

Article

Airborne Measurements of Ethene from Industrial Sources Using Laser Photo-Acoustic Spectroscopy

J.A. de Gouw, S. Te Lintel Hekkert, J. Mellqvist, C. Warneke, E.L. Atlas, F.C. Fehsenfeld, A. Fried, G.J. Frost, F.J.M. Harren, J.S. Holloway, B. Lefer, R. Lueb, J.F. Meagher, D.D. Parrish, M. Patel, L. Pope, D. Richter, C. Rivera, T.B. Ryerson, J. Samuelsson, J. Walega, R.A. Washenfelder, P. Weibring, and X. Zhu

Environ. Sci. Technol., **Article ASAP** • Publication Date (Web): 09 March 2009

Downloaded from <http://pubs.acs.org> on March 9, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Airborne Measurements of Ethene from Industrial Sources Using Laser Photo-Acoustic Spectroscopy

J.A. DE GOUW,^{*,†,‡}
 S. TE LINTEL HEKKERT,[§] J. MELLQVIST,^{||}
 C. WARNEKE,^{†,‡} E.L. ATLAS,[⊥]
 F.C. FEHSENFELD,^{†,‡} A. FRIED,[#]
 G.J. FROST,^{†,‡} F.J.M. HARREN,[∇]
 J.S. HOLLOWAY,^{†,‡} B. LEFER,[○] R. LUEB,[⊥]
 J.F. MEAGHER,[†] D.D. PARRISH,[†]
 M. PATEL,[○] L. POPE,[⊥] D. RICHTER,[#]
 C. RIVERA,^{||} T.B. RYERSON,[†]
 J. SAMUELSSON,^{||} J. WALEGA,[#]
 R.A. WASHENFELDER,^{†,‡} P. WEIBRING,[#]
 AND X. ZHU[⊥]

NOAA Earth System Research Laboratory, Boulder, CO, CIRES,
 University of Colorado, Boulder, CO, Sensor Sense, Nijmegen, The
 Netherlands, Chalmers University, Gothenburg, Sweden, University
 of Miami, Miami, FL, National Center for Atmospheric Research,
 Boulder, CO, Radboud University, Nijmegen, The Netherlands, and
 University of Houston, Houston, TX

Received September 29, 2008. Revised manuscript received
 January 14, 2009. Accepted February 8, 2009.

A laser photoacoustic spectroscopy (LPAS) instrument was developed and used for aircraft measurements of ethene from industrial sources near Houston, Texas. The instrument provided 20 s measurements with a detection limit of less than 0.7 ppbv. Data from this instrument and from the GC-FID analysis of air samples collected in flight agreed within 15% on average. Ethene fluxes from the Mt. Belvieu chemical complex to the northeast of Houston were quantified during 10 different flights. The average flux was $520 \pm 140 \text{ kg h}^{-1}$ in agreement with independent results from solar occultation flux (SOF) measurements, and roughly an order of magnitude higher than regulatory emission inventories indicate. This study shows that ethene emissions are routinely at levels that qualify as emission upsets, which need to be reported to regional air quality managers.

1. Introduction

During the Texas Air Quality Study in 2000, industrial emissions of ethene (C_2H_4) were found to be large and 1–2 orders of magnitude larger than the inventories that summarize the emissions reported by industry for regulatory purposes (1, 2). Ethene and propene were identified as key precursors for rapid ozone formation in industrial plumes in the Houston area (1–5). These conclusions were based on airborne measurements using gas chromatography (GC) both

by airborne instrumentation and canister sampling with subsequent analysis in the laboratory. Both methods are limited in the number of measurements, and consequently, the characterization of ethene plumes from industrial facilities was not as detailed as would be ideal. To fill the need for airborne measurements with much improved temporal resolution, we have developed and used an ethene sensor based on laser photoacoustic spectroscopy (LPAS) (6) that provides fast-response measurements capable of more fully characterizing ethene plumes from industrial facilities.

In an earlier paper, we demonstrated the feasibility of detecting atmospheric ethene by LPAS (7). Here, we used a compact LPAS instrument developed by Sensor Sense to monitor ethene onboard the NOAA WP-3D aircraft during the second Texas Air Quality Study (TexAQs) conducted in September and October of 2006 in eastern Texas. The design of the LPAS instrument is discussed and the airborne performance is described and compared to measurements of ethene from air samples collected in flight. The LPAS measurements were used to locate and quantify the point sources of ethene in the Houston area. Emission flux estimates for the Mt. Belvieu chemical complex are compared with those from measurements with the solar occultation flux (SOF) method (8) deployed in a mobile laboratory by Chalmers University.

2. Measurements

2.1. Airborne Laser Photo-Acoustic Spectroscopy Measurements.

A schematic diagram of the airborne setup developed in this work is shown in Figure 1. The LPAS detector (Sensor Sense) is connected to a gas inlet, which (i) provides the LPAS with a constant sample flow and pressure independent of flight altitude, (ii) allows the sample flow to be

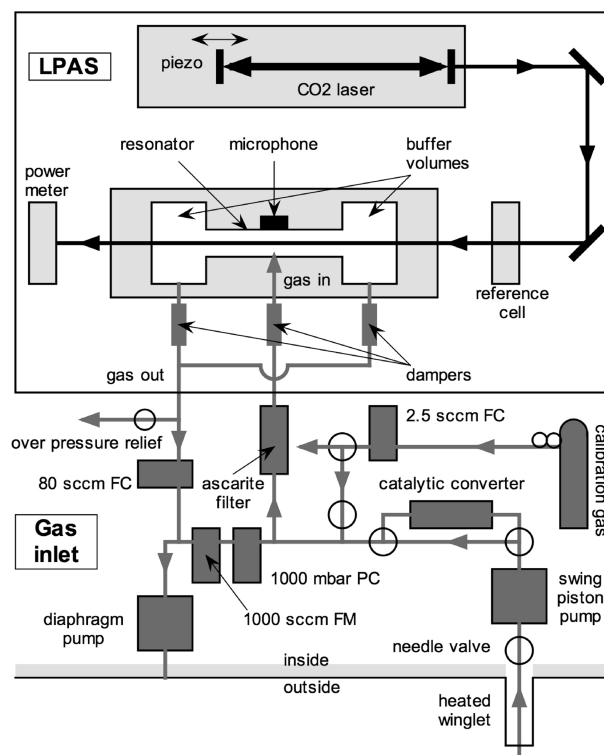


FIGURE 1. Schematic diagram of the airborne setup for measurements of ethene using a laser-photoacoustic spectroscopy (LPAS) instrument. The following acronyms are used: FC = flow controller, PC = pressure controller, and FM = flow meter.

* Corresponding author e-mail: joost.deGouw@noaa.gov.

[†] NOAA Earth System Research Laboratory.

[‡] University of Colorado.

[§] Sensor Sense.

^{||} Chalmers University.

[⊥] University of Miami.

[#] National Center for Atmospheric Research.

[∇] Radboud University.

[○] University of Houston.

passed through a catalytic converter that removes ethene for the determination of system backgrounds, and (iii) allows calibration gas to be added. Both the LPAS detector and the gas inlet system are described below.

2.2. Laser Photo-Acoustic Spectroscopy Detector. In the LPAS, a 1-W tunable CO₂ laser is used to excite trace amounts of ethene in a photoacoustic resonator. The laser is tuned by changing the length of the cavity with a piezo element. The laser is tuned to one of the main absorption features in the ethene spectrum around 10 μm using the photoacoustic signal from a reference cell filled with ethene at a high mixing ratio (~ 100 ppmv). In the photoacoustic cell, ethene is excited by laser light; de-excitation of the molecules through collisional quenching leads to a local heating and pressure increase of the sample gas. The laser power is modulated at the resonance frequency of the photoacoustic cell (~ 1600 Hz). The modulated output signal from the photoacoustic cell is detected using a microphone and amplified with a lock-in amplifier. A power meter behind the photoacoustic cell is used to monitor the laser output.

Temperature stabilization of the photoacoustic cell and the CO₂ laser is essential for the stability of the measurement. As aircraft cabin temperatures in excess of 30 °C occur regularly during summer, the laser temperature was controlled to 29 °C by cooling the instrument with a Peltier element, as opposed to heating in the commercial version of the instrument. To thermally insulate the laser and photoacoustic cell, and to isolate the microphones from aircraft noise, the optical table in the LPAS was packaged in 2.5 cm thick foam. The instrument was found to be insensitive to engine noise. To further limit pressure changes from reaching the resonator, dampers are used in the gas inlet and outlet tubing to the cell.

During operation, the wavelength of the CO₂ laser was stepped between two laser lines, the ¹⁰P₁₄ and the ¹⁰P₁₆ lines around 10 μm . The measurement procedure involved (1) tuning the laser to the ¹⁰P₁₄ line using the signal from the reference cell, (2) measuring the photoacoustic signal at the ¹⁰P₁₄ line, (3) making a fixed step in wavelength to the ¹⁰P₁₆ line, and (4) measuring the photoacoustic signal at the ¹⁰P₁₆ line. The entire cycle took ~ 5 s in flight, $\sim 70\%$ of which was used to collect signal. The absorption coefficients of ethene at the ¹⁰P₁₄ and the ¹⁰P₁₆ lines of the CO₂ laser are called Abs₁₄ ($30.4 \pm 5\% \text{ atm}^{-1}\text{cm}^{-1}$) and Abs₁₆ ($5.07 \pm 10\% \text{ atm}^{-1}\text{cm}^{-1}$), respectively (9). The lock-in signals of the LPAS instrument at these two lines (Sig₁₄ and Sig₁₆) are normalized to the laser power (Pow₁₄ and Pow₁₆), and we can write (6)

$$\frac{\text{Sig}_{14}}{\text{Pow}_{14}} = [\text{ethene}] \times \text{Cal} \times \text{Abs}_{14} + \text{Constant} \quad (1a)$$

$$\frac{\text{Sig}_{16}}{\text{Pow}_{16}} = [\text{ethene}] \times \text{Cal} \times \text{Abs}_{16} + \text{Constant} \quad (1b)$$

where [ethene] is the mixing ratio of ethene. The parameter Cal is the conversion factor from absorption to [ethene]. The parameter Constant is the photoacoustic signal in the absence of ethene, for example from window absorption, which is assumed to be the same at the two laser lines. Equations 1a and 1b can be solved for [ethene]:

$$[\text{ethene}] = \frac{\text{Sig}_{14}/\text{Pow}_{14} - \text{Sig}_{16}/\text{Pow}_{16}}{\text{Cal} \times (\text{Abs}_{14} - \text{Abs}_{16})} \quad (2)$$

In practice, parameter Cal is set by the user to match the instrument output for ethene in calibration gases; the measurement accuracy is not affected by uncertainties in the absorption coefficients.

Other atmospheric trace gases that absorb at the ¹⁰P₁₄ and ¹⁰P₁₆ laser lines include ozone, NH₃, SF₆, ethanol, and

benzene. The absorption coefficients for these compounds are such that interfering signals are not expected at typical ambient mixing ratios (7).

2.3. Inlet System. An inlet system was built to provide the LPAS detector with sample gas at a constant flow (80 sccm) and pressure (1000 mbar) regardless of flight altitude, which is important as the LPAS detector is sensitive to minute changes in pressure and flow. In flight, the ambient pressure is lower than 1000 mbar, and a swing piston pump (KNF) behind a needle valve is used to increase the inlet pressure. A pressure controller (MKS) in front of the photoacoustic cell controls the inlet pressure to 1000 mbar and a flow controller (Unit Instruments) behind the cell controls the flow of 80 sccm. This design kept the cell pressure and flow constant to within 0.2 and 0.8%, respectively, regardless of flight altitude. A flow meter behind the pressure controller measures the excess inlet flow, which is needed to calculate the mixing ratio of ethene when calibration gas is added. The exhaust gas is pumped by a diaphragm pump (Pfeiffer). The sample flow and the volume of the inlet system and photoacoustic cell limit the residence time of gas in the system to ~ 20 s. The sample flow is limited in practice to 80 sccm: at higher flows the air stream generates an acoustic signal in the photoacoustic cell and the noise in the signal increases exponentially.

The presence of CO₂ in sample air leads to a phase shift between the modulated laser power and the photoacoustic signal and therefore affects the output of the lock-in amplifier (7). CO₂ was removed from the sample air just in front of the LPAS instrument using a CO₂/H₂O scrubber consisting of ~ 5 cm³ Ascarite II (sodium hydroxide on silicate, Thomas Scientific) behind ~ 5 cm³ Drierite (calcium sulfate, Hammond Drierite) to keep the Ascarite dry. The volume of the scrubber was kept low to limit any increases in residence time of the sample gas. It was found that a fresh scrubber lasted long enough for one flight in the humid conditions encountered in Texas. No evidence was found for the loss (or production) of ethene in the scrubber.

The inlet flow can be diverted through a catalytic converter, which consists of Pt-coated quartz wool (Shimadzu) at 350 °C. The catalyst removes ethene, CO, CH₄, and other VOCs from the inlet flow and allows the system background to be determined. In-flight calibrations were made using a compressed gas standard containing nitrogen and 1020 ppbv of ethene (Matheson), 2.5 sccm of which was diluted to 2–10 ppbv in VOC-free sample air from the catalytic converter. Based on prior experience with such methods of calibration, we expect the resulting accuracy to be $\pm 10\%$.

2.4. Airborne Operation of the LPAS Instrument. Figure 2A shows the LPAS data from a portion of one flight and is used to illustrate the airborne operation of the instrument. The results were obtained during a nighttime flight, when more sustained periods of elevated ethene were encountered due to its slower photochemical removal at night. The in-flight performance was reduced in turbulent conditions, i.e., daytime flights over land: the 1 σ noise in the 5-s data increased from ~ 0.1 ppbv on the ground to ~ 0.5 ppbv in turbulent flight conditions.

Shaded regions in Figure 2A indicate the periods with calibration and background measurements. The LPAS data have been shifted by -20 s to account for the residence time of air in the instrument. Calibrations were performed every ~ 50 min: sample air was diverted through the catalytic converter for ~ 2 min and a 2.5-sccm flow of calibration gas was added. Background measurements were performed every ~ 15 min by diverting the sample air through the catalytic converter for ~ 90 s. Figure 2A shows that the LPAS signal in the absence of ethene was in many cases negative (-0.5 to -1.0 ppbv). This is explained by slightly different background signals at the ¹⁰P₁₄ and ¹⁰P₁₆ laser lines in the absence of

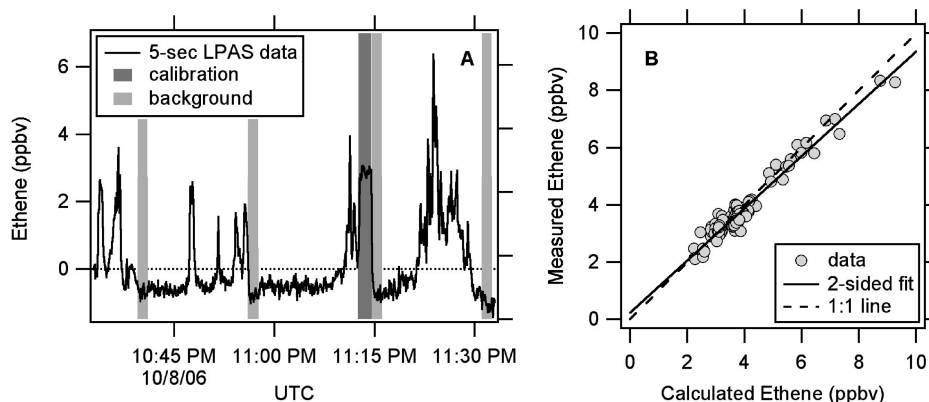


FIGURE 2. (A) Results of the ethene measurements by LPAS from part of a nighttime flight on October 8, 2006. The shaded areas indicate the periods when calibration and background measurements were performed. (B) Results of the calibration measurements from all flights.

ethene (eq 1a), which depend on the laser alignment and the temperature of the instrument. The background measurements were interpolated and subtracted from the signal for ambient air to obtain ambient mixing ratios. Although the background could drift over the course of a flight (by ~ 1 ppbv), the differences between subsequent background measurements were typically small (Figure 2A) and did not significantly enhance the measurement uncertainty.

The data in Figure 2A can be used to estimate the response time of the LPAS measurement. After the instrument switches from calibration to background mode, the 5-s measurement drops sharply from a few ppbv to its background level. The $1/e$ response time for the change was found to be 5.0 ± 1.0 s, and difficult to determine because the change is subsampled by the 5-s data.

The mixing ratio of ethene during calibration periods depends on the inlet flow. At higher altitudes, the inlet flow is smaller and the mixing ratio of ethene during calibrations higher. During the mission, calibration measurements were performed at different altitudes and as a result the calibration mixing ratios ranged from 2 to 10 ppbv. The instrument response during calibrations correlated well ($r^2 = 0.952$) with the value calculated from the composition of the calibration gas and the dilution flow (Figure 2B). The ratio between the instrument response, calculated using the factory-set calibration factor, and the in-flight calibration results was 0.91 ± 0.02 . There was a small offset of 0.23 ± 0.08 ppbv in the instrument response, which is below the detection limit and not explicitly used to correct the data. Based on the results of the in-flight calibrations, the final data were divided by 0.91 relative to the data obtained in the field.

2.5. Other Measurements. The estimates of ethene fluxes from the aircraft are compared in this study with those from a solar occultation flux (SOF) instrument operated by Chalmers University inside a mobile laboratory during TexAQS (8). Details on this measurement have not been published before, and a brief summary of the operating principles is given here. The SOF technique is an optical method utilizing the absorption of direct solar infrared radiation in the $1.8\text{--}14\text{ }\mu\text{m}$ range for retrieval of total columns of ethene, propene, ammonia and the sum of alkanes. The SOF measurements were carried out from a moving vehicle, making it possible to traverse emission plumes downwind from industrial sources and integrate the column density across a plume in real time. By multiplying with the wind speed, determined from balloon sondes launched nearby, the total emission flux is obtained. The uncertainty in the flux is $\sim 30\%$, mainly due to uncertainties in the wind speed. A report on the results from the SOF measurements can be found online (<http://files.harc.edu/Projects/AirQuality/Projects/H053.2005/H053FinalReport.pdf>).

During most flights, a total of 80 whole air samples (WAS) were collected in electro-polished stainless steel gas canisters (10). Sample fill times varied between 7 s at low and 15 s at high flight altitudes. The canisters were transported to the University of Miami, where they were analyzed for an extensive suite of hydrocarbons, alkyl nitrates and halocarbons using gas chromatographic (GC) analyses. In this work, we only use data for ethene and propene, which were reported with a 10% uncertainty (1).

Other measurements used in this study include those of carbon monoxide made by VUV fluorescence (11), formaldehyde (HCHO) made by tunable laser absorption (12), and NO, NO₂, and NO_y made by chemiluminescence (1).

3. Measurement Results and Discussion

3.1. Comparison of Ethene Measurements by LPAS and WAS. Figure 3A shows the LPAS data for ethene from part of a flight on October 13, 2006, along with the data obtained from GC analysis of the whole air samples (WAS). During this flight, the highest mixing ratio of the entire study, 69 ppbv, was observed just downwind from the Bayport chemical complex southeast of Houston. Shown in Figure 3A are the 5-s LPAS data recorded during the flight, as well as the 20-s averaged data. As mentioned before, the in-flight performance of the instrument deteriorated in turbulent conditions and a 20-s averaged data set was reported as a compromise between measurement precision and frequency. Except where otherwise noted, 20-s LPAS data are used in the remainder of this study; the 5-s data are available on request.

The 20-s LPAS and WAS data for all flights were compared on a point-by-point basis by selecting the WAS data within the 20-s averaging intervals of the WAS. The two measurements were correlated with a linear correlation coefficient (r^2) of 0.765 (Figure 3B). The difference in mixing ratio between the two measurements was described well by a Gaussian distribution with a 1σ width of 0.34 ppbv. The differences are due to (i) instrumental noise in the LPAS measurement and (ii) the high variability of ethene in plumes and the fact that the sampling intervals of the two measurements were never exactly the same. From a 2-sided, linear fit of the LPAS relative to the WAS data, we obtained a slope of 0.85 ± 0.03 with a negligible intercept of 0.05 ± 0.06 ppbv. We conclude that the LPAS and WAS data agreed within 15%, just outside the combined $\pm 14\%$ calibration accuracies of the LPAS (10%) and WAS (10%) measurements. The detection limit (DL) of the 20-s LPAS measurement was estimated from the random noise in the background measurements to be ~ 0.7 ppbv. This DL was low enough to observe ethene in industrial plumes, but urban levels of ethene were typically close to or below the DL. The DL of 0.7 ppbv is higher than

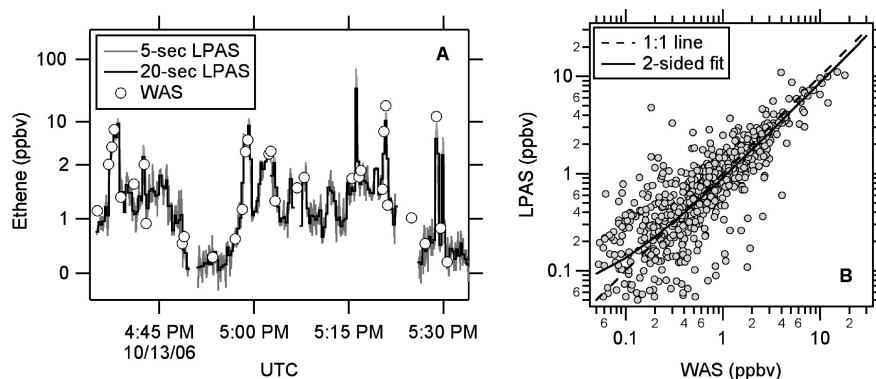


FIGURE 3. Comparison between the ethene measurements by LPAS and WAS (A) for part of the flight on October 13, 2006, and (B) for all data from the entire mission on a point-by-point basis. Note that the left axis in panel A is linear from 0 to 2 ppbv and logarithmic from 2 to 100 ppbv.

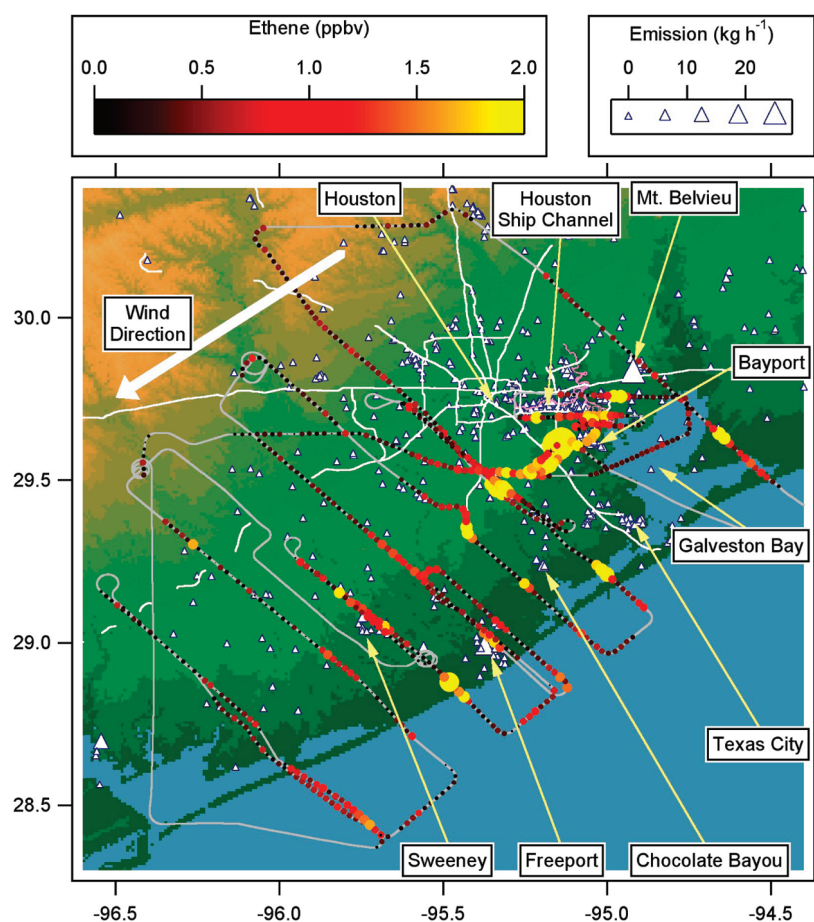


FIGURE 4. Flight track from September 19, 2006, size, and color-coded by the ethene mixing ratios measured by LPAS below 1000 m. The color scale is truncated at 2 ppbv to bring out the smaller plumes in the graph. The white triangles show ethene point sources in the 2004 TCEQ inventory, with the size proportional to the source strength.

for ground-based operation of the instrument, where the 2σ noise in a 20-s measurement is ~ 0.1 ppbv.

3.2. Ethene Sources in the Houston Area. To illustrate our findings on the location of ethene sources in the Houston area and the extent of the ethene plumes, Figure 4 shows the results from a flight on September 19, which sampled outflow from urban Houston, industrial sources near the Houston Ship Channel and a number of isolated sources south of Houston. The prevailing wind direction was northeasterly, and the data show a number of different sources. The highest ethene was measured just south of the Houston Ship Channel near the Bayport chemical complex, and this plume was observed during several downwind transects of the aircraft. High ethene was also observed downwind from the Mt.

Belvieu, Texas City and Freeport industrial complexes, which were also examined in 2000 and 2002 (1). In addition, high ethene was observed east of Galveston Bay. This plume may have originated in the Beaumont–Port Arthur area, but was sampled 10s of kilometers downwind from these sources. All of these point sources are associated with petrochemical plants and/or refineries. Enhancement of ethene from mobile sources downwind from the Houston urban core is not clearly observed in Figure 4.

Figure 5 shows a scatter plot of ethene versus CO for the flight on September 19. Data from Houston are overlaid with data from a flight over Los Angeles (black triangles) performed with the NOAA WP-3D in 2002 (13). It is clear that the data from Houston and Los Angeles are significantly different. In

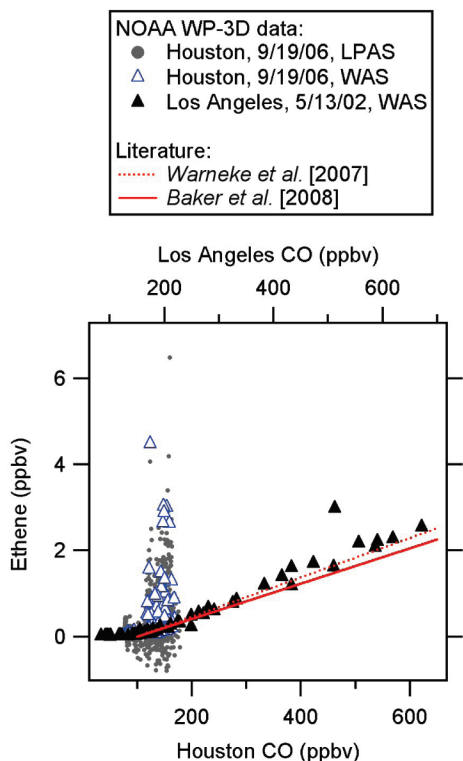


FIGURE 5. Scatter plot of ethene versus CO for the data from September 19, 2006. The results from Houston are overlaid with data obtained from the NOAA WP-3D over Los Angeles on May 13, 2002, and with two recent studies on urban VOC emissions in the U.S. Note that the CO-axis for Los Angeles data is offset by 50 ppbv with regard to the CO-axis for the Houston data in order to account for the seasonal and regional differences in background CO in the U.S.

Los Angeles, VOC emissions are dominated by those from vehicles and ethene and CO were well correlated. The ratio of ethene relative to CO in Los Angeles ($4.92 \text{ pptv ppbv}^{-1}$), defined by the slope of the best fit through the data, agreed within 20% with the emission ratio determined for the northeastern U.S. ($4.564 \text{ pptv ppbv}^{-1}$; red dotted line) (13) and with enhancement ratios averaged for 28 U.S. cities ($4.1 \text{ pptv ppbv}^{-1}$; red solid line) (14). In contrast, ethene and CO were poorly correlated in Houston and the highest ethene mixing ratios were observed at modest enhancements in CO. In agreement with previous work (1), we conclude from the data in Figures 4 and 5 that the plumes with high ethene in Houston were associated with industrial point sources.

On September 19, the NOAA WP-3D flew a pattern around the Houston Ship Channel that was similar to that driven by the Chalmers SOF van on the same day. The results from the two measurements are compared in Figure S1 in the Supporting Information, where the aircraft ethene data are converted to a column density assuming that ethene was uniformly mixed across the height of the boundary layer (BL). The comparison shows that (i) the SOF and LPAS measurements showed enhancements in the same locations and (ii) the column densities from the SOF and estimated from the aircraft agreed within $\sim 50\%$, suggesting that the vertical mixing of the plumes was fairly complete where the plumes were sampled by the aircraft.

3.3. Ethene Flux Estimates. Emission fluxes of ethene from industrial point sources in the Houston area were estimated using the airborne data shortly downwind from the sources, where the source location is unambiguous. By assuming that the plume is uniformly mixed across the BL height h , the flux can be estimated using (15):

$$\text{flux} = h \times \int_t \Delta[\text{ethene}] \times v \times w \times \sin(\alpha) \times dt, \quad (3)$$

where v is the aircraft velocity, w the wind velocity and α the angle between the flight and wind direction. The parameter $\Delta[\text{ethene}]$ is the enhancement in the number density of ethene over the background, i.e., the number density in the plume minus the background outside the plume. The following assumptions and uncertainties are associated with the flux estimates according to eq 3:

- The uncertainty of the ethene measurement of $\sim 10\%$ translates into a similar uncertainty in the flux.
- Calculation of the integral in eq 3 has an uncertainty of $\sim 20\%$ associated with the estimated background concentration of ethene and the limited duty cycle of the LPAS of $\sim 70\%$.
- BL heights were estimated using measured profiles of potential temperature, humidity and CO made near the plume location on the day of the measurement. Differences between multiple profiles during the same flight indicate that there is a $\sim 20\%$ uncertainty in this estimate.
- A large uncertainty comes from the assumption that the plume is uniformly mixed across the BL height. When the aircraft transect is too close to an emission source, the plume may not have mixed completely to the top of the BL, and the flux according to eq 3 may be an over- or underestimate depending on the flight altitude relative to the plume. Multiple passes downwind from the Freeport and Texas City chemical complexes suggest that this may result in an error of $\sim 30\%$, but this number is based on very few data points. Other evidence comes from the comparison of ethene columns from SOF and estimated from the aircraft on September 19 (Figure S1 in the Supporting Information), which agreed within $\sim 50\%$.

• It is assumed in eq 3 that ethene is not chemically removed in between emission and sampling by the aircraft. To evaluate this assumption, we looked at the measurements of formaldehyde (HCHO), one of the photoproducts from ethene, and NO_x and NO_y in the plumes from Mt. Belvieu. On average, $\Delta\text{NO}_x/\Delta\text{NO}_y$ ratios in the plumes were 0.91 ± 0.12 indicating that there had already been some conversion of NO_x into NO_y at the time of sampling. The $\Delta\text{HCHO}/\Delta\text{C}_2\text{H}_4$ ratios in the plumes were 0.3 ± 0.2 on average and were weakly anticorrelated with the $\Delta\text{NO}_x/\Delta\text{NO}_y$ ratios: as NO_x in the plumes was more oxidized, there was more HCHO relative to ethene. At $\Delta\text{NO}_x/\Delta\text{NO}_y$ ratios closest to 1, the HCHO enhancement in the plumes was close to zero, consistent with the notion that most HCHO was not directly emitted but rapidly formed by photo-oxidation of alkenes (2). HCHO is predominantly produced from ethene and propene in these plumes. Based on propene-to-ethene ratios in the Mt. Belvieu plume observed from whole air samples (0.7 on average), the rate coefficients with OH ($k = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for ethene; $k = 26.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for propene) (16) and the number of HCHO molecules formed from each alkene molecule (1.6 for ethene; 1 for propene) (2), we conclude that chemical removal of ethene between emission and sampling was likely $< 10\%$.

We conclude that the uncertainties associated with the assumption of uniform mixing dominate the combined uncertainty in the ethene fluxes according to eq 3. The overall uncertainty of the flux estimates is estimated to be a factor of 2 (-50% , $+100\%$).

Figure 6 and Table S1 in the Supporting Information summarize the results of our estimates for the flux from Mt. Belvieu obtained from 10 different flights. The mean flux was 520 kg h^{-1} with a standard deviation of 140 kg h^{-1} . This variability of $\sim 30\%$ is smaller than the estimated uncertainty of a factor of 2, indicating that (i) the factor of 2 may be a conservative estimate of the uncertainty, and (ii) it is impossible to discern any real variability in the emission flux within the uncertainties of the method. Added to Figure 6

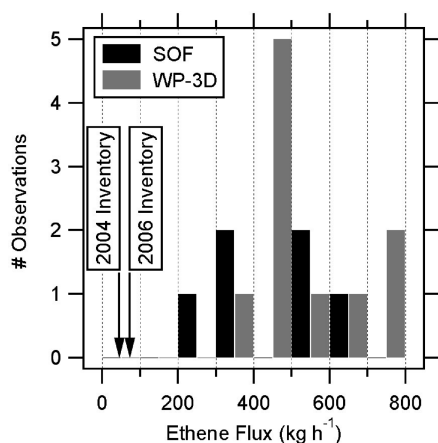


FIGURE 6. Distribution of ethene flux estimates for the Mt. Belvieu chemical complex. Data in gray are from the NOAA WP-3D in and data black from the SOF measurements. The arrows indicate the total fluxes for Mt. Belvieu in the 2004 (45 kg hr⁻¹) and 2006 (73 kg hr⁻¹) TCEQ inventories.

is the distribution of flux estimates from six passes downwind from Mt. Belvieu made by the SOF van on three separate days. The fluxes estimated from the aircraft and SOF measurements varied between 275 and 750 kg h⁻¹. The average from the aircraft estimates (520 ± 140 kg h⁻¹) agreed within the standard deviation with the average from the SOF measurements (450 ± 130 kg h⁻¹).

Both the aircraft and SOF results are significantly higher than the ethene flux for the Mt. Belvieu complex in the inventory of the Texas Commission on Environmental Quality (TCEQ) that summarizes the emissions reported by industry for regulatory purposes. The reported emissions are not measured but modeled from production statistics, assumed leak rates, etc. In the 2004 inventory, the largest single point source in the Mt. Belvieu complex was 29 kg h⁻¹ and the total emissions were 45 kg h⁻¹ by adding in point sources elsewhere in the complex. It is likely that emissions from these different point sources had merged together by the time of sampling with the aircraft. In the 2006 inventory, the total estimated emissions had increased to 73 kg h⁻¹. The 2004 and 2006 inventories are roughly an order of magnitude lower than the measured emissions, consistent with the findings from an earlier field study in the area (1, 2) that did not explicitly focus on Mt. Belvieu emissions. Similarly large underestimates were found for other industrial point sources south of Houston in 2006; these results will be presented elsewhere.

In the Houston area, accidental releases of a single reactive VOC over 45 kg need to be reported to TCEQ (17). This study shows that the Mt. Belvieu complex routinely emits 520 kg h⁻¹ of ethene, i.e., every hour more than 10× the quantity that qualifies as an emission event. Nam et al. studied the ozone formation Houston due to such emission events (3). These authors found that a sudden release of 450 kg of olefins can rapidly generate 0–30 ppbv of ozone in the downwind plume, depending on the time of day of the release, the duration, and chemical composition. Our results show that the emissions of ethene are routinely at the levels studied by Nam et al., suggesting that rapid ozone formation regularly occurs in industrial plumes. Finally, our results in Figure 4 illustrate that ethene emissions from Mt. Belvieu were not exceptionally high; our focus on this particular complex was due to its isolated location, which made the source attribution of plumes unambiguous, and due to the relatively large number of downwind passes made by the NOAA WP-3D and Chalmers SOF van.

Acknowledgments

We are grateful for support from the NOAA WP-3D flight crew, and for useful discussions with John Jolly from TCEQ. This study was financially supported by NOAA's Air Quality and Climate research programs. Participation of Johan Mellqvist and Barry Lefer was supported by the Texas Environmental Research Consortium (TERC).

Supporting Information Available

Figure S1 and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Ryerson, T. B.; Trainer, M.; Angevine, W. M.; Brock, C. A.; Dissly, R. W.; Fehsenfeld, F. C.; Frost, G. J.; Goldan, P. D.; Holloway, J. S.; Hübler, G.; Jakoubek, R.; Kuster, W. C.; Neuman, J. A.; Nicks, D. K.; Parrish, D. D.; Roberts, J. M.; Sueper, D. T.; Atlas, E. L.; Donnelly, S. G.; Flocke, F.; Wert, B. P.; Weidnmyer, C.; Alvarez, R. J.; Banta, R. M.; Darby, L. S.; Senff, C. J. Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas. *J. Geophys. Res.-Atmos.* **2003**, *108*, 4249.
- (2) Wert, B. P. Signatures of terminal alkene oxidation in airborne formaldehyde measurements during TexAQS 2000. *J. Geophys. Res., [Atmos.]* **2003**, *108*, 4104, DOI: 10.1029/2002JD002502.
- (3) Nam, J.; Kimura, Y.; Vizuete, W.; Murphy, C.; Allen, D. T. Modeling the impacts of emission events on ozone formation in Houston, Texas. *Atmos. Environ.* **2006**, *40*, 5329–5341.
- (4) Kleinman, L. I. Ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston. *Geophys. Res. Lett.* **2002**, *29*, 1467, DOI: 10.1029/2001GL014569.
- (5) Kleinman, L. I. Ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston. *Geophys. Res. Lett.* **2003**, *30*, 1639, DOI: 10.1029/2003GL017485.
- (6) Harren, F. J. M.; Cotti, G.; Oomens, J.; te Lintel Hekkert, S. Photoacoustic spectroscopy in trace gas monitoring. In *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; John Wiley Ltd.: Chichester, 2000; pp 2203–2226.
- (7) Kuster, W. C.; Harren, F. J. M.; de Gouw, J. A. Inter-comparison of laser photoacoustic spectroscopy and gas chromatography techniques for measurements of ethene in the atmosphere. *Environ. Sci. Technol.* **2005**, *39*, 4581–4585.
- (8) Mellqvist, J.; Samuelsson, J.; Rivera, C.; Lefer, B.; Patel, M. Measurements of industrial emissions of VOCs, NH₃, NO₂ and SO₂ in Texas using the solar occultation flux method and mobile DOAS Eos Trans. AGU 2007, *88*, 52, Fall Meet. Suppl., Abstract A131-05.
- (9) Brewer, R. J.; Bruce, C. W.; Mater, J. L. Optoacoustic spectroscopy of C₂H₄ at the 9- and 10-μm C12O₂16 laser wavelengths. *Appl. Opt.* **1982**, *21*, 4092–4100.
- (10) Schauffler, S. M. Distributions of brominated organic compounds in the troposphere and lower stratosphere. *J. Geophys. Res.-Atmos.* **1999**, *104*, 21513–21536.
- (11) Holloway, J. S. Airborne intercomparison of vacuum ultraviolet fluorescence and tunable diode laser absorption measurements of tropospheric carbon monoxide. *J. Geophys. Res., [Atmos.]* **2000**, *105*, 24251–24261.
- (12) Weibring, P.; Richter, D.; Walega, J. G.; Fried, A. First demonstration of a high performance difference frequency spectrometer on airborne platforms. *Opt. Express* **2007**, *15*, 13476–13495.
- (13) Warneke, C. Determination of urban volatile organic compound emission ratios and comparison with an emissions database. *J. Geophys. Res.-Atmos.* **2007**, *112*, D10S47, DOI: 10.1029/2006JD007930.
- (14) Baker, A. K. Measurements of nonmethane hydrocarbons in 28 United States cities. *Atmos. Environ.* **2008**, *42*, 170–182.
- (15) White, W. H. Formation and transport of secondary air pollutants: ozone and aerosols in the St. Louis urban plume. *Science* **1976**, *194*, 187–189.
- (16) Atkinson, R.; Arey, J. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* **2003**, *103*, 4605–4638.
- (17) Webster, M. The effect of variability in industrial emissions on ozone formation in Houston, Texas. *Atmos. Environ.* **2007**, *41*, 9580–9593.

ES802701A