Answers to Interactive comment on "Retrieval of absolute SO_2 column amounts from scattered-light spectra – Implications for the evaluation of data from automated DOAS Networks" by Peter Lübcke et al.

Dear Editor,

We like to thank referee #4 for the comments and suggestions. We implemented most of the suggestions into the revised version of our manuscript and give detailed reasons in the cases where we could not follow the reviewer's suggestions. With these changes (and those in response to the other reviewers' we are confident that the revised manuscript has improved considerably. Please find the comments (in normal face) and our detailed answers (in bold face) below:

Anonymous Referee #4
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This paper presents an approach to analyse UV scattered sunlight spectra of volcanic plumes, such that an absolute rather than relative quantification of SO2 slant column amounts can be achieved. The motivation for this approach is that the NOVAC network of scanning UV spectrometers has used since its inception an approach where a reference spectrum from within each scan is used to remove solar spectrum features. SO2 values are then offset by the minimum SO2 value in each scan. This has the advantage of excellent solar feature removal, but also means that if SO2 is ubiquitous then the minimum SO2 value will not represent zero SO2, and an underestimate of column amounts will affect the scan, leading to flux underestimates. On the contrary, by using an absolute method for SO2 retrieval this problem is addressed.
We thank the referee for the comments and the good suggestions, however we do not agree to all of the referee's opinions and will give detailed reasons for this below.

The approach proposed is effectively identical to that reported in Salerno et al. 2009a, which has been applied successfully by INGV Italy to the scanning UV spectrometer SO2 flux monitoring networks on Etna and Stromboli since 2006. Salerno 2009a used a high resolution UV solar spectrum (Kurucz et al., 1984) to model the Fraunhofer features of the solar spectrum, whereas Lubcke et al. use the Chance and Kurucz (2010) Solar atlas.
We strongly disagree with this criticism. While both methods use a version of the Chance and Kurucz Solar atlas spectrum as a baseline to model the FRS, its implementation and details of retrieval are quite different which makes a large difference in both, implementation as well as applicability of the approaches. Salerno et al. 2009a empirically tuned different evaluation parameters in order to reproduce the SO_2 column density of calibration cells with a known column amount. The authors later applied the settings they found for two instruments to three different instruments and found good evaluation performance.
However, their approach suffers from some limitations. For example, during the procedure they made choices that are not reasonable from a physics standpoint. The authors used different instrument line functions for the convolution of the FRS, the O_3 and the SO_2 absorption cross-sections. These errors were most likely made in order to reduce the

influences of the CCD's quantum efficiency as well as the spectrometers grating, which were not explicitly mentioned in their manuscript.
It appears to us that the reviewer did not entirely understand the motivation and aim of our work, we need to correct the properties of spectrometers, which are (or were) in the field and are practically inaccessible for characterization measurements. Our approach allows to evaluate these kind of data sets, even from instruments that are not accessible for laboratory characterization. In our opinion, this is a crucial advantage, since most of the spectrometers in the NOVAC network are installed in remote locations that cannot be easily accessed. While we acknowledge that the approaches by Salerno et al., 2009a and Burton and Sawyer 2016 may have worked for the instruments installed at Mt. Etna or for individual car traverse measurements, they are not feasible for re-evaluating already existing data-sets. As was suggested by Referee #3, it cannot be concluded from single instruments, that the approach and the parameters found by Salerno et al., 2009a would work for instruments that are installed at different locations and are subject to a different variation of, e.g., temperature.

Salerno et al., 2009b examined three years' results using the algorithm described in Salerno et al., 2009a from the automated flux monitoring network on Mt. Etna with traverse flux measurements, which are in many ways much more robust than scanning flux measurements: a clear sky spectrum can be collected which is guaranteed to be SO2 free, and there are no geometric corrections to make for plume height.

We agree that the work of Salerno et al., 2009b deserves greater credit. We will remedy this shortcoming of our manuscript and cite Salerno et al., 2009b in the introduction as well as the discussion of our results. However, we also notice that trying to validate flux measurements taken by two different instruments and measurement strategies has its own issues (as is discussed in Salerno et al., 2009b as well). The results of scanning and traverse DOAS measurements are expected to agree only if sufficient care is taken on controlling the observation geometry in a way that both instruments sample about the same section of the plume at nearly the same time, and the potential influence of radiative transfer effects caused by different pointing directions and distances to the plume. Thus the comparison is limited by the uncertainty of factors like these that usually escape control. The best way to test a retrieval algorithm is therefore by analyzing the same dataset by two methods and looking for physical explanations of the potential cause of differences, as we have done in our manuscript.

We added the following discussion to the conclusions: "Further validation of the results presented here, e.g. with traverse measurements as in Salerno (2009a), would be advantageous. The authors of Salerno (2009a) found good agreement between their specific FRS evaluation for scanning spectrometers and car traverse measurements at Mt. Etna. However, comparing measurements from such different data sets is complex already for a single volcano, and additional error sources must be taken into account. The observation geometry needs to be controlled in a way that both instruments sample the same section of the plume and are subject to similar radiative transfer effects. The complexity of this can lead to an uncertainty, that can be observed in Fig. 6a of Salerno (2009a). Furthermore, the here studied volcanoes are not as easily accessible as Mt. Etna, and regularly conducted traverse measurements can not be obtained. A direct comparison of the differences observed at the two volcanoes would suffer from additional error

sources due to the different set-up locations of the instruments relative to respective volcano, differences in local meteorological patterns (wind speeds and directions), terrain and subsequent dispersion patterns. "

Burton and Sawyer 2016 present an update to the Salerno et al. 2009a work in which they recognise that there are instrumental response features which add a fixed pattern to the measured spectra using CCD-based spectrometers, the 'flat' spectrum. This adds 1-3% noise but can be readily characterised and removed from each spectrometer using lab-based measurements of a broad-band UV source.
Measuring a "flat spectrum" is not a new invention by Burton and Sawyer (2016). It is rather a standard technique used in many CCD detector applications, such as astrophotography, where it is called 'flat field correction'. The first source we found that mentions recordings of a halogen lamp to correct for pixel-to-pixel sensitivity in the context of DOAS measurements is Bussemer (1993), also the approach has been used in the GOME satellite spectrometers. Furthermore, these effects, and possibilities to correct for them are already discussed in the standard literature (Platt and Stutz, 2008). While characterizing these patterns in the laboratory certainly works it does not provide a solution for instruments that are inaccessible.

The issues associated with the standard NOVAC analysis system have been well known for over a decade, since the implementation of the approach of Salerno et al. 2009a. The main objective of the Lubcke paper is that (page 3 line 1-3) "This work will follow the idea of using a high resolution Solar atlas spectrum (Chance and Kurucz, 2010) in order to calculate a gas free background spectrum which is used as an FRS for the DOAS evaluation of SO2.". It appears however that this work has already been done by Salerno et al. 2009, so the novelty of the current work should lie elsewhere.
As discussed above, we see plenty of differences between our approach and Salerno et al. (2009) regarding implementation and applicability. Furthermore, we believe that a technical sound implementation of this important issue is necessary. Moreover, the quote from the manuscript mentions just one single part of the strategy we proposed to deal with the problem. There is much more original work in the article, including the implementation and feasibility of extension to a large operational network, the exploration of the circumstances under which the problem of 'SO_2 contamination' may arise and of the possible origins of the principal components of the residual structures.

This immediately highlights that a major refocussing of the manuscript is needed, because so much of the work has already been developed. A valuable contribution of the Lubcke paper is the comparison of the SO2 offset correction with the Salerno et al. 2009a type retrieval for data from Nevada del Ruiz and Tungurahua. However, with 30 volcanoes in the NOVAC network and the fact that an established method for dealing with the issues of absolute SO2 retrievals has been applied for over a decade, it seems wholly inadequate that only two volcanoes are investigated. My recommendation is therefore to refocus this work from a rehash of previously published methods to a thorough investigation of the full implications of the application of the SO2 offset approach to the NOVAC network. Sincerely, with the time available since this issue was highlighted and a solution shown it is not acceptable to present just for two volcanoes from 30.
While we agree that it is a certainly worthwhile goal of future work to investigate this issue at all 30 volcanoes, we must strongly reject the notion that this manuscript is a mere

rehash of previous work. An in depth discussion of the retrieval approach is mandatory before applying such changes globally. Besides, as laid out above we are convinced that our contribution extends the scientific knowledge of spectroscopic evaluations. Furthermore, different from Salerno et al. (2009b) and Hibert et al. (2016) (who both only investigated one volcano) we added two further volcanoes with different measurement geometries. With the aim to improve the results from NOVAC, we have made a thorough analysis of how often and under which circumstances problems from contaminated reference spectra arise. We have then developed a method that can be implemented on a network basis.

A further requirement for a revised or resubmitted paper is that some comparison with traverse flux data is used. The final objective of all this work is to get as accurate as possible SO2 flux data, not SO2 slant column amounts. The corrections posed may have an angular dependence, leading to unexpected impacts on the reconstructed SO2 fluxes from scans. The only way to evaluate this properly is to compare scanner SO2 fluxes with traverse flux measurements, as performed by Salerno et al., 2009b, which should also be referenced here. I would therefore strongly recommend that such measurements and their comparison be included in a future revision, as otherwise the veracity of the final SO2 flux measurements will remain doubtful.
As mentioned above, we will cite the work by Salerno et al, 2009b where appropriate (e.g. Page 2, Line 30 – 32 and in the conclusions). Regarding the traverse measurements, as the referee correctly points out, there are additional issues due to influences of the geometry and radiative transfer. Salerno et al., 2009b suggests "*that the accuracy of measurements obtained by the network is mostly dependent on the geometry of the plume, thus on the variability of the plume-transport direction***". We therefore believe, that the comparison with SO_2 traverse measurements would not greatly improve the understanding of the matter, in particular we believe that the request is unreasonable as it is not feasible to obtain traverse data at all 30 volcanoes. Not all volcanoes are as easily accessible as Mt. Etna. We suggest to use an FRS evaluation mainly to identify scans that are influenced by contaminated reference spectra and remove them from calculations of the average daily emission rate.**

The final contribution of the Lubcke paper is a PCA analysis which effectively does a qualitative job of removal of the flat spectrum as described by Burton & Sawyer 2016. The PCA approach means the user absolves themselves of responsibility for finding the physical process producing the observed features, which is rather disappointing, as precise physical understanding of the measurement process is how we can improve in the future. The majority of the features captured by PCA are flat spectrum, so this contribution is somewhat redundant, given that a clear physical explanation of the process is given by Burton & Sawyer 2016.
We reject the reviewer's statement that '… is disappointing'. We think that we demonstrated in a large number of previous publications (e.g. Platt and Stutz 2008, Lübcke et al. 2013, Lampel et al. 2015 …) that we do care for and understand the underlying mechanisms influencing the performance of our instruments. The main reason for our careful interpretation of the principal components is that we cannot completely rule out further influences. However, as written in the manuscript, we agree with the referee and believe that the first component most likely corrects for instrumental effects (or as he/she calls it the "flat spectrum"). A constant difference of a trace gas between the Solar atlas

that we used and our measurement spectra could, just as an example, be a further influence on the principal components. We would also like to point out, that the precise physical understanding of the flat spectrum is not a novelty of Burton and Sawyer, 2016. This is rather a standard technique that is already discussed in Platt & Stutz, 2008. We did not apply the PCA for a lack of understanding or disregard of the instrumental effects but to obtain information from instruments that are otherwise inaccessible. To stress the point, in this way the methods allows for re-evaluation of historic data sets and to obtain coherent time series.
Furthermore, we have discussed the possible origins of the principal components and the conditions of appearance of the problem in working monitoring networks. There is nothing in the work cited by the referee that is more 'physical' than we had presented in ours. In both analyses the measured spectra are reconstructed from the adoption of the same physical picture of radiation entering the upper atmosphere and being scattered down into the instrument, and subjected to absorption by O_3 and SO_2 and by an approximation of the Ring effect, according to the extinction law. The broad components of molecular scattering are taken care of by inclusion of a polynomial in both methods, and only the characterization of the instrumental effects are dealt with in a different way in the two approaches (by laboratory characterization or by numerical analysis). Here lies the main disadvantage of Burton & Sawyer (2016) for our application, the need to measure spectra with a broad-band light source, preferably in the laboratory.
We adopted this simplified model because it is practical and works under several conditions for volcanic environments, but we do not claim that it is the most physically sound picture, as a detailed analysis of the physical process will require advanced radiative transfer modelling, e.g. by Monte Carlo simulations, which are as of yet impractical.

The present work is also overly long with a redundant exhaustive explanation of the basic retrieval technique. Significant shortening is essential.
We shortened the introduction and discussion of the basic retrieval technique as suggested by the referee.

Literature:
Burton, M. R. and Sawyer, G. M.: iFit: An intensity-based retrieval for SO2 and BrO from scattered sunlight ultraviolet volcanic plume absorption spectra, Atmospheric Measurement Techniques Discussions, 2016, 1–47, doi:10.5194/amt-2015-380, http://www.atmos-meas-tech-discuss.net/amt-2015-380/, 2016.

Bussemer, M.: Der Ring-Effekt: Ursachen und Einfluß auf die spektroskopische Messung stratosphärischer Spurenstoffe, Diplomarbeit, University of Heidelberg, 1993.

Chance, K. and Kurucz, R. L.: An improved high-resolution solar reference spectrum for earth's atmosphere measurements in the ultraviolet, visible, and near infrared, Journal of Quantitative Spectroscopy and Radiative Transfer, 111, 1289–1295, doi:10.1016/j.jqsrt.2010.01.036, http://www.sciencedirect.com/science/article/pii/S0022407310000610, 2010.

Kurucz, R.L., Furenlid, I., Brault, J.,and Testerman, L., 1984. Solar flux atlas from to 1300 nm, Natl. Sol. Obs., Sunspot, New Mexico, 240.

Lampel, J., Frieß, U., and Platt, U.: The impact of vibrational Raman scattering of air on DOAS measurements of atmospheric trace gases, Atmos. Meas. Tech., 8, 3767-3787, doi:10.5194/amt-8-3767-2015, 2015

Lübcke, P., Bobrowski, N., Arellano, S., Galle, B., Garzón, G., Vogel, L., and Platt, U.: BrO/SO2 molar ratios from scanning DOAS measurements
in the NOVAC network, Solid Earth Discussions, 5, 1845–1870, doi:10.5194/sed-5-1845-2013, http://www.solid-earth-discuss.net/
5/1845/2013/, 2013.

Platt, U. and Stutz, J.: Differential Optical Absorption Spectroscopy - Principles and Applications, Physics of Earth and Space Environments,
35 Springer Berlin Heidelberg, 2008.

Salerno, G.G., Burton, M., Oppenheimer, C., Caltabiano, T., Tsanev, V.I., Bruno, N., 2009a, Novel retrieval of volcanic SO2 abundance from ultraviolet spectra. J. Volcanol. Geotherm. Res. 181, 141–153. doi:10.1016/j.jvolgeores.2009.01.009.

Salerno, G.G., Burton, M.R., Oppenheimer, C., Caltabiano, T., Randazzo, D., Bruno, N., Longo, V., 2009b, 183, 76-83. Three-years of SO2 flux measurements of Mt. Etna using an automated UV scanner array: comparison with conventional traverses and uncertainties in flux retrieval, doi:10.1016/j.jvolgeores.2009.02.013.