Atmos. Chem. Phys. Discuss., 6, S737–S740, 2006
www.atmos-chem-phys.org/acpd/6/S737/
European Geosciences Union

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.

Received and published: 4 May 2006

We like to thank the reviewer for the thorough evaluation which has greatly helped to improve the manuscript.

Our answers are given below the referee's questions.

1) Perhaps the most important issue raised is the memory effect, which the FZJ instrument displays. This effect is now clearly demonstrated in the laboratory and in the atmosphere. Why isn't the memory effect seen on descent in this dataset? For example: (p661 ln 1-3) the ETHZ instrument signal should decrease faster than the FZJ instrument in aircraft descents if the latter has a memory effect. What are the consequences of the observed memory effect for the interpretation of the long-term MOSAIC

dataset?

Answer: The explanation for the similar decrease of the FZJ and ETHZ signals during descent might be due to an so far unexplained memory effect in the ETH measurements after having spent a long time in the stratosphere at high HNO3 mixing ratios. The decay of the MOZAIC NOy signal, when compared with O3, shows the same memory as during ascent, in agreement with the findings by Volz-Thomas et al. (2005) from laboratory tests. We included the descent in Figure 7 and present this argumentation as follows in the section Discussion and Conclusions:

"The discrepancy between the two instruments in the stratosphere, where 90% of NOy is in the form of HNO3 (Neuman et al., 2001), limits the possibility for losses of HNO3 in the Rosemount inlet of the MOZAIC instrument to 10% or less. This finding is important because, as discussed in Volz-Thomas et al. (2005), the use of a Rosemount housing as an inlet for NOy is not undisputed in the literature. Obviously, the design chosen for the Rosemount inlet in MOZAIC has no or very small drawbacks for the sampling efficiency for NOy.

While the memory of the MOZAIC instrument is clearly confirmed by the comparison with the much faster increase in NOy of the ETHZ instruments during the ascent into the stratosphere (Figure 7), there is no corresponding time lag between the two instruments during the final descent. One reason for this behaviour is that the MOZAIC instrument was measuring zero air during the first part of the descent. However, from the comparison with O3 it is suggested that during descent the ETHZ instrument suffered from a similar memory as the MOZAIC instrument, because the decrease in ETHZ NOy occurs much more slowly than the decrease in O3, whereas during ascent, ETHZ-NOy increases simultaneously with O3.

A similar behaviour of the SPURT gold converter has been observed by Lange et al. (2002). A possible explanation is that the memory is only established after the converter has been exposed to high HNO3 mixing ratios for some time. A possible, albeit speculative, explanation is that HNO3 is adsorbed at the outer surface of the tip of the gold tube or at the stainless steel surface of the converter housing. While the corresponding effect may not be significant during the fast ascent, it may show up during descent because of the large amount of HNO3 that has been absorbed on the outer walls of the converter during the long time spent in the stratosphere. Consequently, the effect would depend on the time the aircraft has spent in the stratosphere and on the HNO3 concentrations encountered. It would be quite difficult to quantify this in the laboratory, but would require further dedicated in-flight comparisons.

Both instruments exhibit reduced sensitivities after periods of background determination, i.e., zero air addition to the inlet. The most likely explanation for this behaviour is a memory effect, possibly enhanced by the fact that the zero air contains less water vapour than the ambient air. This effect was only seen because of the otherwise excellent comparison between the two instruments and because both instruments had been operated on the same aircraft so that atmospheric inhomogeneities or time lags between the data sets could be ruled out as possible explanations."

2) How much of the NOy MOSAIC dataset has values below 0.3 ppbv, the minimum value observed on the flight? Are there any uncertainty issues likely to be different at values below 0.3 ppbv?

We include this information as follows: "The intercomparison flight covered a large fraction of the dynamic range of NOy mixing ratios encountered in MOZAIC. On average, 9% of the MOZAIC NOy data are below 300 ppt and 1.5% above 3.5ppb, the lowest and highest concentrations encountered during the intercomparison."

3) The authors are to be applauded for their transparency in showing the ETZH data reduced with the incorrect conversion efficiencies. However, I think it adequate to simply state that the data originally submitted was later adjusted by a common factor due to a recognized error and, thus, panel (a) of Figure 5 can/should be removed.

Answer: 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 1 by removing the erroneous data from Figure 5. 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."

References:

Neuman, J. A., R. S. Gao, D. W. Fahey, J. C. Holecek, B. A. Ridley, J. G. Walega, F. E. Grahek, E. C. Richard, C. T. McElroy, T. L. Thompson, J. W. Elkins, F. L. Moore, and E. A. Ray: In situ measurements of HNO3, NOy, NO, and O3 in the lower stratosphere and upper troposphere. Atmospheric Environment, 35, 5789-5797, 2001.

Volz-Thomas, A., M. Berg, T. Heil, N. Houben, A. Lerner, W. Petrick, D. Raak, and H.-W. Pätz: Measurements of total odd nitrogen (NOy) aboard MOZAIC in-service aircraft: instrument design, operation and performance. Atmospheric Chemistry and Physics, 5, 583-595, 2005.

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