02/09/2014

Dear Prof. Ma,

With regard to the manuscript:

Journal: ACP
Title: Evaluation of tropospheric SO2 retrieved from MAX-DOAS measurements in Xianghe, China.
Author(s): T. Wang et al.
MS No.: acp-2014-10
MS Type: Research Article
Iteration: Major Revision

Please find below our responses to both referees comments. They also contain the changes implemented in the revised version of the manuscript. The latter are highlighted in yellow in the new manuscript.

Sincerely yours,

F. Hendrick (**franch@oma.be**)

Response to Anonymous Referee #1

First, we would like to thank Anonymous Referee #1 for his/her helpful comments.

Please find our replies below. We used the following color code:

Green: Referee's comment

Black: author's reply

Red: modified text in the revised manuscript

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)

I am very impressed about the efforts the authors have spent to account for the referee comments, leading to a significant improvement of the manuscript. I am fully satisfied with the replies on my previous comments and on the modifications of the manuscript, which now also cover a comparison between aerosols and SO2.

I therefore recommend a publication of the manuscript in ACP after the following minor technical issue has been resolved: The rows in the new Fig. 16 show data from different seasons. What do the three different columns mean? Is this data from different years?

The plots in Figure 16 correspond to the different months of the year and not to the seasons. To avoid confusion, the legend of the figure has been modified as follows:

'Figure 16: Scatter plots of aerosol extinction coefficient versus SO_2 concentration in the 0-200m layer for months 1-12 of the March 2010 – February 2013 period (first row from left to right is for J, F, M, respectively; second row for A, M, J; third row for J, A, S; fourth row for O, N, D). The data points correspond to the different MAX-DOAS scans. The red line denotes the linear least-squares fit to the data.'

Response to Anonymous Referee #2

First, we would like to thank Anonymous Referee #2 for his/her helpful comments.

Please find our replies below. We used the following color code:

Green: Referee's comment

Black: author's reply

Red: modified text in the revised manuscript

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)

Comments on "Evaluation of tropospheric SO2 retrieved from MAX-DOAS measurements in Xianghe, China" by Wang T, et al.

In this study, Wang et al. present important ground based MAX-DOAS observations in the urban atmosphere of Xianghe, China. The main results are the seasonal and diurnal variation of in-situ and tropospheric VCD SO2. Even though MAX-DOAS is a powerful technique which can be applied to retrieve several parameters simultaneously the results of SO2 presented here fit well for a publication in ACP after addressing the comments below.

Specific Comments:

In the DOAS analysis section it is mentioned that a daily noon reference spectrum taken at zenith is used for the retrieval of SO2 dSCDs. Past studies have shown that by using the zenith sky reference taken on the same scan the stratospheric and at some degree the free troposphere influence is cancel out, however if you use a single daily reference you might not correct for this. Why the current zenith sky spectra is not used as a reference spectrum for the retrieval of SO2 dSCDs?. For three years of measurements I would expect to some extent and for some days a significant contribution of SO2 in the stratosphere. If you are interested in tropospheric SO2 please expand in how the stratospheric and/or free tropospheric contribution are corrected. How is this treated in the transfer model?. Also, the same is applied for the aerosol extinction retrieval.

The DOAS analysis has been performed using daily zenith radiance spectra around local noon as reference but the bePRO profiling tool is applied for each scan to off-axis DSCDs minus the zenith DSCD interpolated at the time of each off-axis measurement using the zenith DSCDs of two consecutive scans. This allows to remove properly the contributions from the stratosphere during a scan. Nevertheless, we have also performed sensitivity tests using the zenith of the scan as reference for the DOAS analysis and these showed that no significant bias is introduced by making use of a single daily reference spectrum. It should be also noted that making use of a single daily reference allows for

better correction of the time shift between zenith observations and off-axis ones during a scan. For the sake of clarity, the first paragraph of Section 2.3 has been modified as follows:

'SO_2 vertical profiles are retrieved for each MAX-DOAS scan by using the bePRO profiling tool developed at BIRA-IASB (Clémer et al., 2010; see also Hendrick et al., 2014). It is based on the Optimal Estimation Method (Rodgers, 2000) and includes the LIDORT radiative transfer model (RTM) as a forward model. A two-step approach is implemented in bePRO: First, aerosol extinction profiles are retrieved from measured O_4 DSCDs. This step is needed because the aerosols strongly influence the effective light path in the atmosphere and therefore the optical density of trace gases like SO_2. Secondly, bePRO is applied to measured trace-gas DSCDs using the retrieved aerosol extinction profiles for the radiative transfer calculations (see below). Since the DOAS analysis is performed using daily zenith radiance spectra around noon as reference, bePRO is feeded for each scan with SO_2 and O_4 DSCDs obtained by taking the difference between off-axis DSCDs and the zenith DSCD interpolated at the time of each off-axis measurement using the zenith DSCDs of two consecutive scans. Proceeding this way allows to properly remove the contributions of the stratosphere from the measurements and is similar, at least for SZA < 75°, as taking the zenith spectrum of each scan as reference for the DOAS analysis.'

The authors suggest that anthropogenic SO2 plays a dominant role in the aerosol formation in winter compared to other sources, however the only evidence shown is the correlation coefficients of a simple linear correlation between SO2 and extinction coefficient at the surface. Please expand your description of the linear correlation, How was the data treated for this comparison?, was only significant data included?, Was the error in x-y weighted/applied in the correlation?, how are the outliers treated (this can bias the correlation coefficient)?. Also, please include a thorough description of why the correlation coefficients are used here. According with slopes of figure 16, there is not a seasonal variations. How do you explain this?.

As suggested by Referee #2 in the first review round, as well as in published studies (e.g., Lu et al., 2010; Veefkind et al., 2011), the spatial and temporal correlation between aerosols and SO_2 can be used to infer information on the SO_2 conversion and aerosol production, and thus on the contribution of SO_2 to the total aerosol content. That is the reason why the correlation coefficients have been used here. As mentioned in the manuscript (Page 9, line 26 -> Page 10, line 5), the entire paper, and thus also the correlation study between SO_2 and aerosols, is based on MAX-DOAS scans which satisfy the following quality criteria: RMS of the SO_2 retrieval RMS<15%, DFS>0.7 and no negative values in the retrieved profiles. This selection allows the rejection of low-quality retrievals, which represent 30% of the total number of scans.

Regarding the correlation study, we have applied the Pearson linear correlation method to the data points corresponding to individual MAX-DOAS scans. As suggested in the above Referee's comment, we have performed sensitivity tests by (1) removing SO_2 and aerosols data which are not in the 95% confidence interval, (2) taking into account the errors on the SO_2 and aerosols data, and (3) by combining (1) and (2). No significant change is found regarding the correlation coefficient seasonality and the linear least-squares fit after removing outliers and/or taking into account the errors on both SO_2 and aerosols data. So, the results of these sensitivity tests strengthen the marked seasonality of the correlation coefficients we obtained.

We don't have any satisfactory explanation on the absence of seasonality for the slope of the scatter plots. However, it is important to note that the intercept shows a strong seasonality with values much

larger than zero in summer, as can be seen in Fig. 16. This is consistent with the fact that at Xianghe, both SO_2 and aerosols have mainly anthropogenic origins in winter, while aerosol sources other than anthropogenic ones dominate in summer.

We have added these information in the revised manuscript (see our reply to the next comment below).

I am surprised by the suggestion that aerosol formation by SO in higher in winter. The amount and chemical mechanism used in formation of particles SO2 emissions depends largely in the atmospheric oxidants concentration and water vapor. On the other hand, SO2 can form particles as ammonium nitrate (NH4NO3) in the winter months. In order to know whether SO2 plays an important role I suggest to include scientific evidence in terms of water vapor and/or particle composition.

Given the data sets in our possession for the current study, the discussion/interpretation can only be speculative, based as much as possible on the existing literature. That's the reason why we wrote at the end of Sect. 3.4 that co-located measurements of the chemical composition of aerosols in Xianghe would be needed to further support our findings. However, our suggestion that aerosol formation by SO_2 is higher than by other precursors in winter is probably too speculative. What our results show is that anthropogenic SO_2, through the formation of sulfate aerosols, contributes more significantly to the total aerosol content in winter than in spring/summer where other important sources of aerosols are observed (dust, biomass burning). A similar feature was also found by Lu et al. (2010) using the correlation of SO_2 emissions versus AOD measured by the MODIS satellite instrument. Taking also into account the previous comment on the correlation method, Sect. 3.4 has been reformulated as follows:

'SO_2 is known as a major aerosol precursor through its conversion into sulfates and sulfuric acid by reaction with OH (see e.g. Ma et al., 2012). Since aerosol extinction profiles are retrieved in the first step of the SO_2 retrieval (see Sect. 2.3), our data set offers a unique opportunity to investigate the relationship between SO_2 emission and aerosol production in the Beijing suburban area. This will be done through a correlation study as in Lu et al. (2010) and Veefkind et al. (2011).

Fig. 16 shows monthly scatter plots of the SO_2 concentration versus aerosol extinction coefficient retrieved in the 0-200m layer for the March 2010 – February 2013 period. In all plots, data points correspond to MAX-DOAS scans satisfying the selection criteria based on the quality of the retrievals (see Sect. 2.3). A strong correlation (Pearson correlation coefficients in the 0.6-0.9 range) is obtained in J, F, M and O, N, D while a significantly lower correlation is observed in late spring/summer with correlation coefficients around 0.3 in J, J, A. Similar features are found from the scatter plots of SO_2 VCD versus AOD but also when outliers outside the 95% confidence interval are removed and/or the uncertainties on both SO_2 and aerosol data are taken into account (not shown here). The marked seasonality of the correlation between SO_2 and aerosols is further illustrated in Fig. 17 where monthly correlation coefficients for both surface concentration and integrated column are reported. The positive correlation (>0.2) observed throughout the year indicates that in most cases, high pollution events in Xianghe are associated with enhanced SO_2 and aerosol levels (Chan and Yao, 2008; Li et al., 2007). The higher correlation coefficients obtained in winter (>0.6) suggest that anthropogenic SO_2, through the formation of sulfate aerosols, is a major contributor to the total aerosol content during this period of the year. In late spring/summer, the Beijing area is strongly influenced by other sources of aerosols, especially particles emitted from massive agricultural fires in the surrounding region (Xia et al., 2013) as well as dust particles transported from the Kumutage and Taklimakan deserts in western China and from the Mongolian deserts (Yu et al., 2009). In combination to the lower SO_2 concentration, this could

explain the significantly weaker correlation between anthropogenic SO_2 and aerosols obtained in J, J, A. The intercept values much larger than zero found in summer scatter plots (see Fig. 16) further support the fact that aerosol sources other than anthropogenic ones dominate in summer, as also suggested by Lu et al. (2010) from a correlation study between SO_2 emission inventories and AODs measured by the MODIS satellite instrument. It is however important to note that co-located measurements of the chemical composition of aerosols in Xianghe would be needed to confirm our findings.'

The abstract and conclusions have been also modified accordingly.

Technical comments:

- Figure 1. An horizontal scale in the map would help to visualize path lengths in the vicinity of the measurements.

Done.

- In the DOAS analysis section it is explained that a SZA of 75 is used to exclude interference by O3. For clarity I would recommend to include in figure 2 the SZA.

We have added the SZA values corresponding to the local times in Figs. 2 and 3.

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