



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

H.-W. Pätz, A. Volz-Thomas, M. I. Hegglin, D. Brunner, H. Fischer, U.
Schmidt

► **To cite this version:**

H.-W. Pätz, A. Volz-Thomas, M. I. Hegglin, D. Brunner, H. Fischer, et al.. In-situ comparison of the NO_y instruments flown in MOZAIC and SPURT. Atmospheric Chemistry and Physics Discussions, European Geosciences Union, 2006, 6 (1), pp.649-671. <hal-00300951>

HAL Id: hal-00300951

<https://hal.archives-ouvertes.fr/hal-00300951>

Submitted on 18 Jan 2006

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**NO_y instrument
comparison**

H.-W. Pätz et al.

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

H.-W. Pätz¹, A. Volz-Thomas¹, M. I. Hegglin², D. Brunner², H. Fischer³, and
U. Schmidt⁴

¹Institut für Chemie und Dynamik der Geosphäre II: Troposphäre, Forschungszentrum Jülich,
Germany

²Institute for Atmospheric and Climate Science, ETH-Zürich, Switzerland

³Max Planck Institute for Chemistry, Mainz, Germany

⁴Institut für Atmosphäre und Umwelt, Johann Wolfgang Goethe-Universität, Frankfurt,
Germany

Received: 31 October 2005 – Accepted: 11 December 2005 – Published: 18 January 2006

Correspondence to: A. Volz-Thomas (a.volz-thomas@fz-juelich.de)

© 2006 Author(s). This work is licensed under a Creative Commons License.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

EGU

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 6%, 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

NO_y instrument comparison

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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) and 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 (c.f. Crosley, 1996; Brough et al., 2003, and references therein). Potential problems were found with interferences by non-NO_y compounds, e.g. HCN and CH₃CN, and with the inlet configuration in terms of time response or memory, the sampling efficiency for aerosol, and the transmission of HNO₃ (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., 2005). The 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 HNO₃ in the inlet.

NO_y instrument comparison

H.-W. Pätz et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

2. The instruments

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 O₃ and catalytic reduction of the different NO_y compounds to NO with H₂ (0.1 sccm) on a hot gold surface (300°C). Because of the limitations in gas supply, in particular of H₂, for long-term operation (4–7 weeks), the instrument employs a very low sample flow (90 ml/sccm) and thus has a comparably low sensitivity of 0.4–0.7 cps/ppt. The gold converter has a conversion efficiency of >95% for NO₂ and HNO₃ at all altitudes encountered. Interferences by N₂O, NH₃, CH₃CN 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.

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 N₂, 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 NO₂, as determined by gas phase titration of the NO by O₃ remained at 92±4% (2 sigma). Other than for the ETHZ instrument (see below), the conversion efficiency of the MOZAIC instrument is independent of pressure. The overall inaccuracy of the calibration from errors in the flow measurements (3%) and the uncertainty of the conversion efficiency was ±6% (2 sigma). The conversion efficiency for HNO₃ was determined before and after the campaign to >92%. During flight, only the instrumental background was determined by flushing the

NO_y instrument comparison

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

inlet with an excess O₂-flow, in the same way as during MOZAIC operation. NO and NO₂ calibrations were not made during the flight in order to save time for the comparison.

2.1.2. Data treatment and uncertainty assessment

5 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
10 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 zero 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 HNO₃ leads to a
15 potential overestimation of the instrument's real background unless the zero air is applied for much longer 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.

The statistical (2 sigma) precision of an individual 1 s data point was 50 ppt at the
20 detection limit and 3% for the highest NO_y concentrations observed. The overall (2 sigma) uncertainty of an individual 1s NO_y-measurement was estimated by including the uncertainties in the calibration (±6%, 2 sigma) and the instrumental background (±100 ppt, 2 sigma) to

$$\text{DNO}_y = \sqrt{(0.03 \times \text{NO}_y)^2 + (0.06 \times \text{NO}_y)^2 + 50^2 + 100^2} \text{ ppt}$$

25 with NO_y in ppt (cf., Volz-Thomas et al., 2005). The largest contribution to the overall uncertainty usually comes from the uncertainty in the background. Potential errors of 2% in the absolute value of the master NO standard were neglected for the instrument

NO_y instrument comparison

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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.

5 2.2. NO_y-, NO-, and O₃-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 (O₃) was implemented by ETHZ aboard the Learjet 35A aircraft for the
10 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 O₃. Prior to detection, the NO_y-species are reduced to NO using a heated gold-converter with CO (5 sccm, 99.997%, PanGas, Switzerland) as reduction agent (Fahey et al., 1985). The converter is externally mounted on a window blank (Lange et al.,
15 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 NO_y inlet is facing backwards. NO and O₃ are sampled through a forward facing inlet with a diameter of 6 mm mounted below the converter on the same window blank.

20 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 N₂) 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
25 were carried out. This seemed appropriate since previous SPURT campaigns showed

NO_y instrument comparison

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**NO_y instrument
comparison**

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

EGU

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 O₃ 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 O₃-channel was calibrated against a commercial ozone calibrator (Advanced Pollution Instrumentation (API) UV photometric ozone calibrator) at the beginning and 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 O₃-channel were 24.0±0.12 cps ppt⁻¹, 22.4±0.2 cps ppt⁻¹, and 580±10 cps ppb⁻¹, respectively. Beside the instrument's background signal determined for all channels, an additional value of about 105 ppt was subtracted from the ambient 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).

**NO_y instrument
comparison**

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

EGU

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 figure, 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. As discussed in more detail below, the first data set submitted to the referee (see Sect. 3) was calculated with an erroneous pressure dependence of the conversion efficiency leading to an overestimation of the NO_y data by roughly 30% at the highest altitudes.

Interferences for HCN, CH₃CN, and NH₃ were analyzed 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 artifact of probably less than 10 ppt in the background troposphere and the lowermost stratosphere. The conversion efficiency for HNO₃ was determined in laboratory experiments to be approximately the same as for NO₂. Unfortunately the reproducibility of these experiments was much lower than for NO₂ which therefore represents the largest source of uncertainty in the NO_y measurements. Interferences to N₂O are expected to be negligible at a converter temperature of 300°C.

The precision of the NO_y-, NO- and O₃-channels is 11, 9, and 149 ppt s⁻¹, respectively (2-sigma). 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 overall 2-sigma accuracy of the three channels was estimated to $\pm(0.126 \times [\text{NO}_y] + 11 \text{ ppt})$, $\pm(0.045 \times [\text{NO}] + 9 \text{ ppt})$, and $\pm(0.05 \times [\text{O}_3] + 149 \text{ ppt})$.

5 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

15 The comparison was organised in a blind fashion with U. Schmidt 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., 2005). 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.

25 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 NO_y -measurements had been calculated with a preliminary pressure dependence of the conversion efficiency, which led to an overcorrection of about 30% at the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**NO_y instrument
comparison**

H.-W. Pätz et al.

highest altitudes as compared to the correct pressure dependence (in Fig. 1) determined by the subsequent laboratory tests. In addition, the sensitivity of the ETH-CLD was corrected by -3.7% , based 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. For transparency, the originally submitted data are first presented in the following section before the final data are discussed.

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 3:00 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.

Figure 5 shows the NO_y mixing ratios measured by the two instruments together with pressure and the mixing ratios of O₃ measured by ETHZ. The colour coding 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 O₃ in the lower stratosphere as observed in other campaigns (cf., Murphy et al., 1993).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

EGU

**NO_y instrument
comparison**

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

EGU

As noted above, the corrected data (see Fig. 5c), which include the measured pressure dependence of the ETHZ converter, show less disagreement than the data originally submitted to the referee (Fig. 5a). In particular, much smaller deviations are observed in the lower stratosphere. In the following, only the corrected data will be shown.

Figure 6 shows a scatter diagram of the simultaneous NO_y measurements made by the two instruments. The colour coding refers to the different flight sections indicated in Fig. 5. A linear fit to all data and considering errors in both axis gives a slope (FZJ/ETHZ) of (0.940 ± 0.001) , an intercept of $(17 \pm 2 \text{ ppt})$, and a correlation coefficient of $R=0.969$. Considering only level flights improves the correlation ($R=0.983$). The slope becomes slightly lower (0.935 ± 0.001) and the intercept vanishes $(4 \pm 3 \text{ ppt})$. The scatter is dominated by the random noise of the MOZAIC instrument. Exceptions from the good correlation are three ensembles also not included in the linear fit where the ETHZ data (indicated by the red square) or the MOZAIC data (indicated by the blue squares) are somewhat below the average correlation, respectively.

The average deviation of 6% is consistent with the combined 1 sigma inaccuracy of the two instruments ($\pm 6.8\%$). Larger deviations are observed after zero measurements in either instrument and particularly 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 black data points in Fig. 6, identified by the large blue square. This behaviour is highlighted in Fig. 7. While the memory is clearly depicted in the lower right panel, a comparison in form of vertical profiles as shown in the left panel would have suggested very large deviations between the two instruments. The time lag of approximately 120 s is due to a memory of the MOZAIC inlet line for HNO₃ and corresponds almost exactly to what had been determined in laboratory tests (Volz-Thomas, 2005). It is also noted, 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 HNO₃ from very low tropospheric levels to a few ppb than for changes in HNO₃ occurring on a higher background. This

hypothesis will be tested in future laboratory tests.

5. Discussion and conclusions

We presented a comparison between the MOZAIC and the SPURT NO_y instruments, during which 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. In general, there is good agreement between the two instruments within the stated inaccuracies. The average systematic difference of 6% (ETHZ-MOZ) could be indicative of small losses of HNO₃ in the Rosemount inlet of the MOZAIC instrument. On the other hand, residual uncertainties in the ratio between the calibrations of the two instruments could explain at least half of the difference.

As discussed by Hegglin (2004) the temperature of the reaction chamber of the ETHZ instrument is actively controlled whereas the photomultipliers (PMT) are always cooled with maximum power. A comparison with a second ozone instrument operated by FZJ (Engel et al., 2005; Hegglin, 2004) suggests that the response of the O₃-channel is sensitive to PMT temperature (about -2.2%/K). However, the PMT temperature was nearly constant during the intercomparison flight with a decrease of 2°C within the first flight hour only resulting in a maximum variation in the sensitivity of the O₃-channel of 4.4%. The expected change in sensitivity for the NO and NO_y channel is calculated to be somewhat smaller, i.e., 2.3% or less. Temperature fluctuations may therefore indeed have contributed to the observed differences between the first and second half of the comparison flight. In the MOZAIC instrument, PMT and reaction chamber are temperature controlled.

Both instruments seem to exhibit reduced conversion efficiencies after periods of zero air addition to the inlet. A possible cause for this behavior is switching between warmer zero air and cooler ambient air which changes the thermal environment for the conversion reactions. Another possibility might be the change in humidity.

A relevant problem of both NO_y instruments is an observed memory effect when

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

changing from air with high NO_y (HNO_3) to air with low NO_y (HNO_3). During the two descents of the aircraft, the ETHZ NO_y decreases much slower than the MOZAIC NO_y and also the O_3 measurements show a much sharper decrease in mixing ratios.

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. Therefore, the different response to HCN of the two instruments could actually explain the small offset found in the correlation between the two datasets (see Fig. 6). 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 $>1 \mu\text{m}$ (Lange et al., 2002).

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.

The deviation is most significant in the lower stratosphere (LS), where 90% of the NO_y is expected to be in the form of HNO_3 (Neuman et al., 2001). Therefore, the most likely explanation for the difference between the two instruments is a small (<10%) loss of HNO_3 in the inlet of the MOZAIC instrument or a long-term memory for both instruments. The latter could also explain the fact that the two instruments reach slightly better agreement during the second part of the flight, after the aircraft had spent more than 2 h in the LS.

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 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.

 NO_y instrument comparisonH.-W. Pätz et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

**NO_y instrument
comparison**

H.-W. Pätz et al.

Acknowledgements. We gratefully acknowledge funding for MOZAIC by the European Commission, DG Research and for SPURT by the German Ministry for Education and Research (BMBF) as part of the AFO2000 programme. The ETH contribution to SPURT was funded by a research grant of ETH-Zürich and by the Swiss National Science Foundation (SNF). We also
5 kindly acknowledge the expert assistance of the staff of *enviscope* and *GFD* during integration of the instruments and flight operation. Last not least, thanks are due to U. Weers und U. Parchatka for their invaluable technical support during the design and operation of the ETH NO_y-instrument.

References

- 10 Bollinger, M. J., Sievers, R. E., Fahey, D. W., and Fehsenfeld, F. C.: Conversion of Nitrogen Dioxide, Nitric Acid, and n-Propyl Nitrate to Nitric Oxide by Gold-Catalyzed Reduction with Carbon Monoxide, *Analytical Chemistry*, 55, 1980–1986, 1983.
- Brough, N., Reeves, C. E., Penkett, S. A., Dewey, K., Kent, J., Barjat, H., Monks, P. S., Ziereis, H., Stock, P., Huntrieser, H., and Schlager, H.: Intercomparison of aircraft instruments on board the C-130 and Falcon 20 over southern Germany during EXPORT 2000, *Atmos. Chem. Phys.*, 3, 2127–2138, 2003,
15 [SRef-ID: 1680-7324/acp/2003-3-2127](#).
- Crosley, D. R.: NO_y Blue Ribbon Panel, *J. Geophys. Res.*, 101, 2049–2052, 1996.
- Crutzen, P. J.: The Role of NO and NO₂ in the Chemistry of the Troposphere and Stratosphere, *Ann. Rev. Earth and Planetary Sci.*, 7, 443–472, 1979.
- 20 Engel, A., Bönisch, H., Brunner, D., Fischer, H., Franke, H., Günther, G., Gurk, C., Hegglin, M. I., Hoor, P., Königstedt, R., Krebsbach, M., Maser, R., Parchatka, U., Peter, T., Schell, D., Schiller, C., Schmidt, U., Spelten, N., Szabo, T., Weers, U., Wernli, H., Wetter, T., and Wirth, V.: Highly resolved observations of trace gases in the lowermost stratosphere and upper troposphere from the Spurt project: an overview, *Atmos. Chem. Phys. Discuss.*, 5, 5081–5126, 2005,
25 [SRef-ID: 1680-7375/acpd/2005-5-5081](#).
- Fahey, D. W., Eubank, C. S., Hübler, G., and Fehsenfeld, F. C.: Evaluation of a Catalytic Reduction Technique for the Measurement of Total Reactive Odd-Nitrogen NO_y in the Atmosphere, *J. Atmos. Chem.*, 3, 435–468, 1985.
- 30

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**NO_y instrument
comparison**

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

EGU

- Hegglin, M. I.: Airborne NO_y, NO, and O₃-measurements during SPURT: Implications for atmospheric transport, ETH Zurich, Ph.D.-Thesis, 2004.
- Hegglin, M. I., Brunner, D., Wernli, H., Schwierz, C., Martius, O., Hoor, P., Fischer, H., Parchatka, U., Spelten, N., Schiller, C., Krebsbach, M., Weers, U., Staehelin, J., and Peter, T.:
5 Tracing troposphere-to-stratosphere transport above a mid-latitude deep convective system, Atmos. Chem. Phys., 4, 741–756, 2004,
SRef-ID: 1680-7324/acp/2004-4-741.
- Hegglin, M. I., Brunner, D., Peter, T., et al.: Measurements of NO, NO_y, N₂O, and O₃ during SPURT: Implications for transport and chemistry in the lowermost stratosphere, Atmos.
10 Chem. Phys. Discuss., 5, 8649–8688, 2005,
SRef-ID: 1680-7375/acpd/2005-5-8649.
- Keim, E. R., Loewenstein, M., Podolske, J. R., Fahey, D. W., Gao, R. S., Woodbridge, E. L., Wamsley, R. C., Donnelly, S. G., Delnegro, L. A., Nevison, C. D., Solomon, S., Rosenlof, K. H., Scott, C. J., Ko, M. K. W., Weisenstein, D., and Chan, K. R.: Measurements of the NO_y–
15 N₂O correlation in the lower stratosphere: Latitudinal and seasonal changes and model comparisons, J. Geophys. Res., 102, 13 193–13 212, 1997.
- Lange, L., Fischer, H., Parchatka, U., Gurk, C., and Zenker, T.: Characterization and application of an externally mounted catalytic converter for aircraft measurements of NO_y, Rev. Sci. Inst.,
73, 3051–3057, 2002.
- 20 Murphy, D. M., Fahey, D. H., Proffitt, M. H., Liu, S. C., Chan, K. R., Eubank, C. S., Kawa, S. R., and Kelly, K. K.: Reactive Nitrogen and its Correlation With Ozone in the Lower Stratosphere and Upper Troposphere, J. Geophys. Res., 98, 8751–8773, 1993.
- Neuman, J. A., Gao, R. S., Fahey, D. W., Holecek, J. C., Ridley, B. A., Walega, J. G., Grahek, F. E., Richard, E. C., McElroy, C. T., Thompson, T. L., Elkins, J. W., Moore, F. L., and Ray,
25 E. A.: In situ measurements of HNO₃, NO_y, NO, and O₃ in the lower stratosphere and upper troposphere, Atmos. Environ., 35, 5789–5797, 2001.
- Ryerson, T. B., Huey, L. G., Knapp, K., Neuman, J. A., Parrish, D. D., Sueper, D. T., and Fehsenfeld, F. C.: Design and initial characterization of an inlet for gas-phase NO_y measurements from aircraft, J. Geophys. Res., 104, 5483–5492, 1999.
- 30 Singh, H. B., Salas, L., Herlth, D., Kolyer, R., Czech, E., Viezee, W., Li, Q., Jacob, D. J., Blake, D., Sachse, G., Harward, C. N., Fuelberg, H., Kiley, C. M., Zhao, Y., and Kondo, Y.: In situ measurements of HCN and CH₃CN over the Pacific Ocean: Sources, sinks, and budgets, J. Geophys. Res., 108, 8795 (GTE 16-1–16-14), 2003.

Volz-Thomas, A., Berg, M., Heil, T., Houben, N., Lerner, A., Petrick, W., Raak, D., and Pätz, H.-W.: Measurements of total odd nitrogen (NO_y) aboard MOZAIC in-service aircraft: instrument design, operation and performance, Atmos. Chem. Phys., 5, 583–595, 2005, [SRef-ID: 1680-7324/acp/2005-5-583](#).

ACPD

6, 649–671, 2006

**NO_y instrument
comparison**

H.-W. Pätz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

EGU

**NO_y instrument
comparison**

H.-W. Pätz et al.

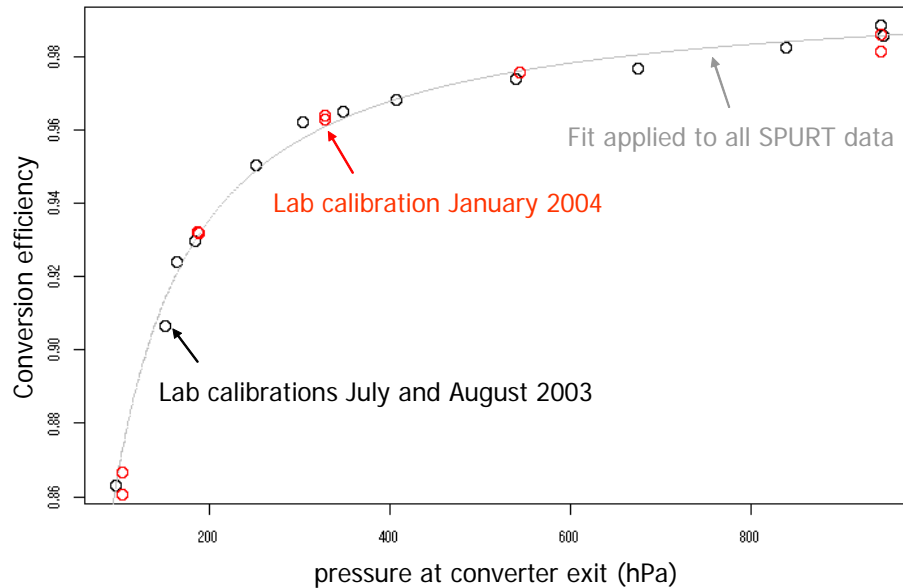


Fig. 1. Conversion efficiency of the ETHZ gold converter for NO₂ as a function of pressure.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

EGU

NO_y instrument comparison

H.-W. Pätz et al.

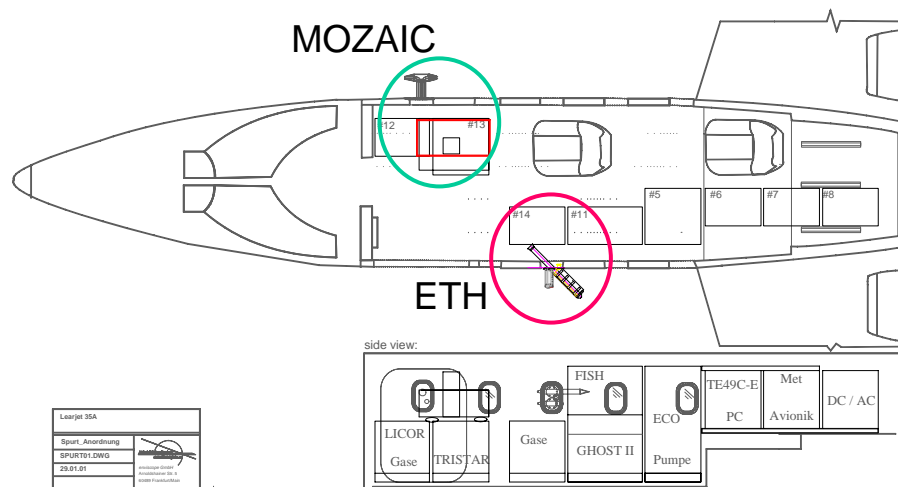


Fig. 2. Installation of the instruments aboard the Learjet during the intercomparison flight within SPURT.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Print Version

Interactive Discussion

**NO_y instrument
comparison**

H.-W. Pätz et al.

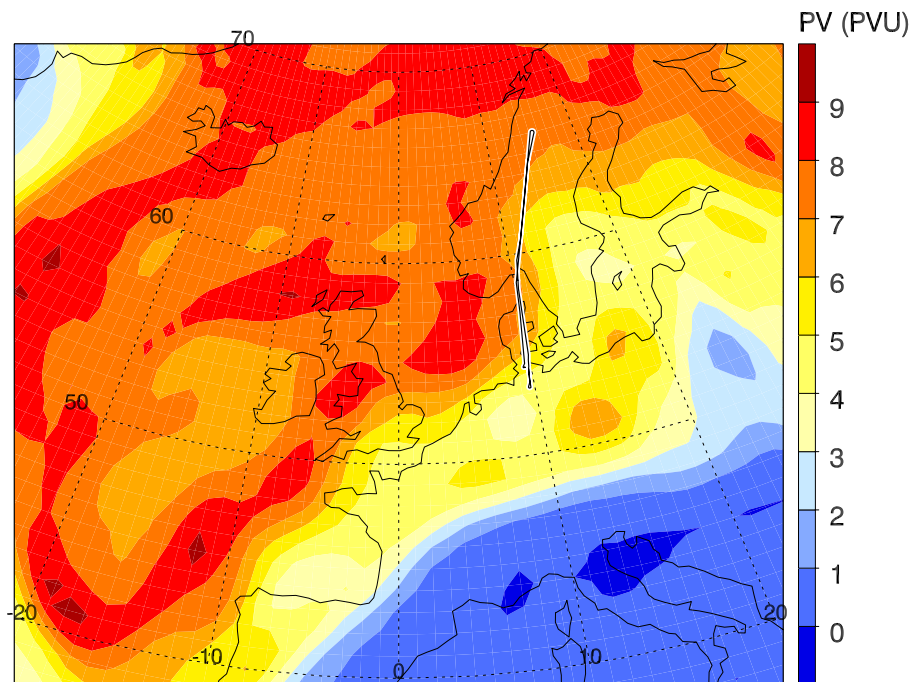


Fig. 3. Flight track of the Learjet itinerary and potential vorticity (PV) on the 220 hPa surface.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

EGU

**NO_y instrument
comparison**

H.-W. Pätz et al.

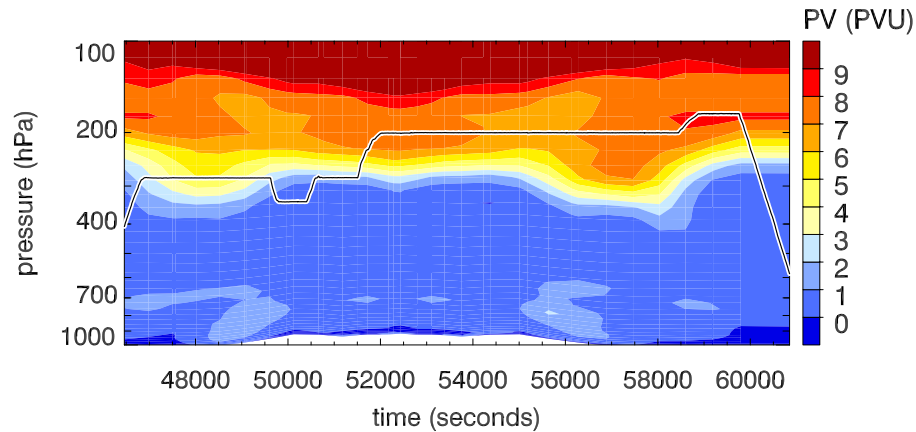


Fig. 4. Height profile of the flight and vertical PV-field interpolated in space and time along the flight track.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

EGU

NO_y instrument
comparison

H.-W. Pätz et al.

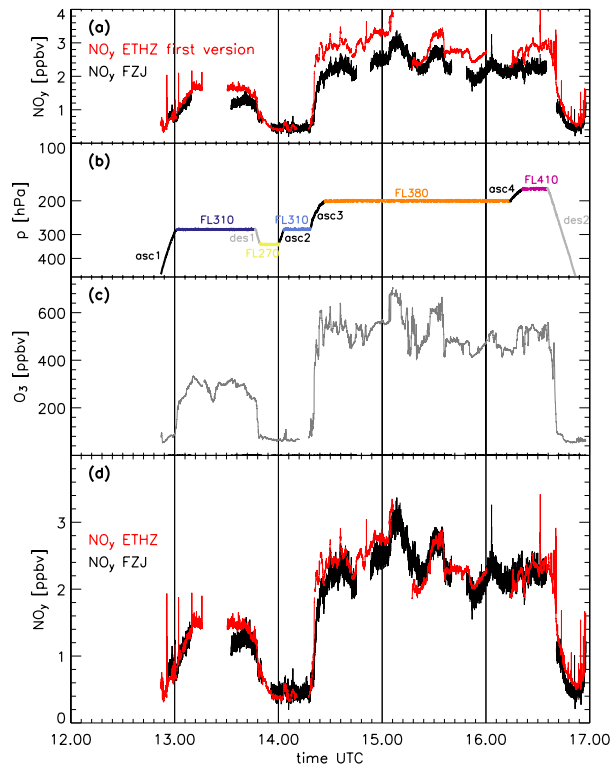


Fig. 5. NO_y mixing ratios measured by ETHZ (SPURT, red) and by FZJ (MOZAIC, black) during the intercomparison flight. Panel (a) shows the original NO_y data as reported immediately after the flight to the referee. Panel (d) displays the data after implementing a corrected pressure dependence of the ETHZ-SPURT converter as explained in the text. Panel (c) shows the ozone mixing ratios measured by ETHZ and panel (b) the pressure during the flight. The different colours are used to identify different flight levels as well as ascent and descent.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

EGU

**NO_y instrument
comparison**

H.-W. Pätz et al.

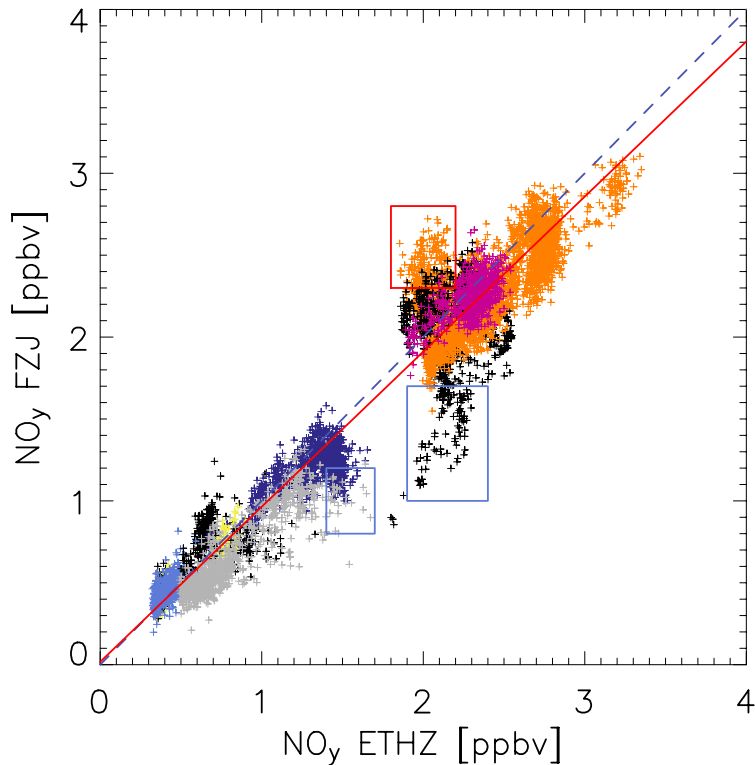


Fig. 6. Correlation between the NO_y-data by ETHZ and FZJ (1 s averages). The colour coding corresponds to the flight segments highlighted in Fig. 5. The boxes denote data collected after calibrations of the instruments. The blue dashed line indicates the one to one correspondence. A linear fit to the data including errors in x and y (red line) yields:
FZJ-NO_y=(0.940±0.001) ETHZ-NO_y+(17±2) ppt; R=0.969
The fit for levels only and excluding the first 5 minutes after calibrations yields:
FZJ-NO_y=(0.935±0.001) ETHZ-NO_y+(4±3) ppt; R=0.983.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

EGU

NO_y instrument comparison

H.-W. Pätz et al.

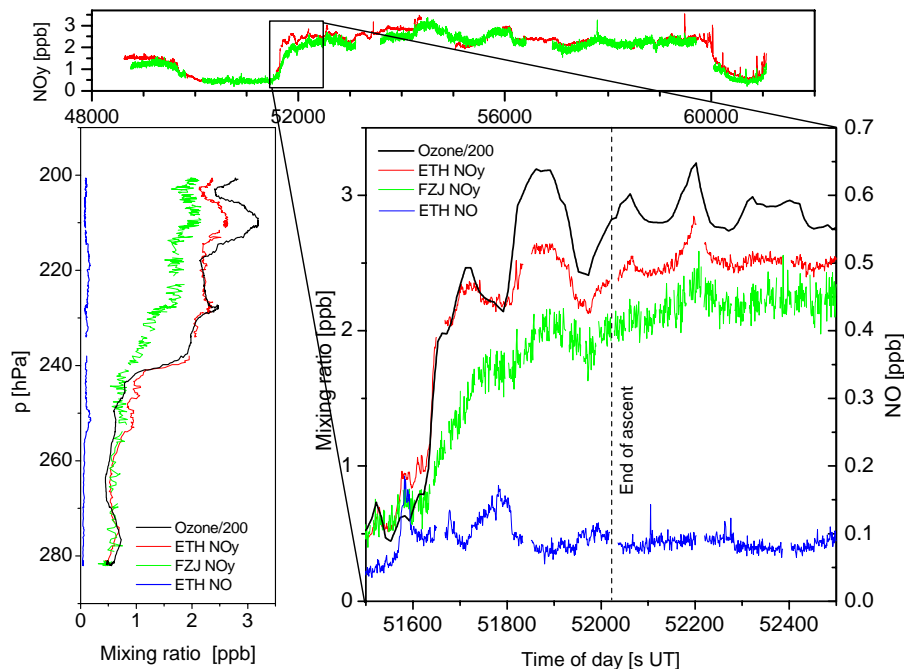


Fig. 7. Blow up of the ascent into the lower stratosphere from flight level 380 to 270 (right panel) highlighting the memory of the FZJ-Instrument (red: ETHZ-NO_y, green: FZJ-NO_y). Ozone (black) and NO (blue) are shown for comparison. The left panel shows the data as vertical profiles.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

EGU