GEOPHYSICAL RESEARCH LETTERS, VOL. 28, NO. 7, PAGES 1175-1178, APRIL 1, 2001

Fine mode particulate sulphur in the tropopause region measured from intercontinental flights (CARIBIC)

Bengt G. Martinsson and Giorgos Papaspiropoulos
Division of Nuclear Physics, Physics Department, Lund University, Lund, Sweden

Jost Heintzenberg and Markus Hermann
Institute for Tropospheric Research, Leipzig, Germany

Abstract. Here the first systematic study of the concentration of particulate sulphur in the upper troposphere and lower stratosphere is presented. The measurements were undertaken in the CARIBIC programme during intercontinental flights from a commercial aircraft, which was equipped with an aerosol inlet and a research payload in the cargo bay. Aerosol samples were collected and analysed for elemental composition. The data set comprises 21 flights between Germany and Male/Colombo in the Indian Ocean. The average fine mode, particulate sulphur concentration was 14 ng/m^3 STP, which is low compared to remote areas at the Earth's surface. A pronounced dependence with latitude with elevated concentrations occurring within the densely industrialised northern hemispheric mid latitudes was observed, thus suggesting anthropogenic influence on the climate from sulphate particles in the tropopause region.

Introduction

Little is known about the mass concentration of aerosol constituents in the tropopause region. The few studies available indicate that the particles are dominated by sulphuric acid, which may be partially neutralised [*Brock et al.*, 1995; *Sheridan et al.*, 1994; *Ferry et al.*, 1999]. Sulphate particles affect climate by scattering solar radiation and by altering cloud properties [*Charlson et al.*, 1992; *Houghton et al.*, 1996]. The sulphate in the tropopause region originates from sources at the Earth's surface and from air traffic [*Brasseur et al.*, 1998]. The latter contributes only marginally to the upper troposphere sulphate concentration [*Ferry et al.*, 1999; *Rodhe*, 1999], and its quantitative effect on climate is unclear [*Brasseur et al.*, 1998; *Penner et al.*, 1999]. In-situ observations of cirrus cloud microstructure show that anthropogenic sulphate contributions to the upper troposphere have the potential to alter its radiative properties significantly [*Ström et al.*, 1997]. Anthropogenic sulphate may also influence climate by extending the lifetime of contrails forming in the effluents from aircraft [*Brasseur et al.*, 1998].

The sulphate concentration in the upper troposphere is currently estimated based on chemical transport models [*Rodhe*, 1999], which need validation from measurements. Here we present the first systematic large-scale study of particulate sulphur in the tropopause region. The data were taken during intercontinental flights on a commercial aircraft. An impaction technique was used to collect aerosol samples, which were analysed for elemental composition with Particle-Induced X-ray Emission.

Paper number 2000GL012257.
0094-8276/01/2000GL012257$05.00

Experimental Methods

The results presented here were obtained in the CARIBIC (Civil Aircraft for Remote Sensing and in situ Measurements in Troposphere and Lower Stratosphere Based on the Instrumentation Container Concept) programme [*Brenninkmeijer et al.*, 1999]. The sampling was undertaken during commercial flights between Germany and Male/Colombo (fig. 1) from a Boeing 767-ER operated by LTU International Airways. The CARIBIC measurement programme includes aerosol elemental characterisation, particle number concentrations in three size channels and several trace gases (in situ O_3, CO and a large number of trace gases and their isotopic abundances from whole air samples). The aerosol sampling inlet is of diffuser-type with a compromise between a blunt and sharp sampling head, placed well outside the aircraft boundary layer. The true air-speed of the aircraft is 240 m/s and the sampling is close to isokinetic. The inlet efficiency was typically 90%, according to particle size-dependent wind tunnel characterisation of the inlet [*Hermann et al.*, 2000].

Here we concentrate on the sulphur results of the aerosol elemental concentration measurements. In order to meet the challenge of aircraft-based measurements in the very low aerosol mass concentration of the tropopause region, sampling and analyses were optimised with respect to detection capabilities [*Papaspiropoulos et at.*, 1999]. An aerosol sampler based on impaction technique was developed, which can take 14 sequential samples. The volume flow-rate in one impactor channel is 3.2 l/min at ambient conditions. The flow in the impactor nozzles is close to isentropic. The 50% cut-off diameter is estimated from impactor theory to be 0.07 μm (lower size limit of the sampling), whereas the upper 50% sampling limit is given by a cyclone and the inlet system and is about two micrometers [*Hermann et al.*, 2000].

Elemental analyses were made with PIXE (Particle-Induced X-ray Emission) [*Johansson and Campbell*, 1988] at the Lund tandem accelerator. PIXE is a multi-elemental method that is characterised by a very high absolute sensitivity. The PIXE detection limits were optimised with respect to the proton beam area, based on Scanning Transmission Ion Microscopy imaging of the aerosol deposit [*Papaspiropoulos et at.*, 1999]. The samples were collected on thin (0.1 μm), high-purity polyimide films (AP1™), which exhibit superior properties with respect to PIXE detection compared to traditional aerosol sampling substrates [*Papaspiropoulos et at.*, 1999]. The detection limit of sulphur for 2.5 h sampling was 3 ng/m^3 (3×10^{-9} g/m^3) STP.

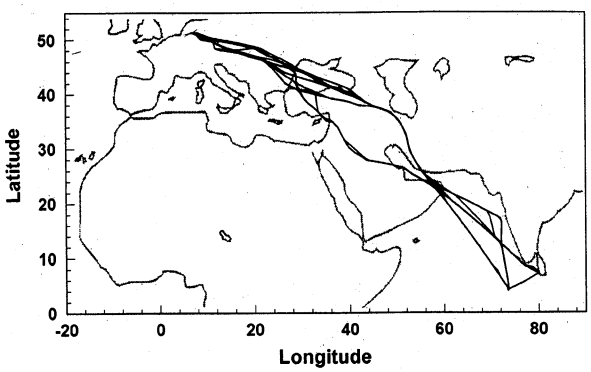

Figure 1. Map over southern Europe, northern Africa and western Asia. The black lines show the routes of the 21 measurement flights.

The sampling during each flight was started automatically as inlet pressure went below 350 hPa, corresponding to approximately 8000 m altitude, and continued until that pressure was exceeded before landing. The altitudes of all the samples were in the range 8800 - 11300 m. One sampling channel was used to collect a total sample during each flight with duration of typically 9 hours. An additional three to four samples, normally with the duration of 2.5 h, were taken sequentially during a flight to obtain geographically resolved elemental concentrations.

Results

Data have been collected from 21 flights. The routes are shown in fig. 1. Due to initial problems with the sample changing, only one sample was collected during each of the first two return flights. 19 samples are available that cover the entire distance of the 21 flights, which are all over approximately the same geographic region. The average particulate sulphur concentration was found to be 14±6.3 ng/m^3 STP. Assuming that all sulphur was in the chemical form of sulphate, which is the dominant sulphur species of the atmospheric aerosol, average sulphate concentration would be 42 ng/m^3. In table 1 it can be seen that the concentrations are generally found to be higher at remote sea level locations, reaching similar concentrations only in polar regions [*Cunningham and Zoller,* 1981; *Leck et al.,* 1996]. Observations at Tenerife [*Putaud et al.,* 2000], Tasmania [*Huebert et al.,* 1998] and the Azores [*Huebert et al.,* 1996] show a decrease with altitude of the sulphate concentration, which is in agreement with chemical transport models [*Rodhe,* 1999]. Earlier measurements [*Clarke,* 1993] of particle size distributions in the tropopause region over the Pacific resulted in a median particle volume concentration of 0.04 μm^3/cm^3 STP (corresponding to the mass concentration 40 ng/m^3 for the density 1 g/cm^3). Thus, the particle volume measurements resulted in concentrations of the same order as the present study, bearing in mind that the particles in addition to sulphate contain cations and other species such as mineral material, organics, soot and strongly bound water.

The measurements spanned latitudes between five and 50 degrees north. The geographically resolved samples were used to examine the latitudinal dependency of particulate sulphur concentration. The data set comprises 52 observations. In two of these observations the concentration was below the detection limit, in which case the concentration was estimated to be half the detection limit. The variability of the sulphur concentration was considerable (fig. 2), ranging from 62 ng/m^3 to below the detection limit of 3 ng/m^3. The long sampling time caused an average latitude span of 11 degrees (latitude dependent) over the measurement, as illustrated by the horizontal bars in fig. 2. Because of that overlap between the measurements, a binning technique was used to evaluate the latitudinal dependency. The influence of each measurement in a bin was estimated by the fraction of its latitude interval falling inside the latitude bin. The average particulate sulphur concentration as a function of latitude, as obtained by this binning technique, is shown in fig. 2. It is clear that sulphur concentrations increase steadily with latitude over the interval studied, increasing on average from 6.9 to 25 ng/m^3 from the lowest to the highest latitude.

Discussion

Sulphate largely is a secondary aerosol constituent forming mainly from precursor sulphur gases. Human activities have increased these emissions during the past century by about a factor of three compared to the global, natural emissions [*Langner et al.,* 1992]. These anthropogenic as well as naturally produced sulphur compounds are transported vertically and a fraction eventually reaches the tropopause region. The residence time of sulphate in the free troposphere is estimated to be a few weeks, which is long compared to the residence time in the planet boundary layer of 2 – 4 days [*Rodhe,* 1999]. As a result, the contribution from a source will be distributed over a larger area. The general circulation pattern of the atmosphere causes the transport in longitudinal direction to be significantly more efficient than the latitudinal transport. The main anthropogenic emissions are located around northern mid latitudes [*Langner et al.,* 1992]. The latitudinal dependency of aerosol sulphur that was observed in the tropopause region thus suggests a strong anthropogenic influence from the heavily industrialised areas of the northern hemisphere.

Previous studies [*Sheridan et al.,* 1994; *Ferry et al.,* 1999] indicate that sulphates are the dominating species of the aero-

Table 1. Mean Aerosol Sulphate Concentration at Various Remote Locations and Altitudes of the Atmosphere.

Location	Altitude (m)	No. Samples	Sulphate concentration (ng/m^3) STP
South Pole (winter) [a]	Sea level	49	87 [f]
South Pole (summer) [a]	Sea level	50	230 [f]
Arctic (summer) [b]	Sea level	59	53 [g]
Tenerife [c]	Sea level	18	320
Tasmania [d]	MBL [h]	90	300
Azores [e]	MBL [h]	27	1300
Tenerife [c]	2370	11	150
Azores [e]	FT [h]	23	420
Tasmania [d]	6000 [h]	40	210
This work	9800 [h]	19	42 [f]

[a] [*Cunningham and Zoller,* 1981]
[b] [*Leck et al.,* 1996]
[c] ACE-2 [*Putaud et al.,* 2000]
[d] ACE-1 [*Huebert et al.,* 1998]
[e] ASTEX/MAGE [*Huebert et al.,* 1996]
[f] Estimated from elemental sulphur (S) measurements by assumption that all S is sulphate.
[g] Median concentration.
[h] Aircraft-based measurements: MBL = marine boundary layer, FT = free troposphere.

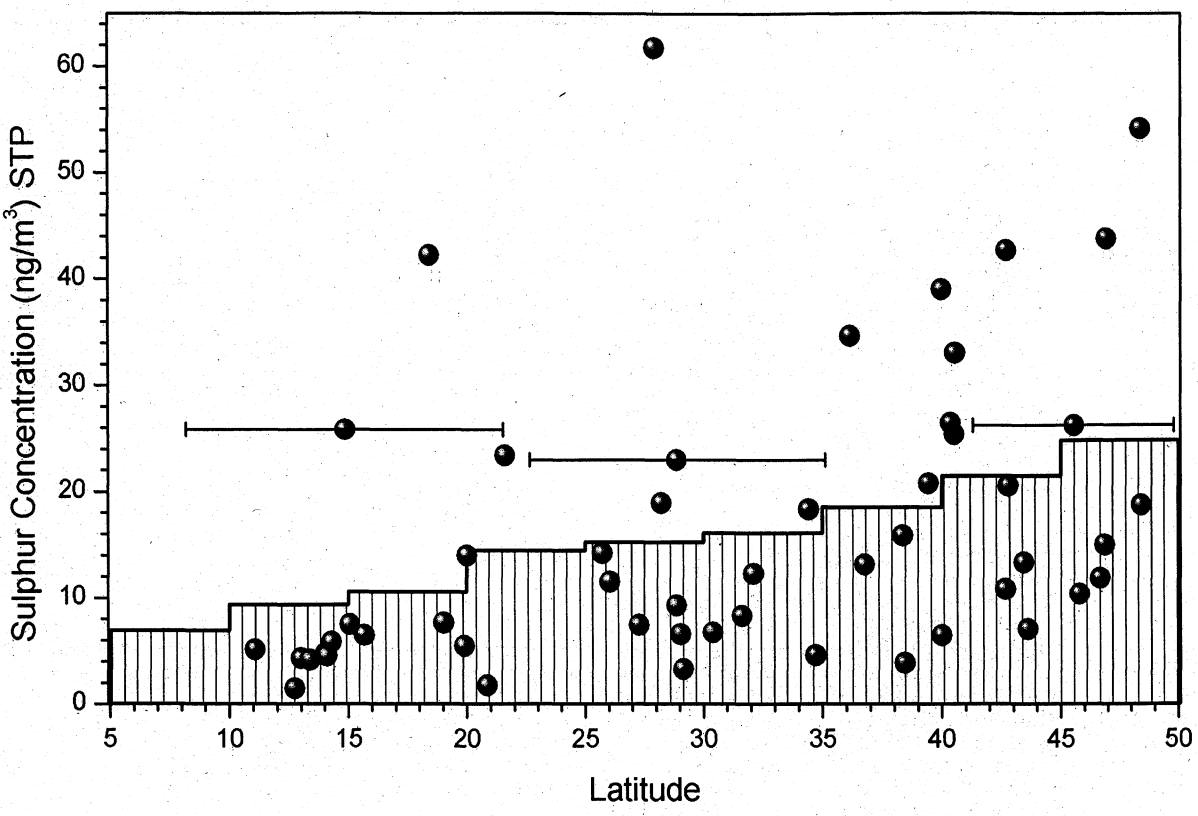

Figure 2. The particulate sulphur concentration as a function of latitude in the tropopause region. The symbols show the results of the measurements and the horizontal bars the average latitudinal interval covered by a sample in three latitude regions. The histogram shows the average particulate sulphate concentration as a function of latitude, obtained by a binning technique described in the text.

sol in the tropopause region. It has been established that increased aerosol concentration affects the microstructure and radiative properties of low-level clouds. A striking example was a pollution outbreak from Europe that was transported more than 1000 km over the ocean before a cloud was formed at Tenerife containing up to 3000 cloud droplets per cubic centimetre [*Martinsson et al.*, 2000], which is 10 times more than the typical concentration. Dry droplet residues smaller than 0.3 μm diameter have been found to dominate the droplet number concentration of cirrus clouds [*Ström et al.*, 1997]. The sulphur-containing particles primarily can be expected to supply cloud condensation nuclei (CCN). The role of CCN in glaciating clouds depends on the concentration of ice forming nuclei as well as the rate of air mass cooling, according to model studies (DeMott et al., 1997). At the low temperature of the tropopause region the CCN are likely to freeze homogeneously. This suggests that increased aerosol concentrations in the fine mode may affect the microstructure and radiative properties of cirrus clouds, similar to the low-level clouds. The strong latitudinal dependency of particulate sulphur thus indicates an important role of anthropogenic sulphate emissions by affecting the radiative properties of cirrus clouds and, hence, the climate.

Conclusions

Experimental observations of mass concentrations of aerosol constituents in the tropopause region are scarce. Particulate sulphur concentrations obtained from 21 intercontinental flights are reported here. The average sulphur concentration was found to be 14±6.3 ng/m^3 STP, which is low compared to remote locations at the surface. This is the first systematic study of particulate sulphur concentrations in the tropopause region. The results are important for the validation of the uncertain vertical transport parameterisations in chemical mass transport models [*Rasch et al., 2000*].

The latitude span of the measurements was five to 50 degrees north. A strong latitudinal dependency was observed, the particulate sulphur concentration being on average 4 times higher at the highest latitudes compared with the lowest. The main source regions of sulphur compounds are located at the heavily industrialised northern mid-latitudes. This suggests that the tropopause region is strongly influenced by anthropogenic emissions that have been transported up from surface sources. Its effect on cirrus cloud microstructure, as well as its radiative properties and interaction with emissions from the increasing air traffic, have the potential to induce significant disturbance to the climate that needs to be quantified.

Acknowledgements. The partners of the CARIBIC collaboration, besides the authors, are Max-Planck-Institute for Chemistry, Mainz, Germany (Project coordinators: P.J. Crutzen, C.A.M. Brenninkmeijer), Institute for Climate Research and Meteorology, Karlsruhe, Germany, Royal Netherlands Meteorological Institute, Utrecht, Netherlands, University of East Anglia, Norwich, UK and LTU International Airways, Düsseldorf, Germany. The work was supported financially by the European Union and the Swedish Environment Protection Agency by research grants ENV-CT95-0006 and 011-121-98-01.

References

Brasseur, G.P. et al., European scientific assessment of the atmospheric effects of aircraft emissions. *Atmos. Environ.* 32, 2329-2418, 1998.

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 tropospheric aerosol. *Science* 270, 1650-1653, 1995.

Charlson, R.J. et al., Climate forcing by anthropogenic aerosols. *Science* 255, 423-430, 1992.

Clarke, A.D., Atmospheric nuclei in the Pacific midtroposphere: Their nature, concentration and evolution. *J. Geophys. Res.* 98, 20633-20647, 1993.

Cunningham, W.C. and W.H. Zoller, The chemical composition of remote area aerosols. *J. Aerosol Sci.* 12, 367-384, 1981.

DeMott P.J., D.C. Rogers and S.M. Kreidenweis, The susceptibility of ice formation in upper tropospheric clouds to insoluble aerosol components. *J. Geophys. Res.* 102, 19575-19584, 1997

Ferry, G.V. et al., Effects of aircraft on aerosol abundance in the upper troposphere. *Geophys. Res. Lett.* 26, 2399-2402, 1999.

Hermann, M., F. Stratmann, M. Wilck, and A. Wiedensohler, Sampling characteristics of an aircraft-borne aerosol inlet system. *J. Atmos. Oceanic Technol.*, In press

Houghton, J.T. et al. (eds), *Climate change 1995: The science of climate change*. University Press, Cambrigde, 1996.

Huebert, B.J. et al. Filter and impactor measurements of anions and cations during the First Aerosol Characterisation Experiment (ACE-1). *J. Geophys. Res.* 103, 16493-16509, 1998.

Huebert, B.J., L. Zhuang, S. Howell, K. Noone, and B. Noone, Sulphate, nitrate, methanesulphonate, chloride, ammonium and sodium measurements from ship, island and aircraft during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol Gas Exchange. *J. Geophys. Res.* 101, 4413-4423, 1996.

Johansson, S.A.E. and J.L Campbell. *PIXE: A novel technique for elemental analysis*. John Wiley & Sons Ltd. Chichester, 1988.

Langner, J., H. Rodhe, P.J. Crutzen, and P. Zimmermann, Anthropogenic influence on the distribution of tropospheric sulphate aerosol. *Nature* 359, 712-716, 1992.

Leck, C. et al., Overview of the atmospheric research program during the international Arctic Ocean expedition of 1991 (IAOE-91) and its scientific results. *Tellus* 48B, 136-155, 1996.

Martinsson, B.G. et al., Validation of very high cloud droplet number concentrations in air masses transported thousands of kilometres over the ocean. *Tellus* 52B, 801-814, 2000.

Papaspiropoulos, G., B. Mentes, P. Kristiansson, and B.G. Martinsson, A high sensitivity elemental analysis methodology for upper tropospheric aerosol. *Nucl. Instr. And Meth.* B150, 356-362, 1999.

Penner, J.E. et al. (eds), *Aviation and the Global Atmosphere. A Special Report of IPCC Working Groups I and III.* University Press, Cambridge, 1999.

Putaud, J.-P. et al., Chemical mass closure and assessment of the origin of the submicron aerosol in the marine boundary layer and the free troposphere at Tenerife during ACE-2. *Tellus* 52B, 141-168, 2000.

Rasch P.J. et al., A comparison of scavenging and deposition processes in global models: results from the WCRP Cambridge workshop of 1995. *Tellus* 52B, 1025-1056, 2000.

Rodhe, H. Human impact on the atmospheric sulphur balance. Tellus 51A-B, 110-122, 1999.

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.

Ström, J. et al., In situ observations of the microphysical properties of young cirrus clouds. *J. Atmos. Sci.* 54, 2542-2553, 1997.

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

J. Heintzenberg and M. Hermann, Institute for Tropospheric Research, Permoserstrasse 15, D-04318 Leipzig, Germany. (e-mail: jost@tropos.de; hermann@tropos.de)

(Received August 25, 2000; revised January 10, 2001; accepted January 10, 2001)