Atmos. Chem. Phys. Discuss., 14, C8659–C8663, 2014
www.atmos-chem-phys-discuss.net/14/C8659/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "OClO and BrO observations in the volcanic plume of Mt. Etna – implications on the chemistry of chlorine and bromine species in volcanic plumes" *by* Gliß et al.

Anonymous Referee #1

Received and published: 30 October 2014

OClO and BrO observations in the volcanic plume of Mt. Etna - Implications on the chemistry of chlorine and bromine species in volcanic plumes

Gliss et al. reported on halogen oxides observations at Mt Etna using MAX-DOAS measurements. This paper is interesting and report on new measurements and should be published after addressing the points below.

Comments

Overall, the methodology is valid and the quality of the results is good. However, the scientific significance of this study is somehow questionable. From the title and the

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

introduction, a reader will have the impression that new conclusions on volcanic halogens formation and chemistry will come out of the paper but in fact it is not really the case. The measurements presented here largely confirm findings from past studies. The only exceptions are the results for young plumes and the discussion on formation time and the results for OClO. My main comment on this study is for the presentation quality.

-The abstract and conclusions should be rewritten. Especially the conclusions part is only a summary of what was presented in previous sections (with a lot of numbers and statistical values, not really necessary). Instead it should reflect what this paper brings compared to previous studies.

-The paper is quite long. The section 2 (methodology) contains a lot of details and are often not very linked with each other. I am worried the reader becomes a bit lost and feels disconnected to the objective of the paper (first results come at page 11!). I am not pushing to revised the complete manuscript structure because it is difficult but I think there are some subsections that could be either simplified, suppressed (section 2.9) or moved to section 3. E.g., section 2.5 could be summarized in five lines, not more. Several other sections could be simplified as well, for instance, on DOAS evaluations and alternative fitting windows. In my opinion, section 2.7 is really where the text is too long. It would be enough to say that τ=l/v and that it has been determined using wind vector an viewing angles (basic trigonometry). The error on τ is calculated by simple error propagation on l and v. I think Fig 4 is not necessary. As an alternative, the authors might want consider to transfer some details of Section 2 in an Annex, to improve the readability of the paper.

-English could be improved.

-Throughout the section3, the author pays a lot of attention to refer to section 2 e.g. for a term definition but I think it is too frequent and it becomes hard to read.

Minor comments

ACPD

14, C8659–C8663, 2014

-p2,l76-83: as it is stated now, the study of volcanic emissions seems to be useful mostly for predicting eruptions and for climate impact. I think it is not what you meant. I suggest to reformulate this sentence and underline the importance notably for ozone/oxidant chemistry.

-p2, l103-104: "In addition, we found evidences of the photochemical nature of the reactions involved." I don't understand this sentence. What else than photochemistry could possibly explain your observations? Please reformulate.

-p3, sect 1.1.2, first paragraph: The release of chlorine and bromine in the gas phase is driven by Cl-/Br- ratio. I think it is an interesting part but it would be useful to give information (if available) on what could possibly determine this ratio (aerosols type, etc)

-p4, section 2.2: it would be good to mention already here why measurements have been performed at different places. Why not at only one site?

-p5, l388: "saturation effects"? what do you mean?

-p6, Table 1: it is not looking as a table.

-Figure 3: features from the Ring effect are clearly visible in the residuals.

-p7, l 514: "radiation transport effects" is vague. "Non-linear retrieval effects" would be more appropriate. The sentence l516-519 is quite odd, please reformulate.

-p10, section 2.8: a stratospheric BrO column of 7.2xE13 cm-2 is definitely too high for a mid-latitude site as Etna. Sinnhuber et al., 2005 showed such high values but it was for the total BrO column at high latitudes (hence including a contribution from polar BL BrO). However, a typical mean value of 4 xE13 cm-2 seems reasonable.

-Figure 6: I don't understand how a BrO or OClO measurement is classified as below/above the detection limit. I would have thought that the detection limits would be fixed SCD values (BrO or OClO)

-p11, l839-841: this statement is untrue because only the measurements within the

ACPD
14, C8659–C8663, 2014

plume are shown here.

-Table A1. For scans with only a few spectra, the statistical parameters are meaningless. I would not present them at all.

- Figure 9b. the drop of OClO after 150 s is due to dilution of the plume (low BrO and low ClO concentrations)

-Figure10: I'm not convinced by Figure 10 (BrO). The diurnal photochemical variation of stratospheric BrO is small for SZA 70-83° but it is still of about 15% or so and would propagate to the observed SCDs by an AMF quite large (twilight measurements). Even if the stratospheric diurnal variation of BrO is zero, an error on stratospheric column (assumed 4e13molec/cm^2) would also propagate with a dependence on SZA through the AMFs used. Sensitivity tests that include realistic stratospheric diurnal variation should be undertaken to verify the results.

-Figure 10: adding SZA in a 2nd x-axis would be helpful. A third panel with OClO/BrO as a function of time could be interesting as well

-p16, l1131-1134: I don't see how it 'underpins' the theory of bromine explosion. It simply shows the importance of local photochemistry on halogen oxides.

-p16, l1151: '(since OClO is likely formed via the "BrO + ClO"- reaction and BrO & ClO via reaction of Br & Cl with O3).' is not necessary

-p16, section 3.1.3: a concentration of 2.7 ppb of BrO is larger than any other published estimates. An error bar (likely dominated by the estimated plume diameter) should be provided. On Fig 11, error bars are shown but it is not mentioned what they represent. I think the fact that OClO is not visible after Tau>4 is to be expected: as the plume ages, the dispersion of the plume makes the concentration of BrO and ClO lower and OClO drops below detection limit very quickly (production rate is non-linear: k[BrO][ClO]). This should be underlined.

-p18, section 3.2: the detection limit of IO is an order of magnitude better than for OIO

ACPD
14, C8659–C8663, 2014

and OBrO, and after looking at the absorption cross-sections, it is clear that it is due to the different performances (SNR) of the instrument in the UV and Visible. This should appear in the text.

Typos

-p2, l75: “difficulties often are associated” → “difficulties often associated”.

-p2, l133: I wonder whether footnotes are allowed in ACP(D). I suggest you include a sentence on BrO/SO2 ratio directly in the text.

-p3, l156: “aquatic” → “aqueous”

-p3, l170: R4f → R4

-throughout the manuscript, the term “radiation transport” is used but in usually “radiative transfer” is preferred by the scientific community.

-for all numbers provided decimals (e.g. correlation coefficients, slope of linear regression), only two digits are needed.

-p12, l899: “tropospheric ozone O3 “ → “tropospheric O3“

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 25213, 2014.