Aircraft observations of NO, NO_y, CO, and O_3 in the upper troposphere from 60°N to 60°S - Interhemispheric differences at mitlatitudes

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[1] Measurements of NO, NO_y, CO, and O_3 made in the middle and upper troposphere over Punta Arenas, Chile (53°S) and Prestwick, Scotland (55°N) during the INCA (Interhemispheric Differences in Cirrus Properties from Anthropogenic Emissions) experiment in 2000 are used to examine the interhemispheric differences in the abundance of these species during local autumn. Median mixing ratios of NO, NO_y, O_3, and CO in the upper troposphere (8 km-tropopause) are 4.5, 3, 1.5 and 1.2 times higher over Prestwick compared to Punta Arenas, respectively. Corresponding enhancement factors for the middle troposphere are 5, 7.8, 1.5, and 1.4. The present data represent a considerable extension of the sparse NO and NO_y data so far available for the middle and upper troposphere at southern midlatitudes. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry. **Citation:** Baehr, J., H. Schlager, H. Ziereis, P. Stock, P. van Velthoven, R. Busen, J. Ström, and U. Schumann, Aircraft observations of NO, NO_y, CO, and O_3 in the upper troposphere from 60°N to 60°S - Interhemispheric differences at mitlatitudes, *Geophys. Res. Lett.*, *30*(11), 1598, doi:10.1029/2003GL016935, 2003.

1. Introduction

[2] Large-scale observations of the meridional distribution of trace gases in the troposphere are important for an understanding of the dynamical and chemical processes that control the globalization of air pollution. Amongst the most important anthropogenic pollutants are nitrogen oxides (NO_x), hydrocarbons, and carbon monoxide (CO) since they control the photochemical production of ozone (O_3) in the troposphere. Ozone plays a key role in determining the oxidizing power of the global atmosphere, and thus the capacity of the atmosphere to cleanse itself. [*Logan et al.*, 1981]. The largest fraction of O_3 precursors is emitted in the Northern Hemisphere (NH) and interhemispheric exchange has a major influence on the global distribution of these gases in the troposphere and on the resulting O_3 abundances [*Hartley and Black*, 1995].

[3] The present knowledge of the large-scale distribution of O_3 precursors in the upper troposphere is largely based on aircraft observations [*Emmons et al.*, 2000]. However, only sparse data are available for mid-latitudes in the SH where anthropogenic NO_x has a particularly large impact on the O_3 abundance and NO_x-levels are near the turnover point for net O_3 production versus net O_3 loss [*Ehhalt and Rohrer*, 1995]. Previous NO_x measurements in the free troposphere at SH mid-latitudes are mainly available from the meridional aircraft campaigns STRATOZ III (Stratospheric Ozone Experiment) in June 1984 [*Drummond et al.*, 1988] and TROPOZ II (Tropospheric Ozone Experiment) in January/February 1991 [*Jonquieres and Marenco*, 1998; *Rohrer et al.*, 1997]. However, the median NO and NO_y concentrations for the middle and upper troposphere from both campaigns differ considerably at SH mid-latitudes. It is not clear whether this is due to different detection limits for the instruments used, the snapshot nature of the observations from only a few flights, or the different seasons in which the measurements have been made.

[4] Here we report on aircraft chemical measurements from 60°N - 60°S performed during the INCA experiment along a similar route as STRATOZ III and TROPOZ II, however, including multiple flights from two main sites at mid-latitudes in the SH and NH. Each campaign covered a period of three weeks, hence these data can provide a more representative picture of the middle and upper tropospheric abundance of nitrogen oxides and other chemical species measured for mid-latitudes and of the interhemispheric difference for autumn conditions. The measurements performed during the flights from Punta Arenas provided the first detailed NO and NO_y distributions near 60°S.

2. Experiment

[5] The INCA expedition included two main field campaigns in Punta Arenas, Chile (53°S) and Prestwick, Scotland (55°N) and used the DLR Falcon with a ceiling altitude of 12 km. The main objective of INCA was to determine interhemispheric differences in cirrus properties of clean compared to polluted air masses for mid-latitudes. The Falcon was mainly instrumented with measurement systems for aerosols and cloud elements. In addition, some selected chemical species were measured to characterize the origin and degree of pollution of the air masses sampled. The Punta Arenas campaign was performed from 23 March to 13 April 2000 and included 10 scientific missions. The second campaign from Prestwick was conducted from 27

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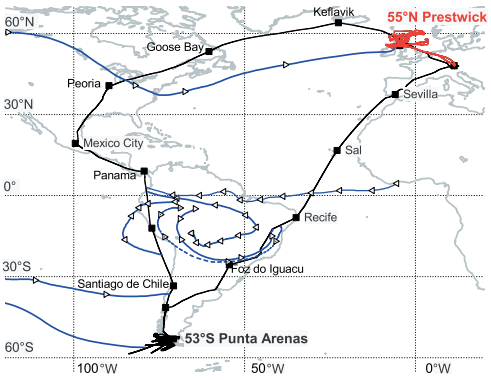

Figure 1. INCA flight tracks and typical backward trajectories (blue) for air masses sampled in the upper troposphere at mid-latitudes and tropical South America (triangles indicate time steps of 1 day).

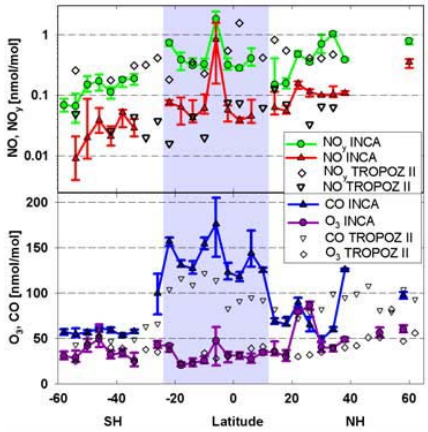

Figure 2. Latitudinal trace gas distributions in the upper troposphere as observed during INCA southbound transit flights (given are median values and 25% and 75% percentiles indicated by whiskers). For comparison, corresponding TROPOZ II data are included. Shaded area indicates measurements in the vicinity of the ITCZ.

September until 12 October 2000 and included 9 scientific flights. In addition, Falcon measurements were performed in the upper troposphere during 14 transit flight sections from Germany to Punta Arenas and back covering an extended latitudinal range from 60°N to 60°S. The locations of the deployment sites and the routing of the local and transit flights are depicted in Figure 1. Also included in Figure 1 are typical backward trajectories to illustrate the transport pathways of the air masses sampled over Prestwick, Punta Arenas and tropical South America.

[6] Measurements used in this study include NO, NO_y, O_3, and CO, photolysis frequency of NO_2, and meteorological parameters. The instruments used have already been described [*Schlager et al.*, 1997; *Ziereis et al.*, 2000; *Gerbig et al.*, 1996]. Briefly, NO was measured using NO-O_3 chemiluminescence with a time resolution of 1 s and an precision/accuracy of 5/10% and 10/15% for concentration levels of 1 and 0. 1 nmol/mol, respectively, and a detection limit of 2 pmol/mol. Total reactive nitrogen (NO_y = NO + NO_2 + NO_3 + PAN + HNO_3 + . . .) was measured using a second NO detector combined with a heated gold converter that reduces oxidized NO_y species to NO [*Fahey et al.*, 1985]. For the NO_y gas phase measurements a backward facing inlet was used preventing enhanced sampling of NO_y contained in aerosols and excluding the sampling of ice particles. O_3 and CO were detected by UV-absorption and VUV-fluorescence, respectively, with an accuracy of 5% for both measurements and a precision of 1 and 6 nmol/mol, respectively. The photolysis frequency (jNO_2) was measured using a filter radiometer with an accuracy of 18%. NO_2 was calculated from measured daytime NO (solar zenith angle <80°), O_3, temperature, and jNO_2 assuming simple photochemical steady state between NO and NO_2 [e.g. *Schlager et al.*, 1997]. Air temperature, static pressure, wind, and aircraft position were available from standard instruments on board the Falcon. In addition, meteorological analyses from ECMWF are used including backward trajectories for air masses sampled during the flights.

3. Results and Discussion

3.1. Meridional Distribution

[7] Figure 2 shows distributions of NO, NO_y, CO, and O_3 measured in the upper troposphere between 60°N and 60°S during the INCA transfer flights from Germany to Punta Arenas. Given are median volume mixing ratios averaged over latitude bins of 4° and altitudes between 7 km and the tropopause or the ceiling altitude of the Falcon, whichever is lower. Data sampled in the stratosphere were excluded based on the measured CO-O_3 and H_2O-O_3 correlations. Threshold O_3 values of 60 and 100 nmol/mol were found appropriate for a safe exclusion of air masses influenced by the stratosphere for southern and northern midlatitudes, respectively. Of all INCA data 15% were classified as sampled in the stratosphere. For comparison, the meridional trace gas distributions measured during TROPOZ II along similar flight routes [*Rohrer et al.*, 1997] are included in Figure 2. The TROPOZ II data were averaged in the same way as the INCA data.

[8] The meridional trace gas distributions observed in the upper troposphere during INCA and TROPOZ II show in general the same features. As expected, mixing ratios measured in the NH are significantly higher compared to the SH. However, at SH midlatitudes NO and NO_y concentrations

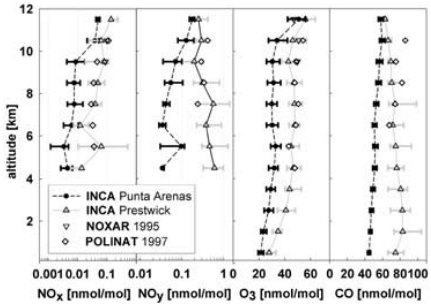

Figure 3. Trace gas profiles from Falcon flights out of Punta Arenas and Prestwick. For comparison median values of POLINAT II (Shannon, Ireland 1997) and NOXAR 1995 (>50°N) are included. Symbols and whiskers indicate median values and 25% and 75% percentiles, respectively.

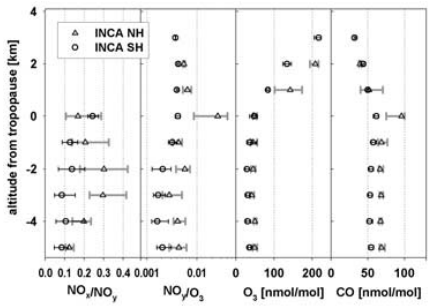

Figure 4. NO/NO_y, NO_y/O_3, O_3 and CO as a function of the distance to the tropopause. Medians and 25% and 75% percentiles are shown.

measured during INCA are much smaller than observed during TROPOZ II. Sharp air mass transitions were observed in the upper troposphere over tropical South America in the vicinity of the ITCZ. Here strongly enhanced CO (118–176), moderately enhanced NO and NO_y (0.04–0.8 and 0.3–1.8) and very low O_3 (21–48) mixing ratios (nmol/mol) were observed in the upper troposphere between 12°N and 24°S. According to backward trajectory analysis corresponding air masses originate mainly from lower heights over the Amazon basin. These air masses encountered deep convection 1–3 days before the sampling time as shown by GOES 8 cloud images. The Large-Scale Biosphere-Atmosphere Experiment in Amazonia [*Gatti et al.*, 2001] revealed that the abundance of CO, NO, and NO_y in the boundary layer in the Amazon basin during the wet season is mostly controlled by biogenic emissions with a small contribution of industrial and traffic emissions and no influence of biomass burning. Typical CO and NO volume mixing ratios measured in the boundary layer during the LBA 2000 wet season campaign were 100–200 and 0.05–0.1 nmol/mol, respectively. These mixing ratios are consistent with the INCA observations in air masses originating from the Amazon basin. During INCA the intense convective activity over the Amazon basin was associated with an upper level anticyclonic flow over tropical South America (see trajectories in Figure 1). According to *Jonquieres and Marenco* [1998] these meteorological conditions occur repeatedly during the wet season and cause enhanced levels of CO in the upper troposphere over a large area. In addition trajectories suggest, that long-range transport of CO from biomass burning sources in Western Africa may have partly contributed to upper tropospheric CO over tropical South America.

[9] At latitudes between 4°S and 8°S remarkably high NO and NO_y mixing ratios of 0.8 and 1.8 nmol/mol, respectively, were observed (see Figure 2). GOES 8 images show large convective cells upwind of this flight section with lightning activity only 8 h prior to the measurements as detected by OTD (Optical Transient Detector). Fresh lightning produced NO_x may explain the high NO and NO_y mixing ratios and the high NO/NO_y ratio of 0.46 mol/mol observed in these samples.

3.2. Interhemispheric Differences

[10] The large data set acquired during the multiple flights from Punta Arenas and Prestwick at the same latitude and local season allows a representative interhemispheric comparison. Figure 3 shows vertical distributions of median NO_x, NO_y, O_3, and CO volume mixing ratios obtained from all local INCA flights from Punta Arenas and Prestwick, respectively. For comparison the POLINAT II and NOXAR values are also included in Figure 3. The NO_y and CO concentrations increase with altitude over Punta Arenas and decrease with altitude over Prestwick. This is typical for remote regions and regions influenced by continental surface sources, respectively. The increasing NO_y and CO mixing ratios with altitude over Punta Arenas indicate that there is a minimal influence of surface sources in the vicinity of the measurement region. Sampling of aged pristine air masses here is also indicated by the small variation of the profiles

Table 1. Median and Mean Concentrations (Standard Deviations in Brackets) of Selected Campaigns For the Middle (4–8 km) and Upper Troposphere (8 km-Tropopause) at Mid-Latitudes in the SH Compared to the NH

				NO pmol/mol		NO_y pmol/mol		O_3 nmol/mol		CO nmol/mol	
							altitude, km				
Campaign	*Location and No. of flights*	*Averaging Area*	*Season*	*4–8*	*>8*	*4–8*	*>8*	*4–8*	*>8*	*4–8*	*>8*
INCA	Punta Arenas: 9	50°–60°S, 68°–84°W	autumn	5 9(27)	9 17(24)	46 58(35)	76 90(60)	31 31(6)	32 33(10)	52 52(4)	57 57(5)
TROPOZ II	Punta Arenas:1	50°–55°S, 68°–74°W	summer	22 24(27)	62 67(62)	176 186(36)	239 275(99)	37 36(7)	43 42(6)	41 44(11)	54 56(17)
STRATOZ III	Punta Arenas: 2	50°–60°S, 68°–84°W	winter	–4[d] 1(9)	5 9(15)	-	-	24 26(7)	32 34(7)	71 68(6)	73 73(6)
AAOE[a]	Punta Arenas: 9	~45°–60°S ~70°W	winter/spring	-	-	200–300 (~250)	250–350 (~250)	40 (10)	40–60 (15)	-	-
INCA	Prestwick: 9	54°–61°N 9°W–4°E	autumn	25 96(234)	41 91(140)	357 760(860)	225 327(364)	46 47(8)	46 48(12)	74 79(14)	68 71(9)
POLINAT II	Shannon: 14	49°–61°N, 5–15°W	autumn	11 14(11)	55 95(114)	241 243(14)	345 378(132)	58 59(17)	81 85(9)	74 73(11)	80 85(9)
SONEX[b]	Shannon: 14	50°–60°N 5–15°W	autumn	18 19	30–98 38–108	235 40	240–265 330	48 45	46 55	80 81	75 75
NOXAR[c] 1995	Zürich: 82	50°–60°N 10°W–8°E	autumn	-	80 131(194)	-	92[e] 152(223)	-	53 54(13)	-	–

[a]Airborne Antarctic Ozone Experiment [*Murphy et al.*, 1993].
[b]Subsonic Assessment Ozone and Nitrogen Experiment.
[c]Measurements of Nitrogen Oxides and ozone along Air routes.
[d]Measurements close to detection limit.
[e]NO_x.

observed from flight to flight. In addition the backward trajectory calculations show that the air masses probed originate from the Southern Pacific Ocean.

[11] Figure 4 depicts mean NO_x/NO_y, NO_y/O_3, O_3 and CO profiles relative to the tropopause of the individual flights. The low NO_x/NO_y ratios (<0.14 mol/mol) in the middle and upper troposphere confirm that relatively clean air was measured over Punta Arenas whereas the profiles over Prestwick show much higher NO_x/NO_y ratios indicating the influence of fresh NO_x emissions. The NO_y/O_3 ratios measured in the lower stratosphere of 0. 004 and 0. 005 in the SH and NH, respectively, are comparable to the ratios found by *Murphy et al.* [1993]. The significantly higher ratio of about 0. 02 observed in the NH tropopause-region reflects the transport of surface emissions by convection into the upper troposphere measured specially during two flights on 12 Oct. 2000. Vertical upward transport occurred repeatedly during INCA in Prestwick because in autumn 2000 the ascent region of the jet stream exit was accentuated close to the UK [*Blackburn and Hoskins*, 2001].

[12] The median concentrations obtained from all INCA mid-latitude flights in the SH and NH for the middle (4-8 km) and upper troposphere (8 km - tropopause) are summarized in Table 1. In the upper troposphere NO, NO_y, O_3, and CO concentrations are factors of 4.5, 3, 1.5 and 1.2 higher over Prestwick compared to Punta Arenas. Corresponding enhancements factors for the middle troposphere are 5, 7.8, 1.5, and 1.4, respectively. For comparison, corresponding median concentrations for previous campaigns are included in Table 1: For the Southern mid-latitudes only data of different seasons were available which exhibit a large scatter possibly due to the more variable nitrogen oxide levels in the different seasons. Significantly higher NO_y and CO values were observed during AAOE and STRATOZ III. These measurements were performed during the dry season with expected long-range transport from biomass burning sites. In addition it is very likely that signal noise contributed to the relatively high NO values reported for TROPOZ II (NO detection limit for these measurements was 50 pmol/mol, [*Rohrer et al.*, 1997]).

[13] For the NH we included only data sampled during major campaigns performed during the same season from POLINAT II [*Schumann et al.*, 2000], SONEX [*Singh et al.*, 1999], and NOXAR 1995 [*Brunner et al.*, 2001]. In general there is a reasonable agreement between the median and mean concentrations calculated for the NH campaigns.

4. Conclusion

[14] During INCA a series of tropospheric profiles of NO_x, NO_y, CO, and O_3 were measured at mid-latitudes in the SH, a region so far only poorly explored. These data provide median NO_x and NO_y mixing ratios for the middle and upper troposphere that can be considered more representative for this region than previous observations from single research flights. These data represents a valuable contribution to a global climatology of reactive nitrogen species and are useful for evaluations of global chemistry transport models.

[15] The INCA measurements over tropical South America agree well with the TROPOZ II data and confirm earlier TROPOZ II observations of an extended upper tropospheric layer of enhanced CO and NO in this region during the wet season. This is due to a persistent anticyclonic flow (Bolivian high) in the upper troposphere which redistributes convectively uplifted air masses from the boundary layer of the Amazon basin over a large area in South America [*Jonquieres and Marenco*, 1998].

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References

Blackburn, M., and B. J. Hoskins, The UK record-breaking wet autumn 2000. Univ. Global Atmospheric Modelling Programme, *UGAMP Newsletter*, *24*, 38–40, 2001.

Brunner, D., J. Staehelin, H. Wernli, and U. Schumann, Nitrogen oxides and ozone in the tropopause region of the Northern Hemisphere: Measurements from commercial aircraft in 1995/1996 and 1997, *J. Geophys. Res*, *106*, 27,673–27,699, 2001.

Drummond, J. W., D. H. Ehhalt, and A. Volz, Measurements of nitric oxide between 0–12 km altitude and 67°N-60°S latitude obtained during STRATOZ III, *J. Geophys. Res*, *93*, 15,831–15,849, 1988.

Ehhalt, D. H., and F. Rohrer, The impact of commercial aircraft on tropospheric ozone, in "The Chemistry of the Atmosphere-Oxidants and Oxidation in the Earth Atmosphere", Proc. of the 7th BOC Pristley Conference, 24–27 June 1994, Lewisburg, USA, edited by A. R. Bandy, Special Pub. No. 170, p. 105–120, 1995.

Emmons, L. K., et al., Data composites of airborne observations of tropospheric ozone and its precursors, *J. Geophys. Res.*, *105*, 20,497–20,538, 2000.

Fahey, D. W., et al., C. S. Eubank, G. Hübler, and F. C. Fehsenfeld, Evaluation of a catalytic reduction technique for the measurement of total reactive odd nitrogen NOy in the Atmosphere, *J. of Atmos. Chem.*, *3*, 435–468, 1985.

Gatti, L. V., et al., Trace gas measurements in the Amazon basin during the wet and dry season, in "A changing atmosphere", Proc. of 8th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, 17–20 Sept., Torino, Italy, edited by J. Hjorth and F. Raes, 2001.

Gerbig, C., D. Kley, A. Volz-Thomas, J. Kent, K. Dewey, and D. S. McKenna, Fast response resonance fluorescence CO measurements aboard the C130: Instrument characterization and measurements made during North Atlantic Regional Experiment 1993, *J. Geophys. Res.*, *101*, 29,229–29,238, 1996.

Hartley, D. E., and R. X. Black, Mechanistic analysis of interhemispheric transport, *Geophys. Res. Lett.*, *22*, 2945–2948, 1995.

Jonquieres, I., and A. Marenco, Distribution by deep convection and long-range transport of CO and CH_4 emissions from the Amazon basin, as observed by airborne campaign TROPOZ II during the wet season, *J. Geophys. Res.*, *103*, 19,075–19,091, 1998.

Logan, J. A., et al., Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, *86*, 7210–7254, 1981.

Murphy, D. M., et al., Reactive Nitrogen and its Correlations with Ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, *98*, 8751–8773, 1993.

Rohrer, F., D. Brüning, and D. H. Ehhalt, Tropospheric mixing ratios of NO obtained during TROPOZ II in the latitude region 67°N-56°S, *J. Geophys. Res*, *102*, 25,429–25,449, 1997.

Schlager, H., et al., In situ observations of air traffic emission signatures in the North Atlantic flight corridor, *J. Geophys. Res.*, *102*, 10,739–10,750, 1997.

Schumann, U., et al., Pollution from aircraft emissions in the North Atlantic flight corridor: Overview on the POLINAT projects, *J. Geophys. Res.*, *105*, 3605–3631, 2000.

Singh, H. B., A. M. Thompson, and H. Schlager, 1997 SONEX airborne mission and coordinated POLINAT activities: Overview and accomplishments, *Geophys. Res. Lett.*, *26*, 3053–3056, 1999.

Ziereis, H., H. Schlager, P. Schulte, P. F. J. van Velthoven, and F. Slemr, Distributions of NO, NO_x and NO_y in the upper troposphere and lower stratosphere between 28° and 61° during POLINAT 2, *J. Geophys. Res.*, *105*, 3653–3664, 2000.

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