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Interactive comment on "Airborne multi-axis DOAS measurements of tropospheric SO_2 plumes in the Po-valley, Italy" *by* P. Wang et al.

P. Wang et al.

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The authors would like to thank the referee for the detailed review. Below, we have replied to the comments point by point, and the corresponding changes have been incorporated in the revised version of the paper.

General comments The manuscript entitled "Airborne multi-axis DOAS measurements of tropospheric SO2 plumes in the Po-valley, Italy" by Wang et al. describes airborne multi-axis DOAS measurements of SO2 during the FORMAT campaign in 2003. In particular, an estimate for the SO2 emissions from a power plant as well as for the vertical column densities over a city are provided.

These are, to my knowledge, the first measurements of SO2 by airborne MAX-DOAS, a

measurement technique which offers the opportunity to determine not only information on the vertical distribution of atmospheric trace gases but also on emission rates by observing SO2 slant column densities (SCDs) in a cross section of an emission plume. The paper therefore presents a novel concept, which addresses measurements of a trace gas with an important impact on atmospheric chemistry, air quality and - due to the potential acidification of rain droplets - the aquatic ecosystem. The analysis and interpretation of the MAX-DOAS measurements uses data from various sources obtained during the FORMAT campaign, such as SO2 in situ measurements, satellite borne measurements of aerosols, and airborne measurements of the boundary layer height, in a synergistic way. The paper is well structured and (as far as I can judge) written in a good English. I recommend the publication of this paper in ACP after some modifications as detailed below.

The detection of SO2 using scattered sunlight is quite challenging, in particular due to the low light intensities in the near UV (below _ 330nm) and, in case of observations pointing towards the ground, the low surface albedo at these wavelengths, as well as the relatively small SO2 optical depth from industrial emissions. A detailed description of the SO2 retrieval is therefore essential. However, I feel that the authors do not provide an appropriate discussion of the spectral analysis, including potential (systematic and random) errors, typical signal to noise ratio, and detection limits of the SO2 retrieval. In particular, it would be interesting to provide the errors of the SO2 SCDs for both nadir and zenith (and also the other viewing directions).

An accurate determination of airmass factors (AMFs) is crucial for the interpretation of MAX-DOAS measurements. In particular, an estimate of the aerosol extinction profile is required for the accurate modelling of the radiative transfer. The authors have demonstrated elsewhere (Wang et al., Measurements of tropospheric NO2 with an airborne multi-axis DOAS instrument, ACP, 2005) that MAXDOAS measurements of the oxygen dimer (O4) provide significant information on atmospheric aerosols and clouds, and that the information on aerosols gained from O4 measurements can serve as an

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input for the modelling of trace gas AMFs. The authors state that the same approach has been used for the determination of the aerosol optical depth for the SO2 measurements (by using the O4 absorption band centered around 360nm?), but do not provide any further details. It would be very informative for the reader to show and discuss a plot of the O4 vertical column densities from different viewing directions during the flight, which would confirm the assumptions made on the aerosol properties, in particular since (as the authors state) it is possible that a higher amount of aerosols (potentially with different optical properties) is present within the exhaust plume. Multi-axis DOAS allows to gain information on the vertical distribution of atmospheric trace gases, or at least to confirm assumptions made on the trace gas profile, by combining measurements performed along different lines of sight. A major weakness of the paper is the fact that the estimation of SO2 emissions from the power plant is based on vertical columns from zenith sky measurements only. Although the signal to noise ratio might be best for zenith sky measurements, the problem is that these measurements are very insensitive to the partial column of SO2 below the aircraft (as the authors mention in the discussion of the measurements at the city of Mantova). This means that even strong variations of the SO2 concentration below the flight altitude should have only a very small impact on the SO2 SCD measured in zenith, and this yields a large uncertainty in the derived VCDs from zenith sky measurements only. It is mentioned in the manuscript that the VCDs from other viewing directions qualitatively agree, but only zenith and nadir SO2 VCDs are shown (Figure 8). I strongly suggest to show the VCDs derived from all available viewing directions. Although an agreement of the VCD from different lines of sight can perhaps not be expected due to the horizontal inhomogeneity of the SO2 concentration within the exhaust plume, at least the integrated VCD along the cross section through the plume (or the respective emission rates) should agree for measurements along different lines of sight. This could confirm that the assumptions made on the vertical distribution of SO2 (as well as on aerosols) are valid.

reply of general comments

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One of the main criticisms of the reviewer is that we have used only two of the 10 viewing directions for the determination of the SO2 flux. In principle, simultaneous retrieval for all viewing directions can provide vertical resolution (see e.g. Bruns et al., 2004 or Pundt et al., 2005) which is one of the main reasons for using the MAXDOAS approach. However, there are several reasons why we have not used the off-axis directions:

1) as mentioned in the text, the signal to noise is best in the zenith direction, reducing fitting errors 2) tomographic inversion of AMAXDOAS measurements is only feasible for low error data (e.g. NO2 measurements) as otherwise error propagation will produce very noisy results. The SO2 data do clearly not have enough signal to noise for tomographic inversion. 3) Use of different viewing directions to deduce the vertical profile of SO2 is complicated by the horizontal gradients, in particular at the plume measurement. The ratio of say nadir and 83 degree viewing direction depends not only on the vertical profile of SO2, but also on the horizontal shape of the plume. Direct inversion is therefore not possible.

Specific comments

1) P2021, L3: It would be interesting to know the horizontal resolution of the measurements. Which horizontal distance corresponds to measurements performed in 1 min time intervals?

The horizontal resolution is about 3.7 km. This information has been added to the paper.

2) Section 3.1: The spectral analysis should be discussed in much more detail, in particular regarding the error budget for the SO2 SCDs from different lines of sight (see general comments).

We have added some more detailed information about the data analysis.

3) Section 3.2: I suggest to include a figure showing the O4 VCDs from different viewing

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directions based on the assumptions for the aerosol scenario (see general comments).

The O4 slant columns in all the viewing directions are compared but due to the large azimuth dependence of the O4 slant columns in the off-axis viewing directions, we could not find proper settings to get the O4 vertical columns similar in all viewing directions. To get the correct optical thickness we used the MODIS data. The Lowtran maritime aerosol with visibility 23 km give similar optical thickness as MODIS data. As the azimuth effect is not important for zenith and nadir viewing directions, we didn't use the SO2 slant columns in off-axis viewing directions for the computation of the vertical columns.

4) P2022, L1: Why is a maritime aerosol used for the AMF calculations at the exhaust plume although there is a northerly wind during the measurements (which means that the air mainly comes from the continent rather than from the sea) and a significant fraction of the aerosols might be directly emitted by the power plant?

The power plant Porto Tolle is close to the sea, so the background aerosol should be closer to maritime aerosol. We calculated the backward trajectory with TRAJKS for 26 and 27 Sep at Porto Tolle. On these two days the airmass at Porto Tolle did come from the sea. It therefore is reasonable to assume a maritime aerosol and that the background air was relatively clean. With respect to possible aerosol contribution from the plume itself it is interesting to note that we didn't see an O4 slant column change when crossing the exhaust plume. This indicates that either few aerosols had been formed at that point or that they do not impact strongly on the radiative transfer.

5) P2024, L9ff, and Figure 4: On Sept. 27, the SO2 SCD is lower at 83_ than at 97_, but one would expect the converse for geometrical reasons. Have you got any explanation for this feature?

We do not know why the SO2 measured in the 83_ viewing direction is higher than SO2 in the 97_ viewing direction on Sept. 27. However, if we assume that the SO2 plume is broadening towards the surface, such a result is possible (note that the 83° peak

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is broader than the 97_ measurement). In general, this type of problems can result from horizontal inhomogeneities of the plume and are one of the reasons why we have restricted ourselves to the nadir and zenith viewing directions for the flux calculations.

6) P2024, L16: Why should the wind speed have an impact on the SO2 SCDs measured downwind, or on the emission rates? Do you suggest that higher wind speeds cause a stronger mixing/dilution of SO2? This would cause smaller SCDs, but would have no impact on the emission rates.

We agree with the viewer on this comment. We wanted to say that higher wind speeds cause a stronger mixing/dilution of SO2.

7) P2024, L23: Are the large variations in the background real or is this variability in SO2 SCDs caused by random errors?

We think the variations in the background in SO2 SCDs are caused by random errors.

8) P2025, L24: It is mentioned that the plume was displaced relative to the local wind direction, and this has been attributed to the large error in measured wind direction. However, this discrepancy could also be explained by the fact that the local wind direction observed on the airplane is not necessarily equal to the average wind direction between the source and the location of the measurement.

We agree with the reviewer that changes in wind direction could also account for the observed displacement and have added this point to the manuscript.

9) P2026, L27ff: Although the signal to noise ratio is probably best in zenith, zenith sky measurements are very insensitive to SO2 below the aircraft. Therefore measurements from other viewing directions should be used for the estimation of the emission flux as well (see general comments).

Use of different viewing directions to deduce the vertical profile of SO2 is complicated by the horizontal gradients, in particular at the plume measurement. The ratio of say nadir and 83_ viewing direction depends not only on the vertical profile of SO2, but

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also on the horizontal shape of the plume. Direct inversion is therefore not possible. It is also difficult to get the accurate AMFs for the off-axis viewing direction. Therefore we don't think that including measurements from the off-axis directions can improve our results for the SO2 emission flux.

10) P2027, L7ff: It would be useful to add the VCDs from the other viewing directions to Fig. 8 to illustrate that they are in agreement with nadir and zenith VCDs. Also, flux estimates should be given for all available viewing directions (see general comments).

See the answer above. We don't think it is useful to calculate the flux from all the viewing directions. The AMF calculations are more reliable in zenith and nadir viewing directionas in the off-axis viewing directions the AMFs are very sensitive to the viewing angle, solar azimuth and aerosol settings.

11) P2027, L24ff: Multiplying the half width of a function with its peak value does not necessarily yield the integral. Why is the integral not calculated using, for example,Pi V Ci ů _ti with _ti being the acquisition time for the measurement of V Ci? The factor cos(_) (sin(_) ??) from Eq. 1 is not mentioned in the description of the flux calculation. Furthermore, it seems that the airplane was flying in a curve through the plume on 26. Sept. (Fig. 6). Do you account for the varying flight direction while crossing the plume?

We actually calculated the flux with formula 1. Later we tried to explain how to use the formula, which apparently was misleading and therefore has been removed. In the formula, the cos(_) should be a sin(_) as also pointed out by the other reviewer. However, the right formula was used in the calculations. We accounted for the variation of the flight direction by using the corresponding flight direction and flight speed at each measurement point.

12) P2028, L19ff: It is mentioned that the fact that SO2 SCDs are measured relative to the background could cause a systematic error in emission rates. But isn't the increase in SO2 relative to the background the quantity that is directly linked to the emission?

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If there is SO2 from local emissions in the background spectrum, it will cause a systematic underestimation of the power plant emission rates. If the background spectrum was well chosen (as we hope), it only contains the background SO2 level which should anyway be removed for the emission estimate as pointed out by the reviewer.

13) P2029, L1: The detection limit is mentioned, but it is neither defined nor quantified anywhere else in the paper. Please add this information to your 'Data Analysis' section.

An accurate determination of the detection limit of the measurements is difficult for DOAS type retrievals. Therefore, we used the short term fluctuations of the background SO2 values as a measure of our detection limit which we estimate to be 1E16 molec/cm2. This information has been added to the manuscript.

14) P2029, L2ff: It is not mentioned which viewing direction is used for the determination of the SO2 VCD at the city of Mantova. As for the measurements of the Porto Tolle plume (see my comments above), I would strongly suggest to show the VCDs derived from all downward viewing directions in order to provide evidence for an SO2 layer height of 500m (or to provide a better estimate of the SO2 layer height).

The SO2 VCD at Mantova in Fig 9 is from the 75- viewing direction. For the other viewing directions, the SO2 VCD is between 9.94e15 and 1.78e16 molec/cm2 on Sep. 26 and 1.60e16 and 3.2e16 molec/cm2 on Sep. 27. Data from the 75° direction have been used as they have the smallest error in slant columns.

15) P2030, L2: It is mentioned that 'The off-axis data of the AMAXDOAS measurements proved to be useful to determine plume altitudes'. I can't see how this has been done. For the Porto Tolle measurements you assume that SO2 is uniformly mixed in the boundary layer, with the boundary layer height determined using data from other in- struments. And for the SO2 layer height above the city of Mantova you only give an upper limit for the layer height of 500m based on the fact that there is no SO2 detected above the flight altitude. As far as I can see, lower SO2 layer heights are also possible. As already mentioned several times above, these assumptions could be easily vali-

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dated by converting the slant columns from all available viewing directions to vertical columns which should be similar if the assumptions on the vertical distribution of SO2 (and aerosols) are realistic.

As the reviewer correctly points out, no quantitative use has been made of the off-axis measurements for the determination of the vertical distribution of SO2. A full inversion of the SO2 measurements is hampered by the relatively large uncertainty of the individual measurements and also by horizontal inhomogeneities which would have to be derived simultaneously using a tomographic approach. We therefore focused on the use of zenith and nadir measurements, employing the off-axis data mainly to derive qualitative information on the vertical distribution. In response to the reviewers comment, we have re-formulated the corresponding section in the conclusions.

16) P2030, L25: It is mentioned that the SO2 measurements '... could be improved ... by optimising the spectrometer for the SO2 retrieval', but it is not stated how this can be done and why the instrument was not optimal during the FORMAT campaign.

During the measurements, the AMAXDOAS instrument was optimized for HCHO and NO2 retrieval, not for SO2 measurements. By improving throughput (use of a grating with a blazing angle at 300 nm, less viewing angles) higher spectral resolution and better straylight rejection (use of cut-off filter) the SO2 retrieval could probably be improved significantly. However, as mentioned by the reviewer due to the low intensity the SO2 signal will always be weaker as for example the NO2 signal. In response to the reviewers comment, we have added some of the above remarks to the text.

17) Technical corrections Please homogenise the spelling regarding U.S./U.K. English. Example: 'center' on L3 and 'centre' on L9 of P2026. P2018, L5: Replace 'sun-light' with 'sunlight'. P2019, L8: Replace 'air-borne' with 'airborne'. P2019, L10: 'Remote sensing measurements of ... have been performed using TOMS .... measurements': delete second 'measurements'. P2023, L2: According to the definition of _ as the angle between flight direction and wind direction, it should be sin(_) rather than cos(_)

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in Equation 1. P2026, L20: Replace "higher altitude" with "higher altitudes".

Changed as requested.

18) P2028, L4: What is 'N' standing for in the unit mg Nm-3?

the N term is an abbreviation of norm or normal. Normal, in this context, means a temperature of 0 degrees Celsius and a pressure of 1.013 bar, the conditions at which one mole of an ideal gas has a volume of 22.413837 litres.

19) P2029, L10: Replace 'or' with 'for'.

Done.

20) Figures 4 and 5: It would be useful for the reader if the locations discussed in the text (Cremona, Mantova, Porto Tolle) would be highlighted in the graphs of the SO2 and NO2 time series.

The figures have been changed as suggested.

21) Figure 6: For which viewing direction are the SO2 SCDs shown?

97 o (see figure caption)

22) Figure 9: From which viewing direction are the SO2 VCDs derived?

In figure 9 The SO2 VCD is calculated from 75_, This has been added in the figure caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 2017, 2005.