Vertical Profiles of O_3, NO_2, SO_2, HCHO, HONO, and NO_3 in Houston

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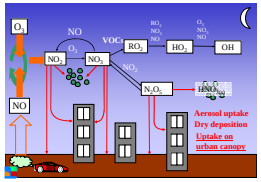
Introduction

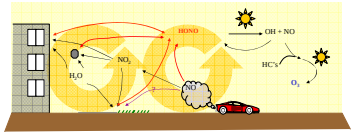
Nocturnal chemistry plays an important role in the urban boundary layer [1, 2, 3]:

- Fresh emissions of NO convert ozone to NO_2 .
- Pollutants emitted near the ground, such as CO and possibly HCHO, accumulate in the nocturnal boundary layer (NBL).
- N_2O_5 uptake on aerosol can lead to a loss of NO_x and the formation of aerosol nitrate.
- NO_3 and N_2O_5 chemistry, together with dry deposition, remove ozone at night .



In addition, radical species and radical precursors can be formed [2, 4] :

- Reaction of ozone with alkenes forms OH radicals.
- NO_3 oxidizes hydrocarbons and leads to the formation of HO_2 and RO_2.
- The mixing of freshly emitted NO at the ground with RO_2 formed aloft can lead to an active OH/HO_2 radical chemistry [3].
- HONO, an OH precursor during the day, can be formed through the reaction of NO_2 on surfaces or direct emissions



Due to weak vertical transport and mixing at night, atmospheric chemistry is highly altitude dependent [1, 2, 3]. To study chemistry in the urban NBL vertical profiles of the most important trace gases need to be measured. Here we present preliminary long-path DOAS measurements of O_3, NO_2, SO_2, HCHO, HONO, and NO_3 in two / three altitude intervals in Houston, TX, during the TRAMP experiment.

References

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5.) Alicke, B., U. Platt, and J. Stutz, Impact of nitrous acid photolysis on the total hydroxyl radical budget during the Limitation of Oxidant Production/Pianura Padana Produzione di Ozono study in Milan, *J. Geophys. Res., 107*, 10.1029/2001JD000075, 2002.

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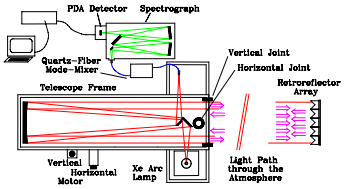
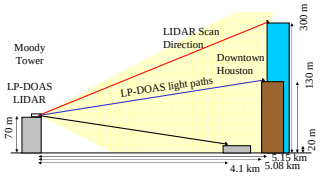
Experimental

All trace gases were measured by long-path Differential Optical Absorption Spectroscopy (LP-DOAS). The instrument (see figures below) consists of a double coaxial Newtonian telescope, which is used to send collimated light from a Xe-arc lamp onto an array of quartz corner cube retroreflectors. The light returning from the retroreflectors is collected by the telescope and analyzed using the DOAS technique. The LP-DOAS telescope was set up at the Moody tower site at the University of Houston ~70m above ground level.
To measure the vertical distribution of trace gases two/three retroreflector arrays (the third array was only installed on Aug 31, 2006) were mounted at different altitudes on buildings in downtown Houston (see figures below). Three altitude intervals can be derived from the data 20-70m, 70-130m, 130-300m. Please note that the data shown here is still path integrated. The upper light-path data covers the interval from 70 – 300m.

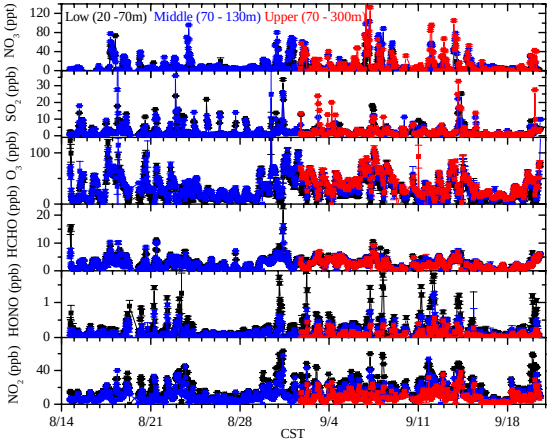


The UCLA LP-DOAS system

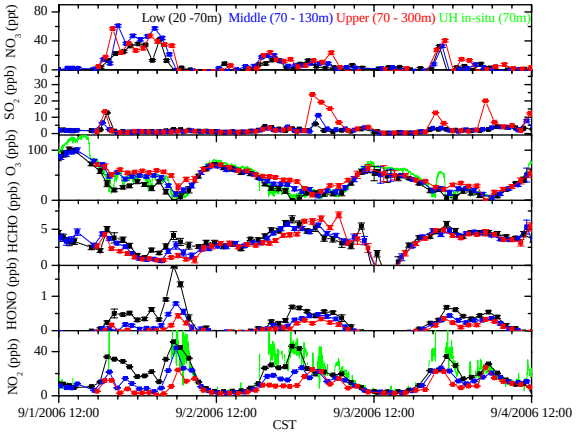


Light path arrangement of the DOAS system during TRAMP. Color codes for the individual light paths are also used in the following graphs.

Overview of Preliminary Data



Discussion of Preliminary Results for Three Days



- Comparison between LP-DOAS and Moody Tower in-situ O_3 and NO_2 data (courtesy of B. Lefer and J. Flynn, UH) shows generally good agreement during the day. At night Moody tower in-situ observations often fall between the lower and middle light-path DOAS mixing ratios.
- Every night ozone is lower near the ground and higher aloft, while NO_2 shows the opposite gradient. The sum of O_3 + NO_2 (not shown) has a much smaller and often negligible gradient.
- HCHO shows higher values near the ground during most nights.
- HONO shows higher values near the ground, reaching mixing ratios of up to 2 ppb.
- NO_3 mixing ratios up to 60 ppt were observed. Vertical gradients are not very pronounced.
- Plumes of SO_2, with mixing ratios above 15 ppb aloft, were observed on 9/3/06 04:00, 9/3/06 21:20, and 9/4/06 05:00. SO_2 plumes were also observed during many other occasions.
- During the SO_2 plume at 9/3/06 4:00, a reversal of the HCHO profile, i.e. higher HCHO aloft, was observed. HCHO plumes correlated with SO_2 plumes were also observed during other times (not shown)

Conclusions and Outlook

- NO emission together with slow vertical mixing leads to a depletion of ozone near the ground due to the NO + O_3 → NO_2 + O_2 reaction. How the extent of this vertical distribution depends on vertical stability and NO emissions will be investigated with a 1D chemical transport model in the future.
- The observed high levels of NO_3 lead to an active radical chemistry at night, which will be investigated in future model studies. Model calculations of the NO_2 - NO_3 - N_2O_5 system will also reveal how important this chemistry is for the NO_x budget in Houston.
- The nocturnal vertical profiles of HCHO point to a surface source of HCHO, which is most likely traffic. The observed plumes of HCHO also show that industrial HCHO point sources seem to influence the Houston area.
- High HONO levels will influence the morning radical budget. Quantification of this source will be achieved by combining our observations with those of other TRAMP participants.
- SO_2 and HCHO plumes will be analyzed by comparing them with aerosol LIDAR data also collected at Moody tower (C. Flynn, PNNL).