

## EXECUTIVE SUMMARY

In summer 2005, Texas Environmental Research Consortium (TERC) supported the Southeast Texas Transport Study (SETTS) in which an improved quasi-Lagrangian aircraft sampling strategy, aided by the newly developed Controllable Meteorological (CMET) balloons, was used to characterize the overnight transport and transformation of the Houston urban/industrial plume as it moved across the state. Three episodic missions, each consisting of one to two CMET balloon launches and three aircraft flights, were made between July 21 and 27, 2005. The CMET balloon launches were made just north of Houston around sunset, under southerly wind conditions, with the result that the Houston plume in each episode was unambiguously tagged and tracked for 200 to 300 km over 8 to 10 hours into north Texas. On nights when two balloons were simultaneously released, one was programmed to make repeated soundings of in situ temperature, moisture, and pressure, while the other, also measuring state variables, was flown in constant-altitude mode set to approximately two-thirds the boundary layer height. Despite the differences in their flight modes, both balloons were typically within 5-10 miles of each other even after ~10 hours of flight, which implies that the balloons successfully served as unique Lagrangian tracers of the Houston urban/industrial plume as it was advected overnight in the residual layer. The leased Twin Otter aircraft used in this campaign was outfitted to measure CO, O<sub>3</sub>, NO<sub>x</sub>, NO<sub>y</sub>, hydrocarbons, aerosol size distribution (0.1-0.4 μm), light scattering at three wavelengths, temperature, pressure, relative humidity, and wind velocity.

This project was focused on the analysis of the SETTS campaign data to address two overarching science questions:

- 1) What is the fate of the Houston urban/industrial pollution plume overnight? Does it completely dilute and blend into the background air or does it remain fairly concentrated during its nocturnal transport?
- 2) How efficiently is NO<sub>x</sub> converted to HNO<sub>3</sub> and stable organic nitrates in the Houston plume at night?

These issues are of great consequence for evaluating and improving air quality models used to simulate the transport and transformation of ozone precursors for the State Implementation Plan (SIP). The overall rate and efficiency with which NO<sub>x</sub> is converted to HNO<sub>3</sub> and stable organic nitrates at night is of great interest because the residual NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> at dawn can photolyze or dissociate back to NO<sub>x</sub> and subsequently produce O<sub>3</sub> in the presence of volatile organic compounds at a downwind location. At the same time, it is important to determine whether the Houston plume remains concentrated or not in the vertically stratified residual layer where sustained NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> related chemistry can occur for several hours at night before the plume is diluted with the background air due to turbulent mixing the following morning.

Analysis of the CMET balloon data showed that the Houston plume experienced appreciable shearing due to the development of the low-altitude nocturnal jet. However, aircraft measurements indicated that pollutant concentrations in the plume remained relatively undiluted even after 8-10 hours of overnight transport due to the lack of turbulent mixing in the residual layer. PTR-MS measurements revealed the presence of high concentrations of olefins (propene, butenes, and pentenes) and acetaldehyde, which were likely of industrial origin. Analysis of aircraft data also yielded evidence for significant conversion of NO<sub>x</sub> to semi-volatile NO<sub>z</sub> species (i.e., gas-phase HNO<sub>3</sub> + particulate inorganic nitrate + particulate organic nitrate) in the plume over this period.

A constrained plume modeling (CPM) analysis of the quasi-Lagrangian aircraft observations was performed using the comprehensive gas-aerosol chemistry box-model MOSAIC (Model for Simulating Aerosol Interactions and Chemistry). A series of sensitivity simulations showed that  $\text{NO}_x$  was likely converted to roughly equal amounts of  $\text{HNO}_3$  and semi-volatile organic nitrates via  $\text{O}_3 + \text{NO}_2$  reaction followed by reactions of olefins and acetaldehyde with  $\text{NO}_3$  and the ensuing chemistry important at night. The semi-volatile organic nitrates have the potential to significantly contribute to secondary organic aerosol mass in such concentrated petrochemical industrial plumes as they are transported overnight. The predicted PAN mixing ratios increased a little or remain unchanged from their assumed levels at the time of sunset. Thus, although relatively less  $\text{NO}_x$  would be available in the plume the following morning than in the absence of olefins, the residual PAN could decompose and serve as a source of  $\text{NO}_x$  to form additional ozone the next morning, especially in the presence of substantial quantities of olefins, aldehydes, and other VOCs which would still be present in the plume.

The overnight transport of concentrated and aged urban/industrial plumes containing substantial amounts of reactive hydrocarbons and PAN could potentially affect the air quality of regions several hundred kilometers downwind the next day. Further field measurements and modeling studies to investigate aerosol evolution and evaluate the overall impact of Houston urban and petrochemical industrial plumes on regional air quality and downwind urban centers should be of considerable future interest.