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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Quantification of the depletion of ozone in the plume of Mount Etna" *by* L. Surl et al.

Anonymous Referee #2

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Review of Surl et al. 2014

Summary:

Surl et al. (2014) present new measurements of ozone depletion in a near-downwind volcanic plume, with ozone quantified alongside SO2 as a 'plume-tracer'. These observations, as well as DOAS measurements of downwind plume column BrO/SO2 are then compared to atmospheric model simulations of the plume reactive halogen chemistry. Overall the experimental work is relevant to the scope of ACP, and the observations in particular present a very useful scientific contribution to this field.

However, I have some questions regarding the modelling part of the study which forms the basis for interpretation of the observations, specifically regarding the validity of

some of the model assumptions, with respect to other studies of Etna plume that have recently been published.

In summary, observations-work is very interesting and merits publication in ACP subject to minor comments, but some major concerns regarding aspects of the modelling need first to be addressed.

Observations part:

Only a few studies have quantified volcanic plume ozone depletion alongside plume-tracer SO2 in volcanic plumes, with only one study to date both mapping the downwind (> 2 km) plume ozone depletion (alongside SO2 at Redoubt volcano), and successfully simulating it with an atmospheric model (Kelly et al., 2013). This study by Surl et al. is one of the first to quantify in-plume ozone observations very near the source (< 1km), noting that the previous measurements of near-downwind ozone depletion reported at Etna (Vance et al., 2010) did not include co-measurements of plume tracer SO2, thus cannot easily be compared to an atmospheric model. Thus, Surl et al. provides a valuable O3-SO2 dataset to better understand Etna plume chemistry and impacts.

The data presented by Surl et al. are very limited in time (only a few days fieldwork), but this is quite acceptable given the challenge of making these observations at the summit of a volcano and analysing the data-sets, particularly of nmol/mol-level ozone in an environment containing 10's μmol/mol SO2, and the effort required for preparation of CrO3 scrubbers for the ozone instrument. Without such scrubbers, SO2 would cause a (positive) interference on the instrument. For sub-μmol/mol SO2 abundances, this interference can in fact be extracted in post-processing to yield a true ozone depletion measurement as shown by Kelly et al. (2013). The approach of Surl et al. (and that of Vance et al., 2010) instead deploys CrO3-scrubbers on the instrument inlet and thus eliminates the cross-sensitivity problem of SO2 already prior to the measurement. This is particularly useful at the high SO2 abundances (10's μmol/mol) of their near-source plume measurements. They thereby successfully observed and quantified in-plume ozone depletion in relatively strong plume close to the Etna summit craters.

The ozone depletion relative to SO2 is found to increase linearly with distance from the crater. The observations indicate ozone depletion relative to SO2 is significant even at time ‘zero’ from the summit crater. This could imply uncertainties in the method (e.g. efficiency of scrubbing SO2 without scrubbing ozone) but the authors make some reasonable arguments that chemical ozone loss can already occur during the period ($\sim$ 1 min estimated) between when the magmatic gases are released from the vent, and transported up to the crater-rim. Thus, these ozone measurements (alongside SO2) are convincing and present a valuable addition to the available literature on ozone in tropospheric volcanic plumes. Also presented are DOAS measurements of column BrO/SO2 made somewhat further downwind, which are useful additional constraint to the model interpretation. Overall this part is of high quality, well presented and justified and of strong scientific interest. I have just a few queries on these observations:

[1] Line 17-25, Page 23645: You state that you passed SO2 gas through the ozone instrument (fitted with CrO3 filters on the inlet) and confirm the efficiency of the filters in trapping SO2. However, you do not comment on how well the filters allow ozone to pass through to the instrument, although you mention daily calibrations were performed. Ozone is highly reactive and typically easily deposits on surfaces, although with time such surfaces can become saturated so that ozone no longer deposits. Did the fitting of CrO3 and particle filters (and all the additional surfaces and tubing) to the inlet cause any ozone loss that had to be accounted for in the calibration? And if so did it vary with time (if so how did you account for this in the field-observations)?

[2] Etna emits mercury (Bagnato et al., 2007). Mercury is known to cause interferences on ozone instruments, particularly at low RH (e.g. Li et al., 2006). This is for obvious reasons given the use of a Hg-lamp to generate a UV light source at 254 nm, where ambient mercury can thus naturally also absorb. However, no mention is made of potential mercury interference on the ozone instrument in the Etna plume measurements, which are at low RH. Do the CrO3 scrubbers also efficiently remove mercury prior to

the measurement – and did you test this in the lab? It seems likely from a chemistry point-of-view. If so, this may present an advantage of the CrO3 scrubbers approach. If not, please comment on the effect of mercury interference on your measurements.

Bagnato et al., Degassing of gaseous (elemental and reactive) and particulate mercury from Mt Etna volcano (Southern Italy), Atmospheric Environment, 41, 7277-7288, 2007.

Li et al., UV-Absorption-Based Measurements of Ozone and Mercury: an investigation on their mutual interferences, Air Quality Research, 6, 4, 418-429, 2006.

[3] Wind-speed was monitored during the campaign, and the data (presumably average values) must be used to convert distance into time downwind from the summit for the ozone measurements (Table 3). Wind-speed estimates must also be used to convert distance to time downwind for the BrO/SO2 measurements (Table 5). However, this wind-data is not fully reported. Please can you add this information to both the Tables?

[4] A cluster of BrO/SO2 measurements are presented in Figure 10, but no error bars are shown. Please can you add error bars (or simply a ‘representative error bar’). This should be in the vertical for BrO/SO2 but also in the horizontal as there must be some uncertainty in the time-distance downwind conversion.

You do state on page 23648 that “The plume ages at the point of measurement were calculated from the wind speed and lateral distance from the craters. In the absence of wind speed data at Etna, speeds from soundings taken at Trapani (37.91 N, 12.50 E, data from http://weather.uwyo.edu/upperair/sounding.html) were used. The 220 km distance between the location of the soundings and the volcano means that there is a relatively large and unquantifiable uncertainty in the calculated plume ages.” However, if the observations of Figure 10 are to be meaningfully compared to the model, there must be some estimate of the error in conversion of the distance-to-time downwind.

[5] Paragraph starting Line 17 page 23649 of “Results”. Please see my questions

about the crystallization RH in my response to the modelling part (below). Given these concerns, perhaps it would be 'cleaner' if you simply state the observational findings here ("Depletion of O3 occurred on 30 July even when the relative humidity was < 10 %") and remove all the interpretation aspects of this paragraph from the 'Results' of your manuscript, leaving the interpretation to later discussion.

You state "No significant increase in humidity due to volcanic H2O was observed at the crater rim", but this is probably expected if the plume is sufficiently dilute – can you confirm this is the case here? The high H2O-content of (almost all) volcanic emissions is not under any question as far as I know. As you state in the later modelling work, a high H2O content is thus expected in very near source plume. This could lead to short-lived elevated humidity. However, for relative humidity you also need to consider the effect of the higher temperature of the very near source plume on (temperature dependent) saturated vapor pressure. Is this considered in the model? How do you predict the temperature of the mixture of magmatic gases and background air?

Further small comments:

Line 10, Page 23643: There is also a recent publication in G3, by Donovan et al. (2014) reporting OClO at Soufriere Hills plume – please add to the list in Line 8.

Line 26, Page 23643: "Active DOAS measurements may be possible, but to the author's knowledge no such measurements have been made at any volcano" Actually, active DOAS measurements were made at Masaya crater-rim by Kern et al. (2009), including performing an O3-retrieval as part of the analysis. As I understand it an ozone depletion signature was not identified. Please check the findings of that study and re-phrase this sentence.

Line 3 page 23651: "The BrO/SO2 column ratios are within the range typically measured both in the Etna plume (Bobrowski and Giuffrida, 2012) and volcanic plumes in general (Boichu et al., 2011; Hörmann et al., 2012)." Still the BrO/SO2 ratio do appear to be very much at the lower end of thedata reported for Etna (Bobrowski and Giuffrida,

2012). I think this is worth mentioning here.

Line 15 page 23650: Assumed twice.

Line 24 page 23650: Can you state which craters this is from?

Modelling part:

I have more serious questions about the assumptions made in the modelling part of this study that is used to interpret the data, viewed in the context of previous work in this area. The observed near-downwind (0-300 s) ozone depletion, as well as BrO/SO2 ratios obtained further downwind ($\sim$1000 s) are compared to output from a numerical atmospheric model , MISTRA. The MISTRA model was previously used to simulate Etna volcanic plume chemistry in the studies of Bobrowski et al., 2007 and Von Glasow, 2010. Here, the focus is initially on the near downwind plume (for comparison to ozone), followed by a comparison of 1 hr simulations to BrO/SO2 further downwind. Simulations are presented for a 'low Br scenario' and a 'high Br scenario' for the Etna emission. The low Br scenario corresponds to the Etna emission slightly before the field-campaign whilst the high Br scenario corresponds to unpublished measurements from another earlier period, and is the same as that used by Von Glasow (2010). The volcanic NOx emission is rather uncertain. Thus simulations are presented both including a volcanic NOx emission (as predicted by HSC noting limitations in use of thermodynamic model for this purpose) and excluding any volcanic NOx emission. Simulations are performed at two background RH's (57% and 21 %). It is stated that the higher RH is above the crystallization of sulphate, whilst the lower RH is below the crystallization of sulphate (43%). Hence heterogeneous chemistry will 'switch-off' when plume RH drops below 43% for the latter case (stated to be after $\sim$1 min downwind). For comparison, simulations with heterogeneous chemistry switched off for the whole time are also presented.

Comparison of the model runs to the near-downwind ozone observations finds that there is very little ozone depletion for the high NOx model runs because reactive bromine is in the form BrNO2. Comparison of the model runs to the BrO/SO2 measured further downwind finds that only the “moist” runs show agreement, even though the meteorology observations indicate low ambient RH. Thus, Surl et al. find that “the model runs which are the best fit for the near-crater O3 and SO2 measurements are not the same runs which best match the BrO/SO2 columns measured further downwind. This is a discrepancy which highlights the need for further investigation into plume chemistry and the relationship between in-plume bromine, NOx and humidity.” (page 23656, Line16). They also conclude that “a comparison of the results from our three different humidity/heterogeneous chemistry cases gives an indication as to the extents that O3 depletion can be ascribed to reactive halogens generated in high-temperature processes within the crater, low-temperature processes within the crater, and low temperature processes further downwind.” (page 23658, Line10).

My major concerns for this modelling work hence the conclusions drawn are:

(i) about the assumed crystallization of the volcanic sulphate aerosol below 43% RH, given work elsewhere (e.g. Roberts et al., 2014a) implies a liquid sulphuric acid aerosol even at low RH.

(ii) about the BrNO2 chemistry scheme assumed in the model that leads to in-plume accumulation of BrNO2 (for cases including a volcanic NOx source), given work elsewhere (Roberts et al. 2014b) predicts less severe BrNO2 accumulation in Etna plume.

(iii) about how other uncertainties could propagate through into the results and affect the conclusions. The Etna plume chemistry modelling of Roberts et al. (2014b) highlights some of these uncertainties to be the choice of VA:VM in the high-temperature initialisation, the surface area provided by the volcanic aerosol emission (poorly constrained even by the data of Watson and Oppenheimer cited by von Glasow 2010), and the rate of plume-air mixing. Considering just the MISTRA model work to date there are three publications (Bobrowski et al., 2007, Von Glasow, 2010, Surl et al., 2014) all reporting ‘agreement’ to observations (to various degrees) yet with somewhat different

predictions of plume halogen chemistry thus impacts. This points towards large model uncertainty. Whilst the manuscript does already express caution regarding uncertainties in model-observation comparison in section 4.3, these are in the context of the observation-side only. I think sources of remaining modelling uncertainty should also be emphasized.

Please can you address these concerns by either pointing out any misunderstanding on my part, or by presenting a wider discussion of the model limitations due to the assumptions made, in the context previous studies of Etna plume both by yourself and others, or by redoing any model runs or revising the conclusions drawn if necessary.

[6-i] Question about the crystallization of sulphate:

Line 5, page 23652: “The crystallisation humidity of sulphate particles is around 43% (depending on contents of other salts see, e.g. Seinfeld and Pandis, 2006) which implies that on the days of this study when simultaneous SO2 and O3 measurements were made the aerosol will have contained only very small amounts of water and will not have been deliquesced.”

Please can you explain exactly which sulphate salts are you considering? Ammonium-sulfate salts could crystallize but we do not expect large quantities of ammonium in the plume particularly this close to the source. Your statement on the volcanic aerosol crystallization seems to contradict the work of Roberts et al. (2014a) that calculates Etna aerosol composition using E-AIM equilibrium model, predicting aqueous-phase aerosol composition even at low RH (based on a sulphuric acid composition). Also, how does your assumption of crystallization fit with the work of Martin et al. (2003), Figures 1,2,3? These seem to predict liquid aerosol provide ammonium content is low.

Roberts et al., 2014a, Re-evaluating the reactive uptake of HOBr in the troposphere with implications for the marine boundary layer and volcanic plumes, Atmos. Chem. Phys., 14, 11185-11199, 2014, www.atmos-chem-phys.net/14/11185/2014/doi:10.5194/acp-14-11185-2014

Martin et al., 2003, Crystallization of atmospheric sulfate-nitrate-ammonium particles, Geophysical Research Letters, 30, 21, 2012, doi:10.1029/2003GL017930.

[7-ii] Question about the BrNO2 chemistry scheme used in the model:

You state Line 25 Pager 23652: "The generation of NOx could significantly perturb bromine chemistry due to the formation of BrNO2 (see e.g. Fig. 2 in von 25 Glasow, 2010). A detailed discussion of volcanic plume Br–NOx chemistry, including a modelling study that includes additional BrNO2 reactions, can be found in Roberts et al. (2014b)."

Please can you clarify what BrNO2 chemistry scheme you are considering in the model? To my understanding this work follows directly that of von Glasow (2010) i.e. Br + NO2 -> BrNO2, with slow ($\sim$min) BrNO2 photolytic dissociation rate. However, the work of Roberts et al. (2014b) actually predicts Etna plume BrNO2 accumulation is much lower if additional reactions (and alternative products) are considered. This seems quite relevant to state in your discussion. If the in-plume BrNO2 accumulation is actually lower than your model assumes then it could potentially allow more BrO chemistry and BrO-mediated ozone loss, even for cases with a volcanic NOx emission.

It is also worth mentioning that this is not the first study to suggest volcanic NOx emissions may be lower than previously assumed in order that models can reproduce downwind observations. This was discussed in Boichu et al. (2011) in the context of both revised DOAS analysis and numerical model simulations (as the previous reports of v high NOx causes BrO to turn into BrONO2), and the NOx emission was also reduced in the simulations of Kelly et al. (2013) that were compared to ozone depletion mapped in Redoubt volcano plume. Conversely, Roberts et al. (2009) and (2014) suggest volcanic (as well as any background) NOx may be rapidly converted into HNO3 via BrONO2, and propose this as a possible source for elevated volcanic plume HNO3 (observed at Etna e.g. Voigt et al., 2014, Martin et al., 2012).

Voigt et al., 2014, Evolution of CO2, SO2, HCl, and HNO3 in the volcanic plumes from

Etna, Geophys. Res. Lett., 41, 2196–2203, doi:10.1002/2013GL058974.

[8-iii] Questions about HSC initialisation and model set-up. A high-temperature initialisation is needed to accelerate the onset of downwind plume BrO chemistry in order for BrO/SO2 to agree with that observed, as shown by previous model studies (Bobrowski et al., 2007, Roberts et al., 2009, Von Glasow, 2010, Kelly et al., 2013, Roberts et al., 2014), and already indicated by calculations of Oppenheimer et al. (2006). Hence the use of HSC thermodynamic model output for this purpose. However, there needs to be a much more open discussion of the limitations of using HSC for this purpose. Please add further comment to your ms on this, in the context of the statements below.

Line 13, page 23651: "Based on previous work (Gerlach, 2004; Martin et al., 2006; von Glasow, 2010) we used the thermodynamic equilibrium model HSC (Roine, 2007) to calculate the composition of the mixture of volcanic volatiles and ambient air in the "effective source region" which is located in the crater where temperatures are high enough so that the assumption of immediate thermodynamic equilibrium is still valid but also enough ambient air has been entrained to oxidise the main volcanic reduced gases (mainly H2S and H2) which leads to a dramatic change in halogen speciation."

The second half of this sentence is incorrect. Gerlach (2004); Martin et al. (2006) and Martin et al. (2009) are the correct references for the thermodynamic modelling. Bobrowski et al. (2007), Roberts et al., (2009), Von Glasow (2010) and Roberts et al. (2014) are relevant references regarding including HSC initialisation into atmospheric models. Importantly, Martin et al. (2009) show that the assumption of thermodynamic equilibrium is not valid as it predicts H2S, H2 and CO oxidise whereas in reality these species are observed thus clearly not oxidised. See Roberts et al. (2014) for further discussion: the 'dramatic change in halogen speciation' a.k.a. 'compositional discontinuity' (Gerlach, 2004) in fact is shifted to lower VA:VM and is no longer really valid as a concept if you prevent H2, CO and H2S from oxidising.

Line 19, page 23651: "Compared to von Glasow (2010) we used a higher ratio of volcanic volatiles : ambient air (95 : 5) which is as rich in volcanic volatiles as possible but already oxidised."

Please add that this is the same choice for VA:VM as was proposed in the model study of Etna plume by Roberts et al. (2014b). Still it remains an uncertainty in the HSC initialisation and is not properly justified on any physical basis. I am not sure what you mean by "which is as rich in volcanic volatiles as possible but already oxidised." As VA:VM increases above 5:95 you still tend to increase SO3 mixing ratio although other species (OH, Cl, Br) tend to decrease.

Overall, it seems there are serious problems with using a thermodynamic model to represent the near-downwind plume chemistry. First there is the question of choice of VA:VM. Second, the HSC output must be modified to avoid oxidising H2, CO, H2S, which are shown to be not oxidised by plume measurements. Furthermore, the HSC prediction of NOx has been shown to be kinetically limited (Martin et al., 2012). On this basis, how much trust can you have in the HSC output? What is the physical basis for deciding H2S is preserved in the plume but HCl and HBr may (partially) dissociate? The HSC predictions of OH, Cl and Br are "kept" because they are needed to accelerate the onset of the BrO chemistry but how do we know they are accurate? I think a more open admission of these uncertainties is needed in section 4.3 and regarding your conclusions. Presumably, a different choice of HSC (coupled to for example a different choice of volcanic aerosol emission, which is also poorly constrained) could affect the details of the Conclusions 23658 Line 10. "A comparison of the results from our three different humidity/heterogeneous chemistry cases gives an indication as to the extents that O3 depletion can be ascribed to reactive halogens generated in high-temperature processes within the crater, low-temperature processes within the crater, and low temperature processes further downwind."

Other comments:

[9] A limitation of the model-observation comparison presented, particularly for the

near-downwind observations (at up to 300 s downwind from the crater) is that you do not actually simulate the early stages of the plume chemistry (estimated at ~1 min travel time from vent to crater-rim), instead use a dilution factor for instantaneous mixing. Why do you do this? Why did you not attempt to simulate the plume more closely to the vent? Do you get the same results if you try to simulate the plume from an earlier stage?

[10] A nice aspect of the near-downwind work is that you show the model prediction of near-downwind SO2 is reasonable compared to that observed, before you compare to O3. This is important, because the plume reactive bromine chemistry or speciation can depend critically on the rate of plume-air mixing (see Roberts et al., 2014b). However, you do not show model nor observed SO2 column further downwind, you only present BrO/SO2 ratios. Whilst SO2 observations from DOAS (being integrated over a column) only partially constrain plume-air mixing, a comparison to the model would be relevant. Please can you include both DOAS column SO2 data and that predicted by the model for two emission compositions?

If other people are to attempt to reproduce your work it would be useful to mention the other important aspects of the model set-up e.g. gas flux, and wind-speed, information on plume dispersion, the volcanic aerosol emission assumed (see Roberts et al., 2014b as well as Von Glasow, 2010 for discussion of some of the important model parameters).

[TYPO] The two lowermost plots within the Figure 9 have the same caption. I assume the plot on the left should be 'no NOx'. Please correct, and also the equivalent figure in Supplementary material (high Br case).

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 23639, 2014.