Atmos. Chem. Phys. Discuss., 6, S56–S64, 2006
www.atmos-chem-phys.org/acpd/6/S56/
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.

Anonymous Referee #4

Received and published: 10 February 2006

General Comments:

The manuscript reports on an intercomparison of two in-situ NOy instruments. Both instruments were operated aboard a Learjet in April 2003 during the SPURT campaign. Both instruments are employing the same measurement technique. One of the two instruments is usually used aboard a civil aircraft within the MOZAIC project on a regular base. Therefore the report is especially useful to assess the quality of the MOZAIC NOy data obtained during several years of operation. The data obtained with the two instruments compare reasonable well. The analysis presented is a valuable contribution to the quality control of this large MOZAIC NOy data set of the UTLS region. Generally speaking the manuscript is well written and addresses a relevant scientific

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

EGU

question. Therefore it deserves publication in ACP after revisions and clarifications as pointed out in the following.

Specific Comments:

Page/line

652:

Also 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!

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.

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.

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.

ACPD

6, S56–S64, 2006

652, 26:

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

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".

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.

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?

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

ACPD

6, S56–S64, 2006

affected by memory effects.

653,25:

Although the incorporation of a formula for the calculation of the uncertainty 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.

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

ACPD

6, S56–S64, 2006

table summarizing the different uncertainty sources and values for both instruments and the accuracy of both instruments for 300 and 3000 pptv.

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.

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.

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?

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

ACPD

6, S56–S64, 2006

agent (CO vs. H2)? What about other NOy instruments?

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.

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

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

ACPD

6, S56–S64, 2006

Interactive Comment

observed on the MOZAIC flights in the upper troposphere, in the lowermost stratosphere? There is no doubt that 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?

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 deviation was larger than the combined uncertainty of your measurements.

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.

ACPD

6, S56–S64, 2006

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?

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.

661, 20:

You are arguing that the most likely reason for the deviation between the two 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.

Technical Comments:

652, 5:

The unit "sccm" seems to be not complete. I guess it should be “sccm/min”?

652,7:

The unit "ml/sscm" also looks strange. I guess it should be 90 ml or 90 sscm/min?

657, 15

ACPD

6, S56–S64, 2006

Interactive Comment

For clarification please add “University of Frankfurt” to the name of U. Schmidt.

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