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Interactive comment on "Measurements of total odd nitrogen (NO_y) aboard MOZAIC in-service aircraft: instrument design, operation and performance" *by* A. Volz-Thomas et al.

A. Volz-Thomas et al.

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We like to thank the reviewer for the detailed comments, which are answered below. We tried to combine the answers thematically

Time response: As pointed out in our reply to referee #1, there have been mistakes concerning the time constants listed in Table 1. The correct value for a 67% response to a step change in NO2 at the entrance of the sampling line is 0.4 s and the corresponding time for a 90% response is 1 s, as shown in Figure 10. The respective times for a step change in HNO3 at the entrance of the sampling line are 20 s (67%) and 150 s (90%) respectively. The 67% response of the inlet manifold alone is quite similar to

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that for the entire inlet. However, the long tailing for reaching 90% response is dominated by the 80 cm FEP tube. We have also repeated the tests with PFA tubes and confirmed the longer time constant compared to FEP. We will include this information in Figure 10 in the revised manuscript.

Actually, a somewhat nonlinear response is also seen in the data by Neuman et al., 1999, 2000, 2002. The 1 s time response quoted by Neuman et al., 2000 is difficult to assess, because the HNO3 is actually added directly at the entrance of the mass spectrometer, i.e., behind the inlet line and the Teflon valve used for flow control. Similarly, in Neuman et al., 2002, the HNO3 is added behind the major part of the inlet line and behind the rotor valve. These data are thus not entirely representative of the total time response of the instrument. Evidence from atmospheric measurements is provided by the good anti-correlation between HNO3 and O3 during the transect of the rocket exhaust plume. However, the conclusion from this experiment is somewhat limited by the extreme and unknown HNO3 concentration and the unknown covariance of O3 and HNO3 in the plume. A somewhat slower response for the last fraction of the HNO3 signal is actually seen at the right hand side of Figure 7 of Neuman et al., (2000). Similarly, a slower response for HNO3 as compared to O3 is seen in the atmospheric data presented in Figure 6 of their paper, i.e. for the rapid change in O3 at 66500 s, albeit somewhat disguised by the noise in the HNO3 data.

The use of the NOy-data from MOZAIC flights is not primarily seen in detailed process studies, because the MOZAIC aircraft cannot be directed into special atmospheric situations. The main aim is to provide data describing the climatology of NOy in the UT and LS in terms of average and variance. The slow time response of the MOZAIC instrument for HNO3 is due to the constraints imposed by the logistics and safety regulations for installation on the A-340 passenger aircraft. While we would have preferred to have the converter installed closer to the inlet, this was not possible because of the safety regulations imposed by the certification process for passenger aircraft. We should like to re-emphasise that obtaining the permission for using H2 aboard a pas-

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senger aircraft already constituted a major achievement. The request was to have all heated components inside the instrument box, which is being continuously monitored by an avionic smoke detection system. Getting the permission for heating of the inlet line was quite difficult because installation of safety switches or a monitoring system was not possible due to space limitations. Therefore, we had to argue the safety on the basis of the materials used and that the total power applied to the heater wouldn't be capable of heating the tube to more than 150 °C when the aircraft is grounded. This temperature limit was set by the need for back flushing of the inlet at ground and the request for not using a shut-off valve at the H2-reservoir, causing a mixture of H2 and O2 being vented through the inlet. With this boundary condition, the heater is not able to heat the tube to more than 20°C at the lowest ambient temperatures encountered at cruise level.

Concerning the usefulness of the NOy data: Given the 20 s for a 67% response, the use of 4s data is certainly limited for NOy. This time interval was simply adopted as it is the principal time interval for the MOZAIC data base. We should like to note, however, that most data users so far have only considered the 1 min averages, which are also stored in the data base. During 1 min, the instruments response is about 80% of a step change.

The term "high resolution" was used because of the vertical resolution provided by the measurements, because of the fact that the MOZAIC aircraft are flying horizontally (i.e., at constant pressure levels) most of the time and thus usually intercept the tropopause at small angles. The vertical resolution in terms of separating stratospheric and tropospheric air is much better than what is currently achieved by satellite instruments measuring NO2 or HNO3. The bias of the NOy data due to the instruments time response will be a slight horizontal (a few km) and "vertical" (corresponding to a relative height displacement of about 100m) displacement of the maximum and minimum concentrations and an under-representation of the true variance. This effect on the climatology is, however, small as is corroborated by the good correlation between

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NOy and O3 in stratospheric air (O3 $>$ 100 ppb) shown in Figure 11 of our manuscript.

The unity response of our NOy instrument to HCN is clearly stated in the paper. The implication for ambient measurements is obvious, as in fact stated by the reviewer. We feel that this is as far as an instrumental paper should go. Any specific implications, e.g. how much of a given NOy-measurement could be due to HCN, depends on the actual atmospheric situation and must be discussed - on the basis of the results described here - in forthcoming papers that deal with the data and their interpretation. CH3CN is not converted significantly in our instrument as discussed in the reply to reviewer#1.

The NOx concentration in the outflow of our HNO3 permeation tube was regularly checked with CLD equaiped with a photolytic converter. The NOx to HNO3 ratio in the outflow was always $<$ 3%, much smaller than what had been observed by Ryerson et al., 1999. Therefore, the time constant determined in our experiments is not corrupted by the much faster time response for NOx. Actually, we have never observed NOx/HNO3 ratios as high as those found by Ryerson et al. with any of our HNO3 permeation tubes, even with self-built tubes that had been used for calibration of our NOy measurements aboard the C-130 of the UK Met Office (Gerbig et al., 1999).

Answers to specific comments:

Abstract: We shall modify the last sentence giving numbers for 67% and 90% response. See also comments above and below. Heating doesn't improve the time response very much, whereas losses by permeation through the tube walls become significant.

NOy-instrument p. 6152-6162: The fact that NO is converted to 90% in the pre-reaction volume does not create a bias, because calibration is done in the same fashion. Potential interferences in the infra red spectral region from O3-olefine reactions are due to OH Meinel bands (c.f. Drummond et al., 1985). Oxygen is indeed used instead of zero air. We shall modify text and Figure 4 in order to avoid confusion. For emission of NOx by the HNO3 permeation tube, see above.

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Table 1: we will clarify the 20 s as being the 67% response and add the value for 90% response.

Figure 6: Heating of the inlet line to 45 °C didn't change the response significantly. Because of the restrictions due to the certification procedure, it was not possible to install a more powerful heater at the tip of the inlet line.

Figure 7: The data were indeed converted to mixing ratio by subtracting the zero and applying the calibration factor. We shall label the Y-axis and add a corresponding note to the figure caption.

Figure 8: We will change the figure as requested.

Literature:

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