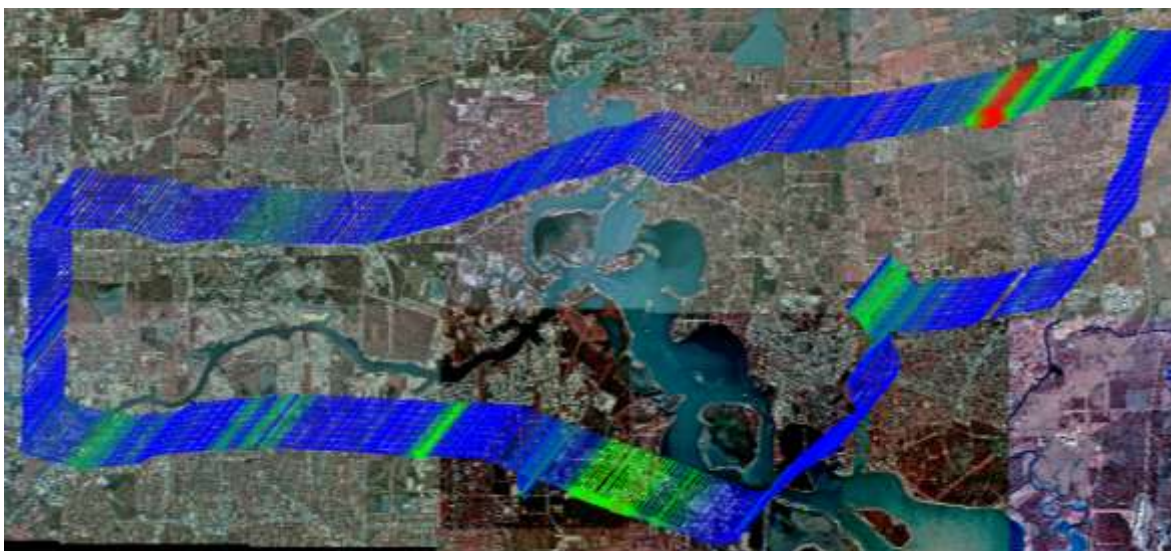


FINAL REPORT

HARC Project H-53

Measurements of industrial emissions of VOCs, NH₃, NO₂ and SO₂ in Texas using the Solar Occultation Flux method and mobile DOAS



Johan Mellqvist, Jerker Samuelsson, Claudia Rivera

Radio and Space Science Chalmers University of Technology,
Hörsalsvägen 11, SE-41296 Göteborg, E-mail: jome@chalmers.se

Barry Lefer, and Monica Patel

Department of Geosciences, University of Houston, 312 SR-1,
4800 Calhoun Road Houston, TX

Aug 20, 2007

Title page: SOF measurement of ethylene in the Houston ship channel on Sep 13 2006 in northerly wind.

Executive summary

In this study the objective has been to to pin-point and quantify the largest industrial emission sources of volatile organic compounds (alkenes, alkanes), NH_3 , NO_2 and SO_2 in the vicinity of Houston and south-eastern Texas. The work is part of the extensive summer campaign TexAQS 2006, included in the Second Texas Air Quality Study (TexAQS II). The study is motivated by the large discrepancy between emissions reported by the industries and those inferred from modelling efforts and airborne measurements made in 2000 by NOAA. The airborne measurements relied on ratio measurements between VOCs and NO_y assuming the NO_y emission to be well understood.

To overcome some of the uncertainties with the previous emission studies, the TexAQS 2006 study used two complementary direct methods to quantify fugitive emissions: the solar occultation flux (SOF) method and mobile DOAS. The SOF technique is an optical method utilizing the absorption of direct solar infrared radiation in the 1.8-14 μm range for retrieval of total columns of various species such as ethylene, propylene, ammonia and alkanes. Mobile DOAS utilizes scattered light in the UV/visible region for measurements of NO_2 and SO_2 . The SOF and mobile DOAS measurements are carried out from a moving vehicle, making it possible to traverse the emission plume downwind of an industry, and thus integrate all the molecules of the plume cross section in real time. By multiplying with the plume wind speed, the total flux emerging from the source is obtained. This technique hence provides a direct measurement of the emissions. The spectroscopic measurements are based on documented retrieval procedures applied in atmospheric research. The calibration is traceable since data from published databases are used. The uncertainties of the spectroscopic data are typically around 3%.

During the month of September 2006 SOF measurements were conducted with the aim of quantifying the largest industrial emission sources of VOCs and other species. About 10 days of measurements were conducted in the vicinity of the Houston ship channel (HSC), 2 days in Texas City, 2 days in Sweeny and 1 day at Freeport and Chocolate Bayou. On a given day multiple measurements of the emission sources were conducted. To eliminate possible background sources, industrial sites were enclosed in a "measurement box" by measuring both upwind and downwind, typically from a distance of 0.5 to 3 km. At this distance downwind, the plume is distributed from the ground up to several hundred meters height and the wind should vary little over the bulk of the plume. This was supported by airborne measurements conducted in parallel by NOAA and Baylor University. Primary wind information was obtained from Global Positioning System (GPS) sondes launched within the project in the near vicinity of the emissions measurements. Additional data were obtained from the La Porte airport wind profiler and SODAR measurements in the eastern and northern part of the HSC, respectively. The various wind measurements were consistent within 30%, which was established as the main uncertainty for the actual SOF measurements, since the wind estimation is the largest source of uncertainty in this technique. The overall uncertainty of technique is estimated to about 35%.

Flux estimates were obtained for the large petrochemical and refining complexes around the Houston Ship Channel, Channelview, Mont Belvieu, Freeport, Chocolate Bayou and Sweeny during September 2006 with abridged results shown in the tables below. The measurements show that the hourly gas emissions from the Houston Ship

channel area correspond to about 1 metric ton of ethylene, 1.5 tons of propylene, 12 tons of alkanes, 1/4 ton of NH₃ and about 5 tons of SO₂ and NO₂. For the VOCs this is an order of magnitude or greater than reported VOC emissions in the 2004 inventory. The observed NO₂ and SO₂ values, on the other hand, are more consistent with the reported values and generally agree within a factor 2 or better. The inventory is based on the one derived in 1999 by the Texas Commission on Environmental Quality (TCEQ), with great detail in chemical speciation, but in which each speciation category has been scaled by the ratio of 2004/1999 total VOCs.

In the measurements conducted during the campaign propene and ethene exhibited high variability, especially the former one, and a significant fraction of these seem to originate from upset releases or frequent flaring. For the Mt Belvieu complex the ethene emission data compared within 50% with airborne measurement conducted by NOAA.

Table I. Measured emission rates obtained by SOF in this study, and the inventory numbers for non methane hydrocarbons

Species	Ethene kg/h		Propene kg/h		Alkanes kg/h		Tot. VOCs kg/h
	Meas.	Invent.	Meas.	Invent.	Meas.	Invent.	Invent.
HSC	860	47	1500	61	12400	1500	3090
Mt Belvieu	404	44	400	9	860	260	265
Baytown	72	6	260	3	980	202	437
Texas City	83	8	-	-	2890	348	686
Channelview	64	11	-	-	-	42	170
Sweeny	163	4	126	4	3630	113	137
Freeport	250	21	-	-	-	44	148
Bayport	170**	4	-	-	-	94	151
Chocolate Bayou	136**	10	273	24	-	107	150

* Nonmethane hydrocarbons corresponding to alkanes and unspciated VOC as in the 2004 inventory database, ** Uncertain due to few measurements.

Table II. Measured emission rates obtained by SOF in this study, and the inventory numbers for SO₂ and NO₂.

Species	NO ₂ kg/h		SO ₂ kg/h	
	Meas.	Invent.	Meas.	Invent.
HSC	4538	3089	5166	2752
Mt Belvieu	271	125		
Baytown	668	344	557	54
Texas City	642	930	1215	660
Channelview	237	715		
Sweeny	398	313	1826	265
Freeport	752	103	1154	285
Bayport	731	47		
Chocolate Bayou	268	327		

For the measurements conducted in the HSC and Mt Belvieu the data reflect the monthly emissions with hourly and day-to-day variations in VOC emissions caused by changes in the wind and process behavior, since the data were collected over 3 to 10 days (depending on site) spread out during September 2006. For Sweeny, Chocolate

Bayou, Texas city and Freeport the data were only gathered on 1 or 2 days and there is hence additional uncertainty about the activities at the industrial sites.

To convert the emission data obtained during the campaign to an annual average one has to consider the seasonal variability in the ambient temperature, solar radiation, wind behavior and industrial activity. VOC emissions which occur from process areas are less dependent on the meteorological factors than tank areas, and this is the case for most of the alkene emissions and a significant fraction of the alkane emissions. Tank emissions on the other hand are driven by vaporization of liquid product and possibly increase both with wind and temperature. During TexAQS 2006 the temperature was 5-10° above the annual mean temperature wherefore the tank emissions possibly were higher than their annual means. The effect is uncertain but calculations using the API model indicate 10-25% higher values. The wind speed, on the other hand, was higher than the annual mean during the HSC measurements, while only slightly lower during the Texas city measurements. Again the effect is uncertain but may be as high as a factor of 2 higher emissions during the HSC measurements.

1. Introduction	7
2. Method	8
2.1 The Solar Occultation Flux method	8
2.1.1 General	8
2.1.2 Retrieval algorithm.....	9
2.2 Mobile DOAS	14
2.3. Flux calculation.....	15
3. The SOF experiment during the TexAQS 2006.....	17
3.1 Wind measurements	19
3.2 Emission inventory data.....	25
3.3 Additional VOC speciation for the alkane channel measurements.....	25
3.4 Error budget	28
4. Results	29
4.1 Ethene.....	29
4.2 Propene.....	38
4.3 Alkanes.....	43
4.4 Ammonia.....	47
4.5 NO ₂ and SO ₂	50
5. Discussion	54
6. Acknowledgements	56
7. References	57

1. Introduction

This study investigates fugitive emissions of highly reactive volatile organic compounds (HRVOCs), alkanes, NO_2 and SO_2 from industrial sources in the vicinity of Houston. The objective of the study was to locate these sources and quantify their VOC emissions. The work is part of the extensive summer campaign TexAQS 2006, included in the Second Texas Air Quality Study (TexAQS II), aiming at understanding the formation of tropospheric ozone.

Ozone is formed by photochemical reactions between VOCs and nitrogen oxides. The main emissions originate from mobile sources but in the Houston area industries may play an important role due to their large number and total VOC emissions. In a previous air quality study in 2000 it was noted that the industries in Texas seem to emit considerably more highly reactive VOCs than reported and that the emissions are important contributors to ozone formation in Texas [Ryerson, 2003; Wert, 2003]. This was found by conducting airborne measurements downwind of several isolated facilities to determine the ratios of HRVOCs to NO_x . The results showed discrepancies between reported and measured values of a factor 20 to 70. Assuming the NO_x emissions are well known, which seemed to be the case, the discrepancy is therefore due to higher than reported VOC emissions. This approach is indirect since it relies on the fact that the NO_x emissions are known and that the relatively few measurement days during which the measurements were conducted are representative of the industries' baseline emissions. For instance, undocumented upsets in process or non-routine operations at the industries studied could possibly have led to increased emissions.

Other indications of discrepancies between actual and reported emissions have been found. Byun [2005] reported that even though the HRVOC emissions are increased by a factor of 7-13 in the model parameterization, the modeled ground concentration is still lower than what is expected observed ground concentrations.

To overcome some of the uncertainties with the previous emission studies, a direct method to quantify fugitive emissions has been applied in the TexAQS 2006 study. This method called the Solar Occultation Flux (SOF) method is relatively new and was developed from a number of different research projects [Mellqvist, 1995 ;1999, Galle, 1999]. The SOF method utilizes the sun as the light source and gas species that absorb in the infrared portion of the solar spectrum are measured. The method has been used operationally in Sweden during the past 5 years to show that the Swedish refineries typically emit 0.03-0.09% of their throughput of oil to the atmosphere, with more than half of the emissions originating from oil and product storage [Kihlman 2005a, 2005b]. The SOF method has also been applied for studies of emissions of ethane, propene and ammonia from the petrochemical industry, for instance to investigate the combustion efficiency of flares [Mellqvist, 2000]. An additional application is measurements of total column CO in cities [Mellqvist 2004, Foy 2007].

2. Method

2.1 The Solar Occultation Flux method

2.1.1 General

The SOF method 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 mirror device that tracks the sun and reflects the light into the spectrometer independent of its position. From the solar spectra it is possible to retrieve the path-integrated concentration (column, see Eq. 1) in the unit mg/m^2 of various species between the sun and the spectrometer. In Figure 1 a measurement system is shown built into a van. The system consists of a custom built solar tracker, transfer optics and a Bruker OPAG FTIR spectrometer with a spectral resolution of 0.5 cm^{-1} , equipped with both an MCT detector and an InSb detector. Optical interference filters are used to optimize the signal to noise ratio (S/N) of the measurements.

To obtain the gas emission from a source, the car is driven in such way that the detected solar light cuts through the emission plume. This is illustrated in Figure 2. To calculate the gas emission the wind direction and speed is also required and these parameters are usually measured from high masts and towers. This calculation is discussed in Section 2.3. The technique has been validated by comparison to other methods and tracer gas releases and it typically has an uncertainty of about 30%, mostly due to uncertainties in the wind field [Kihlman 2005a, 2005b, Samuelsson 2005]. Further discussion of the uncertainty is presented in Section 3.4.



Figure 1 On the left the SOF vehicle is shown while measuring emissions from crude oil tanks not seen in the picture. The solar-tracker shown on the right transmits the solar light into the infrared spectrometer independent of the vehicle's position.

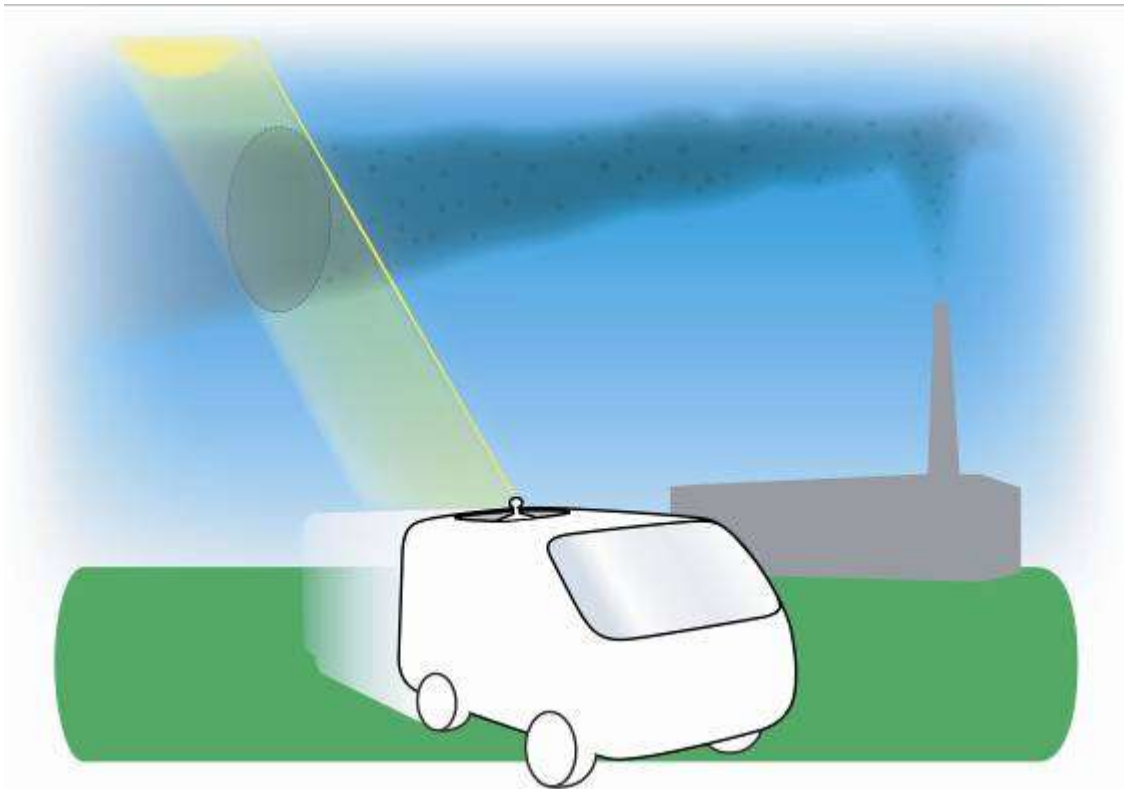


Figure 2. In the Solar Occultation Flux method (SOF) gases are measured by observing solar light in the infrared portion of the solar spectrum. The instrument is placed in a vehicle which is moved across the plume. From the accumulated mass measured across the plume the flux of gas is obtained by multiplication with the wind speed. (Illustration Karin Sjöberg).

2.1.2 Retrieval algorithm

In the infrared region of the solar spectrum utilized by the SOF method, a large number of species, such as aldehydes, alkanes, ammonia, CO, ethene, ethene-oxide, HF, HCl, NO₂, SO₂, propene, terpenes, and vinyl-chloride, can be measured. The spectral retrieval is based on using multivariate analysis in which calibration spectra recorded in the laboratory are fitted to the measured spectra. The calibration spectra are obtained from published reference libraries such as the HITRAN database [Benner 2003] and databases from NIST (www.NIST.gov), Pacific Northwest National Laboratories [PNL 2004] and Hanst [1996].

The retrieval is conducted in a custom software package (QESOF). The results of the spectral fitting algorithm for alkanes have been compared and verified with the results retrieved from the non-linear NLM4 software developed by Griffith [2001]. The agreement between NLM4 and QESOF is very good, within a few percent. Verification of the QESOF software has also been conducted for the volcanic species HCl and SO₂ by comparison with a code developed by Burton [2001] showing good agreement, also with differences of within a few percent.

The retrieval of ethene and ammonia is conducted in the wavelength region between 945 and 979 cm⁻¹ (10.21-10.58 μm) and the retrieval of these species is relatively straightforward without interfering species, except water and CO₂.

Propene is retrieved between 900 and 920 cm^{-1} (10.87-11.11 μm) and in this region 1-butene has a similar absorption feature, although somewhat broader and peaking at slightly lower wave number than propene. The absorption strength per mass unit is similar. In the analysis simultaneous retrieval of the two species was first done but without any realistic response for 1-butene. This species was therefore omitted from the retrieval. This means that part of the propene values retrieved here could correspond to emissions of 1-butene instead. However, 1-butene seems to be much less abundant in the emission plumes. An analysis of the TCEQ auto GC data A169 located at Milby Park, which is west of the HSC shows that at easterly winds the mass ratio of 1-butene/propene is about 0.25. This ratio is even lower when looking at the TCEQ emission database in which propylene is by far dominating. Nevertheless, this means that on average 25% of the propene values could correspond to 1-butene.

For the retrieval of ethene and ammonia calibration spectra from the HITRAN database are used [Benner 2003] while for propene and alkanes the spectra are obtained from the PNL database [PNL 1996]. In addition to the key-species, various interfering species such as H_2O and CO_2 are also fitted in the retrieval procedure. The uncertainty in the absorption strength of the calibration spectra is about 3% for all species.

In the spectral region around 10 μm warm objects radiate heat which creates a thermal background in the absorption spectrum. To achieve the desired spectrum, the thermal background spectrum is recorded at regular intervals by measuring with the solar tracker pointed to the cold sky i.e. away from the sun. The thermal background spectrum can then be removed from each recorded solar spectrum. A further complication is the non-linearity of the detector (photoconductive MCT) used in the 10 μm region. The non-linearity can create artifacts in the spectra, such as offsets in the 100% absorption baseline. This has been compensated for by applying a baseline fit to the spectra. For ethene, propene and ammonia this yields an additional uncertainty to the retrieved values on the order of 1%. This uncertainty can be largely removed by using a photovoltaic detector and a newer spectrometer with less thermal background but it was not available during the TexAQS II campaign.

In Figure 3 solar spectra corresponding to a measurement downwind an industrial facility in the Houston ship channel (HSC) are shown. The solar spectra were measured outside and inside the emission plume. In addition spectral fits of ethene and propene are shown obtained using the QESOF spectral retrieval algorithm. As can be seen there is clear absorption signal of both the ethene and the propene in this case. The retrieval for ethene has a variability of about 0.5 mg/m^2 caused by interference effects and noise due to instrument vibrations and disturbances while driving. For propene the variability is higher, around 3 mg/m^2 , since the sensitivity is less and since the spectroscopic retrieval chosen appears to be more sensitive to instrumental noise features.

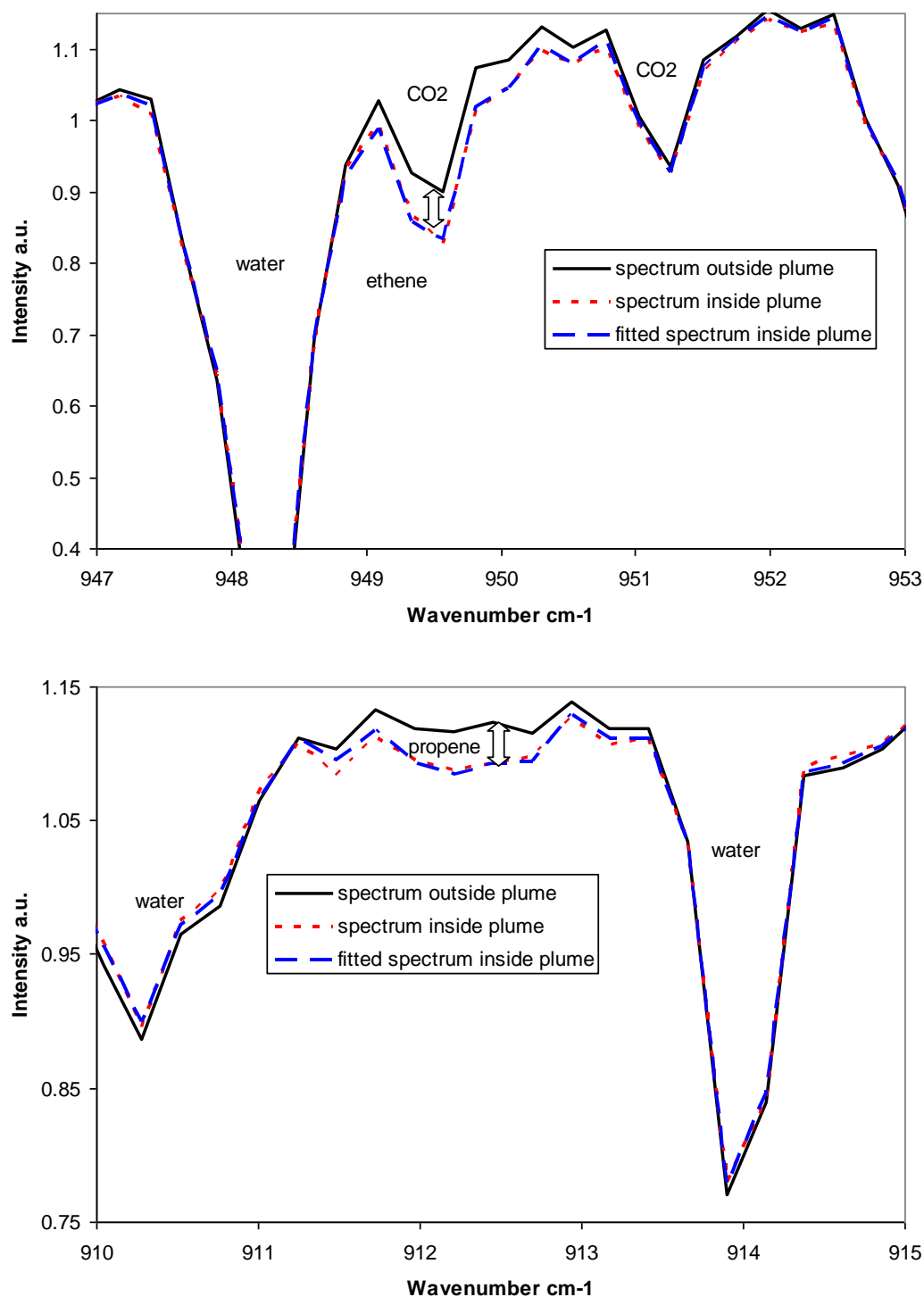


Figure 3. Solar spectra measured outside and inside the emission plume of an industrial plant in arbitrary intensity units. In addition spectral fits of ethene (upper) and propene (lower) obtained using the QESOF spectral retrieval algorithm are shown.

The VOCs leaking from refineries correspond mostly to alkanes (by mass). These compounds are retrieved in the infrared region between 3.3-3.7 μm (2700-3005 cm^{-1}), using the vibration transition in the carbon and hydrogen bond (CH-stretch). The absorption features of the different alkanes are similar and interfere with each other, but

since the number of absorbing C-H-bonds is directly related to the molecule mass, the total alkane mass can be retrieved despite the interference. Aromatics and alkenes also have absorption features in the CH-stretch region, but mainly below 3.33 μm for the most abundant species. The absorption cross section for alkenes is also far weaker here than in the 10.21-10.58 μm region.

The SOF alkane channel retrieval fits calibration spectra of ethane, propane, n-butane, i-pentane and n-octane to the recorded spectra, using a resolution of 8 cm^{-1} . A study of the cross sensitivity of various compounds to this alkane mass retrieval method was conducted by retrieving spectra of all major HSC plume constituents. The results showed that for alkanes (C_2 to C_{10}) the SOF alkane channel mass retrieval retrieve the alkane mass within a factor 0.85 to 1.24 for the different compounds (1.022 on average). For the 12 most abundant alkenes the cross sensitivities varies between 0.000 and 0.305, and the corresponding values for aromatics are 0.000-0.184, see Table 1. For 10 typical hour averages of the HSC plume, as speciated into 36 VOC compounds by an auto-GC-station at Milby Park (TCEQ station CAMS169), the SOF alkane mass retrieval proved to retrieve the total alkane mass within 6.6% (3.5%-6.6% overestimation), see Table 3 in the VOC speciation section.

Table 1. Cross sensitivity for the SOF alkane channel retrieval for the major 36 VOC:s present in the HSC plume. Values correspond to the retrieved alkane mass (e.g. 1 mg m^{-3} n-pentane is evaluated to be 1.003 mg m^{-3} of alkane, and 1 mg m^{-3} of toluene is interpreted as 0.064 mg m^{-3} alkanes).

Alkanes	<u>Cross sensitivity</u> <u>(alkane mass)</u>	Alkenes	<u>Cross sensitivity</u> <u>(alkane mass)</u>
ethane	1.000	ethylene	0.078
propane	1.000	propylene	0.202
n-butane	1.000	acetylene	0.001
i-butane	1.176	1,3-butadiene	0.007
cyclo-pentane	1.037	2-butene (c+t)	0.290
i-pentane	1.000	1-butene	0.283
n-pentane	1.003	i-butene	0.305
2m-pentane	1.015	isoprene	0.100
3m-pentane	0.840	t-2-pentene	0.464
cyclo-hexane	1.239	1-pentene	0.330
2,2-dimethyl-butane	1.084	c-2-pentene	0.316
n-hexane	0.984	styrene	0.000
3m-hexane	0.848	<u>Aromatics</u>	
n-heptane	0.990	benzene	0.000
n-octane	1.000	toluene	0.064
i-octane	1.082	m-xylene	0.118
n-nonane	1.048	p-xylene	0.095
n-decane	1.051	o-xylene	0.170
		ethyl-benzene	0.184

In Figure 4 a solar spectra recorded downwind the Texas City industrial complex on 20 September 2006 is shown. The best fit mix of calibration spectra obtained by the

QESOF spectral retrieval routine is shown along with the recorded spectra, relative to a clean air background spectra recorded immediately before the plume transect.

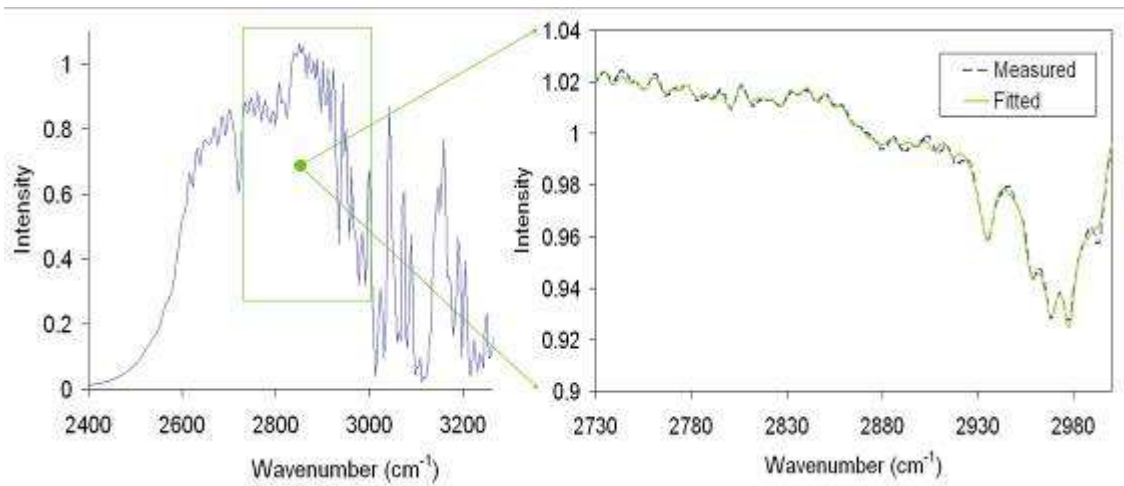


Figure 4. Solar spectra in the alkane CH-stretch region, recorded downwind the Texas City industrial complex 20 september 2006 (left). To the right the measured and the fitted mix of calibration spectra are shown (relative to a clean air background reference), obtained using the QESOF spectral retrieval algorithm.

2.2 Mobile DOAS

In addition to the SOF system, a UV/visible system was used to measure gas fluxes of NO_2 and SO_2 . This system, shown in Figure 5, measures scattered light in the zenith and does not utilize direct solar light in contrast to the SOF instrument. Therefore it is also possible to conduct measurements under cloudy conditions.

The mobile system and spectral retrieval was originally developed for volcanic measurements [Galle 2002] and is based on differential optical absorption spectroscopy (DOAS) [Platt 1979]. The mobile DOAS collects scattered ultraviolet light by means of a telescope coupled to a quartz fiber and the light is transferred into either of two spectrometers with a spectral resolution 0.6 nm and spectral ranges 280-420 nm (SO_2) and 336-480 nm (NO_2), respectively. The column of SO_2 is retrieved between 310-320 nm and NO_2 between 425-435 nm using a custom code (mobile DOAS). This code has the same retrieval routines as the DOASIS package developed at University of Heidelberg by Stephan Kraus [DOASIS]. The calibration spectra for both species are obtained from Vandale [1994] with an estimated uncertainty of a few percent.

The mobile mini-DOAS instrument is mounted in a vehicle and measurements are performed traversing the plume, at different distances from the source, perpendicular to the plume direction. To calculate the gas emission, the wind direction and speed is also required, in the same manner as for the SOF technique (see section 2.3).

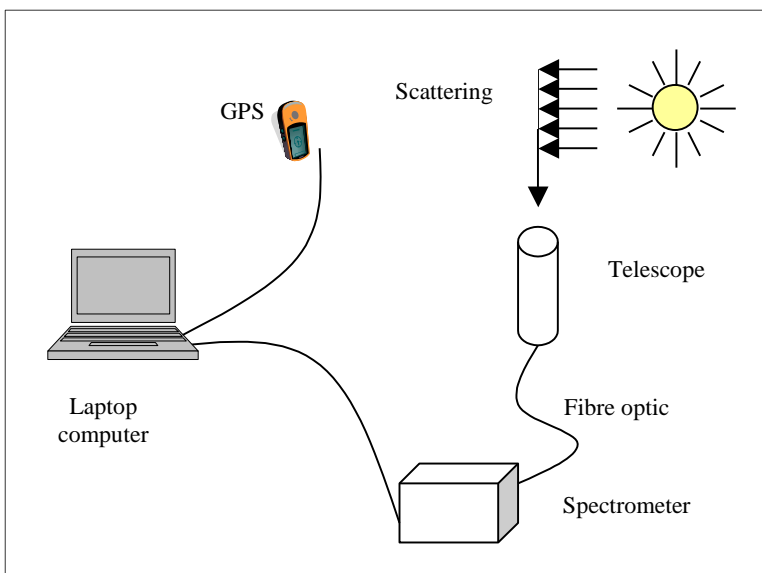


Figure 5. The mobile DOAS system. Scattered solar light is transmitted through a telescope, and an optical fiber to 2 UV/visible spectrometers. From the measured spectra the amount of NO_2 and SO_2 in the solar light can be retrieved. The system is mounted in the vehicle shown in Figure 1.

2.3. Flux calculation

The gas flux in the mobile-DOAS and SOF method is obtained first by adding the column measurements conducted across the gas plume as illustrated in Figure 6. The integrated mass of the key species across the plume is hence obtained. To obtain the flux this value is then multiplied by the average wind speed of the plume, $u_{average}$.

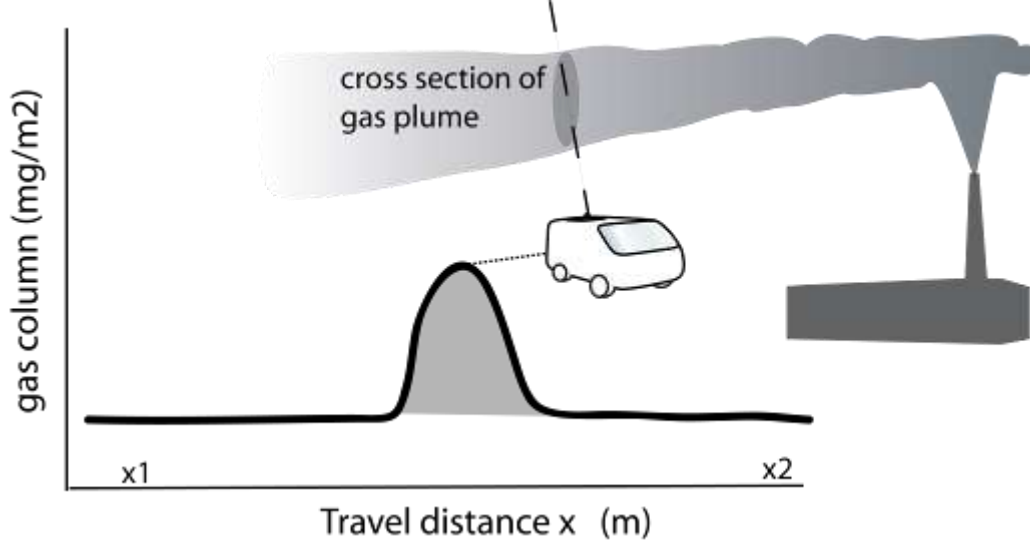


Figure 6. Illustration of the SOF measurement.

The flux calculation is shown in Eq. 1. Here x corresponds to the travel direction, z to the height direction, u' to the wind speed orthogonal to the travel direction (x), Z_{sun} to the distance to the sun, and H_{mix} to the maximum height of the plume. For the solar measurements the slant angle of the sun is compensated for, by multiplying the concentration with the cosine factor of the solar zenith angle.

$$flux = \int_{x1}^{x2} \left(\int_0^{Z_{sun}} conc(z) \cdot u'(z) \cdot dz \right) dx = u'_{average} \int_{x1}^{x2} column(x) dx \quad \text{Eq. 1}$$

$$\text{Where } u'_{average} = \frac{\int_0^{H_{mix}} u' \cdot dz}{\int_0^{H_{mix}} dz}, \quad column = \int_0^{Z_{sun}} conc(z) \cdot dz$$

The wind is not straightforward to obtain since it is usually complex close to the ground and increases with the height. What helps the situation is that SOF measurements only can be done in sunny conditions. This is advantageous since it corresponds to *unstable meteorological conditions* for which wind gradients are smoothed out by convection. Over relatively flat terrain the mean wind varies less than 20% between 20 and 100 m height using standard calculations of logarithmic wind. This is further supported by meteorological sonde measurements conducted during the TexAQS 2006 and modeling [Kihlman 2005b] using the TAPM model [Hurley 2005] (Figure 7). In addition, for such meteorological conditions, with considerable convection, the emission plume from

an industry mixes rather quickly vertically giving a more or less homogeneous distribution of the pollutant versus height through the mixing layer even 10 km downwind. In addition to the atmospheric mixing, the plumes from process industries exhibit an initial lift since they are usually hotter than the surrounding air.

The rapid well-mixed assumption agrees with preliminary results from airborne measurements made by Baylor University [Buhr 2006] and NOAA [personal communication Joost de Gouw] during the TexAQS 2006. The NOAA measurements indicate that the gas plumes from the measured industries mix evenly from the ground to 1000 m altitude, i.e. throughout the entire mixing layer, within 1000-2000 s transport time downwind the industrial plants. This indicates a vertical mixing speed of the plume between 0.5 to 1 m/s. This is further supported by Doppler LIDAR measurements by NOAA from the Ron Brown research vessel showing typical daytime vertical mixing speeds of $\pm(0.5-1.5)$ m/s [Tucker 2007]. During several occasions in the TexAQS 2006 campaign Baylor university [Buhr 2006] did airborne measurements in parallel to the SOF, at different heights, 150-600 m, and at different distances from the sources. Preliminary results for the isolated industrial facility Sweeny, shows that the plume of alkenes, 250 s downwind the source along the same measurements path as the SOF, is found even at 600 m altitude but that it seems to decrease considerably after 300 m altitude. The NO_y on the other hand is well mixed up to 600 m. The difference in vertical distribution may be caused by the fact that the two species have different origins in the industrial facilities, for instance will NO_y from flaring exhibit a strong initial vertical lift. Further downwind the industrial facility, 1500 s transport time, both alkenes and NO_x was well mixed up to 600 m which was the maximum height of the measurements. Similar downwind measurements at Freeport, 250s, showed that the alkene plume was distributed up to 300 m and then decreased while NO_x was evenly distributed between 0-600 m.

In the case of the SOF measurements during TexAQS 2006 the measurements were conducted with a typical plume transport time of 100 s to 500 s, which according to the discussion above means that the emission plumes had time to mix up to heights of several hundred meters above the ground. This is above the first 50 - 100 m where the wind is usually disturbed due to various structures. The wind profile in the bulk of the plume will then be rather smooth and thus the mean wind speed and hence plume transport, varies only slightly (Figure 7).

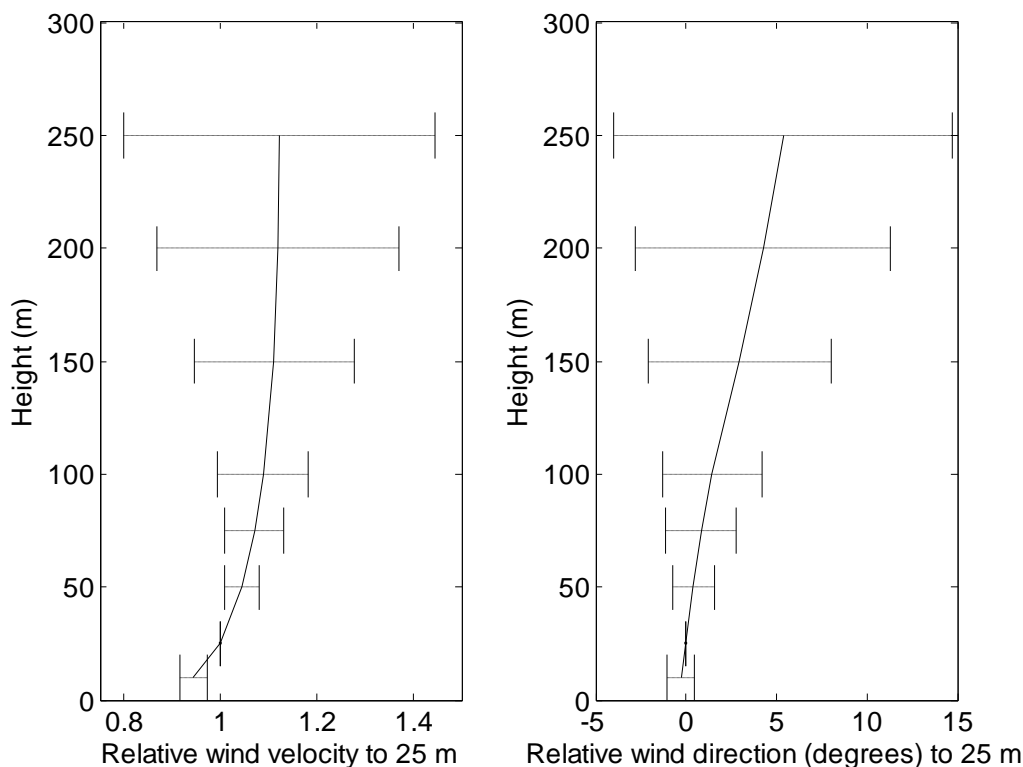


Figure 7. The average daytime wind velocity and wind direction profile retrieved by simulation above Gothenburg averaged over all sunny days during a month with a wind-speed of 3-6 m/s at ground. The error bars indicate standard deviation between daily averages [Kihlmann 2005a].

3. The SOF experiment during the TexAQS 2006

During the month of September 2006 SOF measurements were conducted with the aim of pinpointing and quantifying the largest industrial emission sources of VOCs and other species. About 10 days of measurements were conducted in the vicinity of the Houston ship channel area (HSC), 2 days in Texas City, 2 days in Sweeny and 1 day at Freeport and Chocolate Bayou. On a given day multiple measurements of the emission sources were conducted and the source were enclosed in a “measurement box” by measuring both upwind (to eliminate background sources) and downwind. The SOF experiment is illustrated in Figure 8 and Figure 9. The measurements were typically conducted at 0.5 to 3 km distance from the sources. The assumption, as discussed in the previous section, is then that the plume is distributed from the ground up to several hundred meters height and that the wind varies little with height.

To obtain the wind information Global Positioning System (GPS) sondes were launched within the project. In the analysis the average wind speed up to 200 m or 500 m, has been used depending on the distance to the sources. In addition, we made use of wind profiler data from the Laporte airport and SODAR measurements in the eastern and northern part of the HSC, respectively. This is illustrated in Figure 9 together with various sectors in the HSC that we have studied in more detail during the project.

During the project coordinated measurements with a Twin Otter from the Baylor University and the NOAA WP3 were conducted on several occasions. The Twin Otter carried VOC canisters for speciation and conventional instruments for continuous measurements of NO_x and SO₂. It also carried a “Rapid Alkene detector”, an instrument based on the chemiluminescence technique with a sum response for several alkenes. The NOAA WP3 carried a full suite of measurements and in particular a photo acoustic sensor for ethene. The final data from these platforms were not available during the write-up of this report, and further in depth comparisons will be conducted in the future.

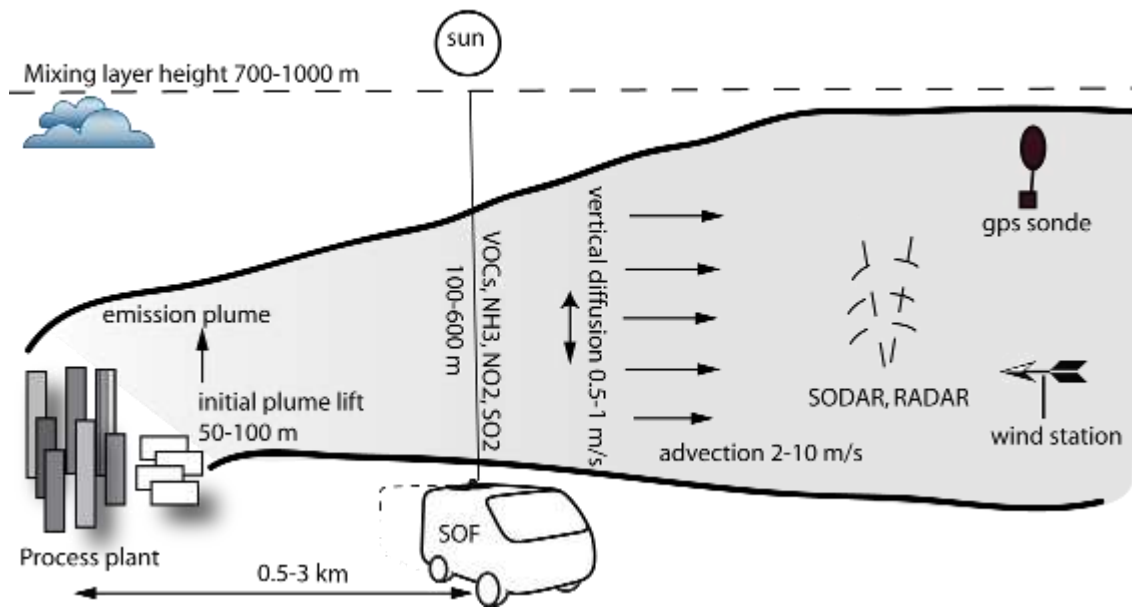


Figure 8. The SOF experiment during the TexAQS 2006 campaign is illustrated here.



Figure 9. SOF sectors in the Houston ship channel . Positions of the wind measurements in the HSC area.

3.1 Wind measurements

Wind soundings were conducted using GPS sondes (RS80-15N-V2D-A-GPS) obtained from Environmental Science Corporation, Boulder, Figure 10. In general three to four soundings were conducted each measurement day. In the HSC the soundings were conducted close to the Lynchburg ferry crossing, in Texas city eastward of the town and in Freeport, Chocolate Bayou and Sweeny downwind the industrial facilities. Frequently the sondes exhibited noise structures, with sharp spikes at some height. These were removed before the wind analysis. The uncertainty in the wind data obtained from the sondes is difficult to assess but part of the uncertainty certainly arises from the fact that the sondes only provide a snapshot of the wind. In addition, to the soundings data was used from a radar profiler operated by the Texas commission of environmental quality (TCEQ) within the NOAA profiler network at the LaPorte airport south of the HSC.



Figure 16. A GPS balloon sounding conducted within the project.

The radar profilers transmit radio wave pulses into the atmosphere and then record the resulting backscattered radio waves to measure winds in the range from 100-3000 meters (above ground level). The data are available as 30 minute averages with the first wind layer starting at about 130 m with a height resolution of about 50 m. The uncertainty of the data is around 1 m/s [Senff 2007].

During the TexAQS 2006 campaign TCEQ also operated two SODAR profilers at the Waterworks and the HRM4 sites, to the west and north of the HSC, Figure 9. The instruments transmit sound pulses into the atmosphere and use the resulting backscattered sound to measure winds in the range from about 15 meters (150 feet) to a varying height between 100-200 m above ground level, with a height resolution of about 15 m. The time resolution for the SODAR data is 5 minutes. The SODARs are better close to the ground, and this can be seen in the data, which often shows errors above 100 m altitude. In addition to the wind profilers TCEQ is operating a network of ground stations with wind measurements at 10 m height which has been used in assessing the wind.

In Figure 11 a comparison is shown between a GPS sonde measurement and the LaPorte wind profiler on August 30 around noon. Noteworthy is the smooth behavior of the wind in the mixing layer as measured with the wind profiler. It hence makes little difference to the SOF estimates at what height one assumes the plume to be. It can also be seen that the sonde and profiler agree quite well, with a 20-25% systematic difference on average, but that the sonde exhibits noisy spikes. The average wind from the ground to 500 m altitude is 4.8 ± 0.4 m/s for the profiler and 6 ± 1.2 m/s for the GPS sonde. The ground speed measured at the Lynchburg ferry was 3.5 m/s and 10° . In Figure 12 a similar comparison is shown for September 13, around noon. The SODAR data above 100 m was here removed. It can be seen that the wind profile is fairly

smooth above 100 m and that there is some structure in the wind below 100 m which is reproduced both by the GPS sonde and the SODAR. The average wind from the ground to 500 m altitude is 4.6 ± 0.4 m/s for the profiler and 4.7 ± 0.8 m/s for the GPS sonde.

To investigate the uncertainties in the wind the various measurements have been compared. In Figure 13 the wind measurements are plotted versus the average GPS wind between ground and 500 m height. The same data has been analysed further in Table 2. It can be seen that all wind speed measurements lie within $\pm 30\%$ of each other, except for the ground stations which on average are 30% lower, as to be expected. For the wind direction all measurements are within $\pm 15^\circ$, which corresponds to a 10% error in most cases in this study.

A conservative estimate of the uncertainty of the wind used in the SOF measurements in the HSC is thus $\pm 30\%$, including measurement errors, systematic geographical wind differences and differences due to averaging times; the profiler and SODARs correspond to 30 minute averages while the GPS sondes corresponds to a 100 s snapshot of the first 500 meters. For measurements conducted in more confined areas, such as Texas City, Freeport, Chocolate Bayou and Sweeny, we expect the wind uncertainty to be less than 30%.

Table 2. Comparison of wind measurements. This comparison includes measurements errors, systematic spatial wind differences, differences due to averaging time-the profiler and SODARs all correspond to 30 minute averages while the GPS sondes travel through the first 500 m layer in 90 s.

Wind measurement	Relative difference from GPS sonde wind speed (0-500m)	Difference from GPS sonde wind direction (0-500m)
Laporte wind profiler (0-500 m)	$(-3 \pm 27)\%$	$(2 \pm 15)^\circ$
GPS sonde (0-200 m)	$(-6 \pm 15)\%$	$(2 \pm 9)^\circ$
SODAR waterworks (0-100 m)	$(-7 \pm 24)\%$	$(7 \pm 16)^\circ$
SODAR HRM4 (0-100 m)	$(-12 \pm 18)\%$	$(2 \pm 18)^\circ$
Ground stations (CAMS, 10 m)	$(-29 \pm 21)\%$	$(12 \pm 21)^\circ$

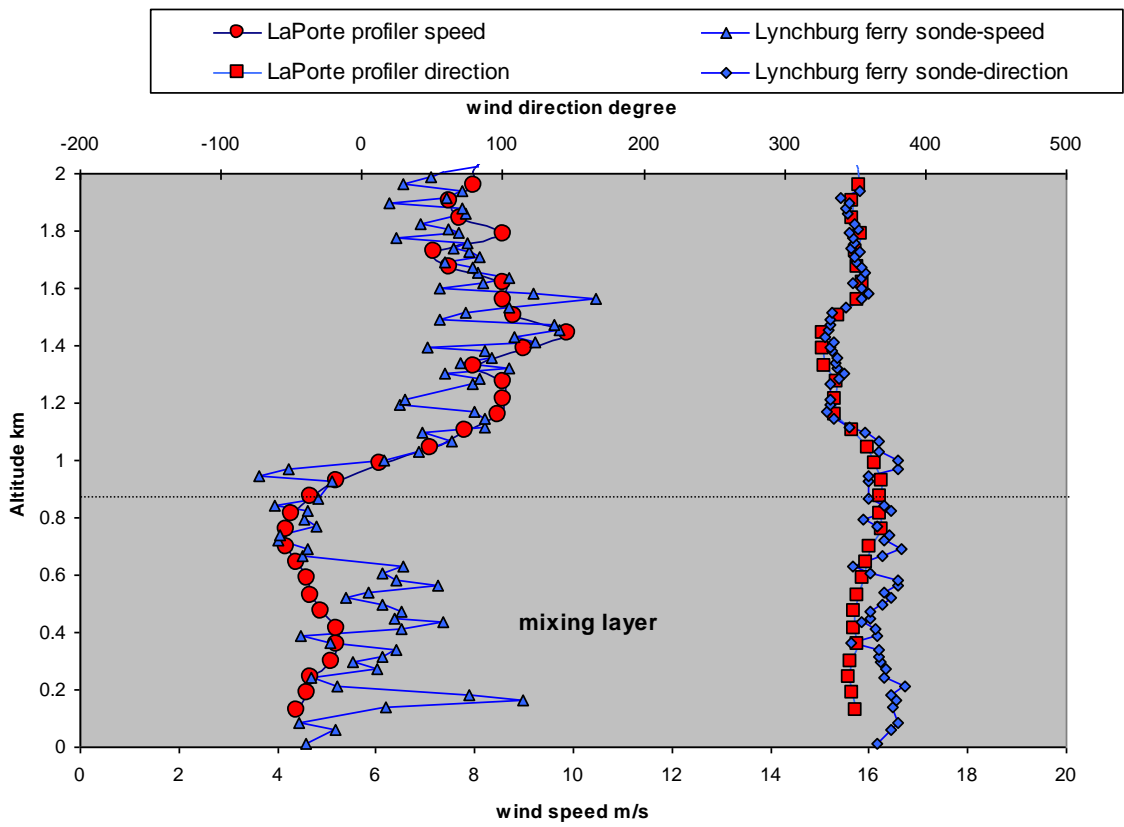


Figure 11. Wind measurements on August 30, 11:50 in the Houston ship channel. The profiler value corresponds to a 30 minute average. The average wind from the ground to 500 m altitude is 4.8 ± 0.4 m/s for the profiler and 6 ± 1.2 m/s for the GPS sonde.

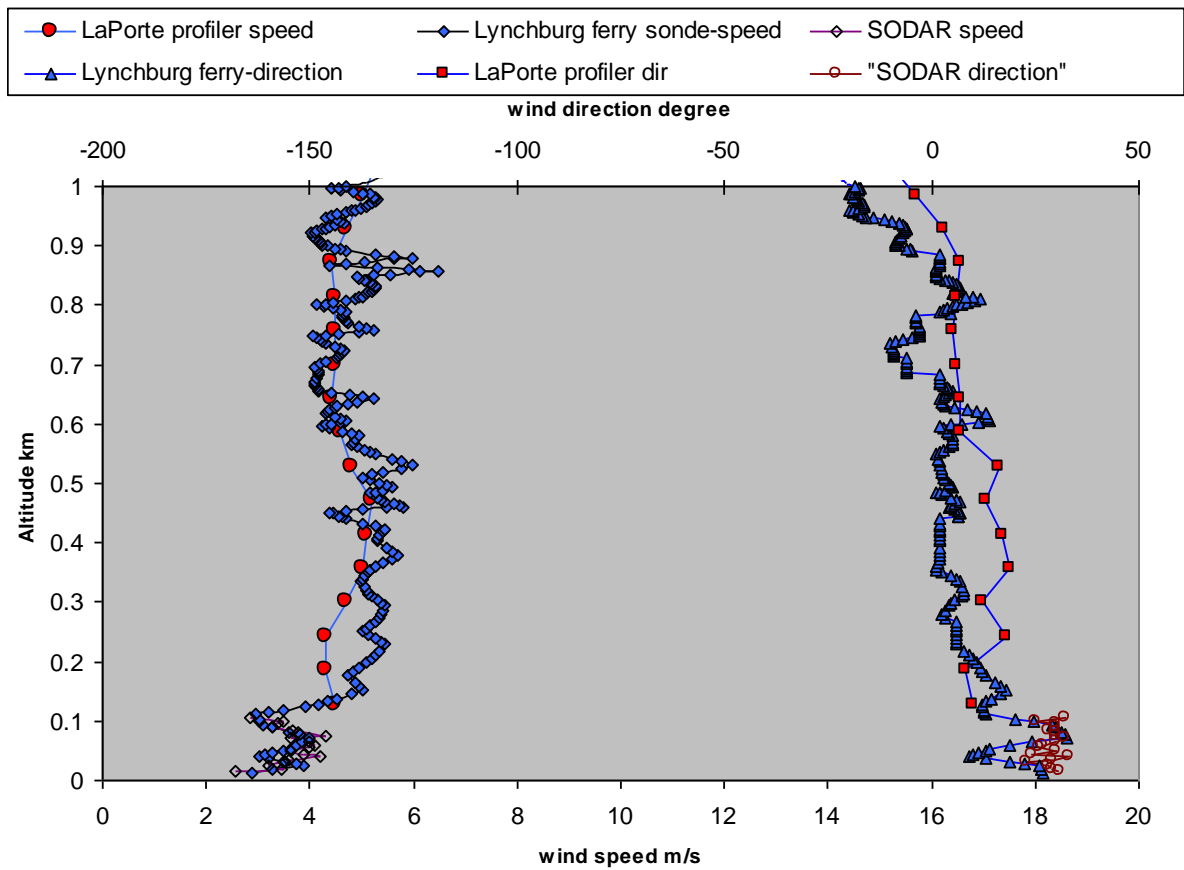


Figure 12. Wind measurements on September 13, 12:00 in the Houston ship channel. The wind profiler value corresponds to a 30 minute average and the SODAR to 5 minute. The SODAR corresponds to measurements at the western part of the HSC (Waterworks). The values above 100 m were removed in the SODAR. The average wind from the ground to 500 m attitude is 4.7 ± 0.4 m/s for the profiler and 4.7 ± 0.8 m/s for the GPS sonde.

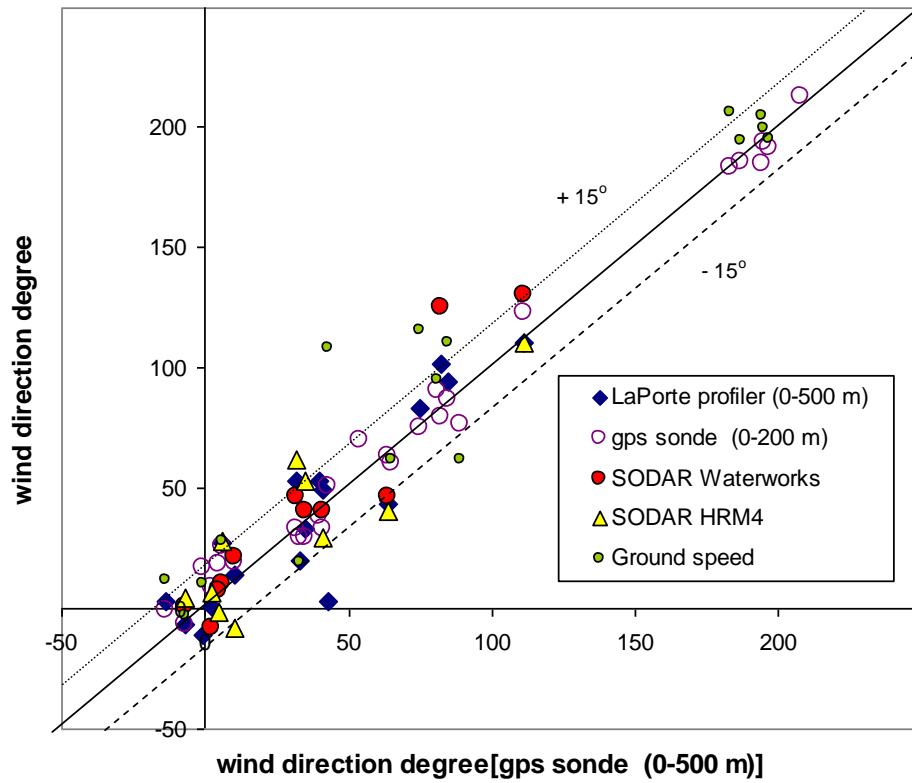
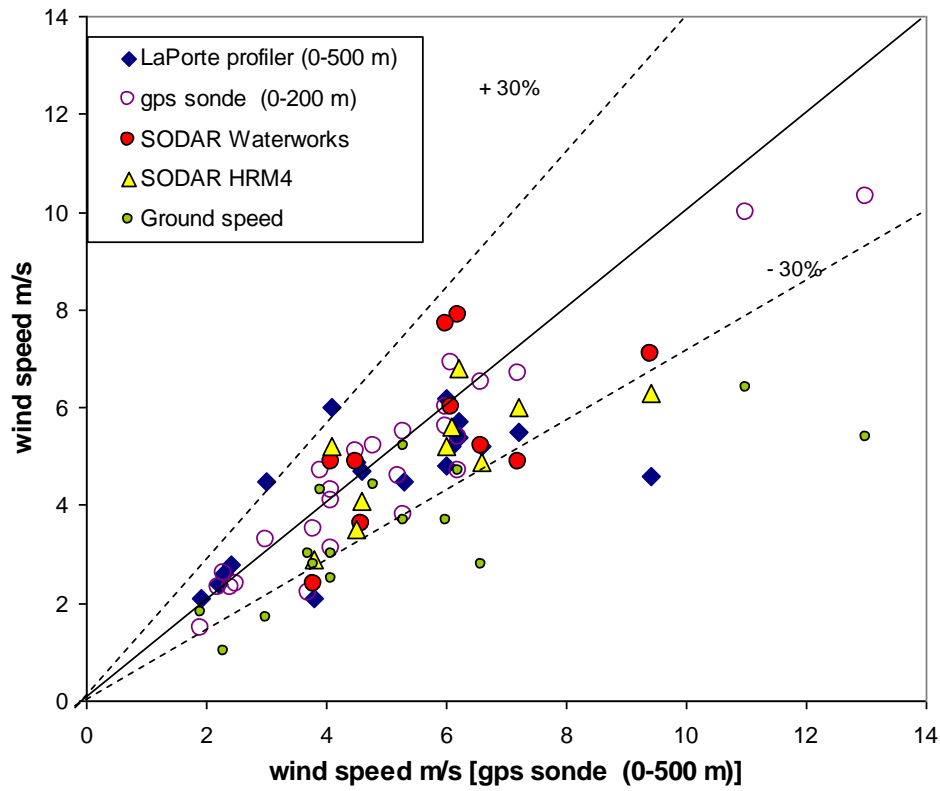


Figure 13. The available wind measurements for the SOF experiment plotted versus the average wind between ground and 500 m height as measured by the GPS sondes. The wind speed and wind direction are shown in the upper and lower figure, respectively.

3.2 Emission inventory data

The emission data obtained in this study have been compared to an emission inventory that has been derived by NOAA [Frost 2006] for the state of Texas including emissions of NO_x, SO₂, CO, total and selected speciated VOCs, PM_{2.5}, and PM₁₀ from 1858 fixed-location pollution sources statewide. The data are based on TCEQ's 2004 annual totals. The 2004 ethylene, propylene and alkane emissions for each point source have been derived from the 2004 total VOC emissions by assuming the same speciation at that point source as in 1999, the last year for which TCEQ provided complete speciation information. An extract of the database is given in appendix II. In the inventory, part of the emissions are reported as unspciated VOC, corresponding to the total of VOC mass whose speciation was not known. In many cases much of the total VOC at a particular facility may in fact be reported as unspciated. Likewise, some facilities will only report emissions in the alkanes and not break things down further. Also, a single facility is composed of hundreds or thousands of individual emission sources. While some of these sources might have good speciation information, others might not, so there may be a mixture of speciated and unspciated emissions from the same facility.

Recently a new emission dataset (2006 hourly inventory) has been released by TCEQ based partly on process monitoring at the industrial sites of for instance flares and cooling towers. According to analysis by Jolly [2007] there is a substantial increase in VOC emissions in the hourly inventory versus the 2004 emission inventory with a 70-80% increase in total VOC, 90% increase in propylene and 50-110% increase in ethylene. He claims flares are a dominant process/point type behind the large increases. Within the scope of this study it was not possible to compare against the new hourly inventory and this should be done in the future. Nevertheless a twofold emission increase in the inventory still does not explain the discrepancy of an order magnitude between the measurements and the 2004 inventory.

3.3 Additional VOC speciation for the alkane channel measurements

As discussed in section 2.1.2 the SOF alkane channel mass retrieval has some interference from alkenes and aromatics. In order to establish the importance of this, the Houston Ship Channel plume composition was studied using data from an auto-GC-station operated by TCEQ (CAMS-169) at the south-western corner of the HSC area, see Figure 14. Ten different hour averages from 5 different days during September 2006 were used. Only periods when wind direction was within the sector 69°-87° and wind speed was above 1.4 ms⁻¹ were used for the analysis (Table 3). The sector was chosen to avoid sample contamination from nearby industries to the east-south-east of the sampling station, and still sample from main part of the HSC area. It was verified that the chosen sector was not severely affected by the neighboring industries by examining the abundance of site specific compounds in the 69°-87°, 110° and 140° directions respectively.



Figure 14. Location of the TCEQ auto-GC-station CAMS-169 at Milby Park in the south-western corner of the HSC area (29.706111°N, 95.261111°W). Auto-GC-data from the wind sector 69°-87° during September 2006 was used for plume speciation into 36 different compounds. (Aerial photo from Google Earth Pro).

Table 3. Hourly averages of mixing ratios of alkanes, alkenes and aromatics as measured by the TCEQ auto-GC station A169 at Milby Park, southwestern corner of HSC. Retrieved alkane mass by the SOF alkane channel for the different plume compositions shown at the bottom row.

Date and time	Mol. mass	2006 Sep 2, 19:00	2006, Sep 4, 17:00	2006,S ep 9 21:00	2006, Sep 9 22:00	2006, Sep 20 11:00	2006, Sep 20 12:00	2006, Sep 26 16:00
<i>Windvel. (ms⁻¹)</i>		1.70	1.43	2.28	1.88	2.55	2.86	1.43
<i>Wind dir (°)</i>		76.00	72.00	87.00	86.00	69.00	76.00	77.00
	<u>gmol⁻¹</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>
Ethane	30.1	17.93	2.59	3.46	4.59	10.51	7.52	3.64
propane	44.1	20.20	1.23	1.71	2.22	9.40	4.84	2.09
n-butane	58.1	12.85	1.14	0.87	0.58	8.74	4.97	1.07
i-butane	58.1	4.87	0.37	0.68	0.60	3.84	2.41	1.03
cyc-pentane	70.1	1.01	0.09	0.16	0.04	0.43	0.23	0.05
i-pentane	72.2	16.07	1.35	1.43	0.47	6.69	4.17	0.74
n-pentane	72.2	12.52	0.80	0.94	0.24	4.23	2.37	0.42
cyc-hexane	84.2	2.17	0.09	0.14	0.04	0.49	0.24	0.04
2,2-dime-but.	86.2	0.33	0.04	0.08	0.03	0.20	0.11	0.02
n-hexane	86.2	2.40	0.18	0.48	0.14	1.21	0.71	0.19
3-me-hexane	100.2	0.45	0.05	0.14	0.05	0.32	0.22	0.05
n-heptane	100.2	0.65	0.05	0.13	0.04	0.33	0.21	0.04
n-octane	114.2	0.31	0.04	0.09	0.02	0.19	0.11	0.03
i-octane	114.2	0.36	0.10	0.18	0.08	0.58	0.24	0.08
n-nonane	128.2	0.07	0.01	0.02	0.01	0.05	0.03	0.01
n-decane	142.2	0.04	0.01	0.02	0.03	0.05	0.03	0.01
ethylene	28.0	4.16	0.46	0.75	0.50	1.96	1.51	0.66
propylene	42.1	3.94	0.24	0.99	0.92	1.66	0.90	0.42
1,3-butadiene	54.1	0.44	0.40	0.16	0.18	0.12	0.12	0.48
t-2-butene	56.1	0.68	0.13	0.09	0.07	0.12	0.10	0.12
1-butene	56.1	0.65	0.14	0.06	0.03	0.36	0.20	0.09
c-2-butene	56.1	0.52	0.07	0.06	0.04	0.09	0.07	0.07
isoprene	68.1	0.20	0.24	0.01	0.01	0.22	0.10	0.10
t-2-pentene	70.1	0.69	0.04	0.07	0.02	0.08	0.05	0.02
1-pentene	70.1	1.07	0.06	0.05	0.02	0.12	0.08	0.03
c-2-pentene	70.1	0.32	0.02	0.04	0.01	0.04	0.03	0.01
styrene	104.1	0.07	0.00	0.29	3.58	0.02	0.11	0.16
benzene	78.1	0.82	0.12	0.21	0.11	0.64	0.57	0.22
toluene	92.1	2.40	0.26	0.49	0.27	0.70	0.54	0.41
m+p-xylene	106.1	0.42	0.07	0.24	0.10	0.25	0.17	0.17
o-xylene	106.1	0.13	0.02	0.10	0.10	0.10	0.08	0.06
ethylbenzene	106.1	0.18	0.03	0.10	0.09	0.09	0.06	0.07
Alkane / Total mass (%)		84.7	76.4	71.1	44.0	87.9	85.3	70.4
Alkene / Total mass (%)		9.4	15.5	15.5	48.9	6.6	7.6	16.3
Aromatic / Total mass (%)		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

The auto-GC speciated the incoming plume into 16 alkanes, 11 alkenes and 5 aromatics. In general the alkane to total VOC mass ratio varied between 70.4-87.9 %. The corresponding mass ratios for alkenes were 6.6-16.4 %, and for aromatics 5.4-16.6 %, respectively. On one occasion (Sep 9, 10 pm), a strong styrene plume were encountered, shifting the mass fractions to 44% alkanes, 48.9% alkenes and 7.0% aromatics. Building composite infrared spectra corresponding to the 10 different plume compositions in Table 3, and evaluating them with the SOF alkane channel retrieval, it was found that the alkane mass could be retrieved within 6.6%.

3.4 Error budget

As discussed earlier and as seen in Table 4, the major source of uncertainty in the SOF and the mobile DOAS measurements, is the uncertainty in the wind field, specifically the wind speed (30%). The absorption line parameters of the retrieved compounds are well established in published databases, stating an uncertainty of 3 % for the spectroscopic part. To this a retrieval uncertainty is added. This is the combined effect of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect. The composite uncertainty is believed to be within 33%-38% for all retrieved compounds. This is the uncertainty in the flux retrieval at the plume measurement traverse. Stating the actual emission from a certain site, one would also have to consider any chemical degradation or change of the plume from the release point to the measurement position. In that sense the given fluxes for ethene, propylene, alkanes and SO₂ are lower end estimates, whereas the NO₂ might be an upper end estimate, considering conversion of primary NO to NO₂ during plume transport.

Table 4. Uncertainty estimation of the flux measurements (the variability of the sources not taken into account).

	Wind Speed	Wind direct	Spectroscopy (cross sections)	Retrieval	Square-root summed uncertainty
Ethene	30%	10%	3%	10 %	33 %
Propene	30%	10%	3%	20 %	38 %
NO₂	30%	10%	3%	10 %	33 %
SO₂	30%	10%	3%	20 %	38 %
Alkanes	30%	10%	3%	10%	34 % *

* Includes an error of 6.6 % in the alkane composite uncertainty, due to interference in different plume compositions.

4. Results

4.1 Ethene

In Figure 15 a SOF transect across the Houston ship channel is shown conducted on August 30, 2006. Blue color represents the lowest and red the highest columns, and the lines are pointing up wind. The total column in mg/m^2 is also shown in the lower part of the figure with a black line. The known point emissions from the TCEQ 2004 database in kg/h are shown in white squares, and also the positions of the wind measurements are shown. There are several distinct source regions as can be seen in the figure, and these usually show up in most measurements. Two measurements across the HSC yielded 1100 and 1400 kg/h ethylene on this particular day while a few weeks later on September 19 three measurements yielded 922 ± 130 kg/h , see cover picture. In our interpretation of the data these measurements include the far away, but large, emissions sources in Mt Belvieu. This means that the HSC and Mt Belvieu are emitting about 1100 kg of ethylene per hour. On this particular day the emissions from sector 3, Deer park, were larger than normal, 340 kg/h compared to the average of 187 kg/h .

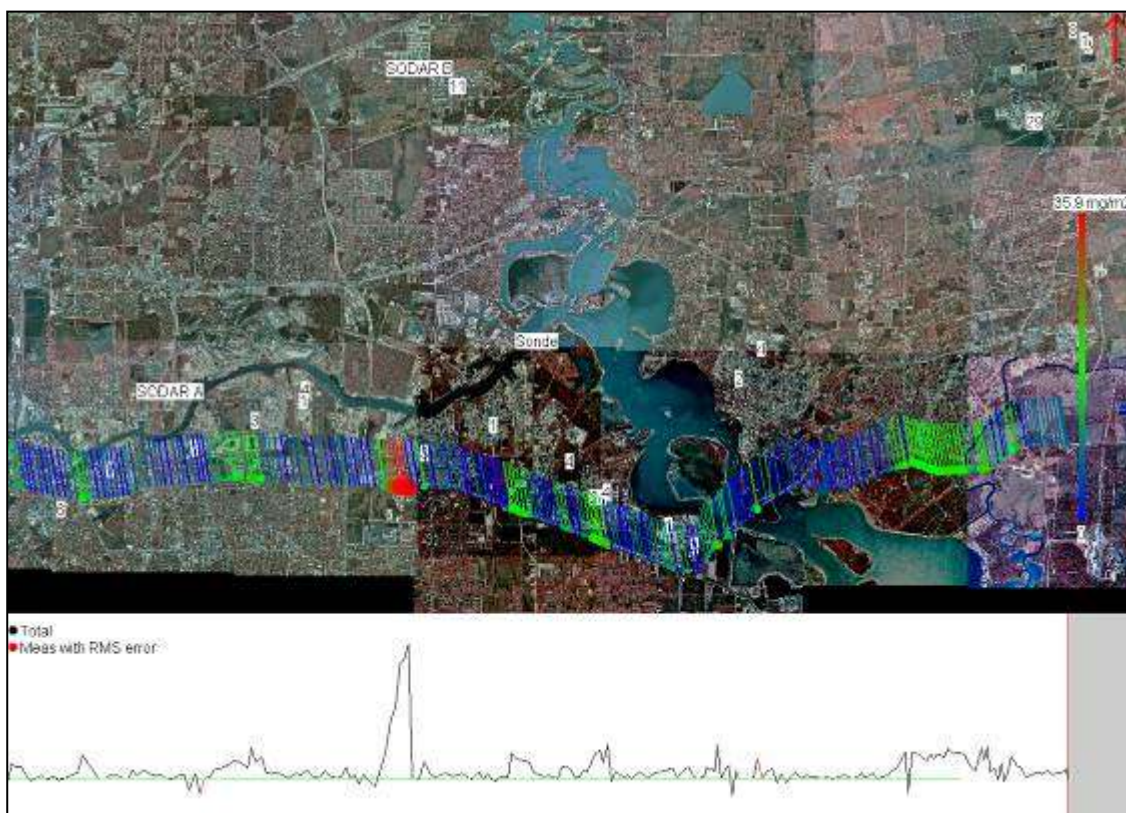


Figure 15 SOF measurement of ethene on August 30 2006, in the Houston ship channel. Blue colour represents the lowest and red the highest columns, and the lines are pointing up wind. Total column in mg/m^2 , known point emissions in kg/h are shown in white squares. The total column values are also shown in the lower part of the figure with a black line. The positions of the wind measurements are shown. Two measurements across the HSC averaged 1290 kg/h on this particular day.

In Table 5 the averaged emissions from the different source regions in the HSC and elsewhere are shown together with the emission database. More detailed information is

given in Table 6. Several of the measurements are also illustrated in Figure 17 to Figure 21.

The largest emission source of ethene at the HSC is the Mt Belvieu complex, emitting around 400 kg/h. Results from the NOAA airborne measurements shows emission values which are within 50% of these numbers [Gouw, 2007] for the same complex. In the 2004 emissions database the emissions of ethene from the Mt Belvieu complex correspond to 41 kg/h, hence an order of magnitude in discrepancy. In Figure 16 measurements at Mt Belvieu are shown for September 26. The emissions this day was higher, 566 kg/h, than for other days when measurements were conducted from this industrial area. The emissions originate from two different industrial sites and the northerly one shows slightly larger (25%) emissions.

A persistent source area of ethylene in the HSC is the region east of Battleground road as shown in Figure 17. Measurements conducted on August 31 and September 14 for easterly wind shows high and slightly variable emissions of 200-400 kg/h coming from this area. This sector corresponds to sector 4 and 5 in Table 5, with an average emission of about 270 kg/h when measured in northerly wind. There is considerable variability in the emissions with apparent upset releases, potentially from flares. This is apparent in the measurements in Figure 17 in which two subsequent SOF transect, 30 minutes apart, yielded emissions of 237 and 95 kg/h, respectively. See section 5 for a further discussion about the variability.

The emissions from the HSC correspond to about 860 ± 180 kg/h when measured over 3 separate days, i.e. August 30, September 13 and 25. The emissions of the individual source areas given in Table 5 sum up to 750 kg/h, which is quite consistent with the 860 kg/h given above. The sum of the emission from the HSC and the Mt Belvieu corresponds to 1260 kg/h. This value is quite close to the average value of 1100 kg/h that was obtained on August 30 and September 19 corresponding to emissions from the HSC and Mt Belvieu in the same measurements, Figure 15, as was discussed above.

For the Freeport complex the SOF measurements show ethene emissions of around 250 kg/h, Figure 20, and 95% of these emissions originate from Freeport A., Figure 3, while the 2004 emissions database states an emission of 21 kg/h, hence a discrepancy of a factor 12.

In Figure 21 a measurement at the Sweeny area is shown. The emissions for two individual days of measurements, i.e. September 21 and 27 showed quite similar results. On the first occasion the personnel at one of the sites indicated that the plant was malfunctioning and that considerable flaring was being conducted.

Table 5. Average ethene emissions for measurements in September 2006. The given variability corresponds to day-to-day variations of the emissions and not uncertainty. The estimated measurement uncertainty is 30%. The sectors in the HSC were measured in northerly wind. The emission inventory is obtained from TCEQ 2004 data, see section 3.2. The error factor corresponds to the ratio between the SOF measurements and the inventory values and it is 25 on average.

Sector/Region	SOF 2006 kg/h	Meas. Days	Emission Invent. 2004 kg/h
1. Allen Genoa Rd	96±15	3	1
2. Davison street	120±24	4	8
3. Deer-Park	187±110	4	3
4. Battleground road WE	92± 47	4	5
5. Miller_cutoff_road	184± 156	4	25
7. Baytown	72 ± 24	2	6
8. Mt Belvieu	404±41	3	41
HSC**	860±180	3	48
Bayport*	170	1	4
Channelview	64±32	3	11
Chocolate-Bayou*	136	1	10
Freeport	250±65	1	21
Sweeny	163±5	2	4
Texas-City	83±12	1	8

*Uncertain since only one measurement, ** Direct measurement over HSC, Mt Belvieu not included

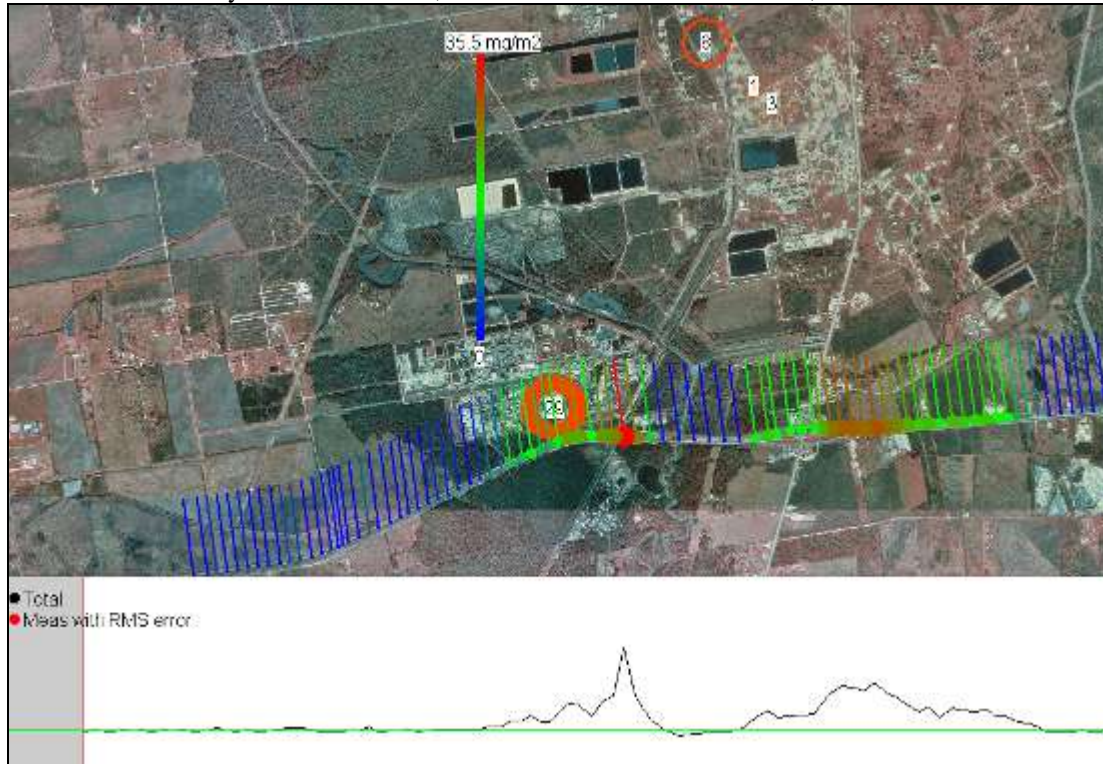


Figure 16. SOF measurements of ethene at Mt Belvieu on September 25, 2006. Two distinct sources can be seen. The emission for three measurements corresponds to 566 ± 35 kg/h, which was considerably higher than the average emission over several days.

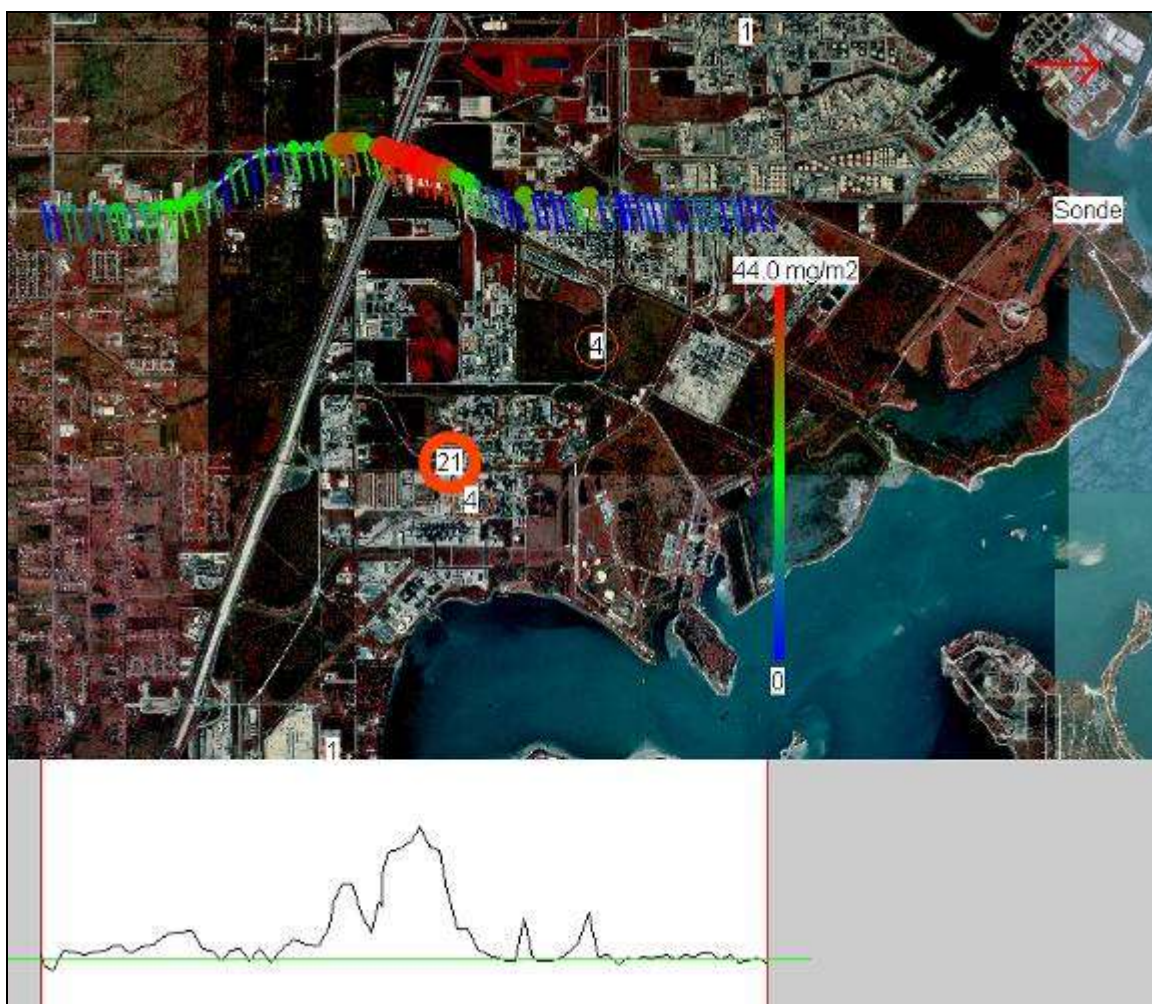


Figure 17. SOF measurements of ethene on Battleground road in HSC (north is to the right) on August 31, 2006 at noon. The emission for four measurements corresponds to 196 ± 80 kg/h. The average of this day and September 14 corresponds to 295 ± 140 kg/h.

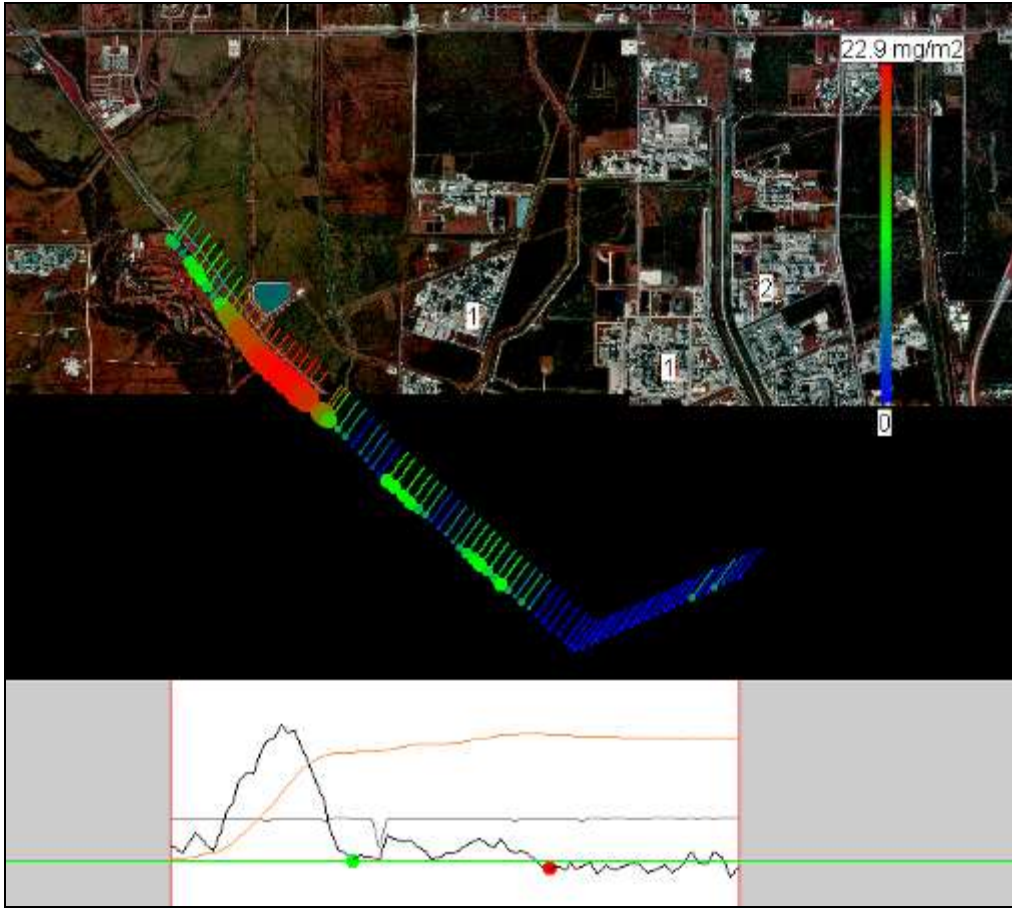


Figure 18. SOF measurement of ethene at Bayport on September 26, 2006. The momentary emission corresponds to 170 kg/h.

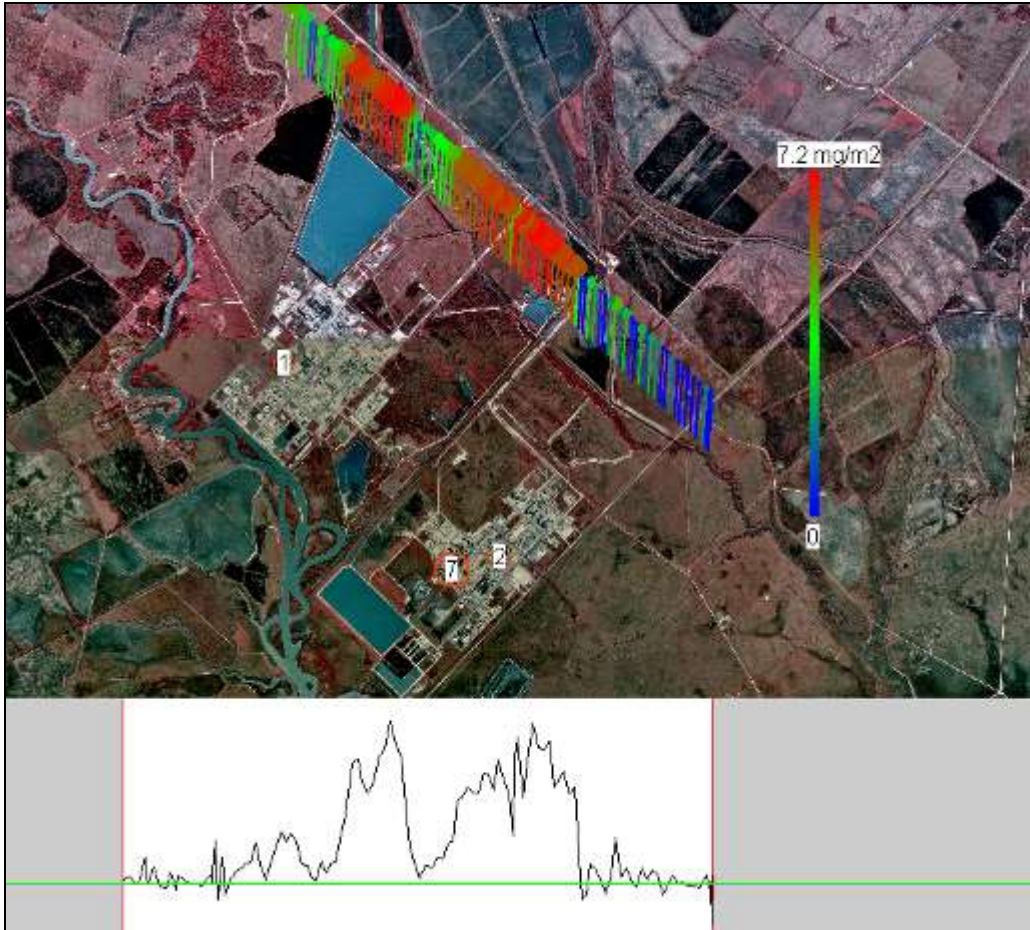


Figure 19. SOF measurement measurements of ethene at Chocolate Bayou on September 26, 2006. The emission corresponds to 129 kg/h.

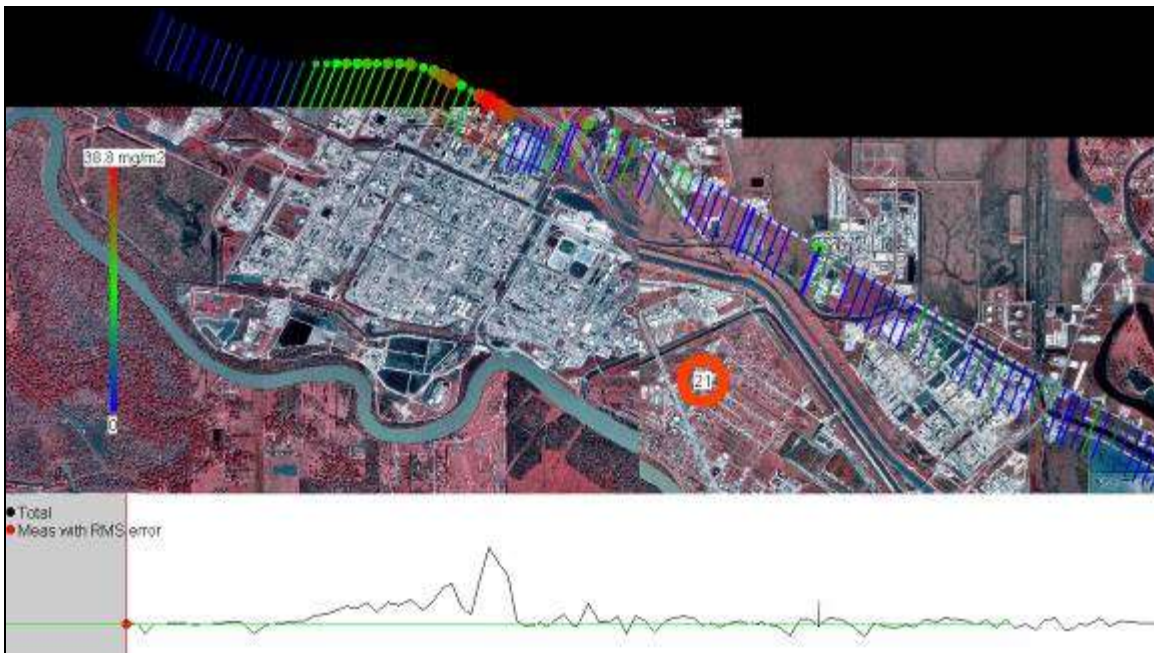


Figure 20. SOF measurement measurements of ethene at Freeport on September 26, 2006. The emission for three measurements corresponds to 250 ± 64 kg/h.

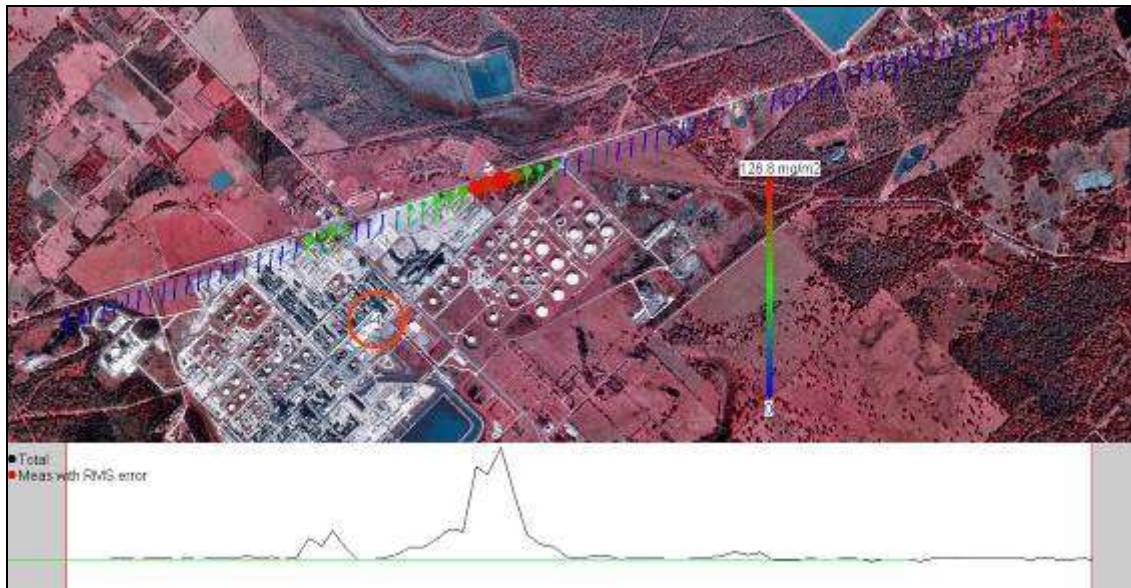


Figure 21. SOF measurement of ethene at Sweeny on September 26, 2006. The emission for three measurements on this day corresponds to 160 ± 34 kg/h.

Table 6. Detailed ethene emission data measured with SOF for various sectors.

Sector	Day	Timespan	Nr of transects	Emission (kg h ⁻¹)	Wind
HSC, sector 1-8					
	060830	105336 - 133757	2	1290± 370	6.0-6.2m/s 1-359deg
	060919	091944 - 152019	3	922± 130	4.5-9.4m/s 35-41deg
HSC, sector 1-8	Average	-	(total 5)	1100 ± 262	-
HSC, sector 1-7					
	<u>060830</u>	105336 - 133757	2	935.7 ± 43.8	6.0-6.2m/s 1-359deg
	<u>060913</u>	143954 - 154606	1	985.3	3.8 m/s 6 deg
	<u>060925</u>	112958 - 123954	1	656.5	7.0 m/s 5 deg
HSC, sector 1-7	Average	-	(total 4)	859.2 ± 177	-
1. Allen Genoa Rd					
1	060830	105705 - 133424	2	82.4 ± 34.6	6.0-6.2m/s 1-359deg
1	060913	153846 - 154556	1	111.4	3.8 m/s 6 deg
1	060919	102544 - 144139	3	93.1 ± 35.4	4.5-9.4m/s 35-41deg
1	Average	-	(total 6)	96 ± 15	-
2. Davison St					
2	<u>060830</u>	110321 - 132401	2	154.5 ± 23.2	6.0-6.2m/s 1-359deg
2	<u>060913</u>	152330 - 152847	1	114.6	3.8 m/s 6 deg
2	<u>060919</u>	101834 - 145016	3	109.4 ± 40.5	4.5-9.4m/s 35-41deg
	<u>060925</u>	121422 - 122338	1	100.8	7.0 m/s 5 deg
2	Average	-	(total 7)	120 ± 24	-
3. Deer Park					
3	<u>060830</u>	111058 - 130741	2	340.3 ± 85.1	6.0-6.2m/s 1-359deg
3	<u>060913</u>	150946 - 151531	1	105.4	3.8-3.8m/s 6-6deg
	<u>060919</u>	100637 - 145802	3	120.4 ± 51.8	4.5-9.4m/s 35-41deg
3	<u>060925</u>	120517 - 121131	1	182.7	7.0 m/s 5 deg
3	Average	-	(total 7)	187 ± 110	-
4. Battleground Rd					
4	<u>060830</u>	111647 - 111947	1	73.9	6.2m/s 359deg
4	<u>060913</u>	150112 - 150614	1	157.9	3.8m/s 6deg

4	<u>060919</u>	100051 - 114110	2	87.9 ± 44.8	9.4m/s 41deg
4	<u>060925</u>	115352 - 115654	1	49.0	7.0m/s 5deg
4	Average		(total 5)	92 ± 47	
5. Miller's Cut Off Rd					
5	<u>060830</u>	111935 - 112342	1	114.8	6.2m/s 359deg
5	<u>060913</u>	145523 - 150126	1	362.7	3.8m/s 6deg
5	<u>060925</u>	114914 - 115413	1	74.6	7.0m/s 5deg
5	Average	-	(total 3)	184.0± 156	-
7. Baytown					
7	<u>060830</u>	112645 - 113500	1	69.7	6.2m/s 359deg
7	<u>060907</u>	122202 - 123633	1	47.3	2.0m/s 75deg
	<u>060913</u>	144844 - 145409	1	104.4	4.6m/s 10deg
7	<u>060925</u>	111946 - 112613	1	67.7	7.0m/s 5deg
7	Average	-	(total 4)	72 ± 24	-
8. Mt Belvieu					
8	<u>060830</u>	113203 - 122843	2	314.6 ± 55.6	6.0-6.2m/s 1-359deg
	<u>060919</u>	131054 - 133246	1	331.3	6.0m/s 32deg
	<u>060925</u>	145616 - 170104	3	566.5 ± 34.0	6.6m/s 353deg
8	Average	-	(total 6)	404 ± 41	-
Sweeny					
	<u>060921</u>	114732 - 150202	3	167.4 ±108.8	10.0m/s 191deg
	<u>060927</u>	161602 - 174958	4	159.9 ± 33.6	2.2m/s 185 deg
Sweeny	Average	-	(total 7)	163±5	-
Channelview					
	<u>060831</u>	164824 - 181336	2	34.5 ± 6	2.0-3 m/s 43-126deg
	<u>060919</u>	135516 - 140833	1	60.7	6.0m/s 32deg
	<u>060926</u>	151530 - 152926	1	97.9	2.8m/s 51 deg
Channelview	Average	-	(total 4)	64±32	-

4.2 Propene

In Figure 22 a SOF transect across the Houston ship channel is shown conducted on September 25, 2006. The momentary emissions here correspond to 900 kg/h. There are several distinct source regions as can be seen in the figure, and these usually show up in most measurements. The point emissions from the TCEQ 2004 database in kg/h are shown in white squares. In Table 7, the average emissions are shown for all measurements during the campaign. As can be seen the emissions from the HSC, excluding Mt Belvieu, correspond to 1500 kg/h on average but show large variability. This corresponds to 25 times the values reported in the emission inventory.

One of the largest emissions sources is Mt Belvieu, Figure 23. An example of large variability is shown in Figure 24 which corresponds to a SOF measurement that was conducted on Battleground road on August 30 in the north to south direction. The emission rate varied from 2000 kg/h down to 200 kg/h within 30 minutes. Similar events also occurred on other days. At the same time ethene varied from 237 to 95 kg/h as was discussed in relation to Figure 17. The reason for the variation is potentially flaring or some other type of upset release, but it is difficult to understand why propene varies more than ethene.

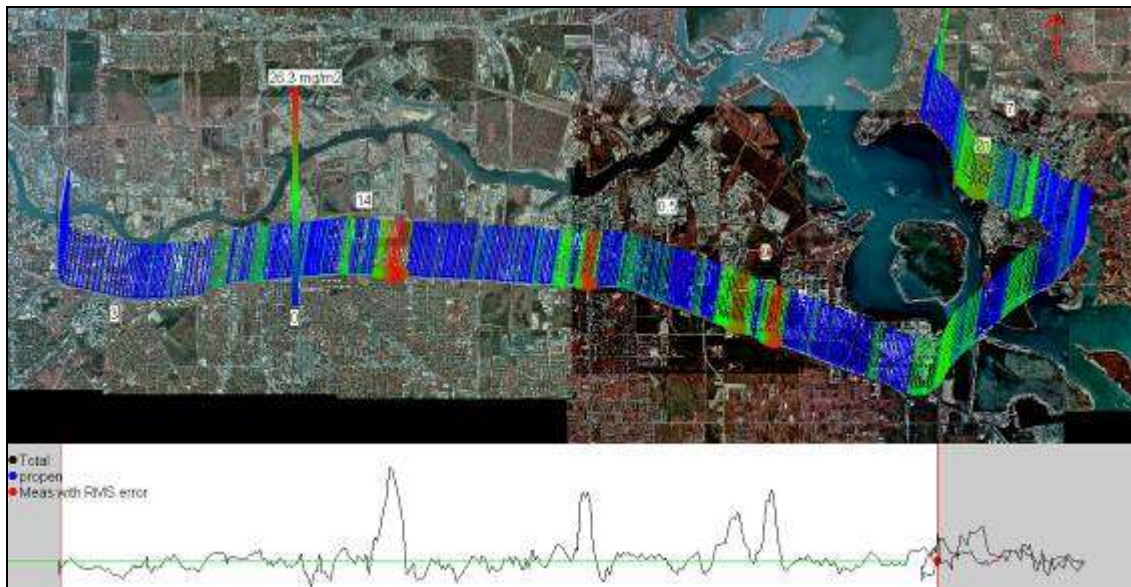


Figure 22. SOF measurement of propene on September 25 2006, in the Houston ship channel. Blue colour represents the lowest and red the highest columns in mg/m^2 and the lines are pointing up wind. Emission sources, white squares, from an emission inventory are given in kg/h. The total column values are also shown in the lower part of the figure with a black line.

Table 7. Average propene emissions for measurements in September. The given variability corresponds to day-to-day variations of the emissions and not uncertainty. The estimated measurement uncertainty is 30%. The sectors in the HSC were measured in northerly wind. The emission inventory is obtained from TCEQ 2004 data, see section 3.2. The error factor corresponds to the ratio between the SOF measurements and the inventory values and it is 35 on average.

Sector/Region	SOF 2006 kg/h	Meas. Days	Emission Invent. 2004 kg/h
2. Davison street	144±75	4	14
3. Deer-Park	282±282	4	8
4. Battleground road	380±390	4	9
5. Miller_cutoff_road	211±70	4	2
7. Baytown	260±95	3	28
8. Mt Belvieu	420±280	2	9
HSC**	1500±500	3	61
Chocolate-Bayou	273.0*	1	24
Sweeny	126±64	1	4

* Uncertain since only one measurement, ** Direct measurement over HSC, Mt Belvieu not included.

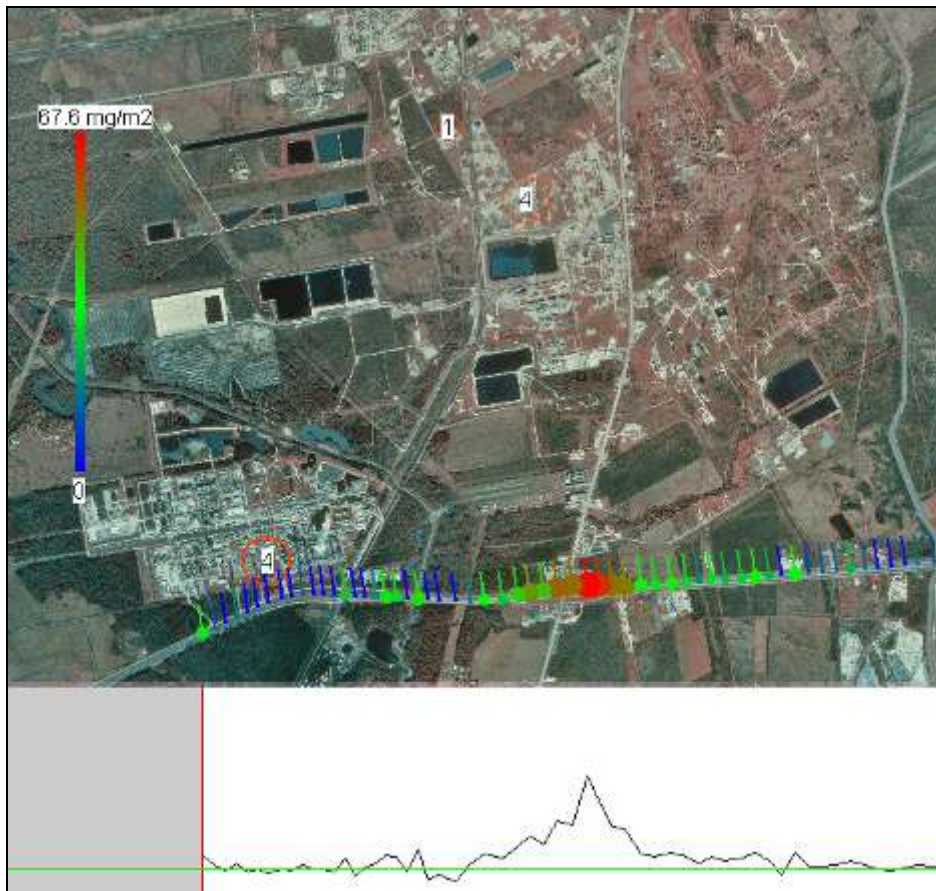


Figure 23. SOF measurement of propene on September 2007, at Mt Belvieu. The emissions correspond to 646 kg/h.

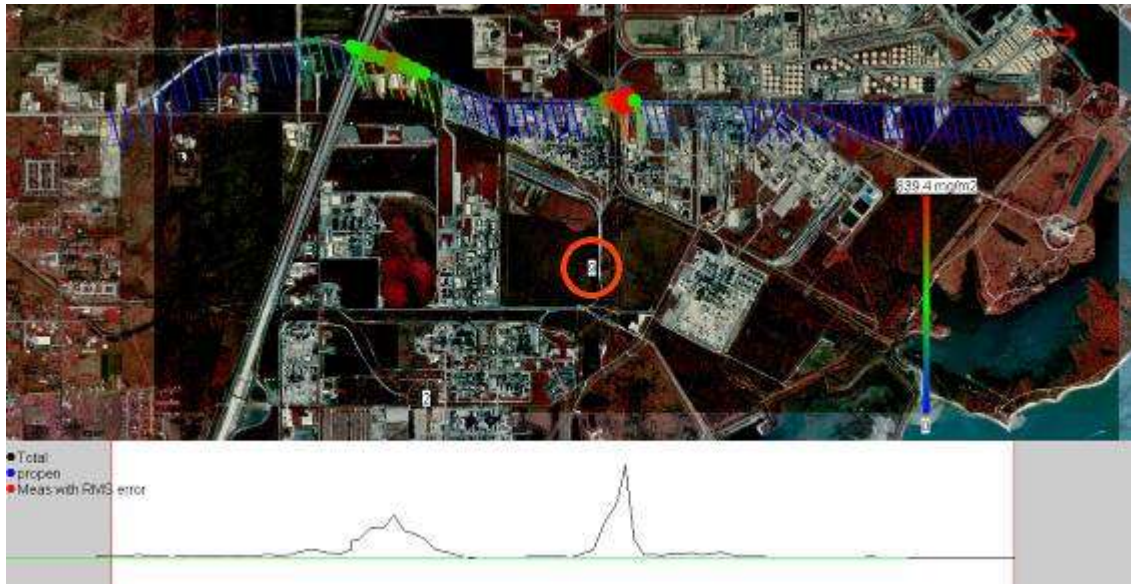


Figure 24. SOF measurement of propene on August 31 2006, on Battleground road. The emission rate corresponds to 2000 kg/h but was down to 200 kg/h within 30 minutes. This also occurred on other days.

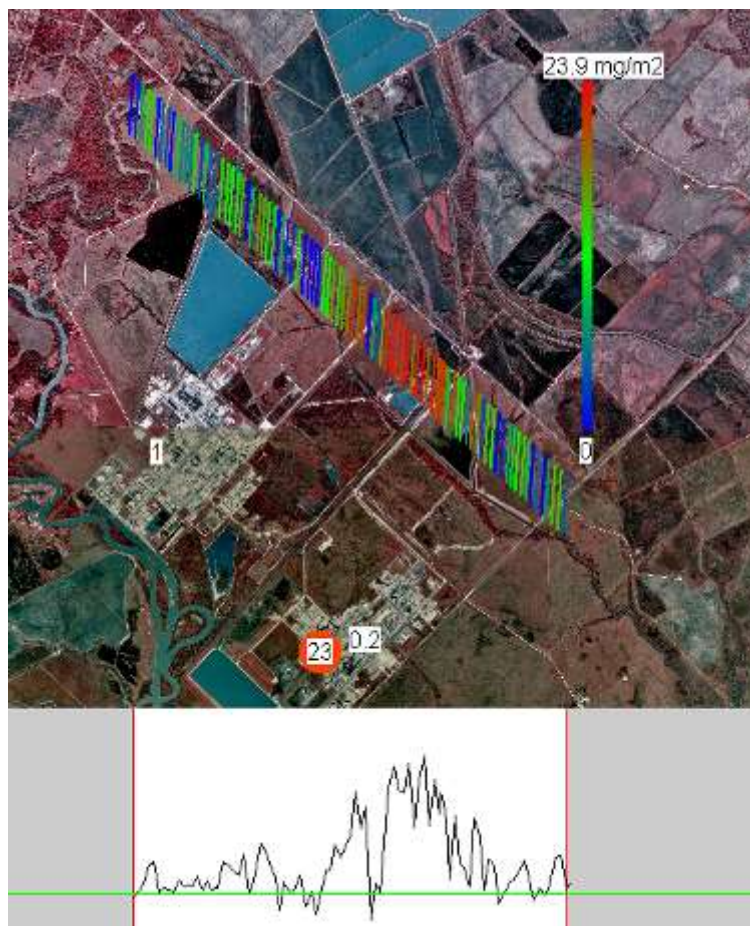


Figure 25. SOF measurement of propene on September 27 2006, at Chocolate Bayou. The emissions here correspond to 273 kg/h.

Table 8. Detailed propene emission data measured with SOF for various sectors

Sector	Day	Timespan	Nr of transects	Emission (kg h ⁻¹)	Wind
HSC, sector 1-7					
	060830	105336 - 113435	1	1859.1	6.2m/s 359deg
	060925	113404 - 122140	1	902.3	7.0-7.0m/s 5-5deg
	060913	144350 - 154534	1	1770.4	3.8-3.8m/s 6-6deg
HSC, sector 1-7	Average	-	(total 3)	1511± 529	-
2. Davison St					
2	060830	110321 - 110859	1	139.1	6.2-6.2m/s 359deg
2	060925	121318 - 122234	1	250.7	7.0-7.0m/s 5-5deg
2	060919	144217 - 145016	1	82.6	4.5-4.5m/s 35-35deg
2	060913	152847 - 154100	1	102.0	3.8-3.8m/s 6-6deg
2	Average	-	(total 4)	144 ± 75	-
3. Deer Park					
3	060830	111058 - 130741	2	689.1	6.0-6.2m/s 1-359deg
3	060925	120413 - 121027	1	140.1	7.0-7.0m/s 5-5deg
	060919	112611 - 145802	2	53.7	4.5-9.4m/s 35-41deg
3	060913	150946 - 151531	1	245.8	3.8-3.8m/s 6-6deg
3	Average	-	(total 6)	282 ± 282	-
4. Battleground Rd					
4	060830	111647 - 111947	1	144.5	6.2m/s 359deg
4	060925	115424 - 115654	1	185.3	7.0-7.0m/s 5-5deg
4	060919	145735 - 150249	1	213.2	4.5-4.5m/s 35-35deg
4	060913	150112 - 150614	1	975.0	3.8-3.8m/s 6-6deg
4	Average	-	(total 4)	380 ± 398	
5. Miller's Cut Off Rd					
5	060830	111935 - 125018	2	262.3	6.0-6.2m/s 1-359deg
5	060925	114821 - 115352	1	161.0	7.0-7.0m/s 5-5deg
5	060913	145523 - 150126	1	240.8	3.8-3.8m/s 6-6deg
5	Average	-	(total 4)	221 ± 53	-
7. Baytown					
7	060830	123153 - 123603	1	237.8	6.0-6.0m/s 1-1deg

7	060925	111935 - 112549	1	362.7	7.0-7.0m/s 5-5deg
	060907	122202 - 123633	1	177.4	2.0-2.0m/s 75- 75deg
7	Average	-	(total 3)	259 ± 95	-
8. Mt Belvieu					
8	060925	155434 - 165947	2	621.3	6.6m/s 353deg
	060919	131610 - 132801	1	223.1	6.0-6.0m/s 32- 32deg
8	Average	-	(total 3)	422 ± 282	-
Sweeny					
	060927	164232 - 173728	3	126.5	2.2m/s 185deg
	060921	114732 - 120129	2	117.9	10.0m/s 191deg
Sweeny	Average	-	(total 5)	122±6	-

4.3 Alkanes

Table 9 summarizes alkane emissions from all regions measured by SOF during the TexAQS II 2006 campaign. The overall alkane emission from the HSC area, as made up by sector 1-8, was found to be 12.4 metric tons per hour. For comparison, the reported alkane emissions from the corresponding regions are 1.5 metric tons per hour, or 8 times lower on average. All individual measurements making up Table 9 are shown in Table 10 along with the time period of the measurement and applied wind conditions. As alkane inventory emissions numbers we have used the sum of speciated alkanes and unspciated VOC, since we expect that most emissions occurring from the refineries, are in the form of alkanes [Kihlman 2005a]. On average this increases the alkane emissions from the largest sources by 30%. In Table 9 the total VOC emissions in the inventory are also shown, which on average are about 70% higher than the alkane numbers.

Table 9. Summary of alkane emissions as measured by SOF. Reported as averages (± 1 standard deviation, where applicable) of the daily values. The emission inventory is obtained from TCEQ 2004 data, see section 3.2. The error factor corresponds to the ratio between the SOF measurements and the inventory values.

HSC sector / Region	SOF 2006 kg/h	Emission inventory (kg h ⁻¹) alkanes *	Total VOC inventory (kg h ⁻¹)
1. Allen Genoa Rd	1739 \pm 759 (3 days)	176	254
2. Davison St	3678 \pm 1165 (3 days)	220	373
3. Deer Park	2983 \pm 1424 (3 days)	143	277
4. Battleground Rd	1264 \pm 343 (3 days)	110	236
5. Miller's Cut Off Rd	420 \pm 123 (3 days)	13	75
6. Sens Rd	468 \pm 340 (2 days)	8	38
7. Baytown	976 \pm 113 (3 days)	202	437
8. Mt Belvieu	863 (1 day)	260	265
Texas City	2889 \pm 399 (3 days)	348	686
Sweeny	3633 (1 day)	113	137

* Sum of alkanes and unspciated VOC as reported in the 2004 inventory

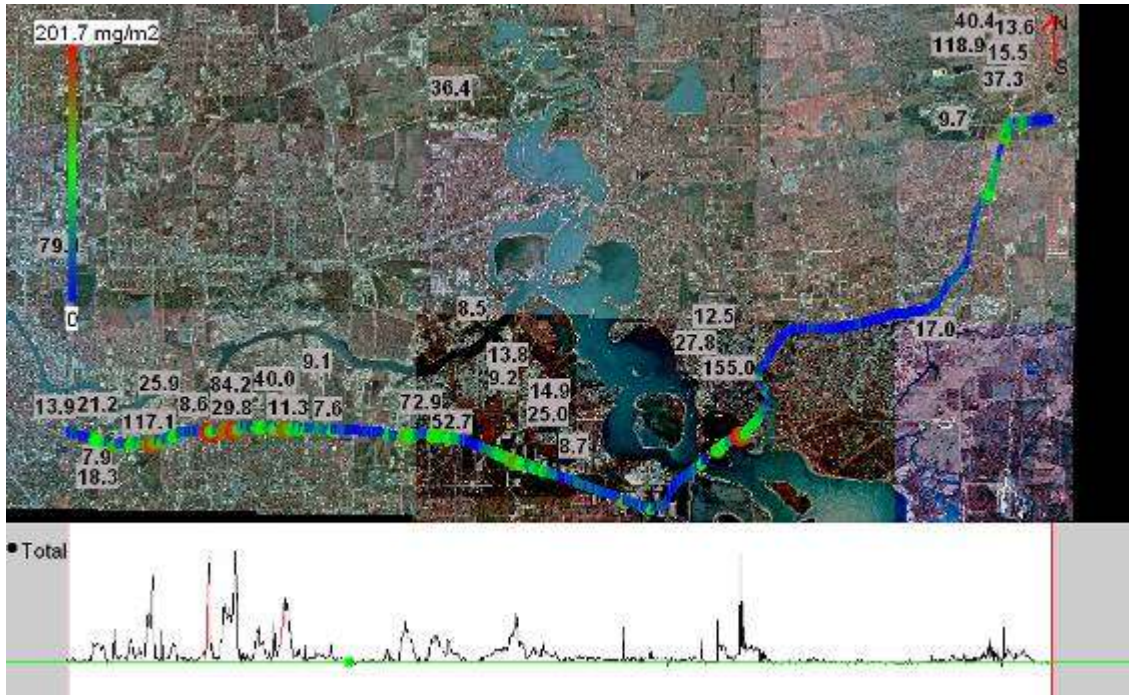


Figure 26. SOF alkane channel measurement south of HSC (sector 1-8) on 25 September 2007, 1:05 pm. Wind from the north (2° , 6.1 ms^{-1}). The emission from the HSC area was found to be 12400 kg/h of alkanes. Reported alkane (+ unspiciated VOC) emissions in bold black on grey background (kg/h).

Figure 27 shows an alkane emission measurement at the Texas City industrial complex on 20 September 2006. Three SOF transects were done on this day, giving an emission of $2905 \pm 118 \text{ kg/h}$. For the measurements in Texas city, wind were measured with GPS-sondes launched at (29.3884°N , 95.0426°W), and by the CAMS100 ground station at (29.3900°N , 94.9194°W), and the CAMS620 ground station at (29.4022°N , 94.9463°W). Comparisons between three GPS-sondes released on 20 September, and the corresponding hour averages of the two ground stations, showed that the ground stations were within -5.2% to $+12 \%$ of the sondes in wind speed, and within 0° to 19° in wind direction.



Figure 27. SOF alkane channel measurement west of Texas City on 20 September 2007, 1:42 pm. Wind from the east (81° , 4.8 ms^{-1}), emission corresponding to 2905 kg/h of alkanes. Reported emissions in bold black on grey background (kg h^{-1}). Ground wind station CAMS100 location shown.

On the 20 September one transect was also done, dividing the Texas City complex into an eastern and a western part, as seen in Figure 28. The alkane emission from the eastern part was found to be 990 kg/h.

In parallel with the SOF measurements on 20 September, canister sampling was performed from an airborne platform (Baylor University) for subsequent GC-analysis (University of Houston). This data set will provide good VOC speciation of the plume, but was not available at the time of reporting. Also plume speciation by NOAA will be added to the final Texas City data analysis. For the measurements in the HSC area and in Sweeny there exists valuable VOC plume speciation and height profile information from the NOAA and Baylor University flying platforms, which will be included as soon as the data sets are presented.

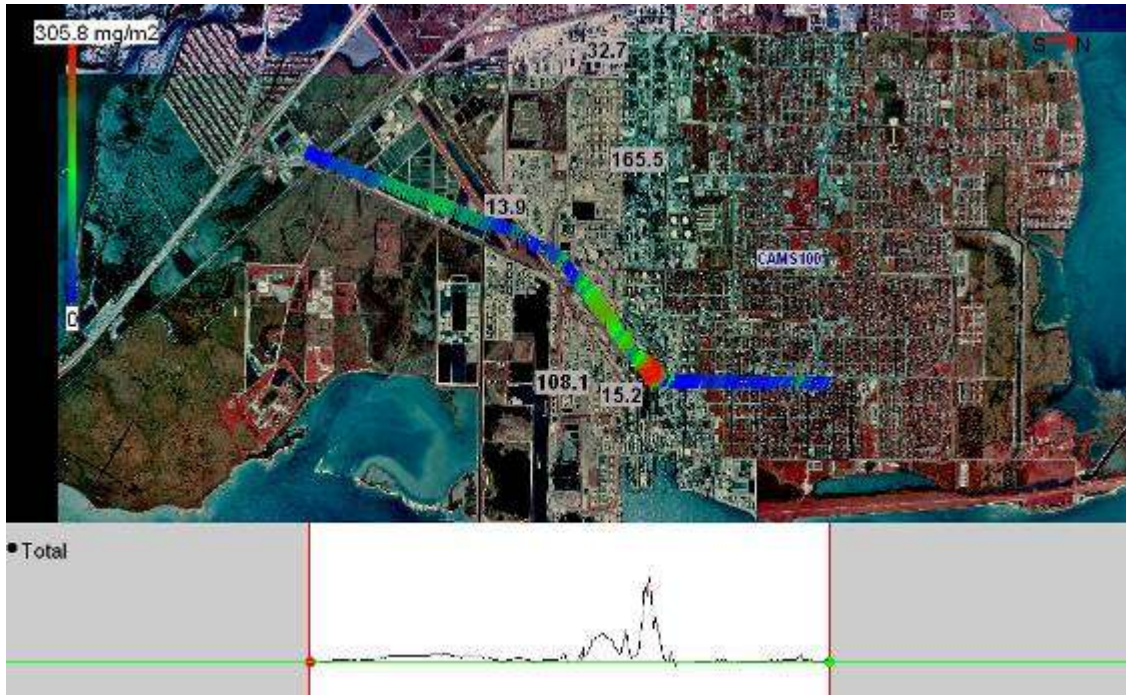


Figure 28. SOF alkane channel measurement of the east half of Texas City on 20 September 2007, 5:00 pm. Wind from the east (109° , 3.0 ms^{-1}), emission corresponding to 990 kg/h of alkanes. Reported emissions in bold black on grey background (kg/h).

Table 10. Detailed alkane emission data measured with SOF for various sectors.

Sector	Day	Timespan	Nr of transects	Emission (kg h^{-1})	Wind
1. Allen Genoa Rd					
1	060913	122515-124109	1	1593.7	4.6 m/s 10 deg
1	060919	174754-175647	1	2560	4.9 m/s 30 deg
1	060925	122734 - 123443	1	1062.8	6.1 m/s 2.0 deg
1	Average		(total 3)	1739 ± 759	-
2. Davison St					
2	060913	121916-122515	1	3061.7	4.6 m/s 10 deg
2	060919	173810-174754	1	5021.2	4.9 m/s 30 deg
2	060925	132118-132751	1	2950.8	6.1 m/s 2.0 deg
2	Average		(total 3)	3678 ± 1165	-
3. Deer Park					
3	060913	121255-121916	1	3632.9	4.6 m/s 10 deg
3	060919	173211-173810	1	3966.6	4.9 m/s 30 deg
3	060925	132751-133633	1	1349.8	6.1 m/s 2.0 deg
3	Average		(total 3)	2983 ± 1424	-
4. Battleground Rd					

4	060913	120933-121255	1	1636.1	4.6 m/s 10 deg
4	060919	172202-173211	1	959.6	4.9 m/s 30 deg
4	060925	133633-134116	1	1195.7	6.1 m/s 2.0 deg
4	Average	-	(total 3)	1264 ± 343	-
5. Miller's Cut Off Rd					
5	060913	120620-120933	1	549.3	4.6 m/s 10 deg
5	060919	171853-172202	1	404	4.9 m/s 30 deg
5	060925	134116-134453	1	305.6	6.1 m/s 2.0 deg
5	Average		(total 3)	420 ± 123	-
6. Sens Rd					
6	060913	120043-120302	1	708.2	4.6 m/s 10 deg
6	060925	134453-134858	1	227.2	6.1 m/s 2.0 deg
6	Average		(total 2)	468 ± 340	-
7. Baytown					
7	060831	151350-152352	1	954.7	3.0 m/s 58 deg
7	060913	115310-120043	1	1098.6	4.6 m/s 10 deg
7	060925	134858-135749	1	874.9	6.1 m/s 2.0 deg
7	Average		(total 3)	976 ± 113	-
8. Mt Belvieu					
8	060925	140544-141615	1	863	5.0 m/s 359 deg
8	Average		(total 1)	863	-
Texas City					
	060902	134924-140045	1	2482.2	3.2 m/s 67 deg
	060914	092643-100709	2	3279.7 ± 758.5	4.0 m/s 73 deg
	060920	132634-164612	3	2904.6 ± 118.0	4.8 m/s 81 deg
Texas City	Average		(total 6)	2889 ± 399	-
Sweeny					
	060921	153950-164442	2	3633.4 ± 1361.9	8.1 m/s 188 deg
Sweeny	Average		(total 2)	3633 ± 1362	-

4.4 Ammonia

In Figure 29 ammonia measurements are shown on September 19. This measurement illustrates the “emission picture” rather well which is further summarized in Table 11 and in detail in Table 12.

The largest emission source of ammonia can be found in sector 2 around Davison street constituting almost half of the 270 kg/h that is being emitted from the HSC. In Figure 30 is shown a close up of such a measurement on August 30.

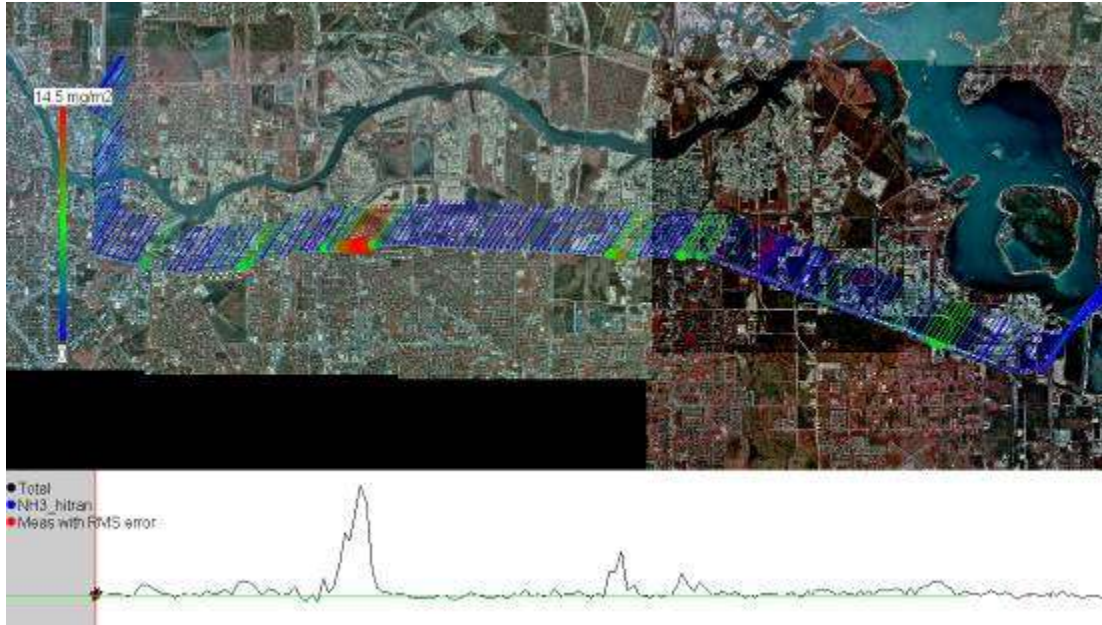


Figure 29. Ammonia measurement on a SOF transect downwind of the HSC on September 19.

Table 11. Average ammonia emissions for measurements in September.

Region/sector	2006	Measurement days
1. Allen Genova	35± 8	3
2. Davison street	115 ± 40	4
3. Deer park	32± 15	3
4. Battleground	40± 12	3
7. Baytown	43± 35	1
8. Mt Belvieu	12	1
Bayport	40	1
Chocolate Bayou	8	1
Freeport A	15	
Freeport B	41	1
Texas city	8.0	1

Table 12. Detailed ammonia emissions measured with SOF for various sectors.

Sector	Day	Timespan	Nr of transects	Emission	Wind
Allen Genova					
1	060913	153814 -154524	1	44.2 kg/h	4.6-4.6m/s 10-10deg
1	060919	102315 -144346	4	34.9kg/h	4.5-9.4m/s 35-64deg
1	060925	122734 -123443	1	27 kg/h	7.0-7.0m/s 5-5deg
1	Average		(total 6)	35± 8 kg/h	-
Davison street					
2	060830	110401 -142524	3	175 kg/h	5.3-6.2m/s 1-359deg
2	060913	152353 -153323	1	111 kg/h	4.6-4.6m/s 10-10deg
2	060919	111755 -144850	2	87 kg/h	4.5-9.4m/s 35-41deg
2	060925	121932 -122504	1	86 kg/h	7.0-7.0m/s 5-5deg
2	Average		(total 7)	115±41 kg/h	-
Deer Park					
3	060830	130535 -143851	3	50 kg/h	6.0-6.0m/s 1-1deg
3	060919	100939 -145541	3	25 kg/h	4.5-9.4m/s 35-64deg
3	060925	120517 -120944	1	22 kg/h	7.0-7.0m/s 5-5deg
3	Average		(total 6)	32±15 kg/h	-
Battlegr					
4	060919	112912 -145957	2	31 kg/h	4.5-9.4m/s 35-41deg
4	060925	115644 -120319	1	50 kg/h	7.0-7.0m/s 5-5deg
4	Average		(total 3)	40±12 kg/h	-
Baytown					
8	060830	112406 -145136	3	84.1 kg/h	5.3-6.0m/s 1-1deg
8	060919	150225 -153731	2	18.8 kg/h	4.5-4.5m/s 35-35deg
8	060925	111818 -114957	2	27.0kg/h	7.0-7.0m/s 5-5deg
8	Average		(total 7)	43±35 kg/h	-



Figure 30. Ammonia measurement on August 30 from sector 2 around Davison street.

4.5 NO₂ and SO₂

Table 13 summarizes the NO₂ emission measurements made with the mobile DOAS system during the TexAQS II 2006 campaign, whereas the SO₂ measurements are presented in Table 14. NO₂ and SO₂ fluxes were quantified in Texas City, Channelview, Sweeny, Freeport, Mt Belvieu, Bayport, Chocolate Bayou and the Houston Ship Channel (HSC) area (specifically also the Battleground-225-Miller's Cut Off Rd circuit and Baytown in this area). A comparison between the measured data and the data in the emission inventory is displayed in Figure 31.

Table 13. Summary of the mobile-DOAS NO₂ measurements during the TexAQS II 2006 campaign. The emission inventory is obtained from TCEQ 2004 data, see section 3.2. The error factor corresponds to the ratio between the SOF measurements and the inventory values.

HSC sector / Region	Mobile DOAS 2006 (NO ₂ kg h ⁻¹)	Emission inventory (kg h ⁻¹)
1-7. HSC box.	4538 ± 1860 (31 transects)	3089
7. Baytown (BT)	668 ± 217 (10 transects)	344
8. Mt Belvieu (BV)	271 ± 111 (9 transects)	125
Texas City (TC)	642 ± 241 (21 transects)	930
Channelview (CH)	237 ± 123 (7 transects)	715
Sweeny (SW)	398 ± 53 (40 transects)	313
Freeport (F)	752 ± 127 (8 transects)	103
Bayport (BP)	731 ± 419 (5 transects)	47
Chocolate Bayou (CB)	268 ± 56 (2 transects)	327

Table 14. Summary of SO₂ measurements during the TexAQS II 2006 campaign. The emission inventory is obtained from TCEQ 2004 data, see section 3.2. The error factor corresponds to the ratio between the SOF measurements and the inventory values.

HSC sector / Region	Mobile DOAS 2006 (SO ₂ kg h ⁻¹)	Emission inventory (kg h ⁻¹)
1-7. HSC box.	5166 ± 2404 (16 transects)	2752
7. Baytown	557 ± 259 (2 transects)	54
Texas City	1215 ± 381 (19 transects)	660
Sweeny	1826 ± 479 (24 transects)	265
Freeport	1154 ± 99 (4 transects)	285

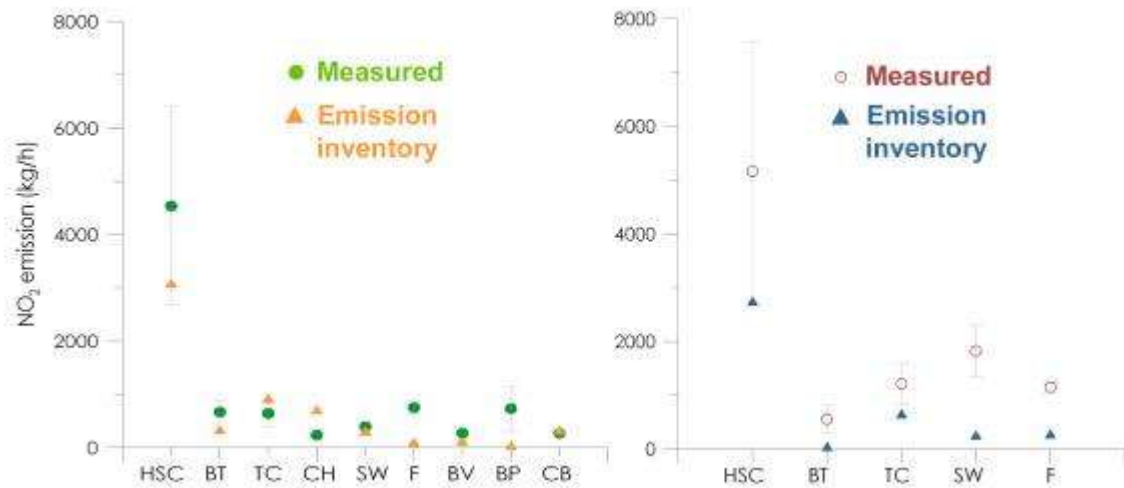


Figure 31. Measured and reported emissions of NO₂ (left) and SO₂ (right), with the sites denominated as in Table 13. The bars show the variability for respectively average, including both measurement error and actual variability in the emissions.

Figure 32 shows a typical transect around the Houston Ship Channel box. An inflow of NO₂ to the box is seen from the north, coinciding with the Channelview location.

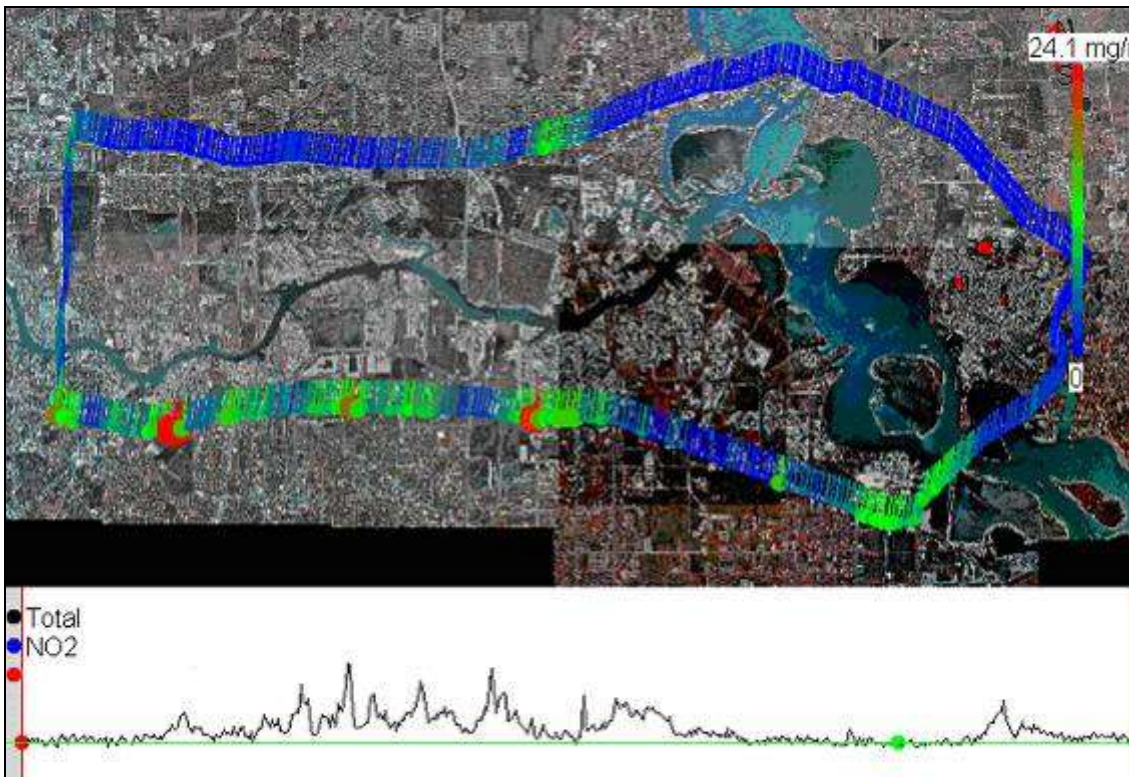


Figure 32. Mobile DOAS measurement of NO₂ around the HSC area. NO₂ in flow to the HSC box is seen centrally in the north from Channelview.

In the following Figure 33 to Figure 36 measurement transects of NO₂ plumes, are shown for Baytown, Texas City, Sweeny and Freeport respectively.

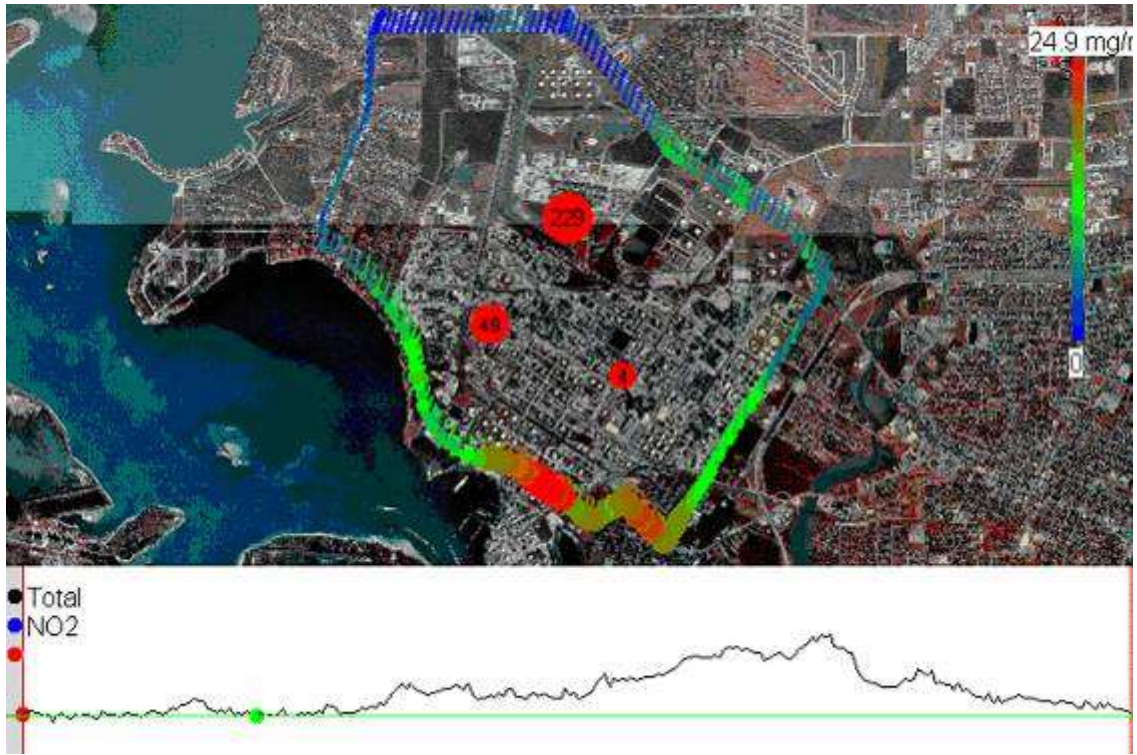


Figure 33. NO₂ transect around Baytown. Emission inventory data as black figures on red circles, (kg/h).

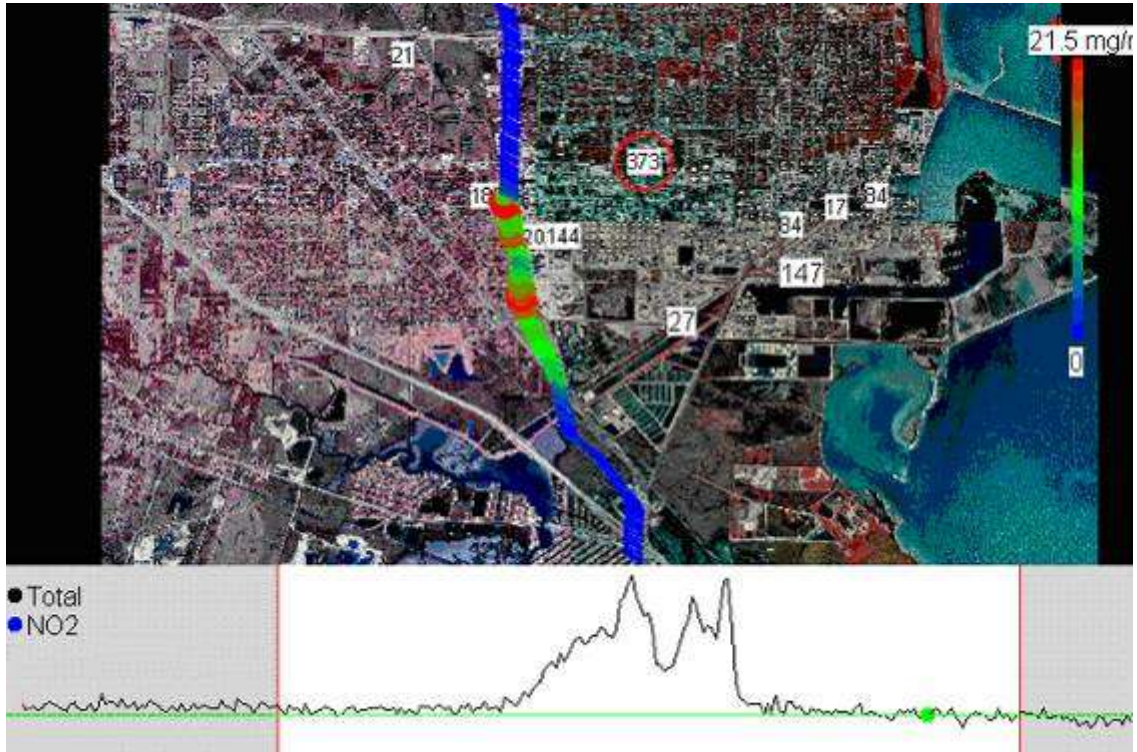


Figure 34. NO₂ measurement in Texas City. Emission inventory data in white boxes (kg/h).

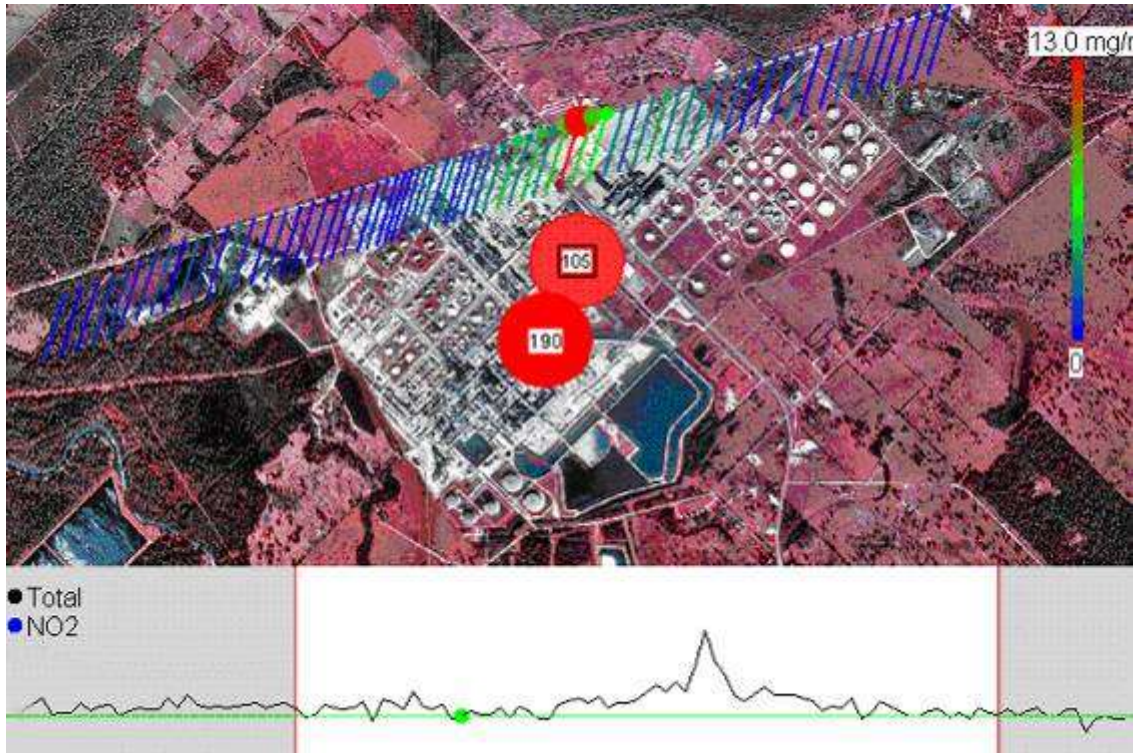


Figure 35. Mobile DOAS measurement of NO₂ in Sweeny on September 21, 2006. Emission inventory data in kg/h on as black numbers on white background (on red circles).

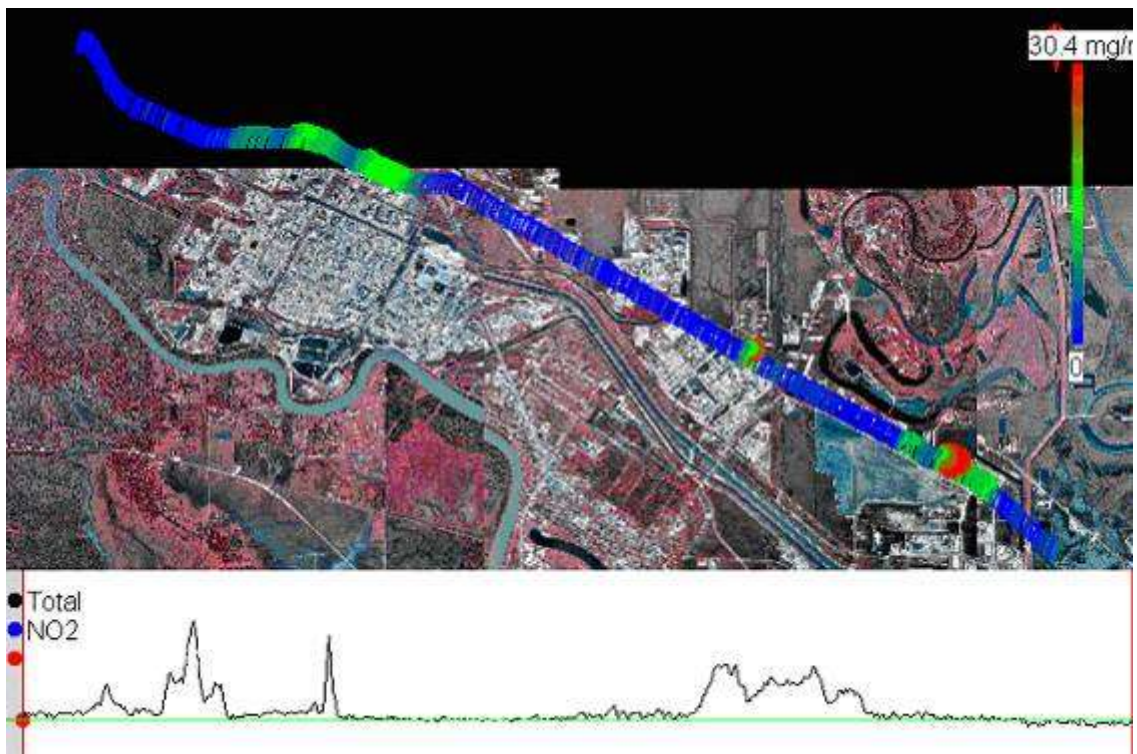


Figure 36. NO₂ flux measurement in Freeport.

5. Discussion

In this study we have shown that the hourly gas emission from the Houston Ship channel area corresponds to about 1 metric ton of ethylene, 1.5 tons of propylene, 12 tons of alkanes, 1/4 ton of NH₃ and about 5 tons of SO₂ and NO₂ each. For the VOCs this corresponds to 5-50 times greater emissions than reported in the 2004 TCEQ inventory. For NO₂ and SO₂ values, the discrepancy is less, factor 1.5 and 1.9, respectively. Similar discrepancies were observed for the other sites. It should be stated that the emission inventory used in this comparison is based on the 2004 TCEQ inventory, as described in section 3.2, and that an improved inventory for the TexAQS 2006 September period has been derived by TCEQ, partly based on continuous emissions monitoring equipment at power plants and monitoring of flares. Apparently the VOC emissions increase by 50-100% in the more recent hourly inventory due to larger emissions from flares [Jolly, 2007], but this still leaves the large discrepancies observed in this study unexplained. The largest single emission source of HRVOCs in the vicinity of Houston was the Mt Belvieu area with emissions of around 400 kg/h for both ethene and propene. This is 10 and 47 times higher, respectively, than the emission inventory. The measured ethene emissions obtained with SOF agreed within a factor 2 with measurements conducted by the NOAA WP3 during TexAQS 2006 [Gouw 2007].

In Table 15 is summarized the ethene and NO₂ measurements for the different regions during the TexAQS II 2006 campaign, along with the inventory data. In the Texas air quality study in 2000 the VOC to NO_x ratio was one of the main ways to estimate the emissions. The ethene to NO₂ ratio in the measured emissions, as obtained with SOF and mobile DOAS, was on average 0.41, which can be compared to the corresponding inventory ratio of 0.08. Earlier reported ethene/NO₂-ratios by Ryerson[2003] and Buhr[2006] for year 2000 and 2001 corresponds to 1.5 to 4 and the measured ratio in this study hence is lower than in the earlier observations.

Table 15. Ethene emissions (kg/h) obtained with SOF for the TexAQS II 2006 campaign. The values have an estimated measurement uncertainty of 35%. The emission inventory has been derived by NOAA [Frost, 2006] from the 2004 TCEQ inventory.

Area	Days	ethene SOF (kg/h)	ethene Inventory (kg/h)	NO ₂ emission (kg/h)	NO ₂ Inventory (kg/h)	ethene/NO ₂ meas.	ethene/NO ₂ invent.	ethene/NO _x Other
HSC (sec. 1-7)	3	859	47	4538	3089	0.19	0.02	
Mt Belvieu (8)	3	404	44	271	125	1.49	0.35	
Baytown (7)	4	72	6	668	344	0.11	0.02	
Texas City	1	83*	8	642	930	0.13	0.01	
Channelview	3	64	11	237	715	0.27	0.02	
Sweeny	2	163	4	398	313	0.41	0.01	3.6 ¹ , 3.7 ² , 1.5 ³
Freeport	1	250*	21	752	103	0.33	0.20	1.5 ¹ , 2 ² , 0.26 ³
Bayport	1	170*	4	731	47	0.23	0.09	
Chocolate Bayou	1	136*	10	268	327	0.51	0.03	2 ¹

* Uncertain, few measurements or other, ¹Ryerson [2003]-2000, ²Buhr [2006] -2001, ³Buhr [2006]-2006.

It is difficult to understand the large discrepancies between measurements and the inventories. One way of doing this is to compare the emissions to the throughput of oil

which seems to relate reasonably well across refineries. Typical refinery emissions measured by SOF in Sweden are 0.03-0.09% [Kihlman, 2005a] of the throughput while other studies with the DIAL technique shows even higher emissions 0.03-0.3% [personal communication Alex Cuclis]. The largest refinery in Texas city claimed a production of 460000 barrels per day in 2004 (i.e. $2.4 \cdot 10^6$ kg/h) with VOC emissions corresponding to about 300 kg/h, which hence corresponds to a relative leakage of 0.01%. According to the emission inventory this refinery stands for about 2/3 of the total emission from Texas City. The VOC emissions that were measured by SOF correspond to about 3000 kg/h. and assuming that 2/3 of this comes from the specific refinery yields a relative leakage of 0.08%. This example is uncertain since we lack information about the actual throughput during the SOF measurements in September 2006 but we believe it could be fruitful to explore this type of analysis further, to understand the large discrepancies.

The SOF emission data has a measurement uncertainty of about 35% as discussed in section 3.4, mainly due to uncertainties in the wind field. The data reflect hourly and day-to-day variation in VOC emissions caused by changes in the wind and process behavior since the data were collected during 3 to 10 days that were spread over September 2006. The measurements on the other hand do not include seasonal variability caused by changes in the ambient temperature, solar radiation and wind behavior.

Temperature and wind has an impact on VOC emissions that are driven by vaporization of liquid product, such as emissions of alkanes from tanks, since this has effect on the vapor pressure and the removal speed of the gas from the tank. Calculations using the API/EPA tank emission model for several typical tanks by O'Connor [1999] indicate an increase in tank emission by a few percent per degree for external floating roof tanks with volatile product, such as crude and gasoline. The measurements in the campaign were conducted at about 25-30°C and since the annual average temperature in Houston is about 20°C this would imply that alkane tank emissions during the campaign were 15-25% higher than the annual mean. These calculations were conducted for 5 typical tank types and the results depend on how well the tank is sealed.

The wind also has an impact on tank emissions, with increasing emissions with increasing wind. For instance O'Connor[1999] claims that the tank emissions have a square dependence to the wind speed but this should depend strongly on type and quality of the sealing and such a strong correlation is not clear in other studies [Kihlman, 2005a]. The SOF measurements of alkanes in Houston and Texas City were conducted at wind speeds between 3-4 m/s at tank height, which is fairly close to the annual mean for Houston of around 3.8 m/s (data for Houston 1998 from www.nrcc.cornell.edu). Assuming a square dependence between the emissions and wind speed yields a maximum underestimation of the annual emissions of 50% for Texas City, and a 10% overestimation for the HSC, for the tank park emissions. For process emissions, which is the main source for HRVOCs and a significant source for alkanes (typically 30% of the overall refinery emission [Kihlman, 2005a]), the temperature and wind in our experience has small impact since these emissions are driven by pressure inside the industrial processes.

During the TexAQS campaign considerable variability of the HRVOC emissions were observed on short time scales, of 30 minutes for the sources in the HSC. Such an example has been discussed already in relation to Figure 17 and Figure 24 in section 4.2 where the emission rates of ethene and propene varied from 2000 to 200 kg/h and 240 to 100 kg/h, respectively, within 30 minutes from emission sources east of Battleground road.

An overview of the VOC emissions and their relative variability for the whole campaign is shown in Table 16. It can be seen that the sectors 4 and 5, again east of Battleground road exhibit strong variability and that propene emissions are more variable than those of ethene. This is consistent with that a considerable fraction of the emissions correspond to upset releases or frequent flaring. Studies conducted in Sweden at a polyethylene plant shows low combustion efficiency of the flares and that the emissions from the flares corresponded to about 50% of the total VOC emissions from the plant [Mellqvist 2000]. The results from the SOF measurements during TexAQS are consistent with a similar behavior.

Table 16. The variability of the VOC emissions measured by SOF during September 2006 is shown for several of the areas studied.

Sector/Region	ethene	propene	alkanes
1. Allen Genoa Rd	96kg/h \pm 16%	1*	1739 kg/h \pm 44%
2. Davison street	120 kg/h \pm 20%	144kg/h \pm 52%	3678 kg/h \pm 32%
3. Deer-Park	187 kg/h \pm 59%	282kg/h \pm 100%	2983 kg/h \pm 48%
4. Battleground road	92kg/h \pm 51%	380kg/h \pm 103%	1264 kg/h \pm 27%
5. Miller Cut-off road	184kg/h \pm 84%	211kg/h \pm 33%	420 kg/h \pm 29%
7. Baytown	72 kg/h \pm 33%	260kg/h \pm 37%	976 kg/h \pm 12%
8. Mt Belvieu	404kg/h \pm 10%	420kg/h \pm 67%	863 *
Texas City	83kg/h \pm 14%	Not detected	2889 kg/h \pm 14%

* Single day measurement.

6. Acknowledgements

This work was funded by the Houston Advanced Research Center (HARC) under project no H53. The authors would like to thank Elisabeth Undén for assisting with the SOF measurements, Brian Offerle for helping out with the report and Creg Clements for conducting some of the GPS soundings. We thank TNRIIS for providing digital maps and TCEQ for supplying auto-GC and wind profiler data.

7. References

- Benner D.C., et al., The HITRAN molecular spectroscopic database: Edition of 2000 including updates through 2001. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2003. 82(1-4): p. 5
- Buhr, M., Alvarez, S., Kauffmann, L., Shauck, M., Zanin, G., Alkene/NO_y Emission Ratios observed from the Baylor Aztec during the 2006 TexAQS II study and Comparison with results obtained during 2001-2002, Rapid science synthesis workshop, Austin, october 12, 2006
- Burton M.R., et al., Diurnal changes in volcanic plume chemistry observed by lunar and solar occultation spectroscopy. *Geophysical Research Letters*, 2001. 28: p. 843-846.
- Daewon Byun, D. et al., HARC Project H12/HRB Final Report
Role of Modeling Assumptions in the Houston Mid-Course Review, HARC Project H12/HRB Final Report, 2005 (www.HARC.edu)
- DOASIS, developed by Kraus., S. Available at: <http://www.iup.uni-heidelberg.de/bugtracker/projects/doasis/>
- Foy, B., "Modelling constraints on the emission inventory and on vertical dispersion for CO and SO₂ in the Mexico City Metropolitan Area using Solar FTIR and zenith sky UV spectroscopy... Mellqvist, J., et al., *Atmos. Chem. Phys.*, 7, 781–801, 2007
- Frost, G. 2006 , *TEXAQS2K6, version 1, 2 August 2006*, personal communication.
- Fransson, K and Mellqvist, J., Measurements of VOCs at Refineries Using the Solar Occultation Flux Technique, Report to Preem Environmental foundation, Göteborg, 2002 (available at www.fluxsense.se)
- Galle, B.; Mellqvist, J., et al., Ground Based FTIR Measurements of Stratospheric Trace Species from Harestua, Norway during Sesame and Comparison with a 3-D Model, *JAC*, 1999, 32, no. 1, 147-164.
- Gouw, J., et al., Measurements of Highly Reactive VOCs Onboard the NOAA WP-3D, Principal Findings Data Analysis Workshop TexAQS II, Austin, May 29-June 01, 2007. (available at www.tceq.state.tx.us)
- Galle B., Oppenheimer C., Geyer A., McGonigle A. and Edmonds M., A miniaturised ultraviolet spectrometer for remote sensing of SO₂ fluxes: a new tool for volcano surveillance. *Journal of Volcanology*, 2002. 119: p. 241-254
- Griffith D.W.T., Synthetic calibration and quantitative analysis of gas-phase FT-IR spectra. *Applied Spectroscopy*, 1996. 50(1): p. 59-70.

Hanst P.L., QASoft '96, Database and quantitative analysis program for measurements of gases. Infrared Analysis Inc., 1996.

Hurley P.J., Physick W.L., and Luhar A.K., TAPM: A practical approach to prognostic meteorological and air pollution modelling. *Environmental Modelling and Software*, 2005. 20(6): p. 737.

Jolly, J. and Nesvacil, D., Examining the 2006 Hourly VOC Emission Inventory, Principal Findings Data Analysis Workshop TexAQS II, Austin, May 29-June 01, 2007. (available at www.tceq.state.tx.us)

Kihlman, M., Mellqvist, J. and Samuelsson, J., Monitoring of VOC emissions from three refineries in Sweden and the Oil harbour of Göteborg using the Solar Occultation Flux method, RR. report (Göteborg) No. 1, , ISSN 1653 333X, 2005a, (available at www.fluxsense.se)

Kihlman, M., Application of solar FTIR spectroscopy for quantifying gas emissions, Technical report No. 4L, Department of Radio and Space Science, ISSN 1652-9103, 2005b, (available at www.fluxsense.se)

Mellqvist, J., Arlander, D. W., Galle, B. and Bergqvist, B., Measurements of Industrial Fugitive Emissions by the FTIR-Tracer Method (FTM), IVL report, 1995, B 1214.

Mellqvist, Johan, Application of infrared and UV-visible remote sensing techniques for studying the stratosphere and for estimating anthropogenic emissions, Chalmers Dissertation, ISBN 91-7197-765-I, Göteborg, 1999

Mellqvist, J., Flare testing using the SOF method at Borealis polyethylene in the summer of 2000, Chalmers report, Aug 2001. (available at www.fluxsense.se)

Mellqvist, J., et al., Ground-based FTIR observations of chlorine activation and ozone depletion inside the Arctic vortex during the winter of 1999/2000, *JGR*, 2002. 107(D20)

Mellqvist, J., Galle, B., Samuelsson, J. and Strandberg, A., Mobile column measurements of CO in megacities". Proceedings of The XVIII Quadrennial Ozone Symposium, Eds C. Zerefos, ISBN 960-630-103-6, 960-630-101-1, pp 612-613, International Ozone Commission, Greece, 2004

O'Connor, S.J, Walmsley, H.L. et al., Measurement of the VOC emission from from the Shell raffinaderi, Göteborg, Shell Global Solution, report OP.99.47110, 1999 (available at provincial government of Västra Götaland, www.o.lst.se)

Pacific Northwest National Laboratory. 2004
Available from: <https://secure.pnl.gov/nsd/nsd.nsf/Welcome>.

Platt, U., Perner, D. and Pätz, H.W., "Simultaneous Measurements of Atmospheric CH₂O, O₃ and NO₂ by Differential Optical Absorption", J. Geophys. Res., 84, 6329-6335, 1979

Ryerson T. B., et al., Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas, J. Geophys. Res., 108 (D8), 4249, doi:10.1029/2002JD003070, 2003.

Samuelsson, J., et. al., VOC measurements of VOCs at Nynas Refinery in Nynäshamn 2005 (Utsläppsmätningar av flyktiga organiska kolväten vid Nynas Raffinaderi i Nynäshamn 2005, in Swedish) Bitumen refinery official report to provincial government 2005, Available at: <http://www.fluxsense.se/reports/N2005.pdf>

Senff, C., et al., Ozone Production and Flux Downwind of Houston and Dallas, Principal Findings Data Analysis Workshop TexAQS II, Austin, May 29-June 01, 2007. (available at www.tceq.state.tx.us)

Tucker, S., Marine boundary Layer dynamics and heights during TexAQS 2006: HRDL measurements from the RV Brown, Principal Findings Data Analysis Workshop TexAQS II, Austin, May 29-June 01, 2007. (available at www.tceq.state.tx.us)

Vandaele, A. C.; Simon, P. C.; Guilmot, J. M.; Carleer, M.; Colin, R. Journal of Geophysical Research-Atmospheres 1994, 99, 25599-25605.

Wert B. P., et al., Signatures of terminal alkene oxidation in airborne formaldehyde measurements during TexAQS 2000, J. Geophys. Res., 108 (D3), 4104, doi:10.1029/2002JD002502, 2003.

Appendix I. Detailed wind measurements used for the flux calculations

Table A. 1. Windspeed (m/s) and wind direction and the standard deviation of these are shown for several wind measurements. Maximum and minimum values are shown in parenthesis.

Date-time (CST)	Sonde 0-200m	Sonde 0-500m	Wind profiler 0-500 m La Porte	SODAR 0-100 m Water-works	SODAR 0-100 m HRM4	Ground station	Comment
2006-08-30 10:00	4.7±0.95 (2.2-5.9) 29±5 (20-36)	6.2±1.5 (2.6-7.9) 33±7 (20-45)	5.4±0.7 20±5	N/A	N/A	4.7 (7) 19±14	HSC, sonde at Lynchburg ferry Ground ay Lynchburg
2006-08-30 11:00			5.4±0.4 3.3±2	N/A	N/A	3.5 (6) 17±18	HSC, sonde at Lynchburg ferry
2006-08-30 11:50	6±1.7 (4.4-9.0) 17±6 (6-26)	6.0±1.2 (4.4-9.0) 359±7 (-13-26)	4.8±0.2 349±5	N/A	N/A	3.7 (7) 10±17	HSC, sonde at Lynchburg ferry
2006-08-30 13:00			4.8±0.5 355±6	N/A	N/A	4.6 (7.5) 7±17	HSC, sonde at Lynchburg ferry
2006-08-30 14:00			4.4±0.2 359±12	N/A	N/A	4.2 (7) 11±17	HSC, sonde at Lynchburg ferry
2006-08-30 15:00	5.5±1.1 (3.5-6.7) 359±7 (350-370)	5.3±1.1 (2.8-6.7) 346±13 (330-370)	4.5±0.4 3±10	N/A	N/A	3.7 (6) 12±18	HSC, sonde at Lynchburg ferry
2006-08-31 09:53	2.6±0.5 (0.7-3.7) 75±10 (50-94)	2.3±0.7 (0.7-3.7) 75±14 (25-94)	2.6±0.5 83±21	N/A	N/A	1 (3) 115±49	HSC, sonde at Lynchburg ferry Ground ay Lynchburg
2006-08-31 11:00			3.0±0.4 87±9	N/A	N/A	1.4 (3) 153±21	HSC, sonde at Lynchburg ferry
2006-08-31 12:00			3.0±0.3 79±30	N/A	N/A	1 (3) 170±27	
2006-08-31 13:00	1.5±0.7 (0.4-3) 87±30 (30-176)	1.9±0.7 (0.4-5.8) 85±34 (30-176)	2.1±0.8 94±40	N/A	N/A	1.8 (3.6) 110±30	
2006-08-31 14:00			1.4±0.8 194±80	N/A	N/A	1.9 (3.7) 108±31	
2006-08-31 15:00	3.3±0.5 (2.4-4.4) 51±8 (31-60)	3.0±1 (1.0-4.6) 43±15 (18-69)	4.5±0.4 3±10	N/A	N/A	1.7 (3.5) 108±31	
2006-08-31			2.0±0.8	N/A	N/A	2 (5)	

16:00			166±118			131±45	
2006-08-31 16:30			1.7±0.8 154±118			1.8±0.5 102±3	Channelview
2006-08-31 17:00			1.7±1 157±64	N/A	N/A	N/A	
2006-08-31 18:00			2.3±0.8 160±28	N/A	N/A	2 (5) 126±12	Channelview
2006-09-07 12:00			3.2±0.6 87±17	2.5±0.3 84±8	N/A		
2006-09-07 13:00	2.3±0.5 (2-3.0) 79±14 (60-88)	2.4±0.7 (2.4-4.4) 82±18 (40-112)	2.8±0.6 101±13	1.8±0.4 125±14	N/A		
2006-09-13 12:00	3.6±1 (1-5.) 19±8 (9-33)	4.6±1 (1-5.) 10±8 (9-33)	4.7±0.35 14±4	3.6±0.5 21±5	4.1±0.5 352±3		
2006-09-13 14:00			3.7±0.4 355±10	3.6±0.3 335±6	3.5±0.5 1±11		
2006-09-13 14:30			3.3±0.6 5±9	1.7±0.3 320±12	2.4±0.5 22±12		
2006-09-13 15:00			4.0±0.4 16±10	2.1±0.4 325±20	3.1±0.6 360±12	2.9 (5) 32±15	
2006-09-13 15:30			2.9±0.5 24±8	2.0±0.2 352±12	2.6±0.7 342±22		
2006-09-13 16:00	3.5±0.7 (2.2-4.5) 26±12 (368-407)	3.8±0.7 (2-5) 6±20 (6-26)	2.1±0.2 27±11	2.4±0.6 10±16	2.9±0.5 28±10	2.8 (5) 28±14	
2006-09-14 09:00						4 (6.5) 73±15	Texas city C100
2006-09-14 10:00						4.7 (7) 70±16	Texas city, C100
2006-09-14 14:00			5.7±0.6 105±6	4.1±0.4 94±5	5.2±1.7 92±15		
2006-09-14 14:30			5.6±0.3 107±3	3.9±0.4 94±5	4.7±1.9 102±13		

2006-09-14 15:00			4.7±0.2 110±7	3.8±0.4 106±1	5.0±2 108±6		
2006-09-14 15:30			5.2±0.2 107±10	4.5±0.5 116±4	4.6±1.5 133±12		
2006-09-14 16:00	4.3±0.8 (2.5-5) 123±5 (110-133)	4.1±0.7 (2.5-5) 111±18 (63-133)	6.0±0.7 110±12	4.9±0.5 130±3	5.2±1.7 110±7		
2006-09-19 09:30			8.1±0.9 45±1.6	7.9±1.6 34±5	7.2±1.4 37±6		
2006-09-19 10:00			6.2±0.4 41±1.9	8.2±1.8 46±2	6.6±1 46±7		
2006-09-19 10:30			5.7±0.3 43±3.5	7.9±1.6 46±5	6.8±1 40±5		
2006-09-19 11:00	7.1±3 (2.6-11) 33±3 (25-37)	9.4±2.6 (2.5-12) 41±8 (25-55)	4.6±0.3 49±5.3	7.1±1.3 40±6	6.3±0.7 29±6		High value of GPS sonde
2006-09-19 11:30			5.7±0.7 43±6	7.7±1.5 38±5	6.8±0.7 28±6		
2006-09-19 12:30	5.6±0.3 (5-6.1) 33±7 (23-48)	6.0±0.6 (5-7.4) 32±8 (18-48)	6.2±0.6 53±4	7.7±1 46±13	5.2±0.7 62±5		
2006-09-19 13:00			6 ±0.5 50±3				
2006-09-19 13:30			6.2±0.6 53±7				
2006-09-19 15:00	5.1±0.8 (3.5-6) 29±7 (18-43)	4.5±0.9 (3-6) 35±10 (18-55)	4.9±0.5 33±3.5	4.9±0.8 40±6	3.5±0.6 53±9		
2006-09-19 17:00							
2006-09-19 17:30							
2006-09-20 09:00						5.3 (8) 70±16	CAMS 100
2006-09-20 10:00						5.0 (8) 62±14	CAMS 100
2006-09-20	5.4±0.3 (5-6)	6.2±0.6 (5-7)					

10:30	63±5(57-70)	64±5(57-73)					
2006-09-20 11:00	3.8±1.1 (2.1-5) 60±7 (50-78)	5.3±1.4 (2-7) 65±7 (49-77)				5.2 (8) 62±14	Sonde at UH research station east of Texas city, CAMS 100
2006-09-20 12:00						5 (8) 72±17	
2006-09-20 13:00						5.0 (8) 72±17	
2006-09-20 13:45	5.2±2 (0.4-10) 90±7 (80-111)	4.8±1.2 (0.4-10) 81±10 (56-112)				4.4 (8) 95±17	
2006-09-20 14:30	4.7±1 (3.2-6.6) 76±9 (66-95)	3.9±0.9 (2.5-6.6) 89±13 (66-114)				4.3 (8) 62±14	
2006-09-20 15:00						4.2 (7) 93±16	
						CAMS	
2006-09-21 10:31	10.3±0.7 (11-12.8) 193±1.5 (191-196)	13±1 (11-15) 195±2 (191-200)				5.4 (11) 199±18	Sweeny, sonde downwind of site, Groundstation: C618
2006-09-21 11:00						6.6 (11) 196±14	
2006-09-21 12:34	10±1.7 (6.6-12) 191±6 (181-199)	11±1 (6.6-13.5) 197±5 (174-214)				6.4 (11) 195±14	
2006-09-21 13:00						6.4 (11) 191±14	
2006-09-21 14:00						6.7 (11) 191±14	
2006-09-21 15:00						6.4 (11) 181±14	
2006-09-25 11:00			5.7±0.9 5±3	5.7±0.8 15±4	5.7±0.6 7.0±7	5.2 (9.9) 7±14	Ground Lynchburg
2006-09-25 11:39	6.7±0.9 (5-12) 18±13 (1-35)	7.2±1 (5-9) 5±10 (-6-35)	5.5±0.4 10±6	4.9±0.8 7±5	6.0±0.8 358.5±4		HSC, Baytown, Sonde at Lynchburg ferry
2006-09-25 12:00			5.4±0.5 359±7	5.3±1 4±4	5.0±0.5 8±4	4.6 (9.9) 6±14	
2006-09-25 12:44	6.9±3.7 (1.5-11) 9±5 (4-20)	6.1±2 (1.5-11) 2±10 (-30-30)	5.2±0.8 360±7	6.0±1 352±4	5.6±0.45 6.7±4		Ground Lynchburg

2006-09-25 15:00			4.8±0.35 358.5±2	5.3±1 355±4	5.5±0.7 359.5±6	3.2 (9.9) 1±14	Mt Belvieu, sonde at Lynchburg ferry, Mt Belvieu ground
2006-09-25 15:55	6.5±0.5 (5-7.6) 353±9 (-17-9)	6.6±0.5 (5-7.6) 353±6 (-20-9)	5.2±0.3 353±2	5.2±0.7 360±4	4.9±0.6 4.7±6	2.8 (9.9) 357±14	Mt Belvieu
2006-09-25 16:30			4.9±0.3 6±2	5.0±0.7 347±6	4.5±0.5 14±6		Mt Belvieu,, sonde at Lynchburg ferry
2006-09-25 17:00			5.5±0.1 11±6	4.3±0.7 352±6	3.3±0.7 31±13		
2006-09-25 17:30			5.8±0.1 10±4	4.0±1.0 2±5	3.8±1 22±11		Mt Belvieu, sonde at Lynchburg ferry
2006-09-26 10:00			1.6±0.3 69±9				
2006-09-26 10:30	2.3±0.4 (1.6-3) 38±13 (8-61)	2.2±0.8 (0.7-3.7) 40±20 (5-87)	2.4±0.2 53±8				
2006-09-26 11:00			2.5±0.3 42±6				
2006-09-26 13:40	3.6±0.7 (1.6-3) 20±10 (7-37)	4.4±0.9 (2-6) 21±8 (7-37)					
2006-09-26 15:00			1.4±0.6 65±46		2.8 ±0.5 51±19	0.6 (3) 48±30	
2006-09-26 16:00	2.4±0.9 (1.6-3) 70±24 (27-99)	2.5±1 (2-6) 54±23 (12-99)					
2006-09-27 09:00						1.7 (5) 193±30	Ground at Mustang Bayou
2006-09-27 10:00	3.1±1.3 (1.5-5) 184±8 (168-195)	4.1±1 (1.5-5) 194±10(167-211)				2.5 (6) 204±26	Ground at Mustang Bayou C619
2006-09-27 11:00						2.8 (6.5) 203±24	Ground at Clute C11
2006-09-27 12:21	4.1±0.7 (3-5) 183±10 (162-198)	4.1±0.7 (3-5.5) 183±10 (156-197)				3.0 (7) 206±25	Sonde only to 300 m
2006-09-27 13:00						3.4 (7.3) 196±20	
2006-09-27	2.2±0.5 (1-3.6)	3.7±1.3 (1-6)				3 (5)	Ground at Danciger

16:21	185±15 (153-204)	187±15 (153-210)				194±14	
2006-09-27 17:00						2.8 (6) 188±13	Ground at Danciger
2006-09-30 16:21	4.6±0.5 (3.8-5.3) 212±6 (200-222)	5.2±1 (3.9-7.6) 208±10 (181-222)					

Locations: 1= Lynchburg ferry crossing, HSC, 2: UH research station east of Texas city, 3 Sweeny

- The ptu sondes travel 500 m in 90 s. while the La porte radar corresponds to a 30 min average. Ground corresponds to nearby CAMS site. SODAR corresponds to 30 minute values, varying height 0-200 m. ndepednet fpr the 2 SODARS

Waterworks sodar=CAMS241

The ground measurements correspond to a 10 m measurement and a 1 hour average.

Appendix II Extract from the emission inventory

The emission inventory (*TexAQS 2006, version 1, 2 August 2006*) used in this study for comparison to the measurements. It has been derived by NOAA [Frost 2006] and it is based on the TCEQ 1999 inventory but with the annual totals scaled to the TCEQ 2004 inventory. The ethylene, propylene and alkane emissions (excl. methane) for each point source have been derived from the 2004 total VOC emissions by assuming the same speciation at that point source as in 1999.

Table All.1 The 50 largest alkene sources in kg/h. The total reported VOC emissions are shown together with some of the speciated species

LAT_04	LON_04	COUNTY	VOC	Alkanes	Ethene	propene	Benzene	Alcohols	Unspeciated
32.43770	-94.68810	HARRISON	398.53	31.76	170.75	13.09	1.82	17.44	40.12
30.63769	-102.94277	PECOS	317.86	191.81	0.00	61.81	0.80	0.00	111.85
28.50928	-96.76941	CALHOUN	91.63	16.71	48.98	9.23	1.59	0.35	3.85
29.82338	-94.92064	HARRIS	47.89	1.66	29.35	0.66	1.37	0.04	8.02
31.82382	-102.32907	ECTOR	84.75	5.06	27.14	1.38	0.59	0.99	8.41
30.05410	-93.75079	ORANGE	65.67	4.64	26.90	0.45	1.57	0.59	10.18
30.06634	-94.23005	JEFFERSON	45.61	11.83	22.26	0.00	0.00	1.59	1.66
28.98220	-95.37430	BRAZORIA	92.41	2.68	21.09	0.58	0.48	0.11	13.30
29.70917	-95.06720	HARRIS	41.38	5.35	21.05	0.12	0.19	0.04	3.40
29.83036	-95.11814	HARRIS	125.25	29.09	11.69	3.42	1.92	2.20	7.30
28.69076	-96.54346	CALHOUN	75.42	9.95	14.35	0.59	0.40	5.92	22.82
29.97613	-94.21540	JEFFERSON	164.60	148.22	0.00	14.39	0.00	0.00	8.28
29.36702	-94.90567	GALVESTON	118.31	52.09	1.81	12.25	0.60	0.77	56.04
29.07439	-95.74696	BRAZORIA	48.54	38.15	4.47	8.88	0.27	0.00	15.36
29.23240	-95.19644	BRAZORIA	59.30	31.86	7.08	2.79	0.79	0.02	1.87
28.67853	-96.94837	VICTORIA	19.89	9.46	9.22	0.00	0.00	0.00	0.07
29.72120	-95.12701	HARRIS	184.28	49.60	3.26	4.86	3.47	1.93	23.33
30.04485	-93.76905	ORANGE	38.83	24.60	7.79	0.03	0.05	0.05	0.76
29.85078	-94.90828	CHAMBERS	10.52	0.00	7.30	0.00	0.00	0.00	3.07
29.70224	-95.25093	HARRIS	11.96	2.89	6.46	0.37	0.28	0.07	0.30
35.48031	-101.04715	GRAY	64.45	26.04	0.00	6.59	0.00	1.93	7.15

29.84633	-94.90254	CHAMBERS	17.62	15.06	3.76	2.39	0.00	0.00	0.46
30.04800	-93.76392	ORANGE	9.22	0.71	5.96	0.08	0.00	0.00	0.20
30.13972	-94.62810	LIBERTY	18.42	13.15	2.29	3.45	0.00	0.00	0.05
28.98343	-95.56025	BRAZORIA	9.16	0.27	5.05	0.07	0.00	0.00	2.58
29.75430	-95.01264	HARRIS	38.54	5.22	4.14	0.92	0.71	0.03	7.32
29.71965	-95.07719	HARRIS	38.97	23.08	4.54	0.43	0.00	0.00	1.93
29.37749	-94.89468	GALVESTON	20.72	5.52	1.50	3.42	1.20	0.40	1.83
29.37121	-94.94602	GALVESTON	79.30	2.40	4.23	0.33	0.10	3.42	30.32
29.38115	-94.92989	GALVESTON	335.38	49.23	0.52	3.97	5.35	120.14	116.26
29.72977	-95.18494	HARRIS	98.13	35.00	2.93	1.52	0.00	0.00	5.02
30.37048	-101.84336	TERRELL	16.55	15.18	0.00	4.29	0.27	0.00	1.06
29.73927	-95.16814	HARRIS	16.79	0.07	4.21	0.00	0.00	1.42	1.63
29.73931	-95.00672	HARRIS	242.12	46.14	0.49	3.70	1.68	2.38	108.84
29.71078	-95.06417	HARRIS	22.21	0.66	4.01	0.10	0.00	0.51	1.13
28.67239	-96.95413	VICTORIA	29.57	2.65	3.71	0.02	0.18	0.02	11.32
29.86993	-94.92756	CHAMBERS	18.48	6.34	3.67	0.00	0.00	0.05	1.28
30.04169	-93.78091	ORANGE	7.79	3.72	3.47	0.02	0.00	0.02	0.35
29.74541	-95.01981	HARRIS	142.69	19.91	1.81	1.58	3.59	0.90	7.85
30.06792	-94.06186	JEFFERSON	15.16	4.01	2.70	0.37	1.57	0.06	1.30
29.63143	-95.05293	HARRIS	30.01	2.38	1.52	1.48	0.00	0.00	14.56
29.72135	-95.20572	HARRIS	51.97	11.22	0.71	2.18	0.50	0.18	18.59
30.01593	-94.03007	JEFFERSON	11.79	3.80	0.46	2.33	0.84	1.91	1.60
29.84512	-94.90322	CHAMBERS	11.23	4.58	0.00	2.78	0.00	0.00	1.21
29.72319	-95.08687	HARRIS	21.78	3.68	0.43	2.31	0.00	0.00	2.43
29.69540	-95.03384	HARRIS	23.33	1.81	2.68	0.00	0.00	6.97	3.40
29.96067	-93.92447	JEFFERSON	2.55	0.00	2.55	0.00	0.00	0.00	0.00
30.11810	-94.63663	LIBERTY	4.93	0.00	2.54	0.00	0.00	0.00	1.98
30.05703	-94.04203	JEFFERSON	2.94	0.00	2.33	0.00	0.00	0.00	0.11
29.73011	-95.15497	HARRIS	11.37	4.19	0.04	2.24	1.27	0.00	0.47

Table All.2 the 50 largest alkane sources kg/h. The total reported VOC emissions are shown together with some of the speciated species.

LAT_04	LON_04	COUNTY	Total VOC	Alkanes	Ethene	Propene	Benzene	Alcohols	Unspeciated
30.63769	-102.94277	PECOS	317.9	191.8	0.0	61.8	0.8	0.00	111.9
29.97613	-94.21540	JEFFERSON	164.6	148.2	0.0	14.4	0.0	0.00	8.3
29.85030	-94.91780	CHAMBERS	20.5	112.1	0.0	2.0	3.9	0.06	6.8
32.42592	-96.84960	ELLIS	58.5	57.4	0.0	0.0	0.0	0.00	0.2
29.36702	-94.90567	GALVESTON	118.3	52.1	1.8	12.2	0.6	0.77	56.0
29.72120	-95.12701	HARRIS	184.3	49.6	3.3	4.9	3.5	1.93	23.3
29.73931	-95.00672	HARRIS	242.1	46.1	0.5	3.7	1.7	2.38	108.8
29.07439	-95.74696	BRAZORIA	48.5	38.2	4.5	8.9	0.3	0.00	15.4
31.12909	-97.33982	BELL	39.1	37.3	0.0	0.0	0.0	0.00	1.7
29.38115	-94.92989	GALVESTON	335.4	49.2	0.5	4.0	5.3	120.14	116.3
29.23240	-95.19644	BRAZORIA	59.3	31.9	7.1	2.8	0.8	0.02	1.9
32.43770	-94.68810	HARRISON	398.5	31.8	170.7	13.1	1.8	17.44	40.1
29.83036	-95.11814	HARRIS	125.2	29.1	11.7	3.4	1.9	2.20	7.3
29.72977	-95.18494	HARRIS	98.1	35.0	2.9	1.5	0.0	0.00	5.0
29.23364	-95.19116	BRAZORIA	27.6	25.7	1.7	0.0	0.0	0.24	0.0
35.48031	-101.04715	GRAY	64.5	26.0	0.0	6.6	0.0	1.93	7.1
29.71965	-95.07719	HARRIS	39.0	23.1	4.5	0.4	0.0	0.00	1.9
29.62480	-95.06175	HARRIS	24.2	22.5	1.0	0.5	0.0	16.48	0.6
26.20899	-97.71871	CAMERON	17.2	21.4	0.0	0.0	0.0	0.00	0.0
29.74541	-95.01981	HARRIS	142.7	19.9	1.8	1.6	3.6	0.90	7.9
29.07083	-95.74855	BRAZORIA	71.4	18.6	0.3	1.2	1.4	0.14	23.2
33.56441	-101.83060	LUBBOCK	14.5	17.3	0.0	0.0	0.0	0.00	0.1
30.04806	-93.78662	ORANGE	30.0	20.1	0.0	0.0	0.0	0.00	0.5
28.50928	-96.76941	CALHOUN	91.6	16.7	49.0	9.2	1.6	0.35	3.8
33.54236	-101.80622	LUBBOCK	16.2	16.1	0.0	0.0	0.0	0.00	0.1
30.37048	-101.84336	TERRELL	16.6	15.2	0.0	4.3	0.3	0.00	1.1
29.84633	-94.90254	CHAMBERS	17.6	15.1	3.8	2.4	0.0	0.00	0.5
35.95205	-101.88045	MOORE	86.4	14.0	0.0	0.7	0.6	0.21	59.2
30.13972	-94.62810	LIBERTY	18.4	13.1	2.3	3.4	0.0	0.00	0.0
29.85725	-93.97144	JEFFERSON	61.2	17.8	0.1	0.8	0.8	0.02	38.2

30.06634	-94.23005	JEFFERSON	45.6	11.8	22.3	0.0	0.0	1.59	1.7
29.69760	-95.25370	HARRIS	54.3	11.5	0.0	0.3	0.0	0.57	6.8
29.72135	-95.20572	HARRIS	52.0	11.2	0.7	2.2	0.5	0.18	18.6
32.18716	-94.26154	PANOLA	65.3	10.7	0.0	0.7	1.1	0.00	53.2
28.69076	-96.54346	CALHOUN	75.4	10.0	14.3	0.6	0.4	5.92	22.8
28.67853	-96.94837	VICTORIA	19.9	9.5	9.2	0.0	0.0	0.00	0.1
32.81012	-97.30894	TARRANT	9.2	9.2	0.0	0.0	0.0	0.00	0.0
35.69828	-101.36863	HUTCHINSON	407.4	14.0	1.7	0.0	1.8	0.00	376.0
30.04485	-93.76905	ORANGE	38.8	24.6	7.8	0.0	0.1	0.05	0.8
29.73607	-95.16857	HARRIS	7.2	7.8	1.0	0.0	0.0	0.00	1.3
29.67948	-95.01328	HARRIS	14.1	7.3	0.0	0.1	0.0	0.41	3.2
29.71746	-95.17703	HARRIS	13.7	6.9	0.0	0.0	0.1	0.00	4.4
29.86993	-94.92756	CHAMBERS	18.5	6.3	3.7	0.0	0.0	0.05	1.3
28.78790	-95.94293	MATAGORDA	8.7	6.2	0.8	0.0	0.0	0.04	1.2
29.37749	-94.89468	GALVESTON	20.7	5.5	1.5	3.4	1.2	0.40	1.8
29.85700	-94.91120	CHAMBERS	51.1	5.5	0.0	1.4	0.0	0.00	34.9
32.21094	-101.93514	MARTIN	10.8	5.8	0.0	1.1	0.2	0.00	3.3
29.75430	-95.01264	HARRIS	38.5	5.2	4.1	0.9	0.7	0.03	7.3