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Atmospheric Chemistry and Physics Discussions

Interactive comment on "SO_2 and BrO emissions of Masaya volcano from 2014–2020" *by* Florian Dinger et al.

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Review

Dinger F, Kleinbek T, Dörner S, Bobrowski N, Platt U, Wagner T, Ibarra M, and Espinoza E, SO2 and BrO emissions of Masaya volcano from 2014–2020, submitted to Atmospheric Chemistry and Physics for discussion.

Summary

This manuscript discusses Differential Optical Absorption Spectroscopy (DOAS) measurements of sulfur dioxide (SO2) and bromine monoxide (BrO) performed at Masaya volcano, Nicaragua. The measurements stem from two monitoring stations of the Network for Observation of Volcanic and Atmospheric Change (NOVAC). The scanning

DOAS instruments at these stations scan the sky from one horizon to the other while collecting scattered solar radiation. When this radiation intersects the volcanic plume, partial absorption occurs at ultraviolet (UV) wavelengths specific to the gas species – in this case SO2 and BrO.

A large part of the manuscript deals with the development of a methodology for consistent analysis of the continuous DOAS data which spans the 2014-2020 time period with only two short interruptions. The authors emphasize the need for applying data quality filters to remove unreliable DOAS scans from the analysis and introduce several corrections for what they deem to be systematic errors in modeled meteorology and measurement geometry parameters.

The resulting time series of SO2 emission rate and BrO/SO2 molar ratio are presented in Figure 9 and appear to show that SO2 emissions averaged around 1000 metric tons per day (t/d) in 2014 - May 2018, then dropped slightly to around 700 t/d. The BrO/SO2 ratio had a significant annual periodicity with relative maxima occurring in March of each year, as well as a general increase in the ratio occurring around the time of the appearance of a lava lake in late 2015. Finally, the implications of these observations are discussed (1) for atmospheric chemistry occurring in the volcanic plume and (2) for volcanic processes occurring at Masaya during the observation period. The authors hypothesize that the seasonal trend of BrO/SO2 may stem from a dilution of bromide in the aerosol phase during more humid times of the year slowing the formation of BrO, and that the drop in SO2 emissions in 2018 was caused by an overall drop in lava lake activity around this time.

General comments

This manuscript provides a wealth of information on methodology for analyzing scanning DOAS measurements of volcanic gas plumes. The authors discuss two different meteorology models (ECMWF ERA-Interim and Operational ECMWF Reanalysis) and compare these with each other and data from a ground-based meteorology station in

Managua. Various methods for filtering and averaging are considered, and finally a correction is developed and applied to the ERA-Interim data. Next, the authors assess methods for retrieving SO2 column densities from the spectral data, developing filters for rejecting data of questionable quality, testing spectroscopic retrievals in multiple wavelength regions, and exploring four different approaches for correcting and/or filtering data associated with contaminated clear-sky reference spectra. The calculation of SO2 emission rates from column densities follows standard methods, but additional filters are then introduced to remove data collected in unstable wind conditions from further consideration. Further testing the reliability of their retrievals, the authors check for and find a significant correlation of SO2 emission rate with wind speed and develop an empirical correction for plume height which appears to improve the quality of their results. Finally, an operational method for retrieving BrO/SO2 ratios representative for each DOAS scan is developed. In the discussion section, all of these topics are again brought up, this time in the context of a critical assessment of each retrieval step and a detailed discussion of potential error sources. All of these topics are well-motivated, described in detail, and appear to be robust, therefore providing a valuable resource for researchers analyzing scanning DOAS data.

At the same time, the other aspects of this manuscript are lacking detail in my opinion, especially the purported link between the measurement results and volcanic processes. Cited extensively throughout this manuscript, a study by Aiuppa et al (2018) developed a fairly detailed conceptual model of degassing at Masaya specifically for the time period examined here, yet there is almost no mention of their conclusions (other than to say that the re-analysis performed here yielded overall higher SO2 emission rates). The authors should consider a much more thorough discussion of this existing degassing model, noting where new information might be added based on their measurements, and work out the volcanological implications of their results compared to those presented in this previous work.

Overall, I wonder whether Atmospheric Chemistry and Physics is the best venue for

dissemination of this manuscript. In its current form, readers primarily interested in the reactive halogen chemistry or volcanic degassing processes will likely find it difficult to identify the information relevant to them. Sections dealing with development, testing, and refinement of measurement strategies make up approximately 2/3 of the manuscript, while the presentation and discussion of results is fairly minor in comparison. The manuscript is already quite lengthy, so this situation might be mitigated by moving significant portions of the methodology to a supplement where those interested in these aspects could find all the details, while expanding on the sections dealing with atmospheric processes and especially volcanology. However, another option might be to move this manuscript to a technical journal such as Atmospheric Measurement Techniques. In this case, the technical information could remain in the body of the manuscript, and less details would be expected in the discussion of atmospheric chemistry and volcanic processes.

Regardless of the path chosen by the authors, I am highly supportive of the content being published for use by the scientific community. In the following section and an attached annotated PDF, I list specific comments which I hope will help the authors in making improvements to their manuscript.

Specific Issues

Abstract - Pending the decision on how to proceed with the publication of this manuscript, the abstract should be revised and shortened to highlight only the key aspects of the study.

L199 – Please clarify how the quality filter based on spectral intensity works. Does the filter only consider the SO2 fit region when rejecting over- or underexposed spectra? Or does it consider the entire spectrum? It would seem to me that spectra could still be used if they are not overexposed in the fit region. Also, I'd be concerned that removing individual spectra from a scan based on their intensity might lead to preferential removal of plume spectra. In my experience, plume spectra often appear brighter than

background sky spectra during clear-sky conditions due to the increased scattering of solar radiation on aerosols in the plume. This will often cause the plume to appear brighter than the sky. The result of this filter could therefore be a removal of some or all the spectra associated with the plume itself. Of course spectra that are oversaturated in the fit region cannot be evaluated, but in such a case the entire scan would need to be discarded, not just the oversaturated plume spectra.

L380 – It didn't become clear to me whether the triangulated plume height was used for the retrieval of SO2 emission rates in cases where it could be determined, i.e. when both scanners detected the plume. Regardless of what was done, one interesting test would be to restrict the dataset to only those emission rates derived using triangulated plume heights. For this subset, does the correlation of emission rate with wind speed disappear? If this correlation really is an artefact of assuming incorrect plume heights, wouldn't we expect it to disappear in cases where the plume height can be measured reliably?

L455 and throughout – I had a hard time understanding the descriptions of volcanic activity presented by the authors. Descriptions such as 'elevation of the lava lake' seem a bit misleading. Aiuppa et al (2018) reported that there was not a lava lake at Masaya prior to December 2015. So do you mean 'appearance of a lava lake' here? I recommend that, when describing volcanic processes, the nomenclature from Aiuppa et al (2018) and other previous studies be adapted as much as possible and those studies be referenced so that it's clear you are referring to the same events. Here, I also don't understand what is meant by 'actual onset of activity in the shallow magma system'. What type of activity? What do you consider the shallow magma system? Do you mean the shallow magma reservoir identified by Rymer et al. (1998) and Williams-Jones et al. (2003)? See Aiuppa et al (2018) for more details on this.

Table 5 – In this section of the manuscript and the accompanying table, a number of suggestions are made for further improving upon the framework utilized by the authors to evaluate the scanning DOAS data. It's understood that there is always room for

improvement, but since one of the central points of this study is to discuss the ideal methodology for analyzing the DOAS data, it seems a bit contradictory to make so many suggestions for improvement beyond what is recommended here. And in many cases, particularly in the table, the suggestions either seem to contradict earlier statements or are too vague for the readers to act upon. For example, I understood that the I0 correction did not improve the SO2 retrieval noticeably. Why then is it recommended that this should always be applied? Similarly, suggestions like 'further optimize filters', 'apply more filters', 'optimize triangulation algorithm', or 'improve calibration' don't provide actionable information. I recommend that this section either be carefully revised such that only specific, actionable suggestions are given, or that this section be removed entirely and these suggestions for possible future investigation simply be given in the methods section.

L782 – The lack of correlation between BrO/SO2 and background ozone concentrations or wind speed is interesting. Others (myself included) have suggested that in-mixing of atmospheric oxidants could be a relevant process limiting BrO formation. For example, this might explain the spatial heterogeneity of BrO/SO2 we observed at Mount Pagan volcano (Kern and Lyons 2018). Here, you write that "The observed correlation coefficients between the BrO/SO2 molar ratios and the ozone mixing ratio and the wind speeds were both rather small, indicating that the BrO conversion is not predominantly controlled by the background ozone mixing ratio or the air in-mixing rate." However, I wonder if in-mixing might be more important than it may seem here. As you point out, the in-mixing rate would likely depend on wind speed, with higher wind speeds leading to greater turbulence and more efficient mixing. But at the same time, a higher wind speed would also reduce the plume transport time from the vent to the DOAS scanning plane, so the measurements would be made in a younger plume. The measurements suggest that the BrO/SO2 ratio is approximately equal, regardless of wind speed. Is it therefore possible that the plume is indeed evolving more quickly (with faster halogen activation) in the high wind / efficient mixing scenario, and that this is the reason that the BrO/SO2 ratio is approximately the same despite the plume being younger?

L786ff – This section needs major revisions in my opinion. As I stated in the general comments above, I strongly recommend the authors take a closer look at the literature available on Masaya's volcanic system and activity. The very first sentence in this section claims that the elevation (= appearance?) of the lava lake was likely caused by the arrival of juvenile magma in the shallow system. How do you know? I don't see how this follows from the measurements presented in the study – in fact I think you could argue the opposite could be true given the observation that the SO2 emission rate hardly increased in this period. At the same time, Aiuppa et al (2018) make some relatively convincing arguments for a shallow intrusion which may have caused a rejuvenation of pre-existing shallow magma. If this is what you are arguing, then please be sure to cite their paper as well as the original references upon which their observations rely. When citing previous work, please also be sure to use the original nomenclature when describing parts of the volcano's plumbing system or types of activity. For example, please clarify what is meant by "shallow system". Other concerns I have for this section include:

- You distinguish between juvenile magma and older magma. Where is the juvenile, where is the older magma? Are they moving up or down? Mixing? Convecting?

- It's not clear that bromine and sulfur would degas at the same depth/pressure. Therefore, it's not clear to me that bromine would have degassed earlier than sulfur from old magma. Isn't it possible that sulfur (and additional brome) are being supplied from juvenile magma and being added to the gas emitted from the older magma?

- Rather than speaking of earlier or later degassing, maybe it's best to describe things in terms of pressure or depth?

- What was the observed 'decrease in lava lake activity in mid 2018? What exactly decreased? How was this determined? I assume this observation is also taken from other studies? Please be sure to cite them.

- Couldn't the decrease in the SO2 emissions simply be caused by depletion of sulfur

in the magma? It's not clear to me why it requires a change in pressure or temperature at degassing depth.

- I don't think the lack of change in BrO/SO2 in 2018 implies that Br and S partitioning are independent of the physio-chemical conditions in the magma. I guess it's also possible that changing conditions combined with varying degrees of depletion of these elements in the magma could lead to a relatively stable ratio. (such an example is actually given in the next sentence).

Overall, I think this section would benefit greatly if the discussion occurred within the framework of a conceptual model for the degassing behavior. Aiuppa et al. (2018) actually present such a model, and this model could be used if desired. In that case, it would be interesting to highlight which information this study adds to the existing framework, which (if any) new observations do not fit well into the exiting model, and which new insights (beyond those already discussed by others previously) can be gleamed from these measurements.

Minor Corrections

Please see the attached annotated PDF for additional comments, suggestions, and minor corrections to the text. I'd like to thank the authors and journal editors for the opportunity to review this manuscript.

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2020-942/acp-2020-942-RC2-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-942, 2020.