

Aerosol elemental concentrations in the tropopause region from intercontinental flights with the Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) platform

Giorgos Papaspiropoulos,¹ Bengt G. Martinsson,¹ Andreas Zahn,^{2,6} Carl A. M. Brenninkmeijer,² Markus Hermann,³ Jost Heintzenberg,³ Herbert Fischer,⁴ and Peter F. J. van Velthoven⁵

Received 20 March 2002; revised 13 August 2002; accepted 21 August 2002; published 3 December 2002.

[1] This study with the Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) platform investigates the aerosol elemental concentrations at 9–11 km altitude in the northern hemisphere. Measurements from 31 intercontinental flights over a 2-year period between Germany and Sri Lanka/Maldives in the Indian Ocean are presented. Aerosol samples were collected with an impaction technique and were analyzed for the concentration of 18 elements using particle-induced X-ray emission (PIXE). Additional measurements of particle number concentrations, ozone and carbon monoxide concentrations, and meteorological modeling were included in the interpretation of the aerosol elemental concentrations. Particulate sulphur was found to be by far the most abundant element. Its upper tropospheric concentration increased, on average, by a factor of 2 from the tropics to midlatitudes, with another factor 2 higher concentrations in the lowermost stratosphere over midlatitudes. Correlation patterns and source profiles suggest contributions from crustal sources and biomass burning, but not from meteor ablation. Coinciding latitudinal gradients in particulate sulphur concentrations and emissions suggest that fossil fuel combustion is an important source of the aerosol in the upper troposphere and lowermost stratosphere. The measurements indicate aerosol transport along isentropic surfaces across the tropopause into the lowermost stratosphere. As a result of the prolonged residence time, ageing via oxidation of sulphur dioxide in the lowermost stratosphere was found to be a likely high-altitude, strong source that, along with downward transport of stratospheric air, could explain the vertical gradient of particulate sulphur mass concentration around the extratropical tropopause.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions; **KEYWORDS:** aerosol, upper troposphere, lowermost stratosphere, elemental composition

Citation: Papaspiropoulos, G., B. G. Martinsson, A. Zahn, C. A. M. Brenninkmeijer, M. Hermann, J. Heintzenberg, H. Fischer, and P. F. J. van Velthoven, Aerosol elemental concentrations in the tropopause region from intercontinental flights with the Civil Aircraft for Regular Investigations of the Atmosphere Based on an Instrument Container (CARIBIC) platform, *J. Geophys. Res.*, 107(D23), 4671, doi:10.1029/2002JD002344, 2002.

¹Division of Nuclear Physics, Lund University, Lund, Sweden.

²Division of Atmospheric Chemistry, Max Planck Institute for Chemistry, Mainz, Germany.

³Institute for Tropospheric Research, Leipzig, Germany.

⁴Institute of Meteorology and Climate Research, Karlsruhe, Germany.

⁵Royal Netherlands Meteorological Institute (KNMI), De Bilt, The Netherlands.

⁶Now at Institute of Meteorology and Climate Research, Karlsruhe, Germany.

1. Introduction

[2] The atmospheric aerosol consists of particles from a large number of sources, both natural and anthropogenic. Large amounts of particulate matter are produced in the atmosphere from various processes of gas-to-particle conversion. Although a minor constituent of the atmosphere, the aerosol particles can affect important properties of the Earth such as the global climate [Charlson *et al.*, 1992; Intergovernmental Panel on Climate Change (IPCC), 2001] via their direct and indirect effects. Other issues associated with the atmospheric aerosol are acidification of

the environment and effects on human health in urban areas.

[3] The atmospheric residence time of aerosol particles is short relative to typical transport times [Rodhe, 1999]. As a result, the aerosol concentration shows high spatial and temporal variability, with high concentrations close to source regions compared to remote areas such as over the oceans. In addition to horizontal gradients, the aerosol concentration is strongly dependent on the altitude with highest concentrations normally appearing in the mixed boundary layer.

[4] The tropopause region is a part of the atmosphere, which is not very well known as far as the concentration and properties of the aerosol are concerned. Previous studies of the chemical composition have been of a campaign-wise nature. Single particle analyses indicate that the aerosol particles mainly consist of sulphuric acid, which can be partly neutralized [Sheridan *et al.*, 1994; Xu *et al.*, 2001]. Long-term measurements of vertical profiles of the particle number concentrations in three particle size intervals have been reported [Hofmann, 1993]. Their measurements often show a minimum concentration of particles larger than 0.3 μm diameter in the tropopause region [Hofmann and Rosen, 1981; Hofmann, 1993]. This size range can also be expected to be a useful indicator of the vertical distribution of the aerosol mass. Mass concentrations of particulate sulphate with limited detection capabilities have been reported from campaigns including measurements in the tropopause region [Dibb *et al.*, 1999]. Lately, systematically repeated measurements in the tropopause region have revealed a strong latitudinal dependency of the particulate sulphur concentration in the northern hemisphere with an average of 4 times higher concentration over midlatitudes compared to the tropics [Martinsson *et al.*, 2001].

[5] In this work by the Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) collaboration [Brenninkmeijer *et al.*, 1999], the aerosol in the upper troposphere and lower stratosphere was investigated. Elemental concentrations, including particulate sulphur, were measured during 31 intercontinental flights between Germany and Sri Lanka/Maldives in the Indian Ocean. The aim was to establish average concentrations, latitudinal and seasonal variations of aerosol constituents and to explore the distribution of particulate sulphur around the tropopause as well as indicating possible source patterns by the aid of ozone and carbon monoxide as tracer gases.

[6] The presence of a fairly concentrated aerosol layer in the stratosphere dominated by sulphuric acid has been known for a long time [Junge *et al.*, 1961]. The aerosol concentration of the stratosphere is strongly influenced by volcanic eruptions [Kent *et al.*, 1995] with clearly observable decay times of several years after strong eruptions [Suortti *et al.*, 2001; Zuev *et al.*, 2001]. During periods of low volcanic influence, model estimates suggest that in situ gas-to-particle conversion of carbonyl sulphide, sulphur dioxide, and to some extent dimethyl sulphide, transported across the tropopause are the major sources of the stratospheric aerosol [Chin and Davies, 1995; Weisenstein *et al.*, 1997; Kjellström, 1998].

[7] In addition to sources of the aerosol in the tropopause region at the Earth's surface, the increasing air traffic contributes to the aerosol in this altitude region of the

atmosphere. The aircraft source is estimated to significantly affect the particle number concentration. Moreover, it could possibly be a significant source of the soot mass, whereas its contribution of sulphate mass in the tropopause region is estimated to be negligibly small [Danilin *et al.*, 1998; Kjellström *et al.*, 1999; Ferry *et al.*, 1999].

[8] The clouds forming in conjunction with upward air motions are highly dynamical systems that depend on a large number of parameters. Elevated aerosol concentrations have been shown to affect cloud microstructure by formation of droplets up to abnormal number concentrations of 3000 cm^{-3} in polluted long-distance-transported, air masses [Martinsson *et al.*, 2000]. These disturbances can, besides affecting the radiative properties of clouds, shift the cut-off particle size of cloud droplet nucleation scavenging toward larger sizes [Martinsson *et al.*, 1997, 1999]. This enhances the cloud interstitial aerosol, which less efficiently is incorporated in precipitation, thus affecting the removal of trace constituents. In addition, the process of precipitation formation could be affected. High concentration of cloud droplets reduces their size, which reduces the efficiency of coalescence. Furthermore, the small droplet sizes delay the ice formation and clouds have been observed by in situ measurements to remain supercooled down to -37.5°C , before the droplets probably freeze homogeneously [Rosefeld and Woodley, 2000]. Satellite-based measurements indicate that these disturbances are frequent, by the presence of pollution tracks from pollution sources and urban areas in widespread clouds [Radke *et al.*, 1989; Rosefeld, 2000]. As a result of air pollution disturbance on the formation of clouds and precipitation, the chemical transport of water substance, aerosols and trace gases thus can be enhanced all the way up to the tropopause.

[9] The efficiency of scavenging and deposition processes depends on a large number of parameters and especially for those substances undergoing wet scavenging the efficiency is poorly known quantitatively [Rasch *et al.*, 2000; Barrie *et al.*, 2001]. Additionally, the resolution of general circulation models presently is too low to allow a detailed representation of clouds. Experimental data on aerosol concentrations, such as particulate sulphur, are thus needed to establish what concentrations appear in the tropopause region and to verify the results of models.

2. Experimental Methods

2.1. Sampling

[10] Aerosol particles in the upper troposphere and lower stratosphere were collected from a passenger aircraft (Boeing 767-300 ER, LTU International Airways) during flights between Germany and Sri Lanka or the Maldives passing over Europe, western Asia and the Indian Ocean, see Figure 1. Sampling was undertaken between March 1999 and January 2001 as part of the CARIBIC program [Brenninkmeijer *et al.*, 1999], which apart from aerosol elemental characterization includes particle number concentrations in three size intervals and a number of trace gases (in situ O_3 , CO and on air samples CH_4 , N_2O , SF_6 , CO_2 , isotopic composition, hydrocarbons and halocarbons).

[11] The aerosol was sampled through a dedicated aerosol inlet 20 cm away from the aircraft body, to prevent possible interference from the aircraft boundary layer. The inlet is of

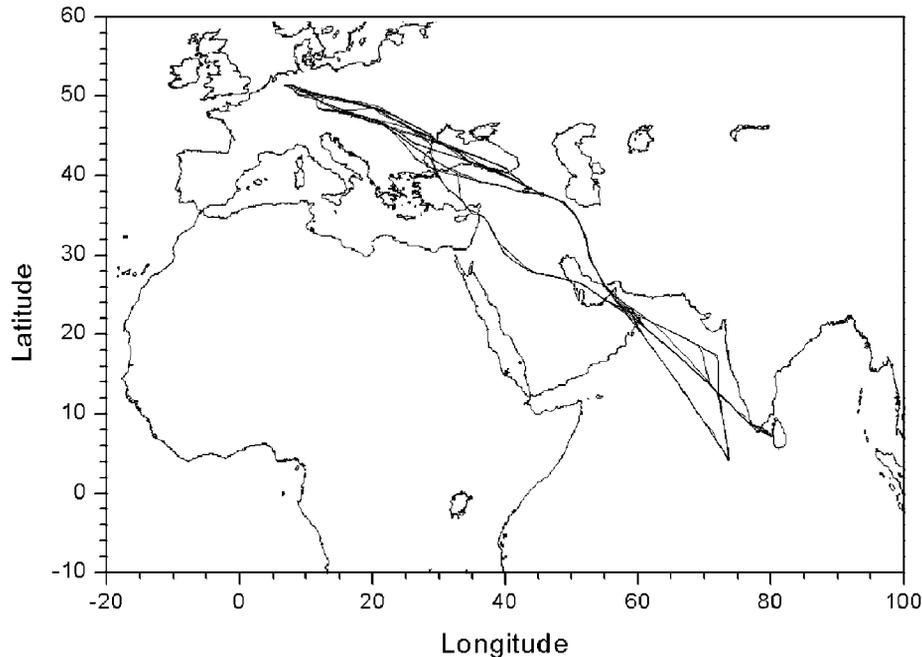


Figure 1. Map of parts of Africa, Asia and Europe showing tracks of the measurement flights between Germany and Sri Lanka/Maldives in the Indian Ocean.

diffuser type with an apex half-angle of 5° . The sampling efficiency of the inlet for the aerosol particle size range important for this work is approximately 90% according to calculations and wind tunnel experiments [Hermann *et al.*, 2001].

[12] Aerosol particle collection was obtained by impaction technique with a specially designed sampler [Papaspriopoulos *et al.*, 1999], yielding spot samples of particles in the size range $0.07\ \mu\text{m}$ – $1.5\ \mu\text{m}$ [Martinsson *et al.*, 2001]. Fourteen identical impactors (3.2 l/min flow rate, ambient conditions) in the instrument provide the capability of sequential and parallel sampling. The protocol in this work comprised two types of samples: sequential and integral. The integral samples covered the entire flight distance, whereas the sequential covered shorter periods. Considering the minimum amount of aerosol mass needed for the subsequent PIXE analysis, the time resolution was normally 2.5 hours (corresponding to ~ 2250 km flight distance), extending down to 1 hour samples in some cases (~ 900 km). The flight time was generally around 9 hours (one way). Sampling was only allowed at ambient pressures below 350 hPa (8200 m pressure altitude) resulting in sampling pressure altitudes of 8800–11,300 m (sample average). With these conditions, typically three or four sequential samples were collected for each flight.

2.2. Aerosol Analysis

[13] The aerosol samples were analyzed with particle-induced X-ray emission (PIXE) [Johansson and Campbell, 1988] at the Lund 3 MV tandem accelerator facility (NEC 3 UDH). A 2.55 MeV proton beam was used to generate the X-rays, which were detected by a Si(Li)-detector from KeveXTM at an angle of 135 degrees. PIXE is a multi-elemental method with high absolute sensitivity. The detec-

tion limits of the present setup have been optimized regarding proton beam area, using Scanning Transmission Ion Microscopy (STIM) imaging of the aerosol deposit [Papaspriopoulos *et al.*, 1999]. The aerosol samples were collected on $0.2\ \mu\text{m}$ polyimide backing films, AP1TM, which have shown superior behavior concerning background levels compared to other commonly used backings in PIXE analyses [Papaspriopoulos *et al.*, 1999]. The typical beam current during the analysis was 60 nA and the total accumulated charge per sample was around $80\ \mu\text{C}$. The setup was calibrated with Micro-MatterTM standards, resulting in 10% inaccuracy in the elemental analysis.

2.3. Detection Limits and Missing Data

[14] The primary analytical objective of this study was to obtain high probability of detection for particulate sulphur, while the second was to make use, as much as possible, of the multielemental nature of PIXE. Inevitably this leads to detection problems that need to be handled.

[15] The minimum detection limit (MDL) of an element in a sample was estimated from the combined uncertainty of the background intensity under the characteristic X-ray peak in the spectrum and the occurrence of the element in blank samples. Two field and two batch blanks were taken for each combination of outbound and return flight. They were analyzed with PIXE in the same way as the aerosol samples. The average blank concentrations were subtracted and the MDL was set to 2.32 standard deviations, corresponding to 99% detection confidence.

[16] Elemental concentrations falling below the MDL of a sample were estimated to be half the MDL, which is the controlled alternative to randomly distributing the estimate between 0 and the MDL. Elements frequently falling below the MDL thus are susceptible to uncertainties in the data

evaluation, for example in estimating the average concentration, because a large fraction of the data in that case is based on estimated concentrations.

[17] In this study the elemental detection frequency varied between 0 and 100%. Due to this span, two different methods were used to estimate average concentrations. For the elements that rarely exceeded the MDL, the concentration was estimated by assigning the MDL concentration to those samples falling below the MDL. The resulting average thus is an estimate of the maximum average concentration. For elements with a higher detection frequency, samples with a concentration below the MDL were estimated to MDL/2, before the average was estimated.

[18] Which of the two methods that was used to describe the average concentration primarily was based on the detection frequency, with the aim of extracting as much information as possible from the data. We found that meaningful estimates of average concentrations could be obtained when the detection frequency exceeded approximately 25%. To substantiate this cut-point between estimating average and maximum average concentration, the influence from the distribution of concentrations below the MDL was investigated. This was done by generating random numbers according to two distributions in the range 0–MDL, to represent cases where the undetected samples are oriented either toward 0 or MDL. The two cases were described as ramp functions extending from 0 to MDL, peaking at 0 and MDL respectively. From this test of the influence from the distribution of the concentration below the MDL, it was found that the average concentrations were within $\pm 15\%$ of the average obtained by assigning the concentration to MDL/2, for all elements exceeding 25% detection efficiency.

2.4. Other Measurement Methods

[19] Aerosol particle number concentrations were measured with 2 s time resolution in three diameter intervals (N_4 with $d > 4$ nm, N_{12} with $d > 12$ nm and N_{18-135} with d between 18 and 135 nm), using three modified condensation particle counters (TSI[®] CPC 7610) [Hermann and Wiedensohler, 2001; Hermann et al., 2002]. The former two particle measurements were used to infer the concentration in the size interval 4–12 nm (N_{4-12}). The ozone (O_3) data used here were measured by a method based on UV absorption (time resolution 17 s). Carbon monoxide (CO) was measured using a gas chromatography technique (2–3 minute time resolution) [Brenninkmeijer et al., 1999]. The data were averaged over 2–3 min sampling intervals of CO, before their use with the aerosol elemental concentrations. The total uncertainty of the particle number concentrations N_{12} and N_{18-135} is estimated to 10%, and to 35% for N_{4-12} [Hermann and Wiedensohler, 2001]. The uncertainty for carbon monoxide is estimated to 3 ppbv and for ozone the greatest of 4% and 4 ppbv [Zahn et al., 2002].

2.5. Methods to Distinguish Between Tropospheric and Stratospheric Air Masses

[20] In order to differentiate between the tropospheric and stratospheric contributions on the particulate elemental concentrations obtained in the present study, two types of

tropopause definitions were used: (i) a seasonally changing ozone tropopause and (ii) the dynamical tropopause.

1. Zahn et al. [2002] showed that along the CARIBIC flight path “Germany–Indian Ocean”, the detection of chemical tropopause can simply be reduced to the measurement O_3 , i.e., to the detection of the ozone tropopause. This is due to the finding that the chemical tropopause is characterized by an O_3 threshold value that is primarily a function of the time of the year. Over central and southeast Europe, where the CARIBIC aircraft intersected the tropopause, the O_3 tropopause threshold value is $O_3^p = 97 + 26\sin[2\pi(\text{Day-of-Year}-30)/365]$ (in ppbv), which maximizes around 1 May at 123 ppbv and minimizes around 1 November at 71 ppbv.

2. For the dynamical tropopause, typical threshold values of the potential vorticity (PV) in the range 1.5–3.5 PVU were taken (potential vorticity unit; 1 PVU = 10^{-6} K m² kg⁻¹ s⁻¹) [Hoerling et al., 1991; Hoinka, 1997]. Here, three PV threshold values of 1.5, 2.5 and 3.5 PVU were used. PV was calculated from archived ECMWF analyses with a resolution of 1x1 degree in the horizontal and 31 (1999) to 60 (2001) vertical hybrid sigma-pressure model levels. The PV values were interpolated linearly in longitude, latitude, log pressure and time to the actual location of the CARIBIC aircraft.

2.6. Grouping of Data

[21] Aerosol samples were collected during 33 flights. In the first combination of an outbound and return flight, particles were collected on a substrate (Kimfol[™]) with inferior PIXE detection capabilities compared to the substrate (API[™]) used in the following 31 flights. Therefore the samples from these first two flights were excluded from the data evaluation. Problems in the sample changing routines during the second combination of an outbound and return flight resulted in an integral sample covering both flight directions. Thus, 30 samples covering the entire flight distance (integral samples) of 31 flights are available. The problem of sample changing also reduced the number of sequential samples available from the first flights. In total, 98 sequential samples are available.

[22] The sequential samples were divided into three latitude groups. These groups approximately represent the northern hemisphere middle-to-upper troposphere of the tropics and the tropopause region of the subtropics and midlatitudes (Figure 2). The tropical, subtropical and midlatitudes groups contain 31, 30 and 37 samples, respectively. Inevitably some overlap between the latitude groups appear, due to the fairly long sampling time. Figure 2 shows that 87–91% of the sampling time was within the boundaries of the respective group. The sample groups thus represent the respective latitude interval fairly well.

[23] The samples were further organized in order to investigate seasonal variation in the aerosol concentration. Two criteria were used to define the seasons. The first was based on structures found in the aerosol elemental concentrations, while the second was the demand that the different groups should be statistically as equal as possible. Based on these criteria three seasonal groups were defined: February–June, July–September and October–January. The number of sequential samples in each category is 35, 34 and 29, while for the integral samples 10, 11 and 9.

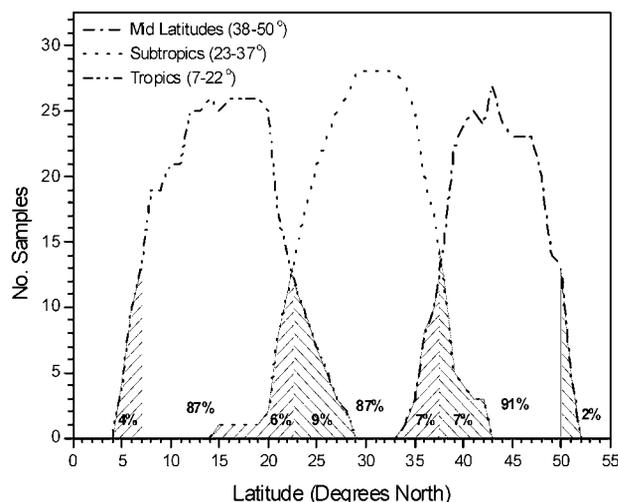


Figure 2. Classification of the sequential samples in three latitude intervals. The vertical axis shows the number of samples classified in each interval as a function of latitude. The hatched area indicates the overlap and the percentages show the time fractions within and outside the defined latitude interval of each group.

[24] Finally, the samples were categorized to determine differences between tropospheric and stratospheric aerosol, using four tropopause definitions (section 2.5). CO, which was used as indicative of pollution from combustion sources [Lelieveld *et al.*, 1997], and particle number concentration data (section 2.4) were included in the data evaluation. These data, which were available with a higher time resolution than the aerosol samples, were averaged over the 1–2.5 h time periods used for aerosol sampling. They were also averaged for subintervals (i.e., tropospheric and stratospheric averages according to the different tropopause thresholds) of the sampling time, and the fraction

of each aerosol sample taken in the stratosphere (F_s) was calculated.

[25] Supporting data for the aerosol elemental data interpretation were missing for two of the aerosol samples (one taken at midlatitudes and one in the tropics). These two samples were excluded from the analysis in section 4, while included elsewhere.

3. Results

3.1. Average Elemental Concentrations

[26] The samples covering entire flights naturally show higher detection efficiency compared to the sequential samples. The integral samples were therefore used to survey the average aerosol elemental concentrations along the flight track. A total of 18 elements with varying detection frequencies were analyzed. The results are summarized in Table 1 for the ten elements that met the statistical demands regarding detection frequency described in section 2.3, whereas the other eight fell below the 25% detection frequency cut-point and only a maximum average concentration can be estimated. Given are the MDL for each element, their detection frequencies, average elemental concentrations in ng/m^3 STP (standard temperature (273.15 K) and pressure (1013.25 hPa)), the standard deviation of the average (σ_A) (i.e., the uncertainty of the average estimate) and the standard deviation of the atmospheric concentration (σ_C).

[27] Sulphur (S) was found to be by far the dominating element with $16 \text{ ng}/\text{m}^3$ STP. The second and third most encountered elements are potassium (K) and iron (Fe), whose average concentrations were about 50 times lower than that of sulphur.

[28] The standard deviation of the atmospheric concentration (σ_C) provides information about the changes in the elemental concentrations, due to conditions in the atmosphere, e.g., seasonal variation and other source-related fluctuations. For S, σ_C was relatively small (around 40%) compared to K and Fe, where σ_C was almost 1.5 times the

Table 1. Chemical Aerosol Characteristics Obtained From Samples Collected During Entire Flights

Element	MDL ^a , ng m^{-3} STP	Detection Frequency, %	Average Concentration, ng m^{-3} STP	σ_A^b , ng m^{-3} STP	σ_C^c , ng m^{-3} STP
Al	2.4	3	<2.5	–	–
S	0.79	100	16	1.7	6.2
Cl	0.32	7	<0.33	–	–
K	0.064	70	0.31	0.10	0.48
Ca	0.25	33	0.28	0.072	0.29
Ti	0.031	27	0.034	0.012	0.045
V	0.010	0	<0.010	–	–
Cr	0.017	7	<0.018	–	–
Mn	0.0069	17	<0.0086	–	–
Fe	0.11	57	0.26	0.078	0.36
Ni	0.013	23	<0.016	–	–
Cu	0.070	3	<0.076	–	–
Zn	0.17	13	<0.19	–	–
Ga	0.0064	47	0.0077	0.0026	0.0059
Ge	0.0088	50	0.0094	0.0030	0.0058
As	0.0091	43	0.0094	0.0031	0.0077
Se	0.011	30	0.0095	0.0036	0.0057
Br	0.020	53	0.028	0.0082	0.023

^a Minimum detection limit for integral samples.

^b Standard deviation of the estimated average concentration.

^c Standard deviation of the atmospheric concentration.

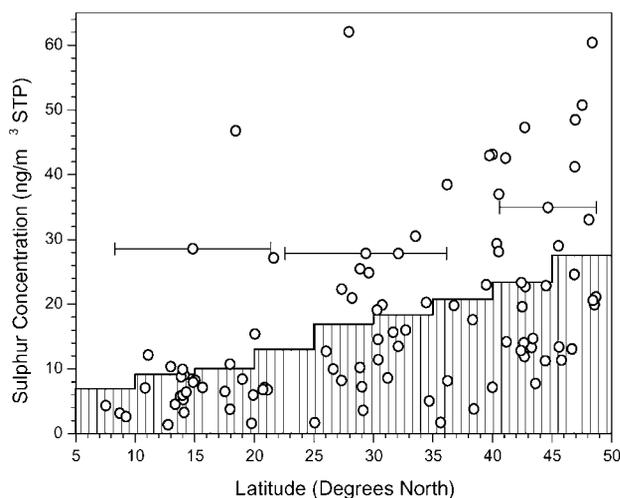


Figure 3. Sulphur concentration as a function of the average latitude of the measurements (open circles). The horizontal bars show the average latitudinal extent of the samples (latitude dependent) and the hatched histogram shows the latitudinal dependency of the concentration as obtained from a binning technique.

average concentration. This is mainly due to a strong variation with season for K and Fe. The issues of seasonality and aerosol sources will be dealt with further in sections 3.3 and 4.

[29] These results were obtained from the integral samples. The following sections mainly address the features observed in the sequential samples.

3.2. Latitudinal Dependency

[30] The flight route investigated in this work spanned the latitude band of 5–52°N and thus enables to investigate latitudinal profiles. Special emphasis is placed on the sulphur, which is a major aerosol constituent as well as the most frequently detected element.

[31] The sequential samples covered, on average, 11° in latitude (dependent on latitude region, see Figures 1 and 3), which causes latitudinal overlap between samples. This was handled by using the binning technique applied by *Martinsson et al.* [2001], where separate concentration averages were calculated for every latitude bin interval of 5°. Each sample influences the bin average by the fraction of its span that lies inside the bin. The result is shown in Figure 3. The open circles represent the individual sequential samples at their mean sampling latitude and the hatched histogram shows the latitudinal profile of the concentration as obtained by the binning technique. It is clearly seen that the concentration increases by a factor of 4 from 5–10° N in the tropics to 45–50° N at midlatitudes. This increase with latitude will be explored with respect to influence from stratospheric aerosol in section 4.

3.3. Seasonal Variation

[32] Almost two years of data with approximately one flight per month makes it possible to study variations in the atmospheric aerosol concentration with the time of year. The three most frequently detected elements, sulphur,

potassium and iron, indeed display seasonality. As mentioned in section 2.6, three seasons were defined for this data set: February–June (“spring”), July–September (“summer”) and October–January (“fall/winter”). In Figure 4 the seasonal dependency for the three elements are plotted for the three latitude groups as well as for the integral samples. For each seasonal group an average and its uncertainty are given (horizontal line and error bar). In some cases (especially for iron in the tropics) there is a problem with too many samples falling below the detection limit and the dotted lines represent the maximum average value for the group (see section 2.3).

[33] Particulate sulphur (Figure 4) has a notably low concentration in the summer compared to fall/winter and spring concentrations in the subtropics and midlatitudes. In the tropics there are deviations from this pattern with low concentrations in the fall/winter period. The integral samples follow the pattern of the two higher latitude groups, which together dominate the total mass sampled in most cases. Potassium (Figure 4) clearly differs from sulphur in its seasonal behavior. The concentration is very low during a large part of the year but rises dramatically in the spring. This pattern holds for all latitude groups, but less clear for the tropics where the spring group is the only one to have sufficiently high detection frequency for an estimate of the average concentration. Iron (Figure 4) shows a similar variation but less pronounced than potassium with elevated concentrations during spring. Also, somewhat elevated concentrations in the fall/winter can be seen at midlatitudes. Detection problems, particularly in the tropics, mask parts of the seasonal variation of iron.

4. Troposphere–Stratosphere Distributions and Exchange

4.1. Sources of the Aerosol

[34] In order to analyze the relations between elemental concentrations and trace gases, particle number concentrations and the fraction of a sample collected in the stratosphere (F_s), a correlation matrix was created (Table 2). Those elements most frequently detected (S, K, Fe) were included as well as one of the tropopause definitions, where the latter was used to test the correlation between the different definitions. The samples from the tropics are not shown in Table 2 because no significant correlations or anti-correlations were found. The detection frequencies of K and Fe at midlatitudes and the subtropics were rather low (23–42%). However, the fact that they were detected means that the concentration was high, compared to samples where they were not detected. Taking also into account the large relative standard deviation of the concentration of both elements (Table 1), these correlation coefficients express whether the other parameters systematically showed high (or low) values when the elemental concentration was high.

[35] In addition to the parameters shown in Table 2, the correlations with the particle number concentrations were investigated. However, no correlations were found. All three particle size intervals can be expected to be dominated (by number) by particles that carry negligible mass compared to the relatively few larger particles that dom-

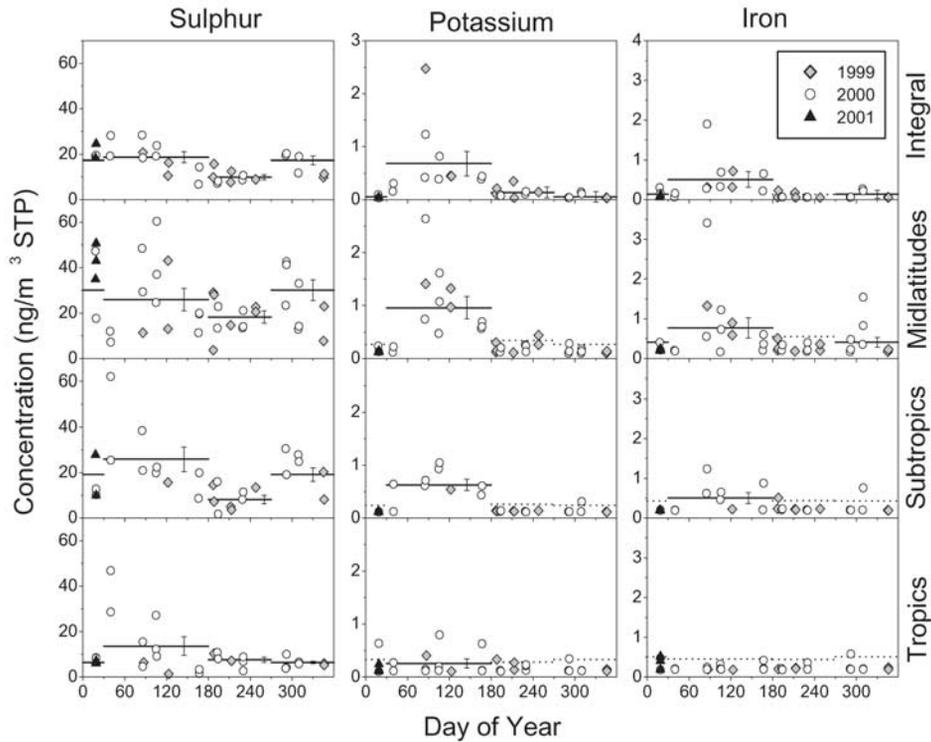


Figure 4. Concentrations of particulate sulphur, potassium and iron as a function of the day of the year for midlatitudes (38–50°N), subtropics (23–37°N), tropics (7–22°N) as well as for samples covering entire flights (“Integral”). The full horizontal lines show the seasonal average concentrations and the error bars the uncertainty of the estimate (± 1 standard deviation). The dotted horizontal lines are estimated seasonal maximum average concentrations. The seasons are February–June, July–September and October–January.

inates particulate mass. For the timescale of this data set (1–2.5 h) it can be concluded that the elemental mass concentrations do not correlate with the number concentration of particles for diameter intervals reaching down to 18 nm or lower. Therefore no further analysis of the number concentrations will be made in this context.

[36] The correlation patterns in the subtropics and midlatitudes are similar. Fe and K are correlated, while the correlation between these elements and S is weak. This

pattern can be compared with properties of aerosol sources and atmospheric processes:

[37] *Stratospheric aerosol contains 0.5–1% Fe in half of the particles as a result of meteor ablation, according to single particle analysis, whereas the K content of that kind of particles is about a factor 100 lower [Cziczko et al., 2001; Murphy et al., 1998]. This is significantly different from the present data set, which was taken at a lower altitude and included a large number of encounters of*

Table 2. Correlation Coefficients

	Midlatitudes				Subtropics			
	S ^a	K ^a	Fe ^a	tpO ₃ ^b	S ^a	K ^a	Fe ^a	tpO ₃ ^b
Detection Frequency ^c	0.97	0.42	0.28	–	0.93	0.30	0.23	–
	<i>Correlation Coefficient</i>							
Particulate S ^a	•	0.31	0.23	0.57	•	0.39	0.18	0.59
Particulate K ^a	0.31	•	0.82	–0.05	0.39	•	0.63	–0.03
Particulate Fe ^a	0.23	0.82	•	0.00	0.18	0.63	•	0.09
CO	–0.14	0.62	0.30	–0.53	0.02	0.49	0.21	–0.42
O ₃	0.59	0.13	0.05	0.79	0.40	0.15	0.23	0.68
Pot. Vorticity (PV)	0.66	–0.10	0.04	0.90	0.46	–0.01	0.13	0.91
F _s (O ₃ > O ₃ ^{tp}) “tpO ₃ ” ^b	0.57	0.05	0.00	•	0.59	–0.03	0.09	•
F _s (PV > 1.5 PVU) ^b	0.57	–0.08	–0.07	0.87	0.53	0.07	0.15	0.88
F _s (PV > 2.5 PVU) ^b	0.58	–0.12	0.02	0.86	0.53	–0.01	0.06	0.90
F _s (PV > 3.5 PVU) ^b	0.65	–0.07	0.10	0.83	0.29	–0.06	0.13	0.74

^a Particulate mass concentration of the element given.

^b Fraction of a sample collected in the stratosphere according to different tropopause definitions.

^c Detection frequency of sequential samples.

stratospheric air, but no entirely stratospheric sample. The K concentration on average was slightly higher than that of Fe (Table 1). As these two elements correlated with each other but not with the indicators of stratospheric air (Table 2), the influence from meteoritic material most probably was minor.

[38] *Crustal material* from the Earth contains appreciable amounts of both K and Fe. However, the K concentration appears to be too high compared to Fe (Table 1) for the crustal source alone [Taylor, 1964]. The IMPROVE network makes use of a simple method to estimate the K concentration in excess of the crust component by subtracting 60% of the Fe concentration from that of K [Gebhart et al., 2001]. Applying that to the present data, results in that, on average, 50% of the K originated in sources other than crust.

[39] *Fossil fuel combustion* emits K and Fe. Contrary to Fe, K correlated with CO (Table 2), thus indicating more influence from combustion sources for the latter element. The influence from various fossil fuel combustion emissions were evaluated in comparison with the detection limits of the present study (Table 1). Motor vehicular emissions contain, in addition to particulate K, significant amounts of Mn, Ni, As and Se [Watson et al., 2001], which should have lifted the average concentration to approximately 4 (Mn) or 3 (Ni, As and Se) times the respective detection limits of Table 1, to explain the excess K. To explain the excess K by oil combustion, significantly increased concentrations of V and Ni (to 20 and 10 times the MDL of Table 1, respectively) would be required [Song et al., 2001] and finally, coal combustion would increase the Se concentration to 2–6 times its MDL [Watson et al., 2001; Song et al., 2001]. The lack elevated concentrations of the mentioned elements, thus indicate that the observed concentrations of particulate potassium cannot be attributed to fossil fuel combustion. The secondary aerosol produced as a result of sulphur dioxide emissions from fossil fuels will be discussed later.

[40] *Biomass burning* emits large amounts of particulate K as well as CO, whereas the emission of all other elements of Table 1 (with the exception of Ge, where no emission data were available) are too low relative to K to significantly affect the concentrations [Turn et al., 1997; Andreae et al., 1998]. In Table 2 it can be seen that particulate K correlates with CO. Elevated concentrations of particulate K appear during spring, with typical concentrations of 1 ng/m³ STP (Figure 4). To compare the concentration of particulate K with CO, the wet deposition of aerosol has to be considered. Studies of rising smoke plumes indicate that 80–95% of the aerosol is deposited before reaching the upper troposphere [Anderson et al., 1996; Andreae et al., 2001]. Making use of emission factors [Andreae et al., 1998] and measurements in biomass smoke plumes elevated to 10 km altitude [Andreae et al., 2001], the change in the CO concentration was estimated to 2 (0.3–7) ppbv for 1 ng/m³ STP change of the particulate K concentration. The monthly mean concentration of CO varies by 30 ppbv over the year in the extratropics along the CARIBIC flight route, with maximum concentration during spring [Zahn et al., 2002]. Biomass burning thus only in part can explain the seasonal variation of CO. Other sources, such as fossil fuel combustion, as well as seasonality in the OH concentration

[Gross and Khalil, 2000], the main sink of CO, influence the CO concentration. Nevertheless, particulate K is a useful tracer of biomass burning [Andreae et al., 1998], suggesting influence from this source, which is further supported by that particulate K shows the strongest correlation with CO of the aerosol constituents investigated.

[41] *Particulate S*, in contrast to K and Fe, is to a large fraction produced in the atmosphere from gas-to-particle conversion processes, including dissolution followed by oxidation in the cloud liquid phase, whereas the other two elements are primary aerosol constituents. This causes differences in the vertical transport of the elements due to differences in uptake by clouds and precipitation associated with phase, water solubility and elemental particle size distributions and therefore in different relationships with the other parameters listed in Table 2. However, Table 2 reveals another feature, namely that particulate S correlates with the indicators of stratospheric air. This will be analyzed next.

4.2. Upper Tropospheric and Lower Stratospheric Particulate Sulphur Concentrations

[42] In order to investigate particulate sulphur concentrations in the upper troposphere and the lower stratosphere, first the question as to whether the average concentrations given above were significantly influenced by stratospheric air will be addressed. The time fraction spent in the stratosphere during the collection of a sample was estimated from the O₃ tropopause definition because of a much better spatial resolution (<50 km in the horizontal) compared to the dynamical tropopause definition (~200 km), see section 2.5. The O₃ tropopause definition thus allows for the resolution of finer spatial details compared to the dynamical tropopause.

[43] Figure 5 shows the measured sulphur concentration as a function of the estimated fraction of sampling time in the stratosphere for the latitude intervals 23–37°N and 38–50°N. It is clear that the stratospheric influence is stronger at more northern latitudes compared to the subtropics, although both the latitude intervals studied were dominated by tropospheric air. There is a considerable variability in the sulphur concentration as a function of the estimated time fraction spent in the stratosphere. In order to investigate the stratospheric influence, the cumulative average sulphur concentration as a function of the stratospheric time fraction was computed, starting from the tropospheric side. In Figure 5a it can be seen that the average concentration was about 18–20 ng/m³ STP when samples with no or little stratospheric influence are included in the average. As more stratospherically influenced samples are included, the average increases and reaches the overall average of 26 ng/m³ STP. From the standard deviation of the average, it is clear that this increase is significant. Similarly the subtropical samples (Figure 5b) show a significant increasing trend in the cumulative average from 12 to 18 ng/m³ STP, although the extreme value for the subtropics of 62 ng/m³ STP affected the average by 1.5 ng/m³ STP. It can thus be concluded that concentrations in the lowermost stratosphere were higher than in the upper troposphere. In particular it is clear that concentrations of about 20 ng/m³ STP or lower were not observed when stratospheric air was dominant (Figure 5).

[44] Due to the variability of the concentration, simple regression analysis to estimate the trend (Figure 5) becomes

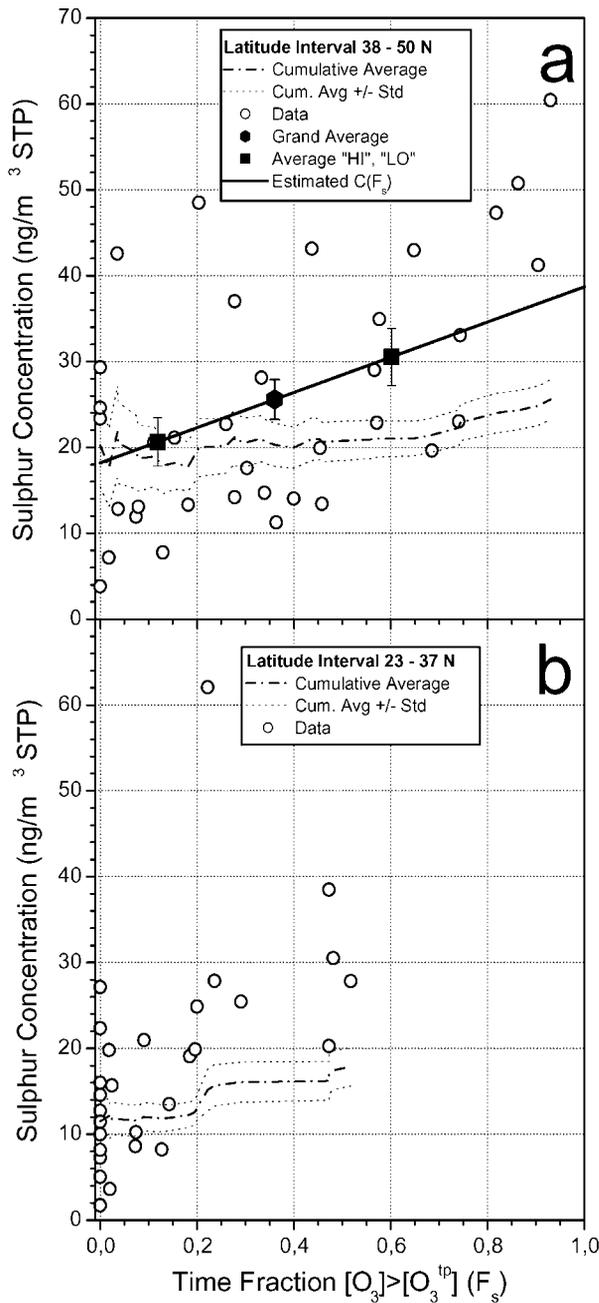


Figure 5. Particulate sulphur concentration as a function of the fraction of the sample collected in the stratosphere according to a tropopause definition based on the ozone concentration. The cumulative averages start with pure tropospheric samples. a) Midlatitudes. b) Subtropics.

very sensitive to the structure in the data. Therefore another, more conservative method was used to estimate the average concentrations in the upper troposphere and lowermost stratosphere. When estimating the average concentrations of two reservoirs from samples representing mixtures of the two, it is reasonable to assume a linear relationship of the average concentration as a function of the time fraction spent in the reservoir. In order to estimate these averages, the average at either side of the mid data point, with respect

to stratospheric time fraction of the sample, was calculated by forming the average concentrations (C_{LO} and C_{HI}) and time fractions spent in the stratosphere (F_{LO} and F_{HI}). Using the linear assumption, these parameters are connected to the average upper tropospheric and lowermost stratospheric average concentrations (C_T and C_S) by $C_{LO} = F_{LO}C_S + (1 - F_{LO})C_T$ and similarly for $C_{HI}(F_{HI}, C_S, C_T)$. From these two equations, the average tropospheric and stratospheric concentrations are obtained by

$$C_T = \frac{F_{HI}C_{LO} - F_{LO}C_{HI}}{F_{HI} - F_{LO}}$$

$$C_S = \frac{(1 - F_{LO})C_{HI} - (1 - F_{HI})C_{LO}}{F_{HI} - F_{LO}}$$

This simple model reproduces the average sulphur concentration ($26 \text{ ng/m}^3 \text{ STP}$) at the average time fraction of the data set spent in the stratosphere (0.36). The average sulphur concentration in the upper troposphere was estimated to $18 \text{ ng/m}^3 \text{ STP}$, which is well in line with the value found from the cumulative average (Figure 5a). The average concentration in the lowermost stratosphere was found to be a factor of 2.1 higher ($39 \text{ ng/m}^3 \text{ STP}$). The data taken over the subtropics were less influenced by stratospheric air and in addition included an extreme data point, which taken together makes these data less suited to estimate the stratospheric concentration. On the other hand, the upper tropospheric air was well represented in the data set, permitting the concentration to be estimated to $12 \text{ ng/m}^3 \text{ STP}$ (Figure 5b). Making the assumption that the concentration in the lowermost stratosphere over the subtropics was the same as over midlatitudes only slightly underestimates the average concentration of the samples from the subtropics, suggesting that the particulate sulphur concentrations in the lowermost stratosphere are similar in both latitude intervals studied.

[45] The results of these estimates are summarized in Figure 6. In the tropics ($7-22^\circ\text{N}$), the stratospheric influence was negligible and the average of $8.9 \text{ ng/m}^3 \text{ STP}$ thus is representative of the upper troposphere. A substantial latitudinal dependency of the upper tropospheric average particulate sulphur concentration was found, with a factor of two increase from the tropics to midlatitudes. The concentration in the lowermost stratosphere was estimated to be significantly higher ($39 \text{ ng/m}^3 \text{ STP}$) over midlatitudes, with similar concentrations over the subtropics.

4.3. Influence on the Results Due to Tropopause Definition

[46] The results of Figure 6 were obtained using the O_3 -based tropopause definition. The effect on the results for the midlatitudes samples was investigated with respect to the method to define the tropopause. From Table 2 it is evident that the O_3 -based tropopause correlated with those based on PV. Tropospheric and stratospheric average concentrations of CO and O_3 as well as the average PV were calculated for the four tropopause definitions used and the particulate sulphur concentrations were estimated in the same way as in the previous section.

[47] Naturally, the average time fraction spent in the stratosphere depends on the definition of the tropopause,

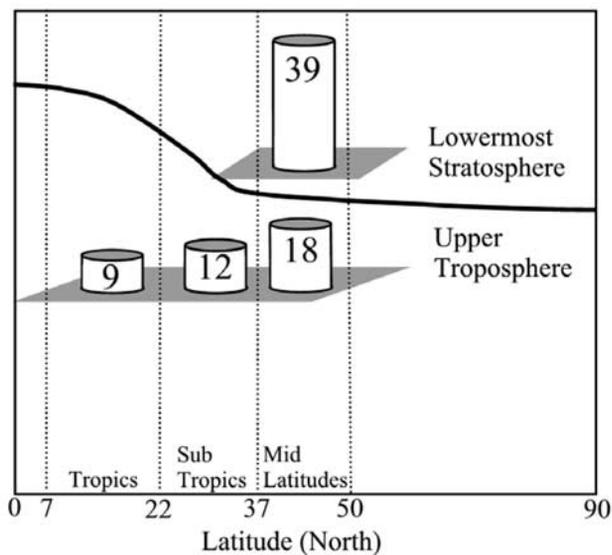


Figure 6. Average particulate sulphur concentration in different sections of the tropopause region of the northern hemisphere. The discrimination between tropospheric and stratospheric air was based on the ozone concentration.

spanning from 19 to 48% for midlatitudes (Table 3). All definitions resulted in clearly different characteristics of the stratosphere compared to the troposphere with respect to PV and CO and O₃ concentrations. The three PV-based definitions show a clear trend of increasing concentrations of O₃ with increasing PV tropopause threshold values, while CO concentrations are decreasing (Table 4). These definitions can be regarded as a scale of increasing stratospheric influence, revealing the gradient of increasing O₃ and decreasing CO in the tropopause region. Based on the averages of Tables 3 and 4, the tropopause defined by the O₃ concentration on average is found between PV values of 1.5 and 2.5 PVU.

[48] The tropospheric concentration of particulate sulphur was not significantly affected by the choice of tropopause definition, the average concentration ranging from 16 to 20 ng/m³ STP (Table 4). Similarly to CO and O₃ concentrations, the stratospheric S concentration strongly depends on the PV tropopause threshold value (36–52 ng/m³ STP). This indicates an average slope of increasing particulate sulphur with altitude in the tropopause region at northern midlatitudes.

4.4. Transport Across the Tropopause

[49] Up to this point the concentrations in the upper troposphere and lower stratosphere have been investigated.

Table 3. Average Fraction Sampled in the Stratosphere According to Different Definitions of the Tropopause

	Midlatitudes	Subtropics	Tropics
F _s (O ₃ > O ₃ ^{tp}) ^a	0.36	0.13	0.01
F _s (PV > 1.5 PVU) ^a	0.48	0.22	0.01
F _s (PV > 2.5 PVU) ^a	0.30	0.09	0.00
F _s (PV > 3.5 PVU) ^a	0.19	0.04	0.00

^aFraction of a sample collected in the stratosphere according to different tropopause definitions.

Table 4. Upper Tropospheric and Lower Stratospheric Characteristics Over Northern Midlatitudes Depending on the Tropopause Definition

	S, ng/m ³ STP	CO, ppbv	O ₃ , ppbv	O ₃ /O ₃ ^{tp}	PV, PVU
<i>Upper Troposphere</i>					
F _s (O ₃ > O ₃ ^{tp}) ^a	18	94	65	0.67	1.1
F _s (PV > 1.5 PVU) ^a	16	94	66	0.68	0.71
F _s (PV > 2.5 PVU) ^a	20	93	75	0.75	1.0
F _s (PV > 3.5 PVU) ^a	19	91	80	0.81	1.3
<i>Lower Stratosphere</i>					
F _s (O ₃ > O ₃ ^{tp}) ^a	39	71	166	1.7	3.9
F _s (PV > 1.5 PVU) ^a	36	76	141	1.5	3.6
F _s (PV > 2.5 PVU) ^a	40	68	165	1.7	4.6
F _s (PV > 3.5 PVU) ^a	52	63	194	2.1	5.5

^aFraction of a sample collected in the stratosphere according to different tropopause definitions.

Next, the transport across the tropopause will be briefly explored.

[50] The K concentration varies strongly with season, showing elevated concentrations during February to June (Figure 7a). In fact, all 16 measurements of K concentrations higher than 0.5 ng/m³ STP at midlatitudes and in the subtropics were recorded during that period. From Figure 7b it can be seen that stratospheric air was encountered throughout the year, with only minor seasonality. This means that high K concentrations were found also when a large fraction of the sample was taken in the stratosphere. To further study this phenomenon, the four samples having the strongest stratospheric influence were investigated (samples marked with a cross in Figure 7). One of these samples was collected during the February–June period. That sample showed high K concentration, whereas the other three did not. Hence, the samples with a strong stratospheric influence (more than 80% of the sampling time in the stratosphere, according to the O₃-based tropopause definition) show the same pattern as the overall seasonal variation of K. According to the O₃ tropopause definition, 93% of the high-K-sample was collected in the stratosphere. The PV always was higher than 2.5 PVU and higher than 3.5 PVU for 84% of the sampling time. The K concentration was the second highest recorded. Thus, it is unlikely that the small fraction sampled in the troposphere was responsible for the high K concentration observed.

[51] A climatology of CO concentration in the upper troposphere showed a shallow maximum in the concentration north of 30°N between February and June [Zahn *et al.*, 2002], similar to Figure 7c, which is based on part of that data (the CO measurements started in 1997, while the aerosol elemental concentrations are available from 1999). The clearest pattern is found at midlatitudes, where the CO concentration was 100 ppb or higher during that season. The same pattern of elevated CO concentration can be seen in the lower stratosphere for the February–June period, the concentration being about 80 ppb or higher, whereas they were mostly lower during the remainder of the year (Figure 7d).

[52] Taken together these results thus show that elevated concentrations of particulate K and CO are transported to the upper troposphere during February to June, most pronounced at midlatitudes but also present in the subtropics. The fact that the elevated concentrations also can be

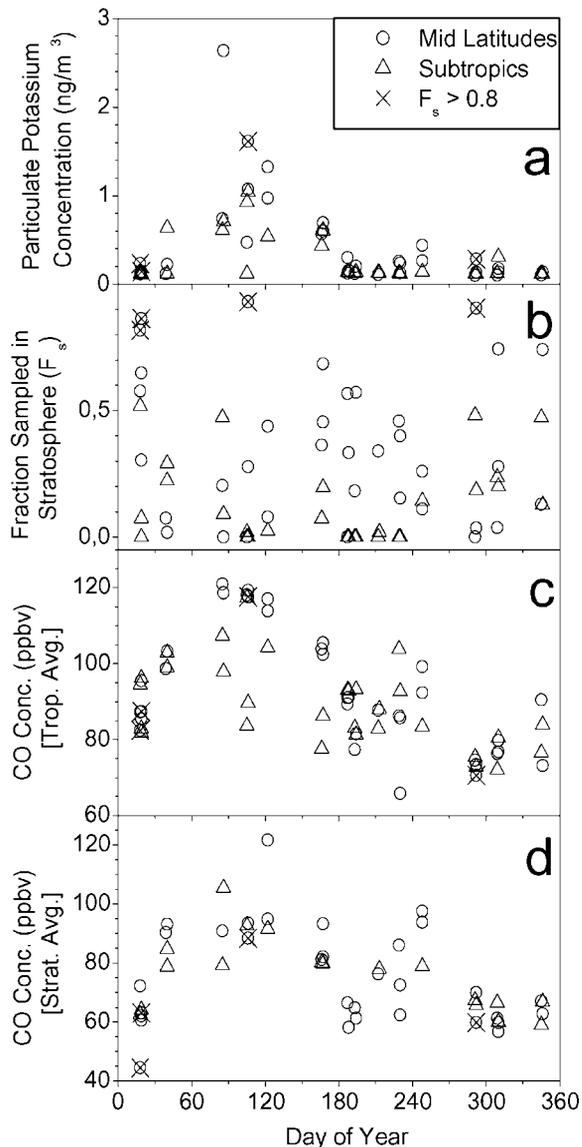


Figure 7. Seasonal dependency of a) particulate potassium, b) fraction of a sample collected in the stratosphere, c) tropospheric average carbon monoxide concentration of the sampling periods and d) stratospheric average carbon monoxide concentration of the sampling periods. The crosses highlight samples where the fraction of the sample collected in the stratosphere exceeded 0.8. The ozone concentration was used to define the tropopause.

observed in the lowermost stratosphere, indicates a transport of aerosol as well as CO across the tropopause.

[53] According to simulations of the large-scale circulation, there is a net downward transport at midlatitudes to the lowermost stratosphere across the isentropic surface of 380 K potential temperature boundary to the stratospheric overworld that is strongest in the northern hemisphere and maximizes during the winter [Holton *et al.*, 1995; van Velthoven and Kelder, 1996]. Due to a seasonal dependency of the mass of the lowermost stratosphere (bounded downward by the tropopause), the maximum net transport from the stratosphere to the troposphere (STE) is shifted to the

spring [Appenzeller *et al.*, 1996]. In addition to these large-scale, diabatic features, transport takes place along isentropic surfaces crossing the tropopause, causing transport in both directions across the tropopause, according to modeling by Dethof *et al.* [2000] and Stohl [2001]. As a result the lowermost stratosphere (LS) contains a mixture of tropospheric air and air from the stratospheric overworld.

[54] Making use of the modeling results, the annual average fraction of the air originating in the stratospheric overworld was estimated to 27% according to Dethof *et al.* [2000] and 33 or 46% according to Stohl [2001], depending on the extension of the dynamical tropopause. These results are averages over the entire LS of the northern hemisphere. The measurements presented here were undertaken at potential temperatures 328 ± 11 K at midlatitudes and are thus not representative for the entire LS. The modeling results by Dethof *et al.* [2000] were given for three potential temperature layers of the LS. Making the assumption that all fluid elements in each layer have equal probability to be transported across layer boundaries in a simple layer model, results in annual averages of 70, 37 and 9% of air from the stratospheric overworld in the potential temperature layers 360, 345 and 330 K of the LS. These results thus indicate that on average 91% of the LS air encountered during the measurements was of tropospheric origin, thus supporting the experimental findings of a strong tropospheric influence on the LS air sampled.

5. Discussion

[55] The measurements presented here were taken during a period of low volcanic influence on the stratospheric aerosol [Halmer *et al.*, 2002]. The latest major volcanic event was the eruption of Pinatubo in 1991, where the effect on the stratospheric aerosol was decayed in the mid 1990th [Zuev *et al.*, 2001]. In periods of low volcanic activity, transport of tropospheric air across the tropical tropopause as part of the large-scale circulation [Holton *et al.*, 1995] has been suggested as the main supplier of newly formed, ultrafine aerosol particles [Brock *et al.*, 1995] and precursor gases to the stratosphere. Carbonyl sulphide has been considered as the main precursor gas of the stratospheric aerosol layer. A reanalysis based on extended atmospheric measurements and refined laboratory studies of reaction rates, indicates that the sulphur dioxide production from carbonyl sulphide is insufficient to sustain the stratospheric aerosol [Chin and Davies, 1995]. Recent modeling studies suggest that transport of tropospheric sulphur dioxide may contribute significantly to the sulphate production in the lower part of the stratosphere [Weissenstein *et al.*, 1997; Kjellström, 1998].

[56] The stratospheric background burden of particulate sulphur has been estimated to 0.08–0.15 Tg [Weissenstein *et al.*, 1997; Kjellström, 1998; Pitari *et al.*, 2002], which corresponds to average concentrations in the range 100–200 ng/m^3 STP. These concentrations are higher than the upper tropospheric concentration of particulate sulphur at northern midlatitudes of the present study. The vertical gradient of particulate sulphur found in the tropopause region thus could be the result of a mixture between stratospheric and tropospheric air, caused by the large-scale extratropical descent of stratospheric air.

[57] *Thornton et al.* [1999] combined the results of sulphur dioxide measurements from several aircraft-based campaigns over the Pacific Ocean. The measurements were undertaken during a period (1991–1996) affected by the Pinatubo eruption, which might have affected the upper tropospheric concentrations due to transport from the stratosphere. The upper tropospheric sulphur dioxide concentration over the Pacific showed a strong latitudinal gradient of about a factor of 10 between 60°S and 60°N, ranging from less than 10 pptv over southern to about 100 pptv (140 ng/m³ STP of sulphur) over northern midlatitudes [*Thornton et al.*, 1999], similar to the gradient of particulate sulphur in the northern hemisphere in the present study. The high concentrations over northern midlatitudes offer another explanation for the observed gradient in the particulate sulphur concentration across the tropopause. As much as 90% of the air encountered in the lowermost stratosphere could have been of tropospheric origin, according to the estimates in section 4.4. The transport from the troposphere to the stratosphere along isentropic surfaces [*Dethof et al.*, 2000; *Stohl*, 2001] prolongs the residence time of the air in the region around the tropopause. The residence time of sulphur dioxide at 10 km altitude in the troposphere is estimated to 10 days and to about a month in the stratosphere [*Weissenstein et al.*, 1997], whereas the ventilation rate of the LS due to isentropic transport is estimated to 6 exchanges per year [*Dethof et al.*, 2000]. The transport of tropospheric air into the lowermost stratosphere thus permits ageing of the sulphur species in the lowermost stratosphere to form particulate sulphur from sulphur dioxide.

[58] According to source estimates, fossil fuel combustion is the dominating source of sulphur species, primarily as sulphur dioxide. The bulk of these emissions originate in northern midlatitudes extending into the subtropics, specifically eastern North America, Europe and eastern and southern Asia [*Smith et al.*, 2001]. Based on the coinciding latitudinal dependency of particulate sulphur and anthropogenic emissions of sulphur dioxide, it is hypothesized that fossil fuel combustion is an important source of aerosol at midlatitudes in the northern hemispheric upper troposphere, at least during periods of low influence from volcanic activity. The high concentrations of sulphur dioxide at northern hemisphere midlatitudes further suggests an influence on the lowermost stratospheric aerosol concentration from anthropogenic sources, which could, at least, be a partial explanation to the observed vertical increase of the particulate sulphur concentration in the region around the tropopause of northern midlatitudes.

6. Conclusions

[59] Aerosol elemental concentrations at 9–11 km altitude were investigated in the CARIBIC project over a two-year-period during 31 intercontinental flights between Germany and Sri Lanka/Maldives in the Indian Ocean. 18 elements were measured and among these elements, particulate sulphur was the dominant with respect to aerosol mass concentration. The average of 16 ng/m³ STP was 50 times higher than any of the other elements. The concentration of particulate sulphur showed a strong latitudinal dependency, increasing a factor of 3 from the tropics to midlatitudes and spanned a factor 4 from 5 to 50°N.

[60] The concentrations of particulate sulphur, potassium and iron showed different seasonal variations. Potassium exhibited the most pronounced dependency with very low concentrations during July to January and peak concentrations during spring. In contrast, the particulate sulphur concentration showed less seasonal variation and was low during July–September over midlatitudes and the subtropics, whereas the concentration over the tropics was lowest during July to January. The seasonality of particulate iron was not as clear, partly due to low detection frequency, but tended to show more similarities with potassium than with sulphur. Just like particulate sulphur, potassium and iron showed highest concentrations over midlatitudes.

[61] Correlation studies indicated that particulate sulphur has a complicated origin of supply both from the ground and via the stratosphere. Concentration gradients of particulate sulphur in the tropopause region were estimated by the aid of tracers of stratospheric air. It was found that the upper tropospheric concentration increased with latitude (northern hemisphere) by a factor of 2 from the tropics to midlatitudes. At midlatitudes, where stratospheric air frequently was encountered, the lowermost stratospheric concentration was estimated to be a factor of 2 higher than the upper tropospheric midlatitudes concentration.

[62] The correlation pattern between the elements and the lack of correlation between particulate iron and the tracers of stratospheric air indicate that meteor ablation was not an important source of the aerosol in the northern hemispheric, extratropical tropopause region. The widespread sources of crustal particulate matter at the Earth's surface could not account for more than about half of the particulate potassium observed. Relating elemental source profiles to the detection properties of the measurements, indicates that fossil fuel combustion cannot account for the potassium concentrations observed and points to biomass burning as a possible source of the elevated concentration during the spring months. The particulate sulphur concentration showed similar latitudinal dependency as the anthropogenic emissions of sulphur dioxide, thus suggesting that fossil fuel combustion is an important source of the aerosol in the extratropical tropopause region of the northern hemisphere.

[63] Elevated concentrations of particulate potassium were found in samples dominated both by tropospheric and stratospheric air. A similar communication between upper tropospheric and lowermost stratospheric concentrations is present in the carbon monoxide data. Aerosol particles as well as carbon monoxide thus were transported up to the upper troposphere and penetrated into the lowermost stratosphere. These experimental observations of a strong influence from tropospheric air on the lowermost stratosphere were made at potential temperatures of 328 ± 11 K at northern midlatitudes. Adapted modeling results of cross-tropopause transport along isentropic surfaces indicate that as much as 90% of the lowermost stratospheric air at that potential temperature level is of tropospheric origin, thus supporting the experimental findings.

[64] A gradient of increasing particulate sulphur with altitude in the midlatitudes tropopause region was found in this study, which was undertaken during a period of low volcanic influence on the stratosphere. This could be

explained both by a large-scale downward transport from the stratospheric overworld and transport along isentropic surfaces from the troposphere to the lowermost stratosphere. In the latter case, sulphur dioxide in the northern extratropical upper troposphere is transported into the lowermost stratosphere, where the prolonged residence time allows for ageing to form particulate sulphur. This process is supported by the strong influence from tropospheric air on the lowermost stratosphere and observations of high concentrations of sulphur dioxide in the upper troposphere of northern hemispheric midlatitudes. As a result, anthropogenic emissions can make an important contribution to the aerosol in the lowermost stratosphere, at least during periods of low volcanic activity. This in turn implies that the tropopause region could be a strong, high-altitude source region and that most of the particulate mass of the tropopause region originates in sources at the Earth's surface.

[65] **Acknowledgments.** The collaboration with LTU International Airways, Düsseldorf, Germany, providing an aircraft modified for the CARIBIC sampling, is gratefully acknowledged. The work was supported financially by the European Union and the Swedish Environment Protection Agency (research grants ENV-CT95-0006 and 011-121-98-01).

References

- Anderson, B. E., et al., Aerosols from biomass burning over the tropical South Atlantic region: Distributions and impacts, *J. Geophys. Res.*, *101*, 24,117–24,137, 1996.
- Andreae, M. O., et al., Airborne studies of aerosol emissions from savanna fires in southern Africa, 2, Aerosol chemical composition, *J. Geophys. Res.*, *103*, 32,119–32,128, 1998.
- Andreae, M. O., et al., Transport of biomass burning smoke to the upper troposphere by deep convection in the equatorial region, *Geophys. Res. Lett.*, *28*, 951–954, 2001.
- Appenzeller, C., J. R. Holton, and K. H. Rosenlof, Seasonal variation of mass transport across the tropopause, *J. Geophys. Res.*, *101*, 15,071–15,078, 1996.
- Barrie, L. A., et al., A comparison of large-scale atmospheric sulphate aerosol models (COSAM): Overview and highlights, *Tellus*, *53B*, 615–645, 2001.
- Brenninkmeijer, C. A. M., et al., CARIBIC—Civil aircraft for global measurement of trace gases and aerosols in the tropopause region, *J. Atmos. Oceanic Technol.*, *16*, 1373–1383, 1999.
- Brock, C. A., P. Hamill, J. C. Wilson, H. H. Jonsson, and K. R. Chan, Particle formation in the upper tropical troposphere: A source of nuclei for the stratospheric aerosol, *Science*, *270*, 1650–1653, 1995.
- Charlson, R. J., et al., Climate forcing by anthropogenic aerosols, *Science*, *255*, 423–430, 1992.
- Chin, M., and D. D. Davies, A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol, *J. Geophys. Res.*, *100*, 8993–9005, 1995.
- Cziczo, D. J., D. S. Thomson, and D. M. Murphy, Ablation, flux, and atmospheric implications of meteors inferred from stratospheric aerosol, *Science*, *291*, 1772–1775, 2001.
- Danilin, M. Y., et al., Aviation fuel tracer simulation: Model intercomparison and implications, *Geophys. Res. Lett.*, *25*, 3947–3950, 1998.
- Dethof, A., A. O'Neill, and J. Slingo, Quantification of the isentropic mass transport across the dynamical tropopause, *J. Geophys. Res.*, *105*, 12,279–12,293, 2000.
- Dibb, J. E., et al., Aerosol chemical composition and distribution during the Pacific Exploratory Mission (PEM) Tropics, *J. Geophys. Res.*, *104*, 5785–5800, 1999.
- Ferry, G. V., et al., Effects of aircraft on aerosol abundance in the upper troposphere, *Geophys. Res. Lett.*, *26*, 2399–2402, 1999.
- Gebhart, K. A., S. M. Kreidenweis, and W. C. Malm, Back-trajectory analyses of fine particulate matter measured at Big Bend national park in the historical database and the 1996 scoping study, *Sci. Total Environ.*, *276*, 185–204, 2001.
- Gross, G. W., and M. A. K. Khalil, OH concentrations from a general circulation model coupled with a tropospheric chemistry model, *Chemosphere*, *Global Change Sci.*, *2*, 191–206, 2000.
- Halmer, M. M., H.-U. Schmincke, and H.-F. Graf, The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years, *J. Volcanol. Geotherm. Res.*, *115*, 511–528, 2002.
- Hermann, M., and A. Wiedensohler, Counting efficiency of condensation particle counters at low pressures with illustrative data from the upper troposphere, *J. Aerosol Sci.*, *32*, 975–991, 2001.
- Hermann, M., F. Stratmann, M. Wilck, and A. Wiedensohler, Sampling characteristics of an aircraft-borne aerosol inlet system, *J. Atmos. Oceanic Technol.*, *18*, 7–19, 2001.
- Hermann, M., J. Heintzenberg, A. Wiedensohler, C. A. M. Brenninkmeijer, G. Heinrich, and A. Zahn, Meridional distributions of aerosol particle number concentrations in the upper troposphere and lower stratosphere obtained by CARIBIC flights, *J. Geophys. Res.*, submitted, 2002.
- Hoerling, M. P., T. K. Schaack, and A. J. Lenzen, Global objective tropopause analysis, *Mon. Weather Rev.*, *119*, 1816–1831, 1991.
- Hofmann, D. J., Twenty years of balloon-borne tropospheric aerosol measurements at Laramie, Wyoming, *J. Geophys. Res.*, *98*, 12,753–12,766, 1993.
- Hofmann, D. J., and J. M. Rosen, On the background stratospheric aerosol layer, *J. Atmos. Sci.*, *38*, 168–181, 1981.
- Hoiinka, K. P., The tropopause: Discovery, definition and demarcation, *Meteorol. Z.*, *6*, 281–303, 1997.
- Holton, J. R., P. H. Haynes, M. E. McIntyre, A. R. Douglass, R. B. Rood, and L. Pfister, Stratosphere–troposphere exchange, *Rev. Geophys.*, *33*, 403–439, 1995.
- Intergovernmental Panel on Climate Change (IPCC), *Climate Change 2001—The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by Houghton et al., Cambridge Univ. Press, New York, 2001.
- Johansson, S. A. E., and J. L. Campbell, *PIXE: A Novel Technique for Elemental Analysis*, John Wiley, New York, 1988.
- Junge, C. E., C. W. Chagnon, and J. E. Manson, Stratospheric aerosols, *J. Meteorol.*, *18*, 81–108, 1961.
- Kent, G. S., P.-H. Wang, M. P. McCormick, and K. M. Skeens, Multiyear Stratospheric Aerosol and Gas Experiment II measurements of upper tropospheric aerosol characteristics, *J. Geophys. Res.*, *100*, 13,875–13,899, 1995.
- Kjellström, E., A three-dimensional global model study of carbonyl sulfide in the troposphere and the lower stratosphere, *J. Atmos. Chem.*, *29*, 151–177, 1998.
- Kjellström, E., J. Feichter, R. Sausen, and R. Hein, The contribution of aircraft emissions to the atmospheric sulfur budget, *Atmos. Environ.*, *33*, 3455–3465, 1999.
- Lelieveld, J., et al., Chemical perturbation of the lowermost stratosphere through exchange with the troposphere, *Geophys. Res. Lett.*, *24*, 603–606, 1997.
- Martinsson, B. G., et al., Experimental determination of the connection between cloud droplet size and its dry residue size, *Atmos. Environ.*, *31*, 2477–2490, 1997.
- Martinsson, B. G., et al., Droplet nucleation and growth in orographic clouds in relation to the aerosol population, *Atmos. Res.*, *50*, 289–315, 1999.
- Martinsson, B. G., et al., Validation of very high cloud droplet number concentrations in air masses transported thousands of kilometers over the ocean, *Tellus*, *52B*, 801–814, 2000.
- Martinsson, B. G., G. Papaspiropoulos, J. Heintzenberg, and M. Hermann, Fine mode particulate sulphur in the tropopause region measured from intercontinental flights (CARIBIC), *Geophys. Res. Lett.*, *28*, 1175–1178, 2001.
- Murphy, D. M., D. S. Thomson, and M. J. Mahoney, In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers, *Science*, *282*, 1664–1669, 1998.
- Papaspiropoulos, G., B. Mentes, P. Kristiansson, and B. G. Martinsson, A high sensitivity elemental analysis methodology for upper tropospheric aerosol, *Nucl. Instrum. Methods Phys. Res., Sect. B*, *150*, 356–362, 1999.
- Pitari, G., E. Mancini, V. Risi, and D. T. Shindell, Impact of future climate and emission changes on stratospheric aerosols and ozone, *J. Atmos. Sci.*, *59*, 414–440, 2002.
- Radke, L. F., J. A. Coakley Jr., and M. D. King, Direct and remote sensing observations of the effects of ships on clouds, *Science*, *246*, 1146–1148, 1989.
- Rasch, P. J., et al., A comparison of scavenging and deposition processes in global models: Results from the WCRP Cambridge workshop 1995, *Tellus*, *52B*, 1025–1056, 2000.
- Rodhe, H., Human impact on the atmospheric sulphur balance, *Tellus*, *51A–B*, 110–122, 1999.
- Rosenfeld, D., Suppression of rain and snow by urban and industrial air pollution, *Science*, *287*, 1793–1796, 2000.

- Rosenfeld, D., and W. L. Woodley, Deep convective clouds with sustained supercooled liquid water down to -37.5°C , *Nature*, *405*, 440–442, 2000.
- Sheridan, P. J., C. A. Brock, and J. C. Wilson, Aerosol particles in the upper troposphere and lower stratosphere: Elemental composition and morphology of individual particles in northern midlatitudes, *Geophys. Res. Lett.*, *21*, 2587–2590, 1994.
- Smith, S. J., H. Picher, and T. M. L. Wigley, Global and regional anthropogenic sulfur dioxide emissions, *Global Planet. Change*, *29*, 99–119, 2001.
- Song, X.-H., A. V. Polissar, and P. K. Kopke, Sources of fine particle composition in the north-eastern US, *Atmos. Environ.*, *35*, 5277–5286, 2001.
- Stohl, A., A 1-year Lagrangian “climatology” of airstreams in the northern hemisphere troposphere and lowermost stratosphere, *J. Geophys. Res.*, *106*, 7263–7279, 2001.
- Suortti, T., et al., Evolution of the Arctic stratospheric aerosol mixing ratio measured with balloon-borne aerosol backscatter sondes for years 1988–2000, *J. Geophys. Res.*, *106*, 20,759–20,766, 2001.
- Taylor, S. R., Abundance of chemical elements in the continental crust: A new table, *Geochim. Cosmochim. Acta*, *28*, 1273–1285, 1964.
- Thornton, D. C., A. R. Bandy, B. W. Blomquist, A. R. Driedger, and T. P. Wade, Sulphur dioxide distribution over the Pacific Ocean 1991–1996, *J. Geophys. Res.*, *104*, 5845–5854, 1999.
- Turn, S. Q., B. M. Jenkins, J. C. Chow, L. C. Pritchett, D. Campbell, T. Cahill, and A. Whalen, Elemental characterization of particulate matter emitted from biomass burning: Wind tunnel derived source profiles for herbaceous and wood fuels, *J. Geophys. Res.*, *102*, 3683–3699, 1997.
- van Velthoven, P. F. J., and H. Kelder, Estimates of stratosphere–troposphere exchange: Sensitivity to model formulation and horizontal resolution, *J. Geophys. Res.*, *101*, 1429–1434, 1996.
- Watson, J. G., J. C. Chow, and J. E. Houck, PM_{2.5} chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in north-western Colorado during 1995, *Chemosphere*, *43*, 1141–1151, 2001.
- Weisenstein, D. K., G. K. Yue, M. K. W. Ko, N.-D. Sze, J. M. Rodriguez, and C. J. Scott, A two-dimensional model of sulphur species and aerosols, *J. Geophys. Res.*, *102*, 13,019–13,035, 1997.
- Xu, L., et al., The composition of individual aerosol particle in the troposphere and stratosphere over Xianghe (39.45°N , 117.0°E), China, *Atmos. Environ.*, *35*, 3145–3153, 2001.
- Zahn A., C. A. M. Brenninkmeijer, W. A. H. Asman, P. J. Crutzen, G. Heinrich, H. Fischer, J. W. M. Cuijpers, and P. F. J. van Velthoven, The budgets of O₃ and CO in the upper troposphere: The CARIBIC passenger aircraft results 1997–2001, *J. Geophys. Res.*, *107*(D17), 4337, doi:10.1029/2001JD001529, 2002.
- Zuev, V. V., V. D. Burlakov, A. V. El'nikov, A. P. Ivanov, A. P. Chaikovskii, and V. N. Shcherbakov, Processes of long-term relaxation of stratospheric aerosol layer in Northern Hemisphere midlatitudes after a powerful volcanic eruption, *Atmos. Environ.*, *35*, 5059–5066, 2001.

C. A. M. Brenninkmeijer, Division of Atmospheric Chemistry, Max Planck Institute for Chemistry, P.O. Box 3060, D-55020 Mainz, Germany.
H. Fischer and A. Zahn, Institute of Meteorology and Climate Research, Research Centre Karlsruhe, P.O. Box 3640, D-76021 Karlsruhe, Germany.

J. Heintzenberg and M. Hermann, Institute for Tropospheric Research, Permoserstrasse 15, D-04318 Leipzig, Germany.

B. G. Martinsson and G. Papaspiropoulos, Division of Nuclear Physics, Lund University, P.O. Box 118, S-22100 Lund, Sweden. (bengt.martinsson@nuclear.lu.se)

P. F. J. van Velthoven, Atmospheric Composition Research, Royal Netherlands Meteorological Institute (KNMI), P.O. Box 3730 AE, De Bilt, Utrecht, The Netherlands.