

# Estimation of background concentrations of trace gases at the Swiss Alpine site Jungfraujoch (3580 m asl)

J. M. Balzani Lööv,<sup>1</sup> S. Henne,<sup>2</sup> G. Legreid,<sup>2</sup> J. Staehelin,<sup>1</sup> S. Reimann,<sup>2</sup> A. S. H. Prévôt,<sup>3</sup> M. Steinbacher,<sup>2</sup> and M. K. Vollmer<sup>2</sup>

Received 7 December 2007; revised 12 August 2008; accepted 19 August 2008; published 27 November 2008.

[1] Extensive trace gas measurement campaigns were performed in 2005 at the Swiss high-altitude station Jungfraujoch, including measurements of ozone  $(O_3)$ , carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>), the sum of reactive nitrogen species  $(NO_{\nu})$ , peroxyacetylnitrate (PAN), formaldehyde (HCHO), oxygenated volatile organic compounds (OVOCs), volatile hydrocarbons (HCs), methane (CH<sub>4</sub>), and nitrous oxide  $(N_2O)$ . The air masses arriving at Jungfraujoch experience particular transport pathways and therefore are expected to have characteristic chemical signatures. These characteristics are often masked by mixing with European planetary boundary layer air. In order to address the influence of European emissions, a method to retrieve "background concentrations" based on backward trajectories and statistics was developed and applied to the trace gas observations at Jungfraujoch. This procedure is important to determine baseline values for subsequent assessment of surface air quality targets. Cluster analysis of backward trajectories for "background conditions" shows that the influence of long-range transport is discernible in most of the clusters. Air masses tend to have lower background concentrations whenever transport conditions favor a higher amount of photochemical degradation (e.g., low latitude or no recent contact to emissions). The results of this study represent an alternative to aircraft measurements which are typically used to determine free tropospheric background conditions. They are valuable for comparison with numerical simulations and for policy making, and provide additional information about free tropospheric chemistry.

**Citation:** Balzani Lööv, J. M., S. Henne, G. Legreid, J. Staehelin, S. Reimann, A. S. H. Prévôt, M. Steinbacher, and M. K. Vollmer (2008), Estimation of background concentrations of trace gases at the Swiss Alpine site Jungfraujoch (3580 m asl), *J. Geophys. Res.*, *113*, D22305, doi:10.1029/2007JD009751.

#### 1. Introduction

[2] The study of variations of air pollutants in background air masses is a challenging task in the currently changing atmosphere. Effects of climate change on chemistry and dynamics [e.g., *Stevenson et al.*, 2005; *Hurrell et al.*, 2004], together with a relocation of emissions (e.g., toward Asia), might affect local and global air quality. According to *Calvert* [1990], background concentration can be understood as "the concentration of a given species in a pristine air mass in which anthropogenic impurities of relatively short lifetime are not present." This definition implies that background conditions only exist for long-lived compounds, which are well mixed in the troposphere away

Copyright 2008 by the American Geophysical Union. 0148-0227/08/2007JD009751\$09.00

from their sources. However, for relatively short-living compounds like  $O_3$  and its precursors a common and generally applicable definition of background and a method to derive it from point measurements does not exist. Medium-lived compounds tend to have a region of influence which is determined by how fast, and in which chemical and physical environment they are transported before their decay. The importance of intercontinental transport of air pollutants has been the focus of various recent studies that highlighted the potential of intercontinental pollution transport [e.g., *Fehsenfeld et al.*, 1996; *Derwent et al.*, 1998; *Jacob et al.*, 2003].

[3] The distribution of tropospheric O<sub>3</sub> is highly sensitive to photochemistry and transport processes, because of its long lifetime (up to 1–2 months in the free troposphere (FT)) [*Ravetta et al.*, 2007]. A recent model study determined that O<sub>3</sub> originating from Asian emissions contributes between 5 and 30 ppb to the annual mean at different locations in the Northern Hemisphere [*Sudo and Akimoto*, 2007]. Several studies investigated the role of long-range transport (LRT) [e.g., *Stohl et al.*, 2007; *Real et al.*, 2007]; however, continuous long-term in situ measurements including the most relevant O<sub>3</sub> precursors in the FT are not

<sup>&</sup>lt;sup>1</sup>Institute for Atmospheric and Climate Science, Swiss Federal Institute of Technology, Zurich, Switzerland.

<sup>&</sup>lt;sup>2</sup>Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Testing and Research, EMPA, Dübendorf, Switzerland.

<sup>&</sup>lt;sup>3</sup>Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen PSI, Switzerland.

available. Most measurement campaigns and programmes using airborne measurements, are limited to only a few species [e.g., Thouret et al., 1998], short periods or sparse sampling. An alternative approach is to perform measurements from a ground station, where no local or regional pollution affects the measurements. These conditions can be met at remote sites like the arctic or at marine boundary layer stations. However, within the planetary boundary layer (PBL) dry deposition and emissions take place, which will characterize measurements at a particular site. While airborne observations allow a direct sampling of specific air masses, a fixed measurement station is exposed to a wide variety of situations, including air which is locally or regionally polluted. In this case appropriate filters have to be used to distinguish between the different conditions. Frequently, filter functions are based on in situ meteorological parameters and/or on trace gas observations directly [e.g., Zellweger et al., 2002; Henne et al., 2005]. These filters have the disadvantage that they need to be adjusted to a particular measurement site. Statistical filter methods can be applied to multiple locations and rely, at different degrees of complexity, on the identification of measurements which deviate from smooth curve fit to the data [e.g., Novelli et al., 1998; Cox et al., 2003]. In addition, the analysis of air mass origins [e.g., Simmonds et al., 1997] can be used to identify baseline conditions. Furthermore, the combination of meteorological filters and statistical approaches has been used [e.g., Tsutsumi et al., 2006].

[4] The information on background concentrations is important for the study of chemical processes in the remote atmosphere, for the calibration and testing of models, for the evaluation of trends, and for the setting of air quality limit thresholds [*McCarthy et al.*, 2006]. A solid knowledge of the compounds primarily emitted to the atmosphere and the compounds which are secondarily produced during the transport is of key importance for the modeling of photochemical ozone production.

[5] In the particular case of Europe the analysis of background concentrations could add further insights on the question why background O<sub>3</sub> concentrations in Europe increased in the last 15 years, despite a significant decrease in the emission of its precursors [Simmonds et al., 2004; Ordonez et al., 2007]. It is still not clear to what extent the increase in ozone at European high mountain sites is caused by increasing transport of ozone from the stratosphere or if it is due to long-range transport [Ordonez et al., 2005]. Auvray and Bey [2005], using a global chemistry transport model, found that in summer  $O_3$  decreased in the Europe boundary layer from 1980 to 1997. This finding reflects the reduction of European ozone precursor emissions (EMEP, 2004). In the free troposphere, this decrease is compensated by the increase in  $O_3$  due to increasing Asian emissions. In contrast, Ordonez et al. [2007] provide evidence for a significant influence of lowermost stratospheric ozone trends on tropospheric ozone changes over Europe. Furthermore, a better knowledge of the background seasonal cycles is of vital importance to understand the often observed and frequently discussed ozone spring maximum [e.g., Monks, 2000].

[6] The aim of this study is to retrieve and analyze background concentrations for 2005 at the high-altitude research station Jungfraujoch (JFJ, Switzerland), consider-

ing both their seasonal and spatial variation. During this particular year routine and campaign measurements allowed the collection of an extensive data set including:  $O_3$ , nitrogen monoxide (NO) and dioxide (NO<sub>2</sub>), the sum of reactive nitrogen species (NO<sub>y</sub>), carbon monoxide (CO), volatile hydrocarbons (HCs), oxygenated volatile organic compounds (OVOCs), and peroxyacetylnitrate (PAN).

[7] A new methodology to retrieve background concentrations was developed in order to minimize the effect of primary European emissions on the Jungfraujoch observations. This approach is based on the analysis of backward trajectories and additionally takes the observations at Jungfraujoch into account. Furthermore, a back-trajectory clustering was applied to describe the influence of the spatial variation of emission sources on the retrieved background concentrations.

### 2. Methodology

## 2.1. Measurement Site

[8] The high alpine station Jungfraujoch (JFJ, 46.55°N, 7.98°E, 3580 meters above sea level (m asl); see Figure 1) is located in the western Swiss Alps, which are a strong barrier for synoptic-scale air flow. The observatory is located on a mountain saddle between the two mountain peaks Jungfrau (4158 m asl) in the west and Mönch (4099 m asl) in the east. This particular topographical condition strongly influences the local wind field. The main wind directions observed at the site are northwest and southwest. The station is located on the first high topographical barrier that an air mass reaching the station from the north (e.g., from the Swiss Plateau) encounters. In contrast, if an air mass arrives from the south (e.g., from the Po Valley, Italy) it needs to cross the inner Alpine region before it arrives at the JFJ observatory.

#### 2.2. Instrumentation

[9] All the measurements used in this study are summarized in Table 1. The majority of the continuous trace gas measurements at JFJ are carried out as part of the Swiss Air Pollution Monitoring Network (NABEL), which is run by the Swiss Federal Laboratories for Materials Testing and Research (Empa) in joint collaboration with the Swiss Federal Office for Environment (FOEN). In addition to the continuous measurements, four seasonal campaigns took place during 2005 focusing on HCHO (winter (20 February to 8 March), spring (15 April to 16 May), summer (9-22 August and 9-18 September), autumn (7 October to 7 November)), on OVOCs (winter (8 February to 15 March), spring (22 April to 30 May), summer (5 August to 19 September), autumn (14 October to 1 November)), and PAN (February 2005 to August 2006). Only results from overlapping HCHO and OVOCs measurements are included in this study.

[10] Air samples were collected using the NABEL stainless steel (SS) inlet with an inner diameter (ID) of 8 cm and a total length of 3.1 m. The air flow was 50 m<sup>3</sup> h<sup>-1</sup> and a heating system provided a constant temperature of 10°C. A glass manifold (ID 4 cm) flushed with 100 L min<sup>-1</sup> is connected to the main inlet. Perfluoroalkoxy (PFA) teflon tubes (ID 6 mm, approximately 2 m) are used in the stream to connect the O<sub>3</sub> and CO instruments to the glass inlet. The



**Figure 1.** A map illustrating the polygon used as latitude and longitude definition of Europe in order to determine the planetary boundary layer contact in this study. The position of JFJ is indicated by a dot.

NO, NO<sub>x</sub>, NO<sub>y</sub>, HCHO, OVOCs, and PAN instruments are directly connected to the main inlet using PFA tubing. Particular care was taken for the NO<sub>y</sub>, PAN, and HCHO measurements by installing the instrument as close as possible to the inlet to avoid adsorption losses or thermal decomposition of the measured compounds themselves. The CH<sub>4</sub>, N<sub>2</sub>O analyzers, and the instrument used to measure volatile hydrocarbons were directly connected to the inlet by a 1/8'' SS tubing.

[11] CO was measured with a commercially available instrument (HORIBA APMA-360) using nondispersive infrared (NDIR) technique. O<sub>3</sub> was measured with a commercially available instrument (Thermo Environmental Instruments (TEI), Model 49C) using UV absorption. NO,  $NO_x$  and  $NO_y$  were measured with a commercially available instrument (CraNO<sub>X</sub>, Ecophysics) using two chemiluminescence detectors (CLD 770 AL pptv) with temperature controlled reaction chambers.  $NO_x$  was measured as NO after photolytic conversion of  $NO_2$  (PLC 760) with a typical conversion efficiency of ~60%. Nitrogen dioxide (NO<sub>2</sub>) was then calculated as the difference between NO<sub>x</sub> and NO. NO<sub>y</sub> species were converted on a heated gold catalyst (300°C) with 2% CO (99.997%, Messer-Griesheim GmbH) as a reducing agent. The instrumentation is described in detail by *Zellweger et al.* [2000].

[12] Reactive hydrocarbons (n-butane, isobutane, npentane, iso-pentane, benzene and toluene) were continuously analyzed, with an integration time of 4 hours by gas chromatography-mass spectrometry coupled with an automated adsorption-desorption system (GC-MS-ADS, Agilent 5793N), which also measured halocarbons [*Reimann et al.*, 2004].

[13] CH<sub>4</sub>, and N<sub>2</sub>O were quasi-continuously measured (every 30 min) using an Agilent 6890N gas chromatograph equipped with a flame ionization detector (FID) and an electron capture detector (ECD) (M. Steinbacher, manuscript in preparation, 2008).

[14] HCHO was measured using a Hantzsch fluorimetric monitor, which is similar to the AERO LASER CH<sub>2</sub>O analyzer AL4021, and based on sensitive wet chemical fluorimetric detection of HCHO [*Kelly and Fortune*, 1994], making use of the Hantzsch reaction [*Nash*, 1953]. The source lamp used in the fluorimeter was a blue lightemitting diode (LED) and a photomultiplier tube as described by *Junkermann and Burger* [2006]. In order to reach higher sensitivity a reduced liquid flow setup was used (0.16 mL min<sup>-1</sup>) and the air was collected with a flow of 1.2 L min<sup>-1</sup>. The precision was ranging from around 20% below 0.5 ppb to 5% at 2 ppb. A recent intercomparison [*Hak et al.*, 2005] showed an accuracy of 12% for this type of instrument. The detection limit, calculated as  $3\sigma$  of the instrumental noise, was found to be 22 ppt.

[15] PAN was measured with a commercially available gas chromatograph (PAN GC, Meteorologie Consult GmbH). The analytical method was based on sampling 2 mL of air in a loop, chromatographic separation, and subsequent electron capture detection (ECD). The overall measurement uncertainty was estimated to be  $\pm 5\%$  (1 $\sigma$ ) and included the uncertainty of the calibration standard, the NO and zero air flow during the calibration, and the integration precision of the GC. The detailed procedure is described by *Zellweger et al.* [2000].

[16] OVOCs were measured using a new GC-MS instrument [Legreid et al., 2008]. The air samples were collected

Table 1. Continuous and Campaign Trace Gas Measurements Performed at JFJ and Used for This Study

Measured Species	Method	Period	Time Resolution	
	Continuous Measurements	Performed by EMPA		
CO	NDIR	continuous	10 min	
O <sub>3</sub>	UV photometry	continuous	10 min	
NO	chemiluminescence	continuous	10 min	
	(after reaction with $O_3$ )			
NO <sub>r</sub>	photolytic conversion	continuous	10 min	
NO <sub>2</sub>	calculated (NO <sub>x</sub> $-$ NO)			
NOv	catalytic conversion 'Au'	continuous	10 min	
HCs	GC-MS	continuous	4 hrs	
$CH_4$	GC-FID	continuous	30 min	
	Campaign Mea	isurements		
НСНО	Hantzsch monitor	4 seasonal campaigns	1 min	
PAN	GC-ECD	4 seasonal campaigns	10 min	
OVOCs	GC-MS	4 seasonal campaigns	50 min	



**Figure 2.** Variation of annual mean concentrations for different compounds as a function of the selected quantile.  $O_3$  and CO concentrations are in ppb,  $NO_y$  and HCHO are in tens of ppt,  $NO_x$ , benzene, toluene, and PAN are in ppt. The right *y* axis indicates the percentage of the European Unpolluted trajectories remaining.

on a two-stage adsorbent system connected to a gas chromatograph-mass spectrometer (GC-MS Agilent HP 6890 -HP 5973N). One measurement cycle took 50 min. The OVOCs were measured with an accuracy of 3-25% (nbutanol: 37%) and a precision of 1-5%, calculated from an intercomparison experiment within the European project ACCENT. The detection limit, calculated as the  $3\sigma$  above the noise of 5 zero air samples, lies in a range of 1-120 ppt depending on the compound.

# 2.3. Backward Trajectories

[17] In this study trajectory calculations were based on European Center for Medium-range Weather Forecast (ECMWF) data with a temporal resolution of 3 hours, horizontal resolution of  $1^{\circ} \times 1^{\circ}$ , and 60 vertical levels. The temporal resolution of 3 hours was achieved by combining analysis fields (0000, 0600, 1200, and 1800 UTC) with forecast fields. The use of a forecasted wind field helps to reduce temporal interpolation errors [Stohl, 1998]. Three-dimensional trajectories were retrieved using the LAGRangian ANalysis TOol (LAGRANTO) described in detail by Wernli and Davies [1997]. An ensemble of 15 days backward trajectories was calculated for each hour of the year 2005. Each ensemble consists of a reference trajectory (centered on JFJ at a mean pressure of 660 hPa) and six displaced trajectories, 4 have an offset of  $\pm 0.5^{\circ}$  in latitude and longitude and 2 are located 20 hPa above and below the reference pressure. The trajectory position was stored with a time step of 1 hour. In total 8757  $\times$  7 trajectories were calculated.

#### 2.4. Background Definition by the Use of Trajectories

[18] The ensemble of trajectories and the associated measurement data were used to identify "Unpolluted Euro-

pean" air masses (hereinafter, UE) applying separately, for each month, the following steps.

[19] 1. The time each trajectory spent in the European PBL (residence time, RT) was calculated for each individual trajectory belonging to the trajectory ensemble  $\Theta$ . Europe was defined using a polygon with a resolution of  $1^{\circ} \times 1^{\circ}$  (see Figure 1), and a constant PBL top of 700 hPa. This PBL height was found to represent an upper limit for the PBL height during summer in Europe [*Matthias et al.*, 2004]. The average residence time,  $\overline{RT}$ , at a specific time was then defined as the weighted mean for each trajectory *i* of the ensemble  $\Theta$ ,

$$\overline{RT}(\Theta) = \sum_{i} w_{i} RT(\Theta)_{i}, \qquad (1)$$

where  $w_i$  is equal to 0.4 for the reference and 0.1 for the 6 displaced trajectories. Each trajectory ensemble was classified as UE only if  $\overline{RT}$  was <0.5 hours. This means, if at least the reference and one displaced trajectory spent one hour in the European PBL, the trajectory of the specific arrival time was discarded. Following this criterion 34.6% of the initial data set was selected as unpolluted.

[20] 2. Each trajectory ensemble  $\Theta$  was classified as UE if the following condition was fulfilled:

$$\Theta: \ x(\Theta) < (0.75)_{q \ x} \ \forall \ x, \tag{2}$$

where  $(0.75)_{q x}$  is the 20 days running 0.75 quantile calculated for a selected group of compounds *x*, which originate from the PBL. The ensemble *x* includes the continuously measured HCs at the site (benzene, toluene, i-butane, n-butane, n-pentane), plus CO and NO<sub>x</sub>, but not NO<sub>y</sub>. Since the HCs were measured every 4 hours



**Figure 3.** Examples of CO measurements and the defined background. The black line gives all measurements, the pink circles are the detected background concentrations, and the green line is a daily running average of the background. Monthly means of the background are also shown as a pink line with its standard deviation (dash-dotted line).

they were interpolated to every single hour between every two consecutive measurements. This criterion leads to a selection of 22.6% of the initial data set as UE.

[21] The overall aim of the use of this procedure is to obtain a data set for which no contact with the European PBL in the previous 15 days before reaching JFJ took place. To assume real "background conditions," these strict criteria were applied. These include the rather elevated height of the PBL and the short European residence time.

[22] Although this method works very well for the colder months, it is less successful for the summer months because trajectories alone cannot sufficiently resolve thermal lifting and mountain venting events (more frequent in spring, summer and autumn), particularly in a complex mountain area as the Alps [*Henne et al.*, 2004]. To overcome these difficulties we eliminated the highest concentrations using a 0.75 running quantile.

[23] However, the selection of data based on the 0.75 running quantile might lead to the exclusion of major transport events, during which longer-lived compounds might be increased especially in periods of low photochemistry. The choice of the 0.75 quantile is a good compromise to maintain enough data points and to remove potential extreme values. As shown in Figure 2, choosing a lower 0.65 quantile would lead to a further 5% loss of data points

during 2005 and a small reduction of the annual mean mixing ratios of different compounds (CO mean by 1.8%, O<sub>3</sub> by 0.3%, and NO<sub>y</sub> 6% with slightly higher variations for NO<sub>x</sub> and PAN).

[24] The background concentration based on the applied conditions is representative of air masses which have not been in contact with the European PBL. Long-range transport events are considered as "background," since they are not affected by Europe and are not depending on European emissions. With this method 22.6% of the total data were maintained. An example of its application is given in Figure 3 for CO concentrations during March and August, where the pink dots represent the selected background. The selected points efficiently mark periods of low, background CO concentrations. These results are then used to calculate a monthly background concentration and its percentiles.

# 2.5. Identification of North American PBL and STT Influence

[25] The retrieved UE background is expected to show specific chemical signatures. Trajectory calculations (number of trajectories which spent more than 5 hours in the North American PBL), show that 24% of the JFJ measurements during 2005 were influenced by NA LRT. However,



Figure 4. Time series of  $O_3$ , CO, and  $NO_y$  observations at JFJ. All measurements are shown in black; the estimated background concentrations are shown in red.

only 7% of the total 2005 measurements represent air directly transported to JFJ without mixing with the European PBL. Furthermore, while retrieving background concentrations it cannot be avoided that applying the 0.75 running quantile excludes some LRT events. However, this is not true for stratosphere to troposphere (STT) extreme transport events, because O<sub>3</sub> is not used in the calculations of ensemble x, therefore a higher observed  $O_3$  concentration would not lead to the exclusion of a particular date. Stratospheric influence (calculated as trajectories with potential vorticity (PV)  $\geq 2$  during the period 5 days prior to the arrival at JFJ (PV = 2 is commonly used to indicate the tropopause height, while lower PV values refer to the troposphere and higher values refer to the highly stable stratosphere) was less important (less than 4%) and most of the air masses seem to mix with European PBL air before arriving at JFJ. Only 1% of the STT influenced air masses during 2005 were not mixed with European PBL before arriving at JFJ. This could have been caused by the PBL definition used in our method (700 hPa) which is very restrictive for the colder months, or by a fast turbulent mixing of dry and colder stratospheric air with warmer, moister, and more polluted tropospheric air [e.g., Brioude et al., 2006], leading to an exclusion of the event from UE background. Furthermore, contact with stratospheric air might have occurred earlier than 5 days prior to sampling [Stohl et al., 2000], which also indicates, that the classification, used in this study does not account for all stratospheric contributions.

#### 2.6. Trajectory Clustering

[26] In order to evaluate the influence of different flow patterns on the background concentration of the different compounds, we applied cluster analysis to the trajectory position. Similar techniques were successfully used in several studies [e.g., Harris and Kahl, 1990; Traub et al., 2003; Henne et al., 2008a] for interpretation of trace gas measurements in relation to large-scale air mass transport. The freeware program PLOTRA v2.1 was used [Sodemann, 2000]. PLOTRA uses Ward's hierarchical clustering method with a 3D Euclidean distance measure on the normalized coordinates of each trajectory point. This accounts for the variations in transport speed and direction in both horizontal and vertical directions simultaneously, yielding clusters of trajectories of similar length, altitude, and curvature. In this study we concentrated on the days 15 to 6 prior to the arrival at JFJ emphasizing the origin of the trajectory. Only

trajectories of the UE background (1978 trajectories with 3 hour time step) were divided into clusters.

#### 3. Results and Discussion

#### 3.1. Performance of Background Estimation

[27] An overview of the selected background concentrations is given in Figure 4 for  $O_3$ , CO, and  $NO_y$ . The method satisfactorily selects lower concentrations, in particular for  $NO_y$ , which is not utilized in the selection procedure (see section 2.4). Table 2 presents the average concentrations and their standard deviations for each compound during the four different astronomical seasons (in order to include the 4 measurements campaigns of OVOCs and HCHO). More detailed results, including complete statistics and detection limits, are given in the auxiliary materials.<sup>1</sup>

[28] Another important result is that the calculated background reduced the diurnal cycle for compounds which are transported to JFJ during daytime by thermal lifting [Zellweger et al., 2002; Henne et al., 2004]. As displayed in Figure 5 the method results in a substantial decrease in CO concentrations in all seasons and an evident reduction in late afternoon concentrations in summer. However, in spring and summer NO<sub>y</sub> is still partially influenced by thermally induced mountain venting. Particularly during spring an increase between 1200 and 1800 CET is observed.

<sup>[29]</sup> In order to evaluate the error due to convection and thermal lifting a monthly Night Relative Error (NRE) was introduced,

$$NRE_i = \left(\frac{UE_i - UEN_i}{UE_i}\right) \times 100\%,\tag{3}$$

where  $UE_i$  is the UE concentration of compound *i*, and  $UEN_i$  is the UE concentration of compound *i* considering only night measurements (from 1500 to 0900 local time). This approach is based on the idea that night or early morning measurements can be used as background concentration, as already shown for JFJ [*Lugauer et al.*, 1998; *Nyeki et al.*, 1998; *Baltensperger et al.*, 1997] and for other high altitude sites [e.g., *Zhou et al.*, 1996; *Henne et al.*, 2008b]. NRE should be considered only for primary pollutants because a secondary produced compound could show higher mixing ratios during daytime compared to nighttime values because of photochemical production. If

<sup>&</sup>lt;sup>1</sup>Auxiliary materials are available at ftp://ftp.agu.org/apend/jd/ 2007jd009751.

	2005	Winter	Spring	Summer	Autumn
O <sub>3</sub> (ppb)	$52 \pm 8.7$	$49 \pm 6.3$	$58 \pm 8.6$	54 ± 9.2	47 ± 5.7
CO (ppb)	$109 \pm 17.4$	$122 \pm 12.6$	$110 \pm 18.4$	$92 \pm 10.6$	$105 \pm 14.1$
NO <sub>2</sub>	$31 \pm 37.8$	$24 \pm 25.3$	$42 \pm 43.3$	$50 \pm 41.7$	$14 \pm 24.3$
NO	$13 \pm 14.0$	$12 \pm 10.8$	$16 \pm 15.4$	$15 \pm 18.5$	$9 \pm 12.0$
NO <sub>v</sub>	$571 \pm 317.8$	$309 \pm 104.0$	$740 \pm 324.0$	$879 \pm 348.0$	$489 \pm 100.4$
NOx	$31 \pm 44.4$	$15 \pm 25.1$	$52 \pm 53.1$	$56 \pm 52.9$	$14 \pm 28.4$
i-Butane	$27 \pm 23.6$	$51 \pm 18.7$	$15 \pm 11.0$	$10 \pm 4.6$	$34 \pm 27.6$
n-Butane	$26 \pm 26.0$	$65 \pm 30.3$	$13 \pm 12.6$	$13 \pm 8.0$	$27 \pm 17.7$
i-Pentane	$19 \pm 10.6$	$25 \pm 10.0$	$17 \pm 8.5$	$19 \pm 13.6$	$14 \pm 8.2$
n-Pentane	$10 \pm 8.4$	$13 \pm 6.3$	$5 \pm 3.3$	$6 \pm 4.3$	$13 \pm 12.4$
HCHO	$290 \pm 126.2$	$143 \pm 30.5$	$351 \pm 174.4$	$353 \pm 93.1$	$272 \pm 62.1$
PAN	$127 \pm 101.4$	$137 \pm 54.1$	$165 \pm 128.4$	$133 \pm 77.4$	$74 \pm 44.1$
Benzene	$20 \pm 16.2$	$46 \pm 14.6$	$12 \pm 9.5$	$11 \pm 5.7$	$19 \pm 11.8$
Toluene	$11 \pm 7.2$	$13 \pm 6.5$	$8 \pm 4.2$	$15 \pm 9.7$	$11 \pm 7.0$
Methanol	$510 \pm 231.4$	$473 \pm 56.4$	$562 \pm 239.4$	$623 \pm 249.8$	$343 \pm 74.5$
Butadiene	$1 \pm 0.7$	$0 \pm 0.1$	$0 \pm 0.6$	$1 \pm 0.9$	$1 \pm 0.8$
Acetaldehyde	- ± -	- ± -	- ± -	$172 \pm 55.3$	$106 \pm 66.9$
Ethanol	$115 \pm 82.5$	$102 \pm 50.1$	$83 \pm 50.4$	$77 \pm 60.4$	$194 \pm 83.9$
Isoprene	$4 \pm 3.2$	$1 \pm 1.2$	$6 \pm 2.3$	$3 \pm 4.5$	$3 \pm 1.8$
Acroleyn	$7 \pm 5.4$	$7 \pm 2.3$	$14 \pm 2.4$	$4 \pm 1.8$	$2 \pm 1.6$
Propanal	- ± -	- ± -	- ± -	$23 \pm 5.9$	$18 \pm 7.5$
Methylacetate	$11 \pm 4.6$	$10 \pm 1.4$	$15 \pm 5.8$	$10 \pm 2.5$	$9 \pm 1.4$
Isopropanol	- ± -	$36 \pm 9.8$	$22 \pm 13.7$	- ± -	- ± -
Acetone	$667 \pm 171.3$	$527 \pm 53.7$	$650\pm200.9$	$746 \pm 156.5$	$631 \pm 122.3$
Propanol	- ± -	$1 \pm 0.6$	$3 \pm 1.2$	$1 \pm 0.6$	- ± -
MTBE	- ± -	- ± -	$4 \pm 2.1$	$8 \pm 10.5$	$9 \pm 4.7$
Methacrolein	$2 \pm 2.3$	$1 \pm 0.3$	$2 \pm 1.1$	$3 \pm 3.6$	$1 \pm 1.1$
Ethylacetate	$8 \pm 3.6$	$8 \pm 2.9$	$8 \pm 3.1$	$11 \pm 6.3$	$7 \pm 2.3$
Butanal	- ± -	- ± -	- ± -	$26 \pm 22.7$	$24 \pm 7.7$
MVK	$7 \pm 5.4$	$5 \pm 2.0$	$7 \pm 4.1$	$10 \pm 6.8$	$3 \pm 2.9$
MEK	- ± -	- ± -	- ± -	$23 \pm 12.8$	$31 \pm 12.1$
MBO	- ± -	$8 \pm 4.3$	- ± -	$7 \pm 3.9$	$3 \pm 0.9$
Penatanal	- ± -	- ± -	- ± -	$11 \pm 2.3$	$5 \pm 1.7$
Butyl-acetate	$3 \pm 1.5$	$1 \pm 0.7$	$3 \pm 1.0$	$2 \pm 1.7$	$3 \pm 1.6$
Hexanal	- ± -	- ± -	- ± -	$10 \pm 2.7$	$11 \pm 2.9$
Benzaldehyde	$6 \pm 3.0$	$2 \pm 0.5$	$8 \pm 2.1$	$4 \pm 1.4$	$8 \pm 2.9$
CH <sub>4</sub> (ppb)	$1823 \pm 17.1$	$1829 \pm 16.6$	$1823 \pm 16.4$	$1821 \pm 21.6$	$1822 \pm 14.3$
$N_2O$ (ppb)	$321 \pm 0.8$	$320 \pm 0.6$	$320 \pm 0.5$	$320 \pm 0.7$	$321 \pm 0.6$

Table 2. Background Concentrations Measured at JFJ During 2005<sup>a</sup>

<sup>a</sup>The yearly and the seasonal averages with the standard deviation of the individual measurements are given. Units are ppt except when specified otherwise.

we use the NRE of NO<sub>y</sub> as an indicator for thermal lifting (as proposed by *Zellweger et al.* [2002]), we find a maximum error of less than 20% during the spring and summer period. Therefore, for spring and summer seasons we should regard the determined background concentrations as un upper limit for the background air.

# **3.2.** Comparison With Measurements at Other Remote Sites

[30] In this section, a brief comparison with selected other measurements at northern hemispheric mountain stations and airplane campaigns addressing "background" measurements is provided. Generally, all background concentrations derived by this method (particularly for anthropogenic primary pollutants) fall within or below the range of values derived from other measurements for northern hemispheric "background" conditions.

[31] CO and O<sub>3</sub> background values for JFJ are in the range of 93–111 ppb for CO and 55–58 ppb for O<sub>3</sub>. For Mount Waliguan (WLG, 36.28°N, 100.90°E, 3816m a.s.l., China) [*Wang et al.*, 2006] found mixing ratios of 103–133 ppb for CO, and 61–58 ppb for O<sub>3</sub> for spring and summer, respectively. At Mount Bachelor (MBO, 44.00°N, 121.70°E, 2763m a.s.l., USA) *Weiss-Penzias et al.* [2006] published CO and O<sub>3</sub> mixing ratios of 179 ppb and 54 ppb

respectively, while for "wet" conditions concentrations they were 40 ppb for  $O_3$  and 150 ppb for CO. *Lewis et al.* [2007] showed an average CO and  $O_3$  mixing ratio of 110 ppb and 55 ppb, respectively, based on measurements of a flight campaign above Azores islands (Atlantic Ocean) during summer 2004.

[32] Benzene background concentrations during winter and summer at JFJ are much lower than at Zeppelin, Spitsbergen [Solberg et al., 2002], and at Pallas in northern Finland [Hakola et al., 2006], and at the rural site Hohenpeissenberg [Plass-Dülmer et al., 2006]. Also the concentrations of all the other hydrocarbons deduced from measurements of JFJ concentrations were lower than at Arctic stations (during both summer and winter), which could be due to the longer lifetime of those compounds at high latitudes. This is related to the existence of a meridional gradient in the concentrations of many pollutants (e.g., CO [see Solberg et al., 2002]).

[33] The low concentrations of primary OVOCs deduced by our approach (e.g., Methyl-tert-butyl-ether) [Legreid et al., 2008] show that PBL influence was effectively removed. Compounds which can be of primary and secondary origin show a slightly more variable behavior. Alcohols were the most abundant OVOCs measured during 2005. Methanol, which is emitted both from anthropogenic and



**Figure 5.** Diurnal cycle of CO and  $NO_y$  (the solid line represents the hourly mean, and the dash-dotted lines represent the standard deviation; the squares show the diurnal cycle of background concentrations.)

biogenic sources, and is secondarily produced in the atmosphere mainly from CH<sub>4</sub> oxidation [Schade and Goldstein, 2006], showed higher values than in the Arctic but similar or lower values than reported from flight campaigns over the Atlantic and the Pacific Ocean [Singh et al., 2000, 2004]. Ethanol at JFJ showed higher concentrations than in the Arctic [Boudries et al., 2002] but was comparable to concentrations at Trinidad Head (USA) [Millet et al., 2004] and encountered during flight campaigns over the Pacific Ocean [Singh et al., 2004]. About 50% of ethanol in the background atmosphere over the Pacific was estimated to originate from primary biogenic sources, while the rest was explained equally by biomass burning, hydrocarbon oxidation, and anthropogenic emissions [Singh et al., 2004]. Acetone was the most abundant carbonyl measured at JFJ. It generally showed lower concentrations than at other background sites like over the Pacific Ocean [Singh et al., 2004] and in the Arctic [Boudries et al., 2002]. Acetone is a globally abundant compound, which can act as a source of  $HO_x$ , peroxy, and alcoxy radicals in the free troposphere [Arnold et al., 1997; Singh et al., 1994]. Jacob et al. [2002] estimated the oxidation of anthropogenic iso-alkanes to be the main source of acetone in the northern hemisphere in all seasons except summer. Acetaldehyde was the second most abundant aldehyde and its concentrations seem to be in the range of measurements performed in the high Arctic [Boudries et al., 2002] and over the Pacific Ocean [Singh et al., 2004]. However, note that acetaldehyde has been measured only in summer and autumn. Other aldehydes were present in much lower quantities decreasing with the length of their carbon chain.

[34] The HCHO background at JFJ was slightly higher than values from campaigns over the oceans [e.g., *Lowe and Schmidt*, 1983] but still lower than observed at coastal sites like Mace Head or Cape Grim [*Ayers et al.*, 1997; *Cardenas et al.*, 2000].

[35] Owing to its smaller thermal decomposition at lower temperature, the background of PAN at JFJ is higher than at MBL stations like Izana in the Atlantic Ocean [Schmitt and Volz-Thomas, 1997] or at the Mauna Loa Observatory [Ridley et al., 1998], but slightly lower than in campaign measurements sampling background air off the west coast of North America [Roberts et al., 2004]. Interestingly, PAN concentrations in 2005 were significantly lower than those reported by Zellweger et al. [2002] for free tropospheric background during measurements at JFJ in 1997–1998. This could be due to the different method used to define "background" samples or due to changed transport conditions in recent years.

# **3.3.** Seasonal Variation of Primary and Secondary Compounds

[36] Figure 6 shows an overview of the seasonal variation of monthly background concentrations of selected compounds at JFJ.

[37] During winter longer lifetimes and higher emissions of primary pollutants (due to domestic heating, cold start engine conditions, etc.) explain the higher concentration of primary compounds measured in the FT at JFJ. Several studies showed higher concentrations of primary pollutants in the remote PBL during winter [e.g., *Solberg et al.*, 1996; *Lightman et al.*, 1990; *Hakola et al.*, 2006]. In this season



**Figure 6.** Background mixing ratios of CO,  $O_3$ , CH<sub>4</sub>, NO<sub>3</sub>, benzene, methanol, formaldehyde, and peroxyacetylnitrate at JFJ. The upper and lower quartiles are represented by the box, the line is the median, and the cross is the mean. The red diamonds show the background mixing ratios calculated using only data from 0300 to 0900 local time. The numbers at the bottom represent the number of valid selected measurements. NRE values are also given as the maximum for each period.

HCs can be transported over long distances. During springtime the degradation of these compounds becomes faster because of higher OH radical concentrations. CO is a primary and secondary pollutant and its concentration decreases by a factor 1.4 between winter and summer. In summer production from the degradation of HCs is an additional important source of CO [*Griffin et al.*, 2007]. Also CH<sub>4</sub> shows a decrease during spring. This is similar to measurements reported from Alaska where the minimum in June was explained by photochemical destruction and the subsequent summer increase due to higher wetland emissions [see *Dlugokencky et al.*, 1997].



Figure 7. Seasonal frequency for each of the eight clusters (for abbreviations of clusters, see text).

[38] The concentrations of secondary OVOCs increase from winter to summer with formaldehyde strongly increasing from winter to summer (by a factor of 2.5). During summer aldehyde concentrations generally show the strongest correlation with  $O_3$ , indicating the importance of photochemical production. Pearson correlation coefficients between  $O_3$  and acetaldehyde, propanal, and pentanal were 0.63, 0.68, and 0.61, respectively. Ketones, in contrast, showed less increase (factor 1.4) and lower correlations with  $O_3$  (R = 0.39, acetone). The increase of alcohols (factor 1.6) is mainly driven by the increase of methanol, which is both a secondary and a primary compound.

[39] Background ozone shows low values in the cold months and a spring maximum (see Table 2). Several factors are believed to contribute to the spring maximum [Monks, 2000]: the general increase in photochemical production during spring, enhanced springtime stratosphere-troposphere exchange, export of primary pollutants from the polar front reservoir, an increased PBL-FT flux, seasonal changes in  $NO_x$  sources, in situ production of  $O_3$  in the FT with a possible O<sub>3</sub> buildup during winter due to favorable condition for high net O<sub>3</sub> production in this season. [Penkett and Brice, 1986] attributed a maximum in PAN background concentrations in May to large photochemical production in combination with enhanced primary pollutant concentrations as consequence of accumulation during winter. In agreement with their results, PAN concentrations at JFJ peaked in spring, but were relatively lower (170 pptv) in the UE background, representing only 24% of the NO<sub>z</sub> (NO<sub>y</sub> – NO<sub>x</sub>) leaving a large unexplained fraction of NO<sub>y</sub>. Zanis et al. [2007] analyzed 6 years of measurements at JFJ and concluded that important sources of NO<sub>x</sub> exist probably in spring, which are not related to the export from the PBL. The same authors highlighted the dominant role of photochemistry in the observed buildup of tropospheric ozone in the winter-spring transition period.

### 3.4. Clustering

[40] The ability to eliminate air masses influenced by European pollution permits to analyze the influence of different large-scale source regions to the receptor point JFJ. The different source regions were identified through different clusters of trajectories as described in section 2.6. The number of clusters was chosen arbitrarily, nevertheless, while increasing the number of clusters, no further significant divisions of clusters were observed. The mean water vapor content in each cluster was consistent with the vertical movement within each cluster, with lower relative humidity (RH) encountered in sinking air masses and higher RH in rising air masses. Furthermore, it is important to notice that the air masses representing UE background at JFJ generally occurred during anticyclonic conditions, while most of the transport from the European PBL results from the movement of fronts linked to low-pressure systems.

[41] The seasonal frequency of each cluster is shown in Figure 7 and their spatial distribution is reported in Figure 8.

**Figure 8.** Spatial distribution of the eight background trajectories clusters. The colors represent the number of hourly trajectory points residing inside a horizontal (1° latitude  $\times$ 1° longitude), or vertical cell (1° longitude  $\times$  100 hPa), thus indicating the probability of the origin of a certain cluster. Only the clustered 15-6 days prior to arrival at JFJ are colored. The black line and the dashed line represent the average and the standard deviation of the final 5-0 days transport before reaching the station. For abbreviations of clusters see text.



Figure 8



**Figure 9.** Overview of  $O_3$  and CO concentrations for the different clusters. The solid circles represent the 2005 average concentrations for  $O_3$  and CO for each cluster together with their 25th to 75th percentiles. The colored triangles ( $O_3$ ) and squares (CO) show the concentrations for each cluster for the different seasons.

An overview of  $O_3$  and CO concentrations for the different clusters is given in Figure 9. In the following the most striking features of dynamics and chemistry for each cluster are discussed, while more complete statistics for the clusters during the different seasons are given in the auxiliary material. In the following a "significant difference" means a 95% confidence limit calculated with a student t-test of the observed cluster against the mean of all the others (i.e., cluster 1 versus the mean of clusters 2 to 8). Particular care was taken to check if the characteristics of a cluster are consistent throughout all the seasons.

[42] Cluster 1 is storm track north (STN). This ensemble is characterized by a fast meridional transport, associated with low-pressure systems moving along the typical midlatitude storm track centered on the 45° parallel at an average level of 410 hPa. This air could encounter strong mixing along the path and arrive at JFJ mainly following an anticyclonic descending flow with relatively high pressure (660 hPa) and 50% RH at the receptor site. Although not directly linked to transport from the North American continent these trajectories could be linked with very long transport, even from the Asian continent. This cluster was more frequent in winter and autumn as expected for this flow type. Regarding CO, this cluster shows higher mixing ratios in all months (significant in autumn; see Figure 9) compared to all other clusters. Regarding O<sub>3</sub>, only slightly higher mixing ratios in summer and autumn are observed, whereas for spring significantly higher concentration of 67 ppb compared to an average of 59 ppb occurred. Cluster 1 shows generally lower  $NO_{\nu}$  concentrations (significant in spring with 0.59 ppb against 0.74 ppb), except for summer. PAN concentrations are higher than average, except for autumn (significant in spring with 0.49 ppb). This leads to a remarkably high yearly PAN/NO<sub> $\nu$ </sub> ratio of 0.83, probably

due to the fact that the air masses move down from higher (colder) altitudes where PAN does not decompose.

[43] Cluster 2 is storm track south (STS). This ensemble is similar to the first but represents air masses on average originating further from the south (41°N) and from lower altitudes (600 hPa), with 50% RH at the receptor site. The STS cluster shows higher CO, in all the months (significant in summer and autumn). O<sub>3</sub> concentrations are higher in all seasons (significant in winter), whereas NO<sub>y</sub> concentrations are lower in all seasons (significant in autumn).

[44] Cluster 3 is anticyclonic Blocking (AB). This cluster exhibits low RH at the arrival (49%) but is associated with slightly lower pressure (657 hPa) and more northerly transport (with an average of 51°N). In contrast to the storm track clusters, the air parcels move slower and cross the Atlantic ocean within two weeks. This is caused by a stable high-pressure system NW of Europe with air flowing around it before reaching JFJ. Contact with the North American boundary layer cannot be excluded but was not resolved in our 15 days backward trajectories. The AB cluster shows higher CO mixing ratios in all seasons except autumn (significant in winter and spring with a maximum of 125 ppb in spring against an average of 110 ppb). This finding is interesting because it could indicate transport from polar regions toward Europe, since air masses travel around a high-pressure system with northerly wind in the mid polar troposphere (above the polar circle). In this region higher concentrations are normally observed in winter and spring [e.g., Hakola et al., 2006; Law and Stohl, 2007]. This is also supported by the significantly lower temperature recorded at the site during these events (e.g.,  $-8.5^{\circ}C$ against an average of  $-2.8^{\circ}$ C for spring). These considerations also apply to other primary HCs and OVOCs. O3 mixing ratios are higher in spring, summer, and winter (significant in spring and autumn). Cluster AB shows generally higher NO<sub>y</sub> mixing ratios except in spring (significant in winter, with 0.37 ppb against 0.31 ppb, and autumn, 0.58 ppb against 0.49 ppb). PAN was close to the average during the winter but significantly higher in spring (0.22 ppb against 0.17 ppb on average), although the PAN/ NO<sub>y</sub> ratio was only 0.33. For summer no data are available but in autumn PAN had the highest mixing ratios among all the clusters (0.11 ppb against 0.07 ppb on average). Nevertheless, another reason for the enhancement of these compounds could be the generally slow transport over Europe accompanied by vertical exchange between FT and PBL.

[45] Cluster 4 is long-range Transport A (LRT-A). Typical conditions related to Warm Conveyor Belts (WCB) were characteristic of this cluster: High RH (66%), an elevated average number of hours spent in the North American PBL during winter and autumn (15 hours in both seasons), fast transport across the Atlantic Ocean (between the last contact with North American PBL and JFJ, respectively of 5.8 and 6.1 days for winter and autumn), and an average temperature gradient of the air mass of  $-2.2^{\circ}$ C d<sup>-1</sup>. The average latitude is 47°N and the average pressure level is 603 hPa. This cluster showed slightly higher concentrations of CO except in winter (significant only in autumn). In contrast, O<sub>3</sub> mixing ratios were lower in all seasons (significant for winter and spring with 54 ppb against 55 ppb).  $NO_{\nu}$ concentrations were generally lower than average (significantly in spring) as well as PAN except for winter.

[46] Cluster 5 is Free Tropospheric (FT). This cluster was represented by an average pressure level of 400 hPa, an average latitude of 43°N, and RH of 52% at the receptor site. The air masses travel below the tropopause at an altitude of 5-9 km a.s.l. before descending toward JFJ. CO mixing ratios in the FT cluster were significantly lower (100 ppb against an annual mean of 109 ppb) throughout all the seasons except for winter. This can be explained by the extended lifetime of CO in winter leading to a better mixing throughout the whole troposphere. Also primary compounds showed lower concentrations. The O<sub>3</sub> mixing ratio was not significantly different from the seasonal averages (except for summer with 59 against 55 ppb). Interestingly this cluster always shows higher mixing ratio of NO<sub>v</sub> (significant only in spring and summer). This high level of  $NO_v$  was neither accompanied by significantly higher PAN mixing ratios (in spring they are even significantly lower with 0.13 ppb compared to an average of 0.17 ppb) nor elevated  $NO_x$  mixing ratios, therefore leaving a large fraction of  $NO_{\nu}$  unexplained. Other major  $NO_{\nu}$  constituents can be HNO<sub>3</sub> and nitrate, which were not measured during this study.

[47] Cluster 6 is long-range Transport B (LRT-B). This case, like the LRT-A cluster, showed a considerable residence time in the North American PBL (20 hours on average), but only in spring. The travel time toward JFJ was longer (8.9 days) and consequently the temperature gradient between the last North American contact and JFJ was only  $-1.2^{\circ}$ C d<sup>-1</sup>. RH is lower (54%), the average traveling latitude was farther south (40°N), and the average pressure level was lower as well (700 hPa), when compared to the LRT-A cluster. LRT-B cluster, on contrary, experienced CO mixing ratios insignificantly higher or around average. No significant differences were found for O<sub>3</sub> as

well. This cluster presents (not significant) lower  $NO_y$  mixing in winter and spring and higher mixing ratios in spring and autumn (significant in autumn), with generally higher PAN mixing ratios (significant in autumn).

[48] Cluster 7 is Marine Boundary Layer (MBL). This very interesting cluster shows air masses originating in the Atlantic Ocean Marine Boundary Layer which then ascended during tropical cyclonic activity before reaching JFJ within an anticyclonic flow (Extratropical Transition). This can also be seen by the very low average traveling latitude (30°N), the high RH (average of 67%) and the very high average temperature. These were the warmest air masses experienced during background conditions (with an average temperature along the trajectory of 1°C) and remain the warmest air masses once they arrive at JFJ despite a fast cooling gradient  $(-3.6^{\circ}C d^{-1})$  during the previous 5 days). The MBL cluster showed higher relative frequency during the warmer seasons. Particularly during summer this could be a pattern for LRT when tropical cyclones are active (with a very fast transport of 5 days). However, only few cases with contact with the North American PBL were observed. The MBL cluster experienced low CO mixing ratios (annual mean of 98 ppb) in all seasons (not significant only in spring). MBL air masses frequently showed low NO<sub>x</sub> concentrations characteristic of a photochemical O<sub>3</sub> destruction regime [Monks et al., 1998]. It should be noted that this cluster together with marine boundary layer air could be influenced by clean southern hemispheric air masses [Novelli et al., 2003]. O<sub>3</sub> mixing ratios were significantly lower for the MBL cluster (during all the seasons with a minimum in autumn with 40 ppb), with photochemical destruction of O<sub>3</sub> in the MBL due to high water concentrations, strong irradiation at lower latitudes and low NOx being the most likely cause. Such conditions will also decrease the lifetime of other compounds subject to OH oxidation. The  $NO_{\nu}$  mixing ratio was lower than average (significant only in summer and autumn with 0.68 and 0.44 ppb) together with low mixing ratios of PAN and  $NO_x$ . All primary HCs showed lower than average concentrations.

[49] Cluster 8 is High PV (HPV). These air masses were characterized by an elevated residence time in the stratosphere (PV > 2 for an average of 122 hours) with average last stratospheric contact 6 days before arrival at JFJ. The average temperature along these trajectories was the coldest among the clusters  $(-40^{\circ}C)$ , and the average pressure level was 550 hPa. The air masses descended to JFJ as indicated by the very high temperature gradient (6.2°C d<sup>-1</sup> during the previous 5 days) which, however, is not followed by a correspondingly strong decrease in RH (50%). This suggests mixing with tropospheric air. Stratospheric influence (PV > 2) was not exclusively observed in the HPV cluster, but also occurred in the STN, STS, and LRT-A clusters, especially during winter. The HPV cluster experienced higher concentration of O<sub>3</sub> for all seasons except autumn (significant in winter and spring), the maximum difference from the average was reached in spring (66 ppb against 59 ppb).  $NO_{\nu}$  concentrations were close to the average, and PAN was slightly, but not significantly, higher than average, particularly in spring. Nevertheless, this cluster represents highly mixed air masses. CO was always higher than the average and significantly higher in summer and autumn



**Figure 10.** Scatterplots of CO and benzene, PAN, and O<sub>3</sub>, including different seasons (for abbreviations of clusters, see text).

together with  $NO_x$  and many OVOCs. Indeed several authors [e.g., *Brioude et al.*, 2006; *Stohl et al.*, 2007] reported turbulent scale mixing during STT events which is not resolved by individual Lagrangian trajectories.

[50] Figure 10 summarizes some of the main features of the analysis (for clarity clusters STN, STS, AB, LRT-A, LRT-B are grouped in a more general LRT cluster): the air masses characterized by LRT tend to have largest concentrations of CO and benzene with rather linear relationships, particularly in winter, when lifetimes are longest and the concentration gradients between PBL and FT are expected to be largest. No linear relationship between the photo-oxidant concentrations of PAN and  $O_3$  was obvious, but the largest  $O_3$  and PAN background concentrations were found during spring with a tendency of a positive correlation in LRT air masses.

[51] Most of the secondary OVOCs did not show significant differences between the clusters. This is partially because of their shorter lifetime and partially because they were measured only during campaigns and were therefore not statistically well represented in all clusters.

[52] From a general point of view clusters STN, STS, AB, LRT-A, LRT-B, reflect a stronger anthropogenic influence as common tendency (not always statistically significant). In the literature higher mixing ratios in background air have been observed on the west coast of North America [e.g., *Parrish et al.*, 1998; *Weiss-Penzias et al.*, 2006]. *Stohl et al.* [2007] showed that it is possible to directly detect Asian Pollution Plumes over Europe and showed also how these air masses could be mixed also with North American polluted air and/or with stratospheric air. Only two clusters exhibited lower than average CO concentrations: FT and MBL. Together they represent 30% of the background conditions. The air masses represented by these clusters traveled slower and this allowed a longer photochemical degradation. In addition, the more southerly advection path played a role in determining the efficiency of the photochemical destruction.

[53] In agreement with the results presented here, *Lewis et al.* [2007], analyzing airplane measurements above the Azores Islands in the Atlantic Ocean, concluded that most of the air masses are influenced by LRT. In a recent model study, *Sudo and Akimoto* [2007] reported that midlatitude  $O_3$  transport from polluted source regions accounts for more than 50% of  $O_3$  even at remote locations. Particularly  $O_3$  formed in the FT after large injections of Asian precursors was simulated to cause a large contribution to the upper tropospheric ozone abundances in the northern hemisphere.

[54] Interestingly  $O_3$  in spring was significantly higher for all the clusters compared to the other seasons (see Figure 9). Smaller intracluster variability exists for winter when VOCs and other short-lived compounds accumulate in the FT. This indicates a common springtime photochemical  $O_3$  production for all transport patterns. Therefore, the influence of variable transport on the  $O_3$  spring maximum seems to be of minor importance.

## 4. Conclusions

[55] In this study we present a method to derive background mixing ratios of trace gases at the high mountain site JFJ (3580 m asl) and separate these from measurements influenced by the European PBL. These air masses were subjected to particular transport and travel through different regions where they could be loaded with non-European emissions. Therefore, they are expected to have a particular chemical signature. However this chemical signature is often disguised by mixing with European PBL and the expected signatures, like LRT or STT events, can be lost.

[56] Background conditions at JFJ were identified by a new method based on backward trajectories and statistics. With this method the European PBL influence was minimized allowing the analysis of FT air masses. This method allowed for the analysis of background concentrations of the trace gases measured at JFJ during 2005 (HCs, OVOCs, NO<sub>x</sub>, NO<sub>y</sub>, O<sub>3</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>O, and PAN). The method proved to work well, although in spring and summer a maximal error up to 20% in the retrieved background concentrations was found. Nevertheless, detected background concentrations were comparable or lower than at other northern midlatitude remote sites. The seasonal variations of background concentrations add new information to the chemistry of the FT: Primary compounds showed to be greatly influenced by LRT during winter, while secondary compounds increased until summer. These also showed a higher correlation with ozone underlining their common photochemical origin.

[57] A relationship exists between a particular flow regime toward a receptor site and the observed chemical composition at the site. This relation was analyzed using trajectory clustering and was found to be less evident in winter because of the general longer lifetime of the compounds. Most of the clusters were influenced by transport from remote emission sources (like North America or Asia). In order to observe low concentrations of O<sub>3</sub> precursors at JFJ air masses had to be transported slowly enough to allow photochemical degradation of these substances between the emission point and JFJ. The two clusters satisfying this condition were one slowly traveling in the mid free troposphere (FT cluster), and one originating and spending most of the time in the Atlantic Ocean marine boundary layer (MBL cluster). An interesting transport pattern toward JFJ representing anticyclonic blocking conditions was represented by the AB cluster. In this cluster the air traveling at northern latitude (in region of lower photochemical activity and colder temperatures) exhibited higher concentrations of primary compounds, particularly during spring.

[58] It is interesting to note that all clusters showed a  $O_3$  spring maximum. This could indicate that the  $O_3$  spring maximum is connected to a large-scale phenomenon and not to specific source regions. This study brought new valuable information to the knowledge of free tropospheric chemistry, and evidence for the importance of long-range transport. The application of this technique to long time series might also improve the detection of long-term trends in background atmospheric composition.

#### References

- Arnold, F., V. Burger, B. Drostefanke, F. Grimm, A. Krieger, J. Schneider, and T. Stilp (1997), Acetone in the upper troposphere and lower stratosphere: Impact on trace gases and aerosols, *Geophys. Res. Lett.*, 24(23), 3017–3020.
- Auvray, M., and I. Bey (2005), Long-range transport to Europe: Seasonal variations and implications for the European ozone budget, *J. Geophys. Res.*, *110*, D11303, doi:10.1029/2004JD005503.
- Ayers, G. P., R. W. Gillett, H. Granek, C. Deserves, and R. A. Cox (1997), Formaldehyde production in clean marine air, *Geophys. Res. Lett.*, 24(4), 401–404.
- Baltensperger, U., H. Gaggeler, D. Jost, M. Lugauer, M. Schwikowski, E. Weingartner, and P. Seibert (1997), Aerosol climatology at the high-alpine site Jungfraujoch, Switzerland, J. Geophys. Res., 102, 19,707–19,715.
- Boudries, H., J. W. Bottenheim, C. Guimbaud, A. M. Grannas, P. B. Shepson, S. Houdier, S. Perrier, and F. Domine (2002), Distribution and trends of oxygenated hydrocarbons in the high arctic derived from measurements in the atmospheric boundary layer and interstitial snow air during the ALERT2000 field campaign, *Atmos. Environ.*, 36(15–16), 2573–2583.
- Brioude, J., J. P. Cammas, and O. R. Cooper (2006), Stratosphere-troposphere exchange in a summertime extratropical low: Analysis, *Atmos. Chem. Phys.*, 6, 2337–2353.
- Calvert, J. G. (1990), Glossary of atmospheric chemistry terms, *Pure Appl. Chem.*, 62(11), 2167–2219.
- Cardenas, L. M., D. J. Brassington, B. J. Allan, H. Coe, B. Alicke, U. Platt, K. M. Wilson, J. M. C. Plane, and S. A. Penkett (2000), Intercomparison of formaldehyde measurements in clean and polluted atmospheres, *J. Atmos. Chem.*, 37, 53–80.
- Cox, M., G. Sturrock, P. Fraser, S. Siems, P. Krummel, and S. O'Doherty (2003), Regional sources of methyl chloride, chloroform and dichloromethane identified from agage observations at Cape Grim, Tasmania, 1998–2000, J. Atmos. Chem., 45, 79–99.
- Derwent, R., P. Simmonds, S. Seuring, and C. Dimmer (1998), Observation and interpretation of the seasonal cycles in the surface concentrations of ozone and carbon monoxide at Mace Head, Ireland from 1990 to 1994, *Atmos. Environ.*, 32(2), 145–157.
- Dlugokencky, E. J., K. Á. Masarie, P. P. Tans, T. J. Conway, and X. Xiong (1997), Is the amplitude of the methane seasonal cycle changing?, *Atmos. Environ.*, *31*(1), 21–26.
- Fehsenfeld, F. C., P. Daum, W. R. Leaitch, M. Trainer, D. D. Parrish, and G. Hubler (1996), Transport and processing of O<sub>3</sub> and O<sub>3</sub> precursors over the North Atlantic: An overview of the 1993 North Atlantic Regional Experiment (NARE) summer intensive, J. Geophys. Res., 101, 28,877–28,891.
- Griffin, R. J., J. J. Chen, K. Carmody, S. Vutukuru, and D. Dabdub (2007), Contribution of gas phase oxidation of volatile organic compounds to atmospheric carbon monoxide levels in two areas of the United States, J. Geophys. Res., 112, D10S17, doi:10.1029/2006JD007602.
- Hak, C., et al. (2005), Intercomparison of four different in-situ techniques for ambient formaldehyde measurements in urban air, *Atmos. Chem. Phys.*, 5, 2881–2900.
- Hakola, H., H. Hellen, and T. Laurila (2006), Ten years of light hydrocarbons ( $C_2 C_6$ ) concentration measurements in background air in Finland, *Atmos. Environ.*, 40(19), 3621–3630.
- Harris, J. M., and J. D. Kahl (1990), A descriptive atmospheric transport climatology for the Mauna-Loa-observatory, using clustered trajectories, *J. Geophys. Res.*, 95, 13,651–13,667.
- Henne, S., M. Furger, S. Nyeki, M. Steinbacher, B. Neininger, S. F. J. de Wekker, J. Dommen, N. Spichtinger, A. Stohl, and A. S. H. Prevot (2004), Quantification of topographic venting of boundary layer air to the free troposphere, *Atmos. Chem. Phys.*, *4*, 497–509.
- Henne, S., M. Furger, and A. S. H. Prevot (2005), Climatology of mountain venting-induced elevated moisture layers in the lee of the alps, J. Appl. Meteorol., 44(5), 620–633.
- Henne, S., W. Junkermann, J. M. Kariuki, J. Aseyo, and J. Klausen (2008a), The establishment of the Mt. Kenya GAW station: Installation and meteorological characterization, J. Appl. Meteorol. Clim, doi:10.1175/ 2008JAMC1834.1, in press.
- Henne, S., J. Klausen, W. Junkermann, J. M. Kariuki, J. O. Aseyo, and B. Buchmann (2008b), Representativeness and climatology of carbon monoxide and ozone at the global GAW station Mt. Kenya in equatorial Africa, *Atmos. Chem. Phys.*, 8, 3119–3139.
- Hurrell, J. W., M. P. Hoerling, A. S. Phillips, and T. Xu (2004), Twentieth century North Atlantic climate change. Part 1: Assessing determinism, *Clim. Dyn.*, 23(3–4), 371–389.
- Jacob, D. J., B. D. Field, E. M. Jin, I. Bey, Q. B. Li, J. A. Logan, R. M. Yantosca, and H. B. Singh (2002), Atmospheric budget of acetone, *J. Geophys. Res.*, 107(D10), 4100, doi:10.1029/2001JD000694.

<sup>[59]</sup> Acknowledgments. The financial support of this work by SNSF (Swiss National Science Foundation) is gratefully acknowledged. We acknowledge that the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG), Bern, Switzerland, made it possible for us to carry out our experiments at the High Altitude Research Station at Jungfraujoch. We also thank the custodian families Fischer and Hemund for the support of our activities. Particular thanks go to D. Brunner, C. Ordonez, J. Dommen, H. Sodemann, and J. Cui for interesting discussions.

- Jacob, D. J., J. H. Crawford, M. M. Kleb, V. S. Connors, R. J. Bendura, J. L. Raper, G. W. Sachse, J. C. Gille, L. Emmons, and C. L. Heald (2003), Transport and Chemical Evolution over the Pacific (TRACE-P) aircraft mission: Design, execution, and first results, J. Geophys. Res., 108(D20), 9000, doi:10.1029/2002JD003276.
- Junkermann, W., and J. Burger (2006), A new portable instrument for continuous measurement of formaldehyde in ambient air, J. Atmos. Oceanic Technol., 23(1), 38-45.
- Kelly, T. J., and C. R. Fortune (1994), Continuous monitoring of gaseous formaldehyde using an improved fluorescence approach, Int. J. Environ. Anal. Chem., 54(4), 249-263.
- Law, K. S., and A. Stohl (2007), Arctic air pollution: Origins and impacts, Science, 315(5818), 1537-1540.
- Legreid, G., D. Folini, J. Staehelin, J. B. Loov, M. Steinbacher, and S. Reimann (2008), Measurements of organic trace gases including oxygenated volatile organic compounds at the high alpine site Jungfraujoch (Switzerland): Seasonal variation and source allocations, J. Geophys. Res., 113, D05307, doi:10.1029/2007JD008653.
- Lewis, A. C., et al. (2007), Chemical composition observed over the mid-Atlantic and the detection of pollution signatures far from source regions, J. Geophys. Res., 112, D10S39, doi:10.1029/2006JD007584.
- Lightman, P., A. S. Kallend, A. R. W. Marsh, B. M. R. Jones, and S. A. Penkett (1990), Seasonal-variation of hydrocarbons in the free troposphere at midlatitudes, Tellus, Ser. B, 42(5), 408-422
- Lowe, D. C., and U. Schmidt (1983), Formaldehyde (HCHO) measurements in the nonurban atmosphere, J. Geophys. Res., 88, 844-858.
- Lugauer, M., U. Baltensperger, M. Furger, H. W. Gaggeler, D. T. Jost, M. Schwikowski, and H. Wanner (1998), Aerosol transport to the high Alpine sites Jungfraujoch (3454 m asl) and Colle Gnifetti (4452 m asī), Tellus, Ser. B, 50(1), 76-92.
- Matthias, V., et al. (2004), Vertical aerosol distribution over Europe: Statistical analysis of Raman lidar data from 10 European Aerosol Research Lidar Network (EARLINET) stations, J. Geophys. Res., 109, D18201, doi:10.1029/2004JD004638.
- McCarthy, M. C., H. R. Hafner, and S. A. Montzka (2006), Background concentrations of 18 air toxics for North America, J. Air Waste Manage., 56(1), 3-11
- Millet, D. B., et al. (2004), Volatile organic compound measurements at Trinidad Head, California, during ITCT 2K2: Analysis of sources, atmospheric composition, and aerosol residence times, J. Geophys. Res., 109, D23S16, doi:10.1029/2003JD004026.
- Monks, P. S. (2000), A review of the observations and origins of the spring ozone maximum, Atmos. Environ., 34(21), 3545-3561
- Monks, P. S., L. J. Carpenter, S. A. Penkett, G. P. Ayers, R. W. Gillett, I. E. Galbally, and C. P. Meyer (1998), Fundamental ozone photochemistry in the remote marine boundary layer: The SOAPEX experiment, measurement and theory, Atmos. Environ., 32(21), 3647-3664.
- Nash, T. (1953), The colorimetric estimation of formaldehyde by means of the Hantzsch reaction, *Biochem. J.*, 55(3), 416–421. Novelli, P. C., K. A. Masarie, and P. M. Lang (1998), Distributions and
- recent changes of carbon monoxide in the lower troposphere, J. Geophys. Res., 103, 19,015-19,033.
- Novelli, P. C., K. A. Masarie, P. M. Lang, B. D. Hall, R. C. Myers, and J. W. Elkins (2003), Reanalysis of tropospheric CO trends: Effects of the 1997-1998 wildfires, J. Geophys. Res., 108(D15), 4464, doi:10.1029/ 2002JD003031.
- Nyeki, S., U. Baltensperger, I. Colbeck, D. T. Jost, E. Weingartner, and H. W. Gaggeler (1998), The Jungfraujoch high-Alpine research station (3454 m) as a background clean continental site for the measurement of aerosol parameters, J. Geophys. Res., 103, 6097-6107.
- Ordonez, C., H. Mathis, M. Furger, S. Henne, C. Huglin, J. Staehelin, and A. S. H. Prevot (2005), Changes of daily surface ozone maxima in Switzerland in all seasons from 1992 to 2002 and discussion of summer 2003, Atmos. Chem. Phys., 5, 1187-1203. Ordonez, C., D. Brunner, J. Staehelin, P. Hadjinicolaou, J. A. Pyle,
- M. Jonas, H. Wernli, and A. S. H. Prevot (2007), Strong influence of lowermost stratospheric ozone on lower tropospheric background ozone changes over Europe, Geophys. Res. Lett., 34, L07805, doi:10.1029/2006GL029113.
- Parrish, D., M. Trainer, J. Holloway, J. Yee, M. Warshawsky, F. Fehsenfeld, G. Forbes, and J. Moody (1998), Relationships between ozone and carbon monoxide at surface sites in the North Atlantic region, J. Geophys. Res., 103, 13,357-13,376.
- Penkett, S. A., and K. A. Brice (1986), The spring maximum in photooxidants in the Northern-Hemisphere troposphere, Nature, 319(6055), 655-657.
- Plass-Dülmer, C., N. Schmidbauer, J. Slemr, F. Slemr, and H. D'Souza (2006), European hydrocarbon intercomparison experiment AMOHA part 4: Canister sampling of ambient air, J. Geophys. Res., 111, D04306, doi:10.1029/2005JD006351.

- Ravetta, F., G. Ancellet, A. Colette, and H. Schlager (2007), Long-range transport and tropospheric ozone variability in the western Mediterranean region during the Intercontinental Transport of Ozone and Precursors (ITOP-2004) campaign, J. Geophys. Res., 112, D10S46, doi:10.1029/ 2006JD007724.
- Real, E., et al. (2007), Processes influencing ozone levels in Alaskan forest fire plumes during long-range transport over the North Atlantic, J. Geophys. Res., 112, D10S41, doi:10.1029/2006JD007576.
- Reimann, S., D. Schaub, K. Stemmler, D. Folini, M. Hill, P. Hofer, B. Buchmann, P. G. Simmonds, B. R. Greally, and S. O'Doherty (2004), Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580 m asl): Continuous measurements and their use for regional European source allocation, J. Geophys. Res., 109, D05307, doi:10.1029/2003JD003923
- Ridley, B., et al. (1998), Measurements of NO<sub>x</sub> and PAN and estimates of O3 production over the seasons during Mauna Loa Observatory Photochemistry Experiment 2, J. Geophys. Res., 103, 8323-8339.
- Roberts, J. M., et al. (2004), Measurement of peroxycarboxylic nitric anhydrides (PANs) during the ITCT 2K2 aircraft intensive experiment, J. Geophys. Res., 109, D23S21, doi:10.1029/2004JD004960.
- Schade, G. W., and A. H. Goldstein (2006), Seasonal measurements of acetone and methanol: Abundances and implications for atmospheric budgets, Global Biogeochem. Cycles, 20, GB1011, doi:10.1029/ 2005GB002566.
- Schmitt, R., and A. Volz-Thomas (1997), Climatology of ozone, PAN, CO, and NMHC in the free troposphere over the southern North Atlantic, J. Atmos. Chem., 28, 245–262.
- Simmonds, P. G., S. Seuring, G. Nickless, and R. G. Derwent (1997), Segregation and interpretation of ozone and carbon monoxide measurements by air mass origin at the TOR Station Mace Head, Ireland from 1987 to 1995, J. Atmos. Chem., 28, 45-59.
- Simmonds, P. G., R. G. Derwent, A. L. Manning, and G. Spain (2004), Significant growth in surface ozone at Mace Head, Ireland, 1987-2003, Atmos. Environ., 38(28), 4769-4778.
- Singh, H. B., D. Ohara, D. Herlth, W. Sachse, D. R. Blake, J. D. Bradshaw, M. Kanakidou, and P. J. Crutzen (1994), Acetone in the atmosphere: Distribution, sources, and sinks, J. Geophys. Res, 99, 1805-1819
- Singh, H., et al. (2000), Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic, J. Geophys. Res., 105, 3795-3805.
- Singh, H. B., et al. (2004), Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, J. Geophys. Res., 109, D15S07, doi:10.1029/2003JD003883.
- Sodemann, H. (2000), Relationships between the origin of air masses and carbon monixide measurements at the Cape Point Trace Gas Monitoring Station, honours thesis, Dep. of Environ. and Geogr. Sci., Univ. of Cape Town, Cape Town.
- Solberg, S., C. Dye, N. Schmidbauer, A. Herzog, and R. Gehrig (1996), Carbonyls and nonmethane hydrocarbons at rural European sites from the Mediterranean to the Arctic, J. Atmos. Chem., 25, 33-66.
- Solberg, S., N. Schmidbauer, N. Wallasch, and R. Junek (2002), VOC measurements 2000, Tech. Rep. 8, Eur. Monit. and Eval. Programme, Geneva.
- Stevenson, D., R. Doherty, M. Sanderson, C. Johnson, B. Collins, and D. Derwent (2005), Impacts of climate change and variability on tropospheric ozone and its precursors, Faraday Discuss., 130, 41-57.
- Stohl, A. (1998), Computation, accuracy and applications of trajectories: A
- review and bibliography, Atmos. Environ., 32(6), 947–966. Stohl, A., N. Spichtinger-Rakowsky, P. Bonasoni, H. Feldmann, M. Memmesheimer, H. E. Scheel, T. Trickl, S. Hubener, W. Ringer, and M. Mandl (2000), The influence of stratospheric intrusions on alpine ozone concentrations, Atmos. Environ., 34(9), 1323-1354.
- Stohl, A., C. Forster, H. Huntrieser, H. Mannstein, W. W. Mcmillan, A. Petzold, H. Schlager, and B. Weinzierl (2007), Aircraft measurements over Europe of an air pollution plume from Southeast Asia-Aerosol and chemical characterization, Atmos. Chem. Phys., 7, 913-937
- Sudo, K., and H. Akimoto (2007), Global source attribution of tropospheric ozone: Long-range transport from various source regions, J. Geophys. Res., 112, D12302, doi:10.1029/2006JD007992.
- Thouret, V., A. Marenco, J. Logan, P. Nedelec, and C. Grouhel (1998), Comparisons of ozone measurements from the MOZAIC airborne program and the ozone sounding network at eight locations, J. Geophys. Res., 103, 25,695-25,720.
- Traub, M., et al. (2003), Chemical characteristics assigned to trajectory clusters during the MINOS campaign, Atmos. Chem. Phys., 3, 459-468.
- Tsutsumi, Y., K. Mori, M. Ikegami, T. Tashiro, and K. Tsuboi (2006), Longterm trends of greenhouse gases in regional and background events ob-served during 1998-2004 at Yonagunijima located to the east of the Asian continent, Atmos. Environ., 40(30), 5868-5879.

- Wang, T., H. L. A. Wong, J. Tang, A. Ding, W. S. Wu, and X. C. Zhang (2006), On the origin of surface ozone and reactive nitrogen observed at a remote mountain site in the northeastern Qinghai-Tibetan Plateau, western China, J. Geophys. Res., 111, D08303, doi:10.1029/ 2005JD006527.
- Weiss-Penzias, P., D. A. Jaffe, P. Swartzendruber, J. B. Dennison, D. Chand, W. Hafner, and E. Prestbo (2006), Observations of Asian air pollution in the free troposphere at Mount Bachelor Observatory during the spring of 2004, J. Geophys. Res., 111, D10304, doi:10.1029/ 2005JD006522.
- Wernli, H., and H. C. Davies (1997), A Lagrangian-based analysis of extratropical cyclones. 1. The method and some applications, *Q. J. R. Meteorol. Soc.*, 123(538), 467–489.
- Zanis, P., A. Ganser, C. Zellweger, S. Henne, M. Steinbacher, and J. Staehelin (2007), Seasonal variability of measured ozone production efficiencies in the lower free troposphere of central Europe, *Atmos. Chem. Phys.*, 7, 223–236.
- Zellweger, C., M. Ammann, B. Buchmann, P. Hofer, M. Lugauer, R. Ruttimann, N. Streit, E. Weingartner, and U. Baltensperger (2000), Summertime NO<sub>y</sub> speciation at the Jungfraujoch, 3580 m above sea level, Switzerland, *J. Geophys. Res.*, 105, 6655–6667.

- Zellweger, C., J. Forrer, P. Hofer, S. Nyeki, B. Schwarzenbach, E. Weingartner, M. Ammann, and U. Baltensperger (2002), Partitioning of reactive nitrogen (NO<sub>y</sub>) and dependence on meteorological conditions in the lower free troposphere, *Atmos. Chem. Phys.*, *3*, 779–796. Zhou, X. L., Y. N. Lee, L. Newman, X. H. Chen, and K. Mopper (1996),
- Zhou, X. L., Y. N. Lee, L. Newman, X. H. Chen, and K. Mopper (1996), Tropospheric formaldehyde concentration at the Mauna Loa observatory during the Mauna Loa observatory photochemistry experiment 2, J. Geophys. Res., 101, 14,711–14,719.

J. M. Balzani Lööv and J. Staehelin, Institute for Atmospheric and Climate Science, ETH Zürich, Universitätstrasse 16, CH-8092 Zürich, Switzerland. (jacob.balzani@env.ethz.ch)

S. Henne, G. Legreid, S. Reimann, M. Steinbacher, and M. K. Vollmer, Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Testing and Research, EMPA, CH-8600 Dübendorf, Switzerland.

A. S. H. Prévôt, Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland.