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Atmospheric Measurement Techniques Discussions

Interactive comment on "Novel SO_2 spectral evaluation scheme using the 360–390 nm wavelength range" *by* N. Bobrowski et al.

N. Bobrowski et al.

nicole.bobrowski@iup.uni-heidelberg.de

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Detailed response to the reviewer 2 comments:

We would like to thank reviewer 2 for the detailed and helpful comments and suggestion he made to improve the quality and clarity of our manuscript.

For reference the original comments are always included followed by our response.

1 Introduction

* It would be better to split section 1 into two sections: an introduction and a section with a more detailed description of the current retrieval approach. In the current introduction, the background information about the ground based measurements is rather limited,

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and a general description of atmospheric SO2 (natural and anthropogenic sources, impact on chemistry and climate etc.) and of satellite SO2 measurements is missing completely.

We are not seeing the point to split the introduction in subsections. In view of the large number of articles and books available on the subject we don't think that the inclusion of background material (on ground based measurements and on atmospheric sulphur) would fit very well in the scope of this article to be appearing in an technical journal, nevertheless we could make the following additions (including additional lit. references) to the introduction, if the editor should as well see the need of a more general introduction to the sulphur subject.

line 24 ff "Sulphur influences chemistry as well as climate and can negatively affect our health. It has been known for long time that sulphur species are naturally released to the atmosphere through volcanism (mainly as SO2 and H2S) or biological processes - decay of organic matter (H2S, CH3SH or CH3SCH3) and sea spray (sulphate). After industrialization anthropogenic sources have increased and are comparable in magnitude to natural ones since the early 20th century. Sulphur aerosol affects the radiation balance of the atmosphere directly (i.e. cooling by sulphate particles) and indirectly by acting as cloud condensation nuclei (CCN). SO2, SO3, H2SO4 are aerosol precursors, which lead to cloud formation and serve as surfaces for heterogeneous chemistry. The modification of the cloud properties by sulfate aerosol is associated with a cooling effect [e.g. Lohmann and Feichter 2005]. The sulphur particles enhance the number of aerosols and therefore increase the albedo. The result is a reduction of the direct incoming sunlight radiation." Since the eruption of El Chichon 1982 SO2 when SO2 was detected by satellite measurements for the first time through the Total Ozone Mapping Spectrometer (TOMS) on the Nimbus-7 satellite (Krueger 1983) and later, the algorithms and instruments to detect SO2 from space are since then under continous improvement (e.g. Eisinger and Burrows, 1998, Khokar et al. 2005, Krotkov et al. 2006, Lee et al. 2008, Krueger et al., 2008)

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Krueger, A.J. (1983) Sighting of El Chichon sulfur dioxide clouds with the Nimbus 7 Total Ozone Mapping Spectrometer. Science, 220, p. 1377-1378.

Krueger, A.J., L.S. Walter, P.K. Bhartia, C.C. Schnetzler, N.A. Krotkov, I. Sprod, and G.J.S. Bluth. (1995) Volcanic sulfur dioxide measurements from the Total Ozone Mapping Spectrometer (TOMS) Instruments. Journal of Geophysical Research, 100, D7, 14,057 - 14,076.

Eisinger, M., and J. P. Burrows: Tropospheric Sulfur Dioxide observed by the ERS-2 GOME Instrument. – Geophys. Res. Lett., No. 25, pp. 4177-4180, 1998.

Khokhar, M. F., C. Frankenberg, S. Beirle, S. Kühl, M. Van Roozendael, A. Richter, U. Platt and T. Wagner, Satellite Observations of Atmospheric SO2 from Volcanic Eruptions during the Time Period of 1996 to 2002, Journal of Advances in Space Research, 36(5), 879-887, 10.1016/j.asr.2005.04.114, 2005

Lee, C., Richter, A., Weber, M., Burrows, J. P., SO2 retrieval from SCIAMACHY using the weighting function DOAS (WFDOAS) technique: comparison with standard DOAS retrieval, Atmos. Chem. Phys., 8, 6137-6145, 2008

Krotkov, N. A., Carn, S. A., Krueger, A. J., Bhartia, P. K., Yang, K., 2006: Band residual difference algorithm for retrieval of SO2 from the Aura Ozone Monitoring Instrument (OMI), IEEE Trans. Geosci. Remote Sensing, AURA Special Issue, 44(5), 1259-1266.

Krueger, A., Krotkov, N., and Carn, S.: El Chichon: The genesis of volcanic sulfur dioxide monitoring from space, Journal of Volcanology and Geothermal Research, 175, (4), 408-414, DOI: 10.1016/j.jvolgeores.2008.02.026., 2008.

* P865, 7-19: It is not fully clear to me with phenomenon is meant here. Does it refer to the I0- effect?

No, we don't refer to the I0-effect her. Rather we describe a phenomenon occuring because of the finite spectral resolution of a DOAS instrument, thus it does not directly measure optical densities,but the light intensity convoluted with the instrumental func-

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tion. For large optical densities (in case of σ times SCD is not much smaller than unity) , the convolution and the exponential function are not commutative (for a detailed explanation, see Wenig et al. 2005 or Platt and Stutz 2008. The common DOAS approach: τ = ln(H x (exp(σ âŃĚ SCD))) = SCD (H x σ) is only valid for weak absorbers! For strong absorbers like SO2 in a volcanic plume an itarative approach like the one from Frankenberg et al. 2005 should be in theory applied. See also comment to Andreas Richter (referee 1)

To keep the text flow we only added some references:

Kern C, Spectroscopic measurements of volcanic gas emissions in the ultra-violet wavelength region. Ph.D. thesis, University of Heidelberg, 318 pages, Heidelberg, 2009. http://www.ub.uni-heidelberg.de/archiv/9574

Volkamer, R., Etzkorn, T., Geyer, A., and Platt, U.: Correction of the oxygen interference with UV spectroscopic (DOAS) measurements of monocyclic aromatic hydrocarbons in the atmosphere, Atmos. Environ., 32, 3731–3747, 1998.

Wenig M., Jähne B., and Platt U. : Operator Representation as a new differential optical absorption spectroscopy formalism, Appl. Optics 44 (16), 3246-3253,2005.

* P866-867: The three problems described here are also related to the use of the traditional DOAS approach in the 310-330 nm wavelength range. It would be interesting to know to what extend these problems can be resolved by applying a modified DOAS method (Marquard et al., 2000) in this wavelength region. Issues like the temperature dependence of the SO2 absorption cross-sections and the strong ozone absorption that complicates the satellite retrieval in this wavelength region should be mentioned here as well.

We added to the following text : “In principle these effects could be corrected for by using modified DOAS approaches (e.g. Marquard et al., 2000). However, especially for very strong absorptions not only the total optical density but also the profile shape

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become important, preventing a simple parametrisation of the correction. In extreme cases the observation might become even completely insensitive for the lowest part of the SO2 plume."

Cross sections of SO2 in various temperatures are available, but the influences of temperature is a minor error of the evaluation accounting for not more than about 15 % in SCD (Kern, 2009, Bobrowski, 2005). In this section, which deals with problems related to radiative transport, it would be confusing for a reader to read about spectroscopical issues recarding cross sections therefore we added only a short sentence including also the mentioned issue of O3 in the introduction section:

"Two other spectroscopic issues can potentially lead to minor errors in the evaluation. For one, the SO2 absorption cross section is slightly dependent on temperature thus leading to an imperfect fit if the temperature of the measured gas deviates from the temperature at which the cross-section was measured. Secondly, the O3 absorption in the lower part of the SO2 evaluation wavelength range can be sufficiently strong to interfere with the SO2 evaluation. Both of these effects are however usually of subordinate importance compared to the other spectroscopic errors mentioned above. "

* 3 Sample measurements and evaluations

P870,10-13: The SO2 spectrum and SO2 Reference in Fig. 1a seem to be a perfect fit. For the very large SO2 column measured here (600 DU), one would expect significant difference between the SO2 spectrum and SO2 Reference (similar to that in Fig 2a) because of the limitations of the classical DOAS approach in this wavelength region. Please clarify.

Figure 1a might seem on the first look a perfect fit, but having a closer look you will note that that the residuum is high with about 70 promille and also the O3 fits bad, with every nm into the lower wavelength region the fit gets even more problems. With the better Figure resolution of Figure 1 you might also notice more clearly that the SO2

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itself does not fit perfect in its minima and maxima.

* P870,15: Why is the estimated error in the slant column density (0.1 molec/cm2) smaller than for the long wave UV window? For the GOME-2 example in section 3.2, the estimated error is larger for the short wave UV window.

The given error is strictly valid only under the assumption that the residuals are of random nature. Especially in the short wavelength range this assumption is clearly not valid.

We added the sentence:"Although the error of the SCD seems to be higher in the longer wavelength region, this is only because the given 'Fit error' assumes a random residuum. As this is obviously not the case for the short wave UV retrieval, the 'Fit error' is not a good measure of the measurement error in this case (see Stutz and Platt 1996) "

* P870,24-26: Are there any independent measurements available to validate the SO2 columns from the mini MAX-DOAS system?

Unfortunately there are no other independent measurements. One possibility is for sure the FTIR technique but this technique can be used only under certain conditions, because of the need of direct view to the light source, either to an artifical one (only close to the source measurements are possible) or direct sun, which requires a clear day. Unfortunately, up to now we did not manage to combine our measurement with FTIR ones, but plan to do it in future field campaigns. If the referee has additional suggestions for other techniques we would be glad to know about it.

* P871,1-6: Point 1 and 3 seems to be closely related. Is Point 3 (a wavelength dependent air mass factor) not one of the effects caused by high optical densities?

Although both effects are related to strong SO2 absorption, they should be kept separated. Also, they are both the result of the standard DOAS approach exceeding its limits. On the end of section 3.1 we added the text :

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"The first point deals with the (apparent) saturation of SO2 absorption lines occurring at high optical densities. In such cases, a convolution of the SO2 absorption cross-section performed in optical density space does not quite match the optical density measured by the instrument (even if the light path of all measured photons is the same). The true measurement can be described by a convolution of the incident intensity with the spectrometer's instrument function. After the measurement, the logarithm is applied to obtain the optical density. For high optical densities, the logarithm and the convolution are not commutative, and the convolution must instead be performed in intensity space (see answers to Reviewer 1 comments and Wenig et al. 2005).

The effect described by point 3 deals with the radiative transfer in and around the volcanic plume. SO2 absorption in the plume is sufficiently strong to significantly influence radiative transfer. The average light path in the plume is much shorter for wavelengths at which absorption is high (peaks of the SO2 absorption cross-section) than at wavelengths where the absorption is weaker (dips in the absorption cross-section). Therefore, the measured column density is a function of wavelength, a fact that is not taken into account in simple DOAS retrievals. However, the dependency of the measured column density of SO2 can be used to gain information on the radiative transfer in and around the plume (Kern et al 2010), thus correcting the associated errors."

* P872,5-8: What is the theoretical background for including this second ozone cross-section in the fit? Is there a reference about this method?

The second O3 reference spectrum was included to consider the wavelength dependence of the O3 AMF caused by Rayleigh scattering (see e.g. Pukite et al., 2010). Especially for strong ozone absorption at large SZA the fit residual could be reduced including this second O3 reference spectrum. The GOME-2 SO2 analysis is briefly described in the following reference:

Heue,K.-P., Brenninkmeijer, C. A. M., Wagner, T., Mies, K., Dix, B., Frieß, U., Martinsson, B. G., Slemr, F., and van Velthoven, P. F. J.: Observations of the 2008 Kasatochi

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volcanic SO2 plume by CARIBIC aircraft DOAS and the GOME-2 satellite, Atmos. Chem. Phys., 10, 4699-4713, doi:10.5194/acp-10-4699-2010, 2010.Âă

PuÄůÄńte, J., Kühl, S., Deutschmann, T., Platt, U., and Wagner, T.: Extending differential optical absorption spectroscopy for limb measurements in the UV, Atmos. Meas. Tech., 3, 631-653, doi:10.5194/amt-3-631-2010, 2010.)

The two references and a brief explanation were added to the text.

* P872,16-17: Can you include a more quantitative comparison of the AMF and vertical column density for the two wavelength regions (in addition to the slant column density comparison)? It should be relatively easy to calculate an AMF for the centre wavelengths of the two fitting windows.

We added figure 7, for further description, see also comment to the review of Andreas Richter (referee 1).

* P872,17-20: The unexplained systematic structures in the residual are not only a result of the dependence of the SO2 AMF on the wavelength. It is likely that the simple treatment of the Ring effect and the strong ozone absorption contribute to the residual structures as well.

We agree with the reviewer, this is indeed possible, we included in the section "satellite measurement examples" the statement : " partly caused by imperfect corrections of the Ring effect and ozone absorption, but mainly by "

* P873,3-4: Please indicate in fig 3 the locations of the GOME-2 measurements with the maximum SO2 columns. Do I understand it correctly that the two DOAS analyses from fig 2 have been done for two different GOME-2 measurements? This should be mentioned in the text.

The pixels with the maximum columns are now indicated. by a white star. The DOAS analyses from fig 2 was of course done for the same GOME-2 pixel for the Kasatochi eruption at 8th of August 2008 (21:25UTC, center pixel coordinates 167.88W 49.69N).

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Thus, it shows the large differences for the two evaluation fit windows (mostly because of the non-linearity effects for the short UV wavelength range).

* P873,11-14: The assumption of a decreased sensitivity for high SO2 columns can be verified by calculating the AMFs for this measurement. One would expect very small values of the AMF in this case.

We added a new Figure (No. 7) showing that there are indeed quite small AMF values for the wavelength region at 315 nm at high VCD's

* 4 Discussion

As explained here, both the sensitivity/detection limit and the signal to noise ratio play an important role for the DOAS fit in the long wave UV region. Can you provide more quantitative information about the detection limit and the estimated slant column density error? (here it is only mentioned that there is a loss in sensitivity of about an order of magnitude) For example, is it possible to detect moderate SO2 enhancements (e.g. 5-10 DU) in the long wave UV region? If so, it would be interesting to include another example of a smaller eruption (e.g. Etna) as well.

Unfortunately 5-10DU units will not be detectable with this long wave UV region, as already stated in the abstract and also later mentioned in the paper; the alternative wavelength range (360-390 nm) works "in conditions where high SO2 column densities prevail"

No changes to the text were made.

* 5 Model studies

P867,5-8: Here, the retrieved slant column densities are compared with the modeled straight column (i.e. without applying an AMF). Is the short wave UV window described as "better" because the AMF for 320 nm is closer to 1? Why is the larger sensitivity of long wave UV window not preferable in this case ?

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The long wave UV window does not exhibit a higher sensitivity to the SO2 in the volcanic plume. While it is true that the SO2 column densities retrieved from the measured spectra using a standard DOAS evaluation are about twice as high than those obtained in the short wave region, this does not imply a higher sensitivity. The sensitivity of a DOAS instrument to a certain absorber is given by the inverse of the instrument's detection limit regarding this species (see Kern 2009, section 3.4.3). This is approximately equal to the product of the absorber's differential absorption cross-section, the square root of the (normalized) incident radiation, and the air mass factor. Although the air mass factor is about twice as high for the long wave UV region as for the short wave region and the square root of the intensity is typically also 2 times higher, the differential absorption cross-section is 2 orders of magnitude smaller. Therefore, the sensitivity is still more than an order of magnitude lower for the long wave UV region than for the short wave UV region.

However, the accuracy of DOAS measurements of volcanic plumes is frequently not limited by the sensitivity of the instrument, but rather by the complex radiative transfer of the measured radiation. The SO2 absorption can be so strong as to completely block radiation at certain wavelengths (where the SO2 absorption cross section peaks) from entering into the interior of the plume. In such cases, no information about this region of the plume can be obtained from the measurement. In these cases, it is better to switch to the long wave region, where sensitivity may be inferior, but where radiation is not as strongly absorbed and can penetrate the plume. Therefore, the long wave region is "better suited" for an accurate retrieval. One such example is given in the manuscript. However, it is clear that this may not be valid for all scenarios. This is now stated more explicitly in the manuscript. See also response to the comment of Andreas Richter.

* P877, 19-21: It would be interesting to know the vertical columns that corresponds to the SCDs plotted in fig. 6.

We added new figures showing the SO2 VCDs (Figure 3d) and the dependence of the

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SO2 AMF on the SO2 VCD (Figure 7) to the revised version of our manuscript.

* P878,9-10: It is not clear to me what is meant with: “Good agreement for the upper bound of measured SO2 SCDs for 315 nm is found for an assumed aerosol optical depth of about 3”

As also pointed out by the other reviewer, the SO2 AMF (and thus also the SO2 SCDs) strongly depend on several parameters (like e.g. the vertical profiles of SO2, aerosols, clouds). Thus the model simulation can not be assumed to be representative for all observations. Interestingly, it is found that the simulations assuming an aerosol OD of 3 seem to be representative for the upper bound of the measured values.

* Minor Comments P864,17: please correct/add references Noxon, 1975 and Perener et al., 1976

done

* P865, 6-7: Since the DOAS method is also widely applied for ozone retrieval in the UV wavelength range, this sentence should be changed.

We changed the sentence "The DOAS method is usually applied to weak absorbers with optical densities below approximately 0.05.“ to: "The DOAS method is usually applied to weak absorbers with optical densities below approximately 0.05 (an exception are retrievals of stratospheric O3).“

* P867-868: Please add a reference to fig. 4 in section 2 as well.

We added a reference to fig 4 to section 2, changing the sentence: "In the following we refer to the two evaluation windows as the “long wave UV” and “short wave UV” windows, respectively.“ to: "In the following we refer to the two evaluation windows as the “long wave UV” and “short wave UV” windows, respectively (see Figure 4).“

* P872,24: please add reference Burkholder et al., 1990 and Vandaele, 1997

The two references were corrected (it should be Greenblatt et al., instead of Burkholder

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et al.) and added in the script.

Greenblatt, G. D., Orlando, J.J., Burkholder, J.B., and Ravishankara A.R.: Absorption Measurements of Oxygen Between 330 and 1140 nm, J. Geophys. Res., 95(D11), 18, 577–18, 582, 1990.

Vandaele, A.C., Hermans, C., Simon, P.C. , Carleer, M., Colin, R., Fally, A., Mérienne, M.F., Jenouvrier, A. and Coquart, B.: Measurements of the NO2 absorption cross-section from 42000ÂăcmÂă−Âă1 to 10000ÂăcmÂă−Âă1 (238–1000Âănm) at 220 and 294ÂăK. Journal of Quantitative Spectroscopy and Radiative Transfer 59 , 171–184, 1997. * P873,14-15: Fig 3c only illustrates the large differences between the two wavelength ranges

We agree that Fig. 3c provides no new information. Nevertheless, we feel that in comparison with Fig. 3a it nicely demonstrates the strength of the effect of the wavelength dependence of the SO2-AMF. We therefore prefer to keep Fig. 3c.

* P884, Fig 1: The quality of this figure could be improved, the lines are not clear (Fig 2 is better)

We increased the resolution of Figure 1 it should have now a quality comparable to Figure 2.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/3/C651/2010/amtd-3-C651-2010-supplement.zip

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