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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-term in situ measurements of NO_x and NO_y at Jungfraujoch 1998–2009: time series analysis and evaluation" *by* S. Pandey Deolal et al.

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We thank the referees for their detailed evaluation and providing useful comments and suggestions.

1. The quality of the NOy measurement depends strongly on its capability to account for HNO3, which is affected by sampling line losses and the conversion efficiency of the NOy converter itself. The authors claim to address the line loss problematic by comparing their NOy measurement to a second measurement using an externally mounted converter. The comparison showed rather good agreement in the October and December, while later comparisons yielded very poor results. The authors argue that most

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likely NOx emission from a snow covered inlet tip of the external converter is responsible for the strong deviation in January/February. In the experimental section 2.2 the authors state, that the inlet line (20 cm Teflon tubing) is heated to 25_C an protected against snow and rain by a Teflon hood. So how does the inlet accumulate snow, and why only in January and February? Was there no snow fall in December? One way to address this last question would be to extend Figure 13 to the whole period. Additionally, comparing Fig. 10 and 11 it seems that the agreement between the two NOy measurements is good for high NOx/NOy ratios (e.g. most of October and December) and poor for low NOx/NOy ratios (e.g. Jan. 12 – 25).

Reply: We understand the difficulty to follow the arguments concerning snow accumulation in the inlet and therefore we attached a supplementary file with sampling inlet pictures to support the understanding of the instrument design and severe snow conditions. Yes, we do state in the experimental section 2.2 that the inlet line (20 cm Teflon tubing) was heated to 25_C and that it was protected by a Teflon hood against snow and rain. However, the heating was only applied to the Teflon tubing while the hood covering the inlet line was not heated. Unfortunately, it turned out that snow could accumulate within the hood under conditions with strong winds (depending on wind direction) moving snowflakes almost horizontally into the hood. Such conditions occurred in January and February while visual inspection in the previous months did not show such accumulation (personal communication by responsible custodians at JFJ). The NABEL inlet is in turn made of stainless steel and is heated to prevent accumulation of snow and ice under all circumstances. Note that since the NABEL inlet is shared by many instruments including a HiVol PM10 sampler, it has a much larger diameter and a very large flow (>800 liters/minute STP) is passing through which minimizes wall losses. Snow photochemistry requires a combination of snow accumulation inside the inlet and sunshine. In December, however, only few sunny days were recorded. For a better understanding we extended Figure 2 of manuscript with an additional schematic of the inlet for the situation of snow accumulation and sunlight-triggered snow photochemistry(attached Fig. 1).

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To better illustrate that the agreement between the two NOy instruments is not restricted to high NOy values we re-plotted Figure 12 of manuscript with an additional inset showing the correlation at low NOy mixing ratios up to 1 ppb. The small inset figure demonstrates that the correlation is not determined only by high NOy values but rather that the slopes are similar for low and high NOy mixing ratios (attached Fig. 2):

The result for the filtered data (black circles in Fig. 2) is NOy_Empa = (0.89 + 0.004) * NOy _ETHZ + (19 + 3) ppt , R2= 0.97 and the slope calculated only at lower NOy mixing ratios (< 1 ppb) is: NOy_Empa = (0.85 + 0.015) * NOy _ETHZ + (38 + 5) ppt , R2= 0.89

2. The authors concede that the conversion efficiency for HNO3 might differ from NO2 and that a degradation of the conversion efficiency could be more severe for HNO3. Nevertheless, all information on the quality assurance for the EMPA instrument is very limited, actually it is restricted to one sentence, indicating that the conversion efficiency of the gold EMPA converter mostly ranged between 95 and 100 %, based on NO2 measurements. I consider this as insufficient, in particular if the authors aim to address potential trends. More information (e.g. a time series) of conversion efficiencies for NO2 AND HNO3 is mandatory to judge on the data quality and exclude instrument artifacts as a potential cause for long term trends as presented in Fig.4. Also, the authors should provide details about maintenance procedures for the EMPA converter (procedure and frequency of converter cleaning). Some of those details (time series of conversion for NO2 and information on cleaning) are only provided for the ETH measurements. Without a better characterization of the EMPA NOy data quality I consider the conclusion drawn by this paper (at least for the trend analysis) as highly superficial.

Reply: Attached Figure 3 shows a time series of the gold converter efficiency determined with NO2. As mentioned in the discussion paper, the efficiency mostly ranged between 95 and 100%. If the efficiency dropped below 95%, maintenance work was undertaken. The maintenance work focused on replacement of the gold tube in the first place; other maintenance procedures included an additional replacement of the

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glass tube that houses the gold tube, the replacement of the cleaning cartridges of the CO gas, cleaning of the critical orifices and adjustment of the flows in the converter and leak tests. The blue lines in Figure 3 illustrate the changes of the gold tube by Empa technicians. The gold tube was changed about twice a year in the beginning whereas the intervals became much longer in recent years. Please take note that low and highly variable converter efficiencies could also be caused by chemiluminescence detector (CLD) problems or calibration failures. We use the same gold converter instrument since the beginning of the NOy time series whereas other parts of the Cranox system such as the calibration unit or the CLDs were replaced since then. Since 2009, Empa's NO-NOx-NOy setup runs with three CLDs (one each for NO, NOx and NOy). Remarkably stable gold converter efficiency is observed since then, providing strong evidence that a large part of the observed converter efficiency variability in the past was caused by Cranox components other than the gold converter itself. Two gold converter tubes were in use since the installation of the converter. After replacement, the tube was cleaned with ethanol, acetone and ultrapure water in the early years. Later, the gold tube was cleaned with sandpaper to remove the (possibly dirty) surface layer. Empa's Cranox setup is also serviced about once a year by the instrument manufacturer (Eco Physics) (see red lines in Fig. 3). The services on-site and/or at Eco Physics took mainly place when problems arose. In recent years, services are also performed preventively in regular intervals. The services seldom targeted the gold converter but mostly other parts of the Cranox setup. Please see reply to comment 3 of reviewer # 2 for HNO3 converter efficiency.

Specific Questions:

3. In the time series of NOy it is shown that the year 2003 is exceptional, which is explained by the authors as being due to the 2003 summer heat wave, causing high pollution levels over Europe, but Figure 7 indicates that the NOy enhancement reach far into the fall and winter of this year. I have a hard time to believe that these are remnants from the 2003 summer pollution. Additionally, the authors should extend

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Figure 4 by inclusion of a NOx/NOy trace. It seems that there is a strong trend for younger air masses (higher NOx/NOy) after 2003, which might indicate a shift in local pollution or a trend in the instrument performance (e.g. decreasing HNO3 conversion).

Reply: We fully agree that the interpretation of enhanced NOy values in fall and winter 2003 is not straightforward and not necessarily related to the summer heat wave particularly winter 2003. Towards the end of the heat wave, several forest fires were reported from southern Europe including major fires from Portugal and Spain (Tressol et al.,2008; Lyamani et al. 2006) during late summer. Therefore we speculate that the autumn values of 2003 might show the influence of fire emissions and remnants of the heat wave which extended till late summer. Interpretation of the high NOy values in winter 2003 (which represents December 2002, January 2003 and February 2003 and therefore a period well before the summer heat wave) is more complicated. Several biomass burning events were also reported in fall 2002 from Eastern Europe and the European part of Russia which increased the background values of several trace gases including CO and O3 (Simmonds et al., 2005;Yurganov et al., 2005;Edwards et al., 2004) and therefore we hypothesize that the winter 2003 NOy values might have increased due to these episodes. It is evident from Figures 8 and 9 in the manuscript that NOx measurements did not show any exceptional increase in fall and winter 2003 which suggests that the high NOy values were caused by a large-scale phenomenon like long-range transport from regions of enhanced biomass burning. Air masses influenced by biomass burning are expected to be enhanced in PAN and other nitrate species (Alvarado et al., 2010) but unfortunately such speciated measurements are not available for this period.

Following the suggestion of the referee we added the time series of NOx/NOy ratios in Figure 4 of the manuscript (attached Fig. 4) which shows that there might be a slightly positive trend in this ratio since 2004 suggesting an increased contribution of fresh air masses in recent years.

4. NOx/NOy ratios would also be helpful in the discussion of the seasonal variation.

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Convective transport as a cause of higher NOy in spring and summer should be characterized by higher NOx/NOy ratios, but Figure 5 (small panel) seems to indicate quite the opposite, with lowest (oldest, most processed air) NOx/NOy ratios in summer. This is in contradiction to the statement on page 2186, line 1, that only in summer the lifetime of NOx is long enough that rapid upward transport to JFJ can generate large NOx pollution events giving rise to large NOy enhancements.

Reply: We agree that the sentence in the original manuscript was wrongly formulated. What we actually meant to say was "This indicates that except for summer the lifetime of NOx is long enough that rapid upward transport to JFJ can generate large NOx pollution events", which is in agreement with Figure 5 of manuscript(small panel). In addition, we will replace the phrase "enhanced convective upward transport" by "enhanced thermally induced transport".

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C12747/2011/acpd-11-C12747-2011-supplement.pdf

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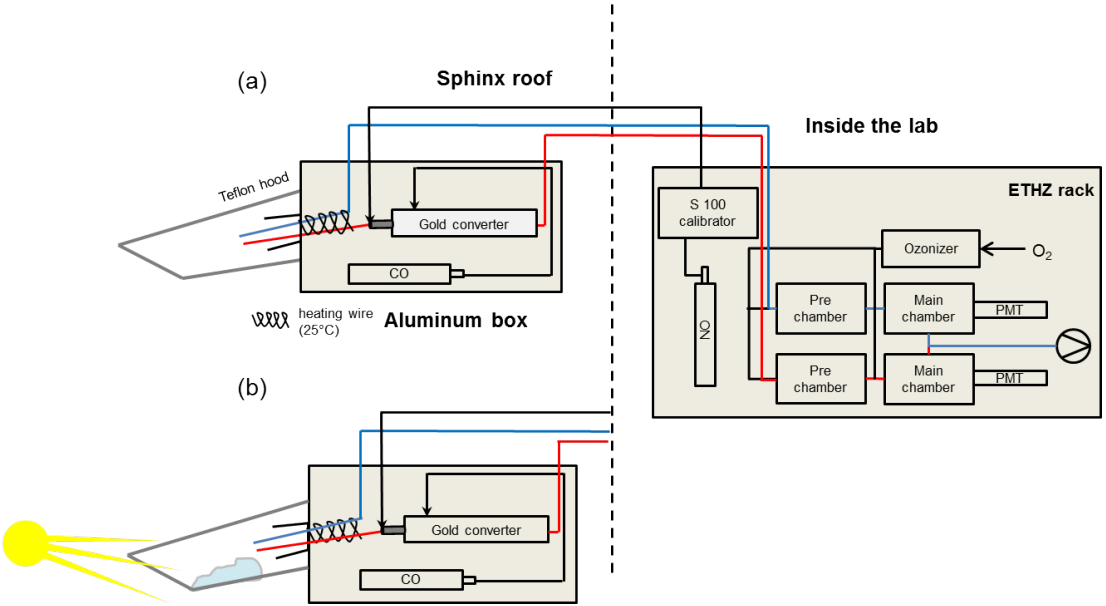

Fig. 1. Schematic of the ETHZ NOy instrument (red: NOy sampling line and blue: NO sampling line) operated during the campaign at Jungfraujoch; (panel b) ETHZ sampling inlet with snow and sunshine

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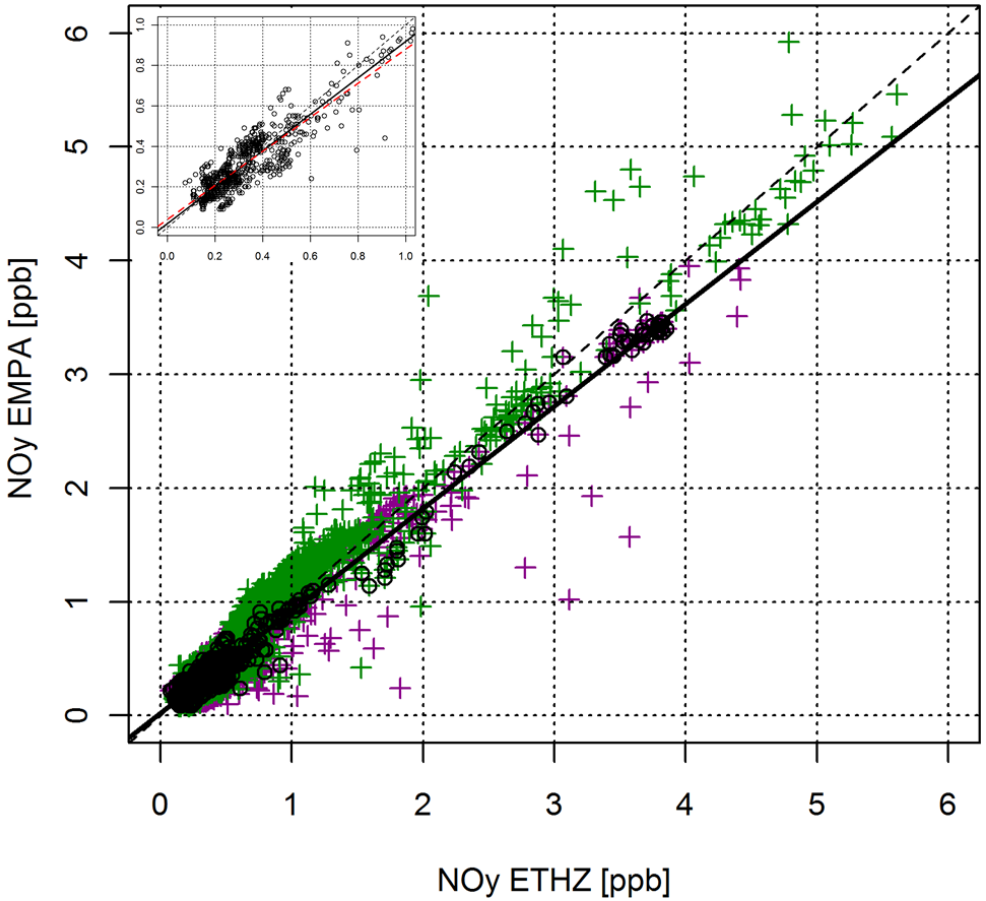

Fig. 2. Inset figure displays the same correlation of filtered dataset at lower NOy values up to 1 ppb. The red line indicates linear fit at lower mixing ratios compared to the whole filtered dataset (black)

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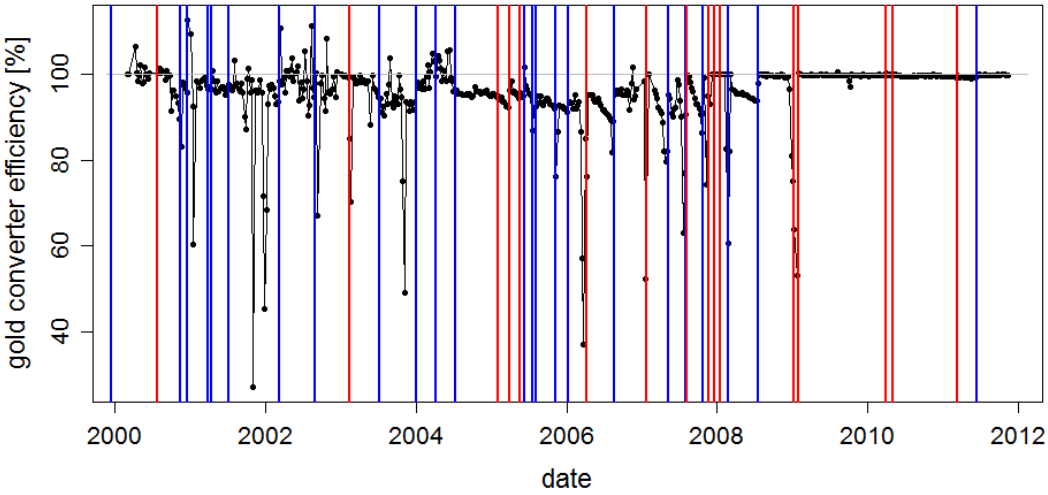

Fig. 3. Time series of converter efficiencies (black) of Empa's gold converter from 2000 till fall 2011. Blue and red lines show maintenance work by Empa technicians and instrument manufacturer respectively

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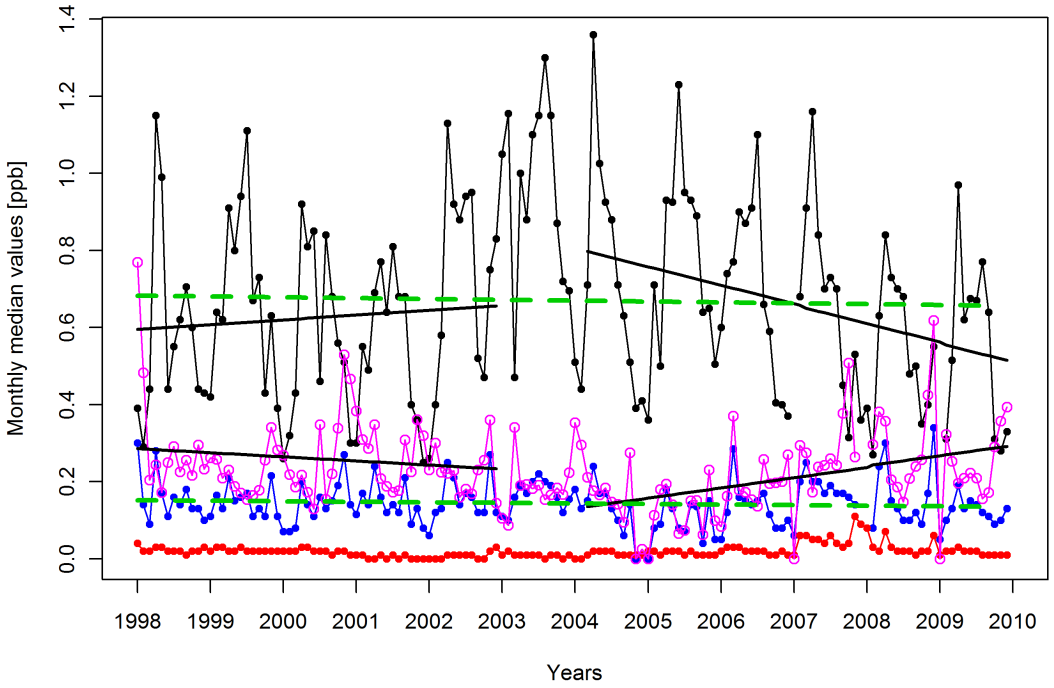

Fig. 4. Monthly median values of NOy (black), NOx (blue), NO (red) and NOx/NOy (magenta) from January 1998 - December 2009. The black thick lines are linear trends before and after 2003 in NOy and NOx/NOy

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