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In-situ comparison of the NO_y instruments flown in MOZAIC and SPURT

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Abstract. Two aircraft instruments for the measurement of total odd nitrogen (NO_y) were compared side by side aboard a Learjet A35 in April 2003 during a campaign of the AFO2000 project SPURT (Spurengastransport in der Tropopausenregion). The instruments albeit employing the same measurement principle (gold converter and chemiluminescence) had different inlet configurations. The ECO-Physics instrument operated by ETH-Zürich in SPURT had the gold converter mounted outside the aircraft, whereas the instrument operated by FZ-Jülich in the European project MOZAIC III (Measurements of ozone, water vapour, carbon monoxide and nitrogen oxides aboard Airbus A340 in-service aircraft) employed a Rosemount probe with 80 cm of FEP-tubing connecting the inlet to the gold converter. The NO_y concentrations during the flight ranged between 0.3 and 3 ppb. The two data sets were compared in a blind fashion and each team followed its normal operating procedures. On average, the measurements agreed within 7%, i.e. within the combined uncertainty of the two instruments. This puts an upper limit on potential losses of HNO_3 in the Rosemount inlet of the MOZAIC instrument. Larger transient deviations were observed during periods after calibrations and when the aircraft entered the stratosphere. The time lag of the MOZAIC instrument observed in these instances is in accordance with the time constant of the MOZAIC inlet line determined in the laboratory for HNO_3.

1 Introduction

Airborne measurements are the only means of obtaining highly resolved information on the distribution of reactive nitrogen compounds in the upper troposphere and lower stratosphere. NO and NO_2 are key in controlling the concentration of the OH radical and ozone formation (Crutzen, 1979), whereas measurements of total odd-nitrogen (NO_y, i.e., the sum of NO and its atmospheric oxidation products) have proven useful for studying transport processes and the budget of odd-nitrogen in the troposphere and stratosphere (Keim et al., 1997, and references therein). The measurement technique for NO_y (i.e., catalytic reduction to NO on a hot gold surface followed by chemiluminescence detection of the NO) was pioneered by Bollinger et al. (1983); Fahey et al. (1985). Since then, a large number of ground-based and airborne data sets have been collected. In the course of the interpretation of such measurements, the quality of NO_y measurements using different kinds of catalytic converters operated under different conditions was called into question (cf. Crosley, 1996; Brough et al., 2003, and references therein). Potential problems were found with interferences by non-NO_y compounds, e.g. HCN and CH_3CN, and with the inlet configuration in terms of time response or memory, the sampling efficiency for aerosol, and the transmission of HNO_3 (cf. Ryerson et al., 1999), which constitutes the major fraction of NO_y in the lower stratosphere (Neuman et al., 2001). Regular instrument comparisons are therefore indispensable for assessing the data quality.

Such comparisons are even more important for the NO_y-instrument deployed in MOZAIC aboard an in-service aircraft of Deutsche Lufthansa in autonomous operation since 2001 (Volz-Thomas et al., 2005). Meanwhile, this instrument has been deployed on more than 2000 long-haul flights collecting more than 15 000 h of NO_y data. In order to assess the data quality of the MOZAIC instrument and to identify potential problems with the inlet configuration, which is sub-optimal because of the certification requirements on passenger aircraft, a blind comparison was conducted between the MOZAIC instrument and a research instrument operated by ETH-Zürich (ETHZ) aboard a research aircraft during the last six of eight measurements campaigns in the framework of the German SPURT project (Engel et al., 2006). The

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Table 1. Summary of the main characteristics and performance of the two instruments. All errors and detection limits are 2σ.

	FZJ-Instrument	ETH Instrument
Manufacturer	FZJ	ECO-Physics, Dürnten, CH
Model	MOZAIC	3-channel CLD 790 SR
Weight	35 kg	96 kg
Sample flow rate	0.1 slm	1.2 slm (per channel)
Converter, T, Reducing agent	Gold tube, 300°C, H_2 (0.2 sccm)	Gold tube, T=300°C, CO (5 sccm)
Inlet	Rosemount housing, 80 cm 1/8″ FEP tube (>20°C)	Converter mounted outside fuselage, backward sampling, no inlet line
Sensitivity NO_y channel	0.46 cps/ppt	24 cps/ppt
Sensitivity NO channel	–	21 cps/ppt
Sensitivity O_3channel	–	0.58 cps/ppt
CLD zero signal:	<200 cps	<1000 cps
NO_y background (fake NO_y)	150±100 ppt	105±50 ppt
Data Acquisition rate	10 Hz	1 Hz
Time resolution	0.2 s (NO, NO_2), 120 s (HNO_3)	0.1 s (NO)
Detection limit NO_y	100 ppt	51 ppt
Detection limit NO	–	10 ppt
Detection limit O_3	–	160 ppt
Precision at 300 ppt NO_y	±52 ppt (17.3%)	±11 ppt (3.7%)
Precision at 3000 ppt NO_y:	±158 ppt (5.3%)	±11 ppt (0.4%)
Total uncertainty at 300 ppt NO_y	±114 ppt (38%)	±63 ppt (21%)
Total uncertainty at 3000 pptv NO_y	±270 ppt (9%)	±381 ppt (12.7%)

previous version of the ETH-instrument, which was used during the first two missions, is described in Hegglin et al. (2004). The improved sensitivity and the optimal inlet configuration of the new instrument deployed during SPURT allow for a critical evaluation of the performance of the MOZAIC instrument, including potential losses of HNO_3 in the inlet.

2 The instruments

A summary of the main characteristics and performance of the two instruments is given in Table 1.

2.1 The MOZAIC NO_y-instrument of FZJ

The MOZAIC NO_y-instrument is described in detail by Volz-Thomas et al. (2005). Briefly, the measurement principle is chemiluminescence of NO with O_3 and catalytic reduction of the different NO_y compounds to NO with H_2 (0.2 sccm) on a hot gold surface (300°C). Because of the limitations in gas supply, in particular of H_2, for long-term operation (4–7 weeks), the instrument employs a very low sample flow (90 sccm) and thus has a comparably low sensitivity of 0.4–0.7 cps/ppt. During MOZAIC operation, the gold converter usually had a conversion efficiency of >95% for NO_2 and HNO_3. Other than for the ETHZ instrument (see Sect. 2.2), the conversion efficiency of the MOZAIC converter is independent of pressure. This was verified in the laboratory, both for NO_2 and HNO_3, 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. Interferences by N_2O, NH_3, CH_3CN are negligible, whereas HCN is converted at almost 100% efficiency (Volz-Thomas et al., 2005). The converter is mounted inside the instrument and is connected via 80 cm FEP tubing (1/8″ OD) to a Rosemount Probe, which provides positive ram pressure and serves as a virtual impactor for separation of atmospheric particles. The inlet line is kept above 20°C by a heating wire. The inlet configuration during the intercomparison flight was exactly the same as in MOZAIC operation.

2.1.1 Calibration

The instrument was calibrated before and after the flight by diluting the FZJ master calibration standard (10 ppm NO in high purity N_2, Air Liquide) with NO_y-free zero air (Linde). The flow rates were measured volumetrically with an automatic soap film flow meter (Gillibrator, Gillian USA). The sensitivity for NO remained constant at 460±18 cps/ppb and the conversion efficiency for NO_2, as determined by gas phase titration of the NO by O_3 was 92±4% (2 sigma), which is somewhat lower than normally observed in MOZAIC. The overall uncertainty of the calibration from errors in the flow measurements (3%) and the uncertainty of the conversion efficiency was U_{CAL}=±6.5% (2 sigma). The conversion

efficiency for HNO_3 was determined before and after the campaign to 92±5%. During flight, the NOy-background (often denoted as fake NO_y) was determined by flushing the inlet with an excess O_2-flow, in the same way as during MOZAIC operation, whereas calibrations with NO and NO_2 were not made during the flight in order to save time for the comparison.

2.1.2 Data treatment and uncertainty assessment

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 NO_y determined from the zero air measurements (fake NO_y) 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 HNO_3 (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 NO_y concentration measured before the zero was initiated. After the flight, the background was 200±35 ppt. The memory for HNO_3 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 ±100 ppt (±67% of the background used as 2 sigma uncertainty as in MOZAIC data analysis).

The statistical (2 sigma) precision of an individual 1 s data point was P_A=±50 ppt at the detection limit and P_R=±5% at the highest NO_y concentrations observed. The overall (2 sigma) uncertainty D_{NOY} (in units of ppt) of an individual 1 s NO_y-measurement was estimated by error propagation (Eq. 1), including the uncertainties in calibration and conversion efficiency, U_{CAL}=±6.5% and in the instrumental background, U_B=±100 ppt (all 2 sigma) to

$$D_{NOY} = \pm \text{sqrt}((P_R^2 + U_{CAL}^2) \times M_{NOY}^2 + P_A^2 + U_B^2) \qquad (1)$$

with M_{NOY} being the NO_y mixing ratio in ppt (cf., Volz-Thomas et al., 2005). Values for D_{NOY} are given in Table 1 for NO_y 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 of the instrument in terms of sensitivity, background signal and conversion efficiency was comparable to that achieved during routine operation in MOZAIC.

2.2 NO_y-, NO-, and O_3-measurements by ETH Zurich

2.2.1 The ECO instrument

A commercial 3-channel chemiluminescence detector (790 SR, ECO Physics, Switzerland) for the measurements of total reactive nitrogen (NO_y), nitrogen monoxide (NO), and ozone (O_3) was implemented by ETHZ aboard the Learjet 35A aircraft for the SPURT project. A detailed description of the experimental setup can be found in Hegglin (2004). The measurement principle is based on chemiluminescence between NO and O_3. Prior to detection, the NO_y-species are reduced to NO using a heated gold-converter, controlled at a temperature of 300°C and using CO (5 sccm, 99.997%, PanGas, Switzerland) as reducing agent (Fahey et al., 1985). The converter is externally mounted on a window blank (Lange et al., 2002). This set-up ensures that the sampled air directly enters the heated gold tube in order to avoid losses of NO_y components in the inlet or other potential sampling artefacts. The NOy inlet is facing backwards. NO and O_3 are sampled through a forward facing inlet with a diameter of 6 mm mounted below the converter on the same window blank.

2.2.2 Quality assurance

Instrument sensitivities were determined before and after the flight by mixing known amounts of NO (5 sccm of 10 ppm NO in N_2) with synthetic air (1400 sccm, purity 5.0, Sauerstoffwerk Lenzburg, Switzerland). In order to maximize the overall measurement time available for comparing the two instruments, no additional in-flight calibrations were carried out. This seemed appropriate since previous SPURT campaigns showed that the sensitivity changed only by 1–3% during single flights. Nevertheless, the determination of the sensitivity added a major uncertainty to the ETHZ NO_y-measurements. The NO calibration gas used during the campaigns as working standard showed an uncertainty of ±3.7% (2 sigma) to the master standard used in the laboratory. This uncertainty originated from the applied calibration procedure. The NO calibration gas was added upstream of the converter and, therefore, NO_y-species potentially present in the working standard were also measured and contributed to the derived sensitivity. The additional signal produced by these NO_y-species, however, was detected and quantified only after the campaign leading to the high uncertainty in the concentration of the used working standard.

The efficiency of the NO_y-converter was determined by gas phase titration of NO with O_3 before and after the campaign. The conversion efficiency did not change significantly over a time of 7 days and was about 98% at ambient pressures of 960 hPa. The reduction of the efficiency at low pressures during flight is described in the next section.

The O_3-channel was calibrated against a commercial ozone calibrator (Advanced Pollution Instrumentation (API)

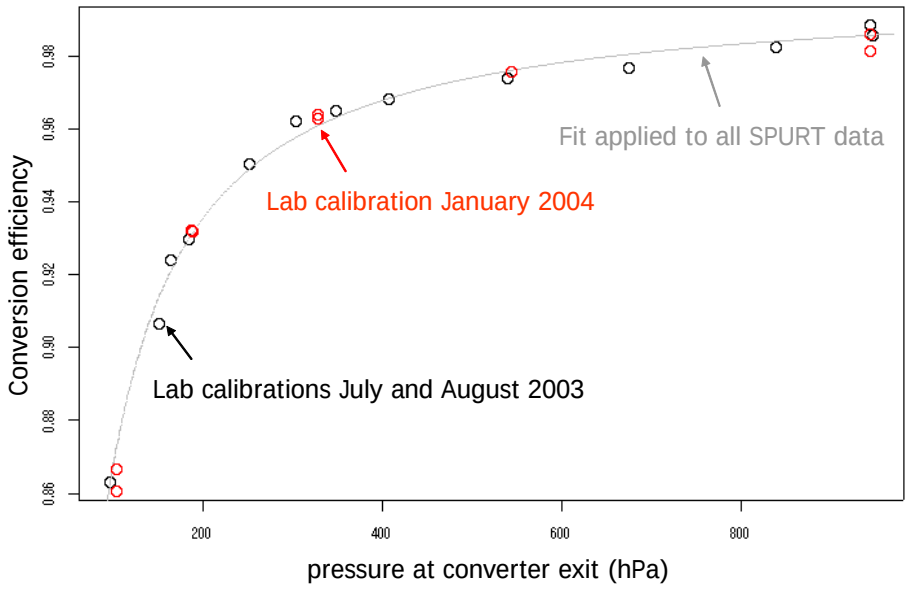

Fig. 1. Conversion efficiency of the ETHZ gold converter for NO_2 as a function of pressure.

UV photometric ozone calibrator) at the beginning and at the end of the campaign.

2.2.3 Data treatment and uncertainty assessment

The data were processed by linearly interpolating the values of the sensitivities and conversion efficiencies obtained by the calibrations of the instrument before and after the flight to each measurement point. The mean sensitivities of the NO_y-, NO-, and O_3-channel were 24.0 ± 0.12 cps ppt^{-1}, 22.4 ± 0.2 cps ppt^{-1}, and 580 ± 10 cps ppb^{-1}, respectively. Besides the zero signal of the CLDs, which is regularly determined and subtracted in all three channels, an additional background of 105 ± 50 ppt was subtracted from the NO_y measurement to account for a "fake NO_y signal", most probably produced by impurities in the CO reduction agent (Fahey et al., 1985). This fake NO_y 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.

The converter exhibits a slight dependence of the conversion efficiency on ambient pressure as reported by Lange et al. (2002). We have repeated these experiments by varying the inlet pressure in the laboratory between about 1000 and 100 hPa. As shown in Fig. 1, the conversion efficiency decreases from about 98% at sea level to 92% at a pressure of 170 hPa, in agreement with the results by Lange et al. (2002) obtained from in-flight-calibrations. The results were used to determine a pressure dependent correction factor f_c for the conversion efficiency $\varepsilon(p)=f_c(p)\times\varepsilon_0$, where $f_c(p)=1/(0.983+15.323/p-91.0481/p^2)$ as obtained from a second order polynomial fit of the inverse pressure to the inverse efficiency shown in the Fig. 1, ε_0 is the conversion efficiency at 1000 hPa, and p is the pressure inside the converter. At cruise speed this pressure is about 15 hPa lower than the static air pressure due to reverse sampling. The pressure dependence of the conversion efficiency can also be derived by using the analytical solution provided by Murphy and Fahey (1987), taking into account the specific converter characteristics.

We like to note that the initial data set submitted after the campaign to the referee (see Sect. 3) had been calculated with an erroneous pressure dependence of the conversion efficiency, that had been obtained with 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 NO_y 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 Fig. 1.

The conversion efficiency for HNO_3 was determined in laboratory experiments by Lange et al. (2002) using the same converter to be approximately the same as for NO_2. Unfortunately the reproducibility of the HNO_3 experiments using the ETH system turned out to be much lower than for NO_2 mainly due to difficulties in the experimental setup of the HNO_3 source. The determination of the HNO_3 conversion efficiency therefore represents the largest uncertainty in the NO_y measurements.

Interferences for HCN, CH_3CN, and NH_3 were analysed by Lange et al. (2002) for the same type of converter and inlet configuration. Interferences from these species were found to be no larger than 5% resulting in an artefact of probably

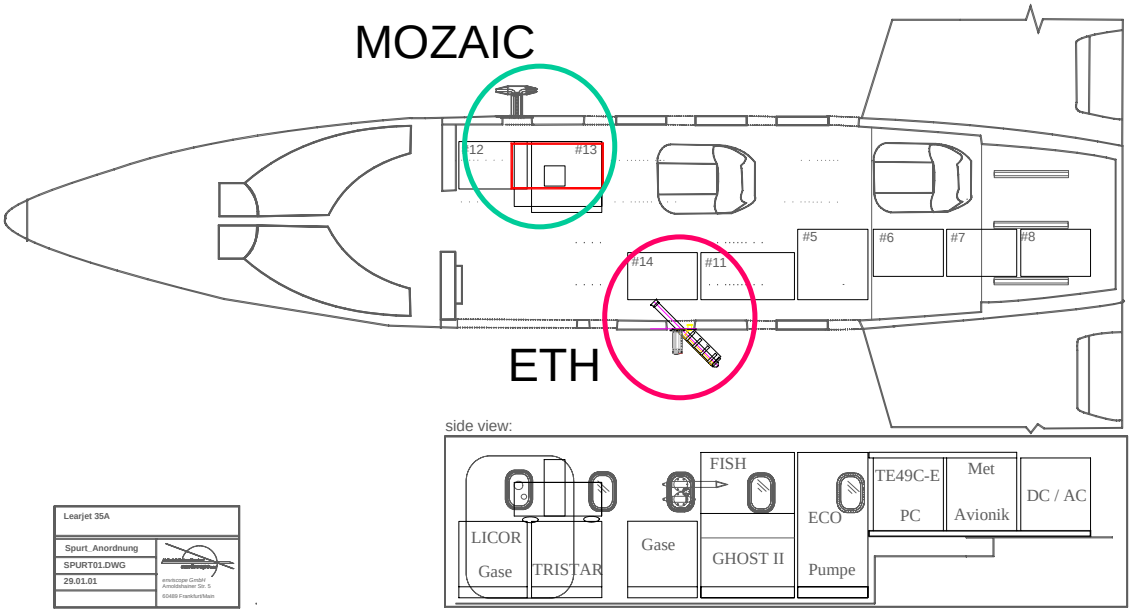

Fig. 2. Installation of the instruments aboard the Learjet during the intercomparison flight within SPURT.

less than 10 ppt in the background troposphere and the lowermost stratosphere. Interferences to N_2O are expected to be negligible at a converter temperature of 300°C.

The precision of the NO_y-, NO- and O_3-channels is less than 11, 9, and 149 ppt, respectively (2-sigma, 1s averages) at the mixing ratios encountered. The accuracy for the NO channel is determined by uncertainties in the NO calibration gas (4%) and the mass flows of the calibration gas and the synthetic air used for dilution (2%). The accuracy of the NO_y-channel contains additional uncertainties in the used calibration gas introduced by additionally converted NO_y species (3.7%, see explanation above), in the conversion efficiency for different species (in particular for HNO_3, 10%), the reproducibility of the conversion efficiency experiments (3%) and the pressure correction (4%). The total uncertainty of the NOy calibration is $U_{CAL}=\pm$ 12.6%. The overall 2-sigma uncertainty D_{NOY} is given by Eq. (2)

$$D_{NOY} = \pm \text{sqrt}(U_{CAL}^2 \times M^2{}_{NOY} + P_A^2 + U_B^2) \quad (2)$$

with M_{NOY} being the mixing ratio of NO_y and with $U_{CAL}=\pm 12.6\%$, $P_A=\pm 11$ ppt, and $U_B=\pm 50$ ppt. Values for D_{NOY} are given in Table 1 for NO_y mixing ratios of 300 and 3000 ppt.

Equation (2) is also used for calculation of the overall uncertainty in the other channels: for NO: $U_{CAL}=\pm 4.5\%$, $P_A=\pm 9$ ppt; for O_3: $U_{CAL}=\pm 5\%$, $P_A=\pm 149$ ppt.

2.3 Installation

The instrument comparison was conducted aboard a Learjet 35A operated by GFD for the German AFO2000 project SPURT. Figure 2 gives a schematic view of the instruments inside the aircraft. The ETHZ instrument was installed at the port side of the Learjet with the NO_y-converter mounted outside the fuselage of the aircraft. The inlet for the NO and O_3 measurements was mounted below the gold converter. The MOZAIC instrument was installed in the front part of the cabin at the starboard side of the aircraft. The Rosemount probe was mounted on a window blank. The configuration of the instrument was exactly the same as in MOZAIC, including the inlet line.

3 Procedures

The comparison was organised in a blind fashion with Ulrich Schmidt, University of Frankfurt, acting as an independent referee. Both groups followed their normal data calibration and evaluation procedures, i.e. those applied by FZJ for MOZAIC operation (Volz-Thomas et al., 2005) and by ETHZ during the SPURT project (Hegglin et al., 2006). The primary NO calibration standards of ETHZ and FZJ had been compared before the campaign and disagreed by less than 0.5%. No further exchange of standards took place during the campaign.

The analysed NO_y-data were submitted to the referee before information was exchanged between the two groups. For the first delivery of the data to the referee, the ETHZ NOy-measurements had been calculated with a preliminary pressure dependence of the conversion efficiency, which led to an overcorrection of about 25% at the highest altitudes as compared to the correct pressure dependence (Fig. 1) determined by the subsequent laboratory tests. In addition, the sensitivity of the ETH-CLD was corrected by −3.7%, based

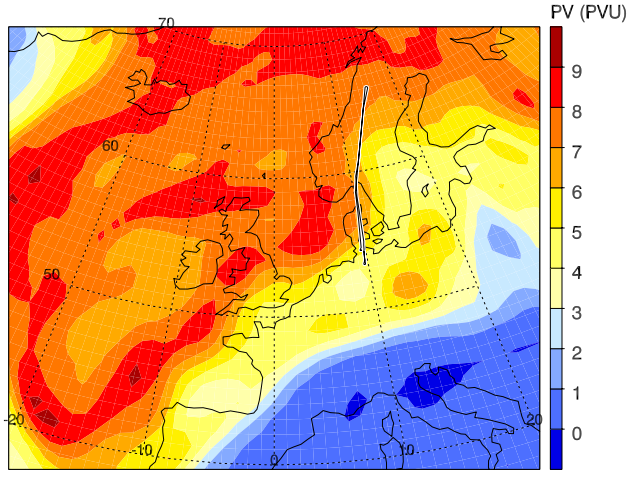

Fig. 3. Flight track of the Learjet itinerary and potential vorticity (PV) on the 220 hPa surface.

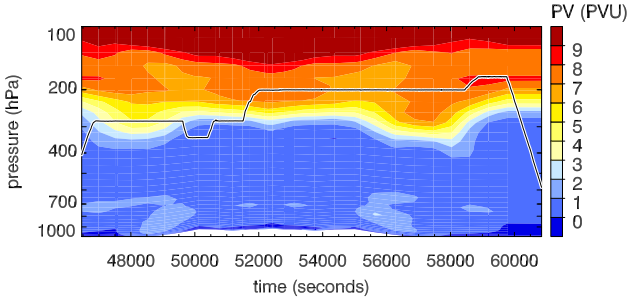

Fig. 4. Height profile of the flight and vertical PV-field interpolated in space and time along the flight track.

on the final evaluation of the working standards used during the campaign against the ETH master standard that had been compared with that of FZJ. These changes were accompanied by written statements explaining the reasons and the implications for the data.

4 Results

The comparison flight took place on 29 April 2003 at the end of the 7th SPURT campaign. As shown in Fig. 3, the aircraft flew from Hohn-Airbase near Rendsburg in Northern Germany towards Kiruna in Northern Sweden reaching 66° N, where it turned around at about 03:00 p.m. and flew back to Hohn. The flight profile is shown in Fig. 4 overlaid on a vertical cross section of potential vorticity (PV) calculated from ECMWF data and temporally and spatially interpolated along the flight path. Judging from PV levels, the aircraft entered the stratosphere during the first level flight. Thereafter, it descended into the troposphere for 20 min and entered the stratosphere again where it remained until the final descent to Hohn.

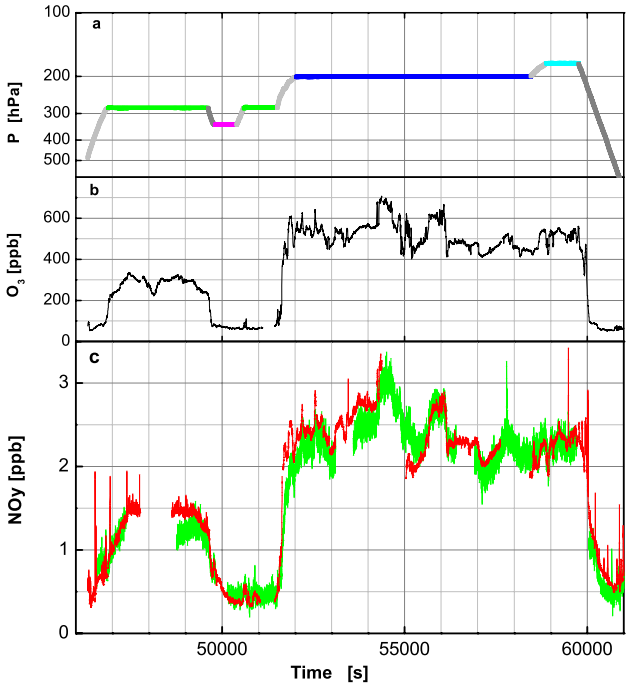

Fig. 5. NO_y mixing ratios measured by ETHZ (red) and by FZJ (green) during the intercomparison flight (panel **c**). Panel **(b)** shows the ozone mixing ratios measured by ETHZ and panel (a) the pressure during the flight. The different colours are used to identify different flight levels as well as ascent and descent.

Figure 5 shows the NO_y mixing ratios measured by the two instruments together with pressure and the mixing ratios of O_3 measured by ETHZ. The colour coding in the pressure trace (panel a) identifies flight segments that should contain comparable data in terms of level flights or vertical profiles. This colour coding is used in the following figures to identify data ensembles.

At first sight, both NO_y-instruments track quite well, both for the large changes during transitions between troposphere and stratosphere and for smaller structures. The noise of the MOZAIC instrument is about 5 times larger than that of the ECO Physics instrument, which is in line with the different sensitivities. Also seen is the good correlation between NO_y and O_3 in the lower stratosphere as observed in other campaigns (cf., Murphy et al., 1993).

Exceptions from the good agreement are seen during the ascend into the stratosphere at 51 500 s, where the MOZAIC instrument significantly lags the ETHZ instrument, which shows a much faster increase in good correspondence with the increase in O_3. Interestingly, the corresponding time lag between MOZAIC and ETHZ is not seen during the final descent at 60 000 s.

There are a few further deviations to be noted:

The MOZAIC instrument exhibits a reduced sensitivity after 48 750 s. This is due to the fact that the instrument had

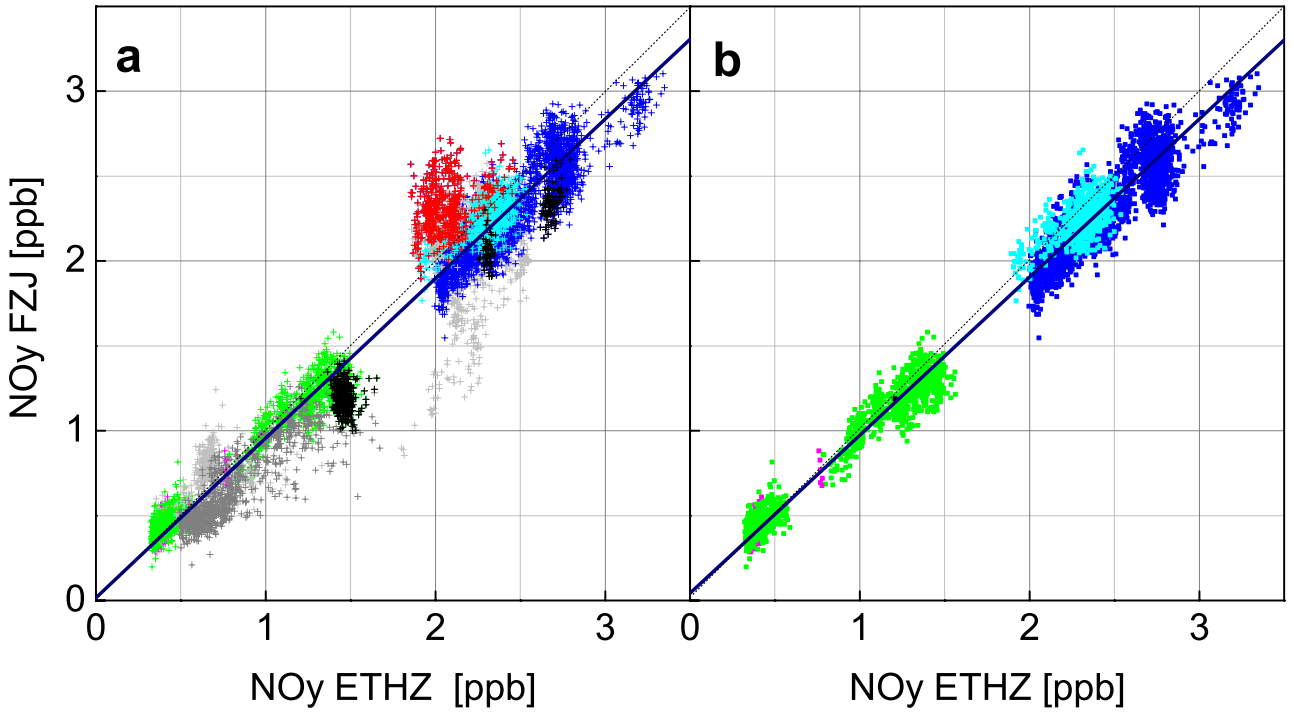

Fig. 6. Correlation between the NO_y-data by ETHZ and FZJ (1 s averages). The colour coding corresponds to the flight segments highlighted in Fig. 5. Panel **(a)** shows all data. Panel **(b)** includes only data that are least affected by memory by excluding profiles (grey points) and the first 5 min 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.

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 NO_y measurements (1 s averages) made by the two instruments. The colour coding refers to the different flight sections indicated in Fig. 5a. Data obtained after periods of zero air measurements are marked black for MOZAIC and red 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 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).

The average deviation of 6–7% from a slope of unity is within the combined 1 sigma uncertainty in the calibration of the two instruments (±7%). As already noted in Fig. 5, however, larger deviations are observed for the ensembles collected after periods of zero air application to either instrument and during the third ascent when the aircraft enters the stratosphere. Here, the MOZAIC instrument lags the ECO instrument significantly, a fact which manifests itself in the light-grey data points in Fig. 6a, which are significantly below the regression line. This section of the flight is highlighted in Fig. 7. While a comparison in form of vertical

profiles, as shown in the left panel, would have suggested very large deviations between the two instruments, the right panel clearly identifies the deviation as caused by the memory of the MOZAIC instrument. The time lag of approximately 120 s corresponds almost exactly to the memory of the MOZAIC inlet line for HNO_3 that had been determined before in laboratory tests (Volz-Thomas, 2005).

It is also noted (see Fig. 5), however, that the correspondence between the two instruments is much better for the subsequent changes in NO_y. It may thus be argued that the memory is stronger for the first increase in HNO_3 from the troposphere with higher humidity (100 ppm, Schiller private communication) and lower HNO_3 levels, than for changes in HNO_3 occurring in the stratosphere at lower water vapour mixing ratios (20 ppm).

5 Discussion and conclusions

During the comparison flight, different air masses of tropospheric and stratospheric origin were probed covering a broad range of NO_y mixing ratios for the testing of both instruments' dynamical range. When considering only data from flight sections at constant pressure level and neglecting the first 5 min after background determinations, in order to exclude data affected by memory of either instrument, the average deviation between the two instruments is 6–7% (ETHZ-FZJ) with an offset of 43 ppt in the FZJ-instrument (Fig. 6b). The significance of this deviation can be judged against the stated uncertainties in calibration and conversion efficiency (the precision term vanishes by averaging over a large ensemble of data pairs). As stated in Sect. 2, these uncertainties are 6.5% for FZJ and 12.6% for ETHZ, yielding a combined 2 sigma uncertainty of 14%. Therefore, the average disagreement between the two instruments is equal to the 1 sigma uncertainty of the calibration. Even, when neglecting the 10% uncertainty estimated by ETHZ for the uncertainty in HNO_3 conversion, because this error term is actually asymmetric (the efficiency cannot be $>100\%$) and hence would tend to go into the wrong direction, the combined 1 sigma uncertainty in calibration would still be 5%.

While this leaves very little room for speculations about the reasons for the deviation, there are a few points to be made:

The discrepancy between the two instruments in the stratosphere, where 90% of NO_y is in the form of HNO_3 (Neuman et al., 2001), limits the possibility for losses of HNO_3 in the Rosemount inlet of the MOZAIC instrument to 10% or less. This finding is important because, as discussed in Volz-Thomas et al. (2005), the use of a Rosemount housing as an inlet for NO_y is not undisputed in the literature. Obviously, the design chosen for the Rosemount inlet in MOZAIC has no or very small drawbacks for the sampling efficiency for NO_y.

While the memory of the MOZAIC instrument is clearly confirmed by the comparison with the much faster increase in NO_y of the ETHZ instruments during the ascent into the stratosphere (Fig. 7), there is no corresponding time lag between the two instruments during the final descent. One reason for this behaviour is that the MOZAIC instrument was measuring zero air during the first part of the descent. However, from the comparison with O_3 it is suggested that during descent the ETHZ instrument suffered from a similar memory as the MOZAIC instrument, because the decrease in ETHZ NO_y occurs much more slowly than the decrease in O_3, whereas during ascent, ETHZ-NOy increases simultaneously with O_3.

A similar behaviour of the SPURT gold converter has been observed by Lange et al. (2002). A possible explanation is that the memory is only established after the converter has been exposed to high HNO_3 mixing ratios for some time. A possible, albeit speculative, explanation is that HNO_3 is adsorbed at the outer surface of the tip of the gold tube or at the stainless steel surface of the converter housing. While the corresponding effect may not be significant during the fast ascent, it may show up during descent because of the large amount of HNO_3 that has been absorbed on the outer walls of the converter during the long time spent in the stratosphere. Consequently, the effect would depend on the time the aircraft has spent in the stratosphere and on the HNO_3 concentrations encountered. It would be quite difficult to quantify this in the laboratory, but would require further dedicated in-flight comparisons.

Both instruments exhibit reduced sensitivities after periods of background determination, i.e., zero air addition to the inlet. The most likely explanation for this behaviour is a memory effect, possibly enhanced by the fact that the zero air contains less water vapour than the ambient air. This effect was only seen because of the otherwise excellent comparison between the two instruments and because both instruments had been operated on the same aircraft so that atmospheric inhomogeneities or time lags between the data sets could be ruled out as possible explanations.

Interferences by HCN, CH_3CN and NH_3 have been found to be negligible ($<5\%$) for the SPURT converter (Lange et al., 2002). In the MOZAIC converter, NH_3 and CH_3CN are not converted either ($<2\%$), whereas HCN is quantitatively converted (Volz-Thomas et al., 2005). 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 NO_y background in both instruments (100 ppt for MOZAIC and 50 ppt for ETHZ), the small offset of 43 ppt found in the correlation between the two datasets (see Fig. 6b) could actually be indicative of the different response of the two instruments to HCN. Aerosol nitrate should not be detected by either instrument as both sampling inlets act as virtual impactors. The ETHZ inlet designed by MPI Mainz discriminates particles with diameters $>1\,\mu$m (Lange et al., 2002).

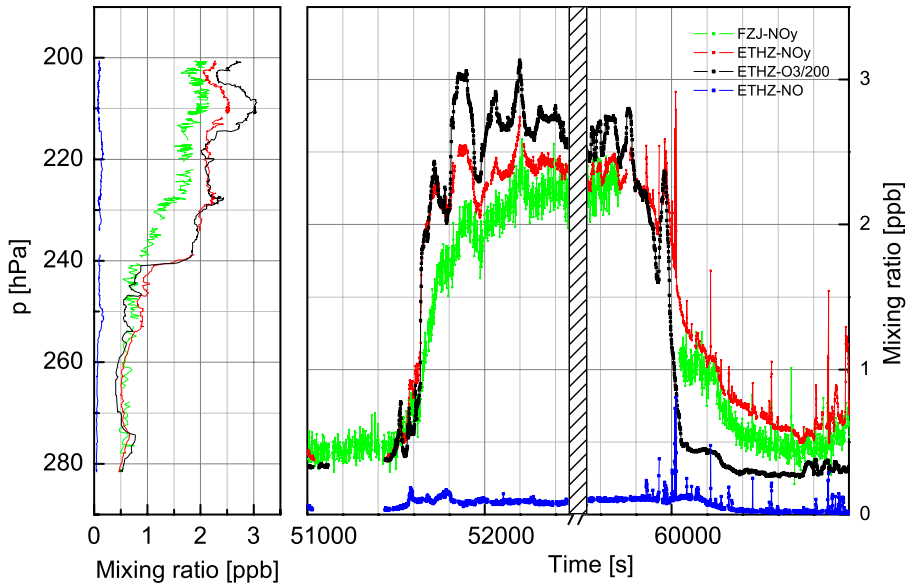

Fig. 7. Blow up of the ascent into and descent from the lower stratosphere between flight levels 380 and 270 (red: ETHZ-NO_y, green: FZJ-NO_y). Ozone (black) and NO (blue) are shown for comparison. The left panel shows the ascent data as vertical profiles.

Interference by atmospheric N_2O was found to be less than 3 ppt for the MOZAIC instrument. Although not explicitly investigated for the SPURT converter, it can be concluded from the comparison that N_2O is unlikely to constitute a significant interference at the converter temperature of 300°C. Because of its nearly constant mixing ratio, N_2O would rather produce a constant offset than the observed relative deviation.

In conclusion, the comparison between the two NO_y instruments led to helpful insight in possible artefacts of the applied measurement systems, which have to be explored in future laboratory and field studies. The generally good agreement between the two instruments, however, shows that the data obtained with both measurement systems provide representative information about atmospheric composition within the stated uncertainties.

The intercomparison flight covered a large fraction of the dynamic range of NO_y mixing ratios encountered in MOZAIC. On average, 9% of the MOZAIC NO_y data are below 300 ppt and 1.5% above 3.5 ppb, the lowest and highest concentrations encountered during the intercomparison.

An important finding is the reduced response after zero determination. It requires the discrimination of somewhat longer periods (ca. 5 min) than originally estimated.

The memory for HNO_3 as discussed in Volz-Thomas et al. (2005) was confirmed. The effect will lead to a slight underestimation of the NO_y mixing ratio during transitions into the stratosphere and a corresponding underestimation during transitions from the stratosphere into the troposphere, thus leading to some reduction in spatial resolution but without bias. The behaviour of the SPURT converter, if confirmed by future tests, would lead to a small overestimation of tropospheric NO_y, depending on the time the aircraft has spent in the stratosphere before descending into the troposphere.

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