

## EXECUTIVE SUMMARY

The purpose of this HARC funded research (H74A) is to conduct ground-based measurements of volatile organic compounds (VOCs) and nitrogen species ( $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$ ) during TexAQS II - 2006. This project includes two tasks: (1) measurements of VOCs using proton transfer reaction mass spectrometry (PTR-MS) at the Aldine site and at the University of Houston Moody Tower. A commercial version of PTR-MS (Ionicon Analytik Ges.m.b.H, Innsbruck, AUSTRIA) was used for measurements of pre-selected highly reactive VOCs (HRVOCs). The species measured with PTR-MS included alkenes and aromatics (such as propene, butenes, toluene, isoprene and etc). (2) Measurements of nitrogen-containing compounds such as  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ , and  $\text{NO}_3$  were made using ion drift-chemical ionization mass spectrometry (ID-CIMS) at the University of Houston Moody Tower. The VOC measurements will help to verify and update the VOC emission inventory, and the measurements of nitrogen containing species will provide an opportunity to assess the nighttime nitrogen chemistry and its role in the  $\text{O}_3$  chemistry. The ultimate objective of the measurements is to facilitate decision-makers in the revision of the State Implementation Plans (SIPs) with up-to-date VOC emission inventory and more detailed nitrogen nighttime chemistry.

We originally proposed to measure VOCs at one level, and particulate matter at three levels from the Williams Tower. However, an agreement for space rental on the Williams Tower could not be reached. Consequently, the research plan was changed to a 3-week campaign carried out during the month of September to provide continuous observations of hydrocarbons, aerosols, and selected trace gases at the Deer Park, Aldine, and Bayland Park air monitoring stations, in collaboration with the Pacific Northwest National Laboratory (PNNL) team led by Dr. Carl Berkowitz. The scientific goals involved the characterization and aging of hydrocarbons and aerosols within the Houston Ship Channel plume, and describing these changes as the plume moves across Houston.

Our field project was divided into two parts. (1) From Aug. 17 to Sep. 9, as part of the TRAMP (TexAQS II Radical Measurement Project), both the PTR-MS and the ID-CIMS were deployed at the University of Houston Moody Tower (Lat 29.71667, Lon -95.33333, Elev 70 m) to measure VOCs,  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$ . (2) From Sept. 14 to Sept. 30, the PTR-MS was relocated to the TCEQ Aldine site (Lat 29.901111, Lon -95.32611, Elev 18 m) to participate in the Houston Triangle Project, while the ID-CIMS continued the VOC and  $\text{HNO}_3$  measurements at the Moody Tower. In addition, the PNNL team deployed an aerosol mass spectrometer (AMS) at the Aldine site from Sept. 15 to 28 to monitor aerosol chemical compositions. After the TRAMP campaign ended on Sept. 30, the PTR-MS remained at the Moody Tower from Oct. 1 to 14. Some extra VOC data were collected.

During the campaign, we detected fourteen individual or group of VOCs, including acetonitrile, propene, acetaldehyde, butenes, acetone, acetic acid, isoprene, methyl vinyl ketone (MVK) + methacrolein (MACR), methyl ethyl ketone (MEK) + methylglyoxal (MGLY), benzene, toluene, C2-benzenes, C3-benzenes, and monoterpenes. Propene and butenes were identified as the major alkene species observed during the campaign and showed influences from the Houston Ship-Channel area and its petrochemical industries. Aromatic VOCs were dominated by automobile emissions. The benzene/toluene ratio was 0.15 indicating the gasoline

benzene content has dropped significantly since TexAQS 2000 [Karl et al., 2003]. Isoprene and monoterpenes showed evidence of both biogenic and industrial sources. VOCs observed at Aldine correlated well with organic aerosol measurements, suggesting that oxygenated VOCs might participate in secondary organic aerosol formation.

The  $\text{HNO}_3$  detection limit of the ID-CIMS was 30 pptv for 10 s integration time. The  $\text{HNO}_3$  diurnal profile followed the solar cycle and the daily high mixing ratios ranged from 0.2 to 2 ppbv in the early afternoon. Occasionally, nighttime peaks were also observed, which could be originated from either  $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$  heterogeneous reactions or transported aged plumes. Preliminary analysis showed that both  $\text{O}_3$  and  $\text{HNO}_3$  time series had similar trends and followed each other very well, consistent with the production mechanism of  $\text{HNO}_3$  during the daytime.