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Airborne multi-axis DOAS measurements of tropospheric SO_2 plumes in the Po-valley, Italy

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Abstract. During the second FORMAT (FORMaldehyde as A Tracer of oxidation in the troposphere) campaign in 2003 the airborne multi-axis DOAS instrument (AMAX-DOAS) performed scattered-light spectroscopic measurements of SO_2 over the city of Mantova and the power plant Porto Tolle, both situated in the Po-valley, Northern Italy. The SO_2 vertical columns and emission flux were derived from two days of measurements, 26 and 27 September 2003. The SO_2 emission flux from the power plant Porto Tolle was calculated to 1.93×10^{25} molec s^{-1} on 26 September and in good agreement with official emission data, which quote 2.25×10^{25} molec s^{-1}. On 27 September the measured flux was much lower (3.77×10^{24} molec s^{-1}) if ECMWF wind data are used, but of comparable magnitude (2.4×10^{25} molec s^{-1}) if the aircraft on-board wind measurements are utilised. Official emission data was 2.07×10^{25} molec s^{-1} indicating only a small change from the previous day. Over the city of Mantova, the observed SO_2 vertical columns were 1.1×10^{16} molec cm^{-2} and 1.9×10^{16} molec cm^{-2} on 26 and 27 September, respectively. This is in good agreement with ground-based measurements of 5.9 ppbv and 10.0 ppbv which correspond to 1.2×10^{16} molec cm^{-2} and 2.2×10^{16} molec cm^{-2} if a well mixed boundary layer of 500 m altitude is assumed.

1 Introduction

Sulphur Dioxide, SO_2 is directly emitted into the atmosphere by volcanoes and also produced by the oxidation of sulphur containing gases in the atmosphere. The main anthropogenic sources of SO_2 are combustion of fossil fuels, for example in electric power plants, refinery emissions, and to a lesser degree biomass burning. In the absence of clouds, SO_2 is converted to H_2SO_4 through homogeneous gas-phase reactions initiated by the hydroxyl radical. Generally only a minority of SO_2 is oxidized in air, the rest is removed by dry deposition. In the presence of clouds a fraction of the SO_2 is dissolved into cloud droplets and oxidized to sulphate ions, SO_4^{2-}, by trace amounts of oxidizing agents such as hydrogen peroxide H_2O_2, and O_3 that are present in the airborne droplets. Eventually it is removed by wet deposition (Wayne, 1991).

SO_2 itself is a respiratory irritant, the effect appearing at concentrations above 1 ppm (Wayne, 1991). SO_2 is oxidized to H_2SO_4 and contributes to acid rain. It increases acidity in the aquatic ecosystem and is harmful for soil and vegetation. SO_2 inhibits photosynthesis in plants and reduces plant growth.

SO_2 concentrations are routinely measured by air quality monitoring networks, such as ARPAV and the Lombardia air quality network (http://www.arpa.veneto.it/indice.htm; http://www.ambiente.regione.lombardia.it/webqa/QualitAmbiente.htm) for the area treated in this study. In-situ measurements of SO_2 were also part of many airborne campaign measurements (e.g. Tscherwenka et al., 1998; Svensson and Klemm, 1998; Thornton et al., 2002; Tu et al., 2003). Remote sensing measurements of SO_2 from space have been performed using TOMS (Krueger et al., 1995; Carn et al., 2004), GOME (Eisinger and Burrows, 1998; Khokhar et al., 2005), SCIAMACHY (Afe et al., 2004) and AIRS (Carn et al., 2004), but are mainly restricted to volcanic eruptions or large scale pollution. The COSPEC (COrrelation SPECtrometer) technique developed in the late 1960s has also been used to study total emissions of SO_2 and NO_2 from various sources, e.g. industrial emissions (Millan

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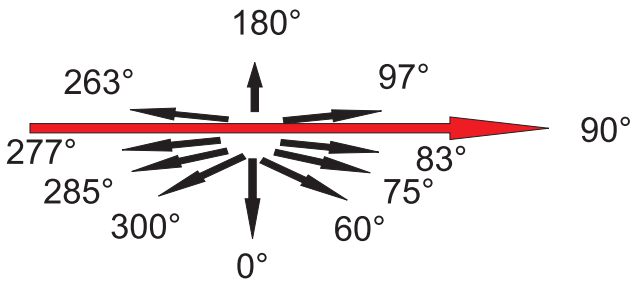

Fig. 1. AMAXDOAS telescope viewing directions. The flight direction is indicated by the red arrow (90°). The ten directions are in the same vertical plane.

et al., 1969; Hoff and Millan, 1981) and volcanic plumes (Hoff, 1992) using ground-based remote sensing.

The airborne multi-axis DOAS instrument (AMAXDOAS) has previously been used on board the high flying aircraft DLR-Falcon in campaigns dedicated to the validation of the SCIAMACHY instrument on ENVISAT (Bovensmann et al., 1999). Several papers have demonstrated its use for measurements of the tropospheric NO_2, and the validation of SCIAMACHY NO_2 (Heue et al., 2005; Wang et al., 2005; Fix et al., 2005). The possibility to retrieve vertical profiles from the measurements has also been reported (Bruns et al., 2004). In summer 2002, the AMAXDOAS instrument was for the first time operated onboard the low flying aircraft Partenavia, to measure HCHO and NO_2 abundances in urban plumes (Pundt et al., 2005a)[1]. During the second FORMAT campaign, the viewing directions were optimized for the measurements of plumes from point sources (Pundt et al., 2005b)[2].

In this study we focus on measurements of the SO_2 flux from the power plant Porto Tolle and the SO_2 concentration at the city of Mantova, both located in northern Italy. The measurements were performed using the AMAXDOAS instrument onboard the aircraft Partenavia in the Po-valley, northern Italy in September 2003. For the power plant plume, the SO_2 emission rate was derived and compared with official emission data. For the city of Mantova, the SO_2 vertical columns were determined and compared with ground-based in situ measurements.

[1]Pundt, I., Heue, K.-P., Wang, P., Richter, A., Friedeburg, C. V., Bruns, M., Laepple, T., Wagner, T., Burrows, J. P., and Platt, U.: Airborne Multi-Axis-DOAS measurements of formaldehyde of the photochemical plume of Milan city, paper in preparation, 2005.

[2]Pundt, I., Heue, K.-P., Song, B.-C., Richter, A., Wang, P., Bruns, M., Platt, U., Burrows, J. P., and Wagner, T.: Airborne Tomographic Measurements of NO_2 Plumes from Point sources using the AMAX DOAS instrument, paper in preparation, 2005.

2 AMAXDOAS setup during the second FORMAT campaign

The AMAXDOAS instrument consists of two grating spectrometers, one operating in the UV between 300–440 nm, the other covering the visible part of the spectrum (400–550 nm). Quartz fibre bundles are used to collect scattered sunlight from two sets of telescopes outside of the aircraft, one on the top and one on the bottom (Wagner et al., 2001). Measurements are performed in ten viewing directions, where the zenith direction is denoted as 180°, the nadir direction is 0°, and the flight direction 90°. The viewing directions are shown in Fig. 1. The signals from the ten directions are detected simultaneously with CCD imaging detectors. During measurements the CCD detectors are cooled down to −30°C and the spectrometers are thermally stabilized at about 40°C to prevent wavelength drifts during the flight. The UV spectra images were recorded with 10 s integration time, and dark current and line lamp calibration measurements were performed after the flight. In order to improve the signal to noise ratio, the measured spectra were averaged over 1 min intervals before further analysis, resulting in a horizontal resolution of about 3.7 km.

3 Data analysis

3.1 SO_2 slant column

The data analysis is based on the Differential Optical Absorption Spectroscopy (DOAS) method (Platt, 1994). For the SO_2 fit, the spectral window of 316.5–325.5 nm was selected. Two O_3 cross sections at 293 K and 221 K, respectively (Burrows et al., 1999), an NO_2 cross section at 293 K (Burrows et al., 1998), the SO_2 cross section at 295 K (Vandaele et al., 1994), the HCHO cross section (Meller and Moortgat, 2000) and a ring spectrum (Vountas et al., 1998) were included in the fit. The spectral resolution of the AMAXDOAS UV spectrometer is about 0.8 nm, and all the cross sections used were convolved with the AMAXDOAS slit function prior to the fit. For each measurement direction, a background spectrum taken in the same viewing direction during the same flight was used. The background spectra were chosen to be close to the SO_2 plume to minimise the effect of potential instrumental changes but in a region where low SO_2 is expected. The result of the DOAS analysis is the differential slant column, which is the slant column relative to the background spectrum. With our background spectrum criteria, the differential slant column is actually the SO_2 slant column of the plume.

3.2 Airmass factor calculation

The slant columns retrieved with the DOAS method have to be converted to vertical columns, usually by dividing through appropriate air mass factors (AMF). The AMF is defined as

the ratio of the slant column and the vertical column of the absorber. In this study, AMFs were calculated with the radiative transfer model SCIATRAN 2.0 full spherical version (Rozanov et al., 2001) for all viewing directions at flight altitude (600 m). One important factor in air mass factor calculations is the aerosol loading. As the power plant Porto Tolle is located near the coast, and as trajectory analysis with the TRAJKS model (Stohl et al., 2001) indicate that the air masses on 26 and 27 September came from the sea, a maritime aerosol is assumed. In contrast, the aerosol type near the city Mantova was assumed to be urban. The aerosol optical depth used in the radiative transfer model was set to about 0.35 (at 550 nm) which is similar to the aerosol optical thickness given by MODIS data on that day (Kaufman and Tanre, 1998). Within the plume from the power plant, aerosol concentrations are expected to be enhanced. However, the O_4 slant columns which can be used as an indicator of light path (Wang et al., 2005) do not show significant variation when crossing the SO_2 plume, and therefore we assume that the effect of aerosol on the measurements is similar inside and outside of the plume. Throughout the measurements, the sky was cloud free, and therefore no clouds were included in the radiative transfer calculations. The surface albedo was set to 0.02 at 320 nm, the central wavelength of the SO_2 fitting window. Using these settings, air mass factors were calculated for solar zenith angles between 40° to 75° with 5° intervals at 320 nm.

During the measurements, two kinds of emission plumes of SO_2 were sampled, one from a power plant, and one from a city. Therefore, two sets of AMFs were calculated with different types of SO_2 profiles. To calculate the SO_2 AMFs for the city, the profile was assumed to be well mixed between 0 and 500 m. This choice is based on the fact that no significant SO_2 slant column increase was observed above flight altitude as discussed in Sect. 4.1. The AMFs for the plume near the power plant were calculated with a well-mixed SO_2 profile in the boundary layer. The boundary layer height at Porto Tolle was about 1.0 km at 10.5 UT on 26 and 27 September according to ECMWF data.

3.3 SO_2 flux calculation

To calculate the emission flux from the power plant Porto Tolle, a simple formula based on the integrated amount of SO_2 in the transect measured from the aircraft and the wind speed perpendicular to the flight direction can be used:

$$Flux = v_{\text{aircraft}}\, v_{\text{wind}}\, \sin\theta \int_{t_1}^{t_2} VC(t)\, dt\,, \qquad (1)$$

where v_{aircraft} is the velocity of the aircraft, v_{wind} is the wind speed, θ is the angle between the wind direction and the flight direction, VC is the SO_2 vertical column and $t_1 ... t_2$ is the time interval flown in the plume (White et al., 1976; Trainer et al., 1995; Melamed et al., 2003). Since there were no clouds and humidity was low (relative humidity about 60%), the SO_2 emitted from the power plant was probably not converted to H_2SO_4 or removed by deposition very fast. If both the wind direction and wind speed are constant throughout the boundary layer, the measurement should give a good approximation of the emission flux from the power plant. If wind speed and direction vary with altitude, the flux can still be calculated if the SO_2 is assumed to be well mixed by adding partial fluxes for the individual layers:

$$Flux = \int_{t_1}^{t_2} v_{\text{aircraft}} \sum_i v^i_{\text{wind}}\, \sin\theta^i\, VC^i(t) dt\,, \qquad (2)$$

where VC_i is the partial SO_2 vertical column in layer i. In this study, the wind speed and direction were taken from either the measurements taken on board the aircraft in flight altitude or ECMWF re-analysis 0.5×0.5° data at 45° N, 12.5° E, which is very close to the power plant (at 44.95° N, 12.5° E).

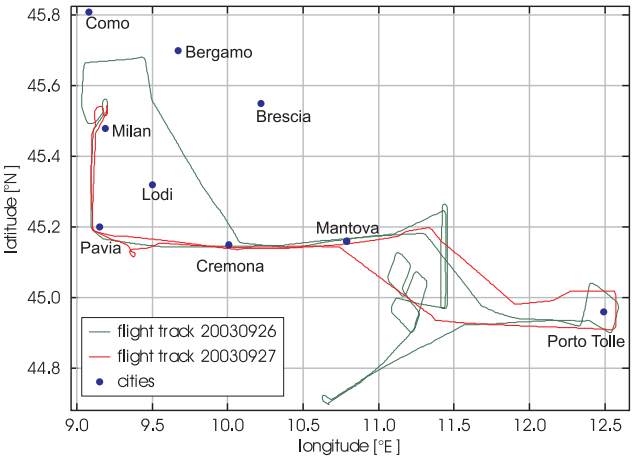

Fig. 2. AMAXDOAS flight tracks on 26 and 27 September 2003.

4 Results and discussion

4.1 Enhanced SO_2 slant columns at Porto Tolle and Mantova

On 26 and 27 September 2003 the flight started from Milan to the south, lead over Pavia, turned to the east, over Cremona and Mantova, then turned around the power plant Porto Tolle, and back to Milan. To measure the plume from the power plant, the aircraft flew around the stacks with a roughly 3 km radius as illustrated in Fig. 2. The flight routes taken on the two days around the power plant Porto Tolle are almost the same. On 26 September on the way back from Porto Tolle the aircraft also flew around another power plant at Sermide and Ostiglia (close to 45.0° N, 11.2° E), and did a comparison flight with the Ultralight aircraft(Junkermann, 2005) at 45.0–45.2° N, 11.45° E. The flight altitude was mainly about 600 m except for the intercomparison flight where it was at

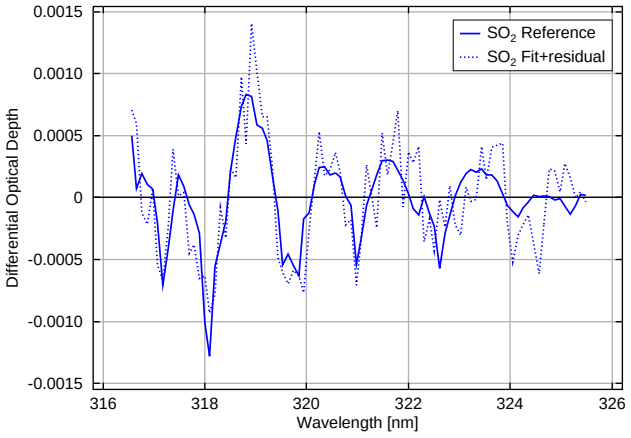

Fig. 3. An example of a SO_2 fit, on measurements close to Porto Tolle at 10:24 UT on 27 September. The solid line is the scaled laboratory reference, the dotted line is the result of the fit after subtraction of all other absorbers and the polynomial.

about 1.8 km. The flight started at 09:00 UT on 26 September, and at 08:55 UT on 27 September.

Enhanced SO_2 values were clearly identified both at Porto Tolle and Mantova. An example of the DOAS fit is shown in Fig. 3. That measurement was in zenith viewing direction, near the power plant Porto Tolle at 10:24 UT on 27 September, at a solar zenith angle of 47.26°. The background spectrum used was measured at 44.94° N, 11.36° E, which is about 90 km west of Porto Tolle. The error of the fit was about 12%. The background spectrum for 26 September was measured at 45.04° N, 12.40° E, the upwind direction of Porto Tolle power plant. For the analysis the assumption is made, that the background spectra contain no SO_2 absorption signature. The SO_2 slant columns were measured in 10 viewing directions. Three representative viewing directions are shown in Fig. 4. On 26 September, three SO_2 plumes were measured at about 9.6 (09:36) UT, 9.9 (09:54) UT, 10.6 (10:36) UT near the city Cremona, Mantova, and the power plant Porto Tolle, respectively. On 27 September the same plumes were measured at about 9.3 (09:18) UT, 9.6 (09:36) UT and 10.4 (10:24) UT. The SO_2 plume from the power plant was observed both in the upward and downward viewing directions. In contrast, the plumes of the cities of Cremona and Mantova were only detected in the downward viewing directions. At Porto Tolle, the SO_2 slant columns of the zenith viewing direction were similar on the two days. The SO_2 slant columns in the 97° and 83° viewing direction were larger than that in the zenith viewing direction due to the enhanced optical path. Over Mantova the SO_2 slant columns measured on 27 September are about two times that of 26 September. The SO_2 plume over Cremona is smaller than the other two plumes. From the SO_2 time series it is also obvious that the slant columns have relatively large variations outside of the plumes, which makes it difficult to detect small SO_2 plumes. On the way back from Porto Tolle, on 26 September the flight didn't cross Cremona, and on 27 September the flight did not cover Mantova.

The NO_2 slant columns in the three viewing directions on 26 September are shown in Fig. 5 for comparison. The fitting window selected for the NO_2 retrieval is 345–380 nm, which does not overlap the SO_2 fitting window. Power plant emissions of SO_2 and NO_x are highly correlated and the difference in lifetime between NO_2 and SO_2 is not relevant close to the stack. As NO_2 measurements have much higher accuracies, the error in the NO_2 slant column fit being about 2% within the plumes, they can be used to test the consistency of the SO_2 measurements. Several different NO_2 emissions contribute to the NO_2 signal and it is difficult to identify individual sources. However, the NO_2 plume from the power plant Porto Tolle can clearly be seen at about 10.6 (10:36) UT. As in the case of SO_2, the NO_2 plume from the power plant is also detected in all viewing directions. The 97° viewing direction has a similar amount of NO_2 as the 83° viewing direction. The similarity of the NO_2 and SO_2 measurements adds confidence to the SO_2 measurement.

4.2 SO_2 emission flux at power plant Porto Tolle

The AMAXDOAS measurements show enhanced SO_2 close to the Porto Tolle power plant. To calculate the emission flux from these measurements, it has to be assured that the plume from the power plant was fully sampled, and the measured slant columns have to be converted to vertical columns to derive the total amount of SO_2 in the plume transect. For the conversion of slant to vertical columns, an assumption has to be made on the vertical distribution of the SO_2. For this, both the AMAXDOAS measurements themselves and in-situ surface measurements were used.

In Fig. 6 SO_2 slant columns (97° viewing direction) are shown around the power plant along the flight track. As can be seen, the location of the SO_2 plume was to the south of the power plant as expected from the wind direction.

On 26 September the wind speed at 10:28 UT (at 44.92° N, 12.28° E) was about 4.5(±2) m/s and the wind direction 345°(±30°) (north is 0°). On 27 September the wind speed at 10:28 UT (at 44.92° N, 12.11° E) was also about 4.5(±2) m/s, however, the direction was 18°(±30°). Both wind speed and direction were measured on the aircraft during flight. The position of the observed plume is in good agreement with the wind direction on 26 September. The plume was displaced to the west relative to the wind direction on 27 September, indicating a change in wind direction or a large uncertainty in the wind direction measured on the aircraft. According to the ECMWF vertical wind profile on 26 September at 45.0° N, 12.5° E, the wind speed at 550 m, which is close to the flight altitude, was 3.7 m/s, with a direction of 30°, comparable to the wind measurements on the aircraft. The wind direction and speed were also stable with altitude, see Fig. 11. On 27 September the wind profile was

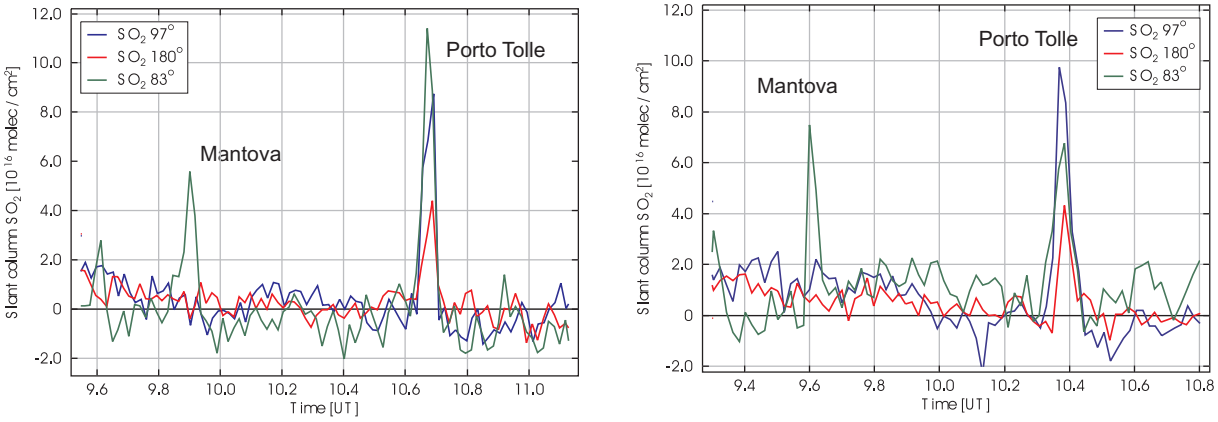

Fig. 4. SO_2 slant columns measured by AMAXDOAS on 26 September 2003 (left) and 27 September 2003 (right) for the flight from Cremona to Mantova, to the Porto Tolle power plant and back to the airport Reggio nell' Emiglia (44.70° N, 10.67° E).

chosen at the same time and location from the ECWMF data, yielding a wind speed of 0.9 m/s and a direction of 264°. These values are clearly very different from those measured on the aircraft. According to the trajectory on 27 September, the wind was very weak and turning around 45° N, 12.5° E. Both wind speed and direction varied strongly in the horizontal and vertical direction. As a result, measurement conditions were not favourable for determination of the SO_2 flux.

The Electric Energy Board (ENEL) operates one central meteorology station at the center of the Porto Tolle power plant and eight air quality measurement stations around the power plant, the one closest to our flight track being at Scardovari (44.9° N, 12.46° E), at the south of the power plant, see Fig. 6. As shown in Fig. 7, the SO_2 concentration at Scardovari showed a large peak between 10:00 and 15:00 UT on 26 September. The station is located downwind of the power plant (the surface wind direction was from north to south measured at the central meteorological station), almost at the centre of the plume, according to the AMAXDOAS measurements. The very large concentrations observed at the station during the AMAXDOAS overpass show that the plume reached the surface and indicate that the boundary layer was probably well mixed. On 27 September, the SO_2 concentration at Scardovari did not vary significantly during the day, also in agreement with the AMAXDOAS measurements that show no indication for enhanced SO_2 close to the station. On 27 September, the Scardovari station did not sample the plume because the surface wind direction was from west to east before 10:00 UT and then turned to east to west, the wind speed being low throughout the day, which also indicated that on 27 September the wind had large variation in that area.

The SO_2 of the power plant Porto Tolle is emitted from a stack of 250 m altitude at a temperature of about 130°C (http://www.gruppoverdier.it/documenti.php). Thus, the plume can easily be transported to higher altitudes and in fact could

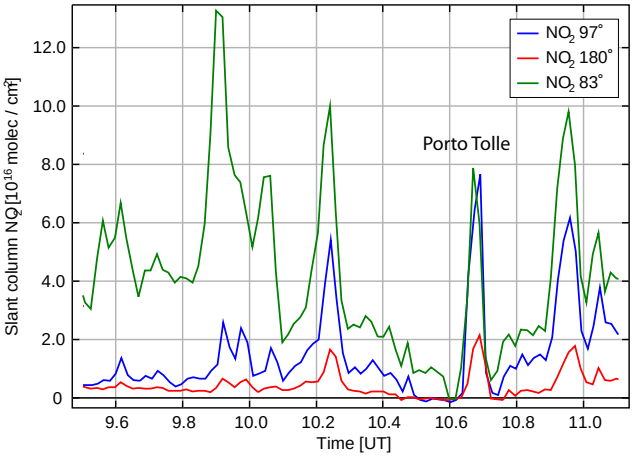

Fig. 5. AMAXDOAS NO_2 slant columns measured on 26 September 2003. The part of the flight shown is from Cremona to Mantova to the Porto Tolle and back to the airport Reggio nell' Emiglia (44.70° N, 10.67° E).

be measured in all AMAXDOAS viewing directions. At noon the turbulence in the boundary layer is usually strong, and the SO_2 could be well mixed in the boundary layer a few kilometres downwind of the stack. The measurements of the SO_2 peak were made at distances of about 5 km (26 September) and 11 km (27 September) from the stack, and therefore the SO_2 profile was assumed to be well-mixed below 1 km, the height of the boundary layer.

The SO_2 vertical columns for the power plant plume are calculated from the zenith viewing direction, as this measurement has a high signal to noise ratio and is insensitive to the relative azimuth angle of the sun. The SO_2 AMF in zenith viewing direction is about 0.73 for the power plant plume using the assumptions described above. Thus, the SO_2 vertical column maximum near the power plant is about

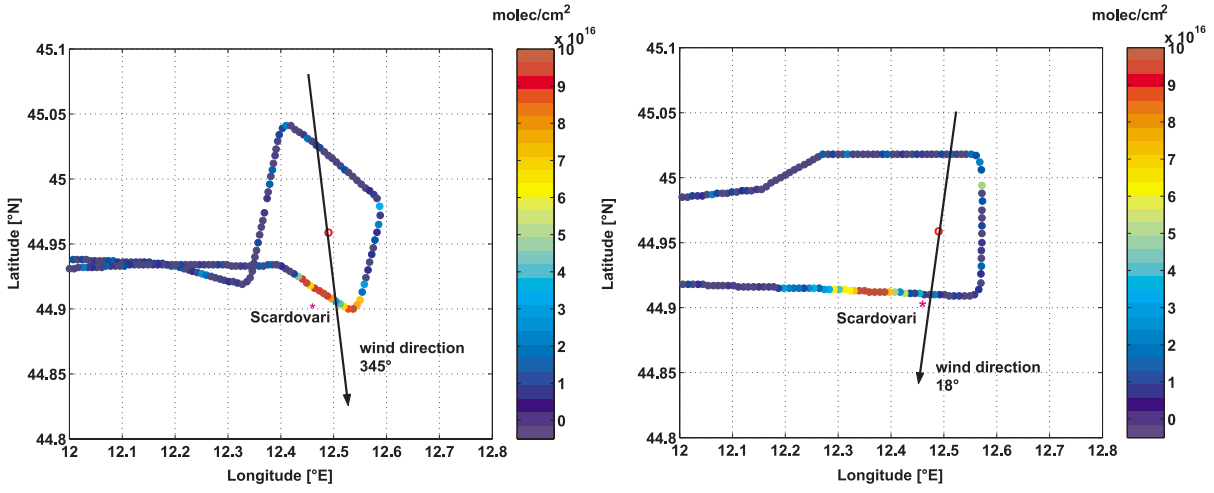

Fig. 6. SO_2 slant columns measured around the Porto Tolle power plant (red circle) in the 97° viewing direction along the flight track on 26 September, (left) and 27 September 2003 (right). The wind directions were measured on the aircraft. Also indicated is the closest ENEL air quality measurement station at Scardovari.

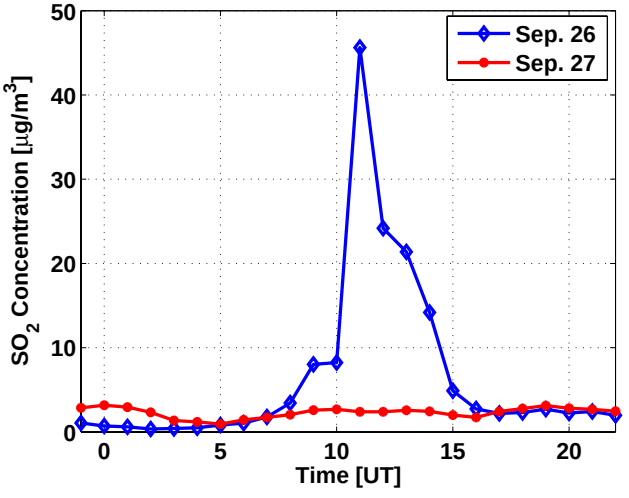

Fig. 7. Hourly averaged SO_2 concentration measured at the ENEL surface station Scardovari on 26 and 27 September, 2003.

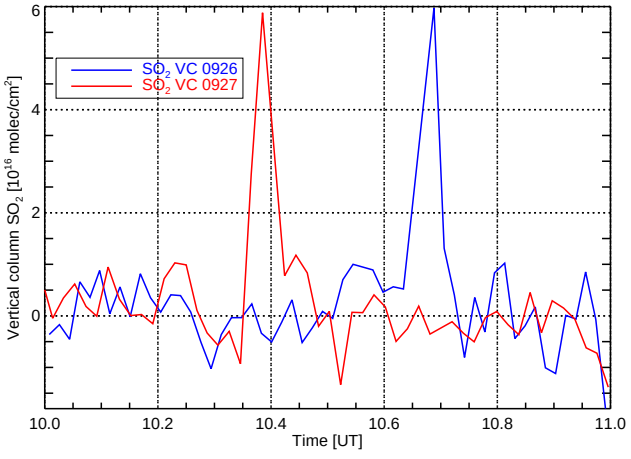

Fig. 8. SO_2 vertical columns measured by AMAXDOAS around the Porto Tolle power plant on 26 and 27 September 2003. These vertical columns are derived from zenith viewing direction.

6×10^{16} molec cm^{-2}. The SO_2 vertical columns measured on both days near the Porto Tolle power plant are shown in Fig. 8.

The AMAXDOAS SO_2 vertical columns are in agreement with the ENEL in situ measurements at Scardovari. The in situ SO_2 concentration at 10:50 UT was about 27 μg m^{-3} or 10.3 ppbv (parts per billion volume mixing ratio) on 26 September. Converting the mixing ratio to a vertical column with the assumption of a well-mixed profile from the surface up to 1.0 km yields 2.5×10^{16} molec cm^{-2}. Since the ground-based measurement was locate downwind of the flight track, a smaller value than in the maximum of the SO_2 plume is to be expected.

Using formula (1), the SO_2 emission flux from the Porto Tolle power plant can be calculated from the measurements. The time needed to cross the plume was about 6 minutes at a flight speed of 230 km h^{-1}. Using only the aircraft measurements and assuming homogeneous wind speed and direction, the SO_2 flux is determined to 2.36×10^{25} molec s^{-1} on 26 September and 2.4×10^{25} molec s^{-1} on 27 September. If the ECMWF wind profile at 45° N, 12.5° E is used according to formula (2), the SO_2 flux is 1.93×10^{25} molec s^{-1} on 26 September and 3.77×10^{24} molec s^{-1} on 27 September. Hourly averaged SO_2 emission data are also measured by the power plant Porto Tolle. The SO_2 concentration of the power unit groups 1-2-3 was about 1500 mg Nm^{-3} at

Table 1. SO_2 emission of the Porte Tolle power plant and surface concentrations inside the plume derived from the AMAXDOAS measurements in comparison with the data measured by the ENEL (* on 27 September the ground station was located outside the emission plume).

Date	AMAXDOAS near Scardovadi ground station (10^{16} molec cm^{-2})	Insitu Data Scardovadi ground station (10^{16} molec cm^{-2})	AMAXDOAS Porto Tolle emission rate (10^{25} molec s^{-1})	Insitu Data Porto Tolle emission rate (10^{25} molec s^{-1})
26 September	6.0 ($\pm$0.7)	2.5	2.36 $\pm$1.2, 1.93 (ECMWF wind)	2.25
27 September	–	1	2.4 $\pm$1.2, 0.377 (ECMWF wind)	2.07

11:00 UT on both 26 and 27 September. As there were no measurements for unit 4 on 26 and 27 September, the averaged concentration between 11 September and 16 November was used, which was 317 mg Nm^{-3}. The SO_2 concentration and power output were very stable with variations being smaller than 1% during the day. The gas flow for each of the power units is calculated from the output power, the burned fuel and its efficiency. The SO_2 emission flux is calculated from the gas flow and the SO_2 concentration. The resulting SO_2 emission flux is 2.25×10^{25} molec s^{-1} on 26 September and 2.07×10^{25} molec s^{-1} on 27 September.

Uncertainties in the SO_2 emission flux derived from AMAXDOAS measurements are introduced by the uncertainty of the SO_2 vertical columns, the wind speed, wind direction, aircraft speed and the time needed to cross the plume. In this case study, the error is dominated by the uncertainty of wind speed and direction. The error bars on the wind speed are 30% for the aircraft measurements and 10% for ECMWF data. However, due to the coarse resolution of the model (0.5x0.5 degree), the wind profile used is not necessarily representative for the plume. In spite of the large error on the wind speed, the fluxes determined using the in-situ wind speed are in good agreement with power plant emission data for both days. In contrast, the analysis using ECMWF data results in a comparable value for 26 September, but a much lower values on 27 in spite of the very similar SO_2 vertical columns measured. This is probably the result of the unstable wind situation on 27 September which is reflected in the spatial and temporal variability of the ECMWF data and also the differences between the wind speed measured on the aircraft and at the station Scardovari. In summary, the situation on 27 September was not well suited for flux measurements with the AMAXDOAS. Another error source of the method are the variations of up to 5×10^{15} molec cm^{-2} SO_2 in the background measurements, which is about 12% of the slant column. The SO_2 calculated here is the SO_2 in the plumes relative to the background. If there is any SO_2 present in area where the background spectrum was taken, the AMAXDOAS measured SO_2 will be too small. The fit error in the SO_2 slant column was between 12–50% depending on the SO_2 signal. The SO_2 emission flux derived from AMAXDOAS and the power plant measurements are summarized in Table 1.

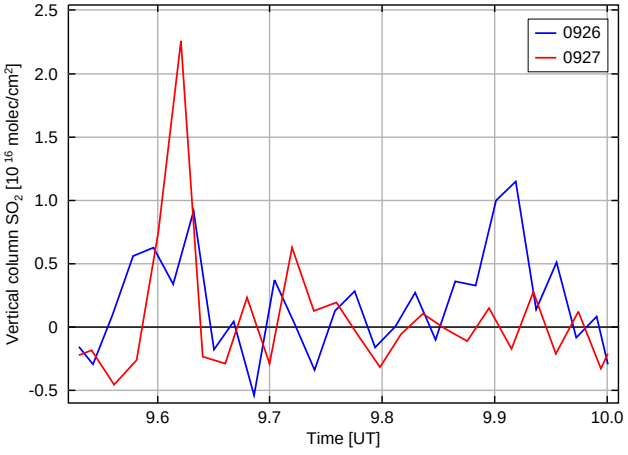

Fig. 9. SO_2 vertical columns measured over Mantova on 26 and 27 September 2003. The peaks at 9.9 UT on 26 September and 9.6 UT 27 September were located over Mantova. The peak at 9.6 UT on 26 September was close to Cremona. The vertical columns plotted here are derived from the 75° viewing direction.

4.3 SO_2 plumes over the city of Mantova

Enhanced SO_2 over Mantova could only be observed in the downward viewing directions, indicating that the source of the SO_2 is close to the surface. At least, no SO_2 had been transported above 600 m, the flight altitude, within the AMAXDOAS detection limit of about 1×10^{16} molec cm^{-2}. Judging from the AMAXDOAS weighting functions for the SO_2 measurements in the zenith and 97° viewing directions, the lack of SO_2 signal in the upwards viewing directions indicates that the plume was lower than 500 m. Accordingly, the AMFs were calculated with a profile where SO_2 is located only in the lowest 500 m.

The SO_2 vertical columns measured over the city of Mantova are shown in Fig. 9 based on the measurements from the 75° viewing direction as it provides the best signal to

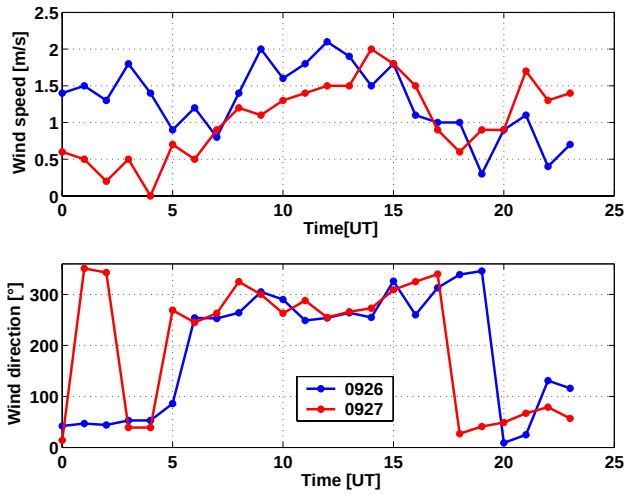

Fig. 10. Wind speed and direction at Mantova (station No. 542) on 26 and 27 September 2003 (data from http://www.ambiente.regione.lombardia.it/webqa/QualitAmbiente.htm).

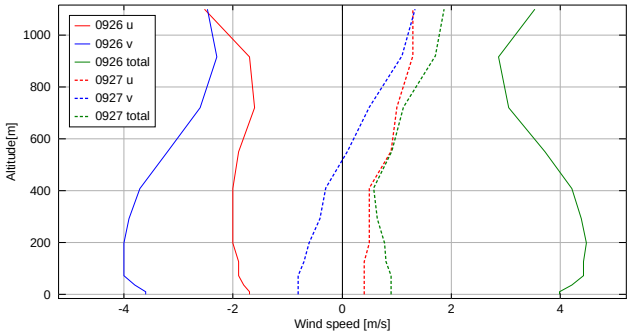

Fig. 11. ECMWF wind profile at 45.0° N, 12.5° E at 10.5 UT on 26 and 27 September 2003. The u, v components of wind speed and total wind speed are shown.

noise. The peaks at 9.9 (09:54) UT on 26 September and 9.6 (09:36) UT 27 September are signals from the SO_2 pollution at Mantova. The peak at 9.6 (09:36) UT on 26 September was close to the city of Cremona. The SO_2 vertical columns measured on 27 September are twice as large as those observed on 26 September. The wind directions on 26 and 27 September were similar (south-westerly), but on 26 September the wind speed was much larger than on 27 September before 10:00 UT, see Fig. 10. Low wind velocities usually contribute to the accumulation of SO_2 which probably is the reason or the larger values measured on 27 September. Compared to the SO_2 amount at Porto Tolle power plant, the SO_2 over Mantova is much less, and the error in the SO_2 slant column is between 13–30%. The closest in-situ station along the flight track at Mantova is the station at 10.82° E, 45.16° N (No. 542). The hourly averaged SO_2 concentration measured at this station between 10:00 and 11:00 UT on 26 September was 5.9 ppbv and 10.0 ppbv on 27 September (http://www.ambiente.regione.lombardia.it/webqa/QualitAmbiente.htm). Assuming that the SO_2 is well mixed below 500 m, this corresponds to vertical columns of 1.09×10^{16} molec cm^{-2} and 1.85×10^{16} molec cm^{-2}, respectively. The AMAXDOAS measurements are 1.2×10^{16} molec cm^{-2} and 2.2×10^{16} molec cm^{-2}, which is in very good agreement with the in situ measurement.

5 Conclusions

In this study, the first airborne multi-axis DOAS measurements of SO_2 pollution are reported. The measurements were performed as part of the second FORMAT campaign in September 2003 in the Po valley, Italy, and covered both a power plant (Porto Tolle) and two cities (Mantova and Cremona).

At the power plant Porto Tolle, both SO_2 and NO_2 were detected in all viewing directions at a cruising altitude of 600 m, indicating that the plume was transported above the flight altitude and probably well mixed in the boundary layer. The SO_2 had also reached the ground according to surface in-situ measurements which reported high SO_2 concentrations. In contrast, SO_2 enhancement over the city of Mantova was detected in the downwards viewing directions only, so that the plume was assumed to be located below 500 m. Using these mixing heights, SO_2 vertical columns were derived from the AMAXDOAS measurements. The values over Mantova were compared to in-situ measurements, and good agreement was found on both days, highlighting the sensitivity of the measurements. For the Porte Tolle power plant, the AMAXDOAS data were used to derive estimates of the power plant emissions using two different approaches. The simple method assuming constant wind speed and direction throughout the boundary layer resulted in $2.4\pm1.2\times10^{25}$ molec s^{-1} on 26 and $2.36\pm1.2\times10^{25}$ molec s^{-1} on 27 September. When vertical wind profiles from ECMWF data were used, a SO_2 emission of 1.93×10^{25} molec s^{-1} was derived for 26 September and 3.37×10^{24} molec s^{-1} for the next day. While the values from the first method are in good agreement with the official emission data of 2.25×10^{25} molec s^{-1} and 2.07×10^{25} molec s^{-1} for 26 and 27 September, respectively, the second approach yields much lower values for the second day. This is probably the result of the low wind speeds and high spatial variability on 27 September making it unfavourable for airborne flux measurement.

Compared to the in-situ measurements, the advantage of the airborne measurements is that neither the exact vertical position of the plume, nor the distance of the measurement from the stack need to be known to establish the emissions. Also, the measurement can be performed for any wind direction whereas the surface network will only pick up SO_2 for

well mixed plumes passing over the measurement site. However the airborne measurement requires stable wind condition during measurements, complex wind condition will lead to large uncertainty of the measurements.

The errors of the estimated emission flux are relatively large, mainly due to uncertainties in wind speed and direction but also as a result of SO_2 measurement errors in particular for smaller values. SO_2 fits could be improved by optimizing the AMAXDOAS spectrometer which was set-up mainly for HCHO measurements for the UV spectral region used in the SO_2 retrieval by increasing throughput and spectral resolution and improving straylight rejection. Emission estimates could be improved in future measurements by using detailed modelling of the vertical wind field and a plume model for the vertical spread of the plume.

Our measurements and the comparison of the results with independent data demonstrate that the AMAXDOAS instrument is a very useful tool for air quality monitoring in a large number of applications ranging from urban pollution to point sources.

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