



March 15, 2023

VIA EMAIL ONLY

Michael Morris, Planning and Rules Manager  
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**RE: Comments on Preliminary Draft Language for Proposed Amended Rule 1178 (Further Reductions of VOC Emissions from Storage Tanks at Petroleum Facilities)**

Dear Mr. Morris:

The undersigned organizations submit these additional comments on the preliminary draft of Proposed Amended Rule (PAR) 1178. We appreciate the opportunity to provide additional input. Before enumerating several deficiencies with PAR 1178 that must be addressed, we would like to note several general concerns about South Coast AQMD's approach in this rulemaking process that are undermining public participation and refinery accountability.

**First, we must highlight that all our comments have been hampered by not having any available emissions data during rulemaking**—neither total emissions for storage tanks, nor emissions for each category of tanks, nor for individual tanks. It seems unprecedented not to include even *total* emissions. The staff reports and presentations only provide *expected reductions*, but not *existing emissions*. This makes it impossible to determine the relative importance and effectiveness of control measures. Further, without this information, we cannot determine whether the proposal meets minimum requirements of the AB 617 Community Emission

Reduction Plan (CERP), which committed to at least 50% cuts in VOCs by 2030 or higher if feasible.<sup>1</sup>

South Coast AQMD staff has informed us that they expect to provide some form of this data in two weeks, which is almost at the point of rule adoption. **Consequently, we may need to propose an unfortunate delay in adoption. This information can certainly affect our recommendations and decisions about whether we support or oppose adoption of PAR 1178.**

**Second, there are already many tradeoffs and exemptions that we do not support.**

One major problem is allowing exemptions from doming external floating roof tanks, and instead allowing occasional vapor pressure measurements that would be kept in-house at the polluting facilities. But adding a permanent roof is far superior to bi-annual parameter measurements that only measure a snapshot of vapor pressure, which can fluctuate widely over shorter periods of time. Many of the tradeoffs are driven by too low cost-effectiveness limits and are further skewed by known underestimation of emissions in the inventory. Large emissions of VOCs, including benzene and other harmful toxics, make strict application of Best Available Control Technologies (BACT) and Best Available Retrofit Control Technologies (BARCT) essential, but without the data we have requested, it is very hard for us to determine to what extent this will be applied, and what percent of reductions will be achieved.

**Third, we urge you to reconsider our recommendation to implement a moratorium on new storage tanks subject to PAR 1178, or, at a minimum, explain to the public and Governing Board how PAR 1178 does not conflict with the 2022 Air Quality Management Plan (AQMP) and the California Air Resources Board (CARB) 2022 Scoping Plan.** Specifically, the AQMP relies on electrification and the deployment of zero-emissions technology to achieve air quality standards in the

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<sup>1</sup> South Coast AQMD, Governing Board Meeting Agenda No. 25C (Sept. 6, 2019) at 4, <http://www.aqmd.gov/docs/default-source/Agendas/Governing-Board/2019/2019-sep6-025c.pdf?sfvrsn=6> [archived at <https://perma.cc/Z3C8-KYLK>].

region.<sup>2</sup> That, in turn, requires a pause of the continued expansion of fossil fuel infrastructure that would undermine reductions secured through the deployment of these technologies. Similarly, the 2022 Scoping Plan to reduce GHG emissions outlines the need to significantly reduce demand for liquid petroleum and fossil fuel use by 2045.<sup>3</sup> In updating regulations, such as PAR 1178, the South Coast AQMD should consider these air quality and climate objectives and identify opportunities to further—and not undermine—those commitments.

**Finally, we urge you to reconsider our recommendation to conduct regular Fluxsense-type studies as part of the regulation.** The 2015 Fluxsense study<sup>4</sup> (published 2017) is the *only* monitoring that uncovered the drastic underestimation of VOCs and BTEX emissions at every single petroleum refinery. This type of study, conducted regularly, will be necessary to confirm whether PAR 1178 amendments have been successfully reducing VOC emissions. The South Coast AQMD expected its earlier updates to Rule 1178 to be much more restrictive of emissions than they

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<sup>2</sup> South Coast AQMD, 2022 Air Quality Management Plan (Dec. 2022) at 4-7, <http://www.aqmd.gov/docs/default-source/clean-air-plans/air-quality-management-plans/2022-air-quality-management-plan/final-2022-aqmp/final-2022-aqmp.pdf?sfvrsn=16> [archived at <https://perma.cc/2XEK-AQS9>].

<sup>3</sup> CARB, 2022 Scoping Plan for Achieving Carbon Neutrality at 2 (Nov. 2022), <https://ww2.arb.ca.gov/sites/default/files/2022-12/2022-sp.pdf> [archived at <https://perma.cc/7M4A-8CAM>].

<sup>4</sup> See generally Johan Mellqvist et al., 2015 *Emission Measurements of VOCs, NO<sub>2</sub> and SO<sub>2</sub> from the Refineries in the South Coast Air Basin Using Solar Occultation Flux and Other Optical Remote Sensing Methods* (Final Report, Apr. 2017), [http://www.aqmd.gov/docs/default-source/fenceline\\_monitoring/project\\_1/fluxsense\\_scaqmd2015\\_project1\\_finalreport\(040717\).pdf](http://www.aqmd.gov/docs/default-source/fenceline_monitoring/project_1/fluxsense_scaqmd2015_project1_finalreport(040717).pdf) [archived at <https://perma.cc/HV28-7CBB>]; CBE Decoder Factsheet (Apr. 2017), <https://www.cbecal.org/wp-content/uploads/2017/05/CBE-Decoder-Socal-Refinery-Study-Emissions-Underreported.pdf> [archived at <https://perma.cc/694N-6MU7>]. The Fluxsense study found drastically under-estimated VOC and benzene emissions for Los Angeles area refineries, likely due to storage tanks. It found normal calculations do not include degradation over time. This is likely true nationally, as indicated by a Fluxsense study in Texas that found similar results. John K. E. Johansson et al., *Emission measurements of alkenes, alkanes, SO<sub>2</sub>, and NO<sub>2</sub> from stationary sources in Southeast Texas over a 5 year period using SOF and mobile DOAS*, 119 *Journal of Geophysical Research: Atmospheres* 1973, 1983 (Feb. 2014), <https://doi.org/10.1002/2013JD020485> (attached as Ex. 1).

turned out to be. We want to ensure this will not happen again. If the South Coast AQMD cannot include this monitoring every three years, at least require it every five years to confirm the regulation is achieving the intended emission reductions.

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As detailed below, we have identified several deficiencies with PAR 1178 that must be addressed before finalizing this amended rule for adoption:

- **South Coast AQMD must require the preparation of doming plans and a verification process to assess compliance with storage tank doming timelines and to confirm whether a petroleum facility intends to obtain a permit modification to exempt certain storage tanks.** PAR 1178 establishes a compliance schedule for all doming external floating roof tanks on a lengthy schedule—by December 31, 2038.<sup>5</sup> Without the development of a plan and verification process, the public is left to speculate on petroleum facilities’ progress towards meeting doming requirements. Moreover, the public is uninformed as to whether a facility claims an exemption to limit “organic liquids stored in the tanks to lower than 3 psia” to avoid doming requirements.<sup>6</sup> Without these requirements, oversight will be difficult for both the public and regulators. Given the number of petroleum facilities and storage tanks that would be subject to these doming requirements, plans should be developed that note which external floating roof tanks would be domed and which would be exempt through permit modifications, along with the proposed timeline for making those changes. Furthermore, emission reductions may not be achieved as expeditiously as feasible, and in compliance with AB 617’s WCWL B CERP toward 50% or more reductions of VOC emissions by 2030.

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<sup>5</sup> PAR 1178(d)(5), <http://www.aqmd.gov/docs/default-source/rule-book/Proposed-Rules/1178/par-1178-preliminary-draft-rule-language.pdf?sfvrsn=6> [archived at <https://perma.cc/UK66-NN33>].

<sup>6</sup> PAR 1178 (j)(5).

- **South Coast AQMD must require that Optical Gas Imaging (OGI) measurements of leaks be made publicly available by mandating that petroleum facilities submit those recordings to the Executive Officer as part of leak reporting requirements.** Under PAR 1178, petroleum facilities are required to record visible vapors from tanks “for a minimum of 5 seconds” that must be “accurately time-stamped and *kept on-site*” as part of inspections conducted using OGI.<sup>7</sup> Petroleum facilities are required to maintain these recordings “for a minimum of 2 years” and to make them “available to the Executive Officer upon request,” which would undermine public access to this information.<sup>8</sup> Since the agency would not have custody of this information, the public would be unable to obtain these recordings through a Public Records Act request. At a minimum, petroleum facilities should be required to submit these recordings to the agency as part of their non-compliance reporting. Under PAR 1178, facilities are not required to submit OGI recordings when reporting a violation of leak requirements identified by an inspection.<sup>9</sup>
- **South Coast AQMD must establish control and monitoring measures during undefined maintenance and repair periods under subdivision (g), rather than allow petroleum facilities to pollute with impunity during these periods.** PAR 1178 waives the “Vapor Tight Condition” requirement during “preventative maintenance or repair specified in subdivision (g) of this rule.”<sup>10</sup> “Vapor Tight Condition” is defined as “a condition that exists when the reading on a portable hydrocarbon analyzer is less than 500 parts per million (ppm), expressed as methane, above background, measured using EPA Reference Method 21.”<sup>11</sup> In effect, under PAR 1178, petroleum facilities would receive an exemption from applicable emission limits and could

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<sup>7</sup> PAR 1178(f)(4), (h)(2)(D).

<sup>8</sup> PAR 1178 (h)(3)(D).

<sup>9</sup> PAR 1178(f).

<sup>10</sup> PAR 1178(d)(1)(B).

<sup>11</sup> PAR 1178(c)(45).

potentially assert an affirmative defense for releasing excess VOC emissions during maintenance and repairs. Moreover, PAR 1178 does not define what constitutes a preventative maintenance or repair, which would inevitably make enforcement difficult and allow petroleum facilities to exploit this loophole by claiming certain significant VOC releases are due to maintenance or repair activities.

- There are many problems with the vapor pressure limits and exemptions under PAR 1178. Some of these issues can be improved but are inherently less permanent and reliable than requiring BACT equipment to be installed.
  - **Recording of vapor pressure determinations are insufficient. The South Coast AQMD must mandate that petroleum facilities record True Vapor Pressure (TVP) determinations at storage tanks, which facilities are currently not required to log and disclose under the updated Rule 1178 Compliance Reports.** Throughout PAR 1178, petroleum facilities are required to make determinations of “True Vapor Pressure”, defined as “vapor pressure of a liquid at actual storage conditions.”<sup>12</sup> Under PAR 1178 test methods and procedures, TVP of organic liquids would be determined using ASTM Method D-323 for Reid Vapor Pressure (RVP) and converted to TVP.<sup>13</sup> Petroleum facilities, however, are not required to log these TVP correlations. Instead, the revised Rule 1178 Compliance Report requires only that facilities record product RVP, leaving the public to speculate as to the TVP.<sup>14</sup> Importantly, recording TVP determinations is not only key in evaluating compliance with Rule 1178, but also with Title V permit conditions that generally specify TVP requirements for storage tanks rather than RVP. Consequently, as written, PAR 1178 would make it difficult to ensure compliance with applicable requirements and undermine enforcement efforts.

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<sup>12</sup> PAR 1178(c)(43).

<sup>13</sup> PAR 1178(i).

<sup>14</sup> PAR 1178, Attachment A.

- **TVP correlations themselves can lead to inaccuracies, making them unsuitable alternatives to more stringent BACT technology installations like permanent doming of tanks.** Requirements in the rule for RVP testing (easier to perform) followed by correlation with TVP nomographs (since TVP is hard to test) can lead to inaccuracies, even when TVP determinations are properly logged. For example, **one oil industry article found that TVP determinations could be 50 to 300% off from actual TVP due to errors that can occur using standard methods that estimate TVP by correlating it with measured RVP.**<sup>15</sup> The South Coast AQMD has not demonstrated that it has set conditions equivalent to doming in its draft regulation. Standardized EPA tests are useful for many reasons, but in this case, not to exempt external floating roof tanks based on inherently less accurate measurements. Tank doming should be a high priority for the South Coast AQMD, as an inherently more reliable means to permanently cut emissions and protect public health. Indeed, **it is also required under AB 617's mandates to install BARCT at refineries.**<sup>16</sup>
- **The frequency of testing is also insufficient to ensure that high-turnover tanks meet the TVP requirement for exemption from doming.** Biannual testing to avoid a requirement to dome a tank through a permit limit of 3 psia TVP is not sufficient to ensure the tank contents stay under this limit throughout the year. For example, crude oil tanks can turn over more than 50 times a year.<sup>17</sup> The South Coast AQMD must demonstrate that RVP and TVP have no potential for changing more frequently, when

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<sup>15</sup> J.K. Henderson, *Test Method for "Actual" True Vapor Pressure of Crude Oils*, *SPE Advance Technology Series* 4 (Aug. 1996), <https://doi.org/10.2118/29740-PA> [archived at <https://perma.cc/9NNTK-PP3L>].

<sup>16</sup> See Cal. Health & Safety Code, § 40920.6(c).

<sup>17</sup> See Final Environmental Impact Report for Tesoro Los Angeles Refinery: Appendix B (SCH No. 2014091020) at B-3-139 (May 2017), <http://www.aqmd.gov/docs/default-source/ceqa/documents/permit-projects/2017/tesorolaric/appb.pdf?sfvrsn=2> [archived at <https://perma.cc/ZHU5-GD6H>]. For TANKS modeling inputs for six new crude oil tanks at 500,000 bbls each (21,000,000 gallons), Annual Turnovers are listed as 51.1. Tank turnovers can go higher.

refineries receive varying crude oil deliveries into their tanks. South Coast refineries receive crude from many nations with varying characteristics. While refineries likely tend to isolate heaviest crudes from lighter crudes in different tanks, individual tanks could still vary sufficiently to meet the exemption limit twice a year, while failing the rest of the year, hiding substantial emissions.

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We appreciate South Coast AQMD staff's consideration of these concerns. We hope the agency will make necessary revisions to address these issues to ensure compliance with PAR 1178 requirements.

Sincerely,

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# EXHIBIT 1

## RESEARCH ARTICLE

10.1002/2013JD020485

## Special Section:

Study of Houston Atmospheric Radical Precursors (SHARP)

## Key Points:

- Total VOC, SO<sub>2</sub> and NO<sub>2</sub> emission fluxes are measured from industries in Houston
- Reported VOC emissions are typically underestimated by an order of magnitude
- Meteorological variations cannot alone explain VOC emission discrepancies

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## Emission measurements of alkenes, alkanes, SO<sub>2</sub>, and NO<sub>2</sub> from stationary sources in Southeast Texas over a 5 year period using SOF and mobile DOAS

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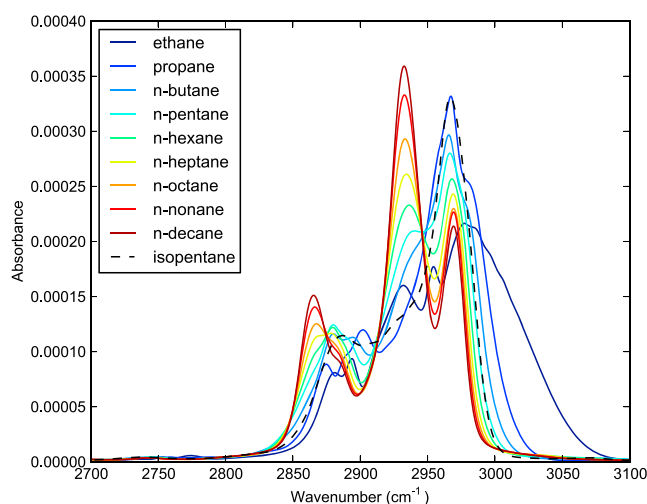
**Abstract** A mobile platform for flux measurements of VOCs (alkanes and alkenes), SO<sub>2</sub>, and NO<sub>2</sub> emissions using the Solar Occultation Flux (SOF) method and mobile differential optical absorption spectroscopy (DOAS) was used in four different studies to measure industrial emissions. The studies were carried out in several large conglomerates of oil refineries and petrochemical industries in Southeast and East Texas in 2006, 2009, 2011, and 2012. The measured alkane emissions from the Houston Ship Channel (HSC) have been fairly stable between 2006 and 2011, averaging about 11,500 kg/h, while the alkene emissions have shown greater variations. The ethene and propene emissions measured from the HSC were 1511 kg/h and 878 kg/h, respectively, in 2006, while dropping to roughly 600 kg/h for both species in 2009 and 2011. The results were compared to annual inventory emissions, showing that measured VOC emissions were typically 5–15 times higher, while for SO<sub>2</sub> and NO<sub>2</sub> the ratio was typically 0.5–2. AP-42 emission factors were used to estimate meteorological effects on alkane emissions from tanks, showing that these emissions may have been up to 35–45% higher during the studies than the annual average. A more focused study of alkene emissions from a petrochemical complex in Longview in 2012 identified two upset episodes, and the elevation of the total emissions during the measurement period due to the upsets was estimated to be approximately 20%. Both meteorological and upset effects were small compared to the factor of 5–15, suggesting that VOC emissions are systematically and substantially underestimated in current emission inventories.

### 1. Introduction

The Houston-Galveston-Brazoria area, which includes eight counties in the vicinity of Houston, Texas, is a nonattainment area for the 2008 National Ambient Air Quality Standard for ozone. Ground-level ozone is formed through a chemical process in the atmosphere, fueled by sunlight and emissions of volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>). Many large metropolitan areas in the U.S. have trouble meeting ozone standards since urban areas generally have a high concentration of anthropogenic sources of VOCs and NO<sub>x</sub>. However, the Houston area is special due to its high concentration of refineries and petrochemical industries. These industries are primarily associated with VOC emissions but also have a significant NO<sub>x</sub> contribution.

Measurements during the 2000 TexAQs (Texas Air Quality Study) and the 2006 TexAQs II indicated that the best emission inventories available at the time significantly underestimate industrial VOC emissions in Houston [Kleinman et al., 2002; Karl et al., 2003; Ryerson et al., 2003; Wert et al., 2003; Jobson et al., 2004; De Gouw et al., 2009; Parrish et al., 2009; Mellqvist et al., 2010b; Washenfelder et al., 2010]. Several studies also concluded that industrial VOC emissions contribute significantly to ozone formation [Kleinman et al., 2002; Ryerson et al., 2003; Wert et al., 2003; Jobson et al., 2004; Gilman et al., 2009; Kim et al., 2011].

Industries are required to report the emissions from their activities to the state governments according to guidelines from the United States Environmental Protection Agency (EPA). The industries typically estimate their emissions with emission factors calculated using methods and formulas described in AP-42, *Compilation of Air Pollutant Emission Factors* [United States Environmental Protection Agency (USEPA), 2013]. VOC emissions from refineries and petrochemical industries are typically dominated by evaporative losses from storage tanks and process equipment. NO<sub>x</sub> and SO<sub>2</sub> emissions, on the other hand, primarily come from external



**Figure 1.** Absorbance spectra for  $1 \text{ mg/m}^2$  of each of the *n*-alkanes from ethane to *n*-decane and isopentane degraded to  $8 \text{ cm}^{-1}$  spectral resolution.

combustion sources. This difference in types of emission sources makes VOC emission estimates inherently less reliable. External combustion is generally intentional and takes place in a limited number of places in a facility, often under controlled conditions with emissions released through flue gas channels which can be monitored to verify emission. Flares are an exception though. Estimates of  $\text{SO}_2$  emissions from combustion are arguably even more reliable due to sulfur mass balance constraints; i.e., they are limited by the amount of sulfur in the burnt fuel. Evaporative losses of VOCs, on the other hand, 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 other indication. These types of irregular emissions can remain unnoticed if measurements of diffuse emissions are not made. Methods for quantitatively measuring these types of VOC emissions exist but are intrinsically more difficult due to the diffuse nature and the large number (tens of thousands) of potential sources. Estimates of VOC emissions from refineries and petrochemical industries 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 0.01–0.02%) of its throughput, emissions would remain insignificant in any type of mass balance even if they were many times larger than reported.

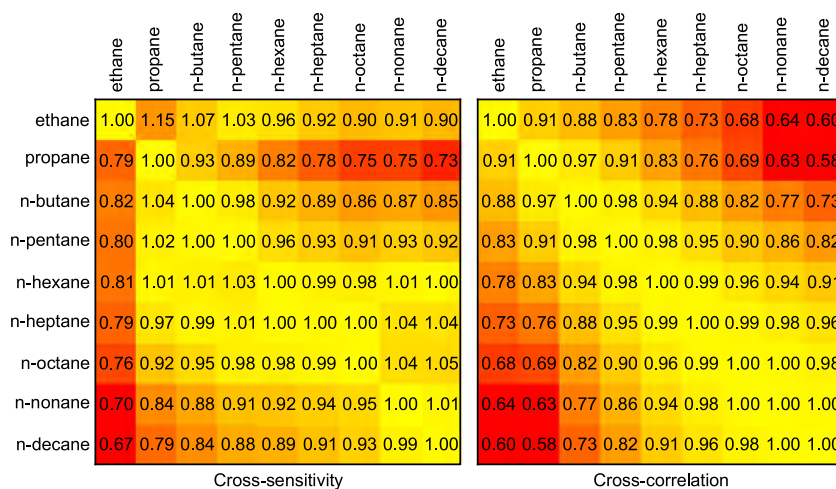
In this paper we present measurements of VOCs,  $\text{SO}_2$ , and  $\text{NO}_2$  from four campaigns in Southeast and East Texas carried out during 2006, 2009, 2011, and 2012. Additionally, a Solar Occultation Flux (SOF) spectral evaluation routine for alkanes is presented in detail and evaluated on the basis of its ability to quantify alkane mass columns in typical VOC mixtures from refineries. The measurement results are compared to emissions reported to the State of Texas Air Reporting System (STARS), and the representativeness of the results is discussed in relation to meteorological conditions, based on the use of the AP-42 emission factors.

## 2. Methods

All emission measurements presented in this article are based on the two methods, Solar Occultation Flux (SOF) and mobile DOAS (differential optical absorption spectroscopy). Both of them are based on the same principles for measuring total fluxes, instead of just concentrations, of industrial emission plumes. They take advantage of the ability of open path absorption spectroscopy methods to measure column concentrations. An emission flux is calculated from a series of column concentrations measured while traversing a plume crosswind together with some form of wind velocity measurement. The difference between the methods is mainly in the spectroscopy. SOF [Mellqvist *et al.*, 2010b] is based on infrared measurements of direct sunlight, while mobile DOAS [Galle *et al.*, 2002] is based on UV measurements of scattered sunlight.

### 2.1. Solar Occultation Flux

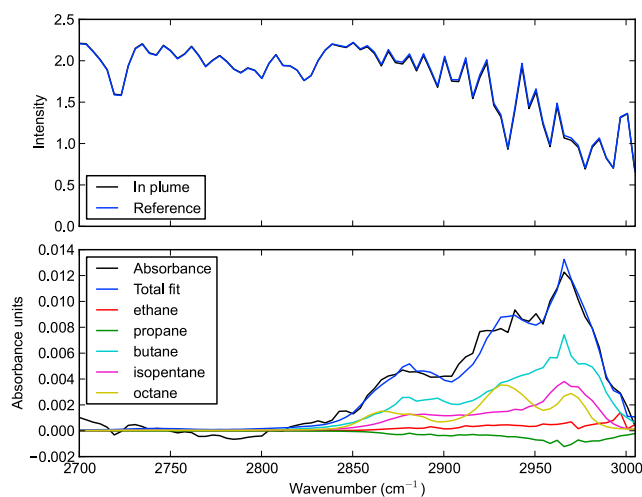
The Solar Occultation Flux method (SOF) is based on infrared measurements of direct sunlight from a mobile platform, typically a small truck, using a Fourier transform infrared (FTIR) spectrometer with a solar tracker.



**Figure 2.** Cross sensitivity and cross correlation between each pair of *n*-alkanes from ethane to *n*-decane. The cross sensitivity is the ratio of the evaluated mass column to the true mass column, when evaluating the species on the y scale as the species on the x scale in a simple linear least squares retrieval in the interval 2700–3005  $\text{cm}^{-1}$ . The cross correlation is the correlation coefficient between the two absorbance spectra in the same interval.

The solar tracker continuously guides the sunlight into the spectrometer as the truck moves and turns, and infrared spectra are recorded consecutively. These spectra are evaluated for absorption by molecular species in the industrial emission plume. A detailed description of the principles for SOF measurements and its application for measurements of ethene and propene is given in *Mellqvist et al.* [2010b].

In addition to ethene and propene, this study focuses on SOF measurements of alkanes. The evaluation of ethene and propene are based on narrow absorption lines in the interval 900–1000  $\text{cm}^{-1}$  which are very specific to each species, while the alkane evaluation is based on a much broader absorption band in the region 2700–3000  $\text{cm}^{-1}$ . This is called the C-H stretch band, since it corresponds to vibrational excitations of carbon-hydrogen bonds. Since C-H bonds are present in most VOCs, they typically have absorption features in this band. Figure 1 shows the absorbance spectra for all *n*-alkanes from ethane to decane downgraded to a spectral resolution of 8  $\text{cm}^{-1}$ , which is typically used for these measurements. They are all fairly similar, and most of the variations are among the shorter alkanes, while the shape seems to almost converge the longer the carbon chain gets. Additionally, all alkanes have almost the same total absorption, i.e., the area under each absorbance spectra, for equal mass columns. These properties make it possible to approximate the combined absorption of any mix of alkanes fairly well with the combination of just a few of their absorbance spectra, and this combination will also approximate the total mass column of the alkane mix. This is important because the number of absorption spectra included in a spectral fitting routine has to be limited to avoid numerical instability, overfitting, and sensitivity to noise. To determine which absorption spectra to include in the evaluation, their similarities were quantified by pairwise calculation of cross sensitivity, i.e., how well the mass column of one alkane is approximated by a simple linear least squares fit to the absorbance spectrum of the other, and cross correlation. The cross sensitivity is a measure of how well a species approximates the mass column of another species in a spectral evaluation, while cross correlation is a measure of how good the spectral fit would be. In a spectral evaluation with several species included, absorption by another species is most likely to be approximated by the species it has high cross correlation with, since the spectral evaluation strives to optimize the spectral fit. The result of this is presented in Figure 2. This confirms the picture that the largest variations are among the shorter alkanes, while the longer ones are more similar to each other. For this reason it is more important to include the absorbance spectra of several shorter alkanes in the spectral fitting routine, while a single long alkane is sufficient to approximate the rest of them. This is also additionally motivated by the fact that gaseous emissions are typically dominated by shorter alkanes since they are more volatile. Accurate determination of alkane columns is further complicated by the presence of branched alkanes and cycloalkanes, which diverge slightly more in cross sensitivity from straight alkanes of similar carbon number. Isopentane is also included in Figure 1 as an example of this, showing that it is fairly similar in shape to straight alkanes but with somewhat lower total absorption, i.e., the area under the graph. However,



**Figure 3.** (top) SOF spectrum measured in a VOC plume and a reference spectrum measured outside of the plume. (bottom) Absorbance in the plume relative to the reference, fitted absorbance, and the fitted components of ethane, propane, butane, isopentane, and octane.

since the fraction of branched alkanes and cycloalkanes in VOC emissions from petroleum industries is typically low, the error of fitting them as straight alkanes is fairly limited.

A combination of ethane, propane, *n*-butane, isopentane, and *n*-octane was chosen to be included in the spectral fitting routine for the alkane measurements in this paper. The inclusion of isopentane was motivated by its relatively high abundance in VOC emissions compared to other branched alkanes and cycloalkanes. Absorption spectra for these species from the Pacific Northwest National Laboratories database [Sharpe *et al.*, 2004] were downgraded to  $8\text{ cm}^{-1}$  resolution and were fitted by multivariate regression to the absorbance in the interval  $2700\text{--}3005\text{ cm}^{-1}$ . Absorption spectra for water and methane, synthesized with line parameters from the HITRAN database [Rothman *et al.*, 2005], were also included in the fitting routine, which was performed in the QESOF software [Kihlman, 2005]. The total alkane mass column was calculated as the sum of the fitted mass columns of all the included alkanes. Figure 3 shows an example of a spectral fit and the alkane components fitted. The  $8\text{ cm}^{-1}$  spectral resolution was empirically determined to be a good compromise between measurement signal-to-noise, sampling time, and sensitivity to spectral interference from other species.

In order to validate the accuracy of the alkane mass columns determined by this spectral fitting routine, data [Texas Commission on Environmental Quality (TCEQ), 2013] from an automated gas chromatograph in a Continuous Ambient Monitoring Station (CAMS), C169 located close to the Houston Ship Channel (HSC) ( $29.7062492^\circ$ ,  $-95.2611301^\circ$ ) and operated by TCEQ (Texas Commission on Environmental Quality), were used to approximate typical refinery VOC compositions in Houston. Data from September 2006, the time of the first measurement campaign, was filtered for hourly averages where wind speed was above  $1.4\text{ m/s}$  and wind direction was in the interval  $69^\circ\text{--}87^\circ$ . In these wind directions the emissions from refineries in the HSC should dominate the VOC concentrations measured at CAMS 169. Seven such instances were found during September 2006. For each of these instances an artificial solar spectrum was synthesized with absorption by different VOCs in the proportions measured by the auto-GC. These spectra were downgraded to the resolution of the spectral retrieval,  $8\text{ cm}^{-1}$ , and evaluated by the spectral fitting routine described above. The evaluated alkane mass columns were then compared to that used for synthesizing the solar spectra. The results of this are presented in Table 1. The evaluated alkane mass overestimated the true alkane mass by 3–7%, which is small compared to the uncertainty in flux calculations due to wind speed uncertainty. This overestimation is due to a combination of the errors of fitting all alkanes to a finite set and the spectral interference from other VOCs with weaker absorption in the same region.

Methane is typically treated separately from other VOC emissions because it has much lower ozone formation potential. Fortunately, the alkane evaluation routine described above has low sensitivity to methane. Methane has absorption in this band but primarily in narrow lines. Because of the relatively high background concentration of methane, these lines are practically depleted of light after passing through the full atmospheric column. This is illustrated in Figure 4. Due to the nonlinearity of Beer-Lamberts law at such strong

**Table 1.** VOC Composition in the Plume Downwind of a Large Refinery Complex in the HSC During Seven Episodes in the 2006 Study as Measured by an Auto-GC at CAMS 169<sup>a</sup>

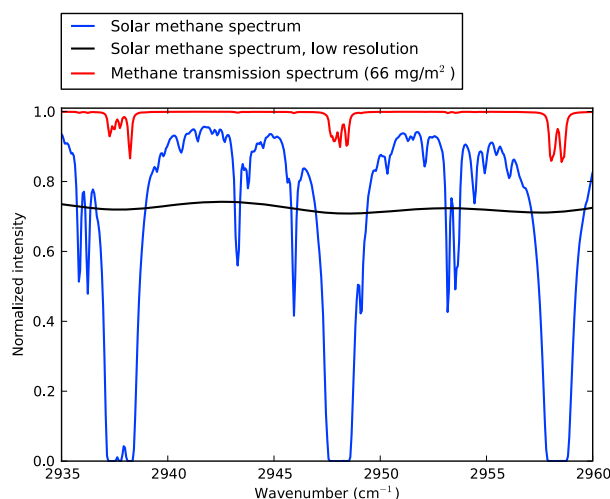
Molar mass	Date and Time							
	2 Sep 2006, 19:00	4 Sep 2006, 17:00	9 Sep 2006, 21:00	9 Sep 2006, 22:00	20 Sep 2006, 11:00	20 Sep 2006, 12:00	26 Sep 2006, 16:00	
Wind speed (m/s)	1.70	1.43	2.28	1.88	2.55	2.86	1.43	
Wind direction (deg)	76	72	87	86	69	76	77	
Units	g/mole	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	
<b>Alkanes</b>								
Ethane	30.1	17.93	2.59	3.46	4.59	10.51	7.52	
Propane	44.1	20.20	1.23	1.71	2.22	9.40	4.84	
<i>n</i> -Butane	58.1	12.85	1.14	0.87	0.58	8.74	4.97	
<i>i</i> -Butane	58.1	4.87	0.37	0.68	0.60	3.84	2.41	
cyc-Pentane	70.1	1.01	0.09	0.16	0.04	0.43	0.23	
<i>i</i> -Pentane	72.2	16.07	1.35	1.43	0.47	6.69	4.17	
<i>n</i> -Pentane	72.2	12.52	0.80	0.94	0.24	4.23	2.37	
cyc-Hexane	84.2	2.17	0.09	0.14	0.04	0.49	0.24	
2,2-Dimethylbutane	86.2	0.33	0.04	0.08	0.03	0.20	0.11	
<i>n</i> -Hexane	86.2	2.40	0.18	0.48	0.14	1.21	0.71	
3-me-Hexane	100.2	0.45	0.05	0.14	0.05	0.32	0.22	
<i>n</i> -Heptane	100.2	0.65	0.05	0.13	0.04	0.33	0.21	
<i>n</i> -Octane	114.2	0.31	0.04	0.09	0.02	0.19	0.11	
<i>i</i> -Octane	114.2	0.36	0.10	0.18	0.08	0.58	0.24	
<i>n</i> -Nonane	128.2	0.07	0.01	0.02	0.01	0.05	0.03	
<i>n</i> -Decane	142.2	0.04	0.01	0.02	0.03	0.05	0.03	
<b>Alkenes</b>								
Ethylene	28.0	4.16	0.46	0.75	0.50	1.96	1.51	
Propylene	42.1	3.94	0.24	0.99	0.92	1.66	0.90	
1,3-Butadiene	54.1	0.44	0.40	0.16	0.18	0.12	0.12	
<i>t</i> -2-Butene	56.1	0.68	0.13	0.09	0.07	0.12	0.10	
1-Butene	56.1	0.65	0.14	0.06	0.03	0.36	0.20	
<i>c</i> -2-Butene	56.1	0.52	0.07	0.06	0.04	0.09	0.07	
Isoprene	68.1	0.20	0.24	0.01	0.01	0.22	0.10	
<i>t</i> -2-Pentene	70.1	0.69	0.04	0.07	0.02	0.08	0.05	
1-Pentene	70.1	1.07	0.06	0.05	0.02	0.12	0.08	
<i>c</i> -2-Pentene	70.1	0.32	0.02	0.04	0.01	0.04	0.03	
Styrene	104.1	0.07	0.00	0.29	3.58	0.02	0.11	
<b>Aromatics</b>								
Benzene	78.1	0.82	0.12	0.21	0.11	0.64	0.57	
Toluene	92.1	2.40	0.26	0.49	0.27	0.70	0.54	
<i>m</i> + <i>p</i> -Xylene	106.1	0.42	0.07	0.24	0.10	0.25	0.17	
<i>o</i> -Xylene	106.1	0.13	0.02	0.10	0.10	0.10	0.08	
Ethylbenzene	106.1	0.18	0.03	0.10	0.09	0.09	0.06	
<b>Mass fractions</b>								
Alkanes		84.7%	76.4%	71.1%	44.0%	87.9%	85.3%	70.4%
Alkenes		9.4%	15.5%	15.5%	48.9%	6.6%	7.6%	16.3%
Aromatics		5.9%	8.1%	13.4%	7.0%	5.4%	7.1%	13.4%
Retrieved/true alkane mass		1.044	1.051	1.062	1.058	1.035	1.036	1.065

<sup>a</sup>The uncertainty of the alkane spectral retrieval has been estimated by applying it to solar spectra with absorption by VOCs added synthetically proportionally to the measured concentrations. The mass ratios between the evaluated alkane columns and the total alkane columns added synthetically are given at the bottom of the table. The mass fractions of alkanes, alkenes, and aromatics are also presented to give an overview of the composition.

absorption, the apparent absorption of additional methane at  $8\text{ cm}^{-1}$  resolution is approximately a factor of 17 lower than it would be without the atmospheric methane background column. The absorption spectrum of methane is still included in the alkane spectral fitting routine but mainly to improve the spectral fit and not to quantify methane. Quantitative measurement of atmospheric methane using solar FTIR is possible but generally requires high-resolution measurements [Angelbratt *et al.*, 2011].

## 2.2. Mobile DOAS

For mobile DOAS measurements UV spectra of solar light scattered in the atmosphere are measured with a UV spectrometer, typically a Czerny-Turner spectrometer with a CCD detector. The spectrometer is typically connected



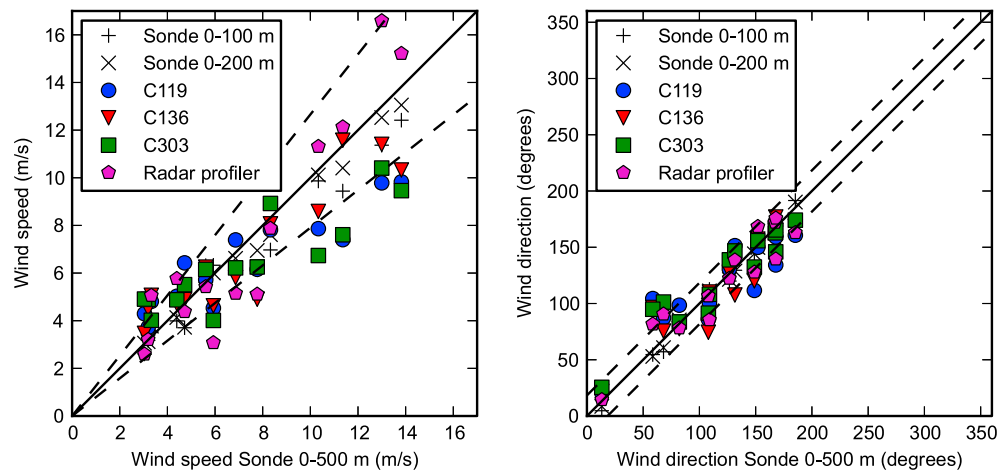
**Figure 4.** High-resolution solar spectrum (blue) after passing through the full atmospheric methane column and the same solar spectrum downgraded to a resolution of  $8\text{ cm}^{-1}$  (black). Although not obvious from the low-resolution spectrum, the strong absorption lines are depleted of light.

with a light guide to a zenith-looking telescope. The principles for mobile DOAS measurements are described in detail by *Galle et al.* [2002], *Johansson et al.* [2008, 2009], *Rivera et al.* [2009, 2010], and *Johansson et al.* [2014] together with its application for measuring  $\text{SO}_2$  and  $\text{NO}_2$  in *Johansson et al.* [2008] and *Rivera et al.* [2009, 2010] as well as formaldehyde (HCHO) in *Johansson et al.* [2008, 2009], *Rivera et al.* [2010], and *Johansson et al.* [2014].

The measurements in 2009, 2011, and 2012 used a 303 mm focal length Czerny-Turner spectrometer (ANDOR Shamrock 303i) with a  $1024 \times 255$  pixel, thermoelectrically cooled CCD detector (Newton DU920N-BU2) which was connected with a liquid light guide, 3 mm in diameter, to a zenith-looking quartz telescope with a 75 mm diameter and a 20 mrad field of view. The holographic grating used (1800 grooves/mm) together with a  $300\text{ }\mu\text{m}$  entrance slit gave a 0.63 nm spectral resolution in the 309–351 nm wavelength region that the CCD was set to cover. The telescope was equipped with an optical band pass filter (Hoya), blocking wavelengths above 380 nm to reduce stray light in the spectrometer. This is a highly light-sensitive DOAS system originally developed for airborne measurements of ship emissions using downward looking DOAS [*Berg et al.*, 2012]. This was the same system and setup as in *Johansson et al.* [2014], and  $\text{NO}_2$  was evaluated with the same spectral fitting routine as formaldehyde in that paper. This routine involved fitting cross sections for HCHO [*Cantrell et al.*, 1990],  $\text{NO}_2$  [*Vandaele et al.*, 1998],  $\text{O}_3$  [*Burrows et al.*, 1999],  $(\text{O}_2)_2$  collision complex [*Hermans et al.*, 1999], a ring spectrum, and a polynomial of order 3 in the 324–350 nm spectral window. Wavelength calibration of the spectrometer was made with respect to the Fraunhofer lines present in all solar spectra.  $\text{SO}_2$  was also evaluated from the same spectra using a 310–325 nm spectral window where  $\text{SO}_2$  [*Bogumil et al.*, 2003],  $\text{O}_3$  [*Burrows et al.*, 1999], a ring spectrum, and a polynomial of order 3 were fitted. Apart from spectral window and cross sections fitted, the two routines were identical. The QDOAS software [*Fayt*, 2011] was used for the wavelength calibration, degradation of cross sections, ring spectrum synthesis, and spectral fitting. Further details of the  $\text{NO}_2$ /HCHO evaluation routine can be found in *Johansson et al.* [2014]. During the 2006 study, a commercial mini-DOAS system was used instead of the one described above. This system collected less light and therefore required longer exposure times to achieve the same accuracy. The mobile DOAS results from this study was previously published in *Rivera et al.* [2010] together with a complete description of the system used.

### 2.3. Wind Measurements

Accurate wind information is of major importance for flux calculations for both SOF and mobile DOAS. Even though considerable effort is put into obtaining high-quality wind measurements, wind uncertainty is typically the largest error source for flux measurements. Measurements of wind height profiles throughout the boundary layer were taken during all four campaigns using GPS tracking radiosondes launched with helium balloons. Since the number of radiosonde launches on a given measurement day varied between five and zero, profiles derived from these launches were not available sufficiently close in time to the measurement



**Figure 5.** Comparison of different wind measurements in the Beaumont/Port Arthur area during the 2011 study. For each radiosonde launch the wind profile averages from ground up to 100 m and 200 m and simultaneous rescaled measurements at the ground stations C119, C136, and C303 and from a local radar profiler are plotted against the profile average from ground up to 500 m. The solid line represents perfect agreement, and the dashed lines show plus/minus the average of the standard deviations of the differences (relative differences for the wind speed) between the ground sources and the radiosonde profile average.

transects. Hence, the radiosonde data were complemented by wind measurements from local ground sites, mainly from the TCEQ-operated network of Continuous Ambient Monitoring Stations (CAMS) [TCEQ, 2013]. Ground wind speed data were normalized to radiosonde measurements to compensate for systematic wind speed differences as a function of height. Average winds over the first 500 m (350 m for the 2012 Longview study) of the wind profiles were used both for flux calculations and for normalization of ground wind data, as described in Mellqvist *et al.* [2010b]. Flux calculations were made using height profile averages when available sufficiently close in time to the measurement transect and normalized ground wind data for other cases. The variations between the different wind data sets were used to estimate the wind uncertainty. This is not a measurement uncertainty but rather the uncertainty due to the variation in the wind on the spatial and temporal scales that the wind measurements differ from the time and place of the column measurements. As an example, Figure 5 shows a comparison between height profile averages and simultaneous normalized ground wind measurements from CAMS sites in the Beaumont/Port Arthur area during the 2011 study. The estimated wind uncertainties based on these comparisons are presented in Table 2 for the different studies. The range of uncertainties given represents the  $1\sigma$  variabilities of a number of ground wind stations compared to sonde profile averages. The estimated uncertainties were similar in most years, with the exception of 2012 in Longview, where especially the wind direction uncertainty was larger. This was suspected to have been at least partly caused by measurement errors in some of the ground wind measurements.

**2.4. Emission Inventories**

Emission inventory data were extracted from the STARS (State of Texas Air Reporting System) emission inventory for comparison to the measured emission rates. Emissions are reported to STARS by the industries on an annual basis and are typically based on calculations using emission factor formulas such as found in AP-42, *Compilation of Air Pollutant Emission Factors* [USEPA, 2013]. Data for 2006, 2009, and 2011 was extracted,

**Table 2.** Wind Speed and Wind Direction Uncertainties for the Four Studies as Estimated From the Variation Between Sonde Profile Averages and Normalized Ground Wind Measurements

Year	Wind Speed Uncertainty	Wind Direction Uncertainty
2006	15–27%	11–33°
2009	11–29%	10–26°
2011	16–30%	11–23°
2012	25–34%	30–34°

and total emissions of the species of interest were computed as the sum of all point source emissions within each studied area. Emission inventories were not yet available for 2012. Speciation in the emission inventories did not perfectly match the speciation of the measurements. For comparison with the SOF alkane measurements, all emissions speciated as either alkanes or alcohols were added, as well as unspciated VOCs and vaguely speciated VOCs, such as “crude oil” and “naphtha.” Alcohols were included since they typically



**Table 3.** Total Number of Sites and Sources and Total Reported Average Emissions in the Emission Inventories for Harris County for All Measured Species and for the Years of the Studies

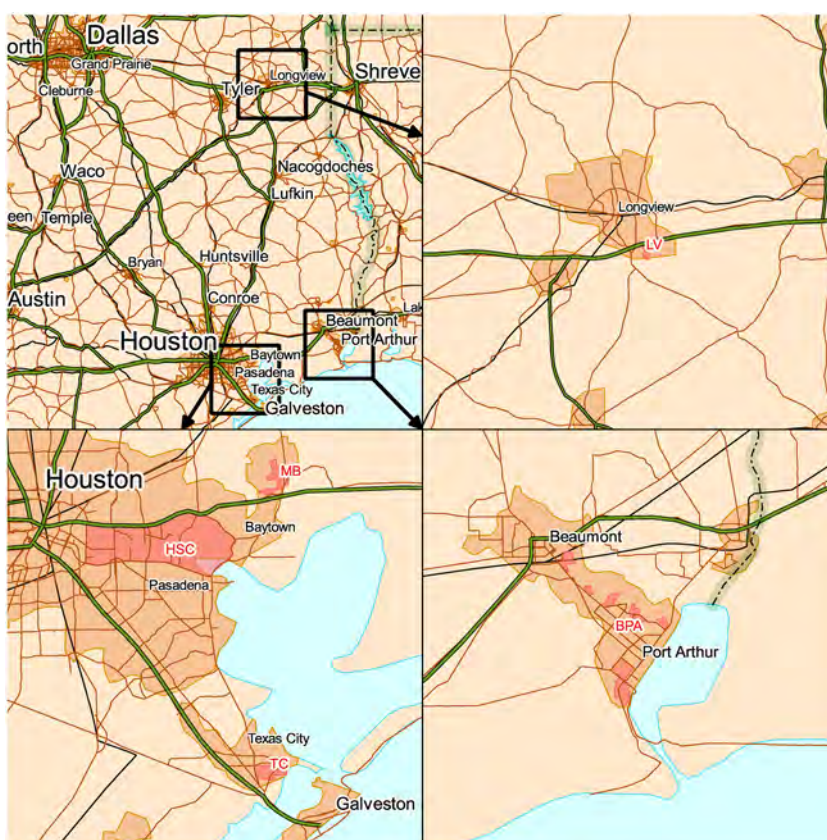
Species	Number of Sites			Number of Sources			Total Emissions (kg/h)		
	2006	2009	2011	2006	2009	2011	2006	2009	2011
Alkanes	261	262	266	10,052	8,398	8,822	1,597	1,224	1,293
Ethene	49	41	51	1,055	798	830	123	104	88
Propene	50	46	53	1,148	844	853	179	102	92
NO <sub>x</sub>	228	234	240	2,449	2,255	2,331	3,241	1,877	1,664
SO <sub>2</sub>	203	207	210	2,192	1,957	2,011	2,730	2,004	1,256

have absorption cross sections similar in shape and strength to alkanes in the C-H stretch spectral region. The unspiciated and vaguely spiciated VOCs were included since they are probably dominated by alkanes in general but may contain some species that the alkane measurements are not sensitive to. NO<sub>x</sub> emissions are reported to the inventories, while only NO<sub>2</sub> is measured with mobile DOAS. According to airborne measurement carried out in parallel to the SOF measurements during the 2006 study [Rivera *et al.*, 2010], the typical NO<sub>2</sub>/NO<sub>x</sub> ratio was 0.75, which suggests that measured NO<sub>2</sub> emissions should be expected to be on average 25% lower than the reported emissions. The measured emissions of ethene, propene, and SO<sub>2</sub> were all possible to compare directly to the equivalent inventory species. Table 3 shows the total number of industrial sites and point sources within those sites reporting emissions of the species of interest to the inventories for Harris County, which contains all of the HSC and parts of Mont Belvieu, in 2006, 2009, and 2011. Alkane emissions (including alcohols and unspiciated VOC) are the most common, and almost every site reports something in this category, while ethene and propene are significantly less common. The number of point sources has stayed relatively constant, although there seems to have been a noticeable dip from 2006 to 2009. To what extent this represents changes in operations, as opposed to changes in reporting procedures, is not known.

The emissions are reported on an annual basis so even when converted to kg/h they should be thought of as annual average emissions. Since there can be large variations in emissions from a source within a year, instantaneous emissions cannot be expected to always match the annual average emissions. However, since each area contains a large number of sources in several independently operated facilities and measurements have been performed on multiple days and in different years, the measured emission should at least be expected to be roughly the same as the reported annual average emissions on average.

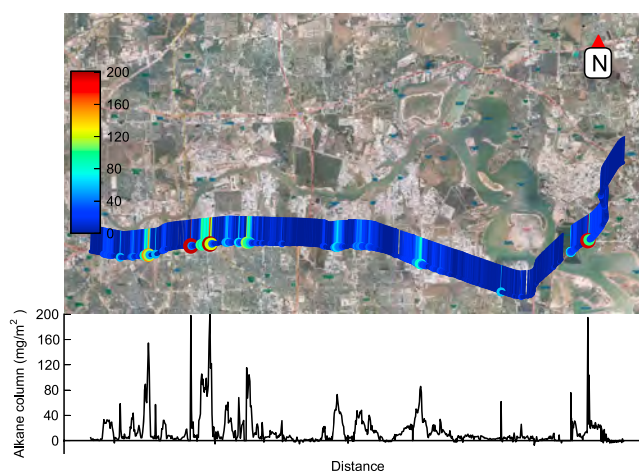
### 3. Results

The measurement results in this article were aggregated from four different studies of industrial emissions performed in Southeast and East Texas in the period 2006–2012. A map of the region is shown in Figure 6. The first study was a part of the Second Texas Air Quality Study (TexAQ5 II) [Parrish *et al.*, 2009], and measurements lasted from August to September 2006. This study tried to cover as many refinery and petrochemical industry areas in the Greater Houston area as possible. As a result, the total number of measurements for each area was fairly low. An example of an alkane measurement series from this study is shown in Figure 7. This measurement was performed on 25 September 2006 in Houston Ship Channel, and separate plumes from a large number of facilities can easily be distinguished in the northerly wind. The second study was a part of the Study of Houston Atmospheric Radical Precursors [Lefer, 2009], and measurements lasted from April to June 2009. In this study, the measurements were focused on three areas: the HSC, Mont Belvieu, and Texas City. This allowed for a larger number of measurements, spread over more days, to be collected. Figure 8 shows an example of a combined alkane and alkene measurement series from this study. This measurement was performed in Mont Belvieu on 5 June 2009, and three separate plumes are detected. The simultaneous measurements of alkane, ethene, and propene suggest that they are only partly coemitted, and especially propene seems to have a separate source. The third study, lasting from April to May 2011, was a stand-alone field study covering the same areas as in 2009, as well as the Beaumont/Port Arthur area. A single day of measurements was also conducted at a petrochemical complex in Longview. An example of an alkane measurement series from this study is shown in Figure 9. This measurement was performed on 3 May 2011 and covered a number of the largest alkane emission sources in the Beaumont/Port Arthur area but not all of them. The fourth study was performed during May 2012 and was focused entirely on the

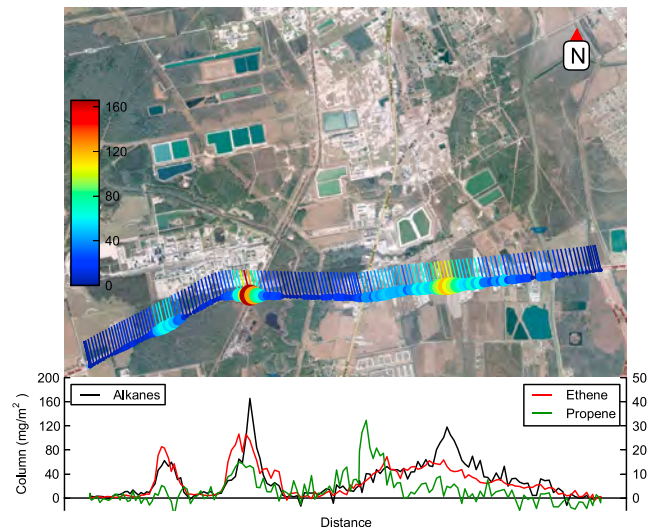


**Figure 6.** Map of Southeastern and Eastern Texas with zoomed in boxes around the areas studied. The areas are marked in red and denoted by their abbreviated names.

petrochemical complex in Longview. This allowed for a comprehensive set of measurements to be collected, giving a clearer picture of day-to-day variations. Figure 10 shows an example of a combined alkene and  $\text{NO}_2$  measurement series from this study. This measurement was performed at the petrochemical complex on 7 May 2012. The measurement series for ethene and propene are closely correlated, but there is a clear spatial



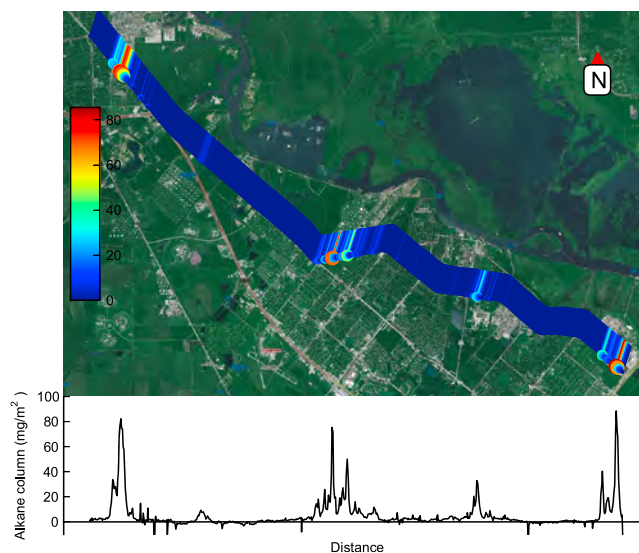
**Figure 7.** Alkane measurement transect covering all of the Houston Ship Channel (HSC) performed on 25 September 2006. Each measurement is indicated on the map with a circle and a line. The size and color of the circle indicates the magnitude of the alkane column measured, and the line indicates the direction the wind is blowing from. Below the map is a plot of the alkane column as a function of crosswind distance. This transect provided one alkane flux measurement for the HSC area.



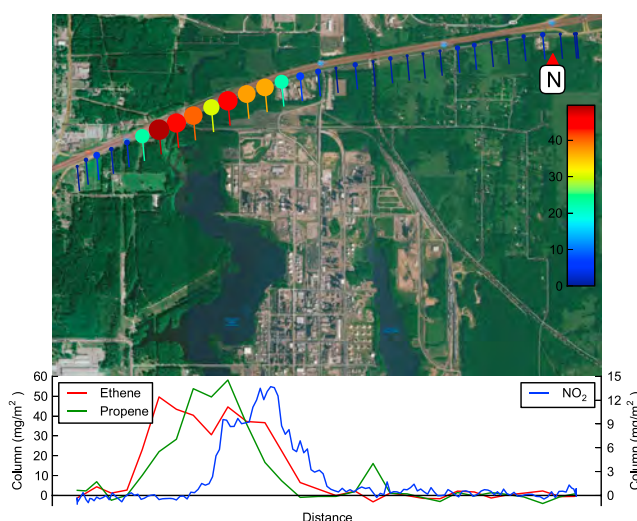
**Figure 8.** Measurement transect of alkanes, ethene, and propene covering all of Mont Belvieu performed on 5 June 2009. Each measurement is indicated on the map with a circle and a line. The size and color of the circle indicates the magnitude of the alkane column measured, and the line indicates the direction the wind is blowing from. Below the map is a plot of the columns of all species as a function of crosswind distance. This transect provided one flux measurement each for alkanes, ethene, and propene from Mont Belvieu.

separation between them and the NO<sub>2</sub> plume. However, this is most likely primarily caused by the different measurement angles of SOF and mobile DOAS. Ethene and propene are measured with SOF, which measures along the path of the direct sunlight, while NO<sub>2</sub> is measured with mobile DOAS, which measures in the zenith direction. This measurement was made in the morning when the sun was fairly low and in the east, which makes the alkene plume appear further to the west. Detailed results from all four studies are presented in Mellqvist *et al.* [2010b, 2007, 2010a] and Johansson *et al.* [2011, 2012].

The measurement results from all these studies have been aggregated to give an overview and enable comparison over time and between the different areas. These aggregated results are presented in Table 4



**Figure 9.** Alkane measurement transect covering a number of industries in the Beaumont/Port Arthur area performed on 3 May 2011. Each measurement is indicated on the map with a circle and a line. The size and color of the circle indicates the magnitude of the alkane column measured, and the line indicates the direction the wind is blowing from. Below the map is a plot of the alkane column as a function of crosswind distance. This transect provided one alkane flux measurement each for five subareas in Beaumont/Port Arthur.



**Figure 10.** Measurement transect of ethene, propene, and  $\text{NO}_2$  covering the petrochemical complex in Longview performed on 7 May 2012. Each measurement is indicated on the map with a circle and a line. The size and color of the circle indicates the magnitude of the ethene column measured, and the line indicates the direction the wind is blowing from. Below the map is a plot of the columns of all species as a function of crosswind distance. This transect provided a flux measurement each for ethene, propene, and  $\text{NO}_2$  from Longview.

together with annual average emissions reported to the emission inventories for the corresponding areas. For each area, species and year, the table shows the total number of measurements, mean and standard deviation of the emission flux measured, and the reported annual average emission. In some cases, total emissions for an area was calculated as a sum of emissions from subareas and the number of flux measurements were not the same for all subareas. For these cases, mean emissions from the subareas were summed, standard deviations were root-sum-squared, and the number of total flux measurements is given as a range from the lowest number of measurements on a subarea to the highest. Reported emissions are the sum of the annual routine emissions for all point sources within an area, converted to average hourly emissions.

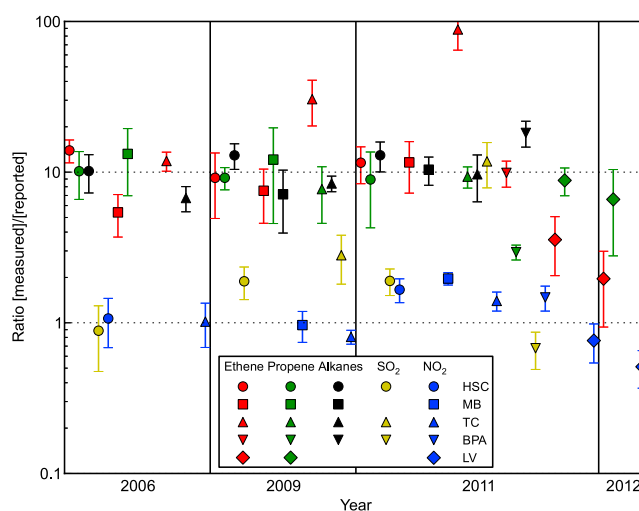
Many emissions seem to have been quite stable over the years. The mean total alkane emissions from the HSC have been within  $\pm 10\%$  of 11,500 kg/h for all three studies. At the same time there are some large differences from year to year. The total propene emissions from the HSC, for example, were approximately 1500 kg/h in 2006 but dropped to roughly 600 kg/h in 2009 and 2011. However, as described in more detail in *Mellqvist et al.* [2010b], the variability in the propene emissions measured from the HSC in 2006 was exceptionally large, indicating temporary upset emissions. Despite some significant variations from year to year and from area to area, there is a clear pattern of measured VOC emissions (alkanes, ethene, and propene) exceeding reported emissions with almost an order of magnitude on average, while no similar pattern exists for  $\text{SO}_2$  and  $\text{NO}_2$ . This pattern is highlighted in Figure 11, where the ratios between measured emissions and reported annual average emissions have been plotted for each year, species, and area. Reported emissions for 2011 were used for the 2012 ratios, since 2012 data were not yet available. Most ratios for  $\text{SO}_2$  and  $\text{NO}_2$  emissions are gathered fairly close to 1, while the ratios for alkanes, ethene, and propene are mostly within the interval of 5–10. There are of course differences between the areas and the years, but they are generally dwarfed by the difference between the species. The most striking exceptions to the overall pattern are the  $\text{SO}_2$  emissions from Texas City. The reported  $\text{SO}_2$  emissions from Texas City have steadily declined during the period of these studies, but no such decrease has been observed in the measurements. Instead, the measured mean emissions increased from 2009 to 2011, giving a measured to reported ratio of almost 12 in 2011. However, all  $\text{SO}_2$  measurements in Texas City in 2011 were performed during a single day, which makes this comparison very sensitive to short-term variations. The unusually large discrepancy in 2011  $\text{SO}_2$  emissions from Texas City might be attributable to large nonroutine emissions during that single day. A large proportion of reported  $\text{SO}_2$  emissions in Texas City are attributed to flares, which might have significant variability. Measurement with Multi-Axis DOAS [Stutz et al., 2011] were performed in parallel with the mobile DOAS measurements during the 2009 study and estimated the average  $\text{SO}_2$  emissions during the period to be 510 kg/h, approximately halfway between the mobile DOAS result and the reported annual emissions.

**Table 4.** Summary of All Total Flux Measurements for Each Area, Species, and Year<sup>a</sup>

Area	Species	2006					2009					2011					2012				
		N	Mean	Std	EI	N	Mean	Std	EI	N	Mean	Std	EI	N	Mean	Std	EI	N	Mean	Std	EI
Houston Ship Channel	Ethene	4	878	152	63	6	614	284	67	4-14	612	168	53	-	-	-	-	-	-	-	-
	Propene	3	1,511	529	149	4	642	108	70	1-9	563 <sup>b</sup>	294	63	-	-	-	-	-	-	-	-
	Alkanes	3	12,276	3,491	1,208	3	10,522	2,032	814	5	11,569	2,598	894	-	-	-	-	-	-	-	-
	SO <sub>2</sub>	3	2,277	1,056	2,570	10-23	3,364	821	1,784	18-25	2,329	466	1,228	-	-	-	-	-	-	-	-
	NO <sub>2</sub>	9	2,460	885	2,303	-	-	-	-	5-16	1,830	330	1,103	-	-	-	-	-	-	-	-
Mont Belvieu	Ethene	6	443	139	82	23	444	174	59	6-9	545	284	47	-	-	-	-	-	-	-	-
	Propene	3	489	231	37	17	303	189	25	1	58 <sup>b</sup>	-	25	-	-	-	-	-	-	-	-
	Alkanes	1	874	-	177	13	1,575	704	221	3	1,319	280	127	-	-	-	-	-	-	-	-
Texas City	NO <sub>2</sub>	-	-	-	-	2-35	168	39	174	2	305	29	155	-	-	-	-	-	-	-	-
	Ethene	3	83	12	7	11	122	41	4	7-9	177	48	2	-	-	-	-	-	-	-	-
	Propene	ND	ND	ND	9	3	54	22	7	5	56 <sup>b</sup>	9	6	-	-	-	-	-	-	-	-
	Alkanes	6	3,010	572	447	12	2,422	288	288	7	2,342	805	242	-	-	-	-	-	-	-	-
	SO <sub>2</sub>	-	-	-	-	17-37	834	298	297	25-26	1,285	428	109	-	-	-	-	-	-	-	-
Beaumont and Port Arthur	NO <sub>2</sub>	11	460	150	452	10	283	30	351	15-16	492	71	352	-	-	-	-	-	-	-	-
	Ethene	-	-	-	-	-	-	-	-	4-7	178	35	18	-	-	-	-	-	-	-	-
	Propene	-	-	-	-	-	-	-	-	1-5	53 <sup>b</sup>	6	18	-	-	-	-	-	-	-	-
Longview	Alkanes	-	-	-	-	-	-	-	-	1-12	7,413	1,448	407	-	-	-	-	-	-	-	-
	SO <sub>2</sub>	-	-	-	-	-	-	-	-	3-22	1,612	447	2,377	-	-	-	-	-	-	-	-
	NO <sub>2</sub>	-	-	-	-	-	-	-	-	3-18	1,422	268	965	-	-	-	-	-	-	-	-
	Ethene	-	-	-	-	-	-	-	-	9	452	191	127	67	249	130	-	-	-	-	-
Longview	Propene	-	-	-	-	-	-	-	-	8	282	59	32	60	211	122	-	-	-	-	-
	NO <sub>2</sub>	-	-	-	-	-	-	-	-	4	176	51	231	92	118	33	-	-	-	-	-

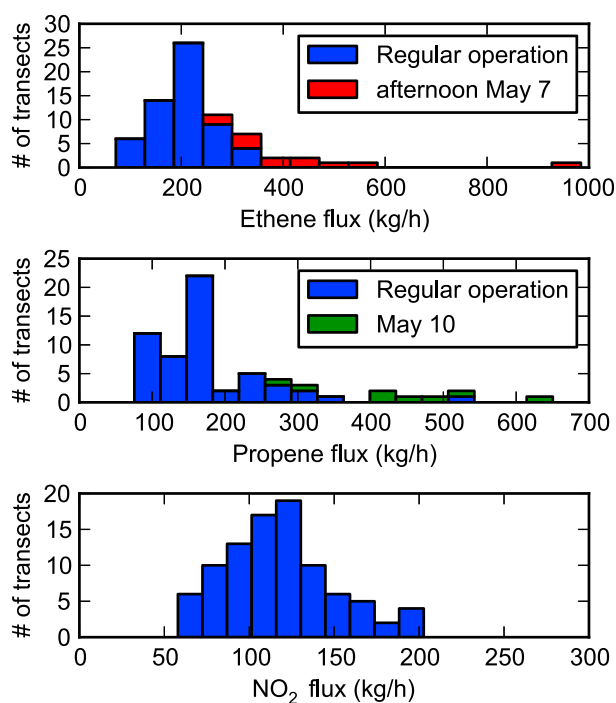
<sup>a</sup>The table gives the number of measurements (N), the mean and standard deviation of the measured fluxes (Mean and Std), and the annual average emissions reported to the emission inventories (EI). All numbers are in kg/h except N, the number of measurements. A range given for N indicates that the mean emissions were calculated as the sum of the mean emissions from a number of subareas. N is the range of the number of measurements for each subarea. The standard deviation was calculated as the root-sum-square of the standard deviations of the subareas for these cases.

<sup>b</sup>Instrumental problems during parts of the 2011 campaign resulted in fewer propene measurements with larger uncertainty.



**Figure 11.** Ratios of emissions measured with SOF and mobile DOAS to annual average emissions reported to State of Texas Air Reporting System (STARS) for each year, species, and area. The markers indicate the ratio of the mean of all flux measurements to the reported emissions, while the error bars indicate ratio of the mean plus/minus one standard deviation to the reported emissions. The error bars only represent the variation in the flux measurements and not the uncertainty in measurements or in reported emissions. The x scale only indicates the year of the measurements; the x position within a year has no meaning. Reported emissions for 2011 were used for the 2012 ratios since 2012 data were not yet available.

Since the Longview study in 2012 was focused on only a single industrial complex, an unusually large number of measurements were performed. In total, 67 measurements of ethene emissions, 60 of propene emissions, and 92 of  $\text{NO}_2$  emissions were performed on 8 different days in a 9 day period. This gives a fairly detailed picture of how much total emissions from an industry varies during a week. The histograms in Figure 12 show the distribution of fluxes for all measurements of these three species. During the measurement period, two episodes with atypical emissions were identified. On the afternoon of May 7, ethene emissions were significantly elevated after having been at more typical levels earlier in the day. Similarly, propene emissions were elevated during May 10. These elevated emissions were suspected to be due to upsets or irregular operation. The measurements from these episodes are shown separately in the histograms in Figure 12. Excluding these two episodes, the variability of the measured fluxes is fairly small for all three species. For ethene the average emission of all SOF transects is  $205 \pm 57$  kg/h, excluding the presumed upset. Similarly, the average propene emission is  $172 \pm 77$  kg/h without presumed upset emissions. No upset episodes were identified for the  $\text{NO}_2$  emissions. The average  $\text{NO}_2$  emission during the whole study was  $118 \pm 33$  kg/h. The flux distributions for ethene and  $\text{NO}_2$ , with the identified upset for ethene excluded, are approximately Gaussian in shape with standard deviations of about 30% of the mean. Measurement variability of this magnitude is often intrinsic to local wind field variability not captured by the wind measurements and not necessarily indicative of the true emission variability. The propene flux distribution, on the other hand, is a bit more irregular with larger variability, even after excluding the identified upset episode. This is probably more than can be explained by wind variability alone, indicating that propene emissions were less constant during the period, although still relatively stable. This study suggests that apart from isolated upset episodes, the total emissions from a petrochemical complex like this is fairly stable on the time scale of slightly more than a week. The average emissions for all transects, including the upset episodes, were  $249 \pm 130$  kg/h for ethene and  $211 \pm 122$  kg/h for propene, which is 21% and 22% higher than without the upset episodes. This is only a single site and a fairly limited period, but if it is taken to be representative of typical conditions, it would indicate that nonroutine emissions account for a relatively small part of total annual emissions, even though they can dominate the momentaneous emissions at times. This conclusion is also compatible with the broad patterns of the measurements in other areas presented in this study, even though the lower number of measurements in those areas makes it more difficult to clearly separate routine emissions from upset events. A notable example to this pattern, however, is the 2006 propene measurement in the HSC, which indicated huge variations in emissions over short time periods. This may, however, have been a rare event, since nothing similar has been seen after that.



**Figure 12.** Histograms showing the distribution of all flux measurements of ethene, propene, and NO<sub>2</sub> during 2012. Ethene emissions were significantly elevated during the afternoon on 7 May, and similarly, propene emissions were higher than usual on 10 May. Fluxes measured during these episodes are plotted as separated additive histograms.

## 4. Discussion

### 4.1. Measurement Uncertainty

The main uncertainty associated with SOF and mobile DOAS flux measurements generally comes from the uncertainty in the wind field. Uncertainties for the measured wind speeds and wind directions were estimated from comparisons of wind profile averages to normalized ground wind measurements. The estimated uncertainties are given in Table 2. Since the calculated flux is proportional to the wind speed, the uncertainty of the wind speed carries over to the flux proportionally. For the wind direction uncertainty, however, the impact on the flux is not linear and also depends on how orthogonal the measurement transect is to the wind direction. To estimate the flux uncertainty due to wind direction uncertainty, measurement situations were simulated with wind errors drawn from a normal distribution based on the estimated wind direction uncertainties, and the average absolute flux error was calculated from a large number of simulations. This was done for 90° and 75° angles between the transect and wind direction to represent the typical range of measurement scenarios and for the estimated wind direction uncertainties of all four studies. The results are given in Table 5. This uncertainty estimate is somewhat conservative, since large wind direction errors can usually be avoided by estimating the wind direction from geometric constraints, i.e., the approximate locations of the sources and where the plume was detected. For the 2012 study, the comparisons of wind profile averages to normalized ground wind measurements gave unusually large wind direction uncertainty estimates, but the simple measurement geometry with only one large industrial complex enabled the actual wind direction uncertainty to be significantly limited by geometrical constraints. To avoid a needlessly conservative uncertainty estimate in this case, wind errors were restricted to a maximum of  $\pm 15^\circ$  in the simulations for this study.

The cross-section uncertainties are generally well established by the experimentalists who have measured them. The infrared cross sections for the VOCs have an uncertainty of 3–3.5% [Sharpe *et al.*, 2004], while the UV cross sections have uncertainties of 2.8% for SO<sub>2</sub> [Bogumil *et al.*, 2003] and 4% for NO<sub>2</sub> [Vandaele *et al.*, 1998]. Additionally, retrieval errors of 10–20% have been estimated for the different species. This is the combined effect of instrument and retrieval stability on the total columns for a plume transect [Mellqvist *et al.*, 2010b]. For the alkane retrieval this also includes the 6% mass retrieval uncertainty established above. All these uncertainty sources have been combined by root-sum-square to a composite flux measurement

**Table 5.** Error Budget for the Flux Measurements During the Different Studies<sup>a</sup>

			Alkanes	Ethene	Propene	SO <sub>2</sub>	NO <sub>2</sub>
Cross-Section Uncertainty			3.5%	3.5%	3.5%	2.8%	4%
Retrieval Error			12%	10%	10%, 20%	10%	10%
Year	Wind Speed	Wind Direction	Composite Flux Measurement Uncertainty				
2006	15–27%	8–12%	21–32%	20–31%	26–36%	20–31%	20–31%
2009	11–29%	7–10%	18–33%	17–32%	24–37%	17–32%	17–33%
2011	16–30%	5–8%	21–33%	20–33%	26–37%	20–33%	20–33%
2012	25–34%	4–12%	28–38%	27–38%	32–41%	27–38%	28–38%

<sup>a</sup>The cross-section uncertainties and estimated retrieval errors depend mainly on the species, while the wind speed and wind direction errors have been estimated separately for each year but apply equally to all species. These four error sources are combined by root-sum-square to a composite flux measurement uncertainty for each species and year. The highest and lowest composite uncertainties in the ranges given were calculated using the lowest and highest uncertainties for both wind speed and direction.

uncertainty range for each species and study. The maximum and minimum for each range were calculated using the maximum and minimum uncertainties of both wind speed and wind direction. These are given in Table 5. In most cases, the composite uncertainty is approximately 20–35%. The high retrieval error estimated for propene (20%) was due to instrumental problems that were primarily present during the 2009 and 2011 studies. These problems primarily affected measurements of small propene columns. Many of the propene measurements actually had a lower retrieval error than this, but 20% was used in the composite errors in Table 5.

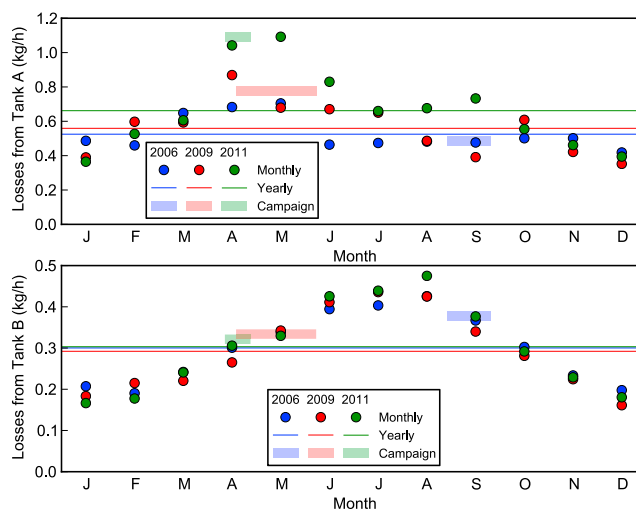
#### 4.2. Representativeness of Measurements

In Table 4 and Figure 11, the results of the SOF and mobile DOAS measurements are compared to reported annual average emissions. The relevance of this comparison depends on whether measurements during shorter periods, a few weeks in these cases, can be expected to be representative for the average emissions over a full year. One argument against this is that temporary emissions or upsets, which only last a limited time period, may be overrepresented in the SOF measurements. Examples of this include emissions occurring during tank cleaning operations, ship loading, flaring, and accidental releases. This type of events occurs rather frequently and might typically last for 1–24 h. Hence, it is likely that some of the SOF measurements include emissions from such events. This type of event is likely to be the explanation for upset emission identified in the Longview measurements in 2012, as illustrated in Figure 12. This example showed that it is possible to discriminate between such upsets and average emissions if a large number of measurements are performed but that the influence of the upset emissions was relatively small on the estimated average emissions.

The industrial areas studied in this paper consist of a large number of independent sites, especially the HSC, and short-term upsets should occur in at least some of the sites during each transect. On the other hand, it is unlikely that they occur in a large fraction of them at the same time, and hence the relative elevation of the total emissions from all of them will be much smaller than for the sites where the upset occurs. The fact that the emissions, for instance, of alkanes from the HSC, show relatively small variations from transect to transect and over several years, as shown in Table 4, indicates that the SOF measurements are representative for long time periods and that the impact of longer term upset emissions is averaged out. On the other hand, this was not the case for the 2006 propene measurements in the HSC, where the emission showed large temporal variability that was attributed to flaring activity in petrochemical plants [Mellqvist *et al.*, 2010b]. These emissions decreased in the later years and have since been more stable. This shows that upsets can have a significant impact on total emissions in some cases and that measurements over longer periods or repeated studies over several years might be needed to make such distinctions.

Another potential reason why the measurements presented in this paper might not be representative for the annual average emissions is that there might be systematic differences in meteorological conditions between the measurement periods and the whole years that could have a large effect on the emission rates of some facilities. All four studies were conducted during the warmer half of the year, during daytime and in clear conditions. All these factors would be expected to contribute to higher than average ambient temperature and solar insolation. Wind speeds might also have been unrepresentative during the studies, which might have caused higher than average emissions. The emission sources most sensitive to meteorological conditions are probably storage tanks for crude oil and for refined products. Ambient temperature and solar





**Figure 13.** Emission rates from Tank A (external floating roof tank with crude oil) and Tank B (internal floating roof tank with gasoline) calculated using emission factor formulas and meteorological data averaged over different time periods. Circles indicate emissions calculated using monthly averages, and bars indicate emissions calculated using averages over the campaign periods, as well as the extent of these campaigns. Yearly averages of the monthly emissions were calculated and indicated with horizontal lines.

insolation affect the liquid surface temperature of the product in tanks which in turn affect the vapor pressure and thereby evaporation. Wind speed primarily affects losses in external floating roof tanks. Ethene, propene, and other products that are gaseous under ambient conditions are stored in pressurized tanks, which should not be expected to have losses significantly affected by meteorology. Temperatures and pressures of feedstocks and products in process steps are typically monitored and regulated and thereby not significantly affected by ambient conditions. Effects of ambient temperatures, solar radiation, and wind speed are included in the formulas for estimation of storage tank losses in *AP-42, Compilation of Air Pollutant Emission Factors* [USEPA, 2013], EPA's primary compilation of emission factor information, which most emission estimates reported to the emission inventories are based on. To estimate the effects of the differences in meteorological conditions, the campaign periods, and the entire years, formulas from *AP-42* were used to estimate the emissions from an external floating roof tank storing crude oil (Tank A) and from an internal floating roof tank storing gasoline (Tank B). These were chosen to represent the most typical tanks with significantly meteorology-affected emissions. Emissions from these tanks were estimated on a monthly basis using monthly averages of the hourly meteorology data. The meteorological data consisted of measurements of ambient temperature, solar radiation and wind speed from the TCEQ monitoring station C1015 [TCEQ, 2013]. Annual average emissions were calculated as the average of monthly emissions for all months in each year. Average emissions during each campaign were calculated using averages of the meteorological data for the duration of the campaign. Figure 13 shows the effects of using meteorological data from these different periods in 2006, 2009, and 2011 on calculated emissions from Tank A and Tank B. Meteorological data were missing from C1015 for October and November 2011, so average values for the same months in 2006 and 2009 were used instead. For Tank B the intrayear variations in emissions are quite similar from year to year, while for Tank A there are larger differences between the years, and especially 2011 stands out. The reason for this is that, according to the *AP-42* emission factors, emissions from external floating roof tanks are sensitive to wind speed, while emissions from internal floating roof tanks are unaffected by wind. During the summer half of 2011, winds speeds were significantly higher than during the same periods in 2006 and 2009, especially in April and May. For this reason, the calculated emissions from Tank A for the campaign period were approximately 65% higher than the annual average, while for 2009 it was only 39% higher and for 2006 it was 8% lower. For Tank B the corresponding differences were smaller: 26%, 14%, and 6% higher during the campaign periods in 2006, 2009, and 2011, respectively.

The differences in calculated emissions presented in Figure 13 are only the seasonal variations. There are of course also day-to-day variations and differences between daytime and nighttime. Assessing these variations

**Table 6.** Average Temperatures, Solar Radiations, and Wind Speeds During the Whole Campaigns Compared to Daytime (9–18) on the SOF-Measurement Days and the Estimated Effects of These Differences in Meteorology on Tank Emissions of Alkanes From an External Floating Roof Tank Storing Crude Oil (A) and From an Internal Floating Roof Tank Storing Gasoline (B)<sup>a</sup>

Year	Tank	Effect of Solar Radiation						Effect of Wind Speed			Total Difference		
		Mean Temperature Campaign (°C)	Mean Temperature Measurement Days (°C)	Effect of Temperature Difference on Emissions	Mean Solar Radiation Campaign (W/m <sup>2</sup> )	Mean Solar Radiation Measurement Days (W/m <sup>2</sup> )	Solar Radiation Difference on Emissions	Mean Wind Speed Campaign (m/s)	Mean Wind Speed Measurement Days (m/s)	Wind Speed Difference on Emissions	Combined Effect on Emissions	Difference Between Campaign and Year	Total Difference Between Measurement Days and Year
2006	A	27.3	26.5	-2.2%	208	677	8.3%	3.8	4.8	40.3%	49.0%	-7.9%	37.2%
	B	24.9	26.3	-4.2%	248	712	17.0%	5.4	4.9	-14.2%	11.5%	25.5%	39.9%
2009	A	24.2	26.1	7.8%	232	649	15.5%	7	7.5	0.0%	25.4%	14.3%	43.3%
	B	24.2	26.1	6.7%	232	649	8.2%	7	7.5	0.0%	15.6%	64.5%	90.2%
				10.8%			13.5%			0.0%	26.7%	6.0%	34.3%

<sup>a</sup>Combined with the effect of whole campaign averages versus annual averages (as shown in Figure 13), the total elevation of alkane emissions due to the meteorological conditions during the measurements is estimated.

using the AP-42 formulas requires applying the formulas on time scales of single days or even hours or at least to averages of meteorological from nonconsecutive time periods on such scales. This is not how the formulas in AP-42 are typically applied and not what they were designed for. Instead, emissions are typically calculated using monthly or even annual averages. Since the campaign periods were of similar time scales as months, the campaign averages in Figure 13 are probably comparable to monthly averages. To estimate the variations on shorter time scales, the AP-42 formulas have been applied to averages of meteorological data from daytime hours (9:00–18:00 CDT) on the days in each campaign when SOF measurements were made. Applying the formulas in this way is likely to give overestimated differences compared to averages for the whole campaign, primarily because the surface temperature in a tank might not follow changes in ambient temperature and solar radiation on the scale of hours or days in the same way as it does on the time scale of months or years. There might be memory effects from the ambient temperatures and solar radiation in previous hours or days, which are likely to be averaged out over a month. The differences given by applying the formulas like this can, however, be thought of as upper estimates of actual differences. Table 6 shows the differences between the daytime averages of the SOF measurement days and whole campaign averages for ambient temperature, solar radiation, and wind speed, and the differences to the calculated emissions from Tank A and Tank B from using averages of measurement days instead of campaign averages. These effects are shown for each meteorological parameter separately as well as the combined effect. Additionally, the last two columns show the differences between campaign averages and annual averages (as shown in Figure 13), as well as the total effect of both seasonal and shorter term variations. The total effect typically adds up to 35–45% for both tanks, with the exception of Tank A in 2011. This exceptionally large effect was due to the strong winds during the campaign. The winds were so strong that the campaign average was outside the applicable range of the AP-42 formulas, 0–15 mph, and hence there was no extra effect due to the short-term variations.

The calculated total effects should be considered as upper estimates, since they assume that there are no memory effects from the cooler nighttime conditions suppressing the daytime emissions. Assuming that storage tanks represent roughly two thirds of the emissions from typical refineries [Kihlman, 2005] and that emissions from process steps are not significantly affected by meteorological conditions, the total meteorological effects estimated above indicate that the alkane emissions measured from refineries in this paper may be 20–30% higher than the annual average.

Neither meteorological effects nor elevated emissions due to upset events seem to be even close in magnitude to the discrepancies between measurements and emission inventories, and hence these discrepancies most likely represent an underestimation of the continuous routine emissions by the inventories.

## 5. Conclusions

Total emissions of alkanes, ethene, propene, SO<sub>2</sub>, and NO<sub>2</sub> from a number of large industrial areas dominated by refineries and petrochemical industries were measured during four measurement campaigns in the period 2006–2012. The measurement error analysis indicates uncertainties typical within 20–35%. In comparison to annual average emissions reported to emission inventories, the VOCs (alkanes, ethene, and propene) stood out with measured emissions typically exceeding reported emissions by factor of 5–15, while measured SO<sub>2</sub> and NO<sub>2</sub> emissions were much closer to reported emissions. A tank model analysis of the effect of wind speed, solar radiation, and ambient temperature on tank emissions shows that the alkane emissions measured from tanks in this study may have been up to 35–45% higher than the annual average, and in 2011 that effect may have been even larger for crude oil tanks due to exceptionally strong winds. These meteorological effects are not nearly large enough to explain the discrepancies between SOF measurements and emission inventories, and they are also not applicable to process emissions and alkene emissions from petrochemical industries. A detailed study of alkene emissions from a petrochemical complex in Longview indicated that upset emissions can cause an increase in total emissions on the order of 20% compared to the continuous routine emissions. Upset emissions are of course highly irregular by nature, but the relatively limited variation in the other VOC emission measurements presented confirms the notion that total emissions are typically dominated by routine emissions rather than by upset emissions.

Since neither upset emissions nor meteorological effects can account for the large emission discrepancies, the conclusion from these results is that current emission inventories, based on emission factor calculations, systematically fail to quantify continuous industrial VOC emissions and that reliable estimates of these emissions can currently only be obtained from measurements.

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