Measurements of Formaldehyde Fluxes in Houston, Texas

Tracy Yelden¹, George Mount², Elena Spinei²

1. Department of Physics, Central College
2. Dept. of Laboratory for Atmospheric Research, Washington State University

Introduction:

Formaldehyde (HCHO) is a chemical compound that has adverse effects on human health and can increase urban ozone levels significantly. Ozone is regulated by the US EPA; the Houston area is often in violation of those standards. Sources of formaldehyde include direct emissions from vehicles, emissions from petrochemical plants, and photochemical production. As part of the Study of Houston Area Radical Species (SHARP) campaign organized by the Houston Advanced Research Consortium (HARC), Washington State University (WSU) and University of California – Los Angeles (UCLA) worked together to collect formaldehyde flux data in Texas City near three oil refineries processing approximately one million barrels of oil per day. The measurements were collected from April 15 - May 31, 2009.

Objectives:

• To determine the HCHO fluxes in Texas City from industrial sources
• To understand the production of HCHO in the area
• To contribute to models of the effects these industrial emissions have on the formation of ozone

Field Methods:

The UCLA site was located upwind and south of the plants; WSU was on the north end and downwind

• Each site had a multi-axis differential absorption spectrometer (MAX-DOAS)
  - Used scattered sunlight as a light source to measure the UV spectrum and deduce the slant column density of HCHO
  - Determined slant column densities [molecules/cm^2] as a function of time at various elevation angles in east and west directions
  - Each instrument scanned the sky at the same angle and similar time approximately perpendicular to the mean wind direction.

MAX-DOAS Schematic

• Formulate box model equation:
  Assumptions that contribute to errors:
  - Uniform emissions from the refineries
  - Test site was approximately 5 km x 2 km
  - HCHO is uniformly mixed vertically
  - No aerosol loading; however, aerosol loading was very large most of the time
  - Planetary Boundary Layer height (PBL) = 700m
  - From LIDAR boundary layer measurements

Box Model equation used:

\[ \text{Flux} = \frac{\text{ASCD(W)}}{d} \times \frac{1}{1} \times 10^3 \times \text{mol}\text{molecule}^{-1} \times \frac{10^-16 \times \text{mol}}{1000 \times \text{kg}} \times \frac{1000 \times \text{kg}}{10^{-6} \text{metric tons}} \times \frac{1}{\text{day}} \]

• Determined average fluxes east and west of the test site

Analysis:

• Compared UCLA and WSU raw data (e.g. 8° elevation)

Graph 1: UCLA and WSU raw data vs. time at 8° elevation angle

• Found differences in HCHO slant column density (downwind minus upwind)

Graph 2: UCLA and WSU’s data with the difference vs. time at 8° elevation

• Used wind speed and direction data for each observed angle to compute fluxes in a box model

Graph 3: Wind speed and direction vs. time

Results:

The above graphs show the fluxes for VZA 75-85°. From these graphs, we can see that the fluxes cluster around two metric tons per day.

Graph 4: Flux vs. time at angles 5-15° elevation (viewing west)
Graph 5: Flux vs. time at angles 5-15° elevation (on May 5th)

The above graph shows the span of the fluxes at different angles. The red indicates fluxes west of the site, whereas the blue are east of the site. The average flux of HCHO is 1.8 metric ton per day (+/- 50% because of our assumptions).

Graph 6: Fluxes from VZA 70° through 85° viewing both east and west vs. time for the entire campaign
Graph 7: A randomly selected day to show the east and west fluxes vs. time

Graph 7 shows how the fluxes sometimes peak around noon local time. This might also suggest secondary formation of HCHO in the atmosphere due to photoysis.

Conclusion:

From these calculations, we determined that the three major refineries in the area produce, either directly or secondary, about 630 metric tons/year of formaldehyde. This is 15% of the total VOC emissions reported by the largest of the three refineries. Therefore, the total HCHO emissions are less than 15% of the total VOC emissions. Since formaldehyde is one contributor to the formation of ozone, this study will provide vital information to those who regulate regional air quality. Monitoring formaldehyde produced in the Houston area would be useful in understanding ozone production and improving air quality in the region.

We plan to identify and use a standardized \( I_0 \) instead of a local \( I_0 \) that was used in these preliminary results, which will likely increase these fluxes by a small amount.

Acknowledgements:

We would like to thank the Houston Advanced Research Consortium (HARC) for organizing the Study of Houston Area Radical Species (SHARP) campaign. We would also like to thank the University of California–Los Angeles (UCLA) for their help in collecting and analyzing the data.

This work was supported by the National Science Foundation’s REU program under grant number 0754990 and HARC grant H104A.