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Atmospheric Measurement Techniques Discussions

Interactive comment on "Comparison of N_2O_5 mixing ratios during NO3Comp 2007 in SAPHIR" *by* H. Fuchs et al.

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We thank the reviewer for his/her comments. Here are our responses to the specific comments:

Comment: After a brief but adequate introduction to the topic of atmospheric NO_X chemistry and the importance of N_2O_5 measurement, a discussion of different measurement techniques follows. Although this comparison is done using a simulation chamber, mentioning also remote measurement techniques (ground based, on planes or satellites) would complete this part of the introduction. The introduction ends with a discussion about the importance of quality assurance and comparisons of methods and instruments which is the main topic of this paper.

Response: We will add on p4913 l26: "Stratospheric NO_3 has also been detected by remote measurement techniques (e.g. from the ground (Allan et al. 2002) and from satellite (Kyrola et al. 2010))."

Comment: The experimental section clearly describes the participating instruments and the related methods of measuring as well as the simulation chamber SAPHIR. On p. 4938, l5-22, the authors should add manufactures and types of the used standard instrumentation or refer to the related literature (e.g. Bohn et al., 2005). Regarding to the chamber, a discussion of a possible NO_X memory effect by the used FEP film and the NO_X formation potential by the silent discharge ozonizer would be interesting.

Response: We will change p4938 l17-22 to: "Besides instruments detecting NO_3 and N_2O_5, a number of other instruments measured O_3 (chemiluminescence detector, modified Eco Physics CLD 770AL, Ridley et al., 1992), NO (chemiluminescence detector, Eco Physics CLD 770AL), NO_2 (chemiluminescence detector, LIF, CRDS, Fuchs et al. 2010a), VOC (PTR-MS, Ionicon, GC, Perkin Elmer) concentrations, and aerosol properties such as number (CPC, TSI 3785) and surface concentrations, size distribution (SMPS, TSI 3936L85) and their composition (HR-TOF-AMS, Aerodyne Research)."

Concerning potential NO_X memory effects and NO_X formation by the ozonizer, which is operated with pure oxygen, we have not observed any NO_X in the clean chamber and after adding ozone to the clean chamber air so far. We will add on p4938 l25: "No NO_X is observed in the clean chamber and after ozone addition to the clean chamber air.".

Comment: The sections Results and Discussion are very detailed but could be more structured according to the types of instruments (RH, photolysis, inorganic and organic aerosols, VOCs) by using sub-chapters. Also figure 1 contains too much information with rather no structure, splitting this figure in parts, representing the different types of experiments, would be very helpful. Also events like e.g. roof opening and VOC addition should be indicated in the figure. A detailed description of the water-vapor

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experiment is missing (p. 4944, 23). Especially a discussion about adsorption of NO_X species on water films in the chamber and the instruments would be very interesting. The influence of the filter used in the inlets is very interesting but not unexpected. The authors could consider adding a figure plotting the change of accuracy as a function of the filter age for the different types of experiments. In general the statistical analysis of the achieved data is very good and could only be improved by discussing the disturbing effects (e.g. filter age) using those tools.

Response: See responses to the specific comments below.

Comment: The conclusions summarize the main results of the comparison and outline the major problems according to the used instruments and methods like inlet transmission efficiency and the presence of aerosols. Giving a general advice for maximum filter age, aerosol particle concentration and relative humidity would increase the outcome of the comparison.

Response: We do not think that it is justified to give a more specific advice than done in the conclusions on p.4948 l20-24. The need for filter change is most likely specific for the design and operational parameters of an individual instrument, so that the recommendation is that a new instrument needs careful characterization of its inlet transmission efficiency for different conditions. We will add on p4948 l27: "The inlet transmission efficiency needs to be characterized for an individual instrument for different conditions before it is deployed in the field.".

Comment: The interaction of atmospheric halogens with nitrogen-oxide species is mentioned within the introduction but their possible interferences with the applied methods is totally neglected. The authors could add some discussion about possible interferences with halogens according to the used instruments.

Response: To our knowledge, the detection of NO_3 by absorption or fluorescence is not disturbed by interferences with halogens, because they do not absorb light at the wavelength used for NO_3 detection. Sampling of air which contains e.g. sea salt

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aerosol may alter the inlet transmission efficiency, but we did not explicitly test the performance of instruments for this case.

We do not see that there is a specific need to discuss the potential for such an interference, because there is no obvious reason such as absorption at the same wavelength or an unexpected behavior of instruments in the presence of halogens, which is reported in literature. Moreover, zero measurements in CRDS are done by titration of NO, so that absorption of other trace gases is included in the zero decay time. We will add p4933 l15: "Because of the specific titration of NO_3, absorption of other trace gases at 662 nm is included in the zero measurements. Since $ClNO_2$ or other halogens compounds likely to be activated from N_2O_5 heterogeneous uptake do not absorb visible light, they are very unlikely to present an interference to any of the optical methods for NO_3 or N_2O_5 detection compared here."

Comment: The result and discussion sections should be more structured according to the type of experiments.

Response: In order to give the Results and Discussion sections a better structure, we will make the following changes:

- We will move the paragraph on p4940 l3-20 to p4941 l20 and add the subsection title "Precision of measurements",
- We will add the subsection title "Time series of N_2O_5 mixing ratios" on p4939 l7
- We will add the subsection title "Regression analysis" on p4941 l20
- We will add the subsection title "Correction for filter aging measurements by UAF-CRDS" on p4943 l17
- We will add the subsection title "Influence of water vapor" on p4944 l20
- We will add the subsection title "Influence of inorganic aerosol" on p4945 l1

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- We will add the subsection title “Influence of organic aerosol” on p4947 l1

Comment: Adding a detailed discussion on the influence of water-vapor, especially of adsorption of NO_X species on water films in- and outside the instruments would be interesting and helpful.

Response: We will add on p4944 l21: “The water mixing ratio was increased in four steps up to nearly 1.2 %.” Adsorption of NO_X on water films did not play any role during these experiments, because relative humidity was always well-below the condensation point in the chamber and in the instruments, so that we cannot draw any conclusion of the performance of the chamber or instruments, if water films occur on the Teflon film of the chamber or on Teflon tubing in the instruments.

Comment: A statistical analysis and discussion of the effect of aged Teflon filters on the accuracy of the used instruments should be added, because it seems to be one of the main results according to problems with the involved methods and instruments.

Response: As concluded from the experiments, the N_2O_5 filter loss in the instruments cannot be easily predicted. Therefore, in our point of view, it does not make much sense to plot the change in accuracy as a function of filter age. The change in the accuracy of measurements depends on how well the change of the inlet transmission efficiency can be quantified. Results shown here indicate that the N_2O_5 filter loss is variable, so that we could only estimate the N_2O_5 filter loss for some instruments from the comparison of measurements. In this case the change in accuracy that can be determined here would depend on the accuracy of the second instrument. Therefore, a general quantitative analysis of changes in the accuracy due to filter aging is not possible. The comparison only allows to identify accuracy problems for the specific conditions encountered during these experiments. In our point of view, the analysis and discussion of these problems in this papers is sufficient.

Comment: Many figures are not readable at black-white prints. Please change data presentation according to this task. Fig. 1 should be split into parts according to types

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of experiments.

Response: The reviewer is correct that the figures are not optimized to be printed as black-white prints. However, because of the high time resolution of the instruments the number of data points in each trace is large, so that only a small size for symbols can be used. Therefore, it is nearly impossible to distinguish the traces by using different symbols. Moreover, it is likely that nearly all readers can get the articles of this journal as PDF-files from the web, so that they can look at the colored figures.

We will add the type of experiment in Figure 1 and add vertical dashed lines to mark opening/closing the roof, if not indicated by the display of j(NO_3). All other events are shown in the time series of O_3, NO_2, H_2O and VOCs. Displaying additional lines to indicate these events would considerably reduce the readability of the figure. We do not think that Figure 1 should be split into several figures. This figure gives an overview about all measurements and the experimental conditions during the experiments. It serves the reader as a reference, if he/she wants to get an overview of the campaign or a specific experiment.

Comment: p. 4930, 10-15: Displaying the reactions as equations and referring to them would be more demonstrative than describing them in the text of the manuscript.

Response: We will add the reactions as suggested by the reviewer on p4930 l14.

Comment: Tab. 1: add the used Teflon filter types (manufactures, quality, material,. . .).

Response: We will add the filter specifications (Teflo, Pall) in Table 1.

Comment: Tab. 2: Clarify the percentage of water – is this relative humidity? Also add ambient temperatures within the simulation chamber.

Response: Water vapor is given as mixing ratio. We will indicate this in Table 2. We will also add a column with temperatures in the chamber.

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Comment: Fig. 4 (and others) caption: add the type of the experiments (not only the dates)

Response: We will add the type of experiment in the captions accordingly.

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