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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 and detailed review which greatly helped to improve the manuscript. Our answers are given below the questions/comments.

Although the detailed description of both instruments might be given in other publications, the reader of this manuscript must get all the necessary information to judge the statements and conclusions of this manuscript. This information is sometimes missing. E.g.: What is the detection limit of the both instruments? This important information is not given!

Answer: A summary of the main characteristics and performance of the two instruments, including detection limits, is now given in Table 1.

652, 9: What is meant by "a conversion efficiency of $>$ 95 % for NO2 and HNO3 at all altitudes encountered"? Is this valid for all flights with this instrument or just for the intercomparison flight? In the referred manuscript of Volz-Thomas it is stated that the HNO3 conversion efficiency is only tested in the laboratory. The above given quotation of your present manuscript gives the impression that the conversion efficiency was tested during flight (at all altitudes). This information is misleading.

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: "During MOZAIC operation, the gold converter usually had a conversion efficiency of $>$ 95% for NO2 and HNO3. Other than for the ETHZ instrument (see section 2.2), the conversion 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.

652,13: Although this information is given later in the manuscript: For better understanding I would recommend to mention already here that the same inlet was used during the intercomparison as during the MOZAIC flights.

Answer: Is now included.

652, 22: Please give an explanation why the FZJ - instrument does not show a pressure dependence of the conversion efficiency while the ETHZ instrument does.

See answer to comment 652,9

652, 26: In 652,9 the conversion efficiency is given as "$>$95 %", in this sentence it is "$>$92 %".

Answer: We clarify this part as follows (see also 652,9 above): "The sensitivity for NO remained constant at 460 +- 18 cps/ppb and the conversion efficiency for NO2, as

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determined by gas phase titration of the NO by O3 was 92 +- 4 % (2 sigma), which is somewhat lower than normally observed in MOZAIC."

653, 5: For the sake of clarity the authors should be more accurate in definitions and terminology. There might be readers who are not deeply involved in this technique. Your usage of “zeros” is not unambiguous. You are writing about “automatic zeros” (“Ozone - zeros”?), “zero air measurements”, “zero-signals” Please be more precise in distinguishing between these two “zeros”.

Answer: We changed the definitions for CLD-zero and NOy-background (fake-NOy) in order to make it clearer.

653,4: Why do you use oxygen for the background determination. From some own measurements performed a long time ago it seemed that the background is not the same using oxygen or purified air for example. Can you please comment on this.

Answer: Oxygen is used in MOZAIC operation because zero air would have required another gas cylinder or a pump plus gas purifier, whereas O2 is present anyway (see Volz-Thomas et al., 2005). Our own tests showed a $<$ 5% change in sensitivity for NO when using oxygen instead of air, but no difference in the CLD-zeros. The 5% difference is taken into account in the calculation of the NOy background albeit insignificant given the large uncertainty of the background.

653,5: This paper is meant to demonstrate the quality of the data obtained during MOZAIC. The reader is therefore interested to read in this manuscript at least some sentences about the calibration procedure during the MOZAIC project. E.g. how often is this instrument calibrated and checked out during a typical operation phase aboard the civil aircraft?

Answer: We started with 3 calibrations (each for NO and NO2) and 3 background determinations in the beginning of MOZAIC operation and later reduced the frequency to 2 and finally 1 per flight. This information will be presented in the forthcoming MOZAIC

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data paper, as it is of relevance to the discussion of the MOZAIC data but not to the intercomparison.

653,18: In the manuscript is written that the instrument was calibrated before and after the flight. But for the determination of the background value (150 pptv) only the value obtained before the flight was taken into account. What is the reason that you only took the value obtained before the flight and not after the flight or a mean of both? As far as I understood only the background determinations obtained during the flight were affected by memory effects.

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 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)."

653,25: Although the incorporation of a formula for the calculation of the uncertainty

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might be of some value (or not) it is rather uncommon to mix parameters (as NOy) and numbers (50, 100). If you want to include this formula you should choose a parameter describing the uncertainty of you background and precision. Additionally it is not clear whether the “0.03” or the “50” in this formula stands for the precision. I guess “0.06” stands for the uncertainty of the sensitivity estimation, please clarify. Which part of this formula addresses the uncertainty of the conversion efficiecy? By and large this formula is not very clear and must be improved. And after all: Usually the readers might not have a pocket calculator with them while reading the paper. Please “help” the readers and calculate your uncertainty “DNOy” for typical concentrations like 300 and 3000 pptv (this is the range of observed concentrations as you have mentioned before). In fact this should be as a matter of course. If I understood your formula in the right way the respective uncertainties would be 114 and 230 pptv (for 300 and 3000 pptv), respectively in absolute values and 38 % and 7.7 % in relative values.

Answer: We changed the formula as suggested and added the uncertainties for 300 and 3000 ppt in Table 1, both in terms of ppt and %. We also revised the text (see also other reviewers’ requests): "The statistical (2 sigma) precision of an individual 1 s data point was PA = +-50ppt at the detection limit and PR = +-5% at the highest NOy concentrations observed. The overall (2 sigma) uncertainty DNOY (in units of ppt) of an individual 1s NOy-measurement was estimated by error propagation (equation 1), including the uncertainties in calibration and conversion efficiency, UCAL = +-6.5% and in the instrumental background, UB = +-100 ppt (all 2 sigma) to

(1) DNOY = +-sqrt((PRˆ2+ UCALˆ2)*MNOYˆ2 + PAˆ2 + UBˆ2)

with MNOY being the NOy mixing ratio in ppt (cf., [Volz-Thomas et al., 2005]). Values for DNOY are given in Table 1 for NOy ambient mixing ratios of 300 and 3000 ppt. Except for the highest mixing ratios, the overall uncertainty is dominated by the uncertainty in the background. Potential errors of 2 % in the absolute value of the master NO standard are neglected for the instrument comparison because of the excellent agreement with the master standard of ETHZ ($<$ 0.5 %). We like to note that the performance

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of the instrument in terms of sensitivity, background signal and conversion efficiency was comparable to that achieved during routine operation in MOZAIC."

These values bring me back to your statement in 650, 14 “the measurements agreed within 6 % i.e. with the combined uncertainty of the two instruments.” This seems to be not correct. As following your formula and taking the highest values observed during the intercomparison of 3000 pptv (650,12) the accuracy of your intercomparison could not be better than 7.7 % (and would be worse for lower concentrations). As you well know the uncertainty of your measurement depends on the actual ambient NOy concentration. Therefore it is not correct to mention an uncertainty value without adding the concentration at which this value is appropriate. To increase the delight of the people reading your manuscript please add at least one table summarizing the different uncertainty sources and values for both instruments and the accuracy of both instruments for 300 and 3000 pptv.

Answer: The statement that the two measurements agreed within 6% (7% when considering levels only) refers to the slope of the regression line in Figure 6 (see below). The 7% deviation from a slope of one is well within the combined uncertainty of the calibration of both instruments, as we now point out more clearly. We like to note that the error propagation for ETHZ is now harmonised with that of FZJ, using a similar equation and including the uncertainty in the background:

655,25: For the FZJ instrument the determination of the “fake NOy” was described. This information is missing for the ETHZ instrument. When was the “fake NOy” signal determined? During the flight? Before and/or after the flight? How was it determined? Also no uncertainty of the fake-NOy determination is given at that point. For the sake of consistency these information should be added to really allow a comparison between the two instruments.

Answer: The following text is added: "Besides the zero signal of the CLDs, which is regularly determined and subtracted in all three channels, an additional background of

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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."

656,5: Again, as mentioned earlier the pressure dependence of the conversion efficiency of NOy converter is well known and can be assessed by theory (e.g. Murphy and Fahey, 1987). Residence time inside the converter and quality of the converter itself influence this dependency.

Answer: We added the reference as suggested. Of course, a significant pressure dependence is only observed for converters which have a length very close to the theoretical limit. The MOZAIC converter has about twice that length and thus doesn’t show a pressure dependence, as is stated in the paper.

656, 14: In the manuscript it is stated that the application of an erroneous pressure dependence leads to an underestimation of the NOy signal by 30 %. I am not sure whether I understand this statement correct. Applying no pressure correction at all would give a conversion efficiency of 98 % for an ambient pressure of 170 hPa. This would not lead to a deviation of 30 % compared to the correct conversion efficiency of 92 %. The deviation would be in the order of about 6 %. Could you please explain more precisely the deviation observed with and without correct application of the pressure dependence of the conversion efficiency?

Answer: The erroneous pressure dependence would have led to an overestimation, not to an underestimation of the NOy mixing ratio. We added the following sentence to page 656 line 11 to clarify this point: "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

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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 overestimation 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."

656, 15:Can you give an explanation for the differences of the two instruments with respect to the HCN conversion efficiency. Is the difference just caused by the different reducing agent (CO vs. H2)? What about other NOy instruments?

Answer: The difference is discussed in detail by Volz-Thomas et al. (see Fig 9 and related text): Briefly, we have tested the conversion of HCN for the MOZAIC converter using H2 and CO. With CO, conversion of HCN requires much higher temperatures than with H2. Kliner et al. (199) also found a larger HCN conversion with H2 as reducing agent.

657, 3:As already mentioned above: Please give numbers for 300 and 3000 pptv. And please be also more accurate when using a formula. “[NOy]”: I guess the respective unit is pptv. So please add this information. Table! With the help of your formula the accuracy at 300 and 3000 pptv would be about 49 and 389 pptv in absolute numbers. This would lead to an accuracy in per cent of 16 % and 13 %, respectively.

Answer: We change the equation and add a Table as requested comparing the numbers for both instruments. The total 2-sigma uncertainty from equation (1) above is +-114ppt (38%) at 300ppt and +-270ppt (9%) at 3000 ppt for the MOZAIC instrument. The uncertainties for ETHZ are +-63ppt (21%) at 300ppt and +-381ppt (12.7%) at 3000ppt. The uncertainties are dominated by the uncertainty in the NOy-background for 300ppt and by the calibration at 3000 ppt.

659,13:In the manuscript is written that three ensembles of data are not included in the linear fit because they would cause a deviation from the average correlation. How do you justify this special treatment of these data point? How would the correlation

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coefficient look like if you included these data ensemble to the linear fit?

Answer: The data are excluded because they are potentially influenced by memory effects. AS we show more clearly now, the fit for all data (nothing excluded) gives almost the same slope as the fit where only data from level flights are included and where the first 5 min after background determinations are excluded. This was solely done to give a better constraint to the deviation in the slope of the regression. We have made this point clearer and highlighted the data in question more clearly in Figure 6, which now contains two panels. The new text for Figure 5 and 6 is: "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 back-flushed 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.

Figure 6 shows a scatter diagram of the simultaneous NOy measurements (1s averages) made by the two instruments. The colour coding refers to the different flight sections indicated in Figur 5a. Data obtained after periods of zero air measurements are marked black for MOZAIC and blue for ETHZ. A linear fit to all data (panel a) considering errors in both axis gives a slope (FZJ/ETHZ) of (0.940+- 0.001), an intercept

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of (17 +- 2 ppt), and a correlation coefficient of R = 0.969. The scatter is dominated by the random noise of the MOZAIC instrument. Figure 6b shows the same scatter plot for the data remaining after excluding flight sections where the aircraft changed altitude (grey data points) and the data from the first 5 min after zero air measurements in either instrument (black and blue data points). As seen from the linear fit, the thus selected data set exhibits a better correlation (R = 0.983). The slope becomes slightly lower (0.93 +- 0.001) and the intercept larger (43 +- 3 ppt).

New caption of Figure 6:

Figure 6. Correlation between the NOy-data by ETHZ and FZJ (1 s averages). The colour coding corresponds to the flight segments highlighted in Figure 5. Panel a shows all data. Panel b includes only data that are least affected by memory by excluding profiles (grey points) and the first 5 min after background determinations (black and red points in panel a). The dotted lines indicate the one to one correspondence and the solid lines are linear fits to the data including errors in x and y. The fit for all data (panel a) yields: FZJ-NOy = (0.94 +- 0.002) ETHZ-NOy + (17 +- 2) ppt; R = 0.969 The fit for the data in panel b yields: FZJ-NOy = (0.93 +- 0.001) ETHZ-NOy + (43 +- 3) ppt; R = 0.983.

659, 16: During the discussion of the accuracies of both instruments 2-sigma levels have been introduced. Now the authors changed to one sigma-level. This is misleading. Please keep to the 2-sigma level. And again: As the accuracy of the measurements of each of the instruments crucially depends on the ambient NOy concentration it does not make any sense to speak about a combined inaccuracy of both instruments as long as the ambient concentration is not mentioned. And what is even more important: The main purpose of this intercomparison exercise is to demonstrate that the MOZAIC data set is, despite the strong restrictions caused by the long term use on a civil aircraft, of such high quality that it can be used for further analysis and study. So the important question is: What are typical concentrations observed on the MOZAIC flights in the upper troposphere, in the lowermost stratosphere? There is no doubt that

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the combined uncertainties of your measurements are reasonable well at high stratospheric concentrations. But what about more or less typical upper tropospheric values with a NOy concentration level of 300 pptv? At this concentration level your given accuracies are 38 % and 16 %, respectively. Could you please comment on the accuracy of your upper tropospheric measurements and its implication for this intercomparison?

Answer: We add a statement on the fraction of NOy measurements above 3.5 ppb and below 300 ppb in the MOZAIC data, in order to comment on this point at the end of the section Discussion and Conclusions: "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."

As the stated uncertainty of the MOZAIC instrument as given in Volz-Thomas et al. (2005) is confirmed by the comparison, this is not an issue of this paper, but will be brought up in the forthcoming MOZAIC data paper, of course.

660, 8-23: Obviously, it is legitimate to think about the reasons for the deviations between the two measurements. But, taking you accuracy treatment seriously, even at 3000 pptv the 2-sigma inaccuracies of your instruments are 7.7 and 13 %, respecitvely. As you pointed out these inaccuracies arise from uncertainties in the calibration procedures, background, precision, etc., etc. Within the combined uncertainties your measurements compare very well. That is fine and a valuable result of your study. The deviation between the two data sets is even smaller than your given inaccuracies. So that's it! You can not you use your data to discuss or speculate on possible effects that are smaller than the accuracy of your measurements. In you manuscript you are trying to explain the difference between the two data sets by PMT temperature effects etc. That is not an appropriate discussion based on the quality of your measurements. Remember, this possible temperature effect is smaller than the accuracy of your measurement. This would be an over-interpretation of your measurements. You only could speculate about additional reasons for the deviations between your two data sets if this

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deviation was larger than the combined uncertainty of your measurements.

Answer: This is mostly agreed and the speculative part on temperature affects is removed. But we disagree that we should not discuss the implication of the small disagreement on possible losses of HNO3 in the MOZAIC inlet, a point which had been raised by Ryerson et al in conjunction with their Rosemount-based inlet (see Volz-Thomas et al., 2005). The comparison puts an upper limit on these losses. The revised discussion makes this point much more explicit, in addition to discussing the memory in both instruments.

660, 23: You did not measure the conversion efficiency during flight, so why do you believe that the conversion efficiency is reduced after zero air periods? There might also be other possibilities to explain this observation. Did you monitor the temperature of the converter? Did you study the conversion efficiency depending on temperature? Which temperature change would be necessary to explain this observation?

Answer: This discussion is indeed quite speculative and thus removed.

661, 10: As the instrument of FZJ shows a higher conversion efficiency towards HCN (100 % ?) the FZJ-NOy signal is expected to be higher than the ETHZ-NOy by about 100 pptv. But this seems not to be the case looking at figures 5 and 7.

Answer: The zero offset of the linear fit in Figure 6b is 43ppt. Albeit this offset is not significant in view of the uncertainty of the NOy background in both instruments, we state in the revised text that this could be due to HCN: "[Singh et al., 2003] found HCN mixing ratios in background air on the order of 100 ppt. Although this concentration is similar to the uncertainty arising from the NOy background in both instruments (100ppt for MOZAIC and 50 ppt for ETHZ), the small offset of 43 ppt found in the correlation between the two datasets (see Figure 6b) could actually be indicative of the different response of the two instruments to HCN."

661, 20: You are arguing that the most likely reason for the deviation between the two

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data sets at expected high HNO3 concentration levels is the HNO3 loss at the inlet. How can you exclude that this might be caused by a HNO3-conversion efficiency departing from the NO2-conversion efficiency for one or both instruments. The authors have stated before that at least for the ETHZ measurements the reproducibility of the determination of the HNO3 conversion efficiency was low. By the way: NO was also measured with the ETHZ instrument. Are these NO - measurements in accordance with the statement given in your manuscript that 90 % of the observed NOy was probably made up by HNO3. Please give the measured NO/NOy (better NOx/NOy) ratio for the stratospheric part of your intercomparison.

Answer: What we wanted to say is that the good agreement limits the potential for HNO3 losses in the MOZAIC inlet, because the two measurements agree within the stated uncertainties (7% deviation from a slope of unity as compared to a 2sigma uncertainty of 14 % in calibration). We revised the text in order to make this point clearer. The NO measurements are included in Figure 7. Overall, the NO/NOy-ratio in the stratosphere was 3-5%. The estimated NOx/NOy ratio using photostationary state calculations for clear sky is about twice as large, i.e., 6-10%.

Technical Comments: 652, 5: The unit "sccm" seems to be not complete. I guess it should be “sccm/min”?

Answer: The term "sccm" stands for standard cubic centimetres per minute and is an official unit.

652,7: The unit "ml/sccm" also looks strange. I guess it should be 90 ml or 90 sccm/min?

Answer: This was a typo and is changed to 90 sccmĚ

657, 15: For clarification please add “University of Frankfurt” to the name of U. Schmidt.

Answer: Is added.

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