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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Vertical profiles of $NO_x$ chemistry in the polluted nocturnal boundary layer in Phoenix, AZ: I. Field observations by long-path DOAS" *by* S. Wang et al.

**S. Wang et al.**

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We would like to thank both referees for their constructive comments. We have considered them carefully. The following is our response to the comments and a description of the changes that were made to the manuscript to address the issues raised by both referees.

**Response to referee 1:**

We agree with the referee that the discussion section is long and that it contains redundant information. To streamline this section, we have removed information that is not essential to the conclusions of the manuscript. We also restructured the review of the



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nocturnal NOx chemistry. These changes have shortened Section 4 by approximately three pages.

It is often difficult to make definitive statements based on field observations due to the large number of parameters influencing atmospheric trace gas concentrations. However, we may have been too careful with our statements. We have rephrased some of our discussion in order to make clear statements on our results. We have also discarded possible speculations and concentrate on discussions of the definitive results.

Our manuscript does refer a number of times to earlier model studies by (Geyer and Stutz, 2004). This manuscript concentrated on highly idealized modeling studies without any constraint to atmospheric observations, due to the lack of corresponding field data. The data presented here fills the gap of field data of vertical profiles of reactive trace species in a polluted urban NBL. While our observations confirm many of the predictions of Geyer and Stutz, 2004, we are presenting and discussing observations in a real urban atmosphere. The experimental proof that strong surface emissions in typical urban environments make the NBL chemistry system of O3-NOx height-dependent, and the direct observations of the impact of vertical stability, is certainly a novel scientific result of our manuscript. The focus of the discussion portion of the manuscript is on the NBL budgets of Ox and how NOx accumulation influences morning O3 levels. None of these topics were discussed in Geyer and Stutz, 2004. In particular, the behavior of Ox in the NBL and the analysis of O3 destruction by NBL chemistry based on the separation of permanent O3 loss processes from the temporary O3 removal have not been reported thus far. We have rephrased some of the text to clarify these points.

It is true that the accurate description of the detailed chemical transport processes requires a chemistry-transport model. However, the observations alone provide rich information about the vertical structure of the NBL chemical system and the possible consequences. The interpretations, although based on some estimates and semi-quantitative discussions, give valuable insights in this complex system. Therefore, we choose to keep the detailed discussions in this manuscript instead of moving it com-



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pletely to the forthcoming model paper. However, we have shortened Section 4 in response to the referee's comments, as discussed above. We believe that this section contributes significantly to the scientific value of this work and allows this manuscript to stand alone without the need of a second publication to understand the observations. We are preparing a follow-up publication presenting the modeling results for the Phoenix case.

**Response to the specific comments of referee 1:**

*- "The used term "vertical profiles" is somehow misleading because it implies continuous measurements along a vertical coordinate, whereas here the "profile" consists of the mean concentrations at three distinct and different altitude intervals."*

We see the point of the reviewer. However, we believe that the term "vertical profiles" describes our observations best. This term is generally used in the literature, even if there is vertical averaging in the data. Examples of vertical profiles that contain vertical averaging are those from satellite retrievals and balloon borne remote sensing experiments. Our manuscript clearly describes our experimental method and we do not believe that the readers will be confused by the term "vertical profile".

*- "Abstract line 24: "vertical profiles of NO3 and N2O5 confirm earlier model results". This implies that NO3 and N2O5 were measured. However, N2O5 was calculated using a model."*

We rephrased this sentence to avoid the misunderstanding. As explained in the text, N2O5 is not calculated using a model. It is calculated based on our measured NO2 and NO3 data, assuming a chemical steady state. We have made clear that this is a calculated value by calling our N2O5 results "steady state N2O5" in the manuscript. How representative steady state N2O5 is for true N2O5 levels will be further discussed in the forthcoming modeling paper.

*- "- Are the ground based measurements of CO, NOx and O3 taken 3 km south-west*



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*of BankOne representative for the air mass probed by the DOAS instrument? As discussed the exact source strength of NO is crucial for the quantitative understanding of the concentrations gradients and this could be considerably different between both sites."*

Considering the spatial averaging of the DOAS measurements we believe that the distance of the ground observation is not a strong limitation. In addition, we only use the in situ NO (and CO) data at different altitudes as an indicator of the relative emission strength for different cases (for example in Figure 12). We also compared the ground data with NO data measured at 50 m and 140 m, which were obtained on BankOne, within our DOAS light paths. The general trends of NO data at these sites are similar.

*- "Page 53, line 5: Have the measurements taken during rapid concentration changes been excluded from the further discussions and which criterion was used?"*

The data generated during the rapid concentration changes are rare. They were easily identified from the original data and were excluded from the discussions. We added a sentence in the manuscript explaining this more clearly.

*- "Conclusions: (I) "NO3 at the ground can be controlled by ground-level emitted NO and VOCs". Have VOCs been measured during the Phoenix campaign? (II) It is stated that denoxification through N2O5 uptake on aerosols may be important. However, in the text this process was ruled out owing to the low RH in Phoenix."*

(I) VOC data during this field experiment was very limited and we did not show them in this manuscript. Generally the VOC levels are low in downtown Phoenix. The NO3 vertical distribution is thus primarily caused by the strong surface emission of NO. We will change the corresponding sentence in the conclusions to make this statement clear.

(II) The reviewer may misunderstand the statement. It is stated that while N2O5 uptake on aerosols does not influence the thermal equilibrium of (R5) much due to the



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low R.H., it may be an important denoxification process that eventually removes O3 from the atmosphere. Because the redundant information has been removed from the discussion of N2O5, this statement is clearer in the revised manuscript.

*- "Information contained in Table 1 could be incorporated in Figure 1 to enhance the information content of the figure. The location of the NO measurements could also be added."*

We have incorporated the corresponding information of heights in Figure 1, as suggested.

Since both Table 1 and Figure 1 explain the setup of DOAS light paths, we did not add NO measurement information. The related information is clearly explained in the text (section 2.3).

*- "Figure 3: Shading used to denote nighttime and daytime seems to be wrong. According to the J(NO2) data, daytime lasts from 0530 to 1930."*

The shading is correct. As explained in the figure caption, “the transition between the colors shows sunrise and sunset periods”. There is no clear line between daytime and nighttime, but rather a transition period during which the solar radiation strength slowly increases or decreases. This is especially clear in the plots of J(NO2) (Figure 5, 8, 9, 10). J(NO2) slowly increases after 0530 in the morning, and the shading background shows a transition between gray (nighttime) and white (daytime).

*- "All figures showing DOAS measurements: With respect to the discussion of the NOx/NO3 chemistry, the order of the panels should be rearranged to O3, NO2, NO3, HONO, and HCHO."*

The involved figures (Figure 3, 4, and 7) have been rearranged as suggested. Please see the new figures.

**Response to referee 3:**



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The referee points out that this manuscript covers not only the vertical profiles of NOx but also those of a number of other trace gases. The focus of the manuscript is NOx chemistry in the boundary layer. This topic covers many reactive species, as well as their chemical reactions. NO, NO2, O3 and several other reactive nitrogen-containing species are the key species of this chemical system. The driving force of this system is the surface emissions of NOx. This altitude-dependent system also governs the accumulation of NOx in the NBL, which has a significant influence on the initial conditions of the boundary layer for photochemistry in the next morning.

While we believe that the term "NOx chemistry" covers species such as NO, NO2, NO3 and ozone, we agree with the reviewer that, at least in the case of ozone, this may lead to some misunderstandings. We have added O3 to the title, changing it to "Vertical profiles of O3 and NOx chemistry in the polluted nocturnal boundary layer in Phoenix, AZ: I. Field observations by long-path DOAS". Although we also show the vertical profiles of other species such as HONO and HCHO, the focus of the manuscript is clearly on ozone and NOx chemistry and the majority of the manuscript discusses this important chemical system. We therefore prefer not to mention other species in the title to avoid misleading readers by suggesting that details of these observations will be discussed.

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 45, 2006.