P1.1

VERTICAL VARIATION OF NOCTURNAL NO_X CHEMISTRY IN THE URBAN ENVIRONMENT OF PHOENIX

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ABSTRACT

During the Phoenix Sunrise Experiment in June-July, 2001, the vertical distributions of NO_2, HONO, NO_3 and several other trace gases were measured with a long-path differential optical absorption spectroscopy system in the downtown area. Strong vertical gradients of all observed species were observed during the night, clearly showing that nocturnal chemistry in this urban environment is height dependent. The disappearance of the gradients in the morning shows the onset of vertical mixing during the transition of a stable boundary layer to a well-mixed layer. During very stable nights, when NO and VOCs emissions were trapped near the ground, mixing ratios of NO_3 up to 200 ppt were found at 110-140m above the ground. Using this information together with the measurements of NO_2, vertical profiles of N_2O_5 can be derived. In addition, the vertical distribution of HONO and NO_2 allows the investigation of heterogeneous HONO formation process on surfaces and the impact of relative humidity on this process. Clear gradients of HCHO were also observed during most nights with high vertical stabilities, suggesting important direct sources of HCHO. The observations will be compared to results from a 1D chemical box model.

1. INTROCUCTION

Nocturnal chemistry in the urban boundary layer is dominated by reactions of NO_x and their products, such as NO_3 radicals and N_2O_5. Due to the high stability of the nocturnal boundary layer (NBL), surface emissions of NO and VOCs are trapped close to the ground, leading to unique vertical profiles of various chemical species throughout the night. These profiles provide rich information about the complex interaction of chemistry and vertical transport. To study this interaction, the Phoenix Sunrise Experiment was performed in June-July, 2001, during which the vertical distributions of O_3 and nitrogen containing trace gases such as NO_2, HONO and NO_3 were measured continuously with a long-path Differential Optical Absorption Spectroscopy (DOAS) system in the downtown area. In-situ measurements of NO and meteorological parameters were also made during the same period of time. We report here the measurement results and discuss their implications for the vertical variations of nocturnal NO_x chemistry with respect to NO titration, the NO_3-N_2O_5 system, and the HONO formation.

2. OVERVIEW OF THE MEASUREMENTS

DOAS is a technique that identifies and quantifies trace gases by their distinctive UV-visible narrow band absorption structures in the open atmosphere. The main advantage of DOAS is the absolute quantification of trace species without disturbing the composition of the observed air mass. The quantification is solely based on the measured optical density and the known absorption cross section of the trace gases. In recent years we have expanded the classical long-path DOAS method to allow us to measure vertical distributions of trace gases.

During the 2001 Phoenix Sunrise Experiment, our DOAS instrument was set up on the 39th floor of the BankOne building, the highest skyscraper in downtown Phoenix. The instrument has been described elsewhere [Alicke et al., 2000] and only a short description is given here. Light from a 500W Xe-arc lamp was fed into a 1.5 m double Newtonian telescope which was used to send a highly collimated light beam onto an array of cubecorner prisms (retroreflectors) and to collect the reflected light. The retroreflectors were mounted on the roofs of three buildings at ~ 3.3 km distance (see figure 1). Since the three retroreflector arrays were located at different heights (see table 1), the average concentrations of trace gases along each light path were monitored by alternating the aiming direction of the telescope periodically. The schematic diagram of the light paths is shown in figure 1.

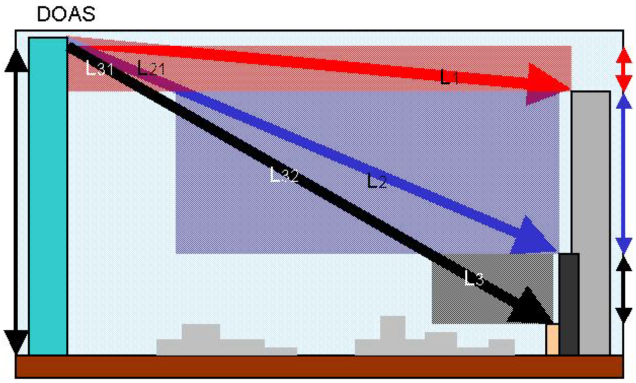

Figure 1. Schematics of the DOAS light paths and the definition of air boxes

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In order to determine vertical profiles, the mixing ratio of each species at different altitudes must be derived. For this purpose, the concept of an “air box” was introduced, as shown in figure 1. Using the following equations the average mixing ratio in each air box (C_i) was calculated from the average mixing ratio along each light path (S_i). All the parameters needed for the calculation are listed in table 1. Due to the error propagation in this calculation, the lower level has larger errors and higher detection limits (table 2).

$$C_1 = S_1$$

$$C_2 = (S_2 * L_2 + S_2 * L_{21} - C_1 * L_{21}) / L_2$$

$$C_3 = (S_3 * L_3 + S_3 * L_{31} + S_3 * L_{32} - C_1 * L_{31} - C_2 * L_{32}) / L_3$$

Building Heights		Light Path Length (km)	
DOAS setup BankOne 39th	~140m		
Upper Retro DEQ Building	~ 110m	Upper	L_1= 3.51
Middle Retro HIL Building	~45m	Middle	L_2+L_{21} =3.29
Lower Retro MLT Building	~10m	Lower	$L_{31}+L_{32}+L_3$ =3.23

Table 1. Light paths and building heights at Phoenix site

	Absorption Structure (nm)	Average Detection Limit (2σ)		
		Upper	Middle	Lower
NO_2	336~371	0.11ppb	0.18 ppb	0.65 ppb
HONO	336~371	0.04 ppb	0.07 ppb	0.25 ppb
HCHO	303~326	0.23 ppb	0.38 ppb	1.4 ppb
SO_2	303~326	0.06 ppb	0.09 ppb	0.34 ppb
O_3	303~326	1.7 ppb	2.8 ppb	10 ppb
NO_3	617~668	3.8ppt	6.5 ppt	20 ppt

Table 2. Detection limits for each measured trace gas

In order to provide detailed meteorological information of the nocturnal boundary layer during the experiment, a number of in-situ measurements of meteorological parameters were performed. Relative humidities and temperatures at different altitudes were measured on top of the DEQ, HIL and MLT buildings. Mixing ratios of NO, as well as the meteorological parameters, were measured at two different floors (16th and 39th) on the BankOne building. Balloon sounding data during most of the nights was also provided.

3. RESULTS AND DISCUSSION

3.1 Vertical Gradients of Trace Gases

In general, our measurements show strong nighttime vertical gradients of all observed trace gases during this two-week field campaign (see, for example, figure 2 and figure 3).

On very stable nights, when NO and VOCs emissions were trapped close to the ground, mixing ratios of up to 200 ppt NO_3 were found at 110-140m height while the mixing ratio in the lower box at 10-45 m level, never reached above 50 ppt.

The clear vertical gradient of HCHO up to 10 ppb/100 m during some of the nights demonstrates the importance of direct emissions from the ground. This shows that photochemical processes may not be the only important source of HCHO.

NO_2 and HONO vertical profiles suggest further investigation of the height dependence of NO_2-to-HONO conversion process.

The disappearance of gradients in the morning coincides with the onset of the vertical mixing during the transition of the stable nocturnal boundary layer to a well-mixed convective layer (figure 2).

3.2 Implications for the Vertical Variation of Nocturnal NOx Chemistry

3.2.1 NO titration

Figure 2 shows the vertical variations of NO_2 and O_3 during the night of June 28-29. In the absence of other major chemical reaction pathways of O_3 and NO_2, NO titration (reaction 1) should be the most important process in determining the gradients of both NO_2 and O_3. NO emissions originating near the ground lead to higher NO_2 and lower O_3 levels at lower altitudes compared to regions aloft. The total amount of O_x, e.g. the sum of NO_2 and O_3, should therefore have no vertical gradient if NO titration is the only major cause for the gradients. The results in figure 2 clearly show the dominant role of NO titration in nocturnal NO_x chemistry.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

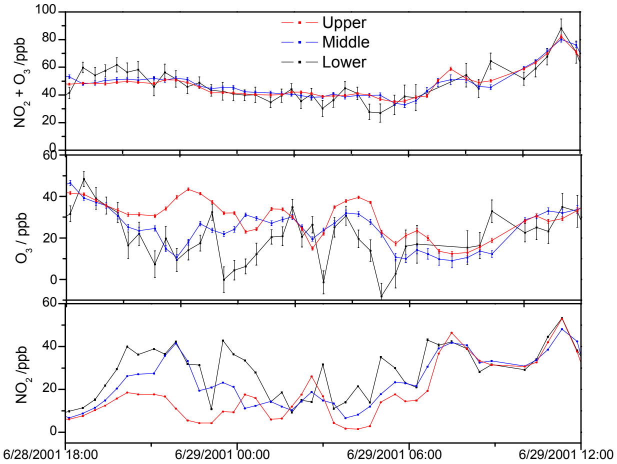

Fig 2. Vertical profiles of NO_2 and O_3 at Phoenix

3.2.2 Vertical profiles of NO_3 and its lifetime

The reaction of NO_2 with O_3 is responsible for the formation of the NO_3 radical (reaction 2), based on which the production rate and the steady state lifetime of NO_3 can be calculated as shown below:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (2)$$

$k_2=1.2\times10^{-13}e^{-2450/T}$ cm^3s^{-1} [*DeMore et al.*, 1997]

NO_3 production rate = $k_2[NO_2][O_3]$

NO_3 steady state lifetime = $[NO_3] / (k_2[NO_2][O_3])$

Figure 3 shows the height profiles of the production rate, lifetime as well as the mixing ratio of NO_3 at the night of June 28-29, 2001 in downtown Phoenix. The NO_3 production rate calculated from our NO_2 and O_3 data was higher at lower altitudes. In contrast, the NO_3 lifetime was shorter near the ground. In many cases, both of the NO_3 mixing ratio and the NO_3 lifetime were below our detection limit in the lower air box. At the upper level the NO_3 radical lifetime was on the order of a few minutes.

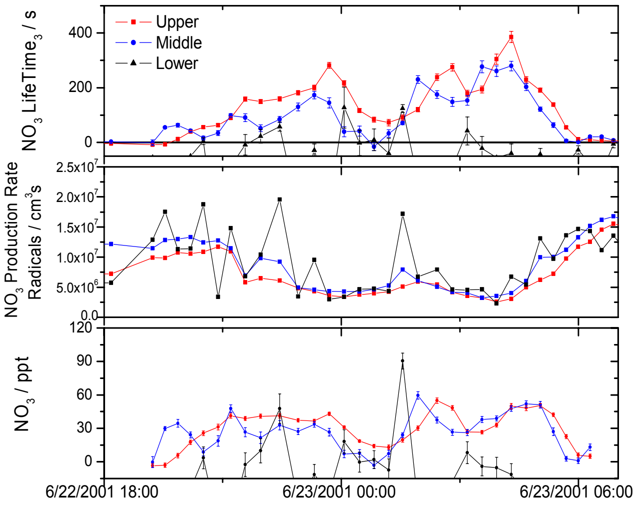

Figure 3. Vertical profiles of NO_3 mixing ratio, NO_3 production rate and NO_3 lifetime

One of the most possible reasons behind these vertical profiles is the direct loss process of NO_3 radical due to reactions with NO and VOCs (reaction 3, 4). Because of their ground based emissions and the limited vertical mixing in the nocturnal boundary layer, mixing ratios of NO and VOCs are generally higher near the ground. And thus a shorter NO_3 lifetime at lower altitude is expected.

$$NO_3 + NO \rightarrow NO_2 + NO_2 \qquad (3)$$

$$NO_3 + VOCs \rightarrow HNO_3 + Products \qquad (4)$$

The uptake of N_2O_5 on aerosols could be another important loss process of NO_3 radicals (reactions 5 followed by 6). The possible height profile of aerosol density could contribute to the gradients of NO_3 and its lifetime. In addition, temperature inversion, increasing temperature with height, could also lead to a positive gradient of NO_3 [Geyer et al., P1.16, AMS 2003].

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \qquad (5)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (6)$$

3.2.3 HONO and NO_2

Unlike NO_3 which is only produced by chemical reactions, HONO originates from both direct emissions and heterogeneous formation processes. Laboratory studies [*Kirchstetter et al.*, 1996]) show that HONO-to-NO_x ratio of motor vehicle exhaust in the United States is 0.3% on average. By subtracting the direct emissions, the corrected secondary HONO can be calculated by the following equation.

$$[HONO]_{corr} = [HONO] - 0.003 \times [NO_x]$$

It is currently believed that the major pathway of chemical HONO formation is a heterogeneous reaction mechanism involving NO_2 and H_2O. Experiments and studies show that the formation of HONO is first order in NO_2 [*Kleffmann et al.*, 1998; *Svensson et al.*, 1987]. Thus the formation rate can be described by the following equation in which S and V are the surface area and reaction camber volume respectively [Svensson et al (1987)]. The ratio of corrected HONO to NO_2 acts as an important indicator of this NO_2 to HONO conversion process. During the Phoenix experiment, although both NO_2 and HONO had clear vertical variation (see figure 4), the $HONO_{corr}$ / NO_2 ratio shows no significant vertical gradient. The influence of relative humidity on this process will be further investigated.

$$\left(\frac{d[HONO]}{dt}\right)_{het} = k_{het} \times \frac{S}{V} \times [NO_2] \times [H_2O] \propto [NO_2] \times R.H.$$

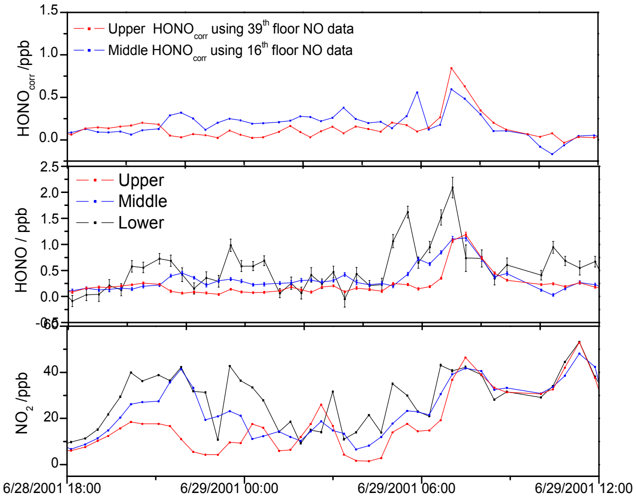

Figure 4. Vertical profiles of NO_2 and HONO

3.2.4 The derivation of N_2O_5 vertical profiles

With the measured mixing ratios of NO_2 and NO_3 as well as the temperature profile, unique vertical profiles of N_2O_5 can be developed.

Due to the formation reaction of N_2O_5 (reaction 5) and its thermal decay, a temperature dependent equilibrium is established between these three species. In the absence of vertical transport and N_2O_5 sinks other than thermal decay (i.e., reaction 6), the steady state mixing ratio of N_2O_5 can be simply determined by the following equation, in which $K_{eq}(T) = 5.5 \times 10^{-27}\ e^{10724/T}$ cm^3 [*Wangberg et al.*, 1997].

$$[N_2O_5] = K_{eq}(T)\ [NO_2][NO_3]$$

These simplifications are justified by model results by Geyer et al. (P1.16, AMS 2003), which show that vertical transport is only important for the N_2O_5 profile at altitudes below 10m. Neglecting the other sinks of N_2O_5 such as the reaction of N_2O_5 with H_2O and aerosol particles may cause less than 10% overestimation of N_2O_5 at the high temperatures at Phoenix.

In this study, the N_2O_5 vertical profile was calculated with the above mentioned simplified equilibrium and will be improved when the aerosol data becomes available in the future.

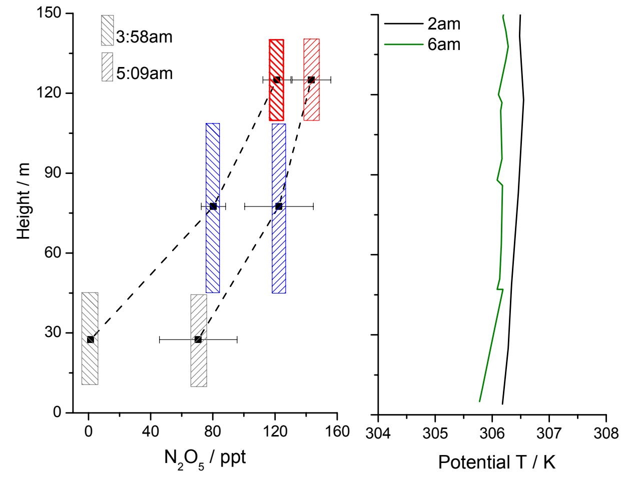

Figure 5. Calculated N_2O_5 profile and sounding data on June 22

Figure 5 shows the results of N_2O_5 profiles during the early morning hours of June 22. The colored bars indicate the height range of the three air boxes. The reported N_2O_5 mixing ratios are the averages in each box. Although this night had a relatively neutral boundary layer as shown in the potential temperature profile, clear vertical gradients of N_2O_5 were observed. During the same period of time, the observation also showed a vertical variation of NO_3 while NO_2 had no detectable gradient. The most likely reason is that surface emissions of NO and VOCs had an impact on the lower level NO_3 and thus also on N_2O_5. A vertical aerosol particle gradient could provide another explanation. This will be compared and discussed with the model results in the next section.

3.3 Comparison With 1D Chemical Transport Model

A 1-dimensional chemical transport model was developed to study the complex interaction of nocturnal NO_x chemistry and the vertical transport in boundary layer (see Geyer et al., P1.16, AMS2003). In general the model predicts distinct vertical profiles of NO_x, NO_3, N_2O_5, O_3 and VOCs under various atmospheric conditions. As observed in Phoenix, NO_3 and O_3 have generally higher mixing ratios at upper altitude while the other trace gases show higher mixing ratios close to the ground.

To learn more about the N_2O_5 profiles shown in figure 5, we performed model simulation of a night with very weak vertical stability assuming initially an even vertical distribution of NO_x and O_3 and allowing a continuous ground emissions of NO and VOCs. The detailed conditions are described by Geyer et al. (see descriptions of run5 in P1.16, AMS2003). After one hour, the NO_3 and N_2O_5 gradients were clearly developed while the vertical NO_2 remained nearly constant. After longer time, the gradient of N_2O_5 decreased. Although the conditions in this model are not exactly the same as the realistic situation in downtown Phoenix, the results, to a certain extent, support the observed N_2O_5 height profile in Phoenix.

4. CONCLUSIONS AND FUTURE WORK

Vertical distributions of various trace gases were measured with a long path DOAS system in downtown Phoenix in June-July, 2001. Strong gradients were observed for all the measured species on nights with a stable nocturnal boundary layer. The observations suggest that the nighttime NO_x chemistry in the urban environment is height dependent. The height profiles disappeared in the presence of vertical mixing after sunrise. The 1D model results are consistent with the measurements in the trend of the vertical variation of these nitrogen containing compounds and O_3.

O_x, the sum of NO_2 and O_3, shows no detectable vertical variation. The opposite vertical gradients of NO_2 and O_3 were therefore caused by titration by NO emitted at the ground.

Both NO_3 concentration and lifetime showed strong vertical gradients. Ground NO and VOCs emissions are believed to be the main reason for the small mixing ratio and short lifetime of NO_3 at low altitude. On stable nights, NO_3 levels of up to 200ppt were observed at 110-140m height.

The HONO formation process by NO_2 conversion was investigated with Phoenix data. It appears that this process is independent of height.

The HCHO gradient suggests the existence of direct emission sources.

The measurement data were compared with model results. Observed N_2O_5 height profiles could be reproduced by the model.

We intend to use the in-situ data of NO, VOCs and aerosols to provide a more detailed picture of the nighttime losses of NO_3 and N_2O_5. The low relative humidities in Phoenix allow the study of the relative humidity dependence of HONO formation processes.

The sources of HCHO direct emission will be investigated in the future.

Acknowledgement

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