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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.

Anonymous Referee #1

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This manuscript presents interesting measurements of the key players of nocturnal NOx chemistry in the heavily polluted environment of downtown Phoenix (AZ) using Long Path Differential Optical Absorption Spectroscopy. The DOAS light path probed different altitude intervals resulting in average concentrations of O3, NO2, NO3, HONO, and HCHO between 10-45 m, 45-110 m, and 110-140 m. Variations in trace gas concentration gradients were observed which are attributed to the interplay of gas phase chemistry, surface emissions (mainly of NO) and atmospheric mixing processes.

The introduction to the scientific problem, the experimental realization of the measure-

ments (including data analysis) and the outcomes of the measurements are clearly presented. The observed time series of trace gas concentrations and the concentration gradients inferred from those are thoroughly discussed in section 3. The figures are adequate and it is shown nicely that NOx nighttime gas phase chemistry and atmospheric transport processed are inseparably linked together making the quantitative analysis of the observations difficult.

My biggest concerns with this paper are related to section 4 (Discussion): This section is very long, contains a lot of redundant information and appears to me kind of unstructured and a bit confused. In the first part of this section the authors present a very detailed and too extensive review of the key processes of chemistry and transport influencing the actual trace gas budgets. Although some mathematics is used to explain the underlying ideas (eqs. 1-6) the discussion remains general and the examples used are of qualitative nature only. Also the following discussion of the field observations contains no quantitative statements. Instead, the authors interpret observations using many 'assumptions', 'speculations', and 'semi-quantitative evaluations'. Terms like 'most likely', 'estimated', 'assuming', 'rather small', 'possibly', etc, are frequently used in this long section, ending in conclusions of general nature. Furthermore many ideas used during the discussion are taken from a previous model work of the authors (Geyer and Stutz, 2004), so the reader could get the impression that most of the findings of this field experiment just confirm their former study and would probably not contribute substantial new insight into the problem.

However, if it is true, and it seems to be so, that the field observations can only be understood using a complex chemistry-transport model (as it is declared several times in the paper) the authors consequently should go this way. The detailed discussion could then better be moved to a succeeding paper where conclusive model calculations constrained by experimental data are used to gain a quantitative understanding of the observations.

I suggest to rewrite this manuscript focusing on the well written experimental part as is,

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extended by a concise presentation of the basic nighttime NOx/NO3/N2O5 chemistry and the key processes which had to be measured in the field in order to feed the model properly. Doing so, would result in a paper that better fits to the title of this manuscript. I'd like to encourage the authors to resubmit the revised manuscript together with the modeling paper as part I and II, respectively.

Specific comments:

- 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.

- Abstract, page 46, line 24f: 'vertical profiles of NO3 and N2O5 confirm earlier model results'. This statement implies that NO3 and N2O5 were measured, however, N2O5 was calculated using a model.

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

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

- Conclusions, page 84f:

I) 'NO3 at the ground can be controlled by ground-level emitted 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.

- Table 1: Information contained in Table 1 could be incorporated in Figure 1 to enhance

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the information content of this figure. The location of the NO measurements could also be added.

- Fig. 3: Shading used to denote nighttime and daytime seems to be wrong. According to the J(NO2) data (figs. 9-11), daytime lasts from 0530 to 1930.

- 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, HCHO.

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