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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. It appears that there was no attempt to filter the data to remove the impact of either local pollution events or strong stratospheric influence. Is it possible to use concurrent measurements of O3, CO, and H2O to at the minimum comment on the possible role of stratospheric NOy? Is NOy and CO tightly correlated.

Reply: An attempt to separate local influences was made in the paper by using only nighttime data (see Figure 15 of manuscript).This efficiently filters out local influences

since thermally induced upward transport from the surrounding valleys as well as touristic impacts are expected to be minimal at nighttime. Figure 15 shows no significant differences in NOy trend between daytime and nighttime data which suggests that these local influences do not have a significant impact on the trends.

We did not try to filter out stratospheric intrusion events as we did not expect a marked influence on NOy. Note that NOy volume mixing ratios in the lowermost stratosphere are of the order of about 0.5-3 ppb (Hegglin et al., 2006) and therefore not much higher than those typically observed at Jungfraujoch. Mixing with free tropospheric air during a stratospheric intrusion event will likely further reduce these concentrations before reaching Jungfraujoch. Based on the referee's suggestion we had a closer look at stratospheric events which are best identified by a concurrent strong increase in ozone and decrease in relative humidity, but didn't observe any significant influence on NOy. As an example for the absence of clear signatures in NOy the stratospheric intrusion of 25 July 2007 is shown in attached Fig. 1.

2. Diurnal (or rather diel) profile in NOy: Does NOy display a strong diel profile? In the free troposphere (unperturbed by local emissions of recent convective activity), I would expect NOy to be relatively constant. This could be an indicator of the impact of local emissions.

Reply: The influence of upward transport from the PBL on diurnal cycles in air pollutant concentrations (e.g. CO) and aerosol parameters at Jungfraujoch has been investigated and documented in numerous previous studies (Baltensperger et al., 1997;Nyeki et al., 1998). A common feature is a more or less pronounced diurnal cycle in all months except winter with maximum PBL influence in the late afternoon around 18:00 local time. The influence depends on weather conditions and is most pronounced during summer under sunny convective conditions. NOy is no exception to this general behavior. This is also the reason why in Figure 15 of manuscript we compared the long-term evolution of NOy for daytime and nighttime measurements separately, since nighttime observations are more representative of free-tropospheric conditions.

3. Inlet characterization: It is hard to imagine high transmission of HNO3 through 1m 3/16 ID PFA. Have the authors directly characterized the transmission efficiency of this inlet, through standard additions to the inlet tip? A comparison of NOy between two instruments does not provide us any information on the transmission efficiency of HNO3 or other sticky compounds, as the slope is weighted heavily by the high NOy points that likely have higher NOx/NOy? What does a comparison of NOz look like? Does the 10C heating refer to 10C over ambient, or is the inlet temperature controlled to a constant 10C. In either case, I would suspect that HO2NO2 or CH3O2NO2 may play an important role in the NOy budget in these air masses. Due their thermal instability, I suspect that they might be included in NOx?

Reply: Unfortunately, no systematic study was performed to quantify the losses of various NOy species in the whole inlet system upstream of the gold converter. Due to the high flow rates of more than 800 l / min it is impossible to do so. The losses of HNO3 in the PFA tube are estimated to be within the overall measurement uncertainty. Neuman et al. (1999) performed a comprehensive study on HNO3 transmission rates for various tubing materials. They reported HNO3 losses of < 5% for a PFA tubing of 30cm length and similar ID and flow rate as used at Jungfraujoch. Empa's main inlet manifold is temperature controlled such that the air temperature measured at one of the ports for the individual instruments (see Fig. 1 of the manuscript) is at constant 10°C.

Fahey et al. (1985) showed conversion efficiencies for a gold converter for both NO2 and HNO3 as a function of temperature in Figure 4 in their publication. Conversion efficiency for HNO3 was somewhat lower than that for NO2 but still above 90% (between 90 and 95%) at similar conditions to our measurement sampling system at Jungfraujoch (1 slpm sample flow, pressure = 623 Torr). Bollinger et al. (1983) reported quite similar conversion fractions for NO2 and HNO3 (even higher for HNO3) at a temperature of 300oC on the gold surface.

Fahey et al. (1985) also investigated the influence of long PFA tubings on NOy losses

using a setup with two parallel converters with and without the PFA tubing upstream of the converter. For a tubing as long as 4.9 m they reported an overall reduction in NOy by only about 10% but a strong decrease in instrument response. The main effect of a long PFA tubing is thus an attenuation of concentration fluctuations and delayed response rather than a complete loss of HNO3 and other NOy components.

Since the ETHZ instrument did not measure NO2 or NOx it is not possible to compare the NOz correlation. However, we added an inset figure to Figure 12 showing the correlation between the two instruments at low NOy mixing ratios below 1 ppb (See our reply to comment 1 referee # 1). The inset figure clearly shows that the slope is not biased by the high NOy values but also holds for low concentrations. We agree that thermal dissociation of HO2NO2 or CH3O2NO2 can potentially bias the NOx measurements (more specifically the NO2 measurement). Mixing ratios of these species have been reported to be in the range of 10 - 15 ppt in the remote atmosphere by Browne et al. (2011) and Kim et al. (2007). Therefore, we assume that interferences from these species have only a minor effect on NOx mixing ratios at JFJ. As mentioned above, the Empa inlet is heated in such a way that the temperature of the sampling air inside the inlet is maintained at a temperature of 10°C (absolute). It should be noted that due to the high flow rate of > 800 l/min the residence time in the 2 m long heated inlet system is less than 2 s (and even shorter in the PFA tube that directs from the main inlet to the photolytic converter) and thus much shorter than the thermal lifetime of HO2NO2 at 10°C (which is more than a minute).

4. Utility of NOx/NOy measurement: The NOx/NOy measurement is a tremendously useful metric for the age of air in the free troposphere. It would be particularly interesting to investigate this parameter in more detail: i) is there a strong diel profile, ii) can PBL influenced airmasses be removed to investigate seasonal variation in NOx/NOy and the role of convection.

Reply: We agree that the ratio NOx/NOy is a very useful measure to asses the photochemical age of the air masses and therefore a good parameter for distinguishing be-

tween freshly polluted and aged air masses. An attempt to minimizing the contribution from PBL influenced air was already made in the manuscript showing nighttime data of NOy and NOx in Figure 15 of manuscript which is mostly representative of background conditions as thermally induced upward transport from the PBL and touristic impacts are expected to be minimal at nighttime. These nighttime measurements do not show any significant effect on long-term trends. Following the suggestion of both referees for using NOx/NOy as an indicator we added the time series of NOx/NOy ratios to Fig. 4 in the manuscript (please also see our reply to comment 3 of referee #1). This shows the long-term evolution of the ratio NOx/NOy as a measure for changes in photochemical age of air masses reaching Jungfraujoch.

As mentioned in our response to point 2 above, NOy shows a clear diurnal cycle in most months except winter. The ratio of NOx/NOy, in contrast, does not exhibit a clear diurnal cycle and we attribute this to two compensating effects: strong upward transport of PBL air to Jungfraujoch mostly occurs on sunny convective days which is exactly those days when photochemistry is most active and NOx lifetime therefore particularly short. Note also that the NOx lifetime is much shorter in summer compared to winter as shown in Figure 5 of manuscript (small panel) of the manuscript. In the warm season when the PBL influence is expected to be largest, the NOx/NOy ratio is smallest due to rapid photochemical depletion of NOx. Therefore, despite low NOx/NOy ratios air masses in spring and summer can often not be interpreted as FT air masses. This demonstrates the problem of using NOx/NOy for a separation between PBL and FT air masses for the JFJ site which intermittently resides in the PBL and FT.

5. Snow photochemistry: Unless the section on snow photochemistry is used to discuss potential artifacts on the NOy measurements, it reads as an aside and does not contribute to the paper. It is also unclear how the ETHZ inlet is buried in the snow? Is it submersed, or close to the snow? It is hard to imagine snow in the inlet if it is heated to 25C?

Reply: We agree, that the explanation of the sampling design of the ETHZ NOy in-

strument in the manuscript was not clear enough. Therefore we modified Figure 2 of manuscript to show the situation when the inlet is affected by snow accumulation. Please refer to comment 1 made by referee #1 and see inlet pictures provided in the supplementary file.

The ETHZ instrument was installed at JFJ to compare the NOy instrument of Empa with measurements from an independent instrument with separate inlet. We found generally a reasonably good agreement, but during particular conditions significant deviations were observed between the two instruments, which we attributed to snow photochemistry in the ETHZ sampling inlet. Several previous studies already indicated that heterogeneous photochemistry on snow could significantly alter the chemical composition of air masses (Grannas et al., 2007;Honrath et al., 1999;Domine and Shepson, 2002). Since our experiment did not aim to study snow photochemistry so we do not have sufficient information to quantify the effects of photochemistry on the snow surfaces surrounding Jungfraujoch on the NOy measurements. Nevertheless, we try to provide a rough estimate of how much NOy enhancement could potentially be observed at Empa's inlet ($\sim$150 m above the glacier surface) using certain assumptions such as the amount of time the sampled air was in contact with a snow-covered surface and the depth of the atmospheric boundary layer in contact with the surface. Please note, these estimates only aims to demonstrate that snow photochemistry is potentially important but do not provide a robust quantitative estimate of the effect due to several uncertain assumptions, therefore we are not intending to include these estimates in the manuscript.

Assumptions:

R = 1 L/min Sampling flow rate C = 1.5 ppb Concentration enhancement between ETHZ and Empa deduced from measurements (from Fig. 13 of manuscript) dt = 6 hrs Duration of enhancement H = 1 km Boundary layer height A = 100 cm2 Surface area of snow in the ETHZ inlet

Then the signal at EMPA's inlet should be:

R * dt * C / (A * H) = 0.05 ppb

Two assumptions used above might bias the result

the sampling inlet has an inner diameter of $\sim$ 10 cm, and the snow could be creeping into it by maybe 10 cm, resulting in the 100 cm2. This might vary anything between 10-500 cm2. The surface area of snow in the inlet of 100 cm2 might be an overestimate/underestimate.

we assume that the NOy exhaled by the snow fields is instantaneously mixed into the entire BL assumed to be 1 km thick. The assumption that all snow in the inlet is exposed to the sun, on the other hand, might bias the result to the high side.

We believe that this section points towards an important question whether snow photochemistry could significantly impact the measurements at high alpine sites such as Jungfraujoch which is snow-covered all year-round. Therefore, a detailed study focusing on this issue would be helpful to confirm our results.

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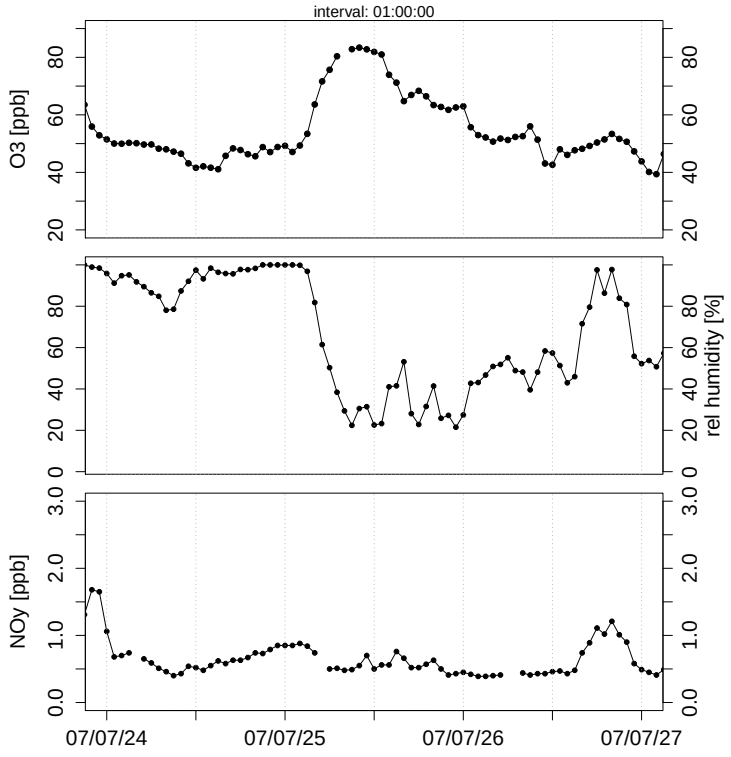

Fig. 1. Stratospheric event on 25 July 2007 based on the trace gas analysis (not to be included in the manuscript)