4.1 INFLUENCE OF VERTICAL MIXING ON NOCTURNAL CHEMISTRY IN THE URBAN BOUNDARY LAYER

Jochen Stutz[*], Andreas Geyer, and Shuhui Wang
Department of Atmospheric Sciences, University of California Los Angeles

Abstract

Nocturnal chemistry in urban areas can considerably influence the composition of the boundary layer (BL) and therefore determine the conditions at sunrise. Since the trace gas levels in the morning BL influence the photochemistry of the day it is crucial to understand the nocturnal processes. Studying the chemical composition of the nocturnal BL is difficult because of the interplay of homogeneous and heterogeneous chemical processes and weak turbulent mixing. This interaction together with direct emissions of NO and hydrocarbons at the ground can lead to strong vertical gradients of all compounds. This is particularly significant for the chemistry of the main oxidants ozone, and NO_3, which are responsible for the removal of NO_x and various VOC's. It also plays an important role in the formation of daytime OH precursors such as nitrous acid.

Here we present data from a number of recent field studies (SOS 1999, Nashville, TN; TEXAQS 2000, Houston, TX; Phoenix 2001, AZ; etc.) showing the vertical distribution of various trace gases measured by differential optical absorption spectroscopy (DOAS). The measurements show vertical gradients of ozone, NO_2, NO_3, and HONO during many nights. A comparison of the results of the individual campaigns and the results from a one-dimensional chemical box model allows us to compose a picture of the chemistry in the nocturnal boundary layer. Common features are elevated HONO levels at the ground, and high NO_3 levels aloft. Our measurements also allow us to determine the significance of processes such as NO_x and VOC removal, as well as the investigation of several heterogeneous reactions. The implications of our findings for air quality monitoring and the photochemistry of the following day will also be discussed.

1. INTRODUCTION

It has been recognized in recent years that chemical processes in the nocturnal urban and sub-urban boundary layer can considerably impact the composition of the atmosphere and therefore influence the starting conditions for photochemical smog formation during the next morning (see for example [*Bey et al.*, 1997; *Geyer et al.*, 2001; *Platt and Heintz*, 1994; *Wayne et al.*,

Corresponding author address: Jochen Stutz, University of California Los Angeles, Dept. of Atmospheric Sciences, 7127 Math Sciences Bldg., Los Angeles, CA 90095-1565;
Email: jochen@atmos.ucla.edu

1991]). Examples of such nocturnal processes are the removal of NO_x and VOCs by NO_3 and the build-up of HONO which serves as a OH precursor after sunrise.

Many investigations of nocturnal chemistry have relied on a 0-dimensional box model approach. While this approach has been used successfully in the well mixed daytime boundary layer, it can be inaccurate at night for the following reasons:

- Vertical mixing is slower than during the day. Therefore gradients of trace gases are more pronounced at night.
- The vertical mixing of direct emissions, for example of NO and VOCs, is slower than their chemical conversion in the NBL. Their concentrations therefore remain elevated close to the ground.
- Radical chemistry is slower and less efficient since OH concentrations are small. The nitrate radical, which takes over the role as dominant radical species at night, only reacts with unsaturated hydrocarbons, in particular with terpenes.
- Heterogeneous reactions appear to play a more important role, for example the formation of HONO and the uptake of N_2O_5.
- In comparison to the day, the ground offers a much larger surface to volume ratio at night.

Based on these considerations we have adopted a 1-dimensional vertical view of the nocturnal chemistry for both our experiments (Wang et al., Poster P1.1) and our modeling efforts (Geyer et al., Poster P1.16).

In the following manuscript we will present our general findings from a number of field experiments, to give a picture of the typical vertical distribution of trace gases. A 1-dimensional vertical chemical transport model is used to interpret our observations, in particular with respect to nocturnal radical levels and the removal of NO_x.

2. Field Observations

2.1 Experimental

To study the variation of nocturnal chemistry with height we have performed a number of field experiments in recent years. All of the experiments had in common that the vertical trace gas gradients were measured by Differential Optical Absorption Spectroscopy (DOAS) [*Platt*, 1994]. Our DOAS instruments consist of a xenon arc lamp, a coaxial sending/receiving telescope, and a spectrograph-detector system. The light beam is folded once by an array of quartz corner-cube-reflectors that are typically mounted in 1 – 6 km distance.

The principle of DOAS is the identification and quantification of trace gases by their narrow band absorption structures. The absorption takes place along the light path. Therefore DOAS measures the concentration averaged over this light path. To measure vertical trace gas gradients we typically mount 2 – 3 reflector arrays at different altitudes and consecutively aim our telescope at the arrays. It is obvious that the DOAS light beam also averages in the vertical and a deconvolution of the height-integrated absorptions has to be performed (see for example Wang et al. P1.1). Typical time resolution for a gradient measurement is ~15 min.

Our field measurements took place in a variety of urban and sub-urban environments in the United States. In Nashville, TN, (SOS 99) and Houston, TX, (TEXAQS 2000) we encountered humid and hot conditions. While the SOS 99 measurements took place in a suburban environment of a city without much industry, the TEXAQS 2000 data was taken in a heavily industrialized area with large direct emissions. In contrast, the conditions during the Phoenix ozone experiment in 2001 (POE 2001) were very dry and the DOAS system was set up in the center of the city (see Wang et al, P1.1 for the POE 2001 results).
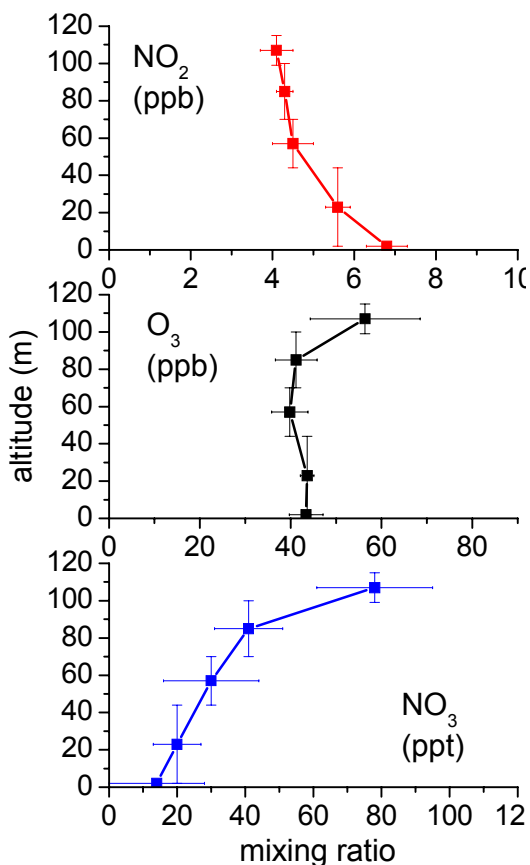

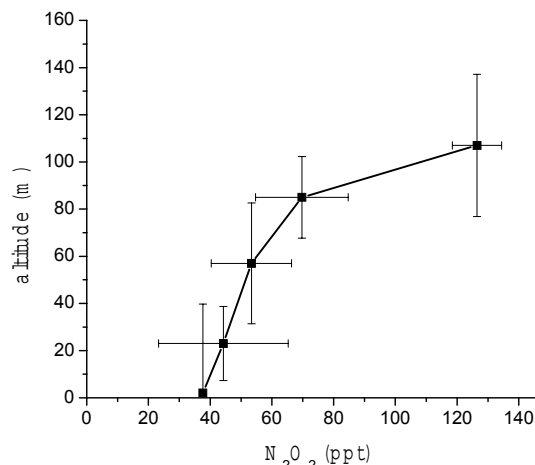Figure 1: Vertical distribution of NO_2, O_3, and NO_3 on 8/31/00 at 22:58 CST at LaPorte near Houston

Figure 2: Vertical distribution of the calculated steady state N_2O_5 mixing ratio on 8/31/00 at 22:58 CST at LaPorte.

2.2   Results

Figure 1 shows an example of the vertical distribution of O_3, NO_2, and NO_3 on Aug 31, 2254 CST in Houston. The data was taken by two DOAS instruments measuring on a total of 5 light paths. The profiles show a negative gradient of NO_2 (more NO_2 at the ground than aloft) and positive gradients of O_3 and NO_3. We have observed similar vertical distributions in all our field studies (see Wang et al, P1.1). The following summarizes the common features of our observations in urban environments:

- Ozone shows a positive gradient, while NO_2 typically shows a negative gradient.
- O_x ($NO_2 + O_3$) shows no gradient, or at least a smaller gradient than O_3 and NO_2
- NO_3 shows positive gradients.
- HONO shows negative gradients.
- HCHO shows positive gradients

In addition to our direct observations we are able to calculate the vertical distribution of the steady state N_2O_5 mixing ratio by assuming the N_2O_5 levels are dominated by the $NO_2 + NO_3 \leftrightarrow N_2O_5$ equilibrium [*Wangberg et al.*, 1997b]. Figure 2 shows the steady state N_2O_5 profile corresponding to the profiles in figure 1. It should be noted that this calculation is only an approximation of the real N_2O_5 mixing ratios since other loss processes of N_2O_5 and temperature effects were not considered here.

3.   Modeling studies

The interpretation of our observation is difficult since it requires an accurate quantification of chemistry, micrometeorology, and direct emissions.

We have therefore developed a 1-dimensional model of the nocturnal boundary layer (NBL) that is described in detail by Geyer et al. (P1.16). In short, the model subdivides the NBL into 14 boxes, with a log-
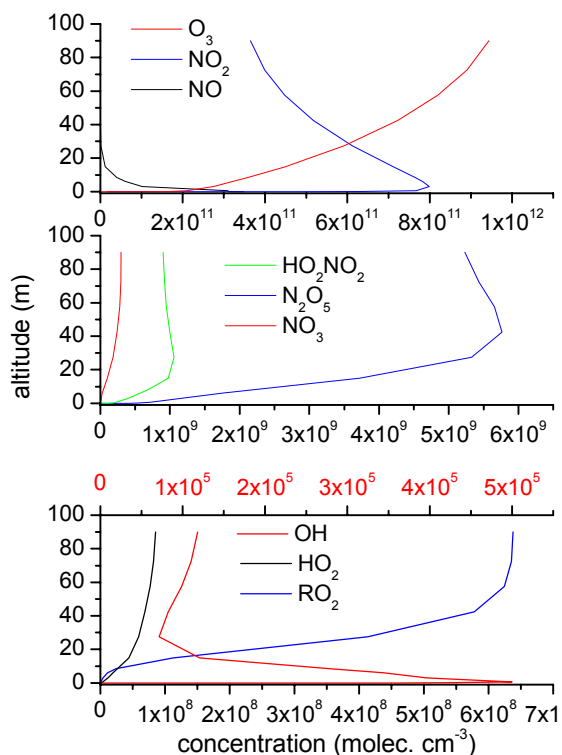
Figure 3: Modeling results after 1 hour for an urban case with an emission of NO of 5×10^{11} molec. s^{-1} at 0.5m height (details of the model are given in Geyer et al., P1.16)

linear spacing. The model contains a chemical mechanism that includes reactions of the NO_x-O_3-NO_3 system, a simplified HO_x/RO_2 reaction scheme, and a small number of VOCs and their degradation pathways representing the more complex VOC mixture found in a city. Vertical transport between the boxes is calculated based on a height dependent turbulent exchange coefficient. Direct emissions of VOCs, CO, and NO at the ground and the lower boxes are also included.

The purpose of the model is to study common features in our observations rather than to simulate the field results in detail. We are specifically interested in studying the height dependence of the removal of NO_x and VOCs, the influence of vertical transport on radical chemistry, and the interaction of NO_x with the ground and other surfaces that lead to the formation of HONO.

3.1   Results

Figure 3 shows the results of a model run after one hour. The model was initialized with a vertically uniform distribution of all trace gases, as is typically observed at the beginning of the night. We chose slightly stable conditions in the NBL, leading to a negligible temperature gradient. The values for NO and CO emissions were chosen to represent a case of an urban or sub-urban environment.

Figure 3 illustrates that the model reproduces the features we have observed in our field studies. In particular, we find a positive gradient of ozone, NO_3, and N_2O_5, while NO_2 and NO show negative gradients.

Figure 3 also shows vertical gradients of the HO_x/RO_2 radical family. While there is currently no experimental data available to verify the vertical distribution of these radicals, the OH concentrations in the lower NBL are in agreement with observations in the field. The large OH, HO_2, and RO_2 gradients are mainly caused by the elevated NO levels close to the ground, which lead to a decrease of the RO_2 lifetime and an accelerated conversion of HO_2 into OH. The latter also seems to explain the very high OH concentrations close to the ground.

3.2   Formation of HO_x radicals

The modeling results (figure 3) show the OH levels increase towards the ground, reaching levels of up to 5×10^5 molec cm^{-3}. This is at first surprising since both ozone and NO_3 levels decrease towards the ground and therefore one would expect that the HO_x formation by NO_3 + terpene reactions and the ozonolysis of VOCs become more inefficient. On the other hand, the levels of VOCs and NO increase towards the ground, which lead to an increased RO_2/HO_2 to OH conversion.

We used our model to investigate if the transport of certain species could be responsible for the radical gradients we found in our model. The most obvious species is ozone, which is continuously destroyed in the lowest region of the NBL by NO. The downward flux of ozone keeps the NO_3 concentration close to the ground elevated and forms HO_x through its reaction with VOCs.

Another trace gas effectively transported is N_2O_5. Our model indicates that due to the positive N_2O_5 gradient a net downward flux exists that leads to a net input of NO_3 following the N_2O_5 thermal decomposition. The magnitude of this effect in the urban NBL is discussed by Geyer et al. (P1.16).

Our model shows that there is a net downward flux of RO_2 radicals in the lowest 20 m of the NBL. This flux leads to the formation of HO_2 following the reaction of RO_2 with NO close to the ground.

We also found that HO_2NO_2 serves as an effective reservoir species for HO_2. The concentration peak of OH at the ground is caused by the downward transport of HO_2NO_2 followed by its thermal decomposition and the HO_2 + NO reaction.

Our model suggests that vertical transport of radicals and radical reservoir species form effective mechanisms to introduce radicals to the lower part of the NBL.

3.3 NO_x loss in the NBL

One of the most important aspects of nocturnal chemistry is the loss of NO_x through different processes. The quantification of these processes is difficult since they are altitude dependent (see figure 4). We used our model to determine the role of different NO_x loss processes:

Deposition of NO_2 is relatively unimportant in our case. It should however be noted that the model uses
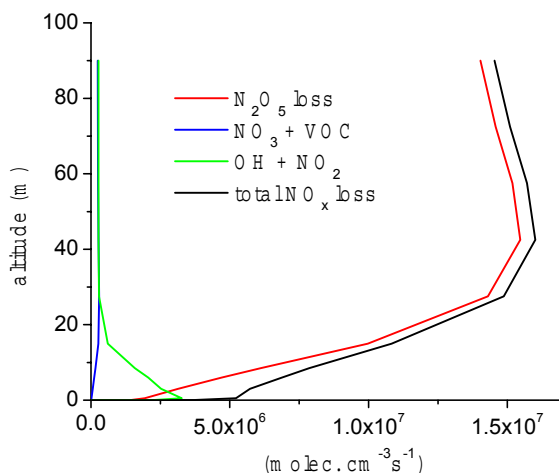
Figure 4: Modeled NO_x removal processes for an urban case (see also figure 3)

the geometrical surface of the ground and this effect is therefore underestimated.

The reactions of NO_3 radicals with VOCs lead to a removal of NO_x. Since we only included α-pinene and isoprene this pathway may also be underestimated in our calculations. One also has to consider that only a part of the nitrogen involved in the reaction is permanently removed. The oxidation of α-pinene by NO_3, for example, releases 80% of the NO_3 back into NO_2 [*Wangberg et al.*, 1997a]. To simplify our calculations we assumed that only ~30% of the NO_3 lost by VOC reactions leads to a removal of NO_x.

The $OH + NO_2$ reaction is the most important loss process during the day. It appears to be clear today that OH radicals are also present in the NBL and that this pathway can lead to a NO_x removal. Using the OH radical concentration predicted by our model, we found that this mechanism can be important in the lowest part of the atmosphere (figure 4).

The most important NO_x loss mechanism in our model is the hydrolysis of N_2O_5 (figure 4). In our model the homogeneous reaction of N_2O_5 with water was considered according to [*DeMore et al.*, 1997]. The heterogeneous uptake of N_2O_5 was determined by assuming a reactive uptake coefficient of 0.05 [*DeMore et al.*, 1997; *Sander et al.*, 2000] and a height independent aerosol surface-to volume ratio of $400\mu m^2 cm^{-3}$. Figure 4 shows that the N_2O_5 hydrolysis is by far the most important loss mechanism and that it is very height dependent. The model also clearly shows that the majority of the removal occurs above 10m height, where the NO_3 and N_2O_5 levels are higher. The total NO_x removal in the lowest 100m calculated by our model is 1.5×10^{11} molec. s^{-1}, which is equivalent to ~30% of the emitted NO_x during the night.

4. Conclusions

Both our field observations and our modeling study show that the chemistry in the NBL is strongly altitude dependent. We have shown that the removal of NO_x occurs predominately in the upper part of the NBL. This yields a picture of nocturnal NO_x chemistry, where NO emitted at the ground is mixed upwards and converted to NO_2 by its reaction with ozone. After further upwards transport it is converted into N_2O_5 and removed through hydrolysis, predominately on surfaces. Our model also shows that the concentrations as well as the chemistry of radicals change with height. We have identified a number of reservoir species that lead to a net downward transport of radicals.

It is clear from our results that a description of nocturnal chemistry omitting vertical mixing is insufficient.

5. References

Bey, I., B. Aumont, and G. Toupance, The nighttime production of OH radicals in the continental troposphere, *Geophys Res Lett*, *24* (9), 1067-1070, 1997.

DeMore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Colc, and M.J. Molina, *Chemical kinetics and photochemical data for use in stratospheric modeling*, 1997.

Geyer, A., B. Alicke, S. Konrad, T. Schmitz, J. Stutz, and U. Platt, Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin, *J Geophys Res-Atmos*, *106* (D8), 8013-8025, 2001.

Platt, U., Differential optical absorption spectroscopy (DOAS), *Chem. Anal. Series*, *127*, 27 - 83, 1994.

Platt, U., and F. Heintz, Nitrate Radicals in Tropospheric Chemistry, *Isr J Chem*, *34* (3-4), 289-300, 1994.

Sander, S.P., R.R. Friedl, W.B. DeMore, A.R. Ravishankara, D.M. Golden, C.E. Kolb, M.J. Kurylo, R.F. Hampson, R.E. Huie, M.J. Molina, and G.K. Moortgat, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Supplement to Evaluation 12: Update of Key Reactions, Evaluation Number 13, JPL, Pasadena, CA, 2000.

Wangberg, I., I. Barnes, and K.H. Becker, Product and mechanistic study of the reaction of NO3 radicals with alpha-pinene, *Environ Sci Technol*, *31* (7), 2130-2135, 1997a.

Wangberg, I., T. Etzkorn, I. Barnes, U. Platt, and K.H. Becker, Absolute determination of the temperature behavior of the $NO_2+NO_3+(M)<->N_2O_5+(M)$ equilibrium, *J Phys Chem A*, *101* (50), 9694-9698, 1997b.

Wayne, R.P., I. Barnes, P. Biggs, J.P. Burrows, C.E. Canosa-Mas, J. Hjorth, G. LeBras, G.K. Moortgat, D. Perner, G. Poulet, H. Sidebottom, The nitrate radical: Physics, chemistry, and the atmosphere, *Atmos. Environm.*, *25A*, 1-203, 1991.