Quantification of Ethylene Emissions from Petrochemical Industries in Houston, Texas: Large Disagreements with Emission Inventories

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ABSTRACT

Reactive alkenes from petrochemical industries are known to play an important role in the formation of ozone in Houston, Texas. In this work we developed a fast-response detector of ethylene based on laser photo-acoustic spectroscopy (LPAS) and used it onboard the NOAA WP-3D aircraft to measure ethylene in industrial plumes around Houston in the summer of 2006. The new LPAS instrument was evaluated by comparison with measurement results from a whole air sampler (WAS), and the two measurements agreed within the combined measurement uncertainties. Emission fluxes of ethylene were estimated (1) by integrating the measured ethylene concentration across the width of industrial plumes, (2) by multiplying the concentration with the orthogonal wind speed measured from the aircraft, and (3) by assuming that the emissions are homogeneously distributed across the height of the boundary layer as estimated using aircraft ascents and descents. The estimated ethylene fluxes were compared with the results of simultaneous Solar Occultation Flux (SOF) measurements inside a mobile laboratory, and the agreement was within a factor of 2. Previous work had indicated that current inventories underestimate alkene emissions in Houston by 1-2 orders of magnitude. These findings were confirmed both by the aircraft and SOF measurements. The measured mixing ratios of ethylene were compared between the results from 2006 and an earlier mission in 2000. In contrast with CO and acetylene, which are predominantly from traffic, ethylene and its photoproduct formaldehyde showed significant decreases between 2000 and 2006.

INTRODUCTION

During the Texas Air Quality Study in 2000, industrial emissions of ethylene (C_2H_4) were found to be 1-2 orders of magnitude larger than emission inventories indicated[1]. In addition, ethylene and propylene were identified as key precursors for rapid ozone formation in industrial plumes in the Houston area[2]. In 2006, the 2nd Texas Air Quality Study (TexAQS II) took place, in which NOAA participated with both the WP-3D research aircraft and the research vessel Ronald H. Brown.

In order to improve the spatial resolution of the ethylene measurements, a new ethylene sensor based on laser photo-acoustic spectroscopy (LPAS)[3] was used onboard the NOAA WP-3D aircraft. In this study, the airborne operation of the new sensor is briefly described and its performance evaluated by comparison with measurements from a Whole Air Sampler (WAS). The fast-response measurements of ethylene are used to locate and quantify the sources of ethylene in the Houston area. Finally, the measurements of ethylene between 2000 and 2006 are compared.

BODY

Ethylene Measurements by Laser Photo-Acoustic Spectroscopy

Airborne measurements of ethylene were made using a laser photo-acoustic spectroscopy (LPAS) instrument (Sensor Sense, Nijmegen, the Netherlands). In the LPAS, a 1-Watt tunable CO_2 laser is used to excite trace amounts of ethylene in a photo-acoustic resonator. The laser is tuned to one of the main absorption features in the ethylene spectrum around 10 μm using the photo-acoustic signal from a reference cell filled with ethylene at a high mixing ratio (~100 ppmv). In the photo-acoustic cell, ethylene is excited by the laser light. The 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 resonator around 1600 Hz. The modulated output signal from the photo-acoustic cell is detected using a microphone and amplified with a lock-in amplifier. Inside the aircraft, the LPAS instrument was hooked up to an inlet system that provided the instrument with a constant flow and pressure across all flight altitudes. In addition, the inlet system allowed the background of the instrument to be determined, i.e. the instrument response in the absence of ethylene, by flowing the ambient air through a Platinum catalyst. In-flight calibrations were made by adding a small flow of calibration gas to the inlet.

Figure 1: Portion of measured ethylene data from a nighttime flight on October 8, 2006. The shaded areas indicate the periods when calibration and background measurements were performed. Results from the WAS measurements are given by the open circles.
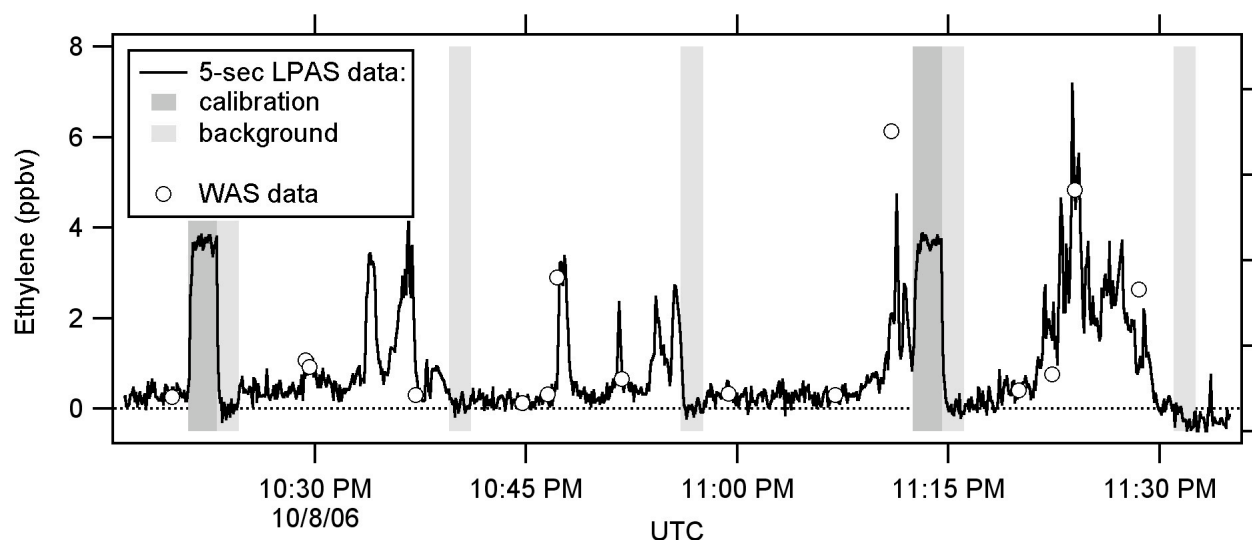

Figure 1 shows a portion of LPAS data and is used to illustrate the airborne operation of the instrument during TexAQS II. The results were obtained during a nighttime flight, when more sustained periods of elevated ethylene were encountered due to the slower chemical removal. The shaded regions in Figure 1 indicate the periods with calibration and background measurements. Background

measurements were performed every 15 min. The LPAS signal in the absence of ethylene was typically slightly negative, depending on the temperature of the instrument; the data in Figure 1 have been corrected for this offset. The data are overlaid with the results of the Whole Air Sampler (WAS) measurements, which consist of canister sampling and post-flight analysis by GC-MS. It is seen that the two measurements agree well. A comparison of all flights showed that the LPAS and WAS measurements generally agreed within 15%, and that the detection limit of the LPAS instrument varied between 200 and 700 pptv.

As an example of the aircraft measurements, Figure 2 shows the results from a research flight on September 26, 2006, when the NOAA WP-3D research aircraft flew downwind from Houston and from petrochemical sources near the Houston Ship Channel and in the Beaumont area, and then followed those plumes downwind. It is easily seen that the highest enhancements of ethylene emerge from sources near the Houston Ship Channel and Beaumont areas. The enhancements of ethylene downwind from Houston are relatively minor. Also shown in Figure 2 are the locations of industrial point sources according to the 2004 point source database of the Texas Commission on Environmental Quality (TCEQ). The sizes of the symbols are proportional to the emission source in the point source database; however, the ethylene observed in the plumes was not obviously correlated with the estimated emissions.

Figure 2: Flight track of the NOAA WP-3D research aircraft on September 26, 2006. The parts of the flight below 1000 m altitude are color-coded by the ethylene measured by LPAS.
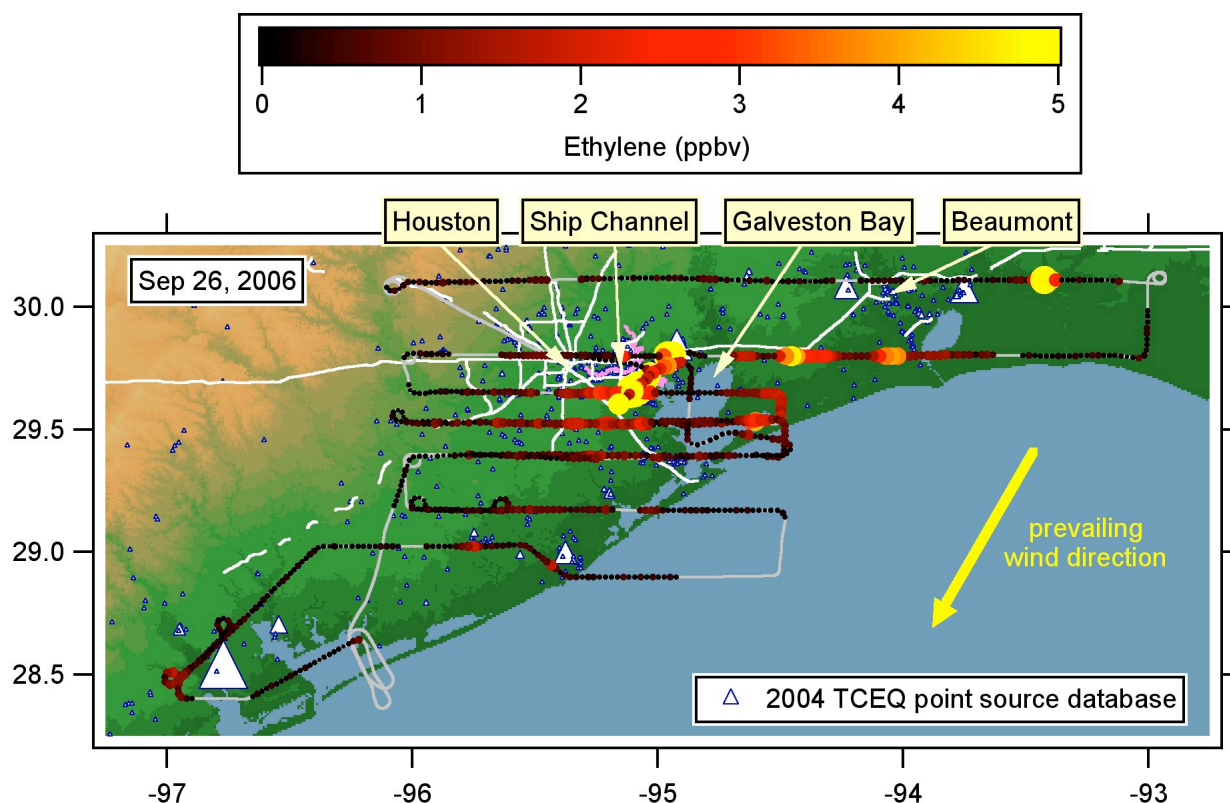

Figure 3 shows a scatter plot of ethylene versus CO for the flight on September 26, i.e. the same data as in Figure 2. The data from Houston are overlaid with data from a flight over Los Angeles (black triangles) performed with the NOAA WP-3D in 2002 as part of the ITCT 2k2 study. It is clear that the data from Houston and Los Angeles are significantly different. In Los Angeles, where most VOCs are dominated by emissions from vehicles, ethylene and CO were well correlated. The ratio of ethylene

relative to CO in Los Angeles, defined by the slope of the best fit through the data, agrees well with the emission ratio determined for the northeastern U.S.[4] (red, dotted line) and with enhancement ratios averaged for 28 U.S. cities[5] (red, solid line). In contrast, ethylene and CO in Houston were poorly correlated and the highest ethylene mixing ratios were observed at modest enhancements in CO. We conclude from the data in Figures 2 and 3 that the emissions of ethylene in Houston were dominated by those from industrial sources.

Figure 3: Scatter plot of ethylene versus CO for the flight on September 26, 2006. Data from the LPAS and WAS for this flight are overlaid with earlier data obtained during a research flight over Los Angeles and from 2 recent summaries in the literature.
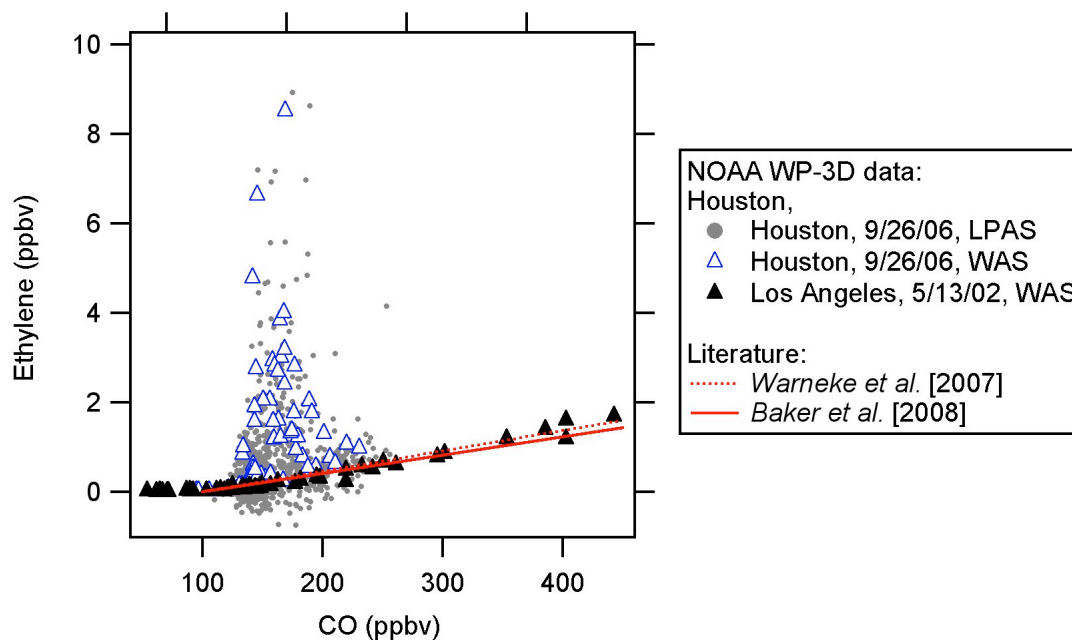
Emission fluxes of ethylene from petrochemical point sources in the greater Houston area were estimated using the airborne data just downwind from industrial point sources, where the source of the emissions is unambiguous. By assuming that the plume is uniformly mixed across the BL height h, the flux can be estimated using:

$$\text{Equation (1)} \quad Flux = h \times \int_t \Delta[ethylene] \times v \times w \times \sin(\alpha) \times dt \ ,$$

where v is the aircraft velocity, w the wind velocity and α the angle between the flight and wind direction. The parameter $\Delta[ethylene]$ is the enhancement in the number density of ethylene over the background, i.e. the number density in the plume minus the background outside the plume. We estimate the uncertainty in the flux estimate according to Equation (1) to be a factor of 2. The largest uncertainty is due to the assumption that the plume is uniformly mixed across the height h of the boundary layer. Other uncertainties that were investigated include the height of the boundary layer and chemical removal of ethylene in between of emissions and sampling by the aircraft.

Ethylene fluxes from the Mont Belvieu chemical complex to the northeast of the Houston Ship Channel were estimated from the results of 10 different flights. The average flux was 520 kg h^{-1} and the standard deviation in this average was 140 kg h^{-1}. This variability of ~30% is smaller than a factor of 2, which we had estimated to be the uncertainty in flux estimates of this kind. The estimated emission flux of 520±140 kg h^{-1} agrees within the combined uncertainties with the average from 3 days of

measurements near Mont Belvieu, 400±40 kg h^{-1}, made using the Solar Occultation Flux method by Chalmers University from Gothenburg, Sweden. Both the aircraft and SOF results are much higher than the combined ethylene flux for the Mont Belvieu chemical complex in the 2004 TCEQ point source database, which sums up to 29 kg h^{-1}. This underestimate of the measured flux in the emission inventory by a factor of 12-23 is consistent with the findings from TexAQS 2000[1]. More details on our flux estimates will be published elsewhere.

We compared our observations of ethylene between 2000 and 2006 from TexAQS I and II. Figure 4B shows cumulative probability diagrams for the airborne ethylene measurements in 2000 and 2006. To make the comparison fair, only data are used that were collected inside the box around Houston and the Ship Channel, shown in Figure 4A, and below 1000 m altitude. The cumulative probability diagram shows the fraction of data with an ethylene mixing ratio below a certain value; these diagrams allow systematic differences between data sets to be seen more clearly than regular distribution plots. Two observations are made from Figure 4B. First, the median ethylene mixing ratio from the LPAS in 2006 was 33% lower than from the WAS measurements. The explanation is that there was a slight tendency to sample WAS canisters inside plumes. Second, the WAS measurements in 2006 were 42% lower than in 2000. We will investigate the possible reasons for this difference in the remainder of this paper.

Figure 4: Comparison between airborne measurements of ethylene in 2000 and 2006. Only data are used that are obtained below 1000 m altitude and inside a box around Houston and the Ship Channel shown in panel A. Median mixing ratios of ethylene are shown in the legend in panel B.
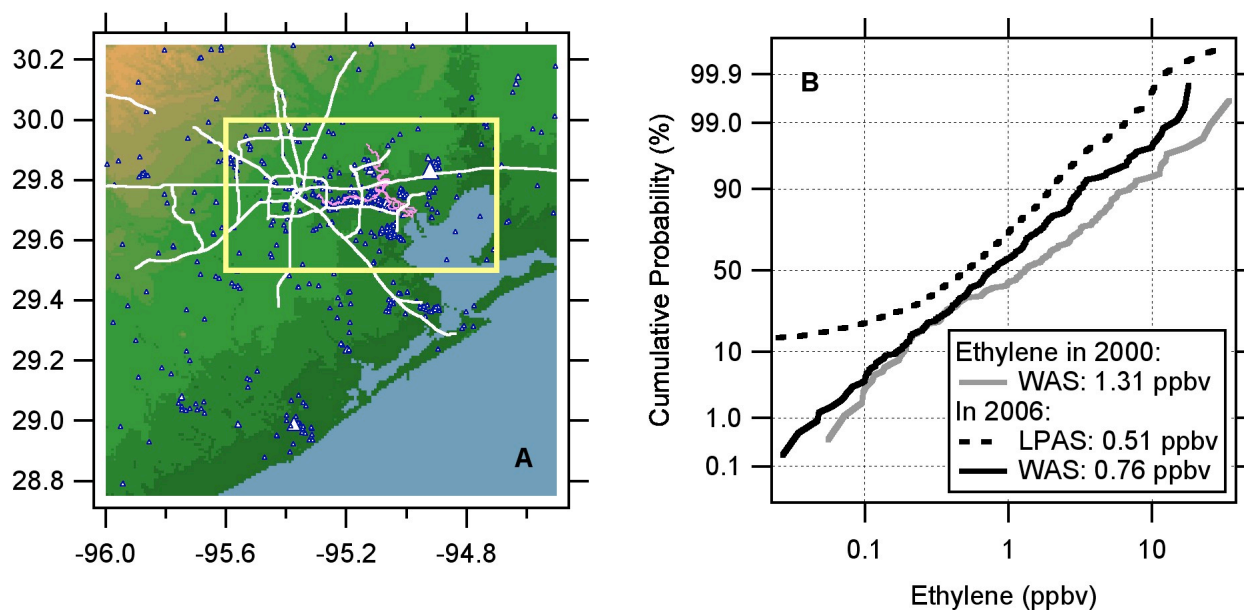
The lower ethylene in 2006 with respect with 2000 may have been caused by a difference in meteorology or a reduction in emissions. The median wind speed was 39% higher during research flights in 2006 and the median temperature almost 5 °C lower. The higher wind speeds in 2006 imply that ethylene emissions were more efficiently diluted in the ambient atmosphere, which is consistent with the observed reduction in ethylene. The lower temperatures in 2006, however, would likely be accompanied by lower boundary layer heights, which would lead to an increase in ethylene as the emissions are mixed into a shallower layer. Clearly, the meteorology in 2006 was very different from 2000 making it very difficult to conclude that ethylene reductions in 2006 were due to lower emissions.

We have also studied trends in other trace gases. The idea is that if all trace gases were reduced by the same fraction, then it is more likely that the differences between 2000 and 2006 were caused by differences in meteorology. If, on the other hand, ethylene was reduced more than some other species, then it is more likely that the differences between 2000 and 2006 were caused by differences in emissions. Figure 5 shows the result of this analysis. The largest reductions between 2000 and 2006 were observed for ethylene and its photoproduct formaldehyde (HCHO), which was measured by laser absorption onboard the NOAA WP-3D aircraft[6]. Reductions were also observed for NOy, which may have been caused by documented reductions in NOx emissions from power pants in Texas. A small reduction between 2000 and 2006 was observed for CO, as expected because the mobile source of CO has continued to decease[7]. No reduction was observed for acetylene and a small increase was observed for SO$_2$. We conclude that the reductions in ethylene between 2000 and 2006 were more likely caused by a reduction in the emissions than by a change in meteorology.

Figure 5: Relative differences between the medians in airborne measurements of several trace gases in 2000 and 2006.
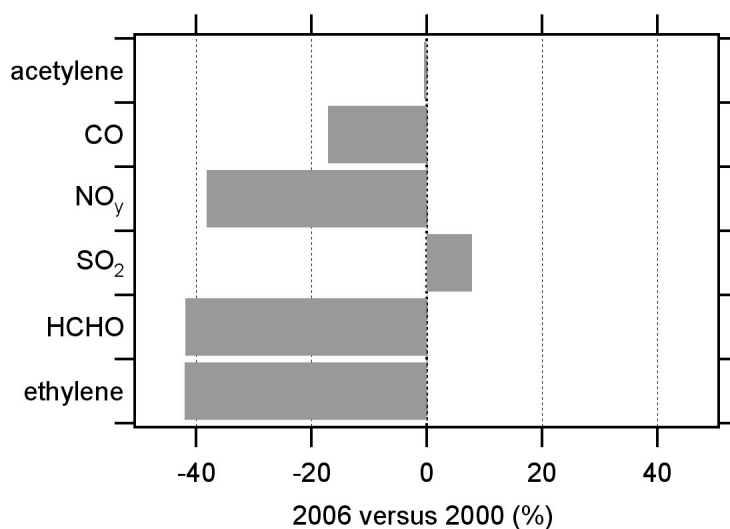
CONCLUSIONS

Ethylene from industrial point sources in the Houston area was measured from the NOAA WP-3D research aircraft using a new method based on laser photo-acoustic spectroscopy (LPAS). The new method was validated by comparison with Whole Air Sampler (WAS) data based on canister sampling and post-flight analysis by GC-MS. Aircraft measurements using LPAS were used to locate and quantify the industrial point sources of ethylene in Houston and the Ship Channel. Emissions from the Mont Belvieu chemical complex were estimated and in agreement with measurements obtained with the Solar Occultation Flux (SOF) technique. Both measurements are 13-23 times higher than the 2004 point source database developed by the Texas Commission on Environmental Quality (TCEQ). This severe underestimate in emissions inventories of the reactive alkene emissions from industrial sources is in agreement with conclusions from an earlier study in Houston. Ethylene mixing ratios in 2006 were 42% lower than in 2000. The weight of evidence suggests that emissions reductions rather than a difference in meteorology caused this decrease.

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KEY WORDS