**Atmospheric
Chemistry
and Physics
Discussions**

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 #1

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Review of the paper "Enhancement of the volcanogenic "bromine explosion" via reactive nitrogen chemistry (Kilauea volcano, Hawaii) by Salerno et al.

In this article by Salerno and co-authors first BrO measurements at a Hot-spot volcano are presented. The BrO mixing ratio measured here is also a new record for BrO measured in the troposphere - 2.3 ppb! The authors further show a strong anticorrelation of NO_2 and BrO (SO_2) and discuss the role of nitrogen for halogen chemistry in volcanic plumes. Unfortunately, the article suffers in imprecise and sometimes contradictory descriptions. But the main problem is the flawed data evaluation. That leads also to the problem that the author needs quite unrealistic interpretations to fit part of the results to

the rest of the argumentation, for instance why a clear sky spectrum taken outside the volcanic plume contains zero SO_2 but still high BrO concentrations. However, because the data analysis is such an essential part of this article I cannot recommend publishing it into ACP. Major changes and a complete re-evaluation of the datasets have to be done, which might result in significant changes in interpretations and discussion. Re-writing and re-submitting might be an option afterwards.

Questions and comments on which work has to be done are listed in the following: Some are similar to the one in the pre-review as they were not properly answered in my opinion. (The list is sorted according to the occurrence in the text):

Page 10317, line 23/24

In the abstract the authors wrote: "Observations were carried out by ground-based Differential Optical Absorption Spectroscopy in 2007 and 2008 at Pu'u'O'o crater and at the 2008 magmatic vent that opened within Halema'uma'u crater." Here and in the following you talk only about one of the Pu'u'O'o crater measurements in 2007 and the one at the Halema'uma'u crater at 2008. Also only these two measurement results are presented in the table. What happened with the measurement of the Pu'u'O'o crater taken in 2008 mentioned in the abstract? Please change the abstract.

Page 10318, line 4

"nominal resolution" what do you mean with that? Have you measured the resolution of the spectrometer or did you calculate it? Or is 0.44 the value which comes from the company where you bought the spectrometer? How did it change when the temperature was not stabilized (see also below for further comments to this argument)?

Page 10318, line 8-10

Did I understand it right? - Your integration time was set to 20 s with a self adjusting exposure-time (?) (around 200ms) and therefore variable number of co-added spectra (up to 100). Please write/state that clearly.

Page 10318, line 11/12

"each survey 3-4 datasets.." if I understood right, you carried out 2 surveys (3.9.2007 and 13.5.2008), meaning on one of this dates you collected 3 datasets of 20 minutes and the other time 4 datasets. In total 7 datasets a 20 minutes, since this is not a huge or infinite number it would be nice if you could add an additional table writing the correct day-time for every dataset carried out, location, weather and ash condition (see below), temperature of the instrument. That would give the reader and maybe later users of the datasets (e.g. modellers) the possibility to have more precise information than just to say we did 1 hour of measurements (3 times 20 min) between 9 am and 4 pm, especially when looking for chemistry, the time of the day might be important.

Page 10318, line 15/16 "For a few datasets in both surveys, the thermo-stabilised instrument was not used"

1) Does this mean you used more than one instrument during the surveys, did the second instrument had the same characteristics described above (295-375 nm, 0.44nm resolution)? Or have you just don't use the thermo-stabilisation but still the same spectrometer. 2) A "few datasets" out of 3 means at least 2 datasets were taken without that the thermostabilisation was used, please add this information to each dataset inside the table mentioned above. How many datasets were taken with thermostabilisation?

Page 10318, line 16/17

You wrote that in cases of no thermostabilisation you took a dark, an offset and a CSR before and after every dataset "to account for instrumental drifts", - Because you studied it, it is a pity not to see the results of it, please add them to the description. How large was the wavelength shift? How much does your instrumental slit function change with temperature? How did you calculate it?

Page 10318, line 24/25

Why did you use a "warm" ozone (293K), but a cold NO2 (223K - a temperature fine

for stratospheric NO2, but not if you want to investigate tropospheric NO2 patterns)? Maybe the numbers are only mixed up? Then just correct it as a typing error otherwise please give an explanation. Did you convolute the references with a Gaussian shape instrument function using the 0.44 nm resolution for both (?) or the instruments or which kind of instrumental function did you assume?

Page 10318/10319, line 29/1

"Each spectrum was shifted and stretched until the best fit was achieved"

Did you allow a first or second order stretch? Did you shifted only the spectrum or also something else - CSR, References of trace gases? In Fig.2 it seems to me that the BrO is shifted, but even more looking up the ozone structure in this wavelength region (which seems to be shifted and streched) I estimate from the example in Figure 2 looking up the O3-cross-section it could be about 1! nm. What else did you shift? How large was the shift usually? 1 nm would be enormous and has no real physical base even without thermostabilisation when you measure only for 20 minutes. In my opinion that gives a strong indication that your results are not certain at all. Further on the high frequency structure of O3 and NO2 are similar to the one of BrO in this small wavelength window, a cross sensitivity check, which I asked for already in the pre-review would result in a relatively high dependency using this wavelength region (345-358nm) especially if you allow a shift. It is easy to check in the Windoas-software you used for your evaluation. The SCD's of O3 in the presented example are unrealistically high 10^20 - how can you explain that?

Page 10319, line 1

"The optimal fitting window" - what do you mean with optimal fitting window? As you read Kern et al. 2009 you probably know that there are some disadvantages to this low wavelength range evaluation, especially regarding the radiative transfer. Also the signal to noise ratio should be relatively bad below 310 nm, isn't it like that? The detector has a small sensitivity in this region and not much light is reaching the surface

due to ozone absorption? The stronger SO2 absorption features in case of low SO2 gas concentration would be the only advantage for this region below 310 nm, but your SO2 absorption at Hawaii are not that small that you need it (it is more the other way around). See also e.g. Yang et al. 2007, or Kern, 2009 or Bobrowski et al. 2010 for SO2 evaluations

Page 10319, line 2 ff

"fitting windows for... BrO and NO2 (345.0 nm - 358.0 nm) were selected to avoid interferences between gases during the retrieval,.."

Have you checked that? What is the cross-correlation coefficient between BrO-O3-NO2? As mentioned already there is a cross sensitivity in this region for these trace gases. You mention that you have done the evaluation in a second wavelength region between 330-370 nm, but you don't mention any result, did you achieve the same values for the SCDs here? Or were there differences - how large was the deviation? Why have you used 345-358nm? These are important information; please add them to the text. Please show also an example for a fit between 330-370 nm in comparison to the one in Figure 2.

Page 10319, line 21ff

SO2 versus BrO does not go through the origin....BrO in the CSR spectrum"

You have no spectrum without BrO even when you are outside the plume you suggest to have BrO that would mean because your 'outside-plume-reference' has BrO, the BrO SCDs inside the plume will be underestimated - right? That first would shift the correlation between So2 and BrO even further away from the origin and second because in the plume is even more BrO than you determined – there would be even higher mixing ratios than 2.3 ppb (which is already a record)! How much O3 do you need to build several ppb of BrO, do you think this is realistic? For NO2 you wrote that there is NO2 in the outside plume reference (similar argumentation as for the BrO, only

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the reason might be different because of different sources) and therefore you get negative SCDs for NO2 in the evaluation caused by a lower or zero concentration of NO2 in the plume - I understood right, didn't I? Thus to be honest I don't understand the BrO argumentation. Could you clear it up? Maybe make a small sketch of the situation showing how you imagine the various trace gases and sources to be distributed.

Do you assume an SO2 free reference or not? Why goes SO2 to zero - BrO doesn't? BrO is not even close to zero, we don't talk about 10^{13} or even 10^{14}, we talk about 10^{15} for the smallest value, 10^{15} molecules/cm^2 is a SCD that has rarely been determined for BrO.

Page 10320, line 6 ff,

For the NOx chemistry even it is applied for other geographical regions there exists also a lot of older citation which should not totally be ignored. For instance Sanders et al., 1999 or another von Glasow and Crutzen, 2003 as an overview about halogen chemistry where the same suggested interaction with nitrogen is discussed. The recent model results of von Glasow, 2010 seems to indicate that the most of NO2 is reacting with Br atoms to form BrNO2; BrONO2 isn't formed in significant amounts in the model result. Please include this new model results in your discussion.

Page 10320, line 22ff

What about the measurements of C. Kern carried out in 2008 (ref: Kern, 2009) as well, which could not detect BrO even with a much lower detection limit than yours (5.4 x 10^{13} instead 3 x 10^{14}). Please include this in your discussion.

Page 10321, line 1/2

"Other factors can contribute to the detection of reactive halogen species, including sensitivity and selectivity of the spectrometer and the spectroscopy"

Did you use the same instruments for both craters? Did you use the same evaluation settings? So you can exclude this reason for your case, right? Write this down.

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Page 10321, line 1/2

"As well as diurnal, seasonal and meteorological factors..

Please describe the differences for your measurements and how they might have influenced your results

Page 10321, line 15/16

"were occasionally ashy.." all 7 datasets or is there any which was taken without ash?

Page 10321, line 17ff

"If we assume that the measured SO2/BrO ratio characterises the near source emission for eruptive vents on Kilauea, then we can take the long-term flux observed for the volcano..."

This assumption can hardly be done for long-term estimates as it is in contrast to other measurements (Kern, 2009). BrO was not or in a quite lower SO2/BrO ratio emitted in March 2008. This has to be mentioned.

Page 10321, line 24 ff

"Gerlach.......are expected to contain less HBr compared with arc gases..." - if that is true you would expect higher SO2/BrO ratios as determined in the past at arc volcanoes, wouldn't you? - but you show that this is not the case - your results show a ratio which is in the same size, even lower as the ones measured at arc volcanoes - so I don't understand why do you write:

"His predictions are thus born out by our detection of BrO"

? Your BrO/SO2 ratio is a surprising result and is in contrast to earlier predictions. Nothing bad with it, but should be written.

Page 10322, line 4-6

" 6 x 10ˆ16 molec/cm2 ... this is equivalent to...50 ppbv"

How did you calculate this value, by using RTM? Or is it estimation, then please add the assumptions you did for it?

Page 10322, line 17 ff

Please add "e.g." for your citation and some older reference like Sander et al, 1999, von Glasow and Crutzen 2003, who wrote overview of halogen reactions, including the possible role of nitrogen.

Figure 1

Your measurements were done at the Halema'uma'u crater pointing in the direction of the vent. Isn't it the point where you assume that NO2 is formed? Why do you have more NO2 in the reference than in the measurement in the plume? Please add the information by coloured areas where hot lava surfaces could be observed during the measurement survey on 13.5.2008.

Figure 3 and 4

None of these correlation figures contain the value of the fitting example in Figure 2 BrO SCD of 8.5 x 10ˆ15 – Did you forget it? Are there other missing points?

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Typing errors:

Page 10316, line 19

Citation von Glasow, just one "s"

Page 10316 line 24

Bobrowski and Platt instead of Bobrowski et al.

Page 10321, line 10

"pertain two plume ages" - add the w in two

References to be added:

Yang, K., N. Krotkov, A. Krueger, S. Carn, P. K. Bhartia, and P. Levelt (2007), Retrieval of Large Volcanic SO2 columns from the Aura Ozone Monitoring Instrument (OMI): Comparisons and Limitations, J. Geophys. Res., 112, D24S43, doi:10.1029/2007JD008825. Sander, R., Rudich, Y., von Glasow, R., 5 and Crutzen, P. J (1999): The role of BrNO3 in marine tropospheric chemistry: A model study, Geophys. Res. Lett., 26, 2858–2860.

von Glasow, R. and P. Crutzen (2003). Tropospheric Halogen Chemistry. In R. Keeling, H. Holland, and K. Turekion (Eds.), Treatise on Geochemistry - Vol. 4 The Atmosphere, pp. 21{64. Oxford: Elsevier/Pergamon.

Kern, C. (2009) Spectroscopic measurements of volcanic gas emissions in the ultraviolet wavelength region, PhD thesis, University of Heidelberg, Heidelberg.

Von Glasow, R. (2010), Atmospheric chemistry in volcanic plumes, PNAS, vol. 107, 6594-6599.

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