Atmos. Chem. Phys. Discuss., 4, S2679–S2683, 2004
www.atmos-chem-phys.org/acpd/4/S2679/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #2

Received and published: 23 November 2004

Review of Volz-Thomas et al., "Measurements of total odd nitrogen (NOy) aboard MOZAIC in-service aircraft: instrument design, operation and performance", ACPD manuscript no. acpd-2004-0142

General comments:

The authors describe and present validation data for an unattended instrument for NO and NOy measurements aboard a civil airliner. This paper is quite relevant to ACPD, discussing a new instrument from which the data will be of interest to a large fraction of the atmospheric chemistry community.

The paper is generally thorough, clear, and well-written. The report describes the instrument design, operation, and performance quite well in most respects. However, there are some additional points of interest regarding data interpretation that were not discussed and should be included before eventual publication in ACP.

One unaddressed issue involves the authors' recommended use of the NOy data in light of the relatively long (2.5 minute!) time constant for instrument response to changes in atmospheric HNO3 mixing ratios. The authors note that a driving force behind this project was the need for regular surveys providing NOy data with high spatial resolution in the upper troposphere/lower stratosphere, especially in the tropopause region (p. 6152). Page 6163 further states, "The response time of the inlet configuration is important for e.g., the interpretation of the correlation between ozone and NOy, because of the strong layering observed ... and in particular the fast transitions observed when the aircraft cross the tropopause." The authors also note that HNO3 makes up 90% of stratospheric NOy, and rapid changes in NOy are common at MOZAIC flight altitudes. However, no discussion of the minimum recommended NOy data interval are included. Under those cases (Common? Rare?) where HNO3 is only a small fraction of NOy, the time response seems to be sufficient to report 4s data, as noted. Unfortunately, with variable composition of NOy it will be very difficult to quantify what time interval represents independent measurements if, a full minute after a change in UT/LS HNO3 concentration, the instrument has not yet reached a single e-folding time.

In those cases, it may be difficult to quantify the reported value for ambient NOy with any confidence. Can these data really be used to quantify NOy distributions at high spatial resolution? At what confidence level are the shortest time response data reported, given unknown NOy compositions and therefore instrument response times? These issues should be carefully and thoroughly addressed, and recommendations developed for the use of the MOZAIC data, before the manuscript is published and the data interpreted.

Another issue involves the nearly unit response to HCN, which is not an NOy con-

ACPD

4, S2679–S2683, 2004

Interactive Comment

stituent. At times the global tropospheric background of HCN of ca. 100 pptv is equivalent to, or exceeds, the clean free tropospheric ambient NOy levels. In those cases (Rare? Common?), the MOZAIC NOy data may be biased high by a factor of two. Certainly the comparison to other NOy measurements (not included here, but in preparation by Pätz et al.) provides an external check on these data, but there will definitely be instances where the known HCN interference of 100% will strongly bias the NOy data. This issue certainly should be addressed in the present report, and quantitatively incorporated in the uncertainty analysis, before publication. CH3CN, found in biomass plumes, may also present an interference and should be mentioned as well.

Finally, in the discussion of HNO3 permeation tube data, no mention of any checks for NO and NO2 permeation is provided. The cited report by Ryerson [1999] mentions that up to 30% of the NOy signal from a HNO3 permeation tube was due to co-permeation of NO and NO2. If either of these two species were also emitted in the MOZAIC instrument tests, an artificially high HNO3 conversion would be calculated, but ambient conversion would be proportionally lower. Were NO and NO2 permeation rates checked from the permeation tubes used here? Was co-permeation of other NOy species accounted for? Please discuss.

This manuscript should make a good contribution to ACP once the authors have discussed data usage and HNO3 permeation tube results in light of these points, and addressed the minor comments given below to the editors' satisfaction.

Specific comments:

Abstract.

p. 6150: "The time response...of the instrument is $<$1 s for NO2 and 150s for HNO3, the latter being caused by memory effects in the 80 cm long inlet line." Neuman et al. (2002) cited in the reference section used a 55 cm long inlet line, with a somewhat shorter residence time, yet report a 1/e instrument response time of approx. 1s for HNO3. These two reports do not seem to be commensurate. Is it possible that factors

ACPD

4, S2679–S2683, 2004

other than the 80 cm inlet cause the 2.5-minute response time to HNO3 in the MOZAIC instrument? One interesting test would be to add HNO3 directly in front of the inlet manifold, bypassing the inlet line, and see how much of the time constant remains. Have the authors tried thermostating the inlet line at higher temperatures to see if that improves the HNO3 transmission time? (See later comments, below).

The NOy instrument.

p. 6152, line 18: "...NO is oxidized to about 90%..." If this were correct, wouldn't there be a 10% bias in all the NO and NOy data as a result of incomplete zeroing of ambient signal in the pre-reactor? Most pre-reactor volumes are sized to give nearly complete reduction, $>$99%, of the ambient signal. Please check this number, and justify if correct.

p. 6152, line 19: "...whereas the concentration of olefins..." Ozone-olefin reactions emit primarily in the blue region of the spectrum, and are efficiently discriminated against by the use of the RG-610 filter in front of the PMT; these reactions likely do not contribute to the background PMT signal in the absence of NO.

p. 6156, line 21: "...which contains ports for the addition of zero air..." according to the text elsewhere, and to the schematic in Figure 1, oxygen is added through this port. Please also amend Figure 4 accordingly.

p. 6162, line 3: For the tests of HNO3 conversion, was the possibility of co-permeation of other NOy species (e.g., NO and NO2; see Ryerson et al., 1999, cited in the references) observed? This eventuality could account for some or all of the 15% discrepancy alluded to in the Pätz et al. report between MOZAIC and NOy data from other research aircraft. Please include this information here.

Table.

The time constant for HNO3 of 20s given here is different than the 150s given in the text and in Figure 10.

Figures.

ACPD

4, S2679–S2683, 2004

Interactive Comment

Figure 6. The text suggests the NOy inlet line was heated to 20 degrees C up to the inlet tip. The 20 C number is above, but relatively close to the 10 degrees C minimum temperature recommended by Neuman et al. [1999] in the cited reference for HNO3 transmission through Teflon tubing. Given the differences noted between this instrument and the Neuman et al. [2002] time responses (150s vs. 1s, respectively), is it possible that a higher inlet line temperature might substantially improve the MOZAIC instrument time response? Neuman et al. [2002] report using 50 C for their inlet temperature and show a much more rapid response time.

Figure 7. Please label the y-axis. These data are described as “raw data” in the caption. However, the text mentions a 200 cps background count rate, but this figure shows the zero mode average at zero. Has a background been subtracted from these data? Are these “raw” data really presented as mixing ratios?

Figure 8. Please label the y-axis. This figure may be hard to decipher for the 10% of the population that have difficulty distinguishing color differences; perhaps use vertical bars to distinguish transitions between modes?. The distinction between NOy and NO zero air mode is not clear; both are in pink. The time constant to attain a stable instrument response after initiating the zero air mode is interesting, and appears to be the 150-s time constant for HNO3 response evaluated in zero air in the laboratory for the instrument. This might be useful information derived from ambient data that the authors might want to present in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6149, 2004.