

Interactive comment on “Enhancement of the volcanogenic “bromine explosion” via reactive nitrogen chemistry (Kīlauea volcano, Hawai’i)” by G. G. Salerno et al.

Anonymous Referee #2

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Salerno et al. present measurements of SO₂, BrO and NO₂ with passive UV spectrometers from the summit and East Rift of Kīlauea volcano, Hawaii. They found very high BrO slant column densities and a strong positive correlation between SO₂ and BrO but a strongly negative correlation between BrO (and SO₂) and NO₂. The authors interpret this as indicative of the reaction of BrO with NO₂ and speculate about the importance of BrONO₂ for the chemistry in volcanic plumes.

Important details of their spectroscopic evaluation remain unclear and the discussion of the negative SCD of NO₂ raises more questions than it answers. More details are given below. I do not support publication of this manuscript.

C3961

Major comments

p. 10317, bottom: Apparently wind data from READY has been used for the calculation of gas fluxes. Is this appropriate? How well do the modeled winds represent the conditions at Kīlauea. I would be surprised if the modeled winds could resolve the real winds realistically and well enough to base flux calculations on it.

p. 10318, l. 16: Why did you do CSR only for the non-temperature stabilized measurements? What are your reference spectra for the other spectra? How did you ensure that you don't have a stratospheric signal in your measurements?

p. 10318, l. 29: It is entirely unclear why you changed the spectra to ensure a “better fit”. What is the physical background for doing this, how do you ensure that you don't distort the data? By how much did you change the spectra? How many lines did you fit for each trace gas?

p. 10319, l. 15/16, 22-25 It is unclear to me from your description if the large background could be stratospheric NO₂. Is this excluded by using the CSR? You suggest that BrO was present in the CSR - do you refer to tropospheric or stratospheric BrO? If this is the case for BrO, why don't you discuss it for NO₂ as well?

p. 10322, l. 12-18 I don't understand how the presence of high NO₂ over lava flows should be related to the presumed presence of high NO₂ in the crater vicinity. How far is the lava flow from the crater where you made the measurements? Not enough information about the location of the Witham measurements is provided but it appears to be at a different location, several kilometers from the crater. To me the best explanation for the high negative NO₂ in the plume is a problem with the retrieval. Free tropospheric background NO_x mixing ratios at Mauna Loa are on the order of several 10ppt (see for example the MLOPEX experiments). Unless there are very strong pollution sources nearby or the lava flows extend over a very large area, the background from which 50ppb of NO₂ is suggested to be missing is unlikely to exist.

C3962

p. 10323, l. 6/7 Please show that the reaction of BrONO₂ on aerosol is fast enough (order of minutes) to support your claims regarding rapid cycling/release of bromine in the early plume. I could not find any relevant information in the cited references.

Minor comments

p. 10316, l. 8-9: It is certainly true that a lot of attention has recently centered on halogens in volcanic plumes, however the claim that “the role of volcanism [...] has become the focus of interest [...]” is a surprising exaggeration.

p. 10319, l. 21 What is the meaning of “BrO emission rate”? To the best of our knowledge, BrO is photochemically produced in the plume, depending on available bromine precursors, reactive surface area, UV radiation, presence/absence of clouds etc. Hence the yield of BrO from the Br precursors will depend on many factors and clearly not be a 24h source, unlike SO₂.

p. 10320, l. 4 How did you determine the path length through the plume?

p. 10321, l. 18-21 See comments above about “BrO emission rate”, they largely hold for “reactive Br” flux as well. Also I get a different numerical value for the quantity that you refer to as Br flux.

p. 10322, l. 10 The reference Witham (2005) is not accessible but referred to for important information; please provide information as to how to access this publication or avoid it. What technique was used for these measurements, what were the details of the sampling?

References:

You refer to three publications from the last AGU meeting. Aren't any better references available?

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 10313, 2010.