

# East Asian SO<sub>2</sub> pollution plume over Europe – Part 1: Airborne trace gas measurements and source identification by particle dispersion model simulations

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**Abstract.** A large SO<sub>2</sub>-rich pollution plume of East Asian origin was detected by aircraft based CIMS (Chemical Ionization Mass Spectrometry) measurements at 3–7.5 km altitude over the North Atlantic. The measurements, which took place on 3 May 2006 aboard of the German research aircraft Falcon, were part of the INTEX-B (Intercontinental Chemical Transport Experiment-B) campaign. Additional trace gases (NO, NO<sub>y</sub>, CO, H<sub>2</sub>O) were measured and used for comparison and source identification. The atmospheric SO<sub>2</sub> mole fraction was markedly increased inside the plume and reached up to 900 pmol/mol. Accompanying lagrangian FLEXPART particle dispersion model simulations indicate that the probed pollution plume originated at low altitudes from densely populated and industrialized regions of East Asia, primarily China, about 8–12 days prior to the measurements.

## 1 Introduction

Atmospheric sulfur dioxide, SO<sub>2</sub>, represents a major air pollutant which has a profound impact on the environment. Its origin is mostly anthropogenic (almost 90% of the atmospheric SO<sub>2</sub> stems from fossil fuel combustion, the Ni-Cu smelting industry or anthropogenic biomass burning) and only to some small extent natural (less than 10% from volcanism and only a few percent from oxidation of other sul-

fur compounds such as dimethyl sulfide (DMS) or carbonyl sulfide (OCS)) (Seinfeld and Pandis, 2006). SO<sub>2</sub> undergoes atmospheric chemical OH-induced conversion to sulfate via gaseous sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, and thereby mediates formation of aerosol particles (e.g. Stockwell and Calvert, 1983; Reiner and Arnold, 1993, 1994; Laaksonen et al., 2000; Seinfeld and Pandis, 2006). H<sub>2</sub>SO<sub>4</sub> undergoes condensation on preexisting aerosol particles or nucleation leading to new and very small aerosol particles due to its very low equilibrium saturation vapor pressure (Brasseur et al., 1999; Seinfeld and Pandis, 2006). The new particles will then grow further up to CCN (cloud condensation nuclei) size, if more condensable gases are available. This favors the formation of clouds and impacts the cloud droplet sedimentation lifetime. In this way climate is affected (Ramanathan et al., 2001; Garrett et al., 2002; Harshvardhan et al., 2002; Andreae et al., 2005). Furthermore SO<sub>2</sub> is toxic and after conversion to sulfate it contributes to acid deposition polluting ecosystems (Rodhe et al., 2002; Huang et al., 2008). Sulfate itself also has a direct effect on the climate by intercepting incoming sunlight and producing a cooling in this way. Atmospheric SO<sub>2</sub> is removed by deposition at the planet's surface and by cloud processes. After dissolution in cloud droplets SO<sub>2</sub> may be washed out or rained out (Seinfeld and Pandis, 2006). However, recent model studies showed that most SO<sub>2</sub> will survive upward transport in clouds (Kreidenweis et al., 1997; Crutzen and Lawrence, 2000). In addition it may also undergo liquid-phase oxidation to condensed-phase sulfate which upon droplet water evaporation resides in the aerosol-phase (on average about 90% of all cloud droplets evaporate again). SO<sub>2</sub> removal by cloud processes is very



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complex. The fraction of SO<sub>2</sub> which is not removed by deposition or cloud processes may then undergo OH-induced gas-phase conversion to gaseous sulfuric acid. The SO<sub>2</sub> lifetime (1/e) with respect to gas-phase oxidation is about 7–14 days depending on atmospheric conditions (estimated on typical upper tropospheric OH concentrations (Logan et al., 1981)). Therefore, SO<sub>2</sub> which has experienced transport to the middle or upper troposphere, where deposition and cloud processes are less efficient and where wind velocities are high, may be transported over large horizontal distances of thousands of kilometers. Hence, it may reach remote and relatively pristine regions free of strong local SO<sub>2</sub> sources. Here it may mediate aerosol formation and contribute to acidification (Rodhe et al., 2002).

Pollution transport the whole way from Asia to Europe from west to east has rarely been measured so far. Examples of intercontinental transport of air pollutants were published by e.g. Jaffe et al. (1999); Cooper et al. (2004); Nowak et al. (2004); Parrish et al. (2004) for intercontinental pollution transport from Asia to North America and by e.g. Arnold et al. (1997); Stohl and Trickl (1999); Stohl et al. (2003); Huntrieser et al. (2005) for transport from North America to Europe.

Pollution from Asia is mainly lifted to the upper troposphere in so-called warm conveyor belts at the eastern seaboard of Asia and subsequently transported by fast air streams in the middle and upper troposphere (Stohl, 2004). Another transport path is the lifting by deep convection in thunderstorms and mesoscale convective systems mainly in summer (Wild and Akimoto, 2001). The most probable lifting process discussed in the present paper is the lifting in a warm conveyor belt. Recently, transport of the pollution tracers CO, NO<sub>y</sub> and O<sub>3</sub> from Asia to Europe was described by Stohl et al. (2007). Arnold et al. (1997) presented a striking example of a SO<sub>2</sub> pollution plume with a maximum mole fraction of 3 nmol/mol detected off the Irish North West coast. Based on trajectory analyses this pollution originated in North East America and traveled about 10 000 km within 5 days.

The present paper will focus on an East Asian SO<sub>2</sub> pollution plume detected off the Irish west coast with maximum SO<sub>2</sub> mole fractions of 0.9 nmol/mol which had traveled the even longer distance of about 20 000 km within 10 days.

Section 2 of this paper describes the methodology and measurement methods that were applied. Section 3 presents the actual measurements of SO<sub>2</sub> in the light of other simultaneously measured trace gases. In Sect. 4 the results of Lagrangian particle dispersion model analyses for the SO<sub>2</sub> pollution source identification are presented and the results are discussed.

## 2 Methodology

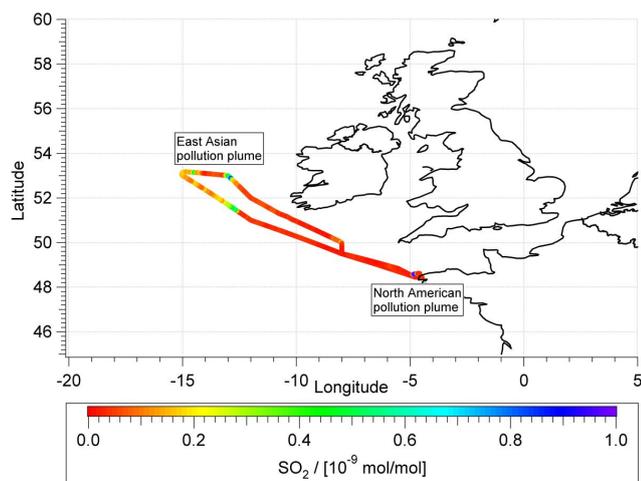
### 2.1 Trace gas measurements

The SO<sub>2</sub> measurement method employed is chemical ionization mass spectrometry (CIMS) with continuous in-flight calibration using isotopically labeled SO<sub>2</sub>. The CIMS-instrument which has been developed by MPI-K (Max-Planck-Institute for Nuclear Physics, Heidelberg) in collaboration with DLR (Deutsches Zentrum für Luft und Raumfahrt, Oberpfaffenhofen) is equipped with an ion trap mass spectrometer. A comprehensive description of the measurement system can be found in Speidel et al. (2007). The method is based on the chemical reaction of CO<sub>3</sub><sup>-</sup> reagent ions with atmospheric SO<sub>2</sub> leading to SO<sub>3</sub><sup>-</sup> ions which in turn react with O<sub>2</sub> leading to SO<sub>5</sub><sup>-</sup>. By measuring the abundance ratio of product and reagent ions with the ion trap mass spectrometer, the SO<sub>2</sub> abundance can be determined. The SO<sub>2</sub> measurements have a time resolution of 1 s and a detection limit (2 sigma level) of about 20 pmol/mol. The relative error is ±12% for SO<sub>2</sub> mole fractions larger than 100 pmol/mol and increases close to the detection limit to ±25% (Speidel et al., 2007).

Simultaneous measurements of other trace gases (CO, NO, NO<sub>y</sub>, H<sub>2</sub>O, O<sub>3</sub>) were carried out on the Falcon by DLR. CO was detected using vacuum resonance fluorescence in the fourth positive band of CO (Gerbig et al., 1999). The accuracy of the CO measurements is ±10% for a time resolution of 5 s. NO (nitric oxide) and NO<sub>y</sub> (sum of reactive nitrogen compounds) was measured using a chemiluminescence technique (Schlager et al., 1997; Ziereis et al., 2000). The NO<sub>y</sub> compounds are catalytically reduced to NO on the surface of a heated gold converter with addition of CO. The accuracy of the NO and NO<sub>y</sub> measurements is ±8% and ±15%, respectively. The time resolution is 1 s. Ozone (O<sub>3</sub>) was measured using an UV absorption photometer (Schlager et al., 1997; Schulte et al., 1997). The accuracy of the ozone detection is ±5%, the detection limit is 1 nmol/mol and the time resolution 4 s.

### 2.2 FLEXPART

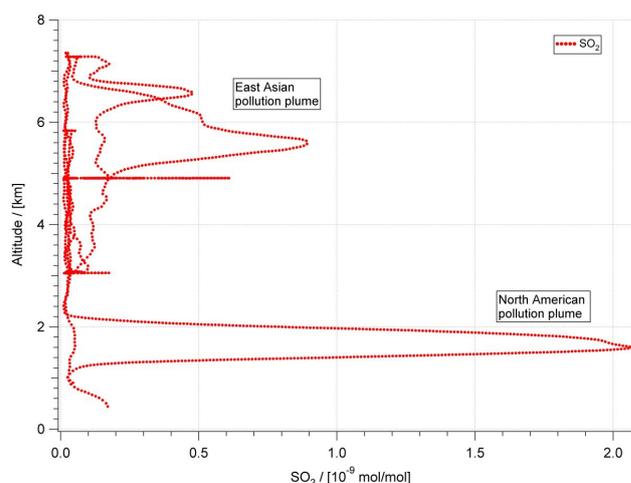
To explore the sources of the observed SO<sub>2</sub> enhancements, the Lagrangian particle dispersion model FLEXPART (Stohl et al., 1998; Stohl and Thomson, 1999; Stohl et al., 2005) was used. FLEXPART simulates the transport and dispersion of linear tracers by calculating the trajectories of a multitude of particles. Particles are transported in the model both by the resolved winds and by parameterized sub-grid motions. FLEXPART parameterizes turbulence in the boundary layer and in the free troposphere by solving Langevin equations (Stohl and Thomson, 1999) and convection by using the parametrization scheme of Emanuel and Živkovic Rothman (1999). The model was driven by global model-level data from the ECMWF (European Center for Medium-Range



**Fig. 1.** Flight path of flight 20060503 color coded with the measured SO<sub>2</sub> mole fraction.

Weather Forecasts) with a temporal resolution of 3 h (analyses at 00:00, 06:00, 12:00, 18:00 UTC; 3-h forecasts at 03:00, 09:00, 15:00, 21:00 UTC), a horizontal resolution of  $1^\circ \times 1^\circ$ , and 91 vertical levels. Over North America, the North Atlantic and Europe, nested input data with a resolution of  $0.36^\circ \times 0.36^\circ$  were used. Alternative simulations were also made with input data from the National Center for Environmental Prediction's (NCEP) Global Forecast System (GFS). For the case discussed here, simulations using the GFS data were consistent with those using ECMWF data and are, therefore, not shown.

FLEXPART can be run both forward and backward in time. For the forward simulations, particles were released in proportion to the SO<sub>2</sub> emissions from the EDGAR (Emission Database for Global Atmospheric Research) emission inventory for the year 2000 (EDGAR version 3.2 FT2000) (Olivier and Berdowski, 2001), with diurnal and weekly emission cycles superimposed. For each flight a few hundred backward simulations were made for small segments along the flight track. For each such segment, 40 000 particles were released and followed backward in time for 20 days, forming what we call a retriplume, to calculate a so-called potential emission sensitivity (PES) function, as described by Seibert and Frank (2004) and Stohl et al. (2003). The word “potential” here indicates that this sensitivity is based on transport alone, ignoring removal processes that would reduce the sensitivity. The value of the PES function (in units of  $\text{s kg}^{-1}$ ) in a particular grid cell is proportional to the particle residence time in that cell. It is a measure for the simulated mixing ratio at the receptor that a source of unit strength ( $1 \text{ kg s}^{-1}$ ) in the respective grid cell would produce. We report the PES function both integrated over the entire atmospheric column (column residence time plot) and for a so-called footprint layer close to the ground (lowest 100 m above ground level),



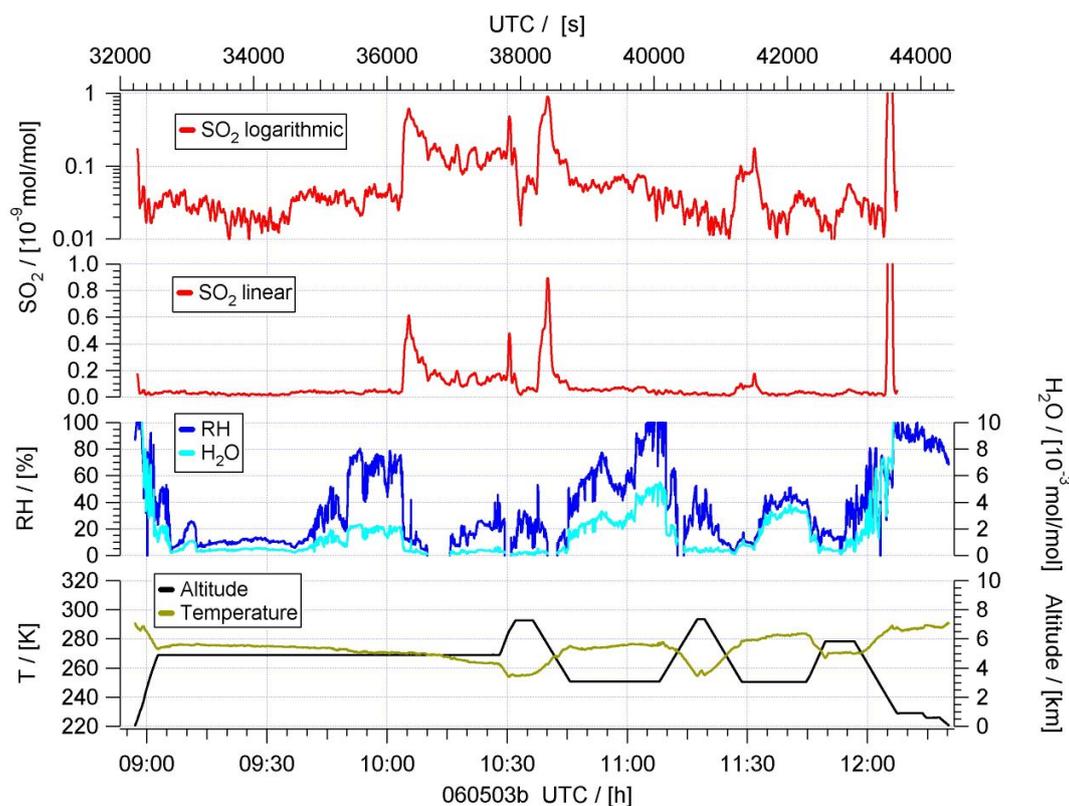
**Fig. 2.** SO<sub>2</sub> mole fraction altitude profile of flight 20060503, smoothed with a running mean over 30 data points.

as anthropogenic emissions occur mostly at or near the surface. Folding (i.e., multiplying) the PES footprint with the SO<sub>2</sub> emission flux densities (in units of  $\text{kg m}^{-2} \text{s}^{-1}$ ) from the EDGAR inventory yields a so-called potential source contribution (PSC) map, that is the geographical distribution of sources contributing to the simulated mixing ratio at the receptor. Spatial integration of the PSC map finally gives the simulated mixing ratio at the receptor.

Note that FLEXPART as used here does not consider chemical conversions or removal processes. Since in reality, SO<sub>2</sub> is subject to removal processes (deposition, cloud processes, photochemical conversion in the gas-phase), observed SO<sub>2</sub> concentrations should always be lower than simulated values both in the forward and in the backward simulations. This makes it difficult to compare model simulations and observations directly. However, the model still helps to reconstruct the plume trajectory and to identify potential source regions of the plume SO<sub>2</sub>.

### 3 Measurements

The measurement flight of the DLR research aircraft Falcon started from Brest in Northern France around 09:00 UTC on 3 May 2006 and was part of the INTEX-B (Intercontinental Chemical Transport Experiment-B) campaign, which is described in detail in the overview paper by Singh et al. (2009). Our measurements took place over the Atlantic Ocean south and west of Ireland. The flight path of the Falcon is depicted in Fig. 1, color coded with the measured SO<sub>2</sub> mole fraction. The objective was to find and to probe an Asian pollution plume, which had been predicted by FLEXPART. The FLEXPART forecasts distinguished between expected transport of pollution from Asian, American or European sources,



**Fig. 3.** Time sequence of atmospheric SO<sub>2</sub> mole fraction (linear and logarithmic representation) measured aboard the Falcon during flight 20060503. Also given are flight altitude, temperature, relative humidity and water vapor mixing ratio.

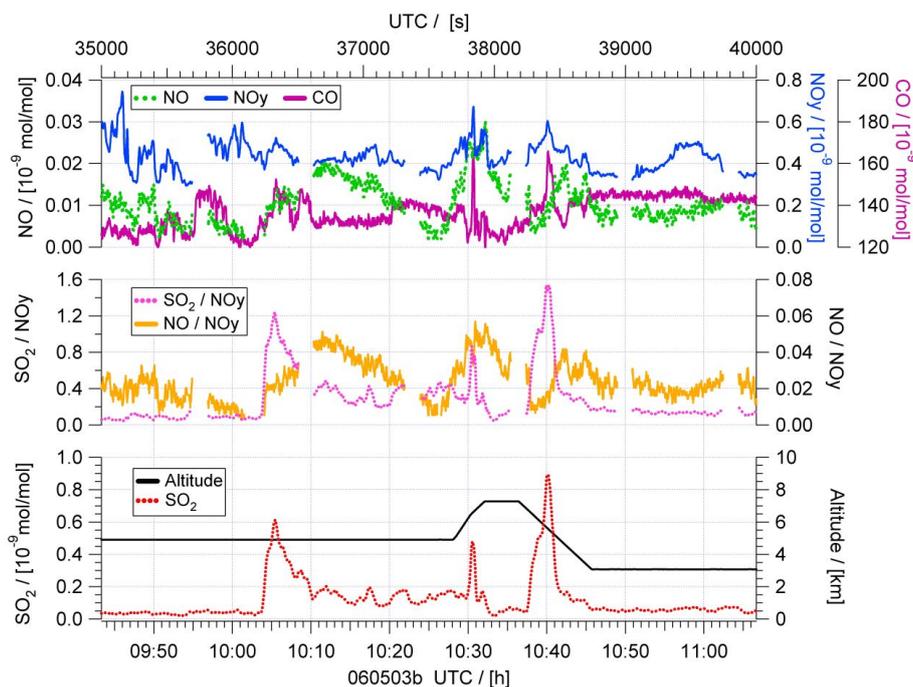
which made a determined search for Asian pollution possible. As can be seen from the color code, two main SO<sub>2</sub> plumes have been detected, according to FLEXPART one of North American origin and one of East Asian origin.

Figure 2 shows the vertical SO<sub>2</sub> mole fraction, smoothed with a running mean over 30 data points. During the flight the Falcon reached a maximum altitude of 7.5 km. Here also the two major SO<sub>2</sub>-rich pollution plumes can be distinguished. One with a peak SO<sub>2</sub> mole fraction of 2000 pmol/mol at 1.6 km and one with a peak SO<sub>2</sub> mole fraction of 900 pmol/mol at 5.6 km. The plumes had entirely different origins. According to FLEXPART, the plume at 1.6 km stemmed from North Atlantic shipping or the USA. This plume will not be further discussed in this paper. The plume at 5.6 km stemmed mainly from East Asia and therefore will be termed the East Asian plume. This paper will focus on the East Asian plume.

Figure 3 presents a time series of SO<sub>2</sub> and meteorological data obtained during the entire flight. The marked SO<sub>2</sub> enhancement with East Asian origin has been detected between 10:05 and 10:50 UTC in a relatively dry air mass (relative humidity 20%, water vapor mixing ratio 200 μmol/mol), whereas the relative humidity before and after the interception of this SO<sub>2</sub>-rich air mass exceeds 60% (water vapor

mixing ratio 2000 μmol/mol). In the pollution plume, the SO<sub>2</sub> mole fraction is generally elevated (150 pmol/mol background) with peak values from 500–900 pmol/mol.

Figure 4 shows the section between 09:50 UTC and 11:00 UTC of the flight in detail. The mole fractions of CO, NO and NO<sub>y</sub> are plotted additionally to SO<sub>2</sub> as well as the molar ratios SO<sub>2</sub>/NO<sub>y</sub> and NO/NO<sub>y</sub>. The SO<sub>2</sub> peaks are accompanied by peaks in NO<sub>y</sub> and CO, but those peaks are less pronounced. The trace gas mole fractions and relative humidity inside the plume as well as the corresponding values of the background atmosphere on that day are listed in Table 1. The NO/NO<sub>y</sub> ratio is quite low (<0.06 mol/mol). For fresh emissions, when no chemical transformation has occurred yet, almost all NO<sub>y</sub> exists in form of NO and the NO/NO<sub>y</sub> ratio is close to one. In this flight the ratio never exceeds 0.06, which means that the originally emitted NO has almost completely been converted to NO<sub>2</sub> and ultimately to PAN and HNO<sub>3</sub>. This is an indication that the pollution plume had experienced substantial aging. However, the individual mole fractions of both NO and NO<sub>y</sub> are quite low (<0.03 nmol/mol, <0.6 nmol/mol) compared to typical middle tropospheric values, which may reach up to several nmol/mol in more freshly polluted air masses.



**Fig. 4.** Trace gases and molar ratios between 09:50 and 11:00 UTC of flight 20060503. The upper panel shows mole fractions of NO, NO<sub>y</sub> and CO, the middle panel molar ratios SO<sub>2</sub>/NO<sub>y</sub> and NO/NO<sub>y</sub> and the lower panel SO<sub>2</sub> mole fraction and flight altitude.

**Table 1.** Measured maximum trace gas concentrations and relative humidity inside the East Asian plume and for comparison the corresponding values of the background atmosphere.

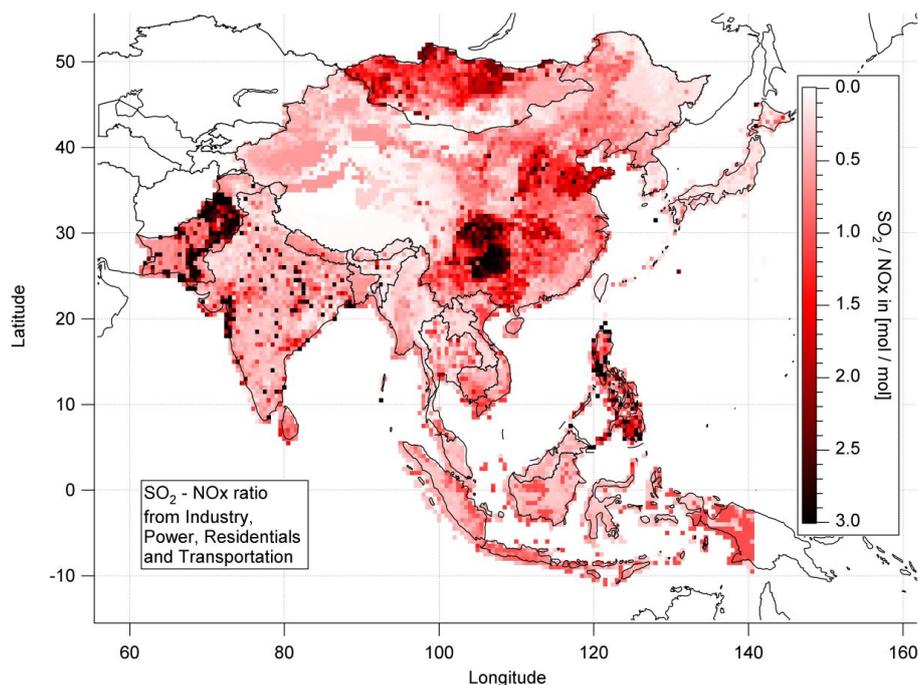
	SO <sub>2</sub> [ppbv]	NO [ppbv]	NO <sub>y</sub> [ppbv]	CO [ppbv]	H <sub>2</sub> O [ppmv]	RH [%]
Maximum	0.9	0.01	0.6	165	200	20
Background	0.02	0.006	0.3	120	500	10

The SO<sub>2</sub>/NO<sub>y</sub> ratio (up to 1.4 mol/mol) suggests combustion of coal or oil as the source. Typical fresh combustion emission ratios of SO<sub>2</sub>/NO<sub>x</sub> range from 0.1 to 5 mol/mol depending on the source type (see Table 2). Figure 5 shows typical molar emission ratios for SO<sub>2</sub>/NO<sub>x</sub> in Asia for the year 2006 and Table 2 lists the same but split into four different source types. The data stem from an emission inventory prepared for the INTEX-B campaign by D. G. Streets and Q. Zhang (Zhang et al., 2009). The data can be accessed at the web site <http://mic.greenresource.cn/intex-b2006>. Especially heavily industrialized areas as e.g. Chongqing and Chendu in central China, the Mongolian region around Ulan Bator or the belt of major cities in Pakistan are clearly visible in Fig. 5. For comparison, Table 2 also lists typical SO<sub>2</sub>/NO<sub>x</sub> ratios for different regions of the world. The values are adopted from the EDGAR inventory of the year 2000 (Olivier et al., 1996; Olivier and Berdowski, 2001). Interestingly, the emission ratios are highest for China and Korea.

**Table 2.** Molar SO<sub>2</sub>/NO<sub>x</sub> emission ratios for four different source types in the East Asian source region for the year 2006 (INTEX-B emission inventory, Zhang et al., 2009). For comparison similar values for other regions adopted from the EDGAR inventory of the year 2000 (Olivier et al., 1996; Olivier and Berdowski, 2001).

INTEX-B East Asia 2006					
	Power	Industry	Residential	Transportation	
SO <sub>2</sub> /NO <sub>x</sub> [mol/mol]	1–3	1–5	2–5	<0.1	
EDGAR inventory 2000					
	USA	Germany	Australia	Russia	India
SO <sub>2</sub> /NO <sub>x</sub> [mol/mol]	0.7	0.9	0.6	1.2	0.9
	China	Japan	Korea	Africa	Brazil
SO <sub>2</sub> /NO <sub>x</sub> [mol/mol]	1.8	0.6	1.4	0.1	0.3

The SO<sub>2</sub>/NO<sub>y</sub> ratio will change during transport due to different chemical conversions of SO<sub>2</sub>, NO<sub>x</sub> and NO<sub>y</sub>. Generally, one can expect that the SO<sub>2</sub>/NO<sub>y</sub> ratio is lowered during plume aging, as SO<sub>2</sub> will be removed by OH reactions in clear sky conditions as well as by wet cloud processes



**Fig. 5.** SO<sub>2</sub>/NO<sub>x</sub> molar emission ratios in Asia 2006 (INTEX-B inventory by D. G. Streets and Q. Zhang (Zhang et al., 2009)).

whereas NO<sub>x</sub> is in first approximation completely converted to NO<sub>y</sub>, whose HNO<sub>3</sub> component may also experience loss by wet cloud processes. The washout coefficient of SO<sub>2</sub> by rain is  $2.6 \times 10^{-5} \text{ s}^{-1}$  times the rate of rainfall (mm/h) (Martin, 1984). HNO<sub>3</sub> on the contrary will be completely removed by rain. Another possible removal mechanism is SO<sub>2</sub> and HNO<sub>3</sub> deposition already before lift to the upper troposphere. The low relative humidity inside the plume (20%) may be an indication that the plume experienced cloud element precipitation. If so, this may imply that in reality HNO<sub>3</sub> and also SO<sub>2</sub> experienced loss.

By contrast to SO<sub>2</sub>, the highly soluble gas-phase sulfuric acid and sulfuric acid aerosols may experience very efficient removal by cloud-processes. Therefore, after transport of a fossil fuel combustion plume through the precipitation formation region of an active cyclone, one may expect, in the very early outflow of the cyclonic system, low concentrations of sulfate aerosols but appreciable mole fractions of SO<sub>2</sub> and large mole fractions of NO<sub>y</sub> (mostly peroxyacetyl-nitrate). Support for this view was previously obtained from airborne measurements of SO<sub>2</sub> made over North East China in the early outflow of a cyclone (Ding et al., 2009). At an altitude of about 2600 m, close to the border of China and North Korea, SO<sub>2</sub> mole fractions of up to 14.6 nmol/mol were detected.

It seems that during ascent or lifting a large fraction of the SO<sub>2</sub> escapes from scavenging by cloud processes. This is consistent with the previous investigations by Ding et al.

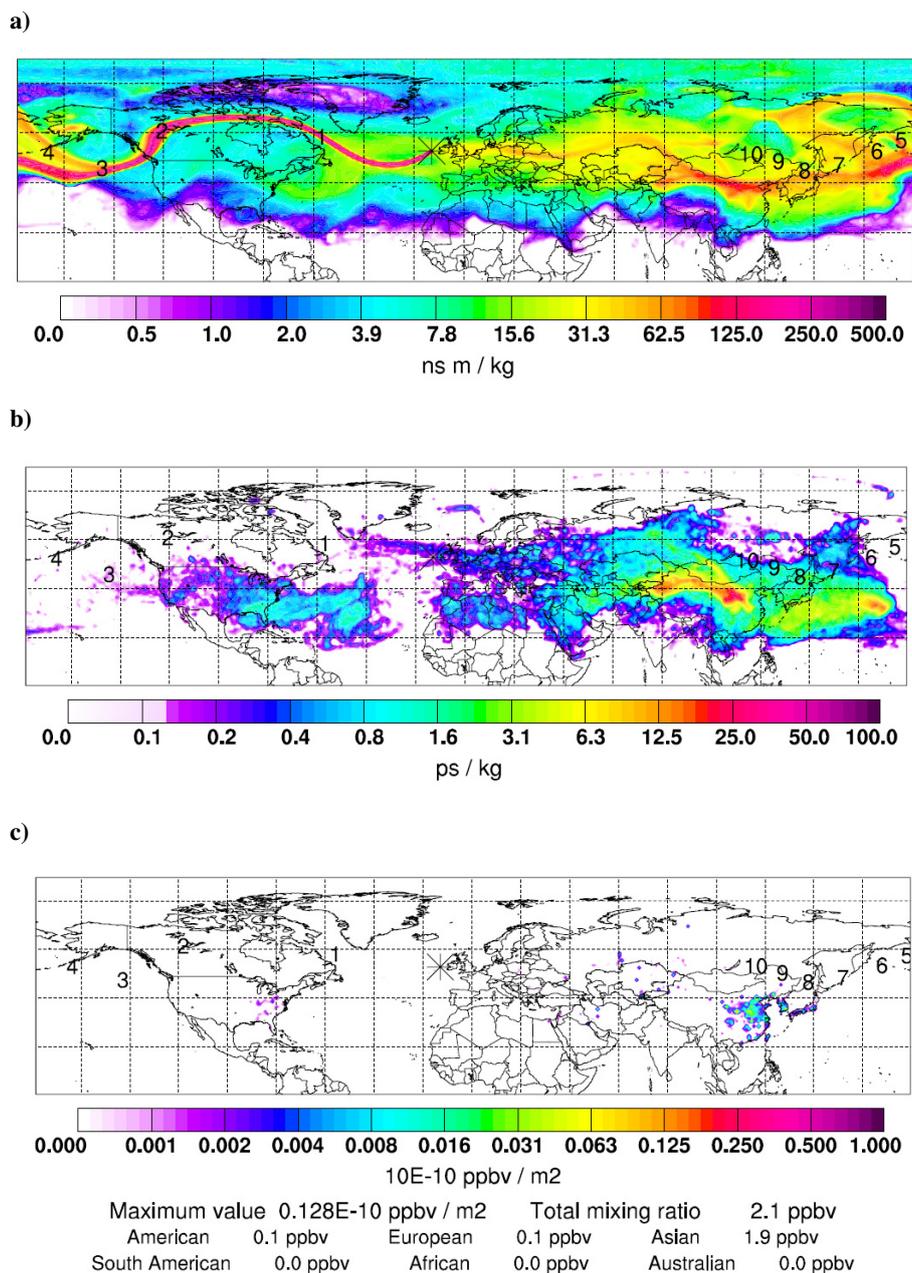
(2009), which suggested that ascent of a pollution plume in a warm conveyor belt may remove relatively little SO<sub>2</sub> but a large fraction of aerosols.

#### 4 Discussion

In order to identify the possible origin of the pollution plume, FLEXPART model simulations have been employed. Thereby it has to be kept in mind that FLEXPART can predict relatively well the position of SO<sub>2</sub> enhancements, but the predicted concentrations at the measurement site are usually too high, as no chemical SO<sub>2</sub> removal during transportation is considered (see above).

Several different FLEXPART products and corresponding graphical representations of the model have been used in this analysis: SO<sub>2</sub> forward calculations as well as backward calculations of column residence time, footprint and source contribution. These FLEXPART products have always been calculated for the highest SO<sub>2</sub> peak, detected at 10:40 UTC.

The column residence time in Fig. 6a shows the vertically integrated residence time of the particles for the air mass with the highest SO<sub>2</sub> signature intercepted by the Falcon at 10:40 UTC. Briefly, this column residence time can also be thought of as the approximate probability that an air parcel reached the measurement location. The numbers superimposed on the shading are the days back in time. This product indicates where the air came from (but without altitude information). The figure suggests that the probed air mass



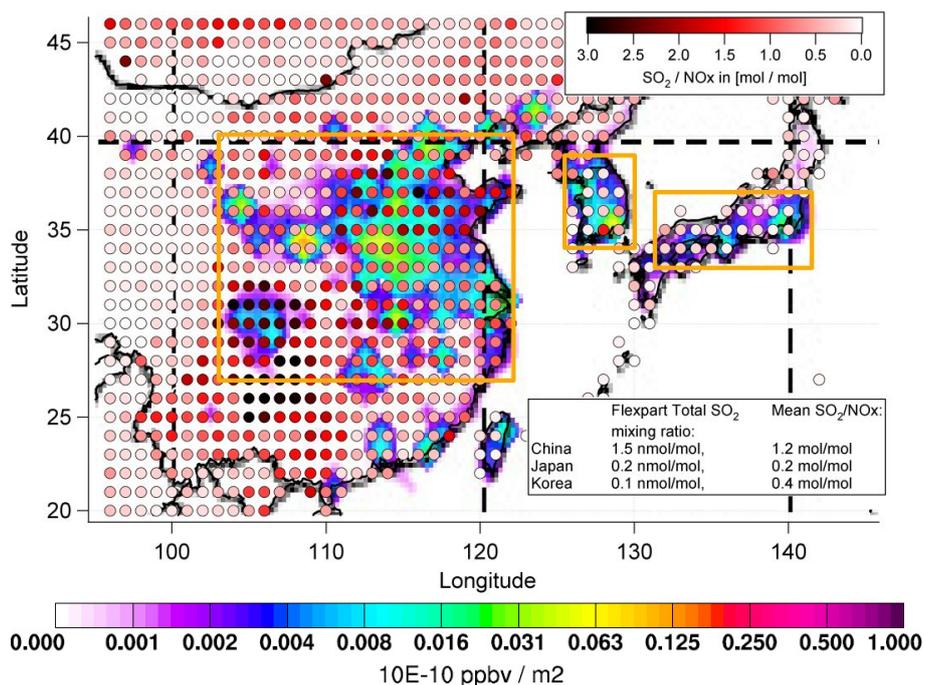
**Fig. 6.** (a) FLEXPART column residence time for the air mass arriving at 10:40 UTC at the measurement site, i.e. the point in time with the highest measured SO<sub>2</sub> mole fraction. The column residence time gives the probability to reach the measurement site for a certain air mass parcel as color code. (b) FLEXPART footprint for the same time. The footprint gives an impression, where the air mass touched the ground and where it most likely took up anthropogenic emissions. (c) FLEXPART SO<sub>2</sub> source contribution for the same time. The numbers superimposed on the shading in all three figures are the days back in time. (ppbv=parts per billion by volume=nmol/mol).

originated 8–10 days prior to the measurements primarily from a region in East Asia.

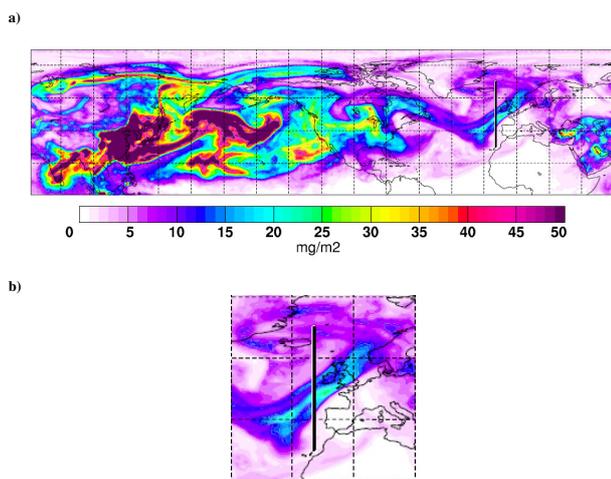
Figure 6b is the so-called footprint emission sensitivity, also for the SO<sub>2</sub> peak at 10:40 UTC. It is actually the same as the column residence time, but summed over the lowest 100 m above ground. As anthropogenic emissions are mostly

released at the surface, this gives an indication where the air mass passed over ground and therefore where emissions were likely taken up. In fact that took place mainly in China.

This is confirmed by another FLEXPART product, the so-called SO<sub>2</sub> source contribution graph. Figure 6c shows the SO<sub>2</sub> source contribution to the measurements at 10:40 UTC.



**Fig. 7.** In the background a zoomed view of the East Asian section of the FLEXPART source contribution map (see Fig. 6c), which is the region with the highest SO<sub>2</sub> source contribution signatures, is plotted (ppbv=parts per billion by volume=nmol/mol). The color coded circles in the foreground represent SO<sub>2</sub>/NO<sub>x</sub> molar emission ratios from the INTEX-B emission inventory (see Fig. 5). The orange boxes mark the three main source regions China, Korea, Japan, for which total Flexpart SO<sub>2</sub> mixing ratios and mean molar ratios SO<sub>2</sub>/NO<sub>x</sub> are also given in the textbox.



**Fig. 8.** (a) Horizontal distribution of the FLEXPART vertical forward column density of SO<sub>2</sub> (mg/m<sup>2</sup>) released from Chinese sources (mean value on 3 May 2006 from 09:00 to 12:00 UTC). Here SO<sub>2</sub> is treated as an inert tracer. The black vertical line marks the approximate location of the plume interception by the Falcon. (b) Zoomed view of the interception area.

The SO<sub>2</sub> source contribution figure also suggests that the SO<sub>2</sub> pollution plume stemmed mostly from East Asia. This FLEXPART product also provides SO<sub>2</sub> mole fractions in ppbv (nmol/mol) split into the different source regions. The total mixing ratio indicated in this figure is 2.1 nmol/mol, which is composed of 1.9 nmol/mol Asian SO<sub>2</sub>, and both 0.1 nmol/mol European and American SO<sub>2</sub>. Consequently, FLEXPART indicates that more than 90% of the measured SO<sub>2</sub> is of Asian origin, 5% is of European origin and 5% of American origin.

Figure 7 depicts a combination of the FLEXPART source contribution map (only the North East Asian section) with the fresh SO<sub>2</sub>/NO<sub>x</sub> emission ratio. The SO<sub>2</sub>/NO<sub>x</sub> ratio is plotted as color coded circles in the foreground. Three sectors can be defined where the sampled air came from: China, Korea and Japan. The Flexpart total emissions are 1.5 nmol/mol, 0.1 nmol/mol and 0.2 nmol/mol, respectively. If we compare these values with the total mixing ratio indicated in Fig. 6c (2.1 nmol/mol), it follows that 71% of the plume were of Chinese, 10% of Japanese and 5% of Korean origin. In China mostly air masses with SO<sub>2</sub>/NO<sub>x</sub> ratios between 1 and 3 mol/mol at the starting point have contributed to the detected plume, the mean molar SO<sub>2</sub>/NO<sub>x</sub> emission ratio there is 1.2 mol/mol. For Korea and Japan the mean molar emission ratio is 0.4 mol/mol and 0.2 mol/mol respectively.

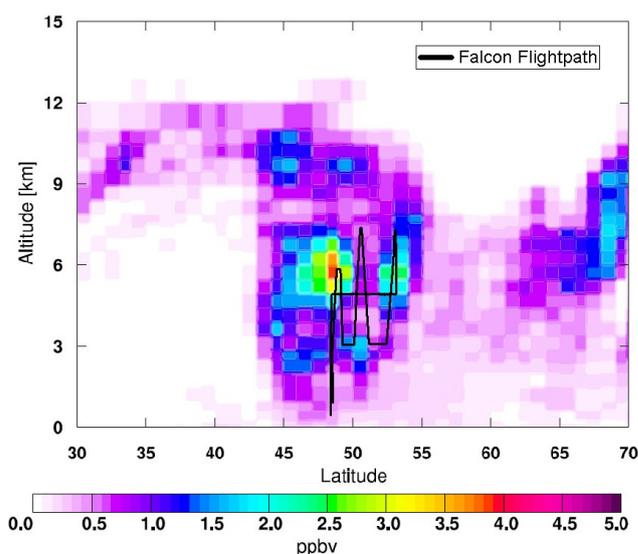
The measured molar ratio SO<sub>2</sub>/NO<sub>y</sub> in the plume off the Irish West coast ranges mostly from 1.2 to 1.4 mol/mol. This is consistent to the most probable Chinese emission sources, but the SO<sub>2</sub>/NO<sub>y</sub> ratio changed most probably largely during transport (view previous paragraph) so that it cannot be compared to the molar emission ratio.

The transport of the polluted air mass most likely occurred in the following way: an analysis of satellite pictures suggests a lifting of the polluted air mass in a cyclone on the East Chinese border on 25 April 2006, which moved further to the ocean south east from Japan on 26–27 April. Convection in the cold air over China on 25 April is less probable and could also not explain the Japanese source contribution. The most probable scenario therefore is the lifting in the warm conveyor belt over China on 25–26 April and later also over Japan.

After having identified East Asia as the preferred source of the 5600 m plume, we have carried out FLEXPART simulations of the geographical distribution of SO<sub>2</sub> of East Asian origin.

Figure 8a shows the geographical distribution (mean value for 3 May 2006 from 09:00 to 12:00 UTC) of vertical column densities of SO<sub>2</sub> emitted from Chinese sources (forward simulation). The FLEXPART model reveals that if this SO<sub>2</sub> behaved like an inert tracer it would be distributed over a large part of the Northern Hemisphere and that one filament would reach the west coast of Europe (zoomed view of this filament in Fig. 8b). The black vertical line in both figures marks the longitude value (12.5°) for the SO<sub>2</sub> vertical latitudinal cross section (see Fig. 9). This line also marks the approximate interception of the plume by the Falcon, but it is not the actual flight path.

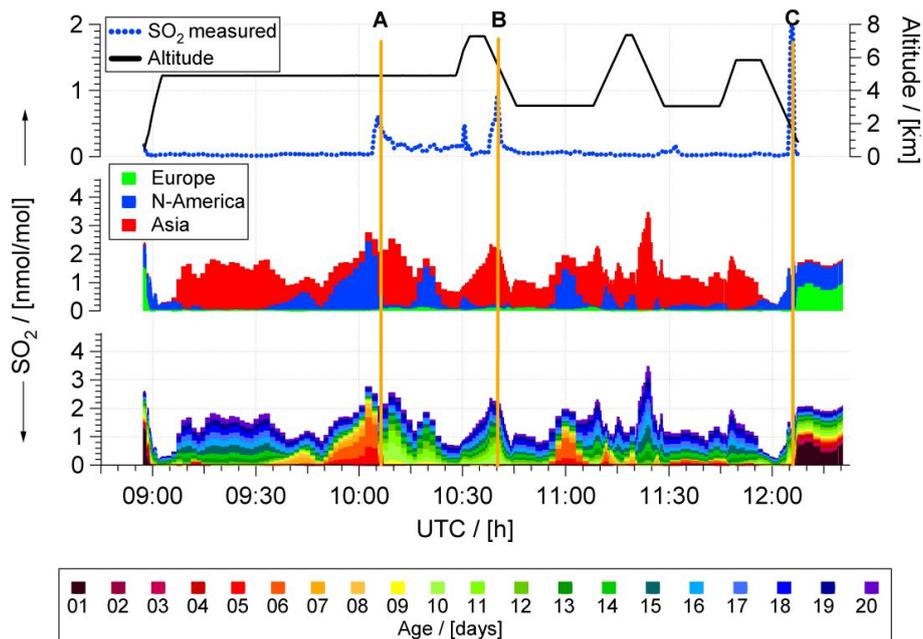
Figure 9 shows for 3 May 2006 (mean value between 09:00 and 12:00 UTC) the altitude-latitude cross section of the atmospheric SO<sub>2</sub> mole fraction at a longitude of 12.5°, the area of plume interception by the Falcon. Here, the Falcon flight path is indicated by a black line, but it has to be taken into account that the Falcon also slightly changed its longitudinal position. The highest SO<sub>2</sub> peaks were detected at the longitude of 12.5°, which was the case for the right-most leg of the flight path indicated in Fig. 9. As can be seen, the Falcon there intercepted air masses with predicted SO<sub>2</sub> mole fractions of up to 2.5 nmol/mol. In comparison, the measured maximum SO<sub>2</sub> mole fraction was 0.9 nmol/mol. This SO<sub>2</sub> deficit is mostly due to the chemical gas phase conversion of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> by OH radicals. In clear sky conditions and with a typical upper tropospheric OH concentration of 1 × 10<sup>6</sup> cm<sup>-3</sup> (Logan et al., 1981), the SO<sub>2</sub> 1/e lifetime is about 10 days. So after 10 days transport in the upper troposphere a SO<sub>2</sub> mole fraction of 2.5 nmol/mol will be reduced to 0.91 nmol/mol without plume dilution, which fits well to our measurements (see also part 2 of this paper, Fiedler et al., 2009). Hence it seems that most SO<sub>2</sub> loss was due to OH-induced gas-phase conversion. If so, this would



**Fig. 9.** FLEXPART vertical distribution of the SO<sub>2</sub> mole fraction at 12.5 degrees Longitude (mean value on 3 May 2006 from 09:00 to 12:00 UTC, ppbv=parts per billion by volume=nmol/mol). Only SO<sub>2</sub> is considered which has been released from Chinese sources. Also given is the vertical footprint of the Falcon flight path (black line).

imply that most SO<sub>2</sub> survived the vertical transport over East Asia.

Figure 10 shows again the time sequence of the SO<sub>2</sub> mole fraction measured during the flight in its top panel (blue dotted line). The middle panel of this figure shows a time sequence of the SO<sub>2</sub> mole fraction predicted by FLEXPART split into SO<sub>2</sub> originating from different continents interpolated on the given flight track. The bottom panel shows the FLEXPART SO<sub>2</sub> age spectrum, i.e. the contribution of air masses with different ages to the total SO<sub>2</sub>. The color code indicates the age. The 3 main SO<sub>2</sub> plumes observed in the measurements (A, B, C) are marked by vertical lines. The times of interception of plumes A and B are approximately predicted by FLEXPART but the mole fractions are markedly overestimated. This overestimation is due to the neglect of SO<sub>2</sub> loss processes by FLEXPART (see above). The age of plume A is more than 9 days, which is a hint that the air mass traveled a long way and originated in Asia. However, an influence of younger air masses originating e.g. in America can not be ruled out, if a slight shift in the time axis of the FLEXPART model prediction is considered. The age of plume B is more than 9 days as well and this air mass seems to be completely uninfluenced by younger air masses. The plume which we discussed before as East Asian plume always was the plume B, detected at 10:40 UTC. The continentally split representation of the FLEXPART results (middle panel) also shows that the main part of the plumes A and B came from Asia.



**Fig. 10.** Top panel: Time sequence of the SO<sub>2</sub> mole fraction measured during the flight and flight altitude. Middle panel: Time sequence of SO<sub>2</sub> mole fractions originating from different continents predicted by the FLEXPART model along the flight path. Bottom panel: Corresponding time sequence of SO<sub>2</sub> mole fractions as predicted by FLEXPART. The color code indicates the SO<sub>2</sub> age. The 3 main measured SO<sub>2</sub> plumes are marked by vertical lines A, B and C.

We do not see the FLEXPART modeled SO<sub>2</sub> increases at 10:00 and 11:00 UTC in the measurements. The measured CO and NO<sub>y</sub> is enhanced at those times. A reason for the “missing” SO<sub>2</sub> enhancements in the measurements could be that the air masses around 10:00 UTC and around 11:00 UTC have much higher relative humidities (70% compared to 20% in the older air mass). Therefore it is at least conceivable, that the SO<sub>2</sub> in the humid air mass has been converted to H<sub>2</sub>SO<sub>4</sub> due to more efficient OH formation and has been removed from the air mass in this way.

Plume C seems to stem mainly from North America (see middle panel of Fig. 10). By contrast to plumes A and B, much of the SO<sub>2</sub> contained in plume C is much younger and the predicted SO<sub>2</sub> mole fraction of plume C is similar to the measurement.

## 5 Summary

For the first time, a SO<sub>2</sub>-rich pollution plume of East Asian origin has been detected over Europe. SO<sub>2</sub> mole fractions of up to 900 pmol/mol have been measured. FLEXPART particle dispersion model simulations clearly indicate East Asia (China, Korea and Japan) as the major source region of the pollution. The plume was lifted to the upper troposphere over the Asian continent most probable in a warm conveyor belt and traveled all the way to Europe across the North Pacific, North America and the North Atlantic. The pollution was

about 8–10 days old and stemmed from densely populated and industrialized areas in East Asia. Investigations of the impact of this SO<sub>2</sub> pollution e.g. on particle formation and growth will follow in the accompanying paper Fiedler et al. (2009).

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