VRU may either trap/bind the VOC to a solid to be disposed of or recover the VOC back as a liquid that can be either disposed of or piped back to the petroleum storage tank. VRUs can be designed to achieve control efficiencies for VOC greater than 98%. VRUs recover the product in the displaced vapors by the use of adsorption or condensation.

(i) Carbon Adsorption

Carbon adsorption is the process of passing the VOC-laden air stream through a bed of adsorbent material, typically activated carbon, although other media may be suitable for certain applications. Hydrocarbons attach to the surfaces of the activated carbon particles.

Carbon adsorbers can be either regenerative or non-regenerative. With non-regenerative carbon adsorption, the adsorbent eventually becomes saturated and loses its effectiveness. The adsorbent needs to be periodically replaced and the spent material disposed of. Due to the cost to replace the spent media and the creation of an additional waste stream, non-regenerative carbon adsorption is not often utilized for high volume, high concentration streams, such as the vapor balance gas stream from gasoline loading.

With regenerative carbon adsorption, hydrocarbons are desorbed and collected, typically by drawing a vacuum on the sorbent bed or by using heated air, steam, or nitrogen. The recovered hydrocarbons can be returned to the petroleum storage tank. A drawback of this control approach is that the adsorbent typically binds strongly to heavy hydrocarbons and is less effective at capturing lighter organics such as propane. Therefore, it may be difficult to desorb some materials which can foul the adsorbent over time. Additionally, lighter materials are even more likely to pass through without being adequately collected if heavy hydrocarbons have already bound to the adsorbent. Therefore, regenerative carbon adsorption is typically used for VRUs associated with the loading of gasoline or distillate fuel and not with heavier hydrocarbon products such as crude oil, residual fuels, and asphalt.

(ii) Condensers

VOC can be removed from an air stream by condensing the product to a liquid. Condensation occurs when an exhaust stream that is saturated with product vapors undergoes a phase change from gas to liquid. The phase change can be achieved in two ways. The system pressure can be increased at a given temperature (i.e., compression), or the temperature may be lowered at a constant pressure (i.e., refrigeration).

For a more volatile product (i.e., a product with a low boiling point and high vapor pressure), larger amounts can remain in the vapor phase at a given temperature. To induce condensation, the exhaust stream must be cooled, compressed, or both. In general, it is more energy-intensive to operate a condenser to control a more volatile product (e.g., gasoline) than a less volatile product (e.g., distillate fuels). However, the less volatile products also often contain heavy, sticky compounds that can stick to the inside of a condenser, reducing its efficiency and effectiveness over time.

(4) Vapor Combustion Units

A vapor combustion unit (VCU) raises the temperature of the exhaust stream to oxidize (burn) the VOC components. VCUs can be designed to achieve control efficiencies for VOC greater than 98%. Types of VCUs include open flares, enclosed thermal oxidizers, and regenerative thermal oxidizers.

(i) Flares

Flaring is a type of thermal oxidizer that directs the VOC-laden exhaust stream through a vertical pipe to a burner assembly located well above ground level. VOC are burned in the open air using a specially designed burner tip, auxiliary fuel, and steam or air to promote mixing. Completeness of combustion in a flare is governed by flame temperature, residence time in the combustion zone, turbulent mixing of the components to complete the oxidation reaction, and available oxygen for free radical formation. Combustion is complete if all VOC are converted to carbon dioxide and water. Incomplete combustion results in some of the VOC being unaltered or converted to other organic compounds such as aldehydes or acids.

The flaring process can produce some undesirable byproducts including noise, smoke, heat radiation, light, sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO), and an additional source of ignition where not desired (i.e., fire hazard).

A major drawback to using an open flare for control of emissions from loading racks is the inability to conduct performance testing. Emissions from most loading racks, especially gasoline loading, are subject to state and federal regulations which establish emission standards, such as a limit on the amount of VOC that can be emitted per liter of product loaded. Due to its open nature, it is impossible to measure actual emissions of VOC after the control device, i.e., after the flame. Therefore, facilities which utilize a VCU for control of VOC emissions from loading racks typically use an enclosed thermal oxidizer instead of an open flare.

(ii) Enclosed Thermal Oxidizers

Enclosed thermal oxidizers (enclosed TOs), also known as ground flares, have burner heads which are inside an insulated shell. This equipment is located at ground level. The shell reduces noise, light, and heat radiation, and provides wind protection.

Enclosed TOs have a defined exhaust point which can be tested for control efficiency and compliance with emission limit regulations.

Enclosed TOs are most often used with exhaust streams with high concentrations of VOC, such as emissions from loading of gasoline. They are less cost-effective when used to control exhaust streams with lower concentrations of VOC. A recent analysis performed for a Maine facility indicated the cost of using a thermal oxidizing system for control of distillate vapors was approximately $600,000 per ton of pollutant controlled.

(iii) Regenerative Thermal Oxidizers

Regenerative thermal oxidizers (RTOs) preheat the inlet emission stream with heat recovered from the exhaust gases generated by their operation. The inlet gas stream is passed through preheated ceramic media and an auxiliary gas burner is used to reach temperatures between 1,450 ºF and 1,600 ºF at a specific residence time. The combusted gas exhaust then passes through a cooled ceramic bed where heat is extracted.

RTOs can very efficiently meet high destruction efficiencies of exhaust streams with a continuous, consistent VOC loading. However, short-term batch process, such as emissions from loading racks, are not well suited for control by an RTO. The intermittent nature of the emissions in the exhaust stream means there could be significant periods of time between high VOC loads, allowing the ceramic media to cool and fail to effectively or efficiently pre-heat the incoming gases. This would result in less efficient operation and the use of more auxiliary fuel.

d. Summary of Control Strategies in Use

(1) Gasoline Loading

Bulk gasoline plants and terminals are subject to state and federal regulations which set emission standards for gasoline loading racks at petroleum storage facilities.

Per *National Emission Standards for Hazardous Air Pollutants for Source Category: Gasoline Distribution Bulk Terminals, Bulk Plants, and Pipeline Facilities*, 40 C.F.R. Part 63, Subpart BBBBBB, bulk gasoline terminals with a gasoline throughput of 250,000 gallons per day or greater are subject to an emission standard for VOC of 80 milligrams per liter (mg/l) of product loaded. Although several facilities in Maine are subject to this standard, all of them are also subject to more stringent standards described below.

Facilities which are categorized as a major source of HAP are subject to an emission standard for VOC of 10 mg/l of product loaded per 40 C.F.R. Part 63, Subpart R. There are no facilities in Maine subject to this standard.

Pursuant to Maine state regulation 06-096 C.M.R. ch. 112, bulk gasoline terminals are subject to an emission standard for VOC of 35 mg/l of product loaded. Bulk gasoline terminals which are categorized as a major source of HAP are subject to an emission standard for VOC of 10 mg/l of product loaded.

Although no petroleum storage facility in Maine is considered a major source of HAP, roughly two thirds of Maine’s licensed facilities which distribute gasoline are subject to the 10 mg/l standard via restrictions incorporated through Best Practical Treatment (BPT) in their air emission license. This includes all three facilities in Maine which are licensed as major sources of VOC.

None of these standards can be met without employing emissions controls at the loading rack. Therefore, all bulk gasoline terminals in Maine operate either a VRU or VCU for control of VOC emissions from the loading of gasoline into cargo tanks.

Texas CEQ's Tier I BACT requires emissions from truck loading of products with vapor pressures greater than 0.5 psia (e.g., gasoline) to be routed to a VOC control device which meets a collection efficiency of 98.7%.

The South Coast AQMD BACT database has one entry for truck loading. This determination applies to products with a vapor pressure greater than 0.10 psia at 70° F (e.g., gasoline). The facility was required to install a thermal oxidizer (VCU) with an assumed overall control efficiency of 95%.

The RBLC contains numerous entries for truck/railcar loading of gasoline or other similar petroleum products which require submerged fill and routing of collected vapors to a VRU or VCU.

All states surveyed require some type of control for the loading of gasoline. Maine's level of control for gasoline loading is equivalent to, or more stringent than, the level of control required in other states surveyed.

(2) Distillate Loading

There are no state or federal regulations which address the control of emissions from loading distillate fuel into trucks or railcars.

Cargo tanks that carry gasoline may also be used to carry distillate fuel, a procedure known as "switch-loading." Since switch-loading can cause a cargo tank being filled with distillate fuel to have emissions similar to gasoline loading, the Department requires licensed petroleum storage facilities to either prohibit switch-loading (i.e., only load dedicated service trucks) or to capture the displaced vapors and route them to a control device (VRU or VCU). These requirements are incorporated into a facility's license under the authority of BPT. However, no such requirement exists for smaller petroleum storage facilities that fall below the Department's licensing thresholds.

The Texas CEQ Tier I BACT for the loading of trucks or railcars with products whose vapor pressure is less than 0.5 psia requires submerged fill or bottom loading of the cargo tank.

The RBLC contains three entries[39] that include emissions from the loading of distillate fuel. The emission limits associated with these entries are equivalent to those for submerged filling without any additional control device. These limits also assume or require the trucks be "dedicated service," i.e., that they carry only distillate fuel and not any other petroleum products.

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[39] RBLC IDs IN-0231, IN-243, and IN-0244

The RBLC contains one entry[40] for 15 loading racks, both truck and railcar, for distillate fuels which required the collection of the displaced gases and routing them to a thermal oxidizer.

There are several RBLC entries that reference distillate fuel products in conjunction with gasoline loading. In those cases, it was impossible to determine whether the controls listed would have been required for distillate fuels alone.

Many states (including Arkansas, Delaware, Illinois, Indiana, Iowa, Louisiana, Maryland, Minnesota, Texas, Washington, and Wisconsin) do not require emissions from the loading of distillate fuel to be controlled unless the truck's most recent previous load was gasoline (i.e., switch loading). However, facilities may often elect to control these emissions as a way to reduce facility emissions below certain permitting thresholds. Some states (including Georgia, Hawaii, and New York) require emissions from all distillate loading to be controlled, typically by a VCU or VRU.

(3) Residual/Asphalt Loading

There are no state or federal regulations which address the control of emissions from loading residual fuel or asphalt into trucks or railcars.

The Texas CEQ Tier I BACT for the loading of trucks or railcars with products with a vapor pressure less than 0.5 psia requires submerged fill or bottom loading of the cargo tank. Note: This is from a Texas CEQ guidance document and not a state regulation.

The RBLC contained only one entry[41] that addressed loading rack emissions for residual fuel. A petroleum storage facility in Chelsea, Massachusetts installed a VCU to control emissions from this process. This control was added at the request of the petroleum storage facility to ensure the facility would continue to be considered a minor source. The system is assumed to have a capture efficiency of 90% and a destruction efficiency of 99% for a combined total control efficiency of 89%.

There were no RBLC entries that addressed product loading of asphalt.

In their response to our survey, the State of Michigan indicated that emissions from the loading of asphalt are sometimes controlled, primarily to reduce odors. The State of North Carolina also indicated that controls on asphalt loading racks are sometimes installed for odor control purposes. No other

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[40] RBLC ID AZ-0046

[41] RBLC ID MA-0040

states reported requiring or considering controls on the loading of residual or asphalt products.

(4) Crude Oil Loading

None of the petroleum storage facilities in Maine load crude oil into cargo vessels. The one facility that stores crude oil offloads from marine barges and transfers the product out of the facility via pipeline. Therefore, cargo loading for crude oil was not investigated as part of this study.

(5) Marine Vessel Loading

There are no state or federal regulations which address the control of emissions from loading marine vessels for products with vapor pressures less than 1.5 psia (e.g., distillate fuels, residual fuels, asphalt).

National Emission Standards for Marine Tank Vessel Loading Operations, 40 C.F.R. Part 63, Subpart Y, applies to marine loading of products with vapor pressures greater than 1.5 psia (e.g., gasoline). Below is a summary of Subpart Y requirements.

(i) Area (minor) Sources of HAP Constructed Prior to 1999

Subpart Y requires use of submerged fill.

Maine has one facility which is licensed for marine vessel loading in this category. In addition to submerged fill, the facility is required to capture vapors from the loading of gasoline and route them to a VCU for destruction.

(ii) Area (minor) Sources of HAP Constructed After 1999 and All Major Sources of HAP

Facilities in this category must load only vapor-tight marine vessels. Vapors from marine loading must be collected and controlled (e.g., through use of a VCU or VRU) by 97% for existing major sources and 98% for area sources or new major sources. Maine has no marine loading facilities in this category.

Texas CEQ’s Tier I BACT requires emissions from marine vessel loading of products with vapor pressures greater than 0.5 psia (e.g., gasoline) to be routed to a VOC control device. There are no requirements listed for marine vessel loading of products with vapor pressures less than 0.5 psia.

The South Coast AQMD BACT database does not contain any entries for marine loading.

There are several RBLC entries that reference marine vessel loading. These entries typically require collection of the displaced vapors and control through use of a VCU or VRU. However, the product being loaded is often not specified, and when it is, is typically gasoline or crude oil, both products with a vapor pressure greater than 1.5 psia. Many entries reference compliance with 40 C.F.R. Part 63, Subpart Y and the requirements listed above.

The State of New York requires facilities which transfer less than 15,000 gallons per day through marine vessel loading to use a vapor balance system. Facilities which transfer more than 15,000 gallons per day through marine loading are required to utilize emission controls with at least a 90% reduction efficiency.

4. Miscellaneous Emissions

Following are additional sources of VOC emissions from petroleum storage facilities not addressed elsewhere:

a. Facility Piping

Operation of a petroleum storage facility equipment will result in some amount of unavoidable fugitive VOC emissions from facility piping, valves, pumps, and other components. Best practices for minimizing these emissions include regular inspections of all facility piping components to check for leaks and/or required maintenance.

b. Roof Landings and Tank Cleanings

(1) Description of Emissions

Floating roof tanks need to be periodically emptied to perform maintenance and required inspections of the tank interior.

When using floating roof tanks, the roof floats on the surface of the liquid inside the tank and reduces evaporative losses during routine operations. However, when the tank is emptied to the point that the roof lands on deck legs or hangers, the roof is no longer floating, and the tank behaves like a fixed roof tank.

After the floating roof is landed, as the liquid level in the tank continues to drop, a vacuum is created which could cause the floating roof to collapse. To equalize the pressure and prevent damage, a breather vent (vacuum breaker) is activated, allowing a vapor space to form between the floating roof and the liquid. The breather vent may remain open until the roof is again floated, so whenever the roof is landed, vapor can be lost through this vent as well as through other deck fittings and past the rim seal. Even in the case of a self-closing breather vent, the vapor space beneath the floating roof is vented via the other deck fittings and the rim seal, which is effectively rendered vapor mounted once the liquid level drops below the bottom of the rim seal. These losses are called "standing idle losses."

The three different mechanisms that contribute to standing idle losses are (1) breathing losses from vapor space; (2) wind losses; and (3) clingage losses. The specific loss mechanism is dependent on the type of floating roof tank and the bottom condition.

For IFRTs or domed EFRTs with liquid remaining in the bottom (liquid heel), the breathing losses originate from a discernible level of liquid that remains in the tank. This is typically the case for IFRTs or domed EFRTs with nominally flat bottoms (including those built with a slight cone), due to the flatness of the tank bottom and the position of the withdrawal line. If the remaining liquid covers the entire bottom of the tank, it is known as a full liquid heel. The liquid evaporates into the vapor space beneath the landed floating roof and daily changes in ambient temperature cause this vapor space to breathe in a manner similar to that seen in a fixed roof tank. A partial liquid heel may be left in tanks with sloped bottoms if the withdrawal of liquid ceases while some free-standing liquid remains in a sump or elsewhere in the bottom of the tank.

For EFRTs, which are not fully shielded from the surrounding atmosphere, wind action across the landed floating roof can create a pressure differential that may cause vapors to flow from beneath the landed floating roof. The higher the wind speeds, the more vapor that can be expelled. These are known as wind losses.

For tanks with a cone-down or shovel bottom, the floor of the tank is sloped to allow for more thorough emptying of the tank contents. Therefore, the amount of liquid remaining may differ significantly from tanks with flat bottoms; see Figure 21.

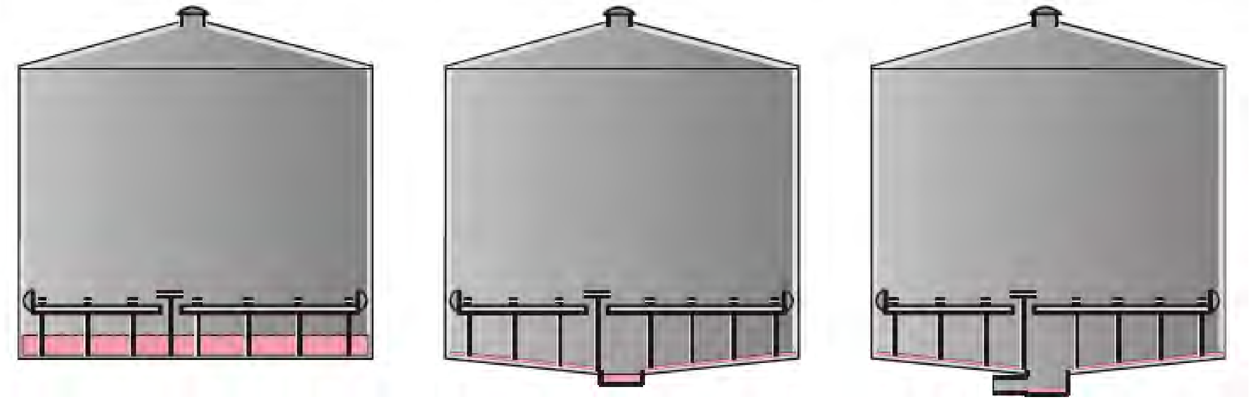

Figure 21:Bottom conditions for landing loss.[42]

Full Liquid Heel	Partial Liquid Heel	Drain-Dry
Standing liquid across the entire bottom	Standing liquid only in or near a sump; clingage elsewhere	No standing liquid, only liquid is clingage

When the emptying operation drains the tank bottom but leaves a heel of liquid in or near the sump, the tank is considered to have a partial liquid heel. A drain-dry condition is attained only when all of the standing liquid has been removed, including from the bottom of the sump. However, due to sludge buildup, irregularity of the tank bottom and roughness of the inside of the tank, a small layer of liquid can remain clinging to the sloped bottom of a drain-dry tank. This layer of liquid will create vapor that can result in clingage losses.

After the tank has been emptied, before inspection or maintenance can be performed, the interior tank vapor space must be purged (also known as cleaning or degassing) to create a safe working environment. The vapor space is purged via forced ventilation using fans or blowers either at the top of the tank or at a shell manhole, cleanout fitting, or other shell fitting. The first exchange of air (i.e., the first volume of air equivalent to the interior tank volume) will have the highest level of VOC. Subsequent air exchanges will have lower concentrations of VOC, but emissions will continue to occur until tank cleaning is complete.

If the tank is subsequently refilled after the inspection or maintenance is complete, there will be vapors generated by the incoming product which would then be expelled from the tank by the rising liquid level. For a fixed

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[42] Courtesy of R. Ferry, TGB Partnership, Hillsborough Hurdle Mills, NC.

roof tank, these refilling emissions are the same as routine working (filling) losses. For a floating roof tank, these emissions are similar to those of a fixed roof tank until the product reaches the level where it makes contact with the roof and the roof is floated off its legs or hangers, at which point they will return to normal levels of operational losses for a floating roof tank.

(2) Potential Control Strategies

(i) Drain-Dry Design

When a drain-dry tank has been emptied, the only stock liquid available inside the tank is a thin layer that clings to the wetted surface of the tank interior. The slope prevents a significant amount of stock liquid from remaining in the tank so that evaporation is much lower than from tanks with liquid heels. Due to the limited amount of liquid clinging to the interior of the tank there would be no liquid remaining to replenish vapors once the clingage layer has evaporated.

(ii) Vapor Control

Emissions from tank cleaning or purging can be routed to either a temporary or permanently installed control device such as a VCU or VRU. The forced ventilation causes a flow through the tank which can be captured and directed to a control device such as a flare.

(3) Summary of Control Strategies in Use

Maine DEP regulation *Petroleum Liquid Storage Vapor Control*, 06-096 C.M.R. ch. 111, requires floating roof tanks to undergo a complete inspection at least once every ten years. This inspection requires the tank to be emptied and degassed. However, facilities are prohibited from emptying and degassing a tank for the purposes of a complete inspection between June 1 and August 31 of each year to limit VOC emissions during the height of the ozone season.

Both *Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After May 18, 1978, and Prior to July 23, 1984*, 40 C.F.R. Part 60, Subpart Ka, and *Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984*, 40 C.F.R.

Part 60, Subpart Kb, require the roofs of applicable tanks to be floated on the surface of the liquid at all times except when the tank is to be fully emptied.

Texas CEQ’s Tier I BACT addresses emissions from the draining and cleaning of fixed and floating roof tanks in a similar manner. If there is any standing liquid within the tank, and the vessel is opened to the atmosphere or ventilated, the vapor stream must be controlled until there is no standing liquid or the VOC vapor pressure is less than 0.02 psia. New floating roof tanks must be designed to drain dry. Degassing (purging) of floating roof tanks must commence within 24 hours of landing. However, bulk gasoline terminals are allowed two uncontrolled landings per tank per year to accommodate any required switching of the type of gasoline stored (i.e., switching between summer and winter gas).

The South Coast AQMD BACT database has one entry for control of emissions from tank degassing. This determination applies to a degassing of tanks containing non-chlorinated petroleum hydrocarbon vapors. The control utilized is a thermal oxidizer capable of 99.9% destruction efficiency.

The RBLC contains numerous entries where tanks are required to capture emissions from tank degassing and route them to a control device, typically a VCU or VRU. These requirements appear to be intended mostly for tanks storing products with a vapor pressure greater than 0.5 psia. The control devices typically achieve greater than 99% control. Degassing is required to commence within 24 hours of the roof being landed on its legs or hangers (to minimize the amount of time the tank behaves as a fixed roof tank) and controls are required to be operated during the purging operation until the VOC concentration in the exhaust stream falls below 5,000 – 10,000 parts per million (ppm) depending on the specific determination. New tanks in the RBLC are often required to be built with a drain-dry design.

c. Heating Equipment

VOC emissions from the petroleum storage facility’s heating equipment are due to any incomplete combustion of the fuel burned for heating. Such emissions are typically very low and managed by efficient operation, which is ensured by performing regular tune-ups of the heating equipment.

d. Control Equipment

Equipment to control VOC emissions may itself be a source of VOC or other pollutants.

VCUs destroy VOC emissions by burning them, releasing emissions of other pollutants which are products of combustion such as particulate matter, sulfur dioxide, nitrogen oxides, and carbon monoxide. Additionally, a VCU must always maintain a pilot flame. If the concentration of the VOC in the exhaust stream is extremely low, additional assist fuel may need to be burned to maintain the pilot light.

VRUs typically adsorb VOC onto another medium such as carbon. If the carbon is not regenerated, it becomes a solid waste that must be disposed of, potentially off-gassing the VOC in another location. If the VRU is a regenerative unit which uses heat to desorb and regenerate the media, a fuel is usually burned to create that heat, which again emits products of combustion.

IV. Methods for Controlling Odors from Petroleum Storage Facilities

A. Background and Evaluation of Odor Regulations in the U.S.

Petroleum products are often associated with distinctive smells or odors. Besides their visual presence, petroleum storage tanks most often garner attention because of associated odors or, as one European study states, "discomfort … due to olfactory annoyance."[43] Odor is not regulated by the U.S. EPA. Some state and local jurisdictions do regulate nuisance odor, including some regulating odors from specific source categories. For example, the Department's *Solid Waste Management Rule for Processing Facilities*, 06-096 C.M.R. ch. 409, includes a standard to assess a nuisance odor from facilities that process wastewater treatment sludge and septage using a modified n-butanol 5-point odor intensity referencing scale.

As part of this project, the Department surveyed each state and, where appropriate, sub-state jurisdictions (for example, California has numerous air quality control districts within the state). The Department received 35 responses to the survey, 32 of which provided answers to questions regarding the regulation of odor. Of the respondents, 10 indicated they had no odor regulations in place. A review of the odor regulations from the 22 respondents with odor regulations in place showed that most considered odor to be a "nuisance" consideration and the requirements were mostly subjective.

Examples of requirements from some of these regulations include the following:

- Prohibiting "unreasonable interference with the comfortable enjoyment of life and property" (MI);
- Defining air pollution as one or more contaminants that "…unreasonably interfere with the enjoyment of life or property." (IL);
- Prohibiting "…the emission of any substance or combination of substances which creates or contributes to an odor beyond the property boundary of the premises that constitutes a nuisance." (CT);
- Prohibiting the cause or allowance of "the emission of an odorous air contaminant such as to cause a condition of air pollution," with possible methods of compliance including scentometer tests, air quality monitoring, and affidavits from citizens and investigators. (DE); and

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[43] Invernizzi M., Ilare J., Capelli L., Sironi S., 2018, Proposal of a method for evaluating odour emissions from refinery storage tanks, Chemical Engineering Transactions, 68, 49-54 DOI: 10.3303/CET1868009

- Requiring no detectable odors when odorous air is diluted with seven or more volumes of odor-free air for residential areas, no detectable odors when odorous air is diluted with 16 or more volumes of odor-free air for other land use areas. (CO).

These regulations are seemingly subjective and therefore difficult to enforce, because what is considered "unreasonable," a "nuisance," "interference," "enjoyment," or "odor-free" will vary from person to person.

More specific and yet still subjective examples of odor regulation come from North Carolina and North Dakota:

- "Objectionable odor" means any odor present in the ambient air that by itself, or in combination with other odors, is or may be harmful or injurious to human health or welfare or may unreasonably interfere with the comfortable use and enjoyment of life or property. Odors are harmful or injurious to human health if they tend to lessen human food and water intake, interfere with sleep, upset appetite, produce irritation of the upper respiratory tract, or cause symptoms of nausea, or if their chemical or physical nature is, or may be, detrimental or dangerous to human health. (NC)
- An odor will be considered objectionable when a department certified inspector or at least 30% of a randomly selected group of persons, or an odor panel (five individuals certified in odor detection) exposed to the odor would deem that odor objectionable if the odor were present in their place of residence. (ND)
- An "odor concentration unit" is defined as a volume of odor-free air mixed with an equal volume of odorous air such that the combination would be at the threshold level of the olfactory senses. The intensity of an odor is determined by the ratio of the volume of odor-free air that must be mixed with a standard volume of odorous air so that a department-certified inspector or at least fifty percent of an odor panel can still detect the odor in the diluted mixture. (ND)

Rhode Island's odor regulation prohibits emissions into the atmosphere of air contaminants which create an objectionable odor beyond the entity's property line. It further specifies that a staff member of the Department shall determine by personal observation if an odor is objectionable, taking into account its nature, concentration, location, duration, and source. Pursuant to this regulation, odor controls consisting of a mist eliminator and carbon absorber were required to be added to the heated tanks at a petroleum storage facility in Providence, RI.

B. VOC vs. Odor

VOC are emitted as gases from certain solids or liquids. Title I of the CAA defines VOC as compounds containing carbon which participate in atmospheric photochemical reactions, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate. An alternate definition provided by the EPA regards VOC as all organic compounds having a vapor pressure exceeding 0.1 mm Hg at standard conditions (20 °C and 760 mm Hg). VOC include a variety of chemical compounds, some of which may have short- and long-term adverse health effects. VOC concentration can be measured, usually in ppm, using standardized test methods and procedures such as EPA Method 25A[44].

Odor can be defined as the sensation created by stimulating the olfactory organs[45] found in the nasal cavity. Odor perception has four major dimensions: threshold, intensity, character, and hedonic tone.

- **Odor threshold** is the lowest concentration of a substance that can be detected by human olfaction. Threshold values are unique for each potentially odorous compound, and they are not fixed physical constants but can vary from one individual to the next.
- **Odor intensity** is the perceived strength of the odor sensation and increases as a function of concentration.
- **Odor character** is what the substance smells like. ASTM publication (ASTM data series DS 61, 1985) provides character profiles for 180 chemicals using a 146-descriptor scale, such descriptors including “fishy,” “nutty,” “creosote,” “turpentine,” “rancid,” “sewer,” ‘ammonia,” and “bananas.” Since odor character can change with intensity, the odor characterization may differ from source to source or from person to person, depending on their individual sensitivity to a given odor.
- **Hedonic tone** is a category of judgment of the relative pleasantness or unpleasantness of an odor. Perception of hedonic tone is influenced by subjective experience, frequency of occurrence, odor character and intensity, and duration. Perceptions vary widely from person to person and are strongly influenced by external factors such as emotions, previous experiences, etc.[46]

Common odor problems are often caused by mixtures of highly volatile compounds with very low threshold detection limits in low concentrations in ambient air. Odors can also be caused by sulfur-containing compounds such as hydrogen sulfide (H_2S). These sulfur-containing compounds also have very low threshold detection limits but are not VOC. VOC and odor are often linked, because many VOC are odorous. However, not all VOC emit odors, and not all odors are caused by VOC.

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[44] See 40 C.F.R. Part 60, Appendix A, Method 25A, *Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer*.

[45] Medical Definition of *olfactory organ*: an organ of chemical sense that receives stimuli interpreted as odors from volatile and soluble substances in low dilution, that lies in the walls of the upper part of the nasal cavity. “Olfactory organ.” *Merriam-Webster.com Medical Dictionary*, Merriam-Webster, https://www.merriam-webster.com/medical/olfactory%20organ. Accessed 4 Nov. 2020.

[46] Murnane, S. S., Lehocky, A. H., Owens, P. D. (2013). Odor Thresholds for Chemicals with Established Occupational Health Standards (2nd Edition). *American Industrial Hygiene Association (AIHA)*. Retrieved from https://app.knovel.com/web/toc.v/cid:kpOTCEOHS 7/viewerType:toc/

Many manufacturing sectors produce gases that contain odorous compounds, including synthetic flavoring manufacturing, paints and coatings manufacturing, paper mills, pharmaceutical industries, and refineries. Odorous components of natural origin are mainly released by industries such as slaughterhouses, breweries, bio-industries, textile industries, coffee roasting plants, yeast and alcohol factories, sewage treatment plants, and solid waste composting facilities.[47]

Perception of a mixture of odorous compounds may be different than perception of individual compounds. Odorous compounds have the potential to interact in an additive fashion, as counteractants (one cancelling out the perception of another), as maskants (one masking the detection of another), or two or more compounds together synergistically amplifying overall perception.

Measurement of odorous compounds is a technological challenge which has not been fully resolved. Olfactometers are instruments that still include human subjectivity to detect and measure ambient odors. To use an olfactometer, an operator controls the sample delivery while the test subject inhales through a sniffing port to detect the presence of odor. Most olfactometers are used in a laboratory setting, but a portable unit, The Nasal Ranger® (St. Croix Sensory, St. Elmo, MN), is available for field use.[48] These devices are not common and still include subjective evaluation by a test subject.

In Europe, there is a standardized method to assess the odor concentration of a gas mixture, EN 13725:2003, using dynamic olfactometry. This method of analysis uses a dilution instrument (olfactometer) to present a specific odor to a panel of trained personnel. The measurement is based on the sensation perceived by the panel and is expressed in units of odor per cubic meter of neutral air (ou_E/m^3). This number is then used with the gas emission flow rate to define the odor emission rate (OER), expressed in ou_E/s. First, though, the maximum potential odor emission rate must be established for each petroleum storage tank. The variability of tank composition, emission periods, corresponding flow rates, and individuals' odor perceptions are all very practical constraints to the use of this method.

Some chemical compounds that contribute to odors associated with petroleum products include butenes, octane, p-tert-butyl toluene, heptanes, hexane, hexene, naphthalene, nonane, and methylcyclohexane.[49] While some of these odorous chemical compounds are pollutants regulated by EPA and the State of Maine, many either have no associated health-based, Maine Ambient Air Guideline (AAG)[50] value or have odors that can be

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[47] Revah S., Morgan-Sagastume J.M. (2005) Methods of Odor and VOC Control. In: Shareefdeen Z., Singh A. (eds) Biotechnology for Odor and Air Pollution Control. Springer, Berlin, Heidelberg. https://doi.org/10.1007/3-540-27007-8_3

[48] Murnane, S. S., et al.

[49] Murnane, S. S., et al.

[50] The Maine Center for Disease Control & Prevention (ME-CDC) develops Ambient Air Guidelines (AAGs) to assist risk managers and the public in making decisions regarding the potential human health hazards associated with chemicals in air. AAGs are not promulgated by rule-making and therefore are not issued as legally enforceable ambient air "standards." Rather, AAGs represent the most recent recommendations for chemical concentrations in

detected at levels significantly lower than their associated AAG. In addition, some of these odorous compounds are not hazardous air pollutants regulated by either the EPA or the State of Maine.

C. Potential Controls

Potential controls for mitigation of odorous compounds from petroleum storage tanks include demisters, carbon beds, biofiltration, thermal oxidizers, and odor masking materials. Several of these control technologies have been discussed previously in this report where VOC controls are addressed. The same possibilities and constraints apply to the use of these technologies for odor control. Biofiltration and odor absorption materials will be discussed in this section.

There is currently no technology routinely applied to mitigate odors from heated petroleum storage tanks storing #6 fuel oil and asphalt. Although there are some specific locations using add-on controls such as demisters and carbon beds, the effectiveness of such controls is not well documented, in part because these technologies are not widespread in the industry and thus have not been thoroughly evaluated for measurable effectiveness. In addition, difficulties in the full and accurate characterization of odorous compounds and quantification of their emission rates provide challenges to the design of effective odor controls.

Additional hinderances to the development of standard odor control technologies for petroleum storage tanks have been identified by researchers who have found no direct correlation between a mixture's chemical composition and its effective olfactory properties (Rice and Koziel, 2015)[51]. This phenomenon is explained by the existence of chemical and physical interactions between various compounds present in odorous mixtures, such that actual olfactory effects may be greater or lesser than the sum of the contributions of the individual substances (Zhao et al., 2014)[52]. Based on the odor contributions of certain compounds, the results of one study revealed that propanol, toluene, and hydrogen sulfide were the dominating odor-causing emissions of industrial facilities included in the study (landfill, WWTP, rendering plant, and ambient air in a town with large petroleum and petrochemical industries).[53]

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ambient air, below which there is minimal risk of a deleterious health effect resulting from long-term inhalation exposure.

[51] Rice, S., Koziel, J.A., 2015. The relationship between chemical concentration and odor activity value explains the inconsistency in making a comprehensive surrogate scent training tool representative of illicit drugs. Forensic Sci. Int. 257, 257–270.

[52] Zhao, P., Liu, J.M., Tang, S.C., 2014. The Interaction of Mixing Odorants with Similar Chemical Properties: A Case Study on Ketone Compounds, in: Advanced Materials Research. pp. 32–37.

[53] Dincer, F., Muezzinoglu, A. (2006). Chemical characterization of odors due to some industrial and urban facilities in Izmir, Turkey. *Atmospheric Environment, 40*(22), 4210-4219. doi:10.1016/j.atmosenv.2005.12.067

1. Biofiltration

   Biofiltration can effectively remove biodegradable odorous compounds from gas streams. In a biofilter, the exhaust gas stream is humidified, then passed through a distribution system beneath a bed of compost, bark mulch, or soil. The media in the bed contains an active population of bacteria and other microbes. As the air stream flows upward through the media, pollutants are adsorbed into the media and converted by microbial metabolism into carbon dioxide and water. In an ideal biofiltration scenario, this technology boasts low capital and operating costs, low energy requirements, and an absence of residual materials requiring further treatment or disposal. Biofiltration controls have been successfully applied to a range of industrial and public sector sources for the abatement of odors, with a purported elimination efficiency of more than 90%, according to manufacturers of biofiltration units.[54]

   Biofilters work best at steady state conditions and cannot tolerate extended periods of downtime. Petroleum storage tanks do not provide those conditions. Controlling tank working losses means large concentration swings, and tank loading does not occur as steady-state operation. Living organisms are crucial to the successful function of biofilters, and freezing temperatures would kill these organisms and, as such, the effectiveness of this control option. Biofilters also typically require a very large footprint which is not always available in retrofit scenarios.

   The successful engineering of a solution to any problem requires clear and accurate definition of the problem and of the desired outcome. Because petroleum products stored in heated tanks, namely #6 oil and asphalt, are each a mixture of several compounds with specific compositions varying from tank to tank and from delivery to delivery, the exact composition of odorous compounds emitted from these tanks will vary. This variation in the target compounds to be removed from tank exhaust gases increases the difficulty in designing the most effective control for each tank.

   To identify an appropriate control method for emissions of odorous compounds, it is crucial to consider the physical, thermodynamic, and reactive properties of the compounds and the controls. For example, results of a field study of the use of biofiltration to treat volatile hydrocarbons from petroleum suggest that the effectiveness varies greatly between compounds. Typically, more than 95% of aromatic compounds, such as benzene and reduced sulfur compounds, can be removed using residence times in the biofiltration unit of one minute or less, while removal of any more than 70% of light aliphatics would require a residence time of several minutes, which would thus require correspondingly larger biofilter volumes

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[54] Altaf H. Wani, Richard M.R. Branion & Anthony K. Lau (1997) Biofiltration: A promising and cost-effective control technology for Odors, VOCs and air toxics, Journal of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology, 32:7, 2027-2055, DOI: 10.1080/10934529709376664

with higher capital costs. This comparison shows that the composition of gases coming from a petroleum storage tank is critical in the selection and design of the most effective control option or combination of options for that tank. Additional considerations are the appropriate selection of filter material, the reliability of the moisture control system, and the level of fluctuation in concentrations of compounds to be removed from the gaseous exhaust.[55] The number and variation of components in the exhaust stream further complicate these considerations.

2. Odor Masking Materials

Some applications, such as landfills, use odor masking materials along the fence line. Such materials are available as liquid to spray or as granules to sprinkle on the ground around property perimeters or to put into socks and hang at intervals around the fence line for the wind to blow through. One such product, Ecosorb ® claims “a proprietary blend of oils including those from pine, aniseed, clove, lime and other sources” to “tackle the toughest smells…” and is billed as an “odor eliminator.” Outside of vendor advertising, research found no independent analysis of the effectiveness of such materials for controlling odors from petroleum storage tanks.

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[55] Leson, G. and Smith, B., 1997. Petroleum Environmental Research Forum Field Study On Biofilters For Control Of Volatile Hydrocarbons. [online] Journal of Environmental Engineering / Volume 123 Issue 6 - June 1997. Available at: <https://doi.org/10.1061/(ASCE)0733-9372(1997)123:6(556)> [Accessed 30 September 2020].

V. Methods of Determining Emissions

A. Background Information: Historical Emissions Estimation Methods

Emissions from air pollution sources, such as industrial boilers and processes, are typically calculated from the measured concentration of a given pollutant in the exhaust stream and the measured flow rate from the emissions source. Direct measurement of emissions from liquid storage tanks is difficult due to the generally low flow rates of the exhaust stream during normal tank operation. Therefore, emissions from liquid storage tanks are generally estimated through the use of equations developed using theoretical energy transfer models. These calculations, developed by the American Petroleum Institute, use information about the tank configuration, tank operation (e.g., throughput, heating, roof landings, cleanings, etc.), properties of the product(s) being stored, and local climate to estimate emissions. The methodology for performing these calculations has been published by EPA in AP-42, *Compilation of Air Pollutant Emissions Factors*, Chapter 7. EPA also published a software program called TANKS designed to assist in calculating emissions from storage tanks using the AP-42 methodology; however, the software contains known errors and is no longer receiving updates or support. Despite this, until recently, TANKS was still commonly used to calculate annual emissions from liquid storage tanks.

Emission sources at petroleum storage facilities other than liquid storage tanks include product distribution, heating equipment, and control equipment. Emissions from these sources are more suitable to direct measurement through testing or estimation by simple and well-established emission factors than storage tanks, and do not require the same use of complex calculations based on theoretical models.

B. Physical Testing vs. Calculating Emissions

Possible methods of determining emissions from petroleum storage facilities are as follows:

- Testing of the facility’s emissions units to develop site-specific emission rates (e.g., pounds of pollutant per hour);
- Calculating emissions using models or complex formulas which take into account the physical properties of the tanks and the products stored;
- The use of continuous emissions monitoring systems (CEMS); and
- The use of forward-looking infrared (FLIR) technology.

The advantages and disadvantages of each method are described below.

1. Physical Testing of Tank Emissions

Testing involves drawing a sample (grab or continuous) from an exhaust stream of an emissions unit or process and analyzing it to determine the concentration of the pollutant(s) of interest. Analysis methods vary, depending on the type of emissions unit and the pollutant(s) of interest. Testing also typically involves measuring the flow rate of the exhaust stream (e.g., flow in cubic feet per minute). Once both the concentration and flow rate are known, the pollutant emission rate (e.g., lb/hr) can be determined.

a. Available Test Methods and Their Limitations

EPA has promulgated test methods, called reference methods, which are used to quantify emissions and demonstrate compliance with both federal and state emission standards[56]. For a liquid storage tank, the typical procedure is to measure vapor pressure in the space inside the tank above the liquid surface. From that vapor pressure measurement and the known vapor pressure of the target pollutant, the concentration of the target pollutant can be calculated.

In any container with material in both liquid phase and gaseous phase, such as petroleum storage tanks, molecules at the gas-to-liquid interface (the liquid surface) will constantly be transitioning from liquid phase to gaseous phase and from gaseous to liquid. The vapor pressure of a substance is the pressure exerted by its particles in the gaseous phase in thermodynamic equilibrium with its liquid phase at a given temperature in a closed system. The equilibrium vapor pressure is an indication of a liquid's evaporation rate. The pressure exhibited by vapor present above a liquid surface is known as vapor pressure.[57]

Potential methods to measure actual emissions of VOC include EPA reference method (RM) 2, *Velocity – S-type Pitot*; RM 25A, *Gaseous Organic Concentration – Flame Ionization*; and RM 18, *Volatile Organic Compounds – Gas Chromatography*. RM 2 is used to measure flowrate. RM 25A is used to determine a generic (single value equivalent) VOC value in terms of propane, methane, or other compound, depending on how the instrumentation is calibrated. RM 18 is used to determine methane concentrations, to be subtracted in order to calculate the NMHC (non-methane hydrocarbons) emission rate.

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[56] See https://www.epa.gov/emc/emc-promulgated-test-methods for a full list of EPA's Air Emission Measurement Center's Promulgated Test Methods and links to each method.

[57] https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Concept_Development_Studies_in_Chemistry_(Hutchinson)/13%3A_Phase_Equilibrium_and_Intermolecular_Interactions#:~:text=The%20situation%20is%20%22equilibrium%22%20in%20that%20the%20observable,of%20the%20liquid%20and%20gas%20do%20not%20change.

Although these reference methods are available, obtaining accurate and reproducible test results from petroleum storage facilities is difficult. Some of the reasons are discussed below.

- Flow rates from normal tank operation (during periods when stored material is not being added or removed from the tank) are lower than the calibrated instrumentation can accurately detect and measure. Most emissions testing from stationary sources is conducted on a source with a continuous, measurable flow. Petroleum storage tanks do not have such flow characteristics. During filling, the tank will demonstrate a flow outward, and while filling trucks, some flow inward. Beyond that, flow can be influenced by wind, solar effects, and ambient temperatures; factors that are both variable and uncontrollable. These flow rates are low enough that they are typically not measurable by EPA Reference Method 2.
- Some of the heavier compounds found in residual oil and asphalt products are problematic in sampling, as they can 'coat' the interior surfaces of the sampling train and equipment, making it difficult to acquire a true value.
- Physical characteristics of asphalt and residual oil products are incompatible with vapor pressure testing methods. Specifically, there is no certified laboratory analysis method for determining vapor pressure from asphalt. Calculated and/or assumed vapor pressure numbers are often used due to the high level of difficulty in obtaining meaningful and repeatable vapor pressure test results using ASTM D2879, the ASTM[58] method listed for determining vapor pressure from #6 fuel oil.

  ASTM D2879 is a laboratory test method that requires the sample being tested be placed in glassware, mostly thin glass tubes with U-bends. At specific temperatures and pressures, the liquid levels inside the glass must be measured very precisely to determine the vapor pressure. An error in measurement can cause the resulting vapor pressure to be off by a significant amount, especially for materials with lower vapor pressures, such as #6 fuel oil and asphalt. The problem lies in taking this measurement. Both products (#6 fuel oil and asphalt) are thick, black, sticky substances. They do not flow easily through the glassware used in the test method, and reading the exact level is extremely problematic.

  In addition, due to the viscosity of #6 fuel oil and asphalt, air or water is often entrained within samples, and both can skew test results. Finally,

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[58] ASTM International, formerly known as American Society for Testing and Materials, is an international standards organization that develops and publishes technical standards for a wide range of materials, products, systems, and services.

ASTM D2879 is designed to determine the vapor pressure of pure substances. These products are complex mixtures of both light and heavy compounds.

A webinar prepared by the American Institute of Chemical Engineers (AIChE), *Evaluating Methods for Determining the Vapor Pressure of Heavy Refinery Liquids*, provides additional information on the difficulties associated with measuring #6 fuel oil and asphalt vapor pressures.[59]

b. EPA Testing Conducted at Two Maine Facilities

EPA required two petroleum storage facilities in Maine to conduct testing from heated petroleum storage tanks in 2012-2014. Results of initial testing showed no standing loss emissions because the flow rate was below the instrumentation detection level and therefore represented as “zero flow.” EPA required the facilities to build a temporary total enclosure (TTE) over the tank’s vents in order to collect any/all emissions and a fan to pull air past the tank vent at a set rate to create a steady, measurable flow rate that could be used with measured concentrations to determine mass emission rates of specific pollutants.

This approach differed from emissions testing conducted for the purposes of a compliance demonstration, which is conducted under conditions representative of a source’s normal operations, excluding a few specific scenarios. (There are some circumstances where non-representative operation is desirable, such as during trial burns, but those are the exception.)

When product is being added to storage tanks, there is an outflow of vapors from the headspace equal to the volume of the product added. This could potentially be measured using typical EPA reference methods without the use of a TTE, though the duration of such filling activities is limited. When product is not being added or removed, storage tanks are in a “resting” state and very little flow occurs.

During periods when no loading or unloading is occurring, tanks can “breathe.” As an uninsulated resting tank heats up during the day due to absorption of solar energy, the change in temperature can cause some of the stored product to volatilize into the headspace of the tank, creating a slight pressure differential between the tank and ambient air, and causing vapors to be released through the vent or vents on the tank in question. Then, as the sun sets and the previously absorbed heat energy is released, the vapors in the tank above the liquid level cool, causing ambient air to be drawn into the headspace of the tank and diluting the vapors. The cooler temperature can also cause some of the vapors to condense

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[59] The webinar is available at https://www.aiche.org/academy/webinars/evaluating-methods-determining-vapor-pressure-heavy-refinery-liquids.

back into liquid form and assimilate back into the main volume of stored product. If a tank has multiple vents, it is possible for ambient air to be drawn in at one vent while vapors are being exhausted at another vent. Throughout this process, the system is trying to reach and maintain a state of equilibrium between liquid and gaseous phases based on the properties of the product, the headspace volume, the surface area of the product exposed to the headspace, pressures, temperatures, solar incidence, etc. Wind movement across the vents can induce drafts, at times, though it would not be as continuous or consistent as artificial flow created by the TTE.

Conditions created by a TTE with a fan inducing a steady vacuum and draft on and across the vents prevents the equilibrium processes described above from happening normally. When evaporation of a liquid occurs in a closed space, molecules of the liquid enter the vapor phase from the liquid phase and vice versa, and a dynamic equilibrium is established between the two phases. At this equilibrium, the rate of evaporation is equal to the rate of condensation. If the liquid is in an open container, the molecules in the vapor phase spread, and some will exit from the container. The required TTE and fan used to pull a vacuum on the tanks during testing potentially pulled gases from the tank that would not have exited the tank without the artificially induced flow. By drawing gaseous components from the tank, the concentration of petroleum molecules in the gaseous phase was lowered, thereby inducing more molecules to move from the liquid surface into the gaseous phase until equilibrium between the two phases was reestablished.[60] By continuously drawing out vapors and preventing the system from reaching equilibrium, it is likely that more of the product became volatilized in the headspace. Continuous exhausting of vapors at the rates created by the fan on the TTE is not “representative” behavior for a petroleum storage tank.

The testing contractor in these specific tests noted that the TTE/fan combination could also have been drawing and exhausting mist/droplets that would otherwise not have exited the tank. During the first portion of sampling, the sample system on the asphalt tank did not include a coalescing filter to remove oil mist/droplets. When a filter was added, there was a noticeable drop in measured VOC concentrations. In the absence of sampling under ambient conditions (no TTE/fan collector), it is impossible to state with certainty that the mist and droplets were not produced by operation of the TTE and associated fan. The tester also noted

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[60] https://blog.siplo.lk/2020/05/19/liquid-gas-equilibrium/

that the emissions concentrations were affected by the fan speed: changing the flow rate in the TTE caused the concentrations being measured to also change[61].

c. Current Testing Requirements for Vessel Loading and Switch-Loading

Maine petroleum storage facilities are required to control emissions from vessel loading from non-heated tanks through the use of a vapor collection system to route vapors to a vapor combustion unit (VCU) or vapor recovery unit (VRU), as identified in individual air emission licenses. These vapor control systems are required to be tested to demonstrate compliance with associated emission limits and control efficiency requirements on a frequency specified in each facility's air emission license. A vapor control method is required to control emissions from the loading process whenever gasoline is loaded or whenever a truck is loaded that carried gasoline as its most recent previous load (a procedure known as "switch loading"). The vapor control system must meet a specified standard (VOC emissions not to exceed a specified limit, in milligrams per liter of product loaded), and each facility must periodically test the loading rack vapor control system to demonstrate compliance with their license requirements.

2. Calculating Emissions

Emissions can also be estimated based on calculations using established emission factors. Typically, those factors are based on a large number of physical samples of actual emissions to give a representative average of emissions from a given type of facility/source.

a. AP-42 (new & old)

The EPA's AP-42, *Compilation of Air Pollutant Emissions Factors*, originally published in 1972, is the primary compilation of EPA's emissions factors and process information for more than 200 air pollution source categories. AP-42 emission factors are developed and compiled from source test data, material balance studies, and engineering estimates. Since the original edition, EPA has published supplements and updates to AP-42. EPA recommends AP-42 for use by states to estimate federally reportable emissions for emission units where source-specific testing results are not required or available.

Chapter 7 of AP-42 presents models for estimating air emissions from organic liquid storage tanks, including petroleum storage tanks. Chapter 7 includes

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[61] Stratton, Anthony M. (2014, 24 November). Anthony Stratton to refineryfactor@epa.gov November 24, 2014 [Letter]. Comments submitted on behalf of Eastmount Environmental Services, LLC and its clients, in response to EPA request for comments on suggested revisions to AP-42.

emissions estimating methodologies for storage tanks of various types and operating conditions. The methodologies are intended for storage tanks that are properly maintained and in normal working condition. They are not intended to address conditions of deteriorated or otherwise damaged structural components or operating conditions that differ significantly from the scenarios described in the chapter.

Estimation methodologies for routine emissions (standing/breathing and working losses) from both fixed roof tanks and floating roof tanks are included. The equations were developed to estimate average annual losses for storage tanks. Provisions for applying the equations to shorter time periods are addressed but have an associated increase in uncertainty.

The equations are a function of temperatures derived from a theoretical energy transfer model. In order to simplify the calculations, default values were assigned to certain parameters in the energy transfer equations. The accuracy of the resultant equations for any individual tank depends upon how closely that tank fits the assumptions inherent to these default values. The associated uncertainty may be mitigated by using measured values for the temperature of the stored product.

In addition to standing and working losses, AP-42 Chapter 7 also includes methodologies for estimating emissions resulting from the landing of a floating roof, emissions resulting from tank cleaning, emissions from variable vapor space tanks, and emissions from equipment leaks associated with pressure tanks designed as closed systems.

AP-42 Chapter 7 received a significant update on November 20, 2019, as well as minor corrections in March 2020 and June 2020. These changes include updates to increase the accuracy of emissions estimation methodologies and are summarized below.

- The original temperature equations in AP-42 Chapter 7 were derived from American Petroleum Institute Publication Chapter 19.1D, *Documentation File for API Manual of Petroleum Measurement Standards Chapter 19.1 – Evaporative Loss From Fixed Roof Tanks*, First Edition, March 1993. The development of these equations included several approximations and substitutions to simplify the calculations. The equations have been revised as follows to more accurately reflect the theoretical derivations.
    - The default expressions for the average liquid surface temperature (T_{LA}) and average daily vapor temperature range (ΔT_V) are based on a uniform assumption of 0.5 for the tank height-to-diameter ratio (H/D). More general forms of these equations are included in the update with H/D as a variable.

  - The equation for calculating the liquid bulk temperature (T_B) was updated to account for solar radiation striking the tank. The new equation was developed from the same theoretical energy transfer model as the other temperature equations.
  - New equations for T_{LA} were added for floating roof tanks, with separate equations for different types of floating roof decks.
  - A new equation for T_B for floating roof tanks was added for use when measured values for T_B are unavailable.
- When alternative equations are available, language was included to indicate which equation is more accurate and what criteria need to be met for simplified forms of the equations to be acceptable.
- An equation was added for calculating the vapor space temperature (T_V). This was incorporated into the equation for calculation of the stock vapor density (W_v), which was previously approximated using the average liquid surface temperature.
- Guidance was added for estimating emissions from fully insulated tanks. Because minimal heat transfer occurs through the roof and shell of an insulated tank, it is assumed that the liquid surface temperature is equal to the liquid bulk temperature, and that there is no generation of breathing loss from the ambient diurnal temperature cycle. Breathing losses may still be driven by temperature cycles in the heating of liquid stock. Equations are provided to estimate heating-cycle breathing losses.
- Guidance was added for estimating emissions from partially insulated tanks. Temperature equations for more accurate modeling of partially insulated tanks were added, rather than modeling the tanks as non-insulated.
- The procedure for estimating floating roof landing losses was updated to use a more accurate equation for the vapor space expansion factor (K_E). Guidance was also added for estimating emission losses from roof landings of less than 24 hours' duration.
- A section was added for estimating emissions resulting from the cleaning of storage tanks.
- A section was added for estimating emissions resulting from evaporation, of material from the sides of the tank structure, also called flashing.
- An explanation was added for why the routine emissions equations are not suitable for estimating emissions for time periods shorter than one month.

b. TANKS 4.09D

A software program entitled "TANKS 4.09D" is available through the EPA website. It was developed based on the emission estimation procedures presented in a previous version of AP-42 Chapter 7 and can calculate VOC and HAP emission from fixed and floating roof storage tanks. TANKS 4.09D was last updated on October 3, 2005, and as such does not include the most up-to-date calculation methodologies presented in the current version of AP-42 Chapter 7. The TANKS 4.09D program contains known errors and is no longer supported by EPA, but it continues to be made available for historical purposes.

c. Commercially Available Software Products

In addition to TANKS 4.09D, other software packages for calculating emissions from storage tanks are available commercially. Some examples include TankESP produced by BREEZE software; ProMax produced by Bryan Research & Engineering, LLC; and E&P Tanks produced by American Petroleum Institute. These software products may use the methodology from AP-42 Chapter 7, other thermodynamic equations, or a combination to calculate emissions. The scope, functionality, and available support differs significantly in the available commercial software options. The cost of this third-party software ranges from $1,000 to over $10,000 per license depending on the sophistication of the software package and level of support provided by the supplier.

3. Continuous Emission Monitoring System (CEMS)

A continuous emission monitoring system (CEMS) is a combination of equipment used to continuously measure specific pollutants in exhaust gases emitted into the atmosphere. A typical CEMS consists of a sample probe, filter, sample line, gas conditioning system, calibration gas system, and series of gas analyzers which reflect the parameters being monitored. Some commonly used gas analyzers include infrared and ultraviolet adsorption, chemiluminescence, fluorescence, and beta ray absorption. A data acquisition and handling system then receives the signal output from each analyzer to collect and record emissions data. CEMS are required by some federal and state regulations as a means to comply with air emission standards. Facilities use CEMS to continuously collect, record, and report the required emissions data. Typical monitored pollutants include sulfur dioxide, nitrogen oxides, carbon monoxide, carbon dioxide, hydrogen chloride, airborne particulate matter, mercury, VOC, and oxygen. CEMS can also measure air flow, flue gas opacity, and moisture content. For each CEMS, the facility is required to perform periodic performance evaluations of the CEMS equipment, including daily calibration error tests, daily interference tests for flow monitors, and quarterly or annual calibration gas audits (CGA) or relative accuracy test audit (RATA) and bias tests.[62]

CEMS are effective on emissions sources with identifiable and relatively consistent flow, such as stacks from power boilers or emissions exhaust points from manufacturing processes. Emissions from petroleum storage tanks are neither readily

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[62] https://web.archive.org/web/20090211082920/http://epa.gov/airmarkets/emissions/continuous-factsheet.html

measurable nor consistent in expected flow rates. For example, the flow rate of breathing losses from heated petroleum storage tanks has not been able to be measured by EPA-required testing at two facilities in Maine due to flow rates being below detection levels of certified and test-method-specified flow meters. Thus, a flow would have to be induced to provide an emissions stream to continuously monitor. This would artificially increase emissions from heated tanks, necessarily resulting in measurement of nonrepresentative emission levels. The flow rates of working losses from heated tanks (during tank filling processes) can be measured, but tank filling events occur relatively infrequently, such that most of the time, the CEMS would sit idle because of the lack of a measurable flow rate.

By design, the gaseous stream collected and routed to odor control equipment recently required for a Maine petroleum storage facility will be a mix of ambient air and vapor emanating from the roof vents of the tanks. During times other than tank filling events, which happen infrequently (one facility reported tank filling events approximately once per month for 12-16 hours of duration), emissions will be from tanks "breathing," and the concentration is expected to be low. Additionally, the exhaust stream is expected to have a relatively high moisture content. VOC components from residual oil and asphalt will tend to be longer-chained (higher molecular weight) molecules that readily condense with moisture droplets. Such an exhaust stream would require preconditioning to remove the condensate to protect against plugging of a CEMS sensor. With the condensate removed, the CEMS measurements would likely be biased low.

Another consideration would be the ability of a CEMS to accurately quantify the VOC concentration given the wide range of VOC compounds. The response factor of the system for measuring short-chain hydrocarbons would be different than a response factor for long-chained hydrocarbons. CEMS currently in use in the petroleum terminal industry are common for gasoline vapors from gasoline loading racks, are only used on the exhaust of carbon vapor recovery control systems as a yes/no indicator for emission breakthrough of the carbon (to then signal to stop gasoline loading). There are no known examples of CEMS in use at residual oil storage facilities equipped with odor controls in the U.S or Canada.

The Department does not recommend requiring the use of CEMS to determine emissions from petroleum storage tanks. The use of CEMS technology is not technically or economically justified at this time.

4. Leak Detection and Repair Using Forward-Looking Infrared (FLIR) Technology

Leak detection using infrared technology is an effective way to identify and minimize losses to the atmosphere of gaseous emissions at petroleum storage facilities. An infrared camera is a non-contact device that detects infrared energy (heat) and converts it into an electronic signal, which is then processed to produce a thermal image or video. Thermal energy is transmitted in the infrared wavelength (1 to

100 micrometers, or µm). Heat sensed by an infrared camera can be used to identify and evaluate the relative severity of heat-related problems.[63] Infrared technology has multiple uses, including surveillance of living things (such as people or animals), watershed temperature monitoring, detection of energy loss or insulation defects in buildings, target acquisition and tracking in military applications, piloting of aircraft in low visibility conditions, locating living things and sources of ignition in firefighting operations, detecting heat in faulty electrical joints, searching for drug labs at night, monitoring active volcanoes, and detecting leaks of natural gas and other gases.

The term FLIR, a US military acronym that officially stands for "forward looking infrared radar," is generally considered to stand for "forward looking infrared" in common usage. This refers to the technology used to create an infrared image of a scene without having to "scan" the scene with a moving sensor. It is also the name of the largest manufacturer of thermal imaging cameras (FLIR Systems Inc.).

FLIR technology can be coupled with optical gas imaging technology to detect and visualize methane, sulfur hexafluoride, and many other industrial gases, which, when detected, appear as plumes of "smoke" in a thermal image or video. In comparison, the Toxic Vapor Analyzer, or sniffer, historically used to detect the presence of gaseous substances, can only detect gas by placing the probe directly on the equipment component or in the suspected stream of emissions, inspecting one point at a time.[64] More and more, FLIR technology is being used in the petroleum industry to conduct routine monitoring for leaks and other sources of emissions to ambient air, enabling faster inspections and more effective leak source identification.

C. Air Quality Monitoring

1. Mobile Devices

Many mobile or portable air quality monitoring devices are available from a variety of commercial sources to measure concentrations of pollutants in the ambient air. These devices represent air quality conditions only at the location where samples are collected. These vary widely in the types of air pollutants they measure, the range of concentrations they are capable of detecting, measurement methods used, methods used for management of data readings, and power sources. Real-time data output is also a typical feature. Cost typically ranges from a few hundred dollars to a few thousand dollars. Some vendors even offer a lease option. While some of the more readily available and widely used devices are those that measure particulate matter

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[63] *English contemporary dictionary. 2014.*

[64] https://www.flir.ca/discover/instruments/gas-detection/insights-from-the-field-how-ogi-cameras-improve-gas-leak-detection-and-environmental-health/

(PM) of different size fractions (e.g., PurpleAir and Clarity sensors), this report only focuses on devices capable of measuring gases such as VOC and polycyclic aromatic hydrocarbons (PAHs), the primary category of HAP emitted by petroleum storage facilities.

The majority of air quality sensor development has been focused on air pollutants for which there are National Ambient Air Quality Standards (NAAQS), such as ozone, carbon monoxide, sulfur dioxide, and nitrogen dioxide. Unfortunately, there are far fewer sensor devices available for gaseous HAP and VOC. Examples of VOC devices include the following:

- UniTech
- ToxiRae
- EPA VOC
- Air Quality Egg

These devices, like most VOC sensors, measure total VOC using a photoionization detection method with a detection limit in the range of 5-20 parts per billion. Measurement of specific VOC, HAP, or PAH require physical sample collection and off-site laboratory analysis.

While portable VOC sensor devices have the advantage of being relatively low-cost, their usefulness is limited due to their inability to measure specific VOC that are typically associated with petroleum storage tanks, as well as their detection thresholds being too high to measure ambient concentrations that can have health impacts. Therefore, using a canister sampling device for VOC or a sorbent tube sampling device for PAHs, coupled with a laboratory analysis of the samples, is both a mobile and more refined approach for measuring the air pollutants of concern in monitoring tank emissions. While the costs of sampling hardware are relatively inexpensive, the need for accompanying laboratory sample analyses (with its associated quality assurance and quality control protocols) adds recurring costs and leads to a delay in obtaining the final results. However, canisters and sorbent tube methods are viable options for municipalities, as demonstrated by Phases 1 and 3 of the South Portland/Portland (SOPO/Po) VOC Air Quality Project (https://www.maine.gov/dep/air/monitoring/spo-voc-monitor.html).

2. Fenceline Monitoring: EPA Method 325

No requirements for fenceline monitoring exist within federal rules for petroleum storage facilities. However, petroleum refineries are required by the EPA[65] to continuously monitor for benzene and VOC from specific emission units within facilities and around facility perimeters using EPA Method 325, *Volatile Organic Compounds from Fugitive and Area Sources*. Method 325 consists of the following two parts:

- Method 325A, *Sampler Deployment and VOC Sample Collection*; and
- Method 325B, *Sampler Preparation and Analysis*.

Method 325A prescribes the methodology and equipment for collection of VOC at or inside a facility property boundary or from fugitive and area emission sources using passive (diffusive) tube samplers specifically tailored to adsorb targeted compounds. This method requires deployment of passive sampling tubes on a monitoring perimeter encompassing all known emission sources at a facility and concurrent collection of local meteorological data. The concentration of airborne VOC collected at or near these potential sources may then be determined using Method 325B. Method 325B describes preparation of sampling tubes, shipment and storage of exposed sampling tubes, and analysis of sampling tubes collected. Method 325B directs thermal desorption/gas chromatography (TD/GC) analysis of the collected samples. The preferred GC detector for this method is a mass spectrometer (MS), but flame ionization detectors (FID) may also be used. Other conventional GC detectors such as electron capture (ECD), photoionization (PID), or flame photometric (FPD) may also be used if they are selective and sensitive to the target compounds and if they meet the method performance criteria provided in this method.

Method 325 is not suitable for particulate pollutants (i.e., fumes, aerosols, and dusts), for compounds too reactive for conventional GC analysis, or for VOC that are more volatile than propane.

A diffusive passive sampler collects VOC from air for a measured time period at a rate proportional to the concentration of vapor in the air at that location. The duration of each sampling period is normally 14 days. Thus, this method may be applied to screening average airborne VOC concentrations at facility property boundaries or monitoring perimeters over an extended period of time using multiple sampling periods (e.g., 26 x 14-day sampling periods). At the end of each sampling period, the

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[65] 40 C.F.R. Part 63, Subpart CC, *National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries*, and Subpart UUU, *National Emission Standards for Hazardous Air Pollutants for Petroleum Refineries: Catalytic Cracking Units, Catalytic Reforming Units, and Sulfur Recovery Units*; and 40 C.F.R. Part 60, Subpart Ja, *Standards of Performance for Petroleum Refineries for Which Construction, Reconstruction, or Modification Commenced After May 14, 2007*; collectively referred to as the Refinery Sector Rule

passive samples are collected, sealed, and shipped to a laboratory for analysis of target VOC by thermal desorption gas chromatography, as described in Method 325B.

Method 325 requires the additional collection of local meteorological data (wind speed and direction, temperature, and barometric pressure). Although local meteorology is a component of this method, non-regulatory applications of this method may use regional meteorological data, but the use of such regional data introduces risk that the results may not identify the precise source of emissions.

The rate of sampling is specific to each compound and depends on the diffusion constants of that VOC and the sampler dimensions, packing, and characteristics as determined by prior calibration in a standard atmosphere. In the sampling time period, gaseous VOC target compounds in ambient air migrate through a constant diffusion barrier (e.g., an air gap of fixed dimensions) at the sampling end of the sampling tube and adsorb onto the sorbent.

At the lab analyzing the samples, heat and a flow of inert carrier gas are then used to extract (desorb) the retained VOC back from the sampling end of the tube and transport/transfer them to a gas chromatograph (GC) equipped with a chromatographic column to separate the VOC and a detector to determine the quantity of target VOC. This method requires the use of field blanks to ensure sample integrity associated with shipment, collection, and storage of the passive samples. It also requires the use of field duplicates to validate the sampling process.

The EPA method includes cautions against general interferences which include possible influencing obstructions to air flow such as trees, walls, buildings, bodies of water, and hills at the monitoring site. The method also includes cautions of background pollution interference, including from nearby or upwind sources of target emissions outside the facility being tested, such as neighboring industrial facilities, transportation facilities (e.g., nearby airports, train/rail traffic, highways), fueling operations, combustion sources, short-term transient sources, and residential sources. Also, because passive samplers continuously sample ambient air, changes in wind direction can cause variation in the level of background concentrations from interfering sources during the monitoring period.

Indicators as to why this monitoring method may not be compatible with monitoring at bulk petroleum storage facilities in Maine include the following:

- The normal working range of sorbent packing for field sampling is 0 – 40 °C (32 – 104 °F). Maine’s ambient temperatures, specifically during the winter season, go below the lower temperature boundary for the sorbent.
- In locating meteorological instruments, the method advises the following: “If possible, locate wind instruments at a distance away from nearby structures that is equal to at least 10 times the height of the structure.” Within the South Portland

area with petroleum storage facilities, for example, some facilities are within closer proximity to one another and to other structures than 10 times the height of a tank (tank height is approximately 50 feet).

Temperature sensors must be located at a distance away from any nearby structures that is equal to at least four times the height of the structure, and at the same time, temperature sensors must be located at least 30 meters (98 feet) from large paved areas.

- Between 12 and 24 monitors are required around the perimeter of each petroleum refinery, based on the size of the facility. Each petroleum refinery covers hundreds of acres. Maine petroleum storage facilities cover areas far smaller than a petroleum refinery.

3. Fenceline Monitoring: Other Methods

There are several air quality jurisdictions in California with fenceline monitoring rules in place: Bay Area Air Quality Management District (BAAQMD), South Coast Air Quality Management District (SCAQMD), San Joaquin Valley Air Pollution Control District (SJVAPCD), Santa Barbara County Air Pollution Control District (SBAPCD), and the California Air Board. These jurisdictions generally require refinery fenceline continuous monitoring, with real-time reporting, for many pollutants including but not limited to total VOC, sulfur dioxide, nitrogen oxides, acrolein, styrene, formaldehyde, benzene, cadmium, manganese, nickel, arsenic, beryllium, hexavalent chromium, diethanolamine, naphthalene, and polycyclic aromatic hydrocarbons (PAHs).

These regulations require a wide variety of instruments to meet the rules, including the following:[66]

- Point monitors (mostly traditional)
  - $PM_{2.5}$, PM_{10}, black carbon, ultrafine PM (BAMs[67], aethalometers, etc.)
  - Metals (XRF[68], filters)
  - Gases (AutoGCs[69], PIDs[70], cavity ringdown, chemiluminescent)
- Open-path monitors
  - Depending on pollutant (UV-DOAS, FTIR, TDLAS, QCL[71])

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[66] Presentation by Clinton P. MacDonald, of Sonoma Technology, for the Air & Waste Management Association 113th Annual Conference & Exhibition, July 2, 2020
[67] Beta attenuation monitor
[68] X-ray fluorescence
[69] Automatic gas chromatograph
[70] Photoionization detector
[71] Quantum cascade laser

  - Mostly gaseous compounds at reasonable MDL[72]
- Low-cost sensors
  - Potential for some gases (e.g., total VOC, NO_x)
  - Evolving technology

Challenges with implementing this type of monitoring system also include the ability to identify and isolate emissions from specific sources, identifying which species to measure for, instrumentation options, data interpretation, and data availability and explanation. Experience at facilities currently complying with these requirements identify additional challenges, including public not believing non-detect results and lack of thorough QA/QC applied to real-time data at the time of publication, which increases the risk of false alarms. In addition, a scientific approach to monitor placement can be inappropriately influenced by the public and political processes. Furthermore, the infrastructure for this type of monitoring is very expensive.

4. Assisting Municipalities with Monitoring

Maine DEP’s Bureau of Air Quality does not have a formalized program for providing assistance to Maine municipalities to monitor ambient air quality. Any past assistance has been provided on an ad hoc basis, as Department resources have allowed, and the Department intends to continue with that approach. The EPA has established air sensor loan programs through various collaborations with community groups, schools, libraries, and others to enable the public to learn about air quality in their communities. These programs are provided to bring new air sensor technology advances to the public for educational purposes. Sensors available through these loan programs are not intended for regulatory use, as those used for regulatory purposes are subject to stringent calibration protocols in order to assure accurate and consistent data. Such calibration is not an available component of the EPA’s loan programs.

EPA Region 1, headquartered in Boston, MA (serving Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont, and ten Tribal Nations) participates in the agency’s Regional Air Sensor Loan Program. The equipment that is available for loan is the ARISense device. It measures carbon monoxide (CO), nitric oxide (NO), nitrogen dioxide (NO_2), ozone (O_3), carbon dioxide (CO_2), particulate matter (PM), solar intensity, noise, wind speed, and wind direction.

The following URLs contain more specific information and details about this program:
https://www.epa.gov/air-sensor-toolbox
https://www.citizenscience.gov/air-sensor-toolbox/

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[72] Minimum detection limit

VI. Conclusions and Recommendations

A. Controlling VOC Emissions

1. Gasoline

The storage and distribution of gasoline is already highly regulated at both state and federal levels. Additional controls beyond those already required would likely not result in any meaningful emissions reductions.

2. Distillate Fuel

Distillate products are often stored in fixed roof tanks. While retrofitting existing fixed roof distillate fuel tanks with a floating roof is unlikely to cause significant emission reductions, the Department has determined as a result of this study that new distillate storage tanks greater than 39,000 gallons should be equipped with a floating roof.

Loading distillate fuel into a truck for which the most recent previous load was gasoline is known as switch-loading. At facilities which are required to have an air emission license, switch-loading is typically prohibited unless vapors displaced during cargo tank loading are sent to a VOC collection and control system. The Department will propose to the Board of Environmental Protection revisions to *Bulk Terminal Petroleum Liquid Transfer Requirement,* 06-096 C.M.R. ch. 112, that prohibit switch-loading at any facility subject to that chapter unless equipped with a VOC collection and control system.

3. Residual Oil and Asphalt

The Department's investigation into the types of add-on control equipment currently being used to control emissions from heated, fixed-roof residual oil and asphalt storage tanks revealed that the majority of tanks of this type being operated in the United States do not utilize any type of add-on control equipment to reduce emissions. There are a limited number of tanks of this type that do utilize add-on control equipment for various other reasons. Some facilities have either been required to install or have voluntarily installed a combination of mist elimination and carbon bed adsorption equipment or in some cases thermal oxidation equipment to reduce emissions (some for odor reduction purposes and others for purposes of ensuring facility-wide VOC emissions remain below major source threshold levels).

Thermal oxidation systems are expected to be very effective in reducing VOC, HAP, and odor-causing compounds from tanks of this type; however, thermal oxidation systems can be very expensive to install and operate.

Carbon adsorbers may be designed to reduce emissions of both VOC and odors from heated, fixed roof storage tanks. However, if carbon adsorbers are not carefully monitored and maintained, they risk increasing emissions instead of reducing them. Therefore, carbon adsorbers should only be considered for tanks at facilities which have an air emission license where monitoring and recordkeeping requirements can be specified and compliance determined through regular inspections. Additionally, the overall effectiveness and longevity on emissions reductions from heated residual oil and asphalt tanks is not known.

Therefore, the Department will evaluate the operational effectiveness of the mist elimination and carbon bed adsorption equipment currently planned to be installed to determine whether this type of equipment should be required on other heated, fixed-roof residual oil and asphalt storage tanks located at bulk storage facilities in Maine in the future.

To accurately evaluate this equipment, characteristics of the material stored in each tank must be identified. Therefore, the Department will require recordkeeping of the amount and type of any material added to heated petroleum storage tanks at licensed facilities, including any additives. The authority for this recordkeeping requirement already exists in the Bureau of Air Quality’s licensing regulations. This requirement has been included in recently issued air emission licenses and will be included as appropriate in the licenses of other petroleum storage facilities state-wide.

The Department will also require that all heated, fixed roof petroleum storage tanks be fully insulated and the temperature of the stored material monitored to minimize temperature fluctuations which lead to breathing losses. This authority already exists in the Bureau of Air Quality’s licensing regulations and is already being implemented.

B. Controlling Odor

The characterization, measurement, and quantification of odors from petroleum storage facilities is complex. There is limited information on the use and effectiveness of existing odor control technologies. Therefore, the recommendations of this report are focused on additional evaluation and data gathering.

Maine will soon have two facilities with operational odor control technologies, and with their debut will come the opportunity to measure their effectiveness. Data showing emissions from the subject tanks and how those emissions are affected by mist elimination and carbon adsorbers will provide important information to inform possible future requirements. The Department will evaluate data from these facilities including the following:

- Emissions prior to controls;

- Emissions post-controls;
- Variations in emissions, seasonally and operationally; and
- Observations in the community of changes in perceptible odors, including both odor intensity and character.

The first three bullets above could be evaluated based on measurable VOC emissions and changes, since VOC are more readily measured and could be used as a surrogate for odorous compounds. When reviewing the use of these controls in practice, the Department will also identify unintended consequences of such controls, either positive or negative, and evaluate such consequences to more fully inform future requirements.

The fourth bullet, as described in the paragraphs above, is a subjective measure and would be best to document for at least a year, since seasonal variations are expected.

Regulatory standards for odor controls would be best approached after conducting studies and documenting the effectiveness of various control options.

C. Determining Emissions

1. Gasoline and Distillate Storage Tanks

   Emissions calculations as described in the most current version of AP-42 are considered the most accurate method for estimating emissions from unheated petroleum storage tanks. Although EPA's TANKS 4.09D will likely still give reasonable results for unheated tanks when compared to the most current AP-42 methodology, that program is no longer updated or supported by EPA, and the Department will not accept its use for compliance with annual emission reporting requirements.

2. Heated, Fixed-Roof Residual Oil and Asphalt Storage Tanks

   The Department will establish requirements in air emission licenses for those facilities installing odor control equipment on heated petroleum storage tanks due to consent agreements with EPA to require emissions testing. The Department will ensure testing is performed both upstream and downstream of the odor control equipment in order to determine the effectiveness of the equipment on reducing emissions (VOC, HAP, and those pollutants expected to significantly contribute to the types of odors being experienced by the community).

   Once completed, this evaluation will be used by the Department to inform decisions about whether this type of equipment should be required on other heated petroleum storage tanks located in Maine. This evaluation will also be used by the Department to determine any operational and maintenance procedures that should be required at facilities operating this type of odor control equipment.

The Department will use existing regulatory authority to require bulk petroleum storage facilities to conduct emissions testing for new or modified heated petroleum storage tanks greater than 39,000 gallons to establish site-specific emission factors that may be used for annual emission reporting and determining compliance with licensed emission limits. The Department will continue to accept use of the most current version of AP-42 emission estimating methods where site-specific testing is not required.

3. Product Loading

Air emission licenses already require control equipment associated with gasoline loading racks to be tested on a regular basis. Additionally, some testing has been performed on the top loading of heated products. The Department will require the use of on-site emissions test data for determining actual emissions whenever such data is available. For the loading of products without representative on-site emissions test data available, the Department will accept the use of the most current version of AP-42 emission estimating methods to determine emissions.

4. Emissions Calculations Software

The Department will explore federal funding opportunities to purchase commercially available software capable of calculating emissions in accordance with the most current version of AP-42.

5. Stack Testing Methods

The Department recommends and supports the development of an EPA standard test method, developed in accordance with EPA criteria for developing test methods as promulgated in the Federal Register, to quantify emissions from tanks with passive vents. Results from application of this method should then be used to update AP-42.

D. Monitoring

1. Ambient Air Monitoring Efforts

The Department supports continuing the ambient air monitoring study, which began in 2019 in coordination with the Cities of South Portland and Portland. This study continues to provide valuable information regarding the air quality within these communities and is being used by the Department and the Maine Center for Disease Control (Maine CDC) to inform the communities. The Department is exploring with EPA the option to use HEM-3 modeling to confirm or otherwise inform ambient air monitoring stations are sited at the most appropriate locations for the purposes of the study.

2. Fenceline Monitoring

   The Department does not recommend fenceline monitoring at this time. Fenceline monitoring is most commonly used around the perimeter of large facilities, such as petroleum refineries, with few or no other emissions sources nearby. Given the proximity of petroleum storage facilities in South Portland to one another and to other significant emissions sources such as highways, railways, marine vessels, and even local traffic and home heating combustion sources, as well as expected emissions release points at tank-top levels, and considering typical air movement and dispersion characteristics, fenceline monitoring for any given facility is not expected to provide much useful data. Emissions from any given source may not impact ground level within the fenceline before being mingled with emissions from other nearby sources, so pollutants detected on fenceline monitors in an area with several potential emissions sources would not necessarily be directly attributable to the facility at whose fences the monitors are located.

3. Continuous Emissions Monitoring Systems

   The Department does not recommend the use of continuous emission monitoring systems (CEMS) to determine emissions from petroleum storage tanks. CEMS are effective on emissions sources with identifiable and relatively consistent flow, such as stacks from power boilers or emissions exhaust points from manufacturing processes. The flow rate of breathing losses from heated petroleum storage tanks has not been able to be measured by EPA-required testing at two facilities in Maine due to flow rates being below detection levels of certified and test-method-specified flow meters. Thus, a flow would have to be induced to provide an emissions stream to continuously monitor. This would artificially increase emissions from heated tanks, necessarily resulting in nonrepresentative levels.

   The Department recommends that forward-looking infrared (FLIR) technology be used at bulk petroleum storage facilities to monitor for vapor leaks around the storage tanks, piping, and fittings associated with their facilities and to inform appropriate equipment repairs. This monitoring should be conducted at least on a monthly basis, and documentation of FLIR findings and associated repairs, as appropriate, be made available to the Department upon request. The Department will propose to the Board of Environmental Protection revisions to *Petroleum Liquid Storage Vapor Control,* 06-096 C.M.R. ch. 111, to include this requirement in licenses with petroleum storage tanks of capacity greater than 39,000 gallons.

E. Summary

The Department has sufficient authority through Maine law and EPA delegation to incorporate all necessary and appropriate requirements into the Department's air emission regulations and air emission licenses, including emission controls, compliance monitoring, and recordkeeping requirements. Based on this analysis, the Department will implement the following measures:

Emission Controls

- New distillate storage tanks with capacity greater than 39,000 gallons will be equipped with a floating roof.
- The Department will propose to the Board of Environmental Protection revisions to *Bulk Terminal Petroleum Liquid Transfer Requirement,* 06-096 C.M.R. ch. 112, to prohibit switch-loading at facilities unless equipped with a VOC collection and control system.
- All heated, fixed roof petroleum storage tanks must be fully insulated and the temperature of the stored material monitored to minimize temperature fluctuations which lead to breathing losses.
- The Department will evaluate the effectiveness of mist eliminators and carbon adsorption equipment, required by EPA consent decrees to control odors from heated tanks at certain Maine terminals, to reduce VOC emissions. If this control technology is proven effective as Best Practical Treatment to control VOC emissions from heated petroleum storage tanks, such technology will be required for all heated tanks in Maine.

Determining Emissions

- The Department will require bulk petroleum storage facilities to conduct emissions testing for new or modified heated petroleum storage tanks greater than 39,000 gallons to establish site-specific emission factors to be used for annual emission reporting and determining compliance with licensed emission limits.
- The Department will require the use of on-site emissions test data for determining actual emissions whenever such data is available. For emissions from facility processes with no available and representative on-site emissions test data, the Department will continue to allow the use of the most current version of AP-42 emission estimating methods to determine emissions.

Monitoring

- The Department will continue to support the ambient air monitoring studies that began in 2019 in coordination with the Cities of South Portland and Portland.

- The Department will propose to the Board of Environmental Protection revisions to *Petroleum Liquid Storage Vapor Control,* 06-096 C.M.R. ch. 111, to require monthly leak detection and repair at all licensed bulk petroleum storage facilities with any petroleum storage tanks of capacity greater than 39,000 gallons. FLIR technology will be required to be used at each bulk petroleum storage facility to monitor for vapor leaks around the storage tanks, piping, and fittings associated with the facilities and to inform appropriate equipment repairs.

In closing, these measures provide a technically sound approach to further reducing VOC and HAP emissions from petroleum storage tanks and facilities in Maine and should provide meaningful reductions in nuisance odors. The Department is also committing to continue its collaborative approach to community scale air quality monitoring in South Portland, Portland and other communities as our resources allow.

Appendix A

Maine Bulk Petroleum Storage Facilities

Following is a list of bulk petroleum storage facilities located in Maine which currently have an Air Emission License. Details on the petroleum storage tanks at each facility and products stored are shown on following pages.

License #	Name	Location
A-97	Sprague Operating Resources LLC	Trundy Road, Searsport
A-161	Penobscot Bay Terminals, Inc.	93 River Road, Bucksport
A-179	Sprague Operating Resources LLC	59 Main Street, South Portland
A-197	Portland Pipe Line Corporation	30 Hill Street, South Portland
A-202	Buckeye Terminals, LLC	730 Lower Main Street, Bangor
A-282	South Portland Terminal LLC	170 Lincoln Street, South Portland
A-390	Gulf Oil Limited Partnership	175 Front Street, South Portland
A-413	Irving Oil Terminals Inc.	52 Station Road, Searsport
A-432	Global Companies LLC	1 Clark Road, South Portland
A-460	Citgo Petroleum Corporation	102 Mechanic Street, South Portland
A-542	Cold Brook Energy, Inc.	809 Main Road North, Hampden

(A-97) Sprague Operating Resources LLC
Trundy Road, Searsport

Tank Number	Capacity (gallons)	Product Stored	Roof Type
1	3,927,756	#6 Fuel Oil	Fixed
2	3,949,890	Asphalt	Fixed
3	6,023,598	Distillate Fuel	Fixed
11	27,848	Distillate Fuel	Fixed
12	27,848	Distillate Fuel	Fixed
101	579,894	Distillate Fuel	Internal Floating
102	2,792,076	Distillate Fuel	Internal Floating
103	4,362,624	Distillate Fuel	Internal Floating
104	4,362,624	Distillate Fuel	Internal Floating
105	5,007,576	Distillate Fuel	Fixed
107	2,014,866	Distillate Fuel	Internal Floating
108	4,362,624	Distillate Fuel	Internal Floating
109	4,362,624	Distillate Fuel	Internal Floating

(A-161) Penobscot Bay Terminals, Inc.
93 River Road, Bucksport

Tank Number	Capacity (gallons)	Product Stored	Roof Type
1	6,200,000	Distillate Fuel	Fixed
2	5,000,000	Distillate Fuel	Fixed
3	2,300,000	Jet Fuel	Internal Floating
4	4,000,000	Distillate Fuel	Internal Floating
5	2,300,000	Jet Fuel	Internal Floating
6	6,200,000	Distillate Fuel	Fixed
7	6,200,000	Distillate Fuel	Fixed

(A-179) Sprague Operating Resources LLC
59 Main Street, South Portland

Tank Number	Capacity (gallons)	Product Stored	Roof Type
3	3,250,296	*See Note a*	Fixed
4	1,320,522	Distillate Fuel	Internal Floating
5	1,337,448	*See Note a*	Internal Floating
7	3,800,370	#6 Fuel Oil	Fixed
13	3,226,398	Distillate Fuel	Fixed
14	4,391,394	Distillate Fuel	Fixed
28	1,715,070	Aviation gasoline	Internal Floating
31	126,000	*See Note a*	Fixed
33	126,000	*See Note a*	Fixed
40	1,281,000	*See Note a*	Fixed
42	6,232,548	*See Note a*	Fixed
101	1,236,438	Distillate Fuel	Internal Floating
103	585,480	*See Note a*	Fixed
104	1,572,270	Distillate Fuel	Internal Floating
105	3,757,488	Distillate Fuel	Fixed
111	2,097,732	Distillate Fuel	Internal Floating
112	2,458,218	Distillate Fuel	Internal Floating
113	2,507,316	Distillate Fuel	Internal Floating
114	2,508,492	Distillate Fuel	Internal Floating
118	3,876,180	*See Note a*	Fixed
201	590,604	Asphalt	Fixed
202	592,242	Asphalt	Fixed
203	592,200	*See Note a*	Fixed
204	16,800	*See Note a*	Fixed
205	16,800	*See Note a*	Fixed
206	193,200	*See Note a*	Fixed
207	1,502,256	*See Note a*	Fixed
208	4,553,766	Asphalt	Fixed
209	3,108,798	Asphalt	Fixed
210	17,136	Distillate Fuel	(Horizontal Tank)
211	17,262	Distillate Fuel	(Horizontal Tank)
212	96,600	*See Note a*	Fixed
215	1,034,460	Asphalt	Fixed
229	18,690	Emulsion	Fixed

[a] These tanks are not currently in use but are being maintained for potential future use.

(A-197) Portland Pipe Line Corporation

30 Hill Street, South Portland

Tank Number	Capacity (gallons)	Product Stored	Roof Type
1	5,796,000	Crude Oil	External Floating
2	5,796,000	Crude Oil	External Floating
3	6,300,000	Crude Oil	External Floating
4	6,300,000	Crude Oil	External Floating
5	6,300,000	Crude Oil	External Floating
6	6,300,000	Crude Oil	External Floating
8	5,670,000	Crude Oil	External Floating
9	5,670,000	Crude Oil	External Floating
10	5,880,000	Crude Oil	External Floating
11	5,880,000	Crude Oil	External Floating
12	5,880,000	Crude Oil	External Floating
13	5,880,000	Crude Oil	External Floating
18	11,256,000	Crude Oil	External Floating
19	6,300,000	Crude Oil	External Floating
20	6,300,000	Crude Oil	External Floating
21	6,300,000	Crude Oil	External Floating
22	6,300,000	Crude Oil	External Floating
23	6,300,000	Crude Oil	External Floating
24	6,300,000	Crude Oil	External Floating
25	6,300,000	Crude Oil	External Floating
26	11,256,000	Crude Oil	External Floating
27	11,256,000	Crude Oil	External Floating
28	11,256,000	Crude Oil	External Floating

(A-202) Buckeye Terminals, LLC
730 Lower Main Street, Bangor

Tank Number	Capacity (gallons)	Product Stored	Roof Type
1	424,454	Distillate Fuel	Fixed
2	635,418	Distillate Fuel	Fixed
6	253,456	Distillate Fuel	Fixed
8	1,027,804	Distillate Fuel	Fixed
9	478,380	Gasoline, Ethanol, Distillate Fuel	Internal Floating
10	373,669	Distillate Fuel	Fixed
11	1,061,298	Gasoline, Ethanol, Distillate Fuel	Internal Floating
16	347,256	Gasoline, Ethanol, Distillate Fuel	Internal Floating
18	183,498	Gasoline, Ethanol, Distillate Fuel	Internal Floating
19	253,429	Distillate Fuel	Fixed
20	967,050	Gasoline, Ethanol, Distillate Fuel	Internal Floating

(A-282) South Portland Terminal LLC
170 Lincoln Street, South Portland

Tank Number	Capacity (gallons)	Product Stored	Roof Type
28	2,204,328	Gasoline, Ethanol, Distillate Fuel	Internal Floating
29	2,228,982	Gasoline, Ethanol, Distillate Fuel	Internal Floating
37	2,674,308	Gasoline, Ethanol, Distillate Fuel	Internal Floating
38	2,675,484	Gasoline, Ethanol, Distillate Fuel	Internal Floating
39	310,548	Gasoline, Ethanol, Distillate Fuel	Internal Floating
40	310,548	Gasoline, Ethanol, Distillate Fuel	Internal Floating
41	310,716	Gasoline, Ethanol, Distillate Fuel	Internal Floating
42	310,338	Gasoline, Ethanol, Distillate Fuel	Internal Floating
43	2,723,784	Gasoline, Ethanol, Distillate Fuel	Internal Floating
44	4,263,630	Gasoline, Ethanol, Distillate Fuel	Internal Floating
30	3,944,766	Gasoline, Ethanol, Distillate Fuel	Internal Floating
32	3,945,102	Distillate Fuel	Fixed
33	2,526,552	Distillate Fuel	Fixed

(A-390) Gulf Oil Limited Partnership
175 Front Street, South Portland

Tank Number	Capacity (gallons)	Product Stored	Roof Type
D1	4,003,566	Gasoline, Distillate Fuel	Internal Floating
D2	3,995,040	Distillate Fuel, Residual Fuel	Fixed
D3	3,828,552	Gasoline, Distillate Fuel	Internal Floating
D4	2,205,042	Distillate Fuel, Residual Fuel	Fixed
D5	3,983,490	Distillate Fuel, Residual Fuel	Fixed
D6	3,992,268	Distillate Fuel, Residual Fuel	Fixed
D7	3,247,062	Gasoline, Distillate Fuel	Internal Floating
D8	5,985,840	Gasoline, Distillate Fuel	Internal Floating
D9	767,466	Gasoline, Distillate Fuel	Internal Floating

(A-413) Irving Oil Terminals Inc.
52 Station Road, Searsport

Tank Number	Capacity (gallons)	Product Stored	Roof Type
1	7,350,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
2	7,350,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
3	3.360,000	Distillate Fuel	Fixed
4	7,350,000	Asphalt, Residual Fuel, Distillate Fuel	Fixed
5	3,360,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
6	5,250,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
7	5,670,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
8	5,670,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
9	4.620,000	Distillate Fuel	Fixed
10	2,100,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
11	1,680,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
12	756,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
13	2,100,000	Distillate Fuel	Fixed
16	168,000	Biofuel, Distillate Fuel	Fixed

(A-432) Global Companies LLC
1 Clark Road, South Portland

Tank Number	Capacity (gallons)	Product Stored	Roof Type
1	2,300,000	#6 Fuel Oil	Fixed
2	2,300,000	#6 Fuel Oil	Fixed
3	2,300,000	#6 Fuel Oil, Asphalt	Fixed
4	1,500,000	Distillate Fuel	Fixed
5	2,300,000	Distillate Fuel	Fixed
6	2,300,000	Distillate Fuel	Fixed
7	2,300,000	Distillate Fuel	Fixed
8	1,550,000	Distillate Fuel	External Floating
9	3,360,000	Asphalt	Fixed
14	410,000	Distillate Fuel	External Floating
15	410,000	Distillate Fuel	External Floating
16	6,800,000	Distillate Fuel	Fixed

(A-460) Citgo Petroleum Corporation
102 Mechanic Street, South Portland

Tank Number	Capacity (gallons)	Product Stored	Roof Type
1	2,800,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
2	4,600,000	Distillate Fuel	Fixed
3	3,800,000	Gasoline, Ethanol	Internal Floating
4	3,800,000	Gasoline, Ethanol	Internal Floating
5	1,300,000	Distillate Fuel	Fixed
6	1,400,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
7	4,200,000	Gasoline, Ethanol, Distillate Fuel	Internal Floating
8	4,200,000	Distillate Fuel	Fixed
9	2,500,000	Gasoline, Ethanol	Internal Floating
10	2,700,000	Gasoline, Ethanol	Internal Floating

(A-542) Cold Brook Energy, Inc.
809 Main Road North, Hampden

Tank Number	Capacity (gallons)	Product Stored	Roof Type
9	1,600,000	Gasoline	Internal Floating
35	420,000	Distillate Fuel	Fixed
44	1,325,000	Distillate Fuel	Internal Floating
66	756,000	Gasoline, Ethanol	Internal Floating
89	240,000	Distillate Fuel	Fixed
90	250,000	Gasoline, Ethanol	Internal Floating
91	252,000	Distillate Fuel	Fixed
92	504,000	Distillate Fuel	Fixed
93	492,000	Distillate Fuel	Fixed

EXHIBIT 10

What Is Activated Carbon?

TIGG LLC - Activated Carbon Equipment, Media, and Services > Resources > Activated Carbon Knowledge Base > What Is Activated Carbon?

Although the term granular activated carbon is used generically, it can refer to dozens of similar – but not identical-adsorbents. Depending on raw material, method and degree of activation and other factors, activated carbons can perform differently in various applications.

What is Activated Carbon?

Granular Activated Carbons are a very versatile group of adsorbents, with capability for selectively adsorbing thousands of organic, and certain in- organic, materials. From medicinal uses of powdered carbons in ancient Egypt, through charred interiors of whiskey barrels, carbon has been activated and used as an adsorbent for centuries. Granular vapor phase

ABOUT TIGG

TIGG has over 40 years of experience in developing a broad range of activated carbon filters, adsorption equipment, and services for environmental remediation all over North America. We develop, design and mar

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activated carbon media was first widely used in WWI military gas masks and, in the years between World Wars, commercially in solvent recovery systems.

Granular liquid phase activated carbons achieved their first prominent applications following WWI', in sugar de-colorization and in purification of antibiotics. Today, there are hundreds of applications — if diverse uses under the general heading of environmental control are counted separately, ongoing applications number in the thousands

Adsorption/Adsorbents/Granular Activated Carbon

Since adsorption is a comparatively specialized technology, a capsule definition of terms may be helpful. Adsorption is a surface phenomenon, in which molecules of adsorbate are attracted and held to the surface of an adsorbent until an equilibrium is reached between adsorbed molecules and those still freely distributed in the carrying gas or liquid. While the atoms within the structure of the adsorbent are attracted in all directions relatively equally, the atoms at the surface exhibit an imbalanced attractive force which the adsorbate molecules help to satisfy. Adsorption can then be understood to occur at any surface, such as window glass or a table top. The characteristic which typifies an adsorbent is the presence of a great amount of surface area; normally via the wall area or slots, capillaries or pores permeating its structure, in a very small volume and unit weight.

The type of adsorption which is dependent primarily on surface attraction, in which factors such as system temperature, pressure, or impurity concentration may shift the adsorption equilibrium, is given the further classification of physical adsorption. The electronic forces (Van der Waal's forces) responsible for adsorption are related to those which cause like molecules to bind together, producing the phenomena of condensation and surface tension. Conceptually, some prefer the analogy of physical adsorption being like iron particles attracted to, and held by, a magnet. Physical adsorption is the most commonly applied type, but an important sub-classification is chemisorption. Chemisorption refers to a chemical reaction between the adsorbate and the adsorbent , or often reaction with a reagent which may be impregnated on the extensive adsorbent surface (see Impregnated Carbons, below). Thus physical adsorption/desorption retains the chemical nature of the adsorbate, while chemisorption alters it.

The surface phenomenon of adsorption may now be contrasted with apsorption, in which one material intermingles with the physical structure of the other; for example, phenol dissolving into fibers of cellulose acetate (absorption) versus being adhered by surface attraction to the outer layer of the fibers (adsorption).

Granular Activated Carbon (activated charcoal) is an adsorbent derived from carbonaceous raw material, in which thermal or chemical means have been used to remove most of the volatile non-carbon constituents and a portion of the original carbon content, yielding a structure with high surface area. The resulting carbon structure may be a relatively regular network of carbon atoms derived from the cellular arrangement of the raw material, or it may be an irregular mass of crystallite platelets, but in either event the structure will be laced with openings to appear, under electron micrographic magnification, as a sponge

removal of trace contaminants from air, water, process liquids, and gases.

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like structure. The carbon surface is characteristically non-polar, that is, it is essentially electrically neutral. This non-polarity gives the activated carbon surface high affinity for comparatively non-polar adsorbates, including most organics. As an adsorbent, activated carbon is this respect contrasts with polar desiccating adsorbents such as silica gel and activated alumina. Granular Activated carbon will show limited affinity for water via capillary condensation, but not the surface attraction for water of a desiccant.

Activity Level

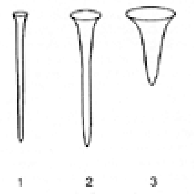
Activity level is often expressed as total surface area per unit weight, usually in square meters per gram. This total exposed surface will typically be in the range of 600-1200 m2/g. Toward the higher end of this range, one might better visualize one pound, about a quart in volume, of granular activated carbon with a total surface area of 125 acres.

To be useful in adsorption, surface area must be present in openings large enough to admit the adsorbate molecule(s). To provide some guidance on this topic, and for quality control purposes, the carbon industry has developed additional standardized vapor and liquid adsorption tests, using adsorbates of varying molecular size and chemical nature such as iodine, phenol, methylene blue, carbon tetrachloride, benzene and the color in standard black strap molasses. However activity level is measured, it is most meaningful when considered with additional characteristics described in the following sections.

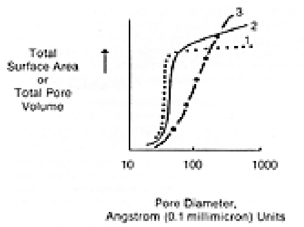
Pore Structure

While openings into the carbon structure may be of various shapes, the term “pore,” implying a cylindrical opening, is widely used. A description of the minute distances between walls of these pores, normally expressed as a function of the total surface area or total pore volume presented by pores of various “diameters,” is the pore structure curve. The following sketches show some sample pore structure curves and what approximate pore shapes are described by the curves. Please note that the average pore shape depicted is derived from a summation of pores of various sizes and shapes. Thus no pore within the activated carbon is likely to have precisely the average shape, but the granular activated carbon overall will often perform as if all its surface area were in pores of that shape.

Depiction of “Average” Pore Shapes



Pore Structure Curve Illustrations



The smallest diameter pores make up the micropore structure, and are the highest adsorption energy sites. Microporosity is helpful in adsorbing lower molecular weight, lower boiling point organic vapors, as well as in removing trace organics in water to non-detectable levels. Larger pore openings make up the macroporosity, which is useful in adsorbing very large molecules and aggregates of molecules, such as "color bodies" in raw sugar solutions. Another important function of the macropore structure is in assisting diffusion of fluids to adsorption sites in the interior of the carbon particle.

Given the above, pore structure. (1) would be effective in adsorbing high volatility solvents, for certain types of odor control, and in removing trace organics from water; the latter with the liability of marginal diffusion characteristics. Pore structures along the lines of. (2) offer a good balance of selectivity for molecules of various sizes, ability to reduce vaporous and liquid contamination to ultra low levels, and good diffusion characteristics. Structure (3) would allow excellent diffusion and can accommodate very large molecular sizes, but has little micro- pore structure and would have very poor retentivity for most organics.

Raw Material

Granular activated carbon can be produced from various carbonaceous raw materials, each of which will impart typical qualities to the finished pro-duct. Commercial grades are normally prepared from coconut and other nut shells, bituminous and lignite coals, petroleum coke, and sawdust, bark and Other wood products. In general, nut shells and petroleum cokes will produce very hard carbons with a pore structure characterized by.(1) above, coals a (2) type structure in comparatively hard carbons, and wood (3) structure in carbons lacking great crush and abrasion resistance. It should be emphasized that specific production techniques may yield carbons that depart from the norm of a given raw material.

Apparent Density

The solid, or skeletal, density of most activated carbons will range between 2.0-2.1 g/cc, or about 125-130 lbs/cubic foot. However, this would describe a material with essentially no surface area and no adsorptive capacity. For GAC, a much more practical density is the apparent density (A.D.), or mass of a given volume of adsorbent particles. This density will be significantly lower than the solid density, due to the presence of pores within particles, and void space between particles. In most commercial GACs, the A.D. variation is between 0.4- 0.5 g/cc, or between 25-31 lbs/cubic foot.

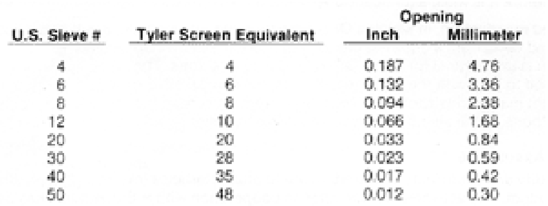
Since granular activated carbons are used in adsorbers of fixed volume, apparent density values can be used to calculate volume activity, which may help determine the work capacity of an adsorber with alternative carbon loadings. For example, assume that carbon A adsorbs iodine to produce a standardized Iodine Number of 1100 mg/g., and has an A.D. of 0.4 g/cc Carbon B has an Iodine Number of 950 mg/g and an A.D. of 0.5 g/cc. Multiplying the A.D. by the weight basis activity value, carbon A has a volume iodine capacity of 440 mg/cc while carbon B has a value of 475 mg/cc. Therefore, carbon B, which has lower activity, might actually do more work and therefore have a longer service life than carbon A of an equal volume. If the price of carbon B permitted filling a given adsorber with the greater weight required, it could thus be the most economical of these adsorbents on a net cost basis.

Since standard activity tests are run with oven dried carbon, it will be immediately apparent why high A.D. values that reflect added moisture will not produce the benefit illustrated above. Similarly, high densities due to significantly low activity levels, or ash or inactive char residue from reactivation, or any non-carbon adulterants will not normally benefit service life nor the adsorbent’s capability to produce highly purified fluids.

Particle Size

The size of most granular activated carbons is given by the U.S. Sieve range that will include the majority of the particles in a distribution of sizes. Typically the range will cover 85-95% of the total product, with a few percent slightly larger and smaller sizes permitted by specification. A similar approach is occasionally used with Tyler Screen or other screen sizes. Pelletized carbon, although not truly granular, often is described by the sieve range method, or by diameter of the pellets.

Common vapor phase U.S. Sieve size ranges are 4×6, 4×8, 4×1 0, 6×16 and 12×30. Liquid phase granular activated carbons are usually somewhat smaller, with 8×30, 12×20, 12×40 and 20×50 being common. Detailed sieve descriptions are found in engineering handbooks, so only a few representative sizes are given here:



U.S. Sieve #	Tyler Screen Equivalent	Opening	
		Inch	Millimeter
4	4	0.187	4.76
6	6	0.132	3.36
8	8	0.094	2.38
12	10	0.066	1.68
20	20	0.033	0.84
30	28	0.023	0.59
40	35	0.017	0.42
50	48	0.012	0.30

Since impurity removal requires the diffusion of adsorbate into the intra particle structure, the rate of adsorption will increase as the particle size decreases. As fluid flows through an adsorber, increased rate of adsorption will require less adsorbent bed depth and contact time for the region in which the adsorbate is being removed. This functional adsorption region is termed the adsorption wave front or ~ transfer zone. However, with any given fluid, decreasing particle size carries the liability of increasing flow resistance or pressure drop. In practice, particle sizes are selected to produce a reasonable balance between the competitive benefits of rapid rate of adsorption and effective removal, versus the liabilities of increased flow resistance and attendant higher pumping costs.

Hardness

Hardness and abrasion resistance are generally beneficial in all granular activated carbons, although their operational usefulness can vary greatly. Within common adsorber designs and operating ranges, all commercial granular activated carbons can withstand their own weight and the pressure effects induced by fluid flow. Thus in systems in which the granular activated carbons will be used once or handled very infrequently, hardness characteristics may be of little or no import. Conversely, if the carbon will be subject to frequent handling for a regeneration step, is subjected to thermal excursions by regeneration in place, or must resist excessive vibration, hardness may become quite important. For example, fines (dust) from handling a soft carbon in a system using thermal reactivation may double or treble the losses in the reactivation furnace itself. In solvent recovery systems using steaming cycles for regeneration, carbons that fracture easily can frequently raise pressure drop enough to require that the adsorbent be re-screened and replenished, or replaced.

In evaluating hardness numbers, it should be remembered that the granular activated carbons hardness test has no relation to the hardness scales used for plastics, metals or minerals. A carbon, of 98 hardness, is appreciably harder than one of 80, but even harder materials such as diamond, steel and copper, even though they differ in actual hardness, will all report as 100 on the basis of the granular activated carbons hardness test.

Ash

If part of the carbon raw material, ash generally varies between 2-20 weight percent in commercial granular activated carbons. A portion of total ash may be water-soluble, normally a greater amount acid soluble, and the remainder deeper within the skeletal structure of the carbon to be effectively insoluble. Ash from wood and nut shell carbons tends to be rich in alkaline metals, while that from coal largely oxides of aluminum, silicon and iron. For the limited instances in which traces of soluble or reactive ash are objectionable, granular activated carbons pre-washed with water or acids are available, or grades based on certain raw materials may minimize the total ash level or particular ash components.

Natural ash is normally not detrimental to the adsorption process, and standard activity tests report granular activated carbons efficiency including the weight of the ash. However, in certain regenerated granular activated carbons, ash that is a residue of previous uses may block some or all of the micropore structure that is vital for removing organics to ultra low levels. Similarly, if ash is due to previous impregnation for another use, or due to any other adulterant, the carbon performance may be seriously compromised.

pH

Water extracts of activated carbons are used for reporting pH. Untreated coal base carbons are typically close to neutrality, while nutshell and wood carbons are more alkaline. Most untreated GACs vary between pH 6-10, but added acids or alkalis may further extend this range.

In purifying water and aqueous solutions, the pH of the granular activated carbons should be contrasted with the preferred pH of the solution. Most organics are best adsorbed from slightly acid, pH 5-7, solution. However, the beginning pH of the GAC will not influence the pH of the treated solution very long (although adsorbates being removed may alter solution pH).

Impregnated Carbons

High surface area per unit weight or volume can make granular activated carbon an effective substrate for dispensing other materials in a manageable form. Impregnants may be catalysts, or they might be reactive chemicals added to improve the rate of adsorption, selectivity, or capacity for certain adsorbates. Examples of the latter would include carbons with a faster rate of removal for hydrogen sulfide and other acid gases, some with capability to remove ammonia and lighter amines, and some with enhanced capacity for reduction of mercury vapor. Impregnated carbons usually retain 75% or more of the physical adsorption capability of the base carbon, so they are often used for combined physical adsorption and chemisorption. Whether an impregnated granular activated carbon will be cost effective frequently depends on whether a particular adsorbate is the only, or primary, removal candidate.

Reactivation

As explained earlier, carbon activation is frequently carried out in high temperature furnaces, under mildly oxidizing conditions. As the name implies, reactivation refers to using a similar process to volatilize and oxidize the adsorbates on spent carbons. The term reactivation might be contrasted with re-Qeneration, which refers to steaming or other methods to restore a portion of the GAC adsorptive capacity, al- though the terms are commonly interchanged. Reactivation will almost always produce measurable changes in pore structure, due to additional oxidative sculpturing of the carbon surface and, frequently, deposits of residual chars or inorganic materials. In a few cases, reactivated granular activated carbons perform better than or as well as the virgin material, but in many others there may be a defined loss of comparative efficiency or a gradually increasing loss of efficiency. When loss of efficiency is encountered, it is normally most pronounced in the micropore structure, therefore it is most significant operationally when the last traces of contamination must be removed.

Dedicated reactivation, in which a granular activated carbon will be segregated and returned to the same use, tends to be more predictable than employing a reactivated GAC from a different previous use, or a mixture of reactivated granular activated carbons from a variety of previous uses. However, dedicated re- activation is impractical for spent GAC quantities under several tons. The cost effectiveness of reactivated versus virgin carbons can be understood to vary with the performance requirements, the comparative volume service life, and the volume cost of the material (cost per unit weight may be misleading, as reactivated carbons frequently have higher apparent densities). Given the possible variations in reactivated carbons, it will also be understood that a reputable supplier should always specify if virgin or reactivated GAC is being offered.

Quality Assurance

Granular activated carbons quality and uniformity will fundamentally relate to characteristics involving: (1) adsorption capacity and (2) a physical description of the product. The activated carbon industry, often in cooperation with A.S.T.M. and other standards organizations, has developed a series of tests that measure these characteristics. As would be expected, such tests can be used both as production controls and, as published specifications, assurance for prospective buyers.

Not all granular activated carbons manufacturers and distributors publish adsorption specifications. Among those that adhere to specifications, the same precise group of tests may not be used. However, some correlation of values is usually possible as, for example, between the vapor phase carbon tetrachloride test used in the U.S. and the benzene and acetone tests more common in Europe and the Far East.

Among physical tests, the methods to determine moisture, apparent density and particle size or distribution are relatively standard among manufacturers. Hardness or abrasion values may require some interpretation or correlation, as above.

Terms such as “high quality; excellent adsorption characteristics; hard; dense; etc.” are inadequate substitutes for specifications. They offer no guidance for comparison, no assurance of quality, and no confidence of uniformity.

Predicting Performance

Many prospective granular activated carbon users will be considering applications that are unique to some extent. Perhaps the mix of impurities is unusual, or the system conditions or performance required may be new. The uncertainty of these situations has historically been resolved by testing. More recently, vapor and liquid computer-assisted correlative techniques have been developed for use when urgency, lack of test fluids, or costs make tests impractical; or to help establish test protocols that will yield the most useful information. A description of TIGG Corporation’s Adsorption Predictive Technique (APTTM) computer service is available on request.

Experimental granular activated carbons tests include adsorption isotherms and column tests. Isotherms are batch tests which require careful evaluation before eventual GAC performance in continuous adsorbers may be predicted. Column tests may vary from laboratory bench to pilot or semi- commercial scale. Sometimes results of such test are termed “treat-ability studies,” and many useful results have been published. Unfortunately, some published data do not describe the methodology or adsorbents used; others employ test methods or data interpretations that are suspect. Therefore the literature can be a risky basis for determining GAC efficiency, although tests performed and interpreted properly are quite dependable. Major GAC manufacturers, as well as firms such as TIGG Corporation which specialize in GAC equipment, can recommend test procedures and may have small scale adsorbers available.

A very important evaluation caveat is that different GACs have differing efficiencies for different applications. Thus a test, literature search or computer projection based on a particular GAC will not necessarily describe the performance to be anticipated from another GAC.

Price

Readers will appreciate that, while not to be ignored, granular activated carbons price is rarely the leading factor in selecting an adsorbent. GACs of diverse efficiencies, qualities, sources and prices are in the marketplace. Price per pound or per cubic foot should be interpreted in terms of effectiveness. Cost effectiveness, in turn, may relate both to the GAC and the adsorber in which it will be applied, since even the optimum GAC will not overcome a deficient adsorber design. We hope that some of the commentary in this guide will assist in selection of the most cost effective adsorbent.

Postscript

An overriding factor in outlining the proper granular activated carbons to use, and predicting expected results, is the clearest possible definition of the application. Eventual performance typically reflects the quality of information used for initial technical judgments, and selecting a GAC follows this truism.

Click here for more information on TIGG's line of activated carbon and other types of filtration media or call us at 1-724-703-3020.

ABOUT TIGG

TIGG has over 40 years of experience in developing a broad range of activated carbon filters, adsorption equipment, and services for environmental remediation all over North

MARKET SECTORS

- PFOA/PFOS
- Municipal Water
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America. We develop, design and manufacture equipment for the removal of trace contaminants from air, water, process liquids, and gases.

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- PCB Removal
- Soil Vapor Extraction
- Vapor Emission
- Odor Removal
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EXHIBIT 11

Air Emission Control Systems & Service

Product Lines

CarbonPure Adsorption Systems

High Control Efficiency

APC Technologies' activated carbon systems can provide 98-99%+ control efficiency for many volatile organic compounds (VOCs), hydrogen sulfide, mercaptans, odors, mercury, Cl2, HCl, other acid gases, siloxanes, and other gaseous contaminants.

Pre-Filter Extends Carbon Life

In cases where fine particulate, oil mist, or aerosol are also present, exhaust gases are first drawn through APC's exclusive Ultra High-Efficiency Filter (UHF®) unit. This filter removes all fine solid- and liquid-phase contaminants from the gas stream, ensuring high removal efficiency and greatly extending the life of the activated carbon bed.

Solvent Recovery or Destruction

If solvent recovery is desired, the saturated carbon bed is periodically regenerated in situ with steam. After the steam has cleaned the bed, solvents are separated from the condensed steam and recycled back to process. Activated carbon can also be regenerated in situ by hot flue gas, and the concentrated VOCs from the regeneration process are oxidized in a small fume oxidizer.

Broad Range of Applications

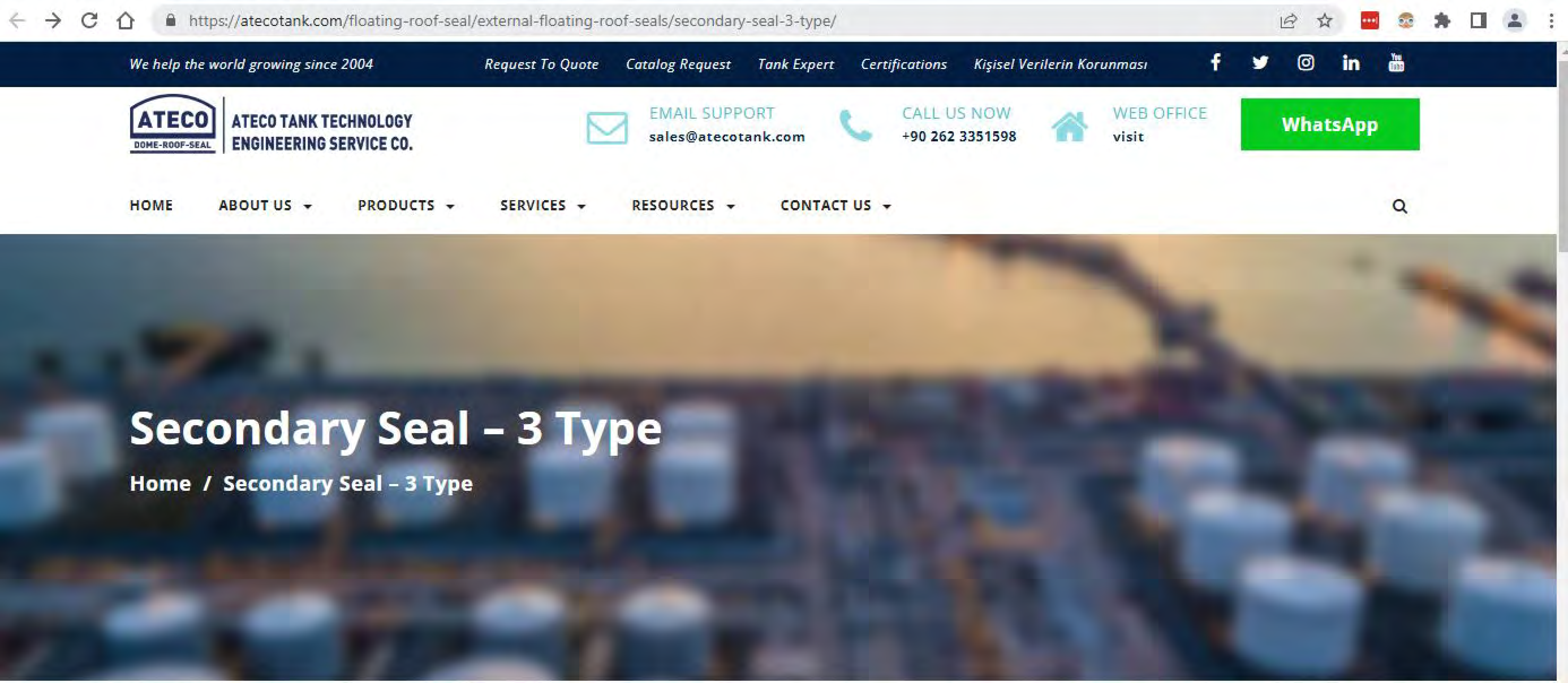
APC's CarbonPure systems provide high-efficiency removal of gas-phase contaminants such as VOCs, hydrogen sulfide, mercaptans, odors, mercury, Cl2, HCl, other acid gases, siloxanes, and other gaseous contaminants.

Applications for CarbonPure systems include: asphalt plants, chemicals, coatings, digester gas cleaning, electronics, foods, groundwater stripping, waste processing, laboratory exhausts, landfill gas treatment, lubricants, oil storage tank vent gas control, oil refineries, petrochemicals, pharmaceuticals, plastics, polymers, resins, printing, roofing manufacture, rubber, siloxane removal, wastewater treatment plants, indoor air quality improvement, and more.

Proven Through Performance

CarbonPure systems have a proven record of reliability and consistent performance across a variety of industries and demanding environments.

EXHIBIT 12



https://atecotank.com/floating-roof-seal/external-floating-roof-seals/secondary-seal-3-type/

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Secondary Seal – 3 Type

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Secondary Seal – 3 Type

Even well designed and properly maintained, primary seals operating in geometrically accurate tank shells permit significant vapour losses from storage tanks. The basic mechanism of loss is due to the swirling, scouring action of the wind. For vapour loss read cash loss. To counter the cash loss, the independently mounted secondary seal of the compression plate type is unequalled. Besides cutting vapour losses, the secondary seal confers other benefits.

Description

The S-Series range of compression plate type secondary seals from ATECO TANK exploits the spring action obtained when custom designed steel plates are compressed to bridge the annular rim gap from tank roof to shell. The plates may be mounted on horizontal or vertical roof rims and made to accept specific bolt pitching. Adjacent compression plates are overlapped, lightly attached and soft gasketed to permit relative movement while presenting an impervious barrier to the passage of vapour. Plates are clamped to the roof rim by channels. As a variant on the above we can provide an option where a flexible vapour barrier is fitted behind the compression plates and the adjacent plates overlap but are not bolted and gasketed. This option is available on request; however, the former details are in our opinion superior for long life and fire safety. Contact with the tank shell is by an extruded S-Series seal polymer tip attached to the upper edge of the compression plates. The form of the extruded tip will be selected from the two styles described below: 1. Single contact: Suitable for butt welded tank shells. High wear resistance. Positive tank shell contact permits removal of waxy deposits. 2. Double contact: Suitable for butt welded tank shells. Lighter contact with shell. Use where shell distorted or very rough, protruding welds, etc. Can be supplied for benzene service. The above are formulated for long life in exposed, arduous conditions.

Available On Request

Fire Protection: note, we can provide access ports in the compression platesfor halon or BCF injection.

Regulatory Compliance

ATECO Tank Engineering seals meet or exceed the allowable gap requirements set forth by the governmental and regulatory agencies throughout the universe. This design will show superior sealing ability throughout the roof travel; accounting for roof shifting, out of roundness, buckling, and the expansion and contraction requirement of each tank.

Guarantee

ATECO TANK warrants its seals to be free from defects in the material and workmanship for a period of two year. Our liability under any express or implied warranty is limited to the purchaser price of any part found defective. Any seal systems installed by ATECO TANK TECHNOLOGY ENGINEERING SERVICE will have an additional two-year warranty.

BASIC INFORMATION	
TYPE	Secondary Seal
DESCRIPTION	Rim Mounted Compression Plate Type Secondary Seal
USED ON	External Floating Roof Tanks
RIM SPACE	Up to 250 mm Nominal. Values of Excess to This Require Modifications to The Pontoon Rim.
SERVICE	Suitable for All Products With Correct Material Selection
API COMPLIANT	Yes
CODRES COMPLIANT	Yes
API 2003 COMPLIANT	Yes
AROMATIC SERVICE	%100
TYPICAL SERVICE LIFE	15-25 years
WEIGHT	11.5 Kg's/mt (Typical Based On 200 mm Rim Space)

Key Benefits Design Features Request For Quote Talk To Tank Expert

Key Benefits

1. The secondary seal can be installed while the tank remains in service. since no hot work is required.
2. Independent overlapping support plates, bolted together, produces greater flexing in the seal to accommodate shell deformities.
3. The extruded seal tip is highly abrasion resistant and can be used in most services, resulting in a long life for a long-term maintenance free operation. Alternative seal tips are available for lap welded and riveted tanks.
4. The secondary seal design diverts most rainwater from entering the primary seal area. The standard vapor seal tip fits vertical with the shell. Seals designed with horizontal tips will not flip in unison causing compliance problems and more internal moisture.
5. The secondary seal is designed for a tight fit to prevent vapor loss. Reduced vapour loss resulting in fewer odour problems and offering a cost-effective way of complying with air quality standards.
6. A continuous fabric is installed as a vapor barrier to eliminate possible vapor leakage that occurs in bolted support plate construction. Fabric can be replaced on underside or on the top side of the support plates, depending on inspection requirements and/or exposure issues.
7. Can be used in almost all service conditions up to 100% aromatics.
8. Easy access for visual inspection.
9. Can be paired with all primary seal types.
10. Enhanced safety by reduced free hydrocarbons above the seal.
11. Irregularly shaped tank shells can be accommodated.
12. Includes seal stand-off wheels to protect against malformed tank shells.

LEAFLET

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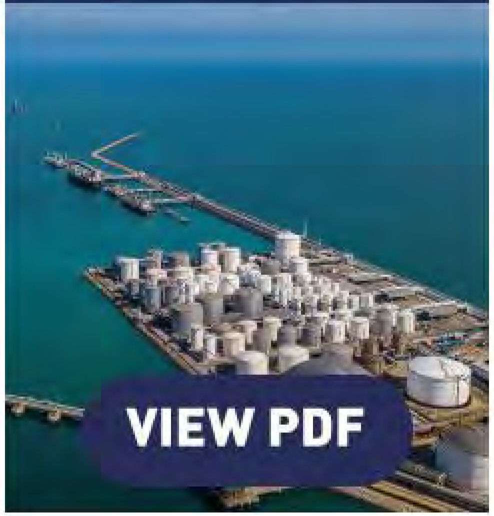
SAMPLE PROJECT



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MATERIAL SPECIFICATION

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SUMMARY SPECIFICATION

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TYPICAL DRAWINGS

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GENERAL SPECIFICATION

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Our Products

- Aluminum Geodesic Dome Roofs
- Internal Floating Roofs
- Floating Roof Seals
- Roof Drain Systems
- Floating Suction Lines
- Emission Control Devices
- Oil Skimmers
- Special Products
- Tank Venting Equipment

EXHIBIT 13

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CTS20

SECONDARY COMPRESSION PLATE SEAL

The CTS20 is an independently rim mounted secondary seal that has developed itself into the leading design for secondary tank seals. Its design is based on compression plates pushing a rubber tip against the tank shell. As the seal design has no complex moving parts it will not encounter problems as a result of corrosion or any other hazards affecting seal performance through time. Each CTS20 seal will be specifically engineered and manufactured to fit the tank involved, making sure the seal will be able to deal with both the product stored as well as with the particular dimensional and design aspects of this tank. Behind the compression plates, fully shielded from weather exposure, is a continuous vapour barrier ensuring excellent vapour tightness.

Features

- Independent rim mounted gastight secondary seal
- Excellent vapour tightness, resulting in maximum emission reduction and eliminating the risk of rim fires
- Eliminating virtually all rain water ingress to the stored product
- Compatible with all stored products, including 100% aromatics, such as Benzene, Toluene and Xylene
- Available in different material combinations, including stainless steel and galvanized steel
- Suitable for both vertical and horizontal roof rim angles, no rim modifications required
- Expected service life in excess of 30 years
- Designed for each specific tank
- Easy installation
- Can be installed while the tank remains in service
- Compliant with all international (environmental) standards such as API, EN, BREF IPPC, EPA, ATEX, NFPA and the specific standards EEMUA, PGS 29, VLAREM, etc.
- Successfully used by all reputed major oil and tank storage companies
- Suitable for both welded and riveted tank shells
- Can be fitted as a primary seal, secondary seal or as a combination of primary and secondary seal (CTS40)

CTS20

Design and engineering

A CTS20 seal is available in many different configurations. Seal tip design as well as seal design are depending on the service requirements and actual tank conditions. CTS designs each individual CTS20 seal for the tank it will be fitted on. CTS considers the rim gap, product properties, tanks specifications and many other design aspects in this process, eliminating the problems that arise when a standard seal is fitted. Our special tank inspection sheet will facilitate this engineering process. The CTS20 secondary seal can be combined with any existing primary seal, fitting both horizontal and vertical rim angles. The seal can be installed while the tank is in service.

Materials

Not just the design of the seal is important for its performance. Correct material selection is very important to ensure a long term adequate performance for any seal. In this respect one also has to realise that fabrics behind secondary seals will be difficult to inspect and malfunctioning seals could represent a hazard, while still mechanically okay.

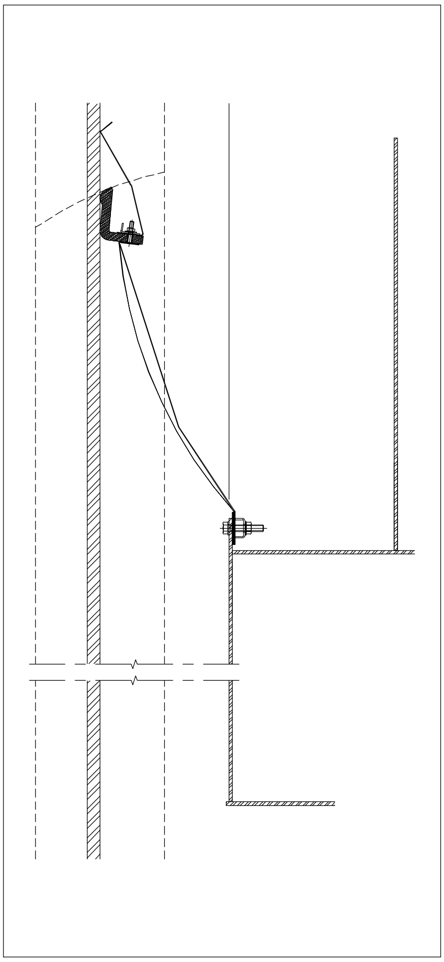
Seal materials have to withstand the stored product, ozone, UV-exposure and rain water contact. CTS is able to give you a profound advise on the optimal combination of materials, resulting in an economic seal design able to deal with the specific conditions.

Seals can be manufactured in a wide variety of materials, including different grades of stainless steel and (fire safe) polymer materials, compatible with 100% aromatics or aggressive chemicals if and when required.

Installation

CTS is capable to install any tank seal on any tank, but our provided detailed drawings and installation manual will give you the choice to have either your own staff or contractor staff installing the seal. The economic advantages of having your own (contractor) staff installing the system could be significant, reducing travelling and lodging costs. Experienced CTS supervision is available upon request.

CTS20L secondary seal with direct foam injection.



CTS20L secondary seal, cross section.

REVISION NO.: 201703

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