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

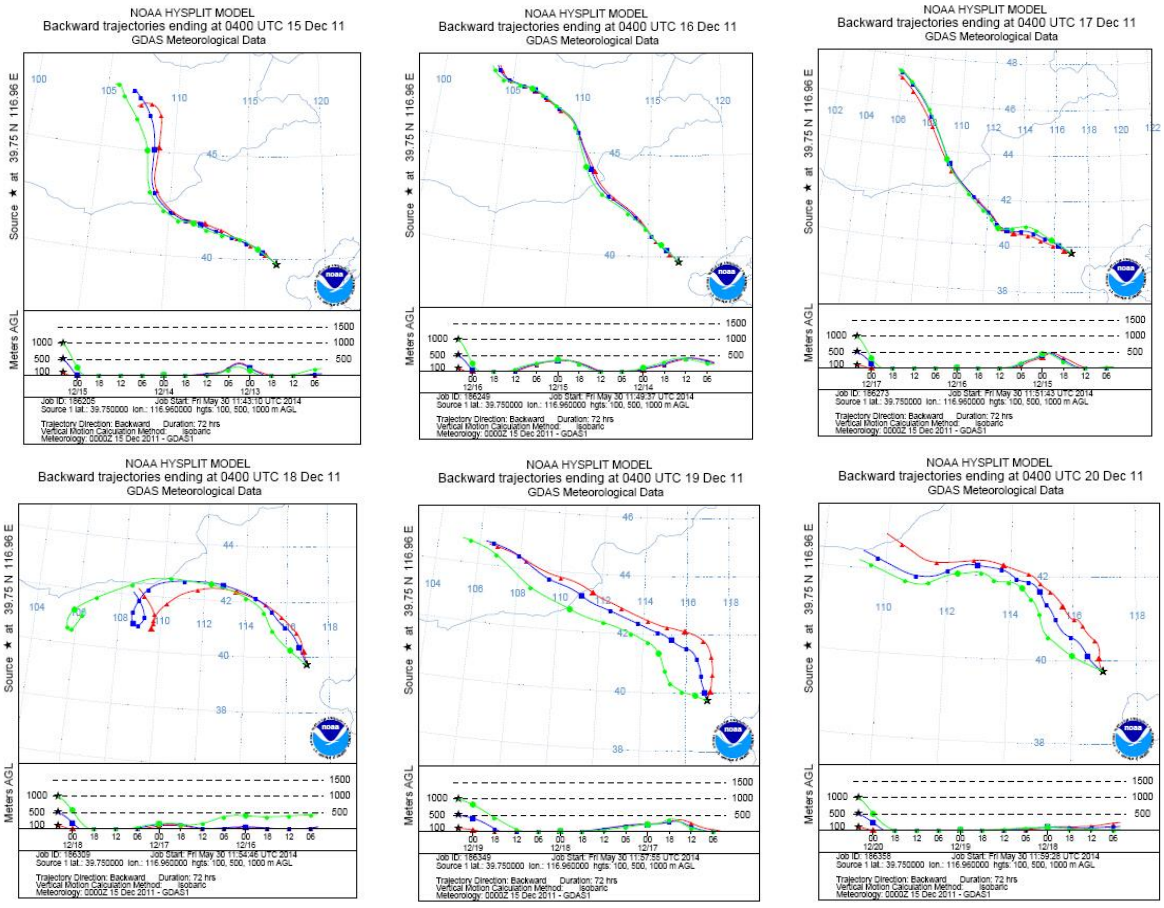
Black: author's reply

Red: modified text in the revised manuscript

The study of "Evaluation of tropospheric SO_2 retrieved from MAX-DOAS measurements in Xianghe, China" by T.Wang et al. presents the seasonal and diurnal variability of SO_2 in the boundary layer of Xianghe, China retrieved by ground based MAX-DOAS. The interpretation of the results is aided by independent in-situ SO_2 and meteorological measurements. The three years of MAX-DOAS measurements in the urban atmosphere of Xianghe, China, demonstrate the importance of this technique for air quality purposes and as indicator of boundary layer in-homogeneity. The manuscript is well written, however, it does not show an evident/noticeable novelty from the three continuous years of MAX-DOAS measurements, as they are not fully exploited. I suggest the publication of this manuscript after considering changes/improvements according to the comments below:

***Referee's comment #1**: According with the authors, the reliability of the SO_2 retrieval vertical profile is demonstrated with the comparison of the near surface concentration retrieval profiles with in-situ and independent SO_2 measurements. However, the sensitivity of air masses is quite distinctive for both methods. In-situ measurements detect air mass close to the instrument and might be able to detect localized air mass while moving close to the site. On the other hand, MAX-DOAS measures/averages the air mass over a long distance. From my point of view, this comparison is actually important in terms of air mass homogeneity in the boundary layer rather than validation process. I would recommend to use backward trajectories at different altitudes to identify air masses, especially aloft. This could help in a deep explanation of the vertical profile extent which is missing in the manuscript.*

Author's reply: To our opinion, the good agreement between MAX-DOAS and in-situ SO_2 measurements means that there is no major horizontal representativeness issues in these comparisons, probably because Xianghe is a sub-urban site not so much affected by local emissions, in contrast to the Beijing City Centre. Moreover, as suggested by Referee #2, we have performed backward trajectory calculations using the HYSPLIT model (https://ready.arl.noaa.gov/HYSPLIT.php) for the 9 days for which MAX-DOAS and in-situ data have been compared. Fig. A shows that in most cases , the air masses corresponding to the three selected altitude levels (100m, 500m, and 1000m) have similar origins and trajectories, coming mostly from the north (pointing direction of our instrument), indicating that in-situ and MAX-DOAS instruments are more likely detecting similar air masses. We have decided to not discuss this point in the revised manuscript.



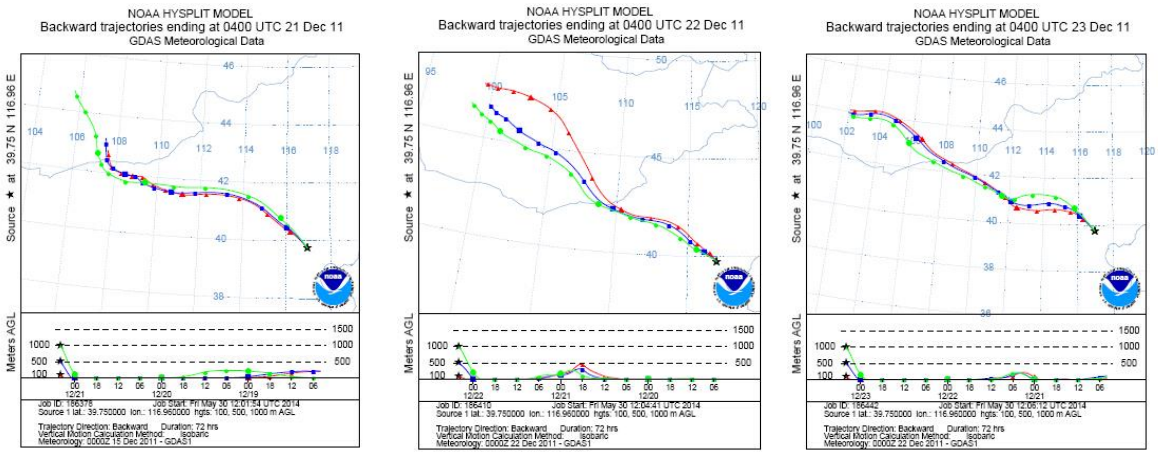


Figure A: Backward trajectories for the 15-23 December 2011 period (upper plots are for 15-17, middle plots are for 18-20, lower plots are for 21-23 December). The selected altitude levels are 100m (red), 500m (blue), and 1000m (green).

***Referee's comment #2**: One important advantage of MAX-DOAS over other techniques, is the capability of measuring several species simultaneously. In the present manuscript, solely results of SO_2 are shown, even though other species can be retrieved, such as NO_2, and aerosol extinction profiles. Undoubtedly the manuscript would improve if results of NO_2 and aerosol extinction (which are actually retrieved in the first step approach) are shown. The ratio of SO_2/NO_2 can be used, for example, as a metric to understand in more detail the emission level and atmospheric transport in the boundary layer. In the current manuscript meteorological conditions and qualitative seasonal domestic heating are used in order to know emission sources, however the metric SO_2/NO_2 ratio could be used adequately to know industry or power plant SO_2 episodes, not only at the surface but also in the vertical profile inside the boundary layer. On the other hand, the correlation of SO_2 and aerosol extinction would be important as an indication of SO_2 conversion and aerosol production.*

Author's reply: We agree with Referee #2 on the fact that the SO_2/NO_2 ratio is an important parameter for investigating the emission sources. This parameter has been investigated in several papers (e.g., Li et al., 2010; Chai et al., 2014). However, we think that looking at particular emission episodes from e.g. power plants and possible transport of SO_2 and NO_2 to Xianghe is beyond the scope of the present study, as it will require an important modelling part. The aim of the present paper is to describe this unique three-year data set of MAX-DOAS SO_2 observations and give reasonable explanations to what we observe. Once published, this data set could then be used for more detailed/dedicated studies like the one suggested by Referee #2.

Regarding point 2, we have included a new Section (3.4) on the relationship between SO_2 and aerosols in the revised manuscript. This relationship has been investigated through a correlation study of SO_2 VCD and surface concentration versus AOD and surface extinction coefficient, respectively. Here is the new Sect. 3.4:

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. A strong correlation (correlation coefficients in the 0.6-0.9 range) is obtained in JFM and OND while a significantly lower correlation is observed in late spring/summer with correlation coefficients around 0.3 in JJA. Similar features are found from the scatter plots of SO_2 VCD versus AOD (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 plays a more significant role in the aerosols formation during this period of the year due to its larger concentration and lower temperatures favoring the formation of sulfates (Lin et al., 2012). In late spring/summer, the Beijing area is more 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 JJA. However, measurements of the chemical composition of aerosols in Xianghe would be needed to further support our findings.

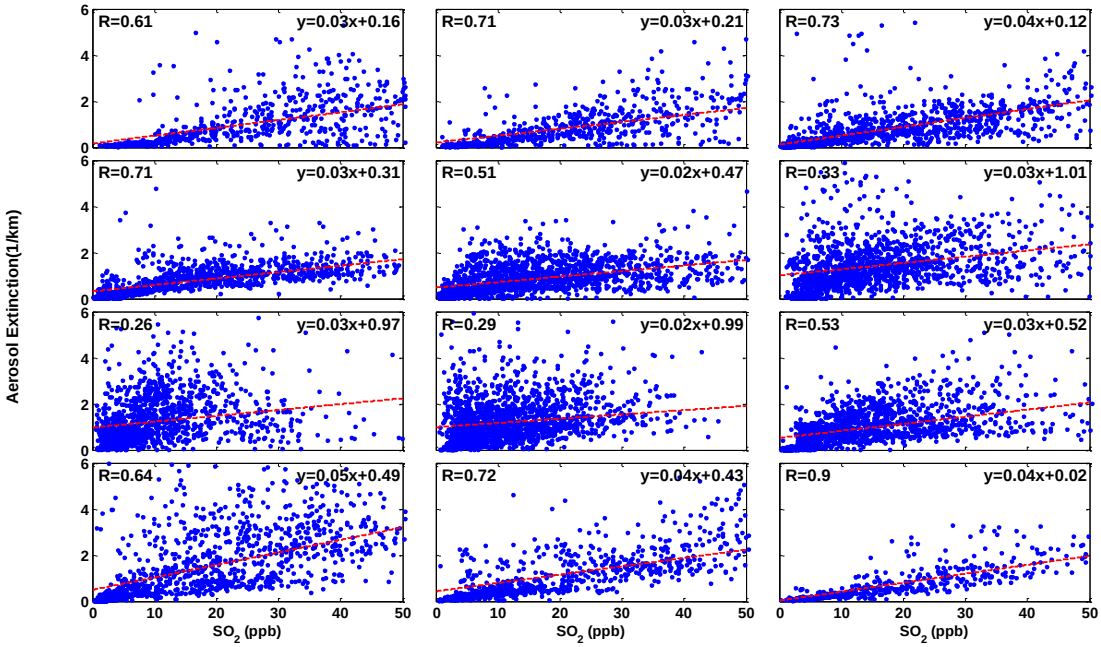


Figure 16: Scatter plots of aerosol extinction coefficient versus SO_2 concentration in the 0-200m layer for months 1-12 of the March 2010 – February 2013 period (first row is for JFM, second row for AMJ, third row for JAS, and fourth plots for OND). The data points correspond to the different MAX-DOAS scans. The red line denotes the linear least-squares fit to the data.

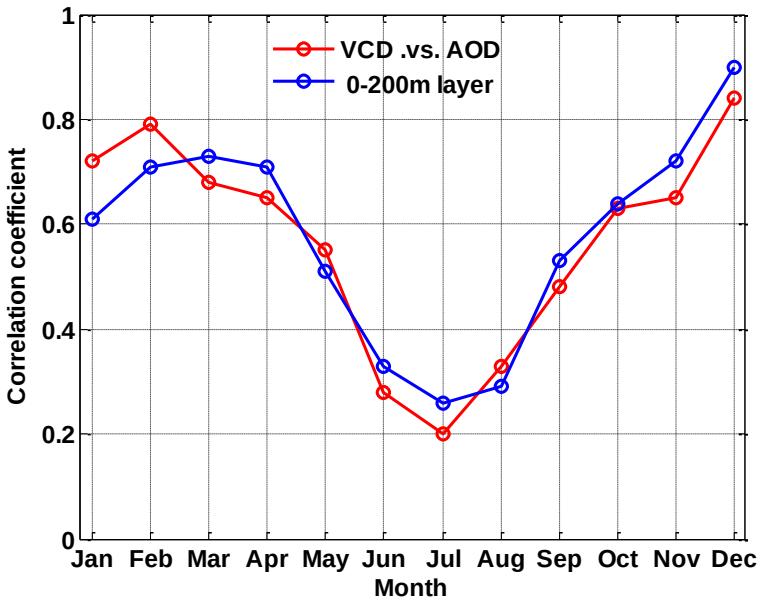


Figure 17: Seasonal variation of the correlation coefficient between SO_2 and aerosols over the March 2010-February 2013 period. The red curve corresponds to VCD versus AOD and the blue curve to SO_2 concentration versus aerosol extinction coefficient in the 0-200m layer.

The abstract and conclusions have been also modified accordingly.

***Referee's comment #3**: As pointed out in the introduction and in the conclusion, these three years of measurements are quite important for tropospheric SO_2 satellite validation/comparison. Have you thought in incorporating existing tropospheric SO_2 VCDs obtained with satellites and compare with your data?. Throughout the manuscript the main results, being the annual and diurnal cycles, are shown in terms of tropospheric SO_2 VCDs. Incorporating SO_2 VCD comparisons with satellite retrievals would improve the quality of the paper.*

Author's reply: We have done comparisons between satellite (OMI, GOME-2, and IASI) and MAX-DOAS SO_2 VCDs, but these will be part of a separate paper about the description of the BIRA-IASB satellite SO_2 products (OMI, GOME-2) and their validation (Theys et al., in preparation, 2014). As an illustration, the comparison with OMI is shown in Fig. B. We see that calculating the SO_2 AMF for OMI by using MAX-DOAS vertical profiles significantly improves the agreement between both data sets.

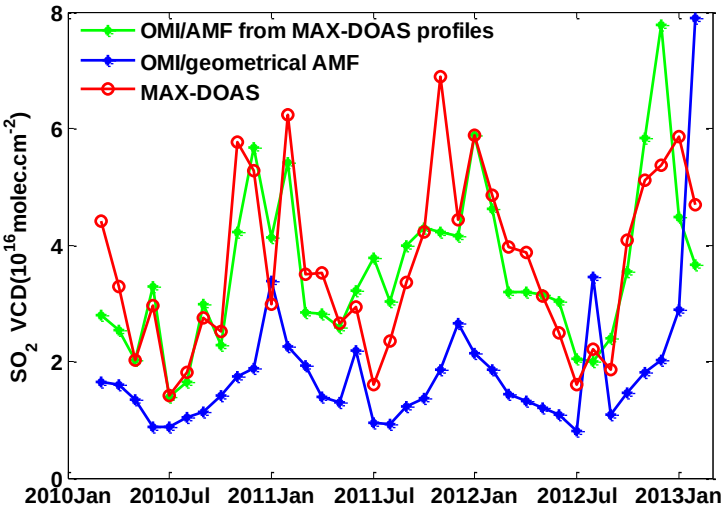


Figure B: Monthly-averaged SO_2 VCD of MAX-DOAS (red line), OMI/geometrical AMF (blue) and OMI/AMF from MAX-DOAS profiles (green) from March 2010 to February 2013.

Specific Comments

6505. DOAS analysis

***Referee's comment**: As pointed out in the introduction, SO_2 retrieval by MAX-DOAS have seldom been conducted in places far away from punctual sources such as volcanoes and/or industry. As far as I know, SO_2 retrieval represent a challenge due to absorption by stratospheric O_3 at the same*

wavelengths (< 325nm). In the DOAS analysis section it is mentioned that sensitivity tests were performed in order to choose the DOAS settings. Therefore, it would be valuable to know what kind of sensitivity tests were performed and applied in this work. I would recommend a detailed explanation and provide these results. This can be part of the supplementary information. Besides O_3 interference and DOAS analysis, more instrumentation details might be necessary For example, were filters used in the spectrometer system? It is known that instrument artifacts might lead to a bias due to noise in the spectral features.

Author's reply: The reliability and stability of the SO_2 DOAS analysis has been investigated through sensitivity tests on several key parameters, such as wavelength interval, choice of absorption cross sections, polynomial order, intensity offset terms. In the revised manuscript, we present the results of the sensitivity tests on the fitting window selection and discuss in more detail the ozone fitting. Here is the new text on DOAS settings (see page 5 line 18 -> page 6 line 17):

SO_2 fitting windows ranging between 303 and 325 nm have generally been used in previous studies (Bobrowski and Platt, 2007; Lee et al., 2008; Galle et al., 2010; Irie et al., 2011). At wavelengths shorter than 303 nm, the limiting factor is the strong ozone absorption which interferes with SO_2, leading to lower signal to noise ratio. At wavelengths longer than 325 nm, the SO_2 differential absorption signal becomes too weak. In order to identify the wavelength interval which minimizes both random and systematic uncertainties on SO_2 retrieval, 6 wavelength intervals have been investigated. The results of these sensitivity tests for two example days are presented in Figs. 2 and 3. On the first day (1st October 2011), the SO_2 content is minimum and stable in time. On the second day (4th October 2011), large variations of the SO_2 content occur, so the ability of the different intervals to give consistent and stable values can be verified. As can be seen, the 305-317.5 nm interval provides the lowest fitting errors throughout the day and the smallest dependence on the solar zenith angle (SZA) for both days. Due to the larger absorption and therefore interference by O_3 at large SZAs, it has been decided to exclude measurements taken at SZAs larger than 75°. For these tests, the following spectral signatures have been included: SO_2, O_3, NO_2, and the Ring effect (Grainger and Ring, 1962; Chance and Spurr, 1997). Daily zenith-sky radiance spectra recorded around local noon have been selected as reference. To account for the temperature dependence of the ozone absorption, cross sections at 2 different temperatures (223°K

and 243°K) were used according to Van Roozendael et al. (2006). A fifth-order polynomial is applied to fit the low-frequency spectral structure due to Rayleigh and Mie scattering and instrumental effects. Attempts to further adjust these settings, e.g. by adding BrO cross-section or by including additional ozone correction terms according to Puķīte et al. (2010) were not successful (less stable retrievals with larger noise on the SO_2 DSCDs).

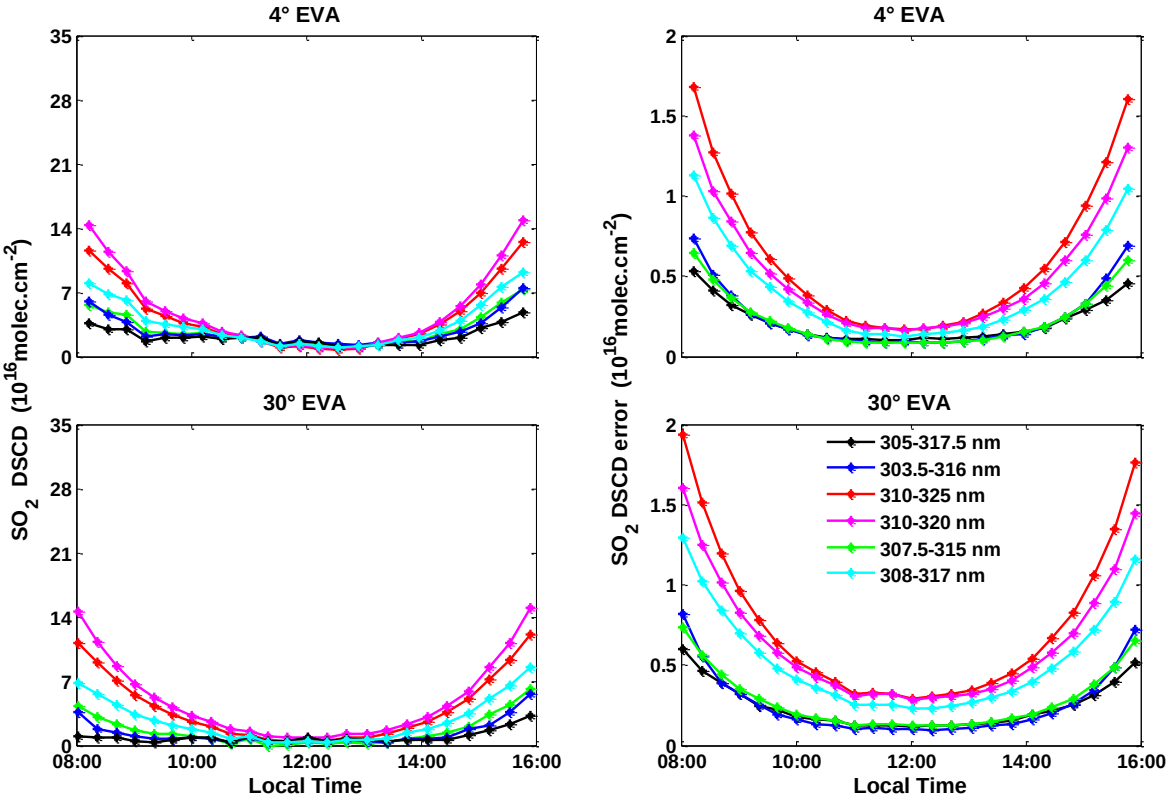


Figure 2: SO_2 DSCDs (1st column) and corresponding fitting uncertainties (2nd column) retrieved at 4° (upper plots), 30° (lower plots) elevation for different wavelength intervals on 1st October 2011.

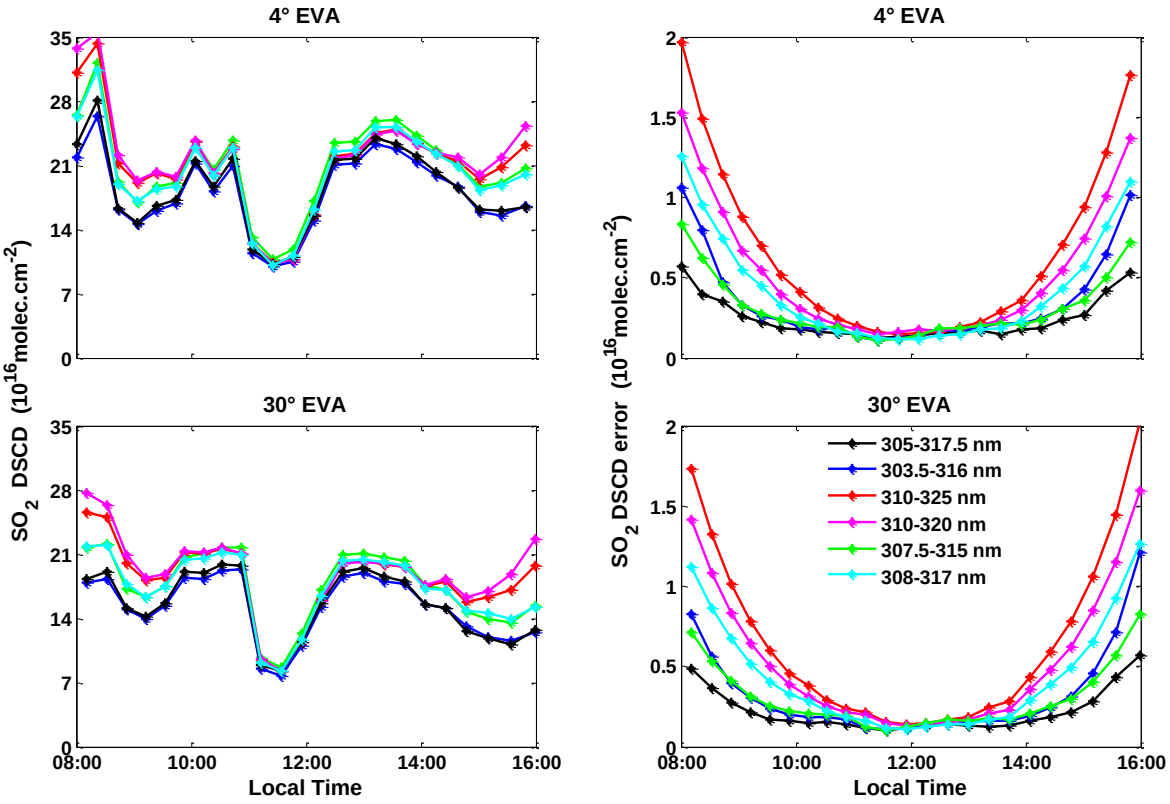


Figure 3: Same as Figure 2, but for 4th October, 2011.

Regarding the second point (instrumental set-up), we used for the UV channel a band-pass filter (Hoya U340) centered at 340 nm in order to avoid stray light from the visible range.

***Referee's comment**: In the same section it is mentioned that the residual achieved in the fitting example is small, ranging from -2×10^{-3} to 2×10^{-3}. Please provide more information about the quality of the DOAS analysis. Please explain why a value of 2x10^{-3} residual error is small? What is considered a good fit residual, and RMS, etc. Since this is the first SO_2 measurements of the MAX-DOAS what would be the detection limit of the MAX-DOAS (or please include a reference where this is mentioned).*

Author's reply: We agree that the sentences 'We see that the residual is small, ranging from -2×10^{-3} to 2×10^{-3}, which indicates a limited retrieval error. In this illustrative case, the retrieved SO_2 DSCD is 7.27×10^{16} molec·cm^{-2}.' suffer from a lack of clarity and can be misleading. We have reformulated this part as follows including a discussion about the detection limit:

'We see that fitting residuals range in between -2×10^{-3} and 2×10^{-3}, corresponding to a root-mean-squares (RMS) of 9×10^{-4}, which appears to be small in comparison to the SO_2

differential structures presented in the lowest panel of the figure. The typical fitting uncertainty on SO_2 DSCDs is of about 1-6x10^{15} molec·cm^{-2} (less than 10%), and for the case illustrated here, corresponds to 2%. For near-noon conditions, the detection limit on the SO_2 DSCD can be conservatively estimated as 3 times the one-sigma uncertainty on the slant column, which means approximately 3x10^{15} molec·cm^{-2}. This detection limit is similar for the vertical columns estimated using the geometrical approximation at 30° elevation (see Sect. 2.3). Vertical columns derived from the full inversion generally have a smaller detection limit, owing to the gain in sensitivity obtained when including near horizontal viewing measurements.'

6506. Profile Retrieval

***Referee's comment**: It is mentioned that aerosol extinction and SO_2 vertical profiles are obtained by means of a non-linear approach. Usually this is the case for strong absorbers such as aerosols. Is SO_2 considered a strong absorber? could you apply a linear inversion and save time in the analysis?*

Author's reply: Actually, both the linear and the non-linear iterative approaches have been implemented in our profiling algorithm. For strong absorbers like O_4, the non-linear iterative approach is used. In case of weak absorbers like NO_2, HCHO, SO_2, the linear method is selected. This is corrected in the revised manuscript (see page 7, lines 12-15).

***Referee's comment**: The retrieval approach is based in a two-step approach. First, the aerosol extinction is retrieved at different wavelengths and then is extrapolated to a shorter wavelength using just the AOD, the Angstrom formula, and an exponential profile shape. The determination of the aerosol extinction based in the O4 has been demonstrated before, but it is not well explained how and why the AOD, the Angstrom formula, and the exponential decrease profile were used here. In order to know the spectral dependence of the aerosol extinction and/or AOD you might need at least two wavelengths. Please describe what wavelengths you used in this step. Also, explain why the AOD was used with an exponential profile shape instead of applying the aerosol angstrom exponent approximation to the aerosol extinction profile?*

Author's reply: The application of the Ångström exponent approximation is discussed into more details in the revised manuscript. In AERONET database, 5 different Ångström exponents are

available: 340-440nm, 380-500nm, 440-675nm, 440-870nm, 500-870nm. The 340-440 nm exponent, which is closest to the SO_2 fitting interval (305-317.5nm) has been used in a first approximation. It is now applied directly to the retrieved aerosol extinction profiles instead to the AODs (and then assuming exponentially decreasing extinction profiles). The corresponding mean scaling factor for converting aerosol extinction profiles from 360 to 313 nm is of 1.16±0.06. SO_2 vertical profiles have been retrieved with these new aerosol extinction profiles and all figures and Table 1 in the revised manuscript have been updated with these new aerosol and SO_2 data sets. Results and findings remain similar to those obtain with the previous data set, except the retrieved profile shape in spring and fall which now displays a maximum in the 200-400m layer instead of in the first layer. The discussion on the profiles is modified accordingly in the revised manuscript (see page 10, lines 18-20).

We have proceeded to the following text changes for addressing this comment: (see page 8, line 16 -> page 9, line 1):

The sentences 'Since the DOAS fitting intervals are different for SO_2 and aerosols, the aerosol extinction profiles utilized as input for the calculation of SO_2 weighting functions have been derived by converting the AODs retrieved in the 338-370 nm wavelength range to the 305-317.5 nm interval using the Ångström formula (Cachorro et al., 2000), and assuming an exponentially decreasing profile shape with a SH of 0.5 km (see Eq. 2).'

have been replaced by

'Since the DOAS fitting intervals are different for SO_2 and aerosols, the aerosol extinction profiles utilized as input for the calculation of SO_2 weighting functions have been derived by directly converting the aerosol profiles retrieved in the 338-370 nm wavelength range to the 305-317.5 nm interval using the Ångström exponents (Cachorro et al., 2000) retrieved from collocated CIMEL/AERONET sunphotometer measurements (Holben et al., 1998; see http://aeronet.gsfc.nasa.gov):

$$\text{Extinction}(z, 313\text{ nm}) = \text{Extinction}(z, 360\text{ nm}) \times (313/360)^{-\alpha} \quad (3)$$

where z is the altitude and α is the Ångström exponent.

The 340-440 nm exponents are used in a first approximation since values for a wavelength range closer to the SO_2 fitting interval (305-317.5 nm) are not available so far. The corresponding mean scaling factor for the March 2010 – February 2013 period is of 1.16±0.06'

Referee's comment (6510):

I suggest to change "A very good agreement is found between both data sets, indicating the good overall reliability and the robustness of our MAXDOAS retrievals" according with the comments above.

Author's reply: For the reasons given above (see our reply to the first general comment), we have decided to keep this sentence as is.

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