

Chinese SO<sub>2</sub>  
pollution over Europe  
– Part 1

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# Chinese SO<sub>2</sub> pollution 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 Chinese origin was detected by aircraft based CIMS (Chemical Ionization Mass Spectrometry) measurements at 3–7.5 km altitude over the North Atlantic on 3 May 2006 during the INTEX (Intercontinental Chemical Transport Experiment) campaign. Additional trace gases (NO, NO<sub>y</sub>, CO, H<sub>2</sub>O) were measured and used for comparison and source identification. All measurements took place aboard the German research aircraft Falcon. The atmospheric SO<sub>2</sub> mole fraction was markedly increased inside the plume and reached up to 900 pmol/mol. The measured ratio SO<sub>2</sub>/NO<sub>y</sub> of 1.4 suggests combustion of coal or fuel with a very high sulfur content as a source of the excess SO<sub>2</sub>. Accompanying FLEXPART particle dispersion model simulations indicate that the probed pollution plume originated at low altitudes over densely populated and industrialized areas in eastern 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> stem from fossil fuel combustion, 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 sulfur compounds 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 (Brosseur et al., 1999; Seinfeld and Pandis,

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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 contributes to acid deposition polluting ecosystems. Atmospheric SO<sub>2</sub> is removed by deposition at the planets surface and by cloud processes. After dissolution in cloud droplets SO<sub>2</sub> may be washed out or rained out. 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 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 in westerly direction has only scarcely been measured so far. Examples of intercontinental transport of air pollutants were published by e.g. Jacob et al. (1999); Jaffe et al. (1999) 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

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and mesoscale convective systems in summer (Wild and Akimoto, 2001). Recently transport of the pollution tracers CO, NO<sub>y</sub> and O<sub>3</sub> from Asia to Europe were described by Stohl et al. (2007). Arnold et al. (1997) presented a striking example of a SO<sub>2</sub> pollution plume detected off the Irish west coast which had probably originated from a Canadian Ni-Cu smelting industry complex near Sudbury and traveled about 10 000 km within 5 days. Now we report on an even more extreme case of long-range transport of SO<sub>2</sub> pollution. This paper will focus on a Chinese SO<sub>2</sub> pollution plume detected off the Irish west coast which had traveled 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 permanent 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 about 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) 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.

## 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 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°×1°, and 91 vertical levels. Over North America, the North Atlantic and Europe, nested input data with a resolution of 0.36°×0.36° 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

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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 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 retroplume, 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 s kg<sup>-1</sup>) 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 kg s<sup>-1</sup>) 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), 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 kg m<sup>-2</sup> s<sup>-1</sup>) 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>.

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### 3 Measurements

The measurement flight of the DLR research aircraft Falcon started from Brest in Northern France around 09:00 UTC on the 3rd of May 2006. The measurements took place over the Atlantic Ocean south and west of Ireland. The flight path of the Falcon is depicted in Fig. 1. 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, which made a determined search for Asian pollution possible.

Figure 2 shows the vertical SO<sub>2</sub> mole fraction, smoothed with a running mean averaging 30 data points. During the flight the Falcon reached a maximum altitude of 7.5 km. Two major SO<sub>2</sub>-rich pollution plumes were detected. 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 preferably from China and therefore will be termed the China plume. This paper will focus on the China plume.

Figure 3 presents a time series of data obtained during the entire flight. Plotted is flight altitude (km) and temperature (K) in the lowest panel, above relative humidity (%) and water vapor mixing ratio (mol/mol), above the SO<sub>2</sub> mole fraction linearly scaled and in the uppermost panel the SO<sub>2</sub> mole fraction logarithmically scaled. The marked SO<sub>2</sub> enhancement 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.

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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 are also 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.

The SO<sub>2</sub>/NO<sub>y</sub> ratio is rather high (0.2–1.4 mol/mol), which suggests combustion of coal or oil with a high sulfur content as 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. 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 stems from an emission inventory prepared for the INTEX campaign by D. G. Streets and Q. Zhang ([http://www.cgrer.uiowa.edu/EMISSION\\_DATA\\_new/index\\_16.html](http://www.cgrer.uiowa.edu/EMISSION_DATA_new/index_16.html), e.g., Streets et al., 2003; Van Donkelaar et al., 2008). 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. For comparison, Table 3 lists typical SO<sub>2</sub>/NO<sub>x</sub> ratios for different regions of the world. The values are based on data from Lelieveld et al. (2001) who adopted data from the EDGAR inventory (Olivier et al., 1996). Interestingly, the emission ratio is highest for China.

The atmospheric SO<sub>2</sub>/NO<sub>x</sub> ratio will of course change during transport due to different chemical conversions of SO<sub>2</sub> and NO<sub>x</sub>. We will nevertheless compare the measured SO<sub>2</sub>/NO<sub>y</sub> ratio to the SO<sub>2</sub>/NO<sub>x</sub> emission ratio in the next section. Generally one can expect that the 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 whereas  $\text{NO}_x$  is in first approximation completely converted to  $\text{NO}_y$ , which is removed mainly by in-cloud processes ( $\text{HNO}_3$ ) or thermal degradation (recycles PAN to  $\text{NO}_x$ ).

## 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  $\text{SO}_2$  enhancements, but the predicted concentrations at the measurement site are usually too high, as no chemical  $\text{SO}_2$  removal during transportation is considered (see above).

Several different FLEXPART products and corresponding graphical representations of the model will be used in this analysis:  $\text{SO}_2$  forward calculations as well as backward calculations of column residence time, footprint and source contribution.

The column residence time in Fig. 6a shows the vertically integrated residence time of the particles for the air mass with the highest  $\text{SO}_2$  signature intercepted by the Falcon at 10:40 UTC. Briefly, this column residence time plot gives as color code a kind of probability for a certain air mass parcel to reach the measurement site. The numbers superimposed on the shading are the days back in time. This product indicates where the air did come from (but without altitude information). The figure suggests that the  $\text{SO}_2$  of the highest observed peak was released 8–10 days prior to the measurements preferably from a source region in North East China.

Figure 6b is the so-called footprint emission sensitivity, also for the  $\text{SO}_2$  peak at 10:40 UTC. It is actually the same as the column residence time, but averaged only over the lowest 150 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 preferably in China.

This is confirmed by another FLEXPART product, the so-called  $\text{SO}_2$  source

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contribution graph. Figure 6c shows the SO<sub>2</sub> source contribution to the measurements at 10:40 UTC. The SO<sub>2</sub> source contribution figure also suggests that the SO<sub>2</sub> pollution plume stemmed mostly from China. This FLEXPART product also gives 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 more than 90% of the measured SO<sub>2</sub> are of Asian origin.

Figure 7 is a combination of the FLEXPART source contribution map (only the North East Chinese 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. As can be seen, 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. In comparison, the measured molar ratio SO<sub>2</sub>/NO<sub>y</sub> in the Chinese plume ranges mostly from 1.2 to 1.4 mol/mol.

After having identified China 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 Chinese 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

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longitude of 12.5°, which was the case for the rightmost 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  $1 \times 10^6 \text{ cm}^{-3}$  (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. Hence it seems that most SO<sub>2</sub> loss was due to OH-induced gas-phase conversion. If so, this would imply that most SO<sub>2</sub> survived vertical transport.

Figure 10 (top panel, blue dotted line) shows again the time sequence of the SO<sub>2</sub> mole fraction measured during the flight. The bottom panel of this figure depicts the time sequence of the SO<sub>2</sub> mole fraction modeled by FLEXPART and interpolated on the given flight track. The color code indicates the approximate age of the predicted SO<sub>2</sub>. 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 plumes A and B is 8–12 days and interestingly this air masses are older than the air masses intercepted before and after the measured SO<sub>2</sub> enhancement (only 4–7 days). We do not see the 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 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. Concerning plume C, the predicted time of the beginning of the interception is correct. However, the predicted time of the end of the

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interception is incorrect. 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

5 For the first time, a SO<sub>2</sub>-rich pollution plume of Chinese origin has been detected over Europe. SO<sub>2</sub> mole fractions of up to 900 pmol/mol have been measured. FLEXPART model simulations clearly indicate China as the major source region of the pollution. The plume was lifted to the upper troposphere over the Asian continent and traveled all the way to Europe across the North Pacific, North America and the  
10 North Atlantic. The pollution was about 8–10 days old and stemmed from densely populated and industrialized areas in East China. The mole fraction ratio of SO<sub>2</sub>/NO<sub>x</sub> was 1.4 mol/mol, which suggests combustion of coal or oil with a high sulfur content. 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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- Andreae, M., Jones, C., and Cox, P.: Strong present-day aerosol cooling implies a hot future, *Nature*, 435, 1187–1190, 2005. 1379
- Arnold, F., Schneider, J., Gollinger, K., Schlager, H., Schulte, P., Hagen, D., Whitefield, P., and van Velthoven, P.: Observation of upper tropospheric sulfur dioxide- and acetone-pollution: Potential implications for hydroxyl radical and aerosol formation, *Geophys. Res. Lett.*, 24, 57–60, 1997. 1379, 1380
- Brasseur, G., Orlando, J., and Tyndall, G.: *Atmospheric Chemistry and Global Change*, Oxford University Press, New York, 1 edn., 1999. 1378
- Emanuel, K. A. and Živkovic Rothman, M.: Development and evaluation of a convection scheme for use in climate models, *J. Atmos. Sci.*, 56, 1766–1782, 1999. 1381
- Fiedler, V., Arnold, F., Schlager, H., and Pirjola, L.: Chinese SO<sub>2</sub> pollution over Europe – Part 2: Simulation of aerosol and cloud condensation nuclei formation, *Atmos. Chem. Phys. Discuss.*, in press, 2009. 1388
- Garrett, T., Radke, L., and Hobbs, P.: Aerosol Effects on Cloud Emissivity and Surface Longwave Heating in the Arctic, *J. Atmos. Sci.*, 59, 769–778, 2002. 1379
- Gerbig, C., Schmitgen, S., Kley, D., Volz-Thomas, A., Dewey, K., and Haaks, D.: An improved fast-response vacuum-UV resonance fluorescence CO instrument, *J. Geophys. Res.*, 104, 1699–1704, 1999. 1381
- Harshvardhan, Schwarz, S., Benkovitz, C., and Guo, G.: Aerosol influence on cloud microphysics examined by satellite measurements and chemical transport modelling, *J. Atmos. Sci.*, 59, 714–725, 2002. 1379
- Huntrieser, H., Heland, J., Schlager, H., Forster, C., Stohl, A., Aufmhoff, H., Arnold, F., Scheel, H., Campana, M., Gilge, S., Eixmann, R., and Cooper, O.: Intercontinental air pollution transport from North America to Europe: experimental evidence from airborne measurements and surface observations, *J. Geophys. Res.*, 110, D01305, doi:10.1029/2004JD005045, 2005. 1379
- Jacob, D., Logan, J., and Murti, P.: Effect of rising Asian emissions on surface ozone in the United States, *Geophys. Res. Lett.*, 26, 2175–2178, 1999. 1379
- Jaffe, D., Anderson, T., Covert, D., Kotchenruther, R., Trost, B., Danielson, J., Simpson, W., Berntsen, T., Karlsdottir, S., Blake, D., Harris, J., Carmichael, G., and Uno, I.: Transport of Asian air pollution to North America, *Geophys. Res. Lett.*, 26, 711–714, 1999. 1379

---

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Laaksonen, A., Pirjola, L., Kulmala, M., Arnold, F., Raes, F., and Wohlfrom, K.-H.: Upper tropospheric SO<sub>2</sub> conversion into sulfuric acid aerosols and cloud condensation nuclei, *J. Geophys. Res.*, 105, 1459–1469, 2000. 1378

Lelieveld, J., Crutzen, P. J., and Ramanathan, V., et al.: The Indian Ocean Experiment: Widespread Air Pollution from South and Southeast Asia, *Science*, 291, 1031, doi:10.1126/science.1057103, 2001. 1384, 1395

Logan, J., Prather, M., Wofsy, S., and McElroy, M.: Tropospheric chemistry: a global perspective, *J. Geophys. Res.*, 86, 7210–7254, 1981. 1379, 1387

Olivier, J. G. J. and Berdowski, J. J. M.: Global emissions sources and sinks, in: *The Climate System*, edited by: Berdowski, J., Guicherit, R. and Heij, B. J., A.A. Balkema Publishers/Swets & Zeitlinger Publishers, Lisse, The Netherlands, 33–78, 2001. 1382

Olivier, J. G. J., Bouwman, A. F., van der Maas, C. W. M., et al.: Description of EDGAR Version 2, RIVM Report 771060002, 1996. 1384

Ramanathan, V., Crutzen, P., Kiehl, J., and Rosenfeld, D.: Aerosol, climate, and the hydrological cycle, *Science*, 294, 2119–2124, 2001. 1379

Reiner, T. and Arnold, F.: Laboratory flow reactor measurements of the reaction SO<sub>3</sub>+H<sub>2</sub>O+M → H<sub>2</sub>SO<sub>4</sub>+M: implications for gaseous H<sub>2</sub>SO<sub>4</sub> and aerosol formation in the plume of jet aircraft, *Geophys. Res. Lett.*, 20, 2659–2662, 1993. 1378

Reiner, T. and Arnold, F.: Laboratory investigations of gaseous sulfuric acid formation via SO<sub>3</sub>+H<sub>2</sub>O+M → H<sub>2</sub>SO<sub>4</sub>+M: measurements of the rate constant and products identification, *J. Chem. Phys.*, 101, 7399–7407, 1994. 1378

Rodhe, H., Dentener, F., and Schulz, M.: The global distribution of acidifying wet deposition, *Environ. Sci. Technol.*, 36, 4382–4388, 2002. 1379

Schlager, H., Konopka, P., Schulte, P., Schumann, U., Ziereis, H., Arnold, F., Klemm, M., Hagen, D. E., Whitefield, P. D., and Ovarlez, J.: In situ observations of air traffic emission signatures in the North Atlantic flight corridor, *J. Geophys. Res.*, 102, 10 739–10 750, 1997. 1381

Seibert, P. and Frank, A.: Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode, *Atmos. Chem. Phys.*, 4, 51–63, 2004, <http://www.atmos-chem-phys.net/4/51/2004/>. 1382

Seinfeld, J. and Pandis, S.: *Atmospheric Chemistry and Physics*, John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 2nd edn., 2006. 1378

Speidel, M., Nau, R., Arnold, F., Schlager, H., and Stohl, A.: Sulfur dioxide measurements in the

- lower, middle and upper troposphere: Deployment of an aircraft-based chemical ionization mass spectrometer with permanent in-flight calibration, *Atmos. Environ.*, 41, 2427–2437, 2007. 1380, 1381
- 5 Stockwell, W. and Calvert, J.: The Mechanism of the HO-SO<sub>2</sub> reaction, *Atmos. Environ.*, 17, 2231–2235, 1983. 1378
- Stohl, A.: *Intercontinental Transport of Air Pollution*, Springer Verlag, Berlin, Heidelberg, Germany, 1st edn., 2004. 1379
- Stohl, A. and Thomson, D.: A density correction for Lagrangian particle dispersion models, *Bound.-Lay. Meteorol.*, 90, 155–167, 1999. 1381
- 10 Stohl, A. and Trickl, T.: A textbook example of long-range transport: Simultaneous observations of ozone maxima of stratospheric and North American origin in the free troposphere over Europe, *J. Geophys. Res.*, 104, 30 445–30 462, 1999. 1379
- Stohl, A., Hittenberger, M., and Wotawa, G.: Validation of the Lagrangian particle dispersion model FLEXPART against large scale tracer experiment data, *Atmos. Environ.*, 32, 4245–4264, 1998. 1381
- 15 Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H., Wilhelm, S., Arnold, F., and Cooper, O.: A backward modeling study of intercontinental pollution transport using aircraft measurements, *J. Geophys. Res.*, 108(D12), 4370–4387, 2003. 1379, 1382
- 20 Stohl, A., Forster, C., Frank, A., Seibert, P., and Wotawa, G.: Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, *Atmos. Chem. Phys.*, 5, 2461–2474, 2005, <http://www.atmos-chem-phys.net/5/2461/2005/>. 1381
- Stohl, A., Forster, C., Huntrieser, H., Mannstein, H., McMillan, W., Petzold, A., Schlager, H., and Weinzierl, B.: Aircraft measurements over Europe of an air pollution plume from Southeast Asia–aerosol and chemical characterization, *Atmos. Chem. Phys.*, 7, 913–937, 2007, <http://www.atmos-chem-phys.net/7/913/2007/>. 1380
- 25 Streets, D., Bond, T., Carmichael, G., Fernandes, S., Fu, Q., He, D., Klimont, Z., Nelson, S., Tsai, N., Wang, M., Woo, J.-H., and Yarber, K.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, *J. Geophys. Res.*, 108, 8809, doi:10.1029/2002JD003093, 2003. 1384, 1400
- 30 Van Donkelaar, A., Martin, R. V., Leaitch, W. R., Macdonald, A. M., Walker, T. W., Streets, D. G., Zhang, Q., Dunlea, E. J., Jimenez, J. L., Dibb, J. E., Huey, L. G., Weber, R., and Andreae, M. O.: Analysis of aircraft and satellite measurements from the Intercontinental

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Chemical Transport Experiment (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada, *Atmos. Chem. Phys.*, 8, 2999–3014, 2008, <http://www.atmos-chem-phys.net/8/2999/2008/>. 1384

5 Wild, O. and Akimoto, H.: Intercontinental transport of ozone and its precursors in a three-dimensional global CTM, *J. Geophys. Res.*, 106, 27 729–27 744, 2001. 1380

Ziereis, H., Schlager, H., Schulte, P., van Velthoven, P., and Slemr, F.: Distributions of NO, NO<sub>x</sub>, and NO<sub>y</sub> in the upper troposphere and lower stratosphere between 28° and 61° N during POLINAT 2, *J. Geophys. Res.*, 105, 3653–3664, 2000. 1381

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9, 1377–1405, 2009

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**Table 1.** Measured maximum trace gas mole fractions and relative humidity inside the Chinese plume.

SO <sub>2</sub> (nmol/mol)	NO (nmol/mol)	NO <sub>y</sub> (nmol/mol)	CO (nmol/mol)	H <sub>2</sub> O (μmol/mol)	RH (%)
0.9	0.01	0.6	165	200	20

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**Table 2.** Molar SO<sub>2</sub>/NO<sub>x</sub> emission ratios for four different source types in the East Asian source region (INTEX emission inventory by D. G. Streets and Q. Zhang, see text).

	SO <sub>2</sub> /NO <sub>x</sub> [mol/mol]
Power	1–3
Industry	1–5
Residential	2–5
Transportation	<0.1

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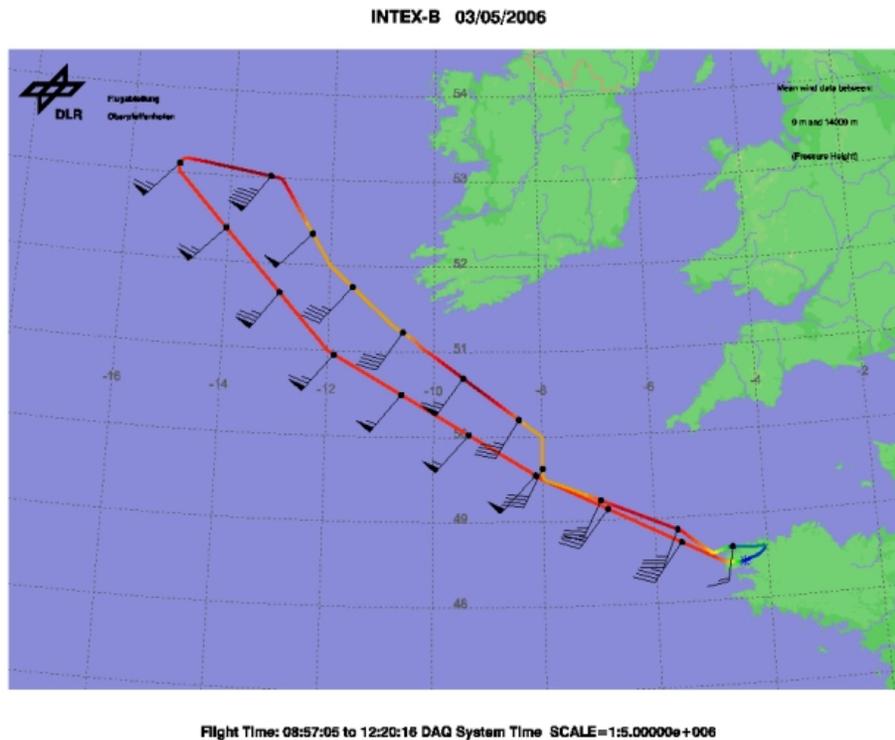
**Table 3.** Mean anthropogenic molar SO<sub>2</sub>/NO<sub>x</sub> emission ratios for different regions derived from the total emissions of one year. (Based on data from Lelieveld et al., 2001).

	N America	Europe	India	China	E Asia
SO <sub>2</sub> /NO <sub>x</sub> [mol/mol]	0.7	1.5	0.6	1.8	0.8

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**Fig. 1.** Flight path of flight 20060503 color coded according to flight altitude (0 km (blue) to 7 km (red)). Distance of the wind direction markers is 10 min.

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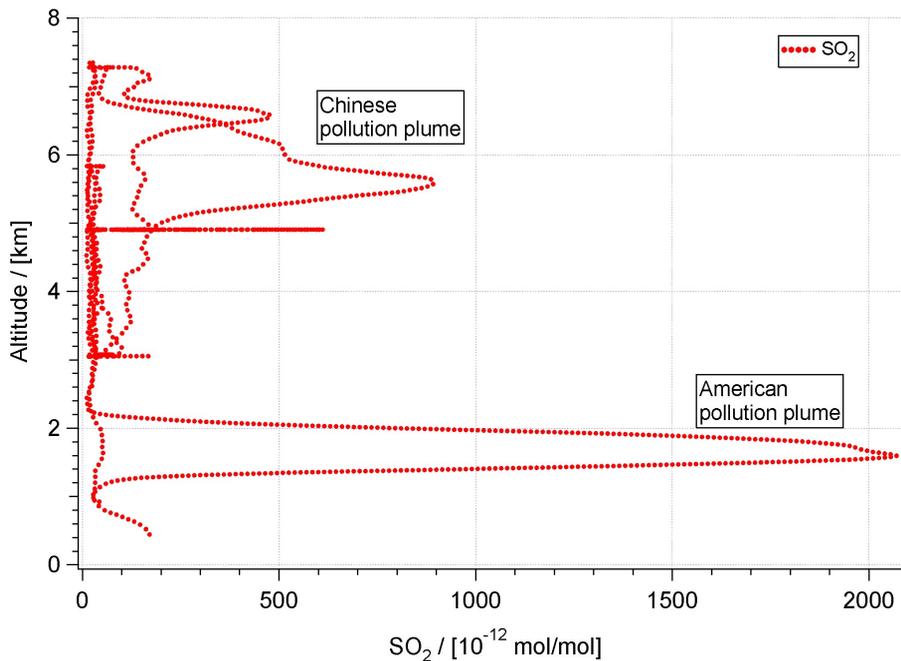
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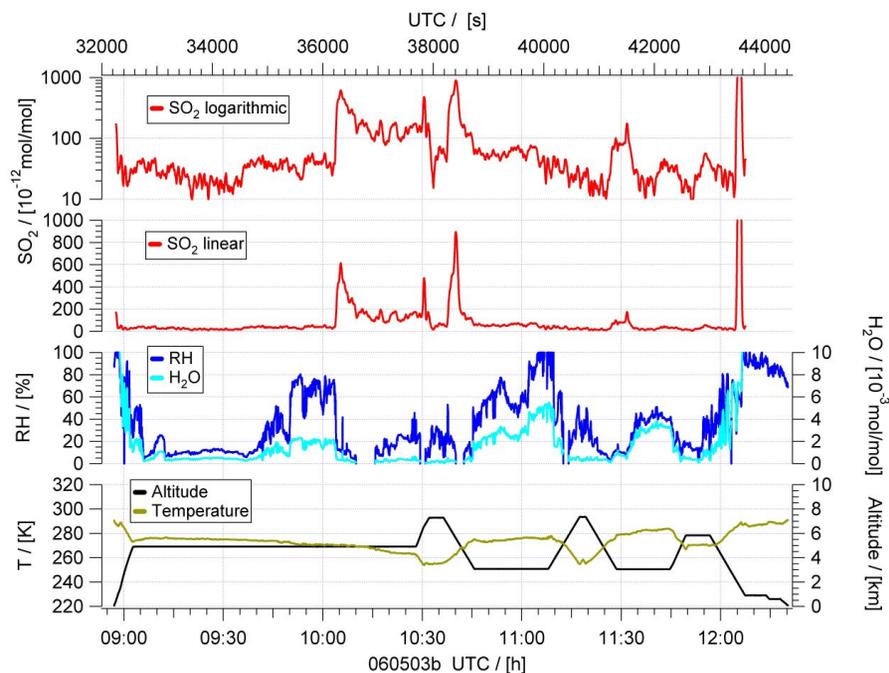


**Fig. 2.** SO<sub>2</sub> mole fraction altitude profile of flight 20060503, smoothed with a running mean averaging 30 data points.

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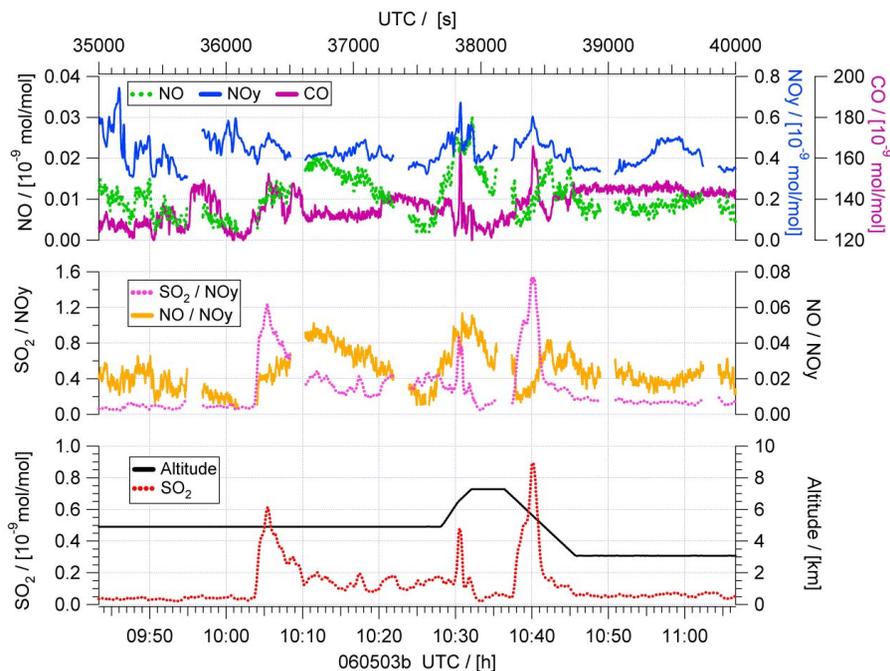


**Fig. 3.** Time sequence of atmospheric SO<sub>2</sub> mole fraction (linear and logarithmic representation) measured aboard the FALCON during flight 20060503. Also given are flight altitude, temperature, relative humidity and water vapor mixing ratio.

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**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.

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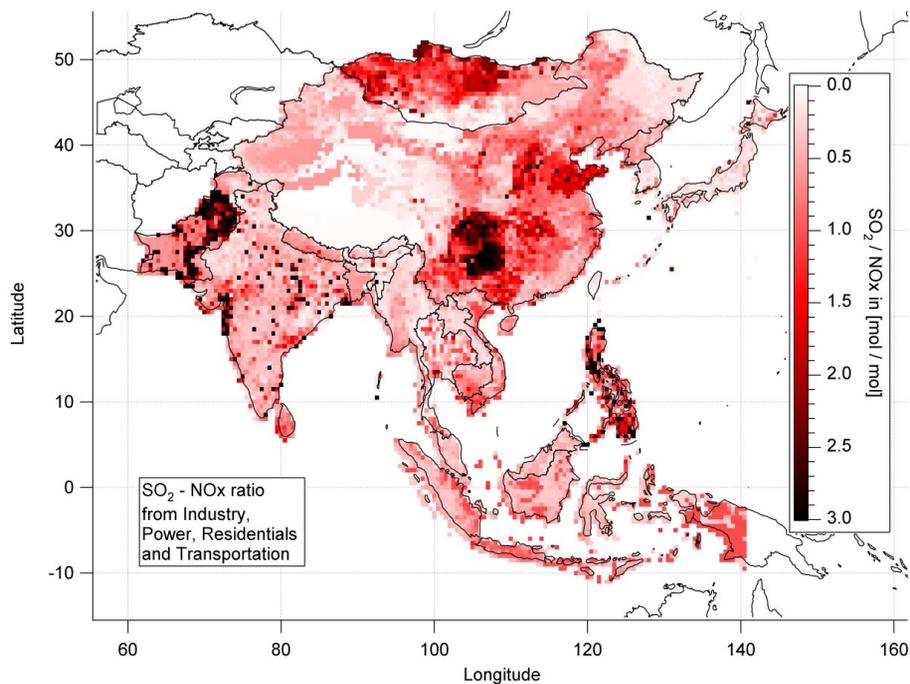
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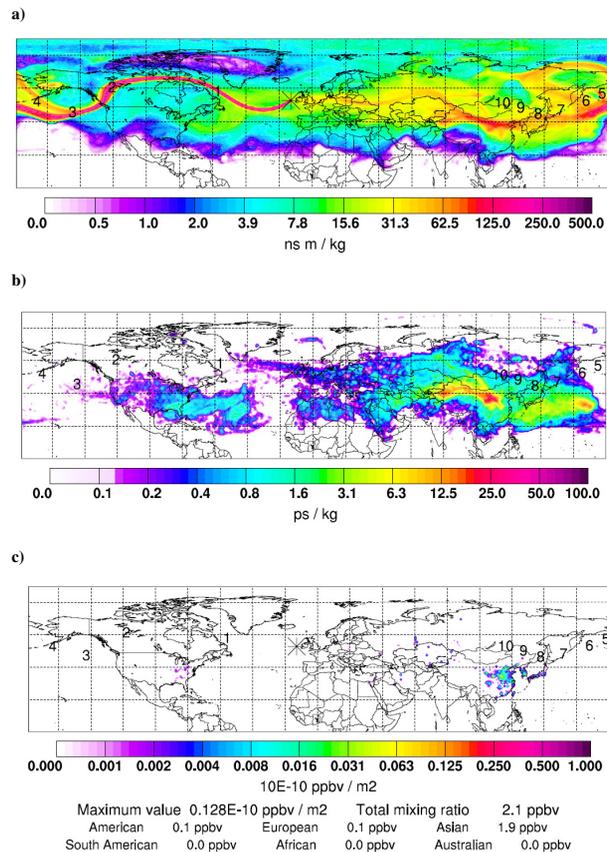


**Fig. 5.** SO<sub>2</sub>/NO<sub>x</sub> molar emission ratios in Asia 2006 (Inventory by D. G. Streets and Q. Zhang, e.g. Streets et al., 2003).

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**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. (ppbv=parts per billion by volume=nmol/mol)

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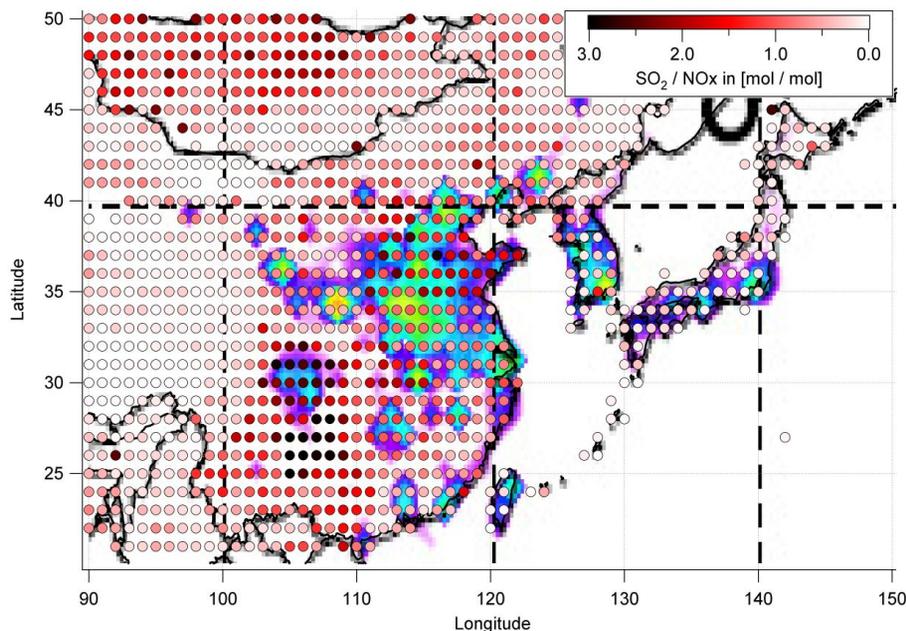
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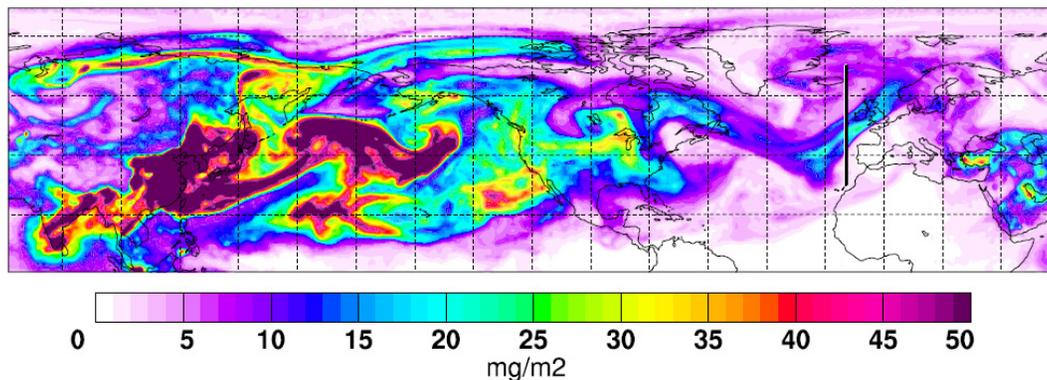
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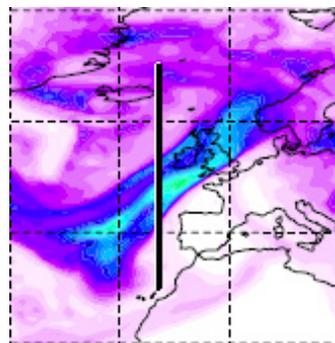
**Fig. 7.** In the background a zoomed view of the East Chinese section of the FLEXPART source contribution map (see Fig. 6c), which is the region with the highest SO<sub>2</sub> source contribution signatures (ppbv=parts per billion by volume=nmol/mol). The color coded circles in the foreground represent SO<sub>2</sub>/NO<sub>x</sub> molar emission ratios from the INTEX B emission inventory (see Fig. 5).

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a)



b)



**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 footprint of the plume interception by the Falcon. (b) Zoomed view of the interception area.

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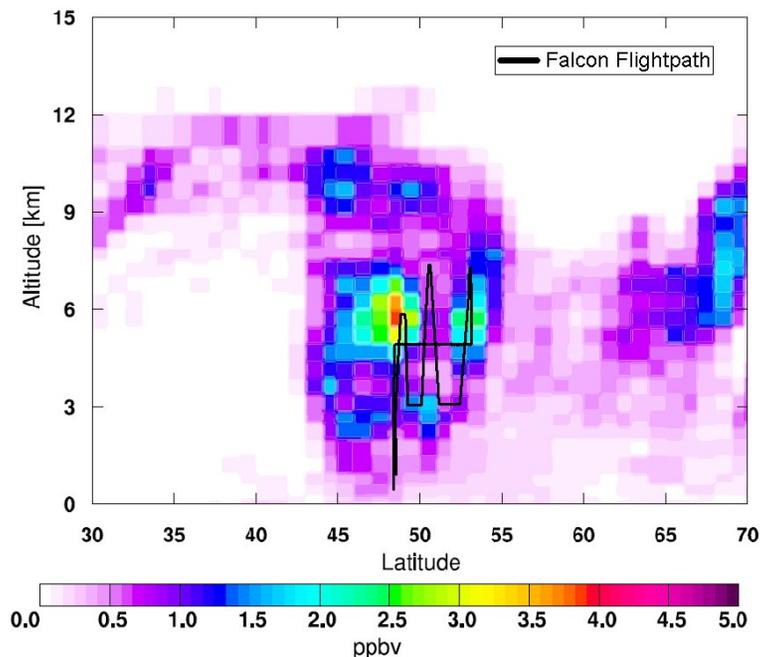
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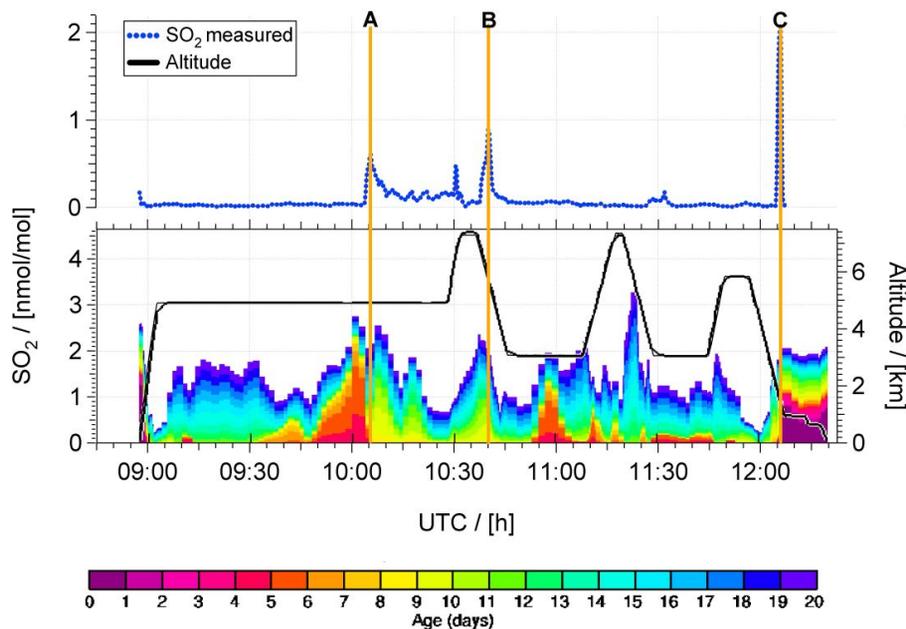


**Fig. 9.** FLEXPART vertical distribution of the SO<sub>2</sub> mole fraction at 12.5 degrees longitude (mean value on 3 May 2006 from 09:00 to 12:00 UTC, ppbv=parts per billion by volume=nmol/mol). Only SO<sub>2</sub> is considered which has been released from Chinese sources. Also given is the vertical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

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**Fig. 10.** Top panel: Time sequence of the SO<sub>2</sub> mole fraction measured during the flight. Bottom panel: Corresponding time sequence of SO<sub>2</sub> mole fractions predicted by the FLEXPART model. 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.

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