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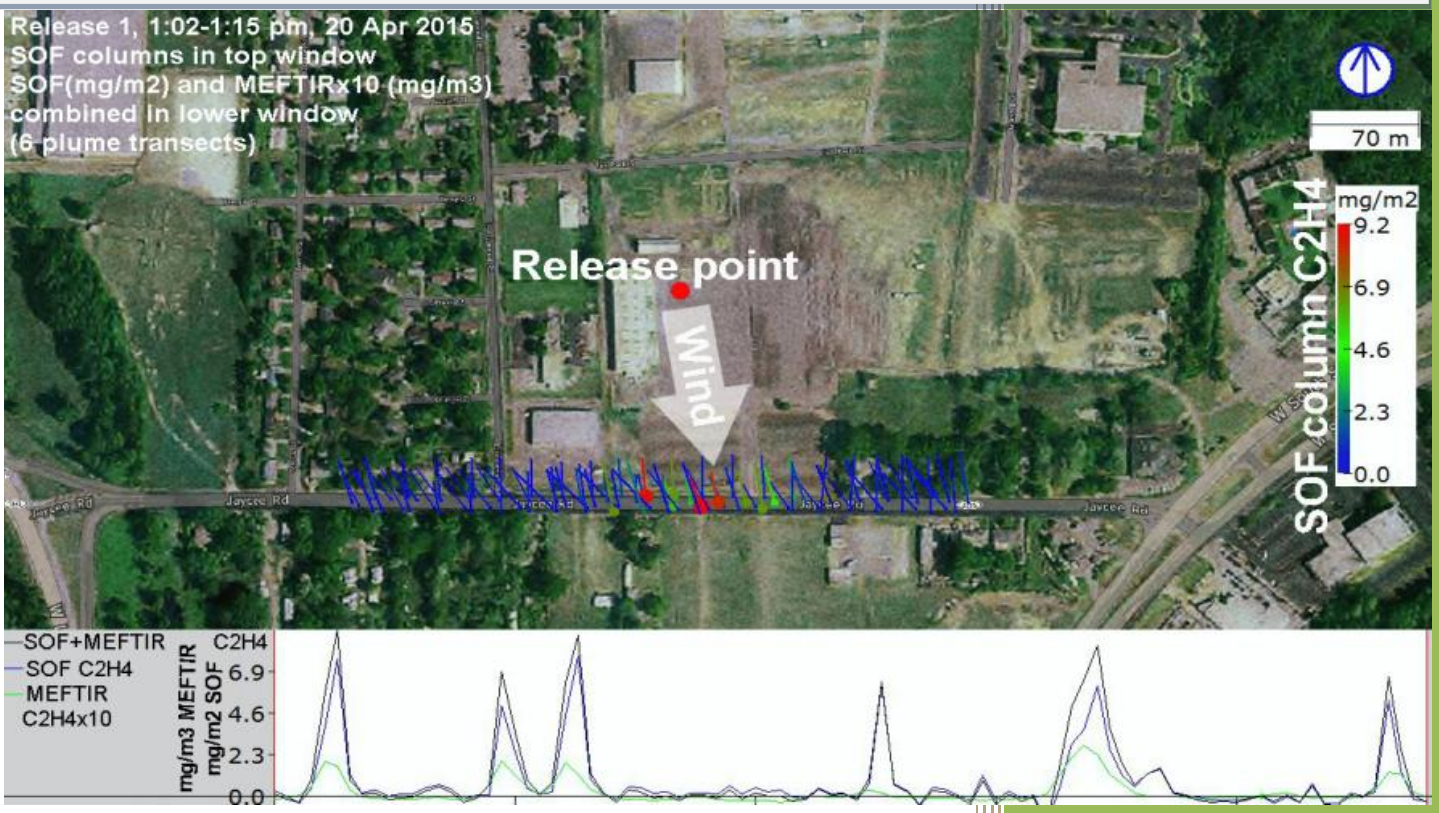
Controlled ethylene release study to evaluate the SOF method



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[Cover: Plume transect examples from the controlled ethylene release at the fairgrounds near Maude Cobb Convention Center, Longview, TX, on April 20, 2015. Six plume transects by two instruments are shown: SOF measured vertical columns (mg/m^2) and MeFTIR measured ground level concentrations x 10 (mg/m^3 x10). Each measured (SOF) spectrum is represented with a point in the upper figure, which color and size indicate the evaluated concentration of ethylene in mg/m^2. A line from each colored point indicates the direction from which the wind is blowing. North is upwards in the figure. The ethylene column (SOF, dark blue) and concentration (MeFTIR, green) by distance driven through the plume is also shown in the lower part of the figure.]

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EXECUTIVE SUMMARY

On April 20, 2015, a controlled ethylene release was conducted at the Longview Fairgrounds, near the Maude Cobb Convention Center in Longview, TX, with the purpose of testing the ability of the SOF method to quantify ethylene point source emissions. The release was run as a so called "blind test" where an independent party (City of Longview representative) managed the release rates, and the SOF team attempted to quantify the unknown emission rates. At the end of the release experiment all data related to the actual release rates were submitted to and kept secret by the City of Longview attorney's office until the SOF team had presented quantified release rate estimates.

The first four controlled ethylene releases (i.e., release #1-#4) in the blind study were conducted in valid conditions, and the reported SOF release rates differed by -45%, +1.4%, +14%, and -10% from the true release rates. Emitted rates ranged from 1.85 to 10.85 kg ethylene per hour. The last two releases (i.e., #5 and #6) were done late in the day, with atypical SOF conditions of low sun angle, low wind speeds, cirrus clouds and limited number of plume transects due poor measurement conditions and lack of time. The last two releases are thus not considered appropriate as validation releases.

Some challenges were encountered in this study compared to an industrial SOF plume case. The limited turbulence at the single release point, and the smooth surface surrounding the release location, resulted in very narrow and sometimes branched plumes, in contrast to typical industrial plumes that are broad and continuous, and therefore easier to completely locate and measure. Industrial plumes are broader and mixed better because sources are near large structures that create turbulent wakes and/or fans and heat sources that introduce strong turbulence.

In summary we believe the blind release study showed that the SOF technique is well capable of measuring ethylene fluxes of only a few kilograms per hour (far smaller than for typical industrial studies) and it reproduced the dynamics of the release range of 1.85-10.85 kg/h, retrieving the smallest and largest rates within +14% and +1% respectively. One of four releases under valid conditions had a retrieval error (-45%) outside the typical accuracy range for industrial SOF studies (± 30%), possibly due the atypical narrow and branched plume dispersion.

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1. Introduction

A controlled ethylene release validation experiment was conducted at the Longview Fairgrounds, near the Maude Cobb Convention Center in Longview, TX, on April 20, 2015. The purpose of the release was to examine objectively how well the SOF method can quantify the emission rate of ethylene from a single point source.

The release was run as a so called "blind test" where an independent party managed the release rates, and the SOF team attempted to quantify the unknown emission rates. This would allow for comparisons between known release rates and fluxes independently derived from SOF measurements. The "blind" nature of the experiment would ensure that neither the conduct of the SOF measurements nor the analysis of the SOF data would be influenced by knowledge of the true release rates. Assuming that the conditions are favorable, the SOF measurements should be expected to determine the true release rates within ± 30%.

Six different release ethylene rates were run, ranging from 1.85-10.85 kg/h. An engineer from the City of Longview acted as the independent release operator. At the end of the experiment all data related to the actual release rates were transferred by the engineer to the City of Longview attorney's office for undisclosed storage until the SOF team had presented the quantified release rate estimates.

2. Methods

Two methods based on infrared absorption spectroscopy were used in parallel in the release study to probe the ethylene emissions. The SOF technique used infrared radiation from the sun to derive vertically integrated average columns of ethylene, which were combined with wind measurements to derive the emission rates. Mobile extractive Fourier Transform spectroscopy (MeFTIR) measured concentrations of ethylene at ground level (2m height), by pumping ambient air through an optical gas cell placed between an infra-red light source and an FTIR spectrometer. The MeFTIR data was combined with the vertical column data from SOF to obtain vertical plume dispersion information, which was then used in assessing the wind profile for the SOF emission rate estimates. Both SOF and MeFTIR were mounted on a vehicle, and measured while the vehicle was driven back and forth through the ethylene release plume. Figure 1 gives an overview of the release site, and Table 1 presents an overview of the instrumentation used.

Table 1 Overview of the instrumentation used for the controlled release study.

Instrumentation	Measured quantity
Solar Occultation Flux (SOF)	Total columns of ethylene (mg/m^2)
Mobile extractive FTIR (MeFTIR)	Ground level (2 m) concentrations of ethylene (mg/m^3)
Wind LIDAR (Light detection and ranging)	Continuous wind profiles from 40 to 200 m (130 to 560 feet) in 20 m layers, wind speed (m/s) and wind direction (0-360 degrees)
Tower wind meters at 3m and 10m above ground	Wind speed (m/s) and wind direction (0-360 degrees)
Mass flow controller and precision scales	Control of the ethylene release rate (kg/h)
Video camera and control computer	Monitor the release experiment in case any review is needed afterwards
GPS	Time synchronization of all systems and position logs

The wind speed and wind direction data needed for the SOF method, were obtained by three wind monitors: a 3 m tower with a prop and vane monitor providing one minute averages, a 10 m tower with a sonic anemometer providing 1 second data, and a wind LIDAR system providing vertically resolved profiles of wind speed and wind direction from 40-200 m, in 20 m segments, also with 1 second time resolution.

Ethylene gas (99.95% purity) was released from cylinders by means of a mass flow controller, on which the release operator could set the wanted release rate. The cylinders were also continuously weighed on precision scales, logging the cylinder weights with 1 Hz time resolution. The ethylene was released 10 m above ground, at the top of the wind meter tower. A video camera was placed near the release operator position, overlooking the complete site and recording for the complete duration of the experiment.

As winds were predominantly from the north, the SOF and MeFTIR measurements were conducted in the plume south of the site, back and forth through the plume along Jaycee Dr at about 200 m distance downwind of the release point. SOF and MeFTIR measurements along the Jaycee Dr in between the controlled release episodes verified that there were no other significant ethylene sources in the area but for the controlled release itself.

Figure 2 shows the SOF and MeFTIR instrumentation installed on the measurement truck.

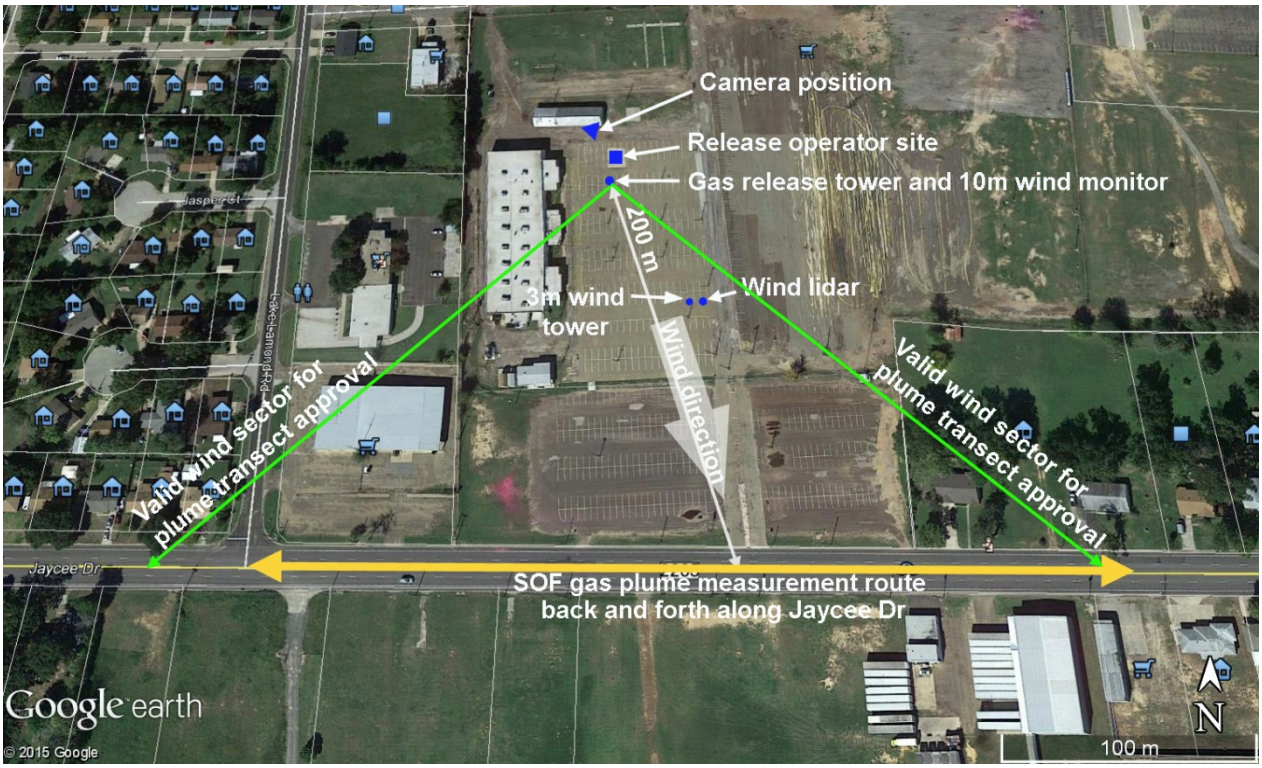

Figure 1 Overview of the controlled release site at the Longview Fairgrounds, near the Maude Cobb Convention Center. The ethylene was released 10 m above ground, from the top of the wind meter tower. As winds were predominantly from the north, the SOF and MeFTIR measurements were conducted along the Jaycee Dr about 200 m south of the release point. The positions for the 3m wind tower and the wind lidar are indicated, as well the camera position monitoring the experiment. The green lines (±45º from north from the release point) indicate valid sector for the plume measurements.

Figure 2 Instrumentation mounted on the measurement truck: SOF for vertical ethylene columns, MeFTIR for ground level ethylene concentrations, GPS and supplemental wind at the truck, wind LIDAR for vertical wind profiles. (SkyDOAS and GPS balloon sondes were not used in the release study, but in an adjacent study).

2.1 Gas release setup

Ethylene gas with ultra high purity of 99.95% supplied by Matheson (product code G19219801) was used for the release. Three gas cylinders initially containing together 41 kg gas was connected to a single line of ½" PFA (perfluoroalkoxy alkane) tubing, via three two-stage gas regulators (Matheson SEQ1253-350). The single flow was then connected to a mass flow controller (MFC). A Vögtlin MFC was used (model GSC-D9SA-BB13), that had been recently calibrated and tested by Vögtlin for ethylene flows in the range 3.46-173 l/min. Specified accuracy is ±1% of full scale and an additional uncertainty of 5% of the reading. The three gas cylinders were replaced with three new ones after two release runs, in order to ensure adequate gas supply throughout the study.

Table 2 Predefined ethylene release intervals for the blind release.

Release rate interval	Min range (l/min)	Max range (l/min)	Min range (kg/h)	Max range (kg/h)	Dynamic range of interval
low	15	60	1.1	4.5	4
medium	40	100	3.0	7.5	2.5
high	80	150	6.0	11.2	1.875

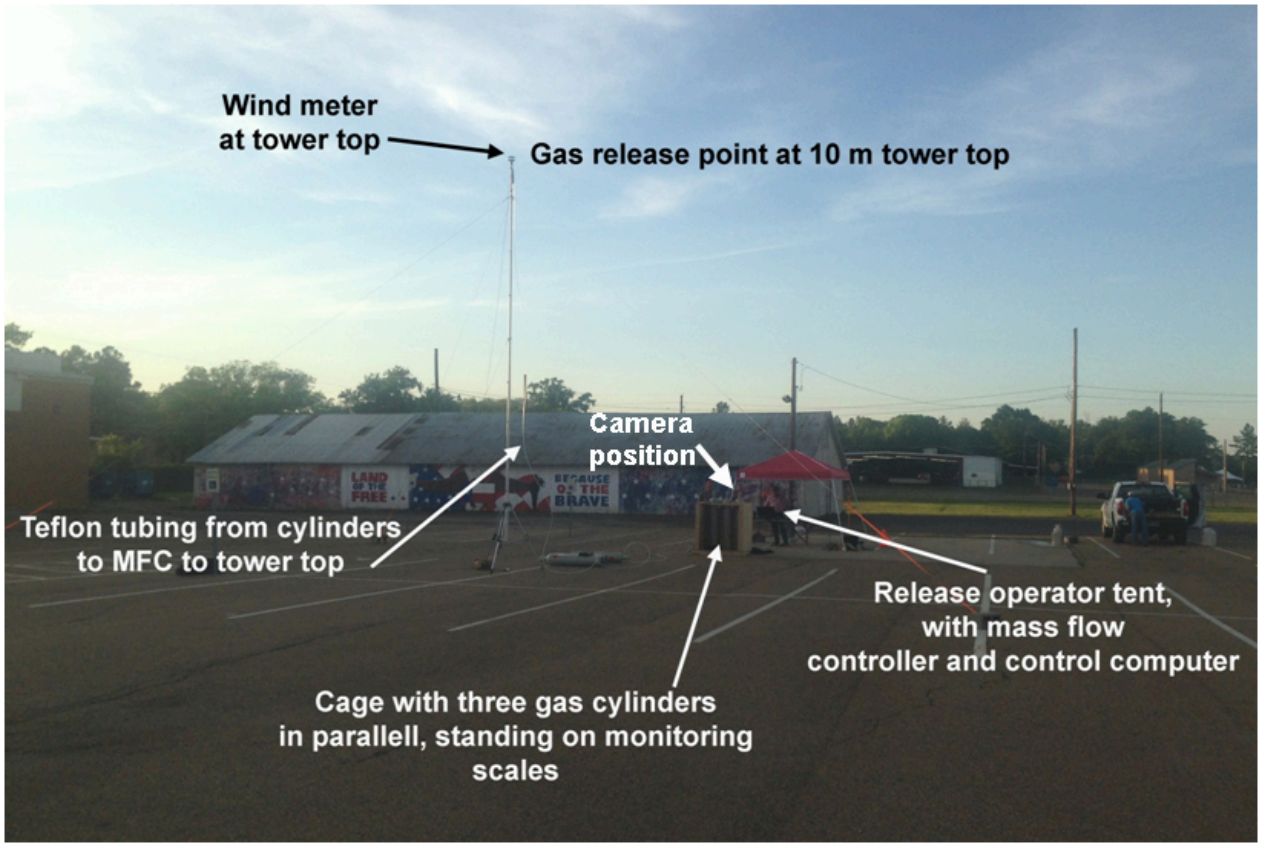

Figure 3 Overview photo of the release setup, facing north. Gas release of pure ethylene controlled by a mass flow controller (MFC) and monitored by precision scales logging the cylinder weights. A video cam recorder, facing south, was located by the barn in the rear.

The MFC was operated through Vögtlin's software (Get read-y). The actual flow rate was continuously logged onto a computer. As a backup and independent check of the release rate reading by the MFC, each gas cylinder was continuously weighed on a precision scale logging the weight with 1 Hz onto the computer. The scales (Vetek VB2-100-10) have 2 g resolution and 100 kg capacity. The scales were calibrated by sequentially adding three certified 5 kg- weights onto the scales after each experiment to check the response.

An independent operator from City of Longview managed the gas release operations, and made the choice of which release rate to apply. The release operator's task was to select ethylene release rates from three rate intervals (low, medium, high) specified in Table 2. Six experiments were run, and each rate interval was to be selected at least once. The independent operator chose the order in which the intervals were run, and the rate within each interval. At all times the independent operator kept secret from the measurement team what release rates were chosen. Note that the interval ranges in Table 2 overlapped in order to make it difficult for the measurement team to make any guesses about release rates. The duration of each release was approximately 30-60 minutes, in order to allow several measurements of each release to be completed (according to wind conditions, cloud cover, traffic interference or instrumental problems). At least ten valid measurements of each release was the goal of the measurement team.

2.1.1 Data integrity

In order to keep the actual release rates secret from the SOF survey team until they had reported their emission rate estimates, the independent release operator from City of Longview secured all data (mass flow control data, video cam recordings, gas cylinder scale logs and operator note book) into a FedEx box at the end of the experiment. The box was then sealed and delivered to the City of Longview attorney's office, for future disclosure only upon reported emission estimates from the SOF survey team.

A video cam recording and control computer screen captures were taken throughout the experiment, for stakeholders to review in case of any ambiguities. At the end of the release study the independent operator released an undisclosed amount of gas so that the final cylinder weight did not reveal the amount released during the release study.

2.2 The SOF method

The SOF method [Mellqvist 1999, 2010; Johansson 2014] is based on the recording of broadband infrared spectra of the sun with a Fourier transform infrared spectrometer (FTIR) that is connected to a solar tracker. The latter is a telescope that tracks the sun and reflects the light into the spectrometer independent of its position. Using multivariate optimization it is possible from these solar spectra to retrieve the path-integrated concentrations (referred to as column concentrations), in the unit mg/m^2, of various species between the sun and the spectrometer, see Figure 4. The system used in this project consists of a custom built solar tracker, transfer optics and a Bruker EM27 FTIR spectrometer with a spectral resolution of 0.5 cm^{-1}, equipped with an MCT (Mercury Cadmium Telluride) detector.

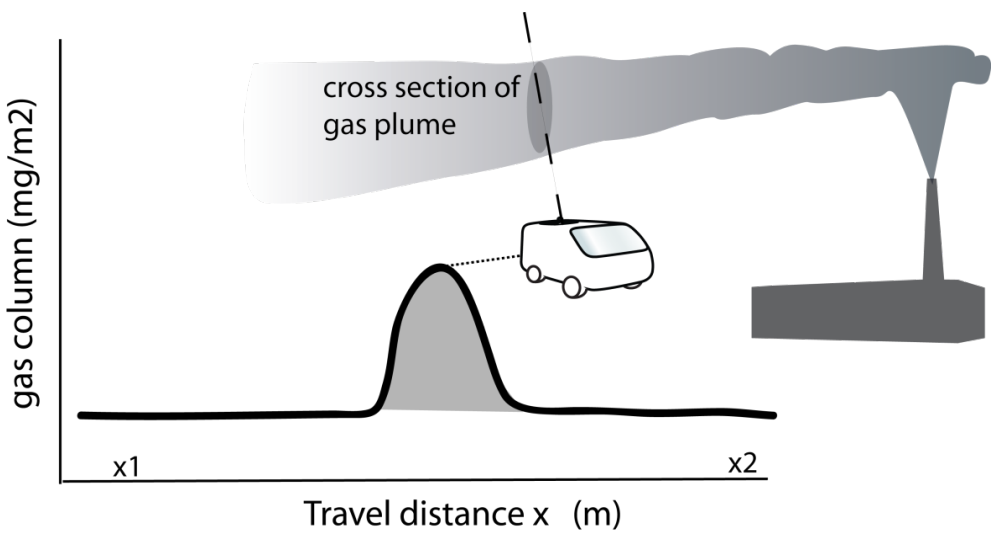

Figure 4 Schematic view of the SOF approach. Vertical gas columns are measured from a vehicle moving cross the emission plume, thus integrating the mass in the plume cross section. By multiplying the plume mass with the wind speed, the emission rate is derived (kg/h).

The system is installed in a measurement vehicle which allows consecutive column concentration measurements to be performed while driving. The flux of a species in a plume from an industry is measured by collecting spectra while driving the vehicle so that the light path from the sun to the

instrument gradually cuts through the whole plume, preferably as orthogonally as possible to wind direction. For each spectrum a column concentration of the species is retrieved using custom software (QESOF, i.e. *Quantitative evaluation of SOF*) [Kihlman 2005]. These column concentrations, together with positions recorded with a GPS (Global Positioning System) receiver and the solar angle calculated from the time of the measurements, are used to calculate the area integrated column of the species in the intersection area between the plume and the light path. The flux of the species is then obtained by multiplying this area integrated mass with the wind speed.

In this project the SOF method was used to measure ethylene using a spectral evaluation in the wavenumber region from 940 to 970 cm^{-1} applied to 0.5 cm^{-1} resolution spectra. An example of a spectral fit in this region is shown in Figure 5.

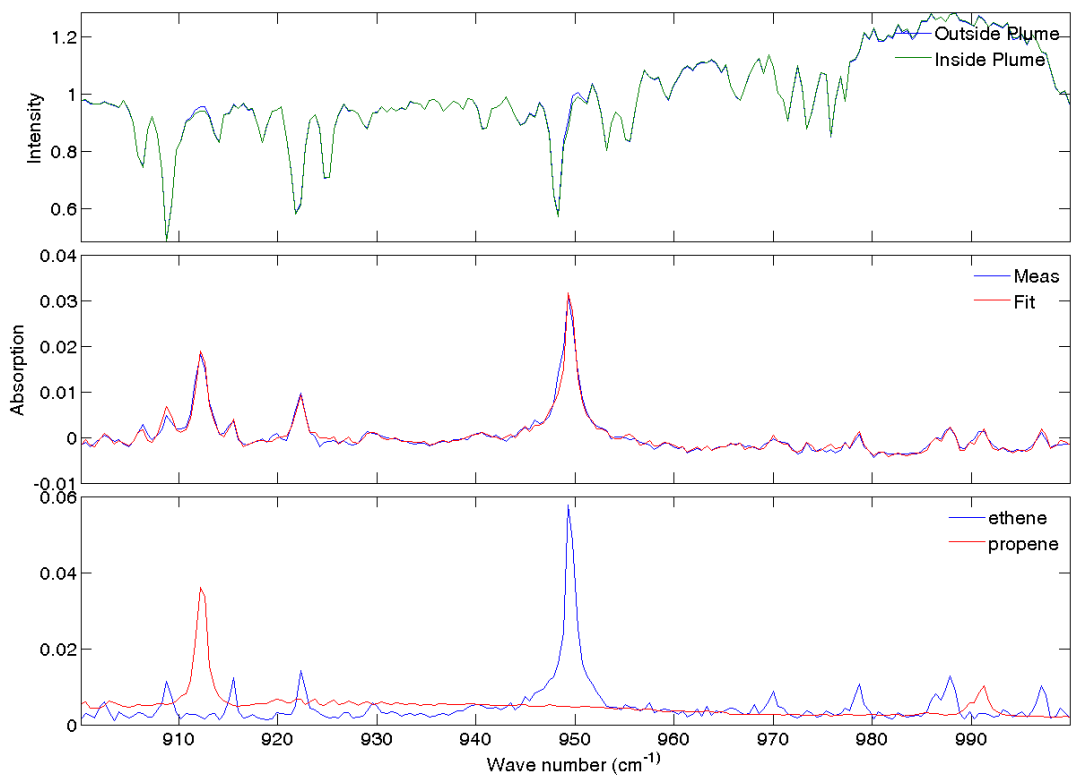

Figure 5 SOF spectrum containing ethylene and propylene. Upper graph shows two intensity spectra as a function of wavenumber (cm^{-1}, 1/wavelength), the blue is taken outside the plume and the green within the alkene plume. Mid graph shows the resulting absorption spectrum (blue) of the green plume spectrum referenced to the blue from the upper graph. The red line in the mid graph corresponds to the fitted calibration spectra of ethylene and propylene, seen in the lower graph.

The SOF spectra are analyzed by fitting a set of calibration spectra based on the HITRAN infrared database (Rothman 2003) in a least-squares fitting routine. Absorption by background atmospheric trace gases is accounted for in this spectral evaluation by inclusion of calibration spectra for water, carbon dioxide and ammonia in addition to the one for ethylene. The high resolution of the measured spectra enables the spectral evaluation to clearly distinguish between the absorption "finger print" of ethylene and those of the background species. The root-mean square error (RMSE) of the spectral fit is used as a

quality indicator to control for interference from unknown absorbers or other effects not accounted for by the spectral evaluation.

The spectral retrieval for SOF is handled by custom software (QESOF) [Kihlman 2005] in which calibration spectra are fitted to the measured spectra using nonlinear multivariate analysis. Calibration data from the HITRAN database are used to simulate absorption spectra for atmospheric background species at the actual pressure, temperature and instrumental resolution of the measurements. The same approach is applied for several retrieval codes for high resolution solar spectroscopy [Rinsland 1991; Griffith 1996] and QESOF has been tested against these with good results. The uncertainty in the absorption strength of the calibration spectra is about 3.5%. The QESOF code has been evaluated against several developed published codes with good agreement, better than 3%.

2.3 The MeFTIR technique

Mobile Extractive FTIR (MeFTIR) (Galle 2001, Borjesson 2009, Mellqvist 2010) in combination with tracers has been used to quantify VOC emissions from refinery and petrochemical sources in Europe and, to a lesser extent, in the U.S. Alkanes and alkenes are typically measured, but also methane and other climate gases can be retrieved. MeFTIR is an optical technique capable of monitoring gas concentrations at ppb-sensitivity in mobile field operations. It is used both independently for concentration mapping and flux measurements, but often combined together with SOF flux measurements to provide more detailed VOC speciation of plumes and for plume height assessments. The method is extractive because air samples are collected and mobile because the instrumentation is mounted on a vehicle driven through the studied emission plume.

The MeFTIR system contains a mid-infrared spectrometer (Bruker IR Cube) with medium resolution (0.5 cm^{-1}). It utilizes an internal glow bar as an infrared radiation source, and by customized optics this light is transmitted through an optical multi-pass measurement cell with selectable path-length of 9.6-107.2 meters. In this survey a path-length of 77 m was used. The system is mounted on a vibration dampening platform to allow for real time plume mapping from a mobile platform, such as a vehicle or boat.

The transmitted light is detected simultaneously with an InSb-detector (Indium Antimonide) in the 2.5–5.5 µm (1800–4000 cm^{-1}) region and a MCT (Mercury Cadmium Telluride) detector in the 8.3–14.3 µm (700–1200 cm^{-1}) region. Ethylene was analyzed at 949.4 cm^{-1}. Temperature and pressure in the cell are averaged over the duration of each measurement. Atmospheric air was continuously pumped at high flow rate through the optical cell from the outside, taking in plume air from the roof of the vehicle (2 m height) through a Teflon tube. A high flow pump is used to ensure that the gas volume in the cell is fully replaced within a few seconds. Spectra are typically recorded with one sample integrated during 13 seconds. A GPS-receiver was used to register the position of the vehicle every second.

The concentration in the spectra is analyzed in real time by fitting a set of calibrated spectra from the Hitran infrared database (Rothman 2003) and the PNL database (Sharpe 2004) in a least-squares fitting procedure. Compounds being analyzed include ethylene, propylene, water, methane, CO, CO_2 and N_2O.

The analysis routines are very similar to the ones for SOF, but less complex because strong absorption by atmospheric trace gases (water, methane, CO_2) has less consequence at the shorter path-length in the MeFTIR measurement cell.

The MeFTIR tracer approach has been validated in a so called gas release "blind test" together with other techniques in U.S. (EREF 2011, Babilotte 2009). In that study, methane was released from an area-distributed source in four different configurations and flow rates ranging from 1.1-3.3 g/s. At a downwind distance of 400 meters MeFTIR retrieved the fluxes within 6% in 3 cases and 19% in the fourth. This is consistent with other validation experiments, showing a flux estimate accuracy of better than 20%. Concentration measurement by FTIR is a widely used procedure, and the main uncertainties are associated with the absorption cross sections (typically < 3.5%) and spectral retrieval, with an aggregate uncertainty better than 10% in the analysis.

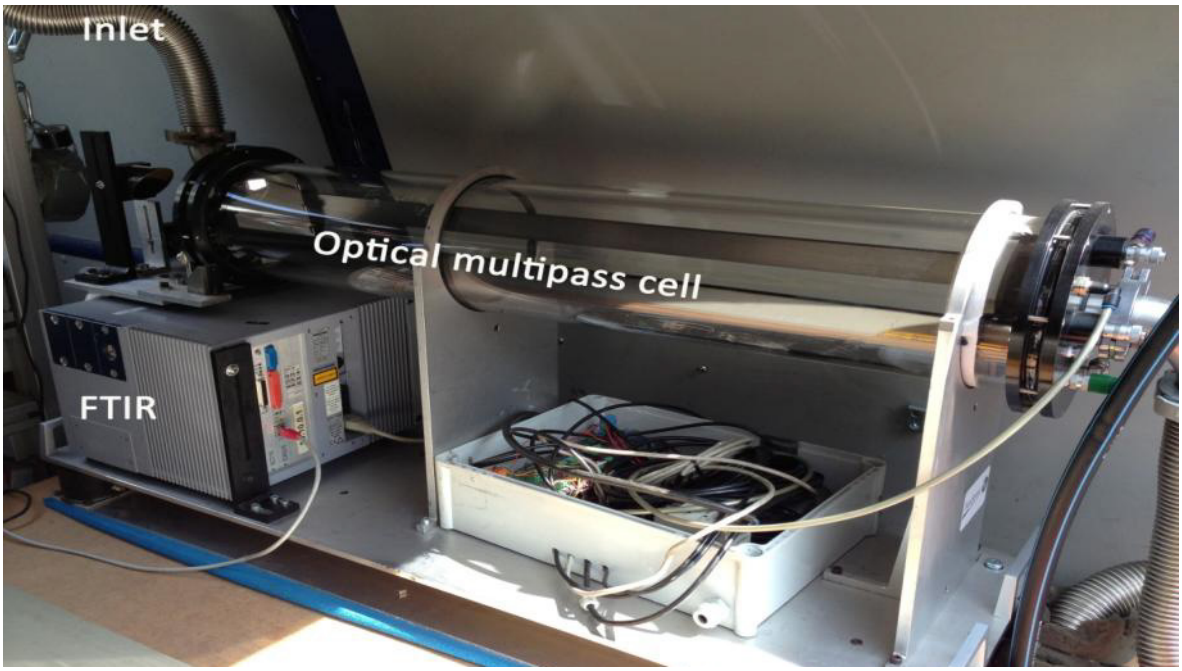

Figure 6 MeFTIR instrumentation: FTIR spectrometer coupled to an optical multi-pass cell. Atmospheric air from roof level is continuously pumped through the cell.

2.4 Estimation of plume dispersion height

The wind speed used for flux calculations should be the average speed of the gas in the emission plume of interest. Since wind speeds tend to vary with height, due to ground retardation, the height dispersion of the plume is an important parameter to consider when assigning plume speed for the flux calculations. In situations with steep height gradients in the wind speed and narrow plumes, the potential for error due to assumptions about plume height increases. Fortunately, the conditions needed for SOF measurements, clear and sunny weather, is typically associated with strong convection which causes fast vertical mixing in the boundary layer. This leads to a smoothing effect on vertical gradients in both wind speed and plume concentration, which mitigates this problem. The longer the plume transport time is, the more mixed the plume will also be.

Figure 7 shows a schematic plume dispersion pattern for different type of sources. Far away from the source, after longer plume mixing times, all sources will tend to have a well-mixed plume vertically from ground and upwards, as exemplified in Figure 7d. How fast this mixing happens depends on turbulence and meteorological conditions. This case is the normal when measuring far downwind of an industrial site, introducing strong turbulence and good mixing. The plume dispersion height corresponds to height from ground up to the roof of the plume in this case.

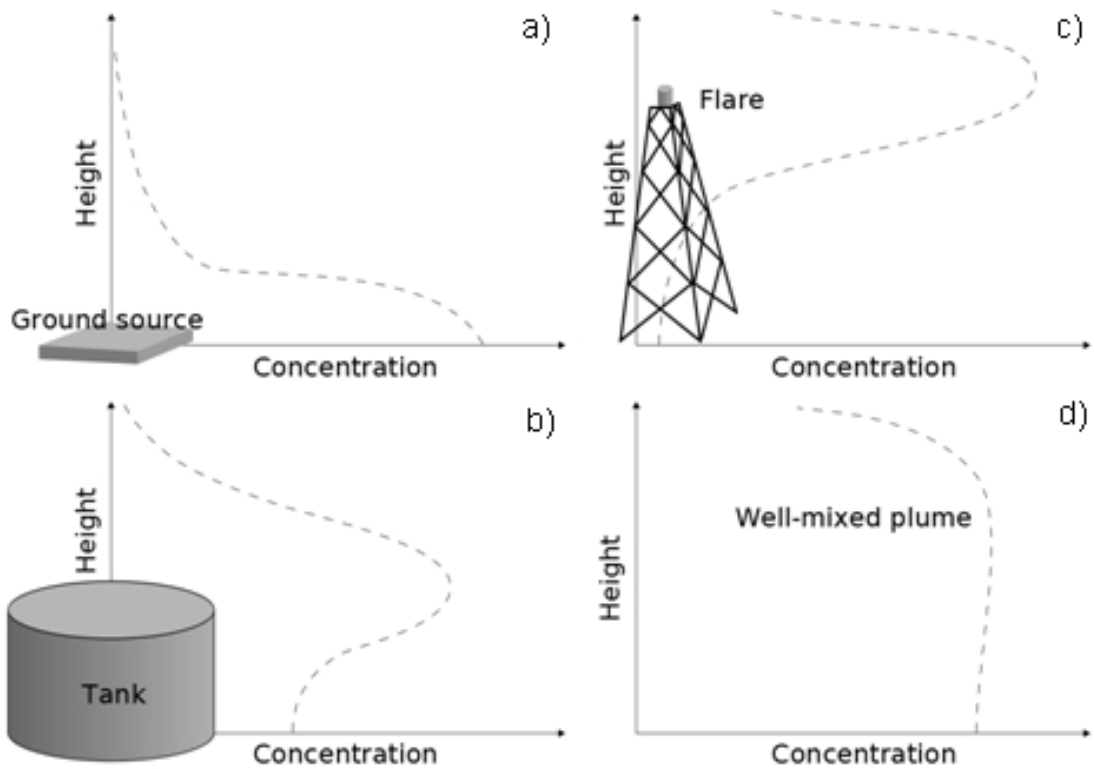

Figure 7 Schematic vertical plume dispersion from different type of sources. a) Corresponds to a ground level source where the concentration near the source is highest close to ground and decreases with height. b) An example of a somewhat more elevated source, where the concentration near the source is highest at the release height but the plume is dispersed both upwards and downwards. c) A high, and in this case also hot, source. The concentration near the source is highest above the release height, and the plume is dispersed more upwards than downwards initially. d) Far away from the source, after longer plume mixing times, all sources will tend to have a well-mixed plume vertically from ground and upwards, as exemplified here. How fast this mixing happens depends on turbulence and meteorological conditions.

Figure 8 shows four examples of what the concentration of a species may look like in the crossection of an emission plume, with reference to corresponding cases in Figure 7. Example d) is an idealized case with a uniform well mixed plume concentration. For this example the plume dispersion height would represent the upper edge for the rectangle. In reality plumes tend to form a more Gaussian distribution as they disperse in the atmosphere. Example a) might represent the distribution of a plume from a ground source at a medium distance. In this case the calculated plume dispersion height by comparing ground level concentration (MeFTIR) and integrated vertical concentration column (SOF), would be somewhat lower than the highest reach of the plume. The plume dispersion height would still be a good estimate of where most of the plume is located, and hence the average wind for this height range would generally be representative of the average plume velocity.

In example b) and c) the plume core is aloft and only partially, if at all, dispersed down to the ground. The estimated plume dispersion height using the ground level concentration would in these cases overestimate the actual height for the plume mass center. Still it's evident that the plume is aloft and not close to ground. Aloft the wind gradient with height is far less steep than close to ground, and with the plume aloft the flux calculation becomes less sensitive to actually picking the true plume height in the wind profile assessment.

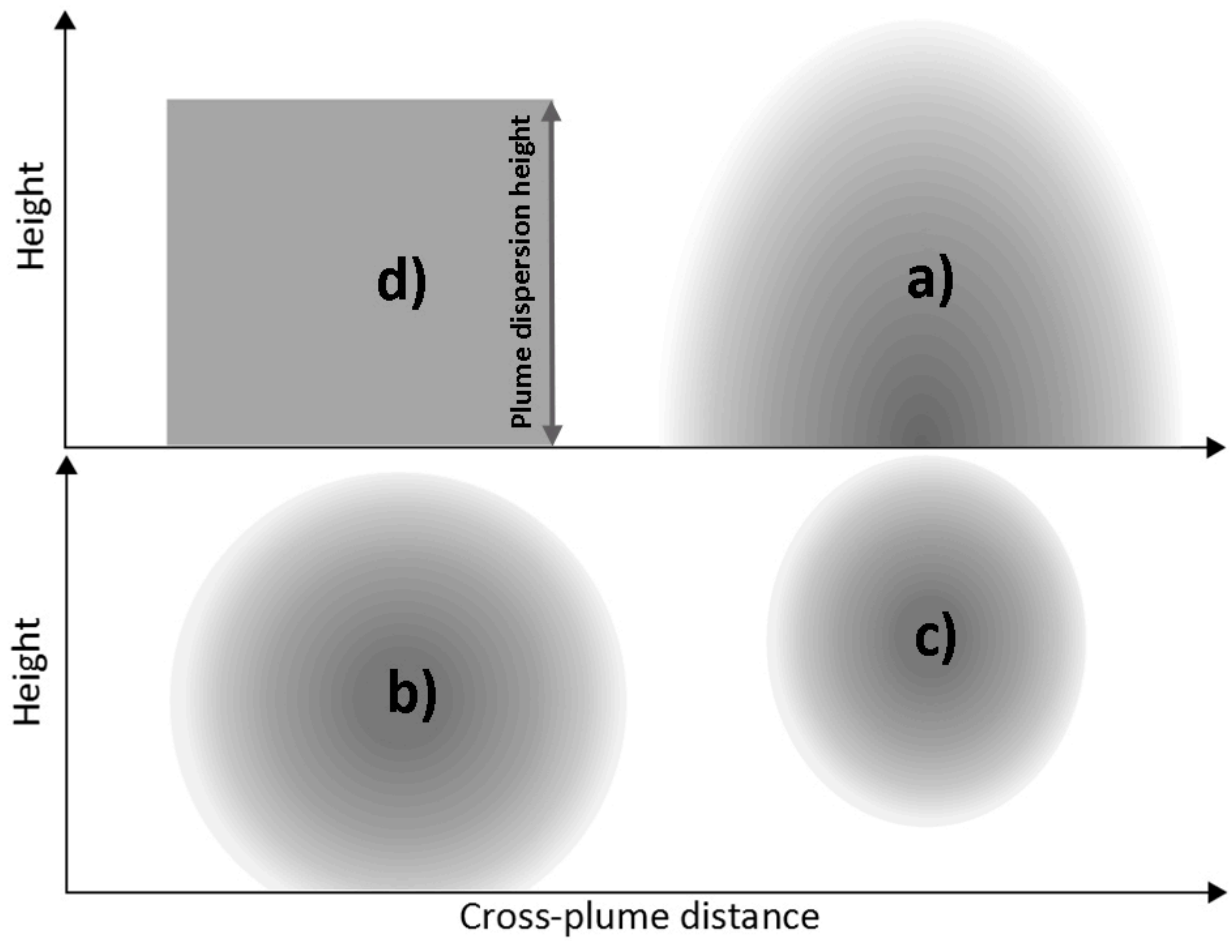

Figure 8 Four examples of what the concentration distribution of an emitted species might look like in a plume. Darker shades of gray indicated higher concentrations. Plume example annotation with reference to Figure 7.

In the controlled release experiment, the measurements were generally performed within 60 seconds downwind of the release point. For a single point source at such close range and limited time for dispersion, the plume distribution may not be accurately approximated by a Gaussian distribution at any specific point in time. Instead the distribution may be highly irregular and varying over time due to local turbulence and winds. However, the average distribution of the plume concentration over a longer time may still be considered to be fairly Gaussian. For this reason, calculating a plume height estimate as described above for every single plume transect can give large variations, partly because the actual plume height varies and partly because of occasional situations as in example c) in Figure 8. By averaging the integrated values of concentration and columns for a number of plume transects before calculating

the plume dispersion height estimate, a more statistically robust estimate can be achieved, which will be representative of the plume dispersion height of the average plume. This average plume dispersion height can then be used to determine the suitable height interval for which the winds are representative of the plume velocity.

In summary:

- The plume dispersion height is calculated by comparing the MeFTIR ground level concentration to the vertically integrated SOF column, assuming uniform plume mixing.
- SOF column (mg/m^2) = MeFTIR ground concentration (mg/m^3) x PlumeDispersionHeight (m)
- The plume dispersion height is used to indicate if the plume is close to ground or aloft to support wind profile assessment in the SOF flux calculation

2.5 Criteria for valid SOF plume transects in the blind release study

As seen in Figure 1, the release site was set up for northerly winds, based on meteorological forecasts for the day. Due to the complexity of the release instrumentation with heavy gas cylinders, meteorological towers, precision scales etcetera, the position of the release point could not be altered once the release study was started.

SOF plume transects are preferably done with as close to orthogonal plume passage as possible, compared to the wind direction, in order to limit uncertainties due to any occurring wind shifts. In order to allow for some wind deviations from the forecasted northerly wind, a sector of within ±45º deviation from north was defined as a valid sector for the plume to be measured in for the release study. Still when skewed winds push the plume to the edge of this sector, uncertainties will inherently be larger than for orthogonal (northerly) winds, since any wind shifts will have a larger impact on the retrieved flux at higher skew angle. A 10º uncertainty in the wind direction measurement would inherently induce an uncertainty in the flux retrieval of 1.5% for an orthogonal plume transect, 4.7% uncertainty for a 75º angle transect and 17.4% uncertainty for a 45º transect angle. As seen in Figure 1 there were some buildings and homes at the borders of this ±45º sector. These introduced enhanced surface roughness, in meteorological terminology, and more efficient plume dispersion rather than blocking the plume transport.

During the day on April 20, the wind unfortunately shifted a little towards northwest compared to the forecast, and the plume was occasionally pushed out of the valid sector. This was especially the case for release episode #5 and #2, limiting the number of valid transects (only five and three respectively).

Release #5 and #6 were pushed very late in the day, and conducted under atypical and non-favorable conditions for SOF studies. As the sun was setting, the wind speed dropped off and was often below 2.5 ms^{-1} which was the lower bound for valid SOF measurements established in the quality assurance project plan (QAPP) prior to the study. At such low wind speeds, the turbulent dispersion is less effective and uncertainties in the plume wind speed assessment increase.

Figure 9 shows the solar zenith angle (SZA) (elevation above ground = 90º - SZA) and azimuth (East-South-West) angle during the different release episodes. For release #1 conducted at noon, the sun was about 70º above the horizon, whereas for the last two episodes the sun was setting and only at about 25º and 15º above the horizon, respectively. The elevation angle, in combination with the azimuth angle, determines how the solar beam cuts through the plume to the SOF vehicle. This becomes a pronounced effect only at low solar elevation (high SZA).

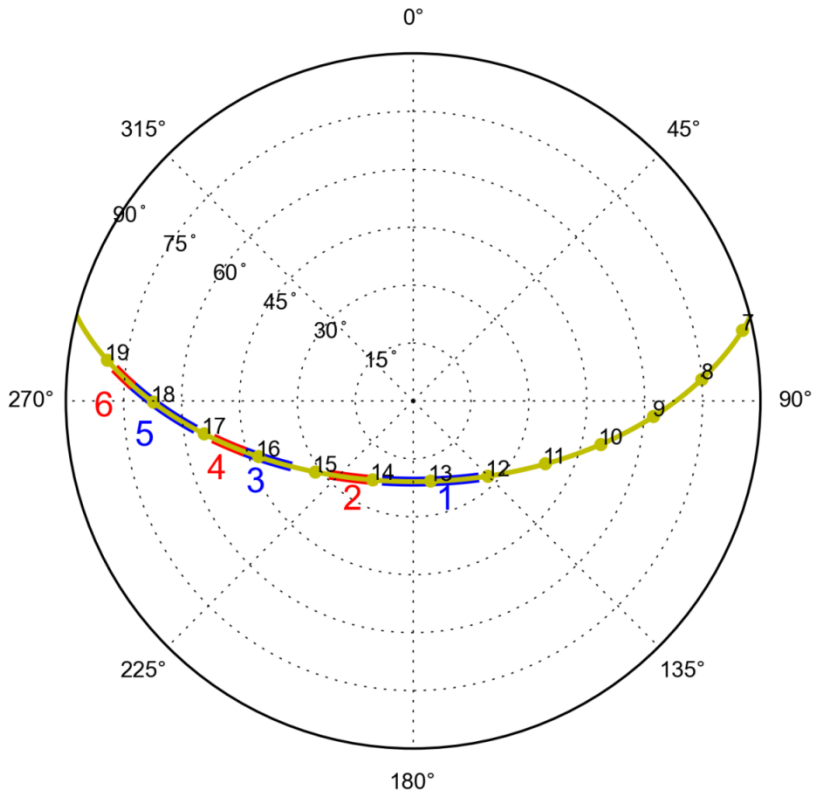

Figure 9 Solar zenith angle (SZA) and solar azimuth angle as function of time of day is shown by the green line. Hour of day is given for the period 7 am – 7 pm, and the duration of the release episodes are indicated by the blue and red colored lines along the green time line (release # given in blue and red numbers). The aiming angle from the horizon to the sun is 90º-SZA, so for example for release #1 the sun was at about 70º above the horizon, whereas for release #5 and #6 only at about 25º and 15º elevation only.

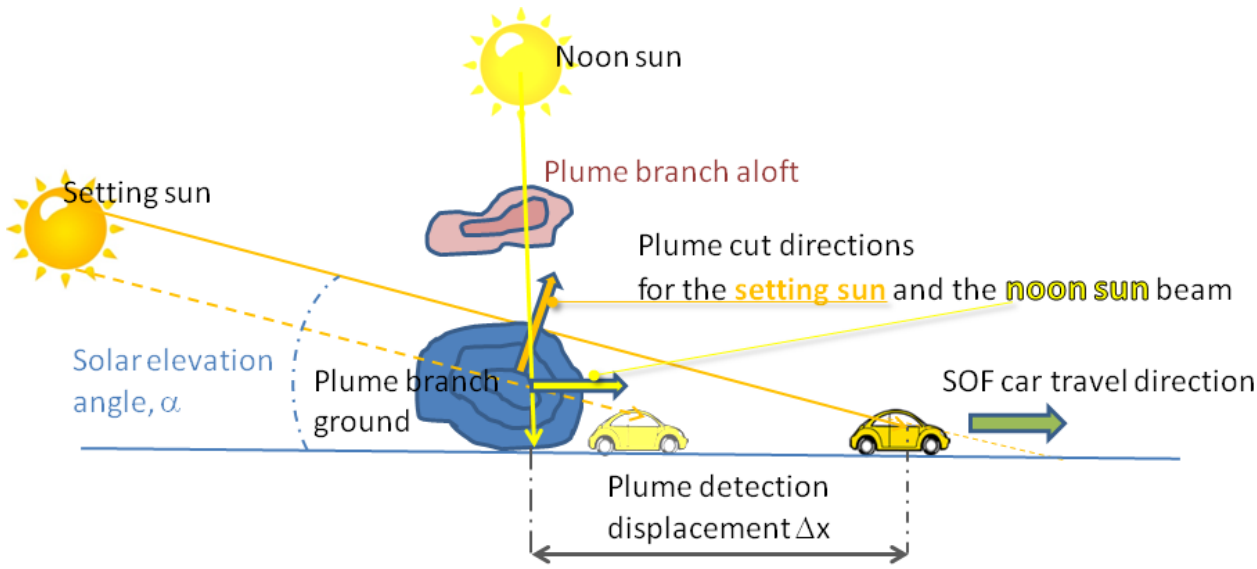

Figure 10 Schematic over the SOF plume scanning orientation at noon versus setting sun elevation angles α, and the apparent plume displacement Δx along the travel direction when the sun beam shines parallel to the SOF travel direction, at low angles. The wind is coming out of the paper plane in the graph, and the plume cross section is shown. Being close to source the plume might not be totally mixed yet, and may have different parts as shown by the ground blue and aloft magenta plume parts here.

Figure 10 shows a schematic of the plume transect situation for high solar elevation angle (noon) and low solar angle (setting sun) respectively. In the figure the wind is northerly, and the plume is coming out of the paper plane towards you. The SOF truck is travelling eastward across the plume, with the setting sun beam shining through the plume from the west at a low elevation angle α. As the car is moving eastward, the setting sun beam is cutting through the plume almost upwards, in contrast to the noon case where the sun beam is shining vertically and cutting the plume almost along the travel direction horizontally. As can be seen in Figure 10 a low sun elevation angle results in an apparent horizontal displacement Δx along the travel direction, to the plume detection point. In other words, at low solar angles one has to drive far out of the real plume to make sure the full vertical extent of the plume cross section is captured. In the case of separate plume branches there is an inherent risk of entirely missing the aloft plume branch, especially if the road is geographically restricted.

The setting sun schematic in Figure 10 illustrates the conditions during controlled releases #5 and #6. For release #6 with solar elevation angle of about 15º a plume branch at 35 m elevation above ground would be displaced (detected) 130 m eastward along Jaycee Dr (see Figure 1) as compared to the length of the ±45º valid wind sector of about 300 m on Jaycee Dr. Given the geographical constraints at the site makes the number of valid transects quite limited at such conditions, and uncertainties increase.

In contrast, at higher solar elevation angles, as exemplified by the noon case, any aloft plume branches would be captured by the vertical sun beam at the same time as any ground plume parts, and there is little risk of missing any vertically split plume branches in this case. Still, one must make sure to travel far enough outside the plume edges, in order to capture any plume branches that has split away from the core plume in the transverse direction.

To summarize, in the release validation study a plume transect was considered valid if:

- The plume was not pushed out of the sector ±45 deg from north (north wind = orthogonal plume pass) and the plume pass was not obstructed by severe shadows or traffic delays
- Wind speed was above 2.5 ms^{-1}
- Solar elevation angle was above 30º (solar zenith angle below 60º)

The conditions in release #5 and #6 did not fulfill the valid transect criteria, and are not considered as appropriate cases for validation. Still, measurements for these two periods have been reported for transparency.

3. Results

3.1 Results summary

On April 20, 2015, a controlled ethylene release study was conducted at the Longview Fairgrounds adjacent to the Maude Cobb Convention Center in Longview, TX.

In total six different ethylene release rates were included in the study, ranging from 1.85 kg/h to 10.85 kg/h. Due to long set-up time for the release site, the release measurements were started first at 12:15 pm and conducted until 6:45 pm, thus spanning from peak sun at noon to approaching sun set at the last release. Table 3 and Figure 11 summarize the results for the controlled release episodes.

For the first 4 releases, the reported SOF release rates were within -45%, +1.4%, +14%, and -10% of the true release rates, which ranged from 1.85 to 10.85 kg ethylene per hour. The last two release episodes were done late in the day, with atypical SOF conditions as low sun angle, cirrus clouds (see Figure 14), low wind speeds and limited number of plume transects due to the wind and the setting sun. These two releases are thus not considered appropriate as validation releases.

Table 3 Reported ethylene emission rates using SOF, and actual release rates. Note the footnote comments submitted with the SOF estimates prior to disclosure of the actual release rates.

Gas release #	Time	Number of plume transects	SOF reported ethylene emission (kg/h)	True ethylene release (kg/h)	Deviation from true release rate (%)	Wind speed range (m/s)
Release #1	12:18-12:30 + 13:02-13:39	17	**3.3 ± 1.1**	**6**	**-45%**	2.7-5.5
Release #2	14:03-14:20	3	**11.0 ± 2.3** [a]	**10.85**	**+1.4%**	3.4-3.4
Release #3	15:36-16:14	7	**2.1 ± 0.9** [b]	**1.85**	**+14%**	3.1-5.6
Release #4	16:26-17:11	12	**3.6 ± 1.6**	**3.99**	**-10%**	2.7-5.6
Release #5	*17:27-18:18*	*5*	*3.6 ± 1.2* [a,c]	*8.8*	*N.A.*	*1.6-3.9*
Release #6	*18:30-18:44*	*4*	*2.9 ± 0.5* [a,c]	*5.1*	*N.A.*	*1.9-2.8*

[a] Low number of valid plume transects – higher uncertainty. A transect was considered valid if wind direction was within ±45 deg from north (north wind = orthogonal plume pass) and the plume pass was not obstructed by severe shadows or traffic delays

[b] A small release as this one gives concentrations and columns closer to the instrument's detection limits (lower Signal to Noise Ratio), which adds relative uncertainty

[c] Atypical conditions for SOF with too low wind speeds, low sun angles, cirrus clouds and limited number of plume transects. Not considered appropriate validation releases, N.A. Measurements presented for transparency.

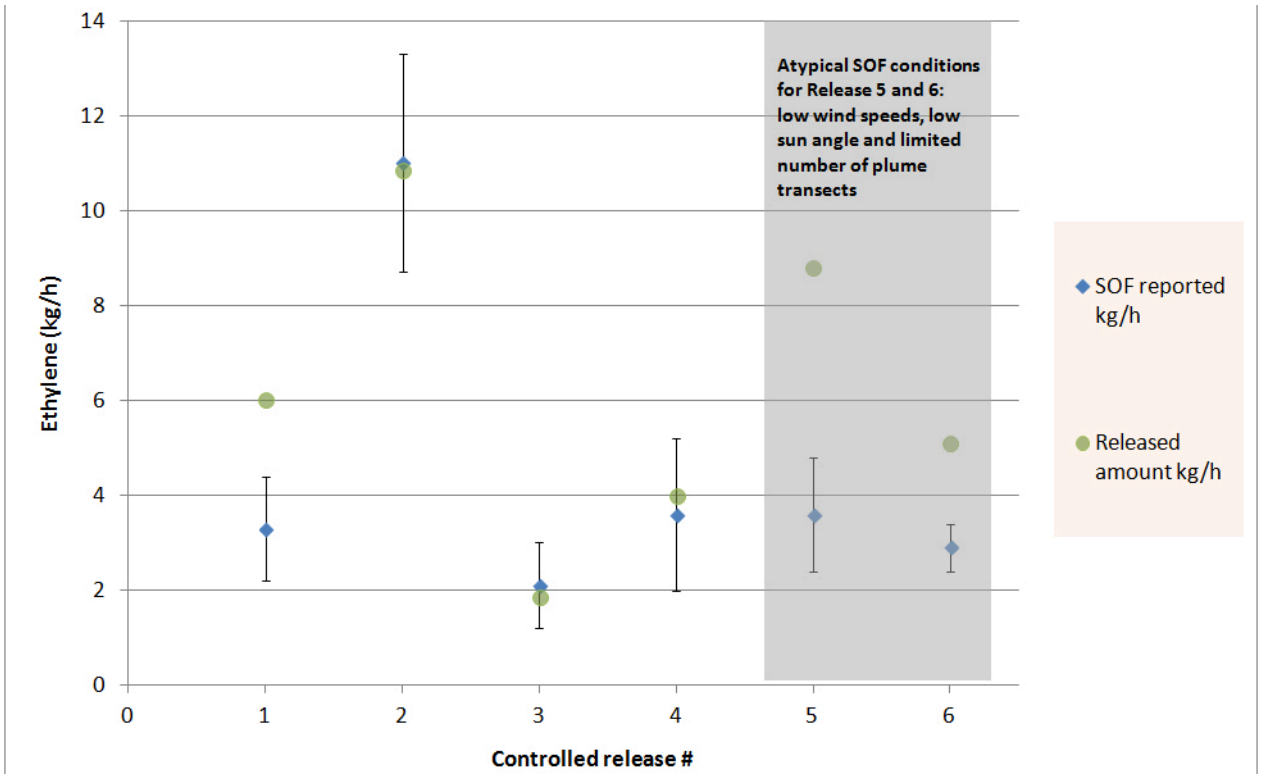

Figure 11 Overview of the results for the six controlled ethylene release episodes. For release #1 the reported SOF value are within 45% of the true release rate, for release #2, #3 and #4 within 1.4%, 13.5% and 10% respectively. Release #5 and #6 were done very late in the day during atypical conditions for SOF with low wind speeds, low sun angles, and very limited number of plume transects, thus not considered as appropriate validation releases.

Figure 12 shows example plume transects from the controlled release survey conducted at the Longview Fairgrounds on 20 April, 2015. Six plume transects from the first release configuration are displayed, including both vertical ethylene columns measured by SOF (unit mg/m^2) and ground level concentrations measured by MeFTIR (mg/m^3). The measurements were done along Jaycee Drive, at about 200 meters downwind of the controlled release point (release at 10 m above ground). The MeFTIR concentration data were combined with SOF vertical column data to assess the vertical plume dispersion height. Figure 13 shows four plume transects (MeFTIR only) from release configuration #4.

As seen both in Figure 12 and Figure 13 the concentrations at ground level varied greatly, as did the plume width, despite a constant emission rate. This variation reflects the short dispersion time in combination with the release being done from a single point source with limited turbulence at the release point. For some transects the plume was so narrow that a single data point constitutes the plume detection. Plume transport time from the release point to the measurement plume transect was typically about 60 seconds (3.5 m/s wind speed and 210 m distance).

Ground level ethylene concentrations in the range 10-350 µg/m^3 were in general observed during the controlled release experiment, with large variability also within each release configuration. SOF and MeFTIR measurements along the Jaycee Dr in between the controlled release episodes verified that there were no other significant ethylene sources in the area bit for the controlled release itself.

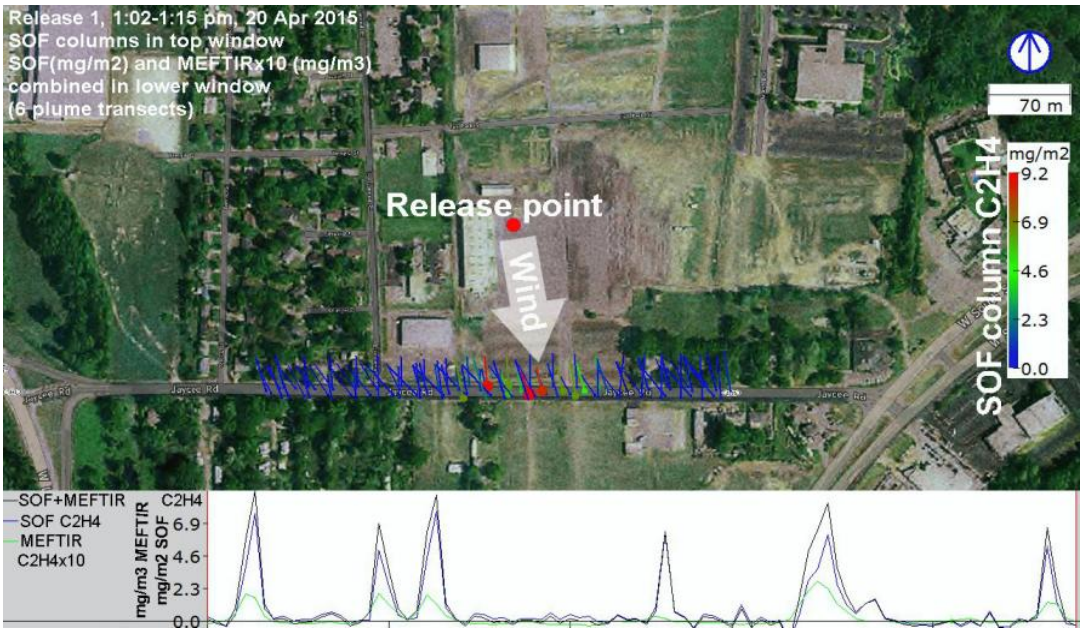

Figure 12 Plume transect examples from the controlled ethylene release at Maude Cobb Convention Center, Longview, TX, on April 20. Six plume transects by two instruments are shown: SOF measured vertical columns (mg/m^2) and MeFTIR measured ground level concentrations x 10 (mg/m^3 x10). Each measured (SOF) spectrum is represented with a point in the upper figure, which color and size indicate the evaluated concentration of ethylene in mg/m^2. A line from each colored point indicates the direction from which the wind is blowing. North is upwards in the figure. The ethylene column (SOF, dark blue) and concentration (MeFTIR, green) by distance driven through the plume is also shown in the lower part of the figure. (The black line is a software sum of SOF+MeFTIR which can be ignored here).

Figure 13 Four MeFTIR plume transect examples for controlled release configuration #4, 16:26-16:40. Each measured spectrum is represented with a point, which color and size indicate the evaluated concentration of ethylene in mg/m^3. The ethylene concentration by distance driven through the plume is also shown in the lower part of the figure (multiple transects back and forth). A line from each colored point indicates the direction from which the wind is blowing. North is upwards in the figure. Note the variability of a factor of 4 in the ground level concentration, due to dispersion effects.

3.2 Wind measurements

Figure 15 and Figure 16 show the wind speed and wind direction measurements for the 3 m tower, the 10 m tower and the LIDAR 40 m level for the duration of the controlled release study. Figure 17 shows the vertical wind speed at 40 m, 60 m, 80 m and 100 m as obtained by the wind LIDAR. Based on the plume dispersion height calculations, see section 3.5, a 0-35 m composite wind profile was derived based on the 3 m, 10 m and 40 m levels, which was used for the SOF release rate estimates. Note how the wind speed drops off for release #5 and #6, often being below 2.5 ms^{-1}, stated as the limit for suitable conditions for SOF measurements.

The temperature was in the range 19-22ºC (66-72ºF) for the duration of the experiment, and atmospheric pressure was stable at 989 mbar.

The sky was clear for the most of the day, with cirrus clouds appearing during release #5 and worsening during release #6, eventually making SOF measurements impossible since the SOF needs to see the sun, see Figure 14.

Figure 14 Sky cover during the controlled release episodes #1-#6. View facing south, with the red release operator tent in the foreground, the wind mast to the right and in the background Jaycee Dr where the SOF measurements where conducted. SIrrus clouds where apparent during release #5 and #6, and looking at the solar intensity and the shadow contrast on the concrete ground by the tent, it is evident how the solar light intensity decreased for release #5 and #6.

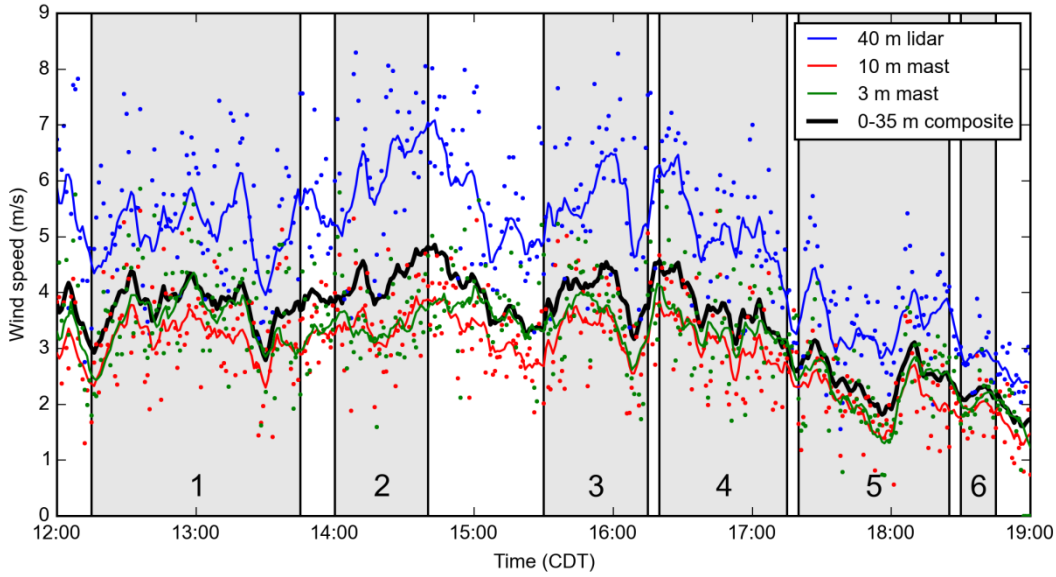

Figure 15 Wind speed measurements during the controlled release study. 1-minute average data shown for the 3 meter tower, 10 m tower and the LIDAR 40 m level, and a composite wind 0-35 m made up by the three linearly interpolated to 35m. Solid lines correspond to 10 minute running averages. Numbered grey sectors correspond to the duration of the release episode.

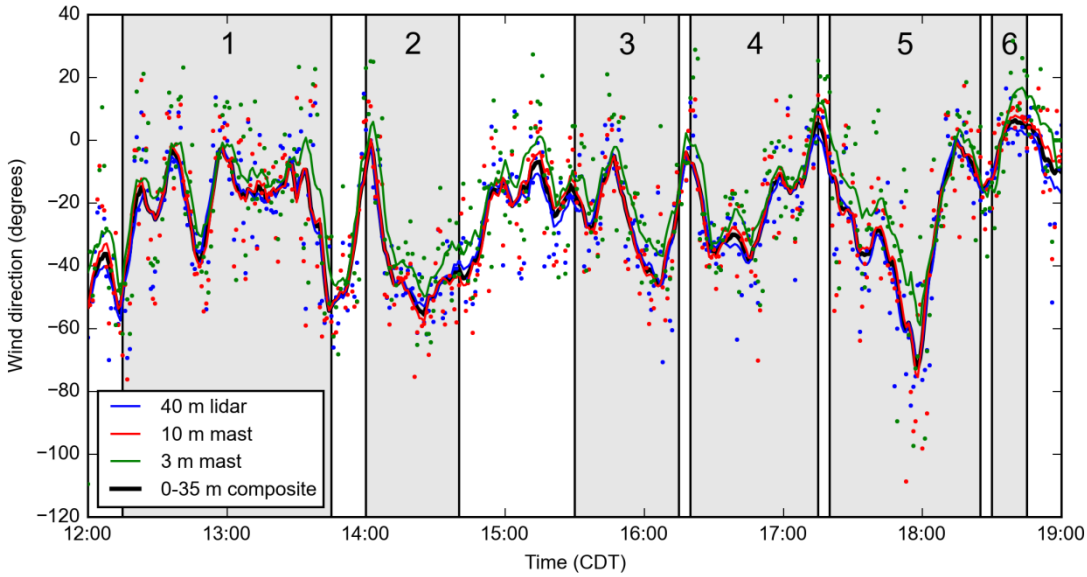

Figure 16 Wind direction measurements during the controlled release study, expressed as deviation from northerly wind. 1-minute average data shown for the 3 meter tower, 10 m tower and the LIDAR 40 m level, and a composite wind 0-35 m made up by the three linearly interpolated to 35 m. Solid lines correspond to 10 minute running averages. Numbered grey sectors correspond to the duration of each release episode.

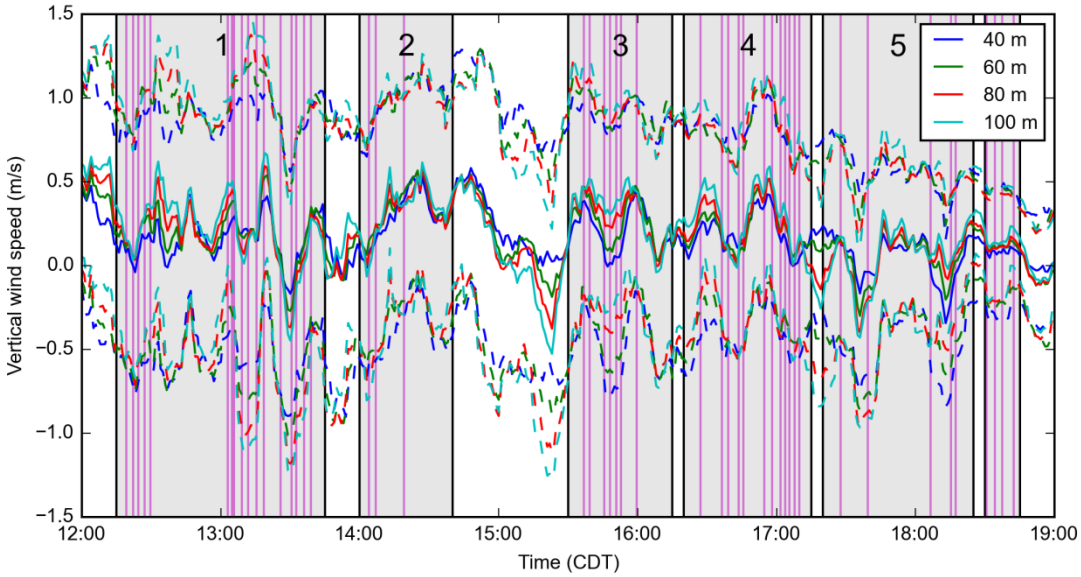

Figure 17 Vertical wind speed measurements during the controlled release study. Solid lines correspond to running 10-minute averages, and the dashed lines to ± 1 standard deviation. The amplitude and spread gives an indication of the dispersion strength, but it's really only at the two last release episodes one can see a decrease, as the sun is setting. Note that negative winds for the LIDAR means winds from ground and upwards and positive means downward winds. Vertical magenta bars indicate time for the SOF plume transects within each release episode.

3.3 Gas release rates

Figure 18 shows release rates for all the release episodes, as obtained from the weight decrease by time (slope) for all scales for the duration of each release respectively. The figure for release #1 shows the time period (~12:50 CDT) when the release was halted to fix a leak.

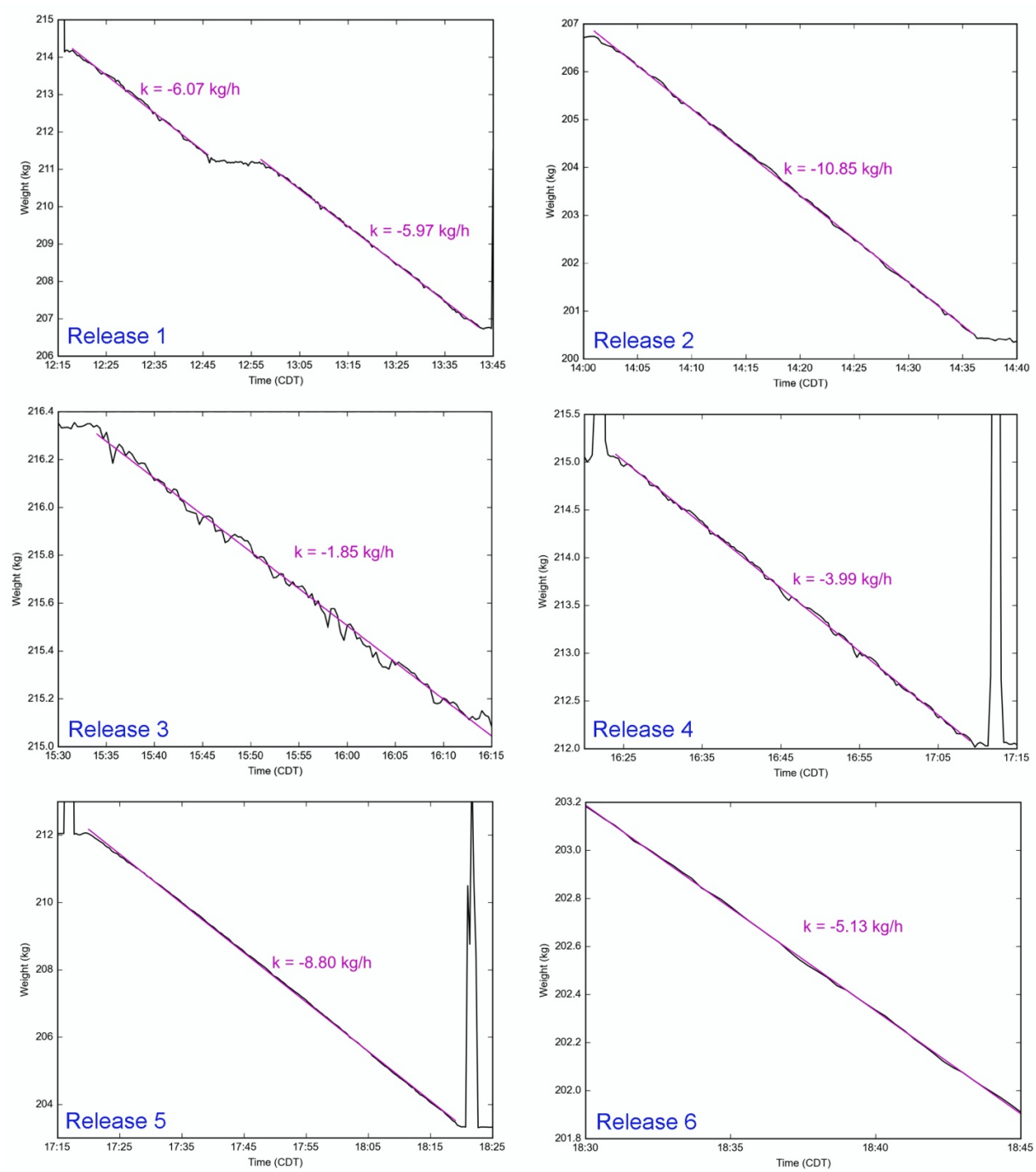

Figure 18 Ethylene release rates for release episodes #1-#6. The MFC and the scales indicated the same the release rates. Presented release rates correspond to the weight decrease by time (slope) for all scales for the duration of the release. The peaks occasionally seen at the beginning and end of some of the releases, are due to scale calibration by three 5 kg – weights put onto the scales.

Table 4 Ethylene release rate comparison between the mass flow controller (MFC) set point and the precision scales.

Release #	MFC flow set point kg/h	Released amount (precision scales) kg/h	Release rate comparison MFC set point / Scale slopes
1	6.00	6.02	1.00
2	10.87	10.85	1.00
3	1.87	1.85	1.01
4	4.12	3.99	1.03
5	8.62	8.8	0.98
6	5.25	5.1	1.03
Average:			**1.008**

As seen in Table 4, the mass flow controller (MFC) set rate and the rate obtained from the weight decrease on the precision scales compared very well, within 1% on average. This implicates that the MFC were well calibrated and had a linear response over the rates used, and that there were no severe leakages in the release system (apart from the leak that was identified and corrected during release #1).

As a check for the scale response, three certified 5 kg calibration weights were sequentially put on and off each scale prior to and after each release episode. The scales showed good response and no anomalies, see Figure 19 and Figure 20.

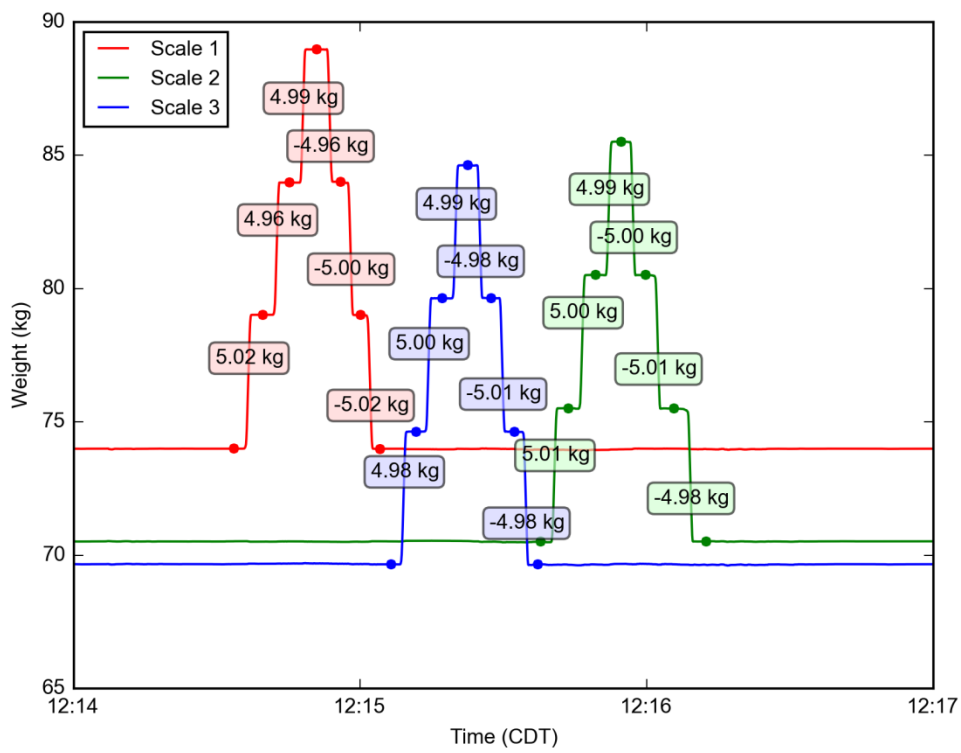

Figure 19 Response check of three scales were done prior to and after each release episode, by sequentially putting three 5 kg - calibration weights onto and off each scale. The graph shows the response check prior to the first release. The somewhat differing baseline weight for the scales is due to the different tare weights for the three ethylene cylinders.

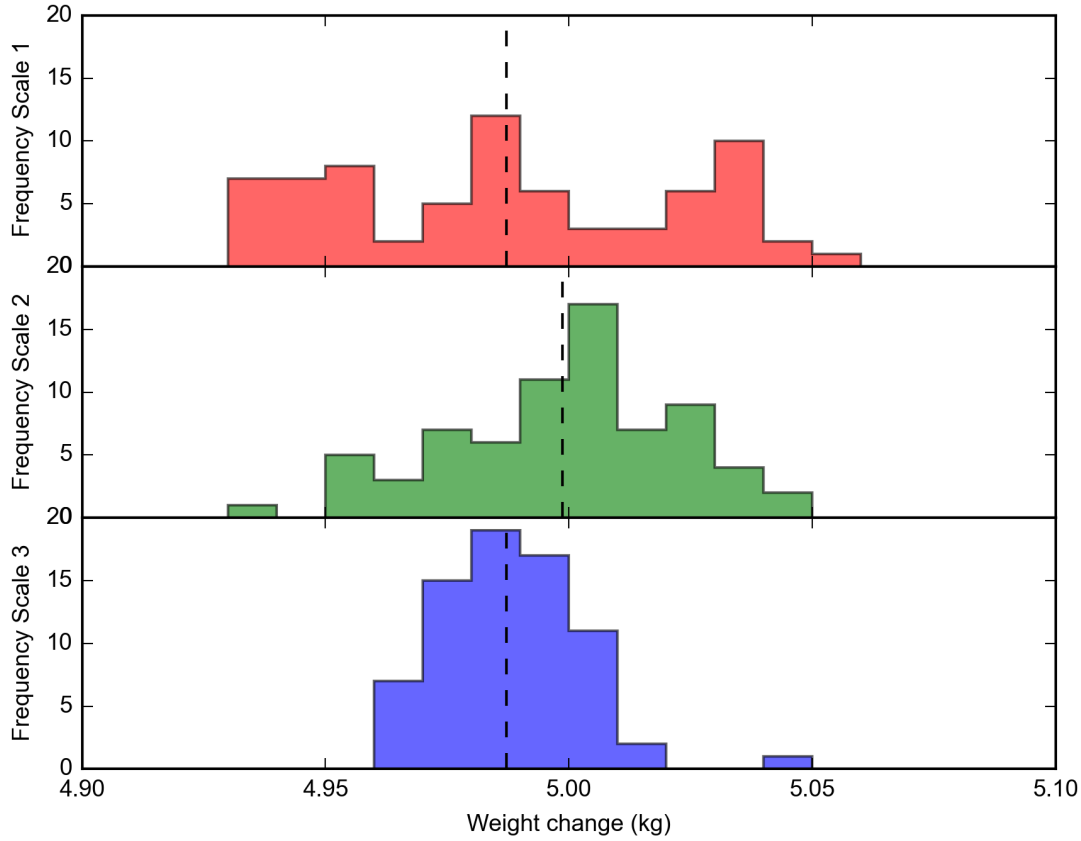

Figure 20 Histogram plot summarizing all the scale calibrations done during the release episodes. In each calibration three 5kg-weights were sequentially put on and off each scale, and the plot shows the frequency of the scale response for each scale.

3.4 Plume dispersion height estimates

The plume from a single point source will disperse horizontally and vertically due to wind turbulence over time tend to follow a Gaussian dispersion pattern. For short downwind distances, such as in this case, the plume distribution may still be highly non-Gaussian at any given time, but the average distribution of the plume over a longer period may still be assumed to approximate a Gaussian pattern. Hence it should be possible to make a statistically robust estimate of the average dispersion height, by averaging as many observations of the plume as possible. Thus, the integrated plume mass of all SOF plume transects and all MeFTIR plume transects were averaged for all plume transects during the whole controlled release experiment. All together 66 simultaneous plume transects with SOF and MeFTIR were used to assess the plume dispersion height.

Based on these averages a plume dispersion height of 35 m (i.e. plume extent from ground to 35 m above ground) was determined to be representative of the average conditions during the whole release experiment. Table 5 shows average plume dispersion heights calculated similarly for each individual release episode. However, the limited number of transects within each release episode does not allow for any significant conclusions or comparisons to be done between the individual release episodes regarding plume dispersion height.

Table 5 Plume dispersion height estimates based on all the controlled release episodes, comparing SOF vertical columns and MeFTIR ground level concentrations, integrated across the plume transects, and summed up for all the plume transects.

Release #	N	Integrated cross plume ratio of: SOF vertical mass column / MeFTIR ground mass concentration (m)
1	18	30.2
2	8	45.9
3	13	41.4
4	15	26.4
5	8	54.1
6	4	21.8
ALL	**66**	**35.4**

3.5 Detailed SOF measurements data from the different releases

Table 6 - Table 11 summarizes individual SOF plume transects for the six controlled release configurations. The wind data presented for each transect correspond to the 0-35 m composite wind profile averaged for the duration of the plume transect. This wind data were also used in the flux calculation.

Table 6 Summary of SOF plume transects for Release #1. Wind speed and direction data correspond to the 0-35 m composite wind profile.

Timespan	Emission (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
121847-121949	3.9	3.7	324
122125-122244	2.3	3.5	344
122337-122456	4.7	4.3	7
122650-122734	2.1	4	320
122911-122955	5.7	5.5	315
130225-130327	2.7	3.2	336
130428-130521	2.4	3.8	352
130512-130605	3.5	3.6	358
130852-130927	2.2	4.3	352
131055-131240	4.1	3.1	346
131417-131620	3.8	4.3	349
131756-131915	2.3	4.4	342
132533-132600	1.7	3.6	344
133010-133103	4.5	3.6	8
133155-133323	4.5	2.7	339
133535-133618	2.5	4.7	358
133822-133923	3.7	4.1	354
Average	**3.3±1.1 (34.4%)**	-	-

Table 7 Summary of SOF plume transects for Release #2. Wind speed and direction data correspond to the 0-35 m composite wind profile.

Timespan	Emission (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
140325-140427	12.1	3.4	339
140630-140722	8.4	3.4	354
141839-141940	12.6	3.4	318
Average (±1 SD)	**11.0±2.3 (20.9%)**	-	-

Table 8 Summary of SOF plume transects for Release #3. Wind speed and direction data correspond to the 0-35 m composite wind profile.

Timespan	Emission (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
153627-153711	1.9	4.7	325
153847-153940	2.3	3.1	330
154438-154632	3.9	4.5	2
154734-154827	2.2	4.3	344
155012-155113	1.5	3.9	359
155224-155307	1.4	5.6	322
155841-160035	1.5	4.2	324
Average	**2.1±0.9 (41.8%)**	-	-

Table 9 Summary of SOF plume transects for Release #4. Wind speed and direction data correspond to the 0-35 m composite wind profile.

Timespan	Emission (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
162645-162738	6.6	4.2	322
163549-163659	4.1	4.5	330
163853-163928	1.5	3	333
164312-164414	4.9	4	327
164515-164608	3.5	5.6	325
165420-165503	2	3.9	352
165724-165852	6	3.4	345
170049-170225	1.8	2.8	349
170309-170410	2.5	3.1	353
170446-170613	2.5	3.7	329
170724-170816	3.6	4.6	337
170909-171028	4.1	2.7	359
Average	**3.6±1.6 (45.4%)**	-	-

Table 10 Summary of SOF plume transects for Release #5. Wind speed and direction data correspond to the 0-35 m composite wind profile.

Timespan	Emission (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
172701-172811	3.7	3.4	355
173834-174010	2.8	1.6	338
180554-180705	5.3	3.9	335
181413-181625	4.1	2.6	357
181642-181753	2	1.8	353
Average	**3.6±1.2 (34.6%)**	-	-

Table 11 Summary of SOF plume transects for Release #6. Wind speed and direction data correspond to the 0-35 m composite wind profile.

Timespan	Emission (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
183007-183109	2.6	2	345
183341-183500	2.7	1.9	2
183642-183809	3.7	2.8	5
184130-184307	2.7	2.6	6
Average	**2.9±0.5 (17.5%)**	-	-

4. Discussion

The first four controlled ethylene releases (i.e., release #1-#4) in the blind study were conducted in valid conditions, and the reported SOF release rates differed by -45%, +1.4%, +14%, and -10% from the true release rates. Emitted rates ranged from 1.85 to 10.85 kg ethylene per hour. The last two releases (i.e., #5 and #6) were done late in the day, with atypical SOF conditions of low sun angle, cirrus clouds, low wind speeds and limited number of plume transects due poor measurement conditions and lack of time. The last two releases are thus not considered appropriate as validation releases.

The short plume dispersion time of about only 60 seconds between the single release point and the plume transect road about 200 m downwind from the source exacerbates some sources of uncertainty that are minor for typical industrial SOF measurements. With limited turbulence over the smooth surface surrounding the single release point, dispersion of the plume was not very effective resulting in very narrow plumes, and often also a branched plume with multiple peaks observed. In contrast industrial sites typically have large structures that create wakes, fans and heat introduces strong turbulence, leading to broad and continuous plumes that are easier to locate and measure completely.

The narrow and sometimes branched plume of the tracer release occasionally introduced difficulty in capturing the full plume, especially given the geographical constraints along the plume transect road. It is likely that some transects did not capture all branches of the plume, and restricting the analysis to transects with winds in the sector ±45 degrees from north does not protect against this difficulty. Another uncertainty factor with narrow point source plumes of only a few measurement points occurs when the plume sweeps sideways with (or opposing) the driving direction, resulting in the plume appearing artificially broadened (or narrowed) and the resulting emissions over (or under) estimated. Averaging many plume traverses suppresses this effect.

Studying the plume widths for release #1 and release #4, wind conditions made plumes comparably more narrow in release #1, with on average two measurement points fewer through the plume cross section for release #1, inducing higher uncertainty. During release #1 the release operator reported a leak occurring at the gas cylinder regulators midway into the experiment. The measurements were at this point put on hold, and the leak was tightened and the measurements were then resumed. In the analysis, the period immediately preceding the service stop was left out, and looking into the scale responses we don't expect this to have affected the rate much.

The plume dispersion height assessment, based on comparing measured ground level ethylene concentrations (MeFTIR, mg/m^3) to the integrated vertical columns (SOF, mg/m^2), implicated a plume dispersion height of 35 m. The presented flux rates were accordingly based on a composite wind profile (0-35 m), combining wind measurements from 3, 10 and 40 m height. A vertical plume extent of about 35 m compares well with a tracer release in France (Connan et. al.). Their study was conducted in sunny springtime urban conditions (comparable Pasquill stability classes for the dispersion in Longview) and showed that a ground level (2 m) tracer release were dispersed to heights of typically 20-40 m at a downwind distance of 100-300 m, and occasionally higher.

A sensitivity study on how the retrieved flux rates would change assuming a more elevated plume, was done by extending the composite wind profile to 60 meters height. The retrieved fluxes would increase due to stronger winds in the upper layer, and in this case differ to the true release rates by -37%, +17%, +35%, +5% for release #1-#4, as compared to -45%, +1%, +14%, -10% in the original estimate using the 35 m wind profile.

In summary we believe the blind release study showed that the SOF technique is well capable of measuring ethylene fluxes of only a few kilograms per hour, and it reproduced the dynamics of the release range of 1.85-10.85 kg/h, retrieving the smallest and largest rates within +14% and +1% respectively. One of four releases under valid conditions had a retrieval error (-45%) outside the typical accuracy range for industrial SOF studies (± 30%), possibly due the atypical narrow and branched plume dispersion. The observed uncertainty range is considered normal for fugitive plume measurements. In a controlled release of ammonia (NH_3) in France in 2012, INERIS (L'Institut National de l'Environnement Industriel et des Risques, French public research body of industrial and commercial character) governed an experiment to examine the SOF ability to quantify ammonia from a single point source. In four release configurations, the SOF technique retrieved the true release rates on average within 20% (range -31% to +19%), which is in line with the Longview release results.

The SOF method has also been compared against other techniques. In an experiment at the Nynas refinery in Sweden a fan was mounted outside the ventilation pipe, sucking out a controlled VOC flow from the tank. The pipe flow was measured using a so called pitot pipe and the concentration was analyzed by FID (Flame ionization detector) by a third party consultant firm that measured the in situ VOC emission rate to 12 kg/h. SOF measurements were carried out in the plume at a distance corresponding to a few tank heights, yielding an emission rate of 9 kg/h, hence within 26 % in this case. Similar measurements from a joint ventilation pipe from several Bitumen cisterns yielded a FID value of 7 kg/h and 1% higher emission from the SOF measurements (Samuelsson, 2005).

As mentioned, some challenges were encountered in this study. The limited turbulence at the single release point and the smooth surface surrounding the release location, resulted in atypical narrow and branched plumes at the plume transect road, being only 60 seconds downwind the release point. A future controlled release should introduce better dispersion at the release point to better simulate a real industrial SOF measurement case, where turbulence is stronger and plumes are more dispersed. A future set up should allow for alternative plume transect roads due any wind shifts, and ideally allow for plume transects at different distances downwind the release point. It would also be beneficial to focus on fewer release rate configurations, which would allow for better statistics on the ones conducted.

For the autumn of 2015 a controlled propane release study is to be conducted in the Los Angeles basin, comparing the SOF and DIAL (Differential Absorption LIDAR) techniques, both considered Best Available Technologies (BAT) in Europe for quantification of fugitive emissions.

5. References

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