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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "In-situ comparison of the $NO_y$ instruments flown in MOZAIC and SPURT" *by* H.-W. Pätz et al.

**H.-W. Pätz et al.**

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We like to thank the reviewer for the thorough evaluation and the detailed comments which have helped to improve the manuscript significantly.

General Comments:

1. We refrained from long technical explanations because the MOZAIC instrument is described in detail in the same Journal (Volz-Thomas et al., 2005) and the ETHZ used a commercial instrument. Therefore, we constrained ourselves to the main differences, i.e. the inlet configuration and operating conditions. We have now added a Table summarising the main technical features and performance of both instruments.

2. As this was a formal and blind comparison, we had thought that showing the original

data delivered to the referee would be appropriate. On the other hand, we had to use the final data, of course, in order to learn most about the performance of the MOZAIC instrument. We followed, however, the suggestion of this and of reviewer 2 by removing the erroneous data from the Figure. Instead, we include now a clearer statement on the magnitude and source of the initial error in the ETHZ data. "We like to note that the initial data set submitted after the campaign to the referee (see section 3) had been calculated with an erroneous pressure dependence of the conversion efficiency, that had been obtained with an inappropriate experimental setup and showed an apparent drop of the conversion efficiency from 98% at 1000 hPa to 70% at 170 hPa, thus leading to an over-estimation of the ETHZ NOy data by about 25% at the highest altitudes. In the following, we only show the revised data which were calculated with the correct efficiency as shown in Figure 1."

Specific Comments

652, 21: The conversion efficiency of 92% is lower than stated above (652, 9).

Answer: The number of 95% referred to the MOZAIC operation in general, whereas a conversion efficiency of 92% was actually determined before and after the comparison flight (we used the MOZAIC instrument without special cleaning). In order to clarify this point, the wording is changed to: "The sensitivity for NO remained constant at 460 +- 18 cps/ppb and the conversion efficiency for NO2, as determined by gas phase titration of the NO by O3 was 92 +- 4 % (2 sigma), which is somewhat lower than normally observed in MOZAIC."

652, 22: “conversion efficiency of the MOZAIC instrument is independent of pressure”; was this tested? Please show results or give a reference if available.

Answer: The conversion efficiency of the MOZAIC converter was tested between 1000 and 150 hPa. As discussed in Volz-Thomas et al. (2005), the conversion efficiency remains constant because the MOZAIC-converter is longer than required. The wording is changed to: "Other than for the ETHZ instrument (see section 2.2), the conversion



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efficiency of the MOZAIC converter is independent of pressure. This was verified in the laboratory, both for NO2 and HNO3, in the pressure range 150 - 1000 hPa (Volz-Thomas et al., 2005) and is due to the fact that the converter is longer than theoretically required for the flow rate applied."

652, 23: Please revise the terminology; inaccuracy might not be the correct term here; use overall uncertainty instead.

Answer: We followed this suggestion.

652, 25: The uncertainty of the conversion efficiency (above 652, 24) might be underestimated: Did you use the +-4% from the NO2 conversion to calculate the overall uncertainty? Do you have an explanation why the conversion efficiency of HNO3 was $>$92% and for NO2 “only” 92+-4%? I would expect the conversion efficiencies for NO2 to be higher when compared to HNO3.

Answer: The "$>$" actually was a typo and should have been "$\tilde{}$". We now state the conversion efficiency for HNO3 with its uncertainty (92+- 5%) and use the larger uncertainty for HNO3 in the calculation of the overall uncertainty, which is thereby increased from 6% to 6.5%. We like to note, however, that we always observed the conversion efficiency for HNO3 to remain similar and sometimes even slightly higher than that for NO2 for converters that began to degrade due to contamination.

653, 24: You account for the uncertainty of the background with 100 ppt (2 sigma). How was this number calculated? And why did you choose 150 ppt for background correction? Do you assume that the 200 ppt measured after the flight was still affected by memory effects? I also expect the “memory” effect to contribute significantly to the uncertainty of an individual measurement point, because some NOy is measured with delay.

Answer: Yes, we assume that the value after flight is still affected by memory from stratospheric HNO3 levels. (See also answer to reviewer 4) and we used 30% of the



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background as 1-sigma uncertainty as in MOZAIC. The text is revised in order to make the point clearer: "The data were analysed in the same way as during routine operation in MOZAIC by interpolation of the automatic zeros of the NO detector. In addition, the average background signal for NOy determined from the zero air measurements (fake NOy) was subtracted. The latter was 150+-30 ppt (2 sigma) before the flight. The background determinations during the flight suffered from memory effects of the gold converter due to the long tail of the memory curve for HNO3 (Volz-Thomas et al., 2005). The memory manifested itself by the fact that the background signals were still decreasing at the end of the zeroing intervals and that the remaining signals (370 to 620 ppt) were correlated with the ambient NOy concentration measured before the zero was initiated. After the flight, the background was 200+-35 ppt. The memory for HNO3 leads to a potential overestimation of the instrument's real background unless the zero air is applied for much longer times than the 5 min employed during the comparison flight. Therefore, the background value of 150 ppt as determined before the flight was used in the data reduction, because this value was assumed to being least affected by memory. The uncertainty of this background value was estimated to +-100ppt (+-67% of the background used as 2sigma uncertainty as in MOZAIC data analysis)."

The memory effect contributes to the uncertainty of an individual data point, depending on the rate of change. We added a section on memory to the discussion.

654, 13: Converter temperature?

This information is now added: "Prior to detection, the NOy-species are reduced to NO using a heated gold-converter, controlled a temperature of 300°C and using CO (5 sccm, 99.997%, PanGas, Switzerland) as reducing agent (Fahey et al., 1985)."

655, 25: How was the 105 ppt determined? Please add more details. Was this number derived from zero checks?

Answer: The following paragraph is added and the uncertainty in the background is now included in the error analysis for ETH: "Besides the zero signal of the CLDs, which



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is regularly determined and subtracted in all three channels, an additional background of 105+-50 ppt was subtracted from the NOy measurement to account for a “fake NOy signal”, most probably produced by impurities in the CO reduction agent (Fahey et al., 1985). This fake NOy signal was determined in the field before the mission flights using zero air produced by a pure air generator. The in-flight background calibrations suffered from a memory effect similar to the MOZAIC instrument and could therefore not be used for these evaluations."

656, 20: Please explain in more detail what you mean by “reproducibility of these experiments was much lower than for NO2”.

The explanation is now included as follows: "The conversion efficiency for HNO3 was determined in laboratory experiments by Lange et al. (2002) using the same converter to be approximately the same as for NO2. Unfortunately the reproducibility of the HNO3 experiments using the ETH system turned out to be much lower than for NO2 mainly due to difficulties in the experimental setup of the HNO3 source. The determination of the HNO3 conversion efficiency therefore represents the largest uncertainty in the NOy measurements."

659, 13: Do you have an explanation why the three ensembles show “somewhat” higher or lower values? How were these three ensembles chosen? I can see data points which are more off compared to the data in the squares but which were still considered to be valid. General: I believe that a reason should be given when data is not considered for the evaluation. This is done only for one of the three squares. It is also not clear to me if this data was not considered at all (linear fit to all data) or not considered when level flights were compared.

Answer: The ensembles are now better identified by giving the time of occurrence in Figure 5 (see also new text below). In addition, we are now showing two panels for figure 6 to make clear that the first fit includes all data, whereas the second fit is made for level data only and excluding the first 5 min after a background determination in ei-



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ther instrument: "Exceptions from the good agreement are seen during the ascent into the stratosphere at 51500 s, where the MOZAIC instrument significantly lags the ETHZ instrument, which shows a much faster increase in good correspondence with the increase in O3. Interestingly, the corresponding time lag between MOZAIC and ETHZ is not seen during the final descent at 60000 s. There are a few further deviations to be noted: The MOZAIC instrument exhibits a reduced sensitivity after 48750 s. This is due to the fact that the instrument had been turned off and restarted several times for unknown reasons, possibly by a malfunction of the gear-compressed signal which was simulated by an external switch for the comparison flight. As was seen in the housekeeping data after the flight, the MOZAIC data acquisition system had switched the instrument several times into standby mode, in which the gold converter is being backflushed to prevent contamination during landing in automatic operation. Furthermore, both instruments exhibit slightly reduced responses after background determinations, i.e., after periods when the inlets and gold converters were exposed to zero air (ETHZ) or oxygen (MOZAIC) for several minutes."

660, 8: Review the terminology; I think inaccuracy should be replaced by uncertainty in this context.

Answer: We changed to uncertainty, as suggested.

660, 23: The discussion should more focus on the differences between the two instruments and the uncertainties of the other available data sets e.g. from MOZAIC. The explanations given for the differences are not all convincing to me; e.g. why should a change from warmer zero air to cooler ambient air reduce the conversion efficiency? The converters are heated, and the conversion efficiency increases with temperature. Thus such a behaviour is not expected at all and should be further discussed.

Answer: Following the suggestion, we removed this (quite speculative) part from the discussion, as it doesn't really lead to a conclusion (see also reply to ref. 4). The discussion is thoroughly revised also in response to the other reviewers.



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References:

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 649, 2006.