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.

L. Surl et al.

l.surl@uea.ac.uk

Received and published: 19 January 2015

We would like to thank the reviewer for their helpful comments, most of which we have used to make revisions to the manuscript. The numbers in these responses relate to the numbering of the comments by the reviewer.

(1) Following the reviewer's comment we have extended our explanation of the O3 monitor calibration in section 2.2. We hope this now makes clear that the calibration process resulted in a correction of the 'raw' O3 results, and that uncertainties in this calibration are incorporated in the assessed error.

(2) Regarding the reviewer's comments on the potential for mercury interference with the ozone detection, we have added the following paragraph which explains why this is

not something compensated for in the post processing. As the O3 monitor used in the campaign utilised an external scrubber, an empirical study such as that by the EPA is of more direct applicability for quantifying the potential effect than Li et al., 2006.

"Gaseous elemental mercury is known to be emitted by Etna (Bagnato et al., 2007) and has the potential to cause interference with UV-based ozone monitors (EPA, 1999), giving false O3 signal when in the sampled air. The inlet and CrO3 scrubbers were not tested against mercury interference. If elemental mercury was entering the monitor in the mixing ratios observed by Bagnato et al. (2007), and causing interference of the magnitudes seen by EPA (1999), it would have caused us to make underestimations of the depletion of O3 on the order of 10 nmol/mol. However, this would assume that all the mercury emitted from the volcano was primarily in the elemental form. This is unlikely as modelling studies (von Glasow, 2010) indicated that much on the mercury is oxidized within the plume. In addition, mercury measurements at Etna contemporaneous with our campaign (Mather and Witt, pers. comm.) indicate that the mercury loading of the craters' plumes were significantly less than that which was measured by Bagnato et al. (2007) in 2004–2007 and confirmed that much of the observed mercury was in an oxidized or particulate form. It is also probable that the two CrO3 scrubbers scavenged or oxidised much of the elemental mercury in the sampled air, as the system is not heated and the scrubbers are changed daily it is unlikely that mercury scavenged by the scrubber would be re-volatilized as elemental mercury. No compensation for this potential effect was made in the post-processing as we believe that the potential for this interference is very low and because the observed anti-correlation of the O3 and SO2 signals is the inverse of what would be expected from such interference."

(3) The reviewer's suggestion that wind speed values were added to tables 3 and 5 has been implemented. Additionally, values for distance from craters to point of measurement have been added to table 5.

(4) Regarding the reviewer's suggestion of including error bars to the measurement data points on figure 10, we do not feel that we have sufficient information to give a

quantification of the error in either the x or y dimension for the spectroscopic data. A qualitative discussion of the uncertainties involved in this data can be found in the text. We believe it would be misleading to the reader to include error bars for this data as choosing such values would involve several assumptions.

(5) Regarding the comment about the potential for volcanic H2O to cause a significant increase in humidity at the crater rim, we have added text explaining that we do not believe this is occurring because there was no such signal in our humidity measurements. The short discussion of crystallisation in the results section has been retained so as to give context for this measurement result.

(further small comments on observations) We added a reference to Donovan et al (2014) in the suggested place. As per the reviewer's suggestion the Kern (2009) active DOAS O3 measurements have been discussed. As per the reviewer's suggestion, we have added a qualification to the statement that the BrO/SO2 ratios observed were "within the ranges" of prior measurements. We thank the reviewer for spotting typos in the manuscript. These have been corrected. As per the reviewer's suggestion the crater from which the Wittmer (2014) results have been used has been noted. Please note that this part of the manuscript has been substantially amended - this is discussed in a separate interactive comment.

(6-i) Regarding the comment on the crystallisation humidity of volcanic aerosol. The reviewer is right in pointing out that mixed, highly concentrated volcanic aerosol particles might have (much) lower crystallisation humidities than what we listed in the manuscript. The composition of volcanic aerosol is poorly defined and was not measured to the required precision during this campaign. We modified the text, wording the description of deliquescence/crystallisation more carefully. The text section now reads: "Following Seinfeld and Pandis (2006) a crystallisation humidity of 40% for sulphate containing particles is assumed in the model but other studies suggest sulphate containing particles to remain liquid at lower relative humidities (e.g. Martin et al 2003). Regardless of the exact composition and crystallisation humidity of the volcanic aerosol

present on the days of this study when simultaneous SO2 and O3 measurements were made we wanted to test the implications of crystallised aerosol in the model. We therefore ran the model at three different settings regarding the deliquescence of the aerosol:"

(7-ii) Regarding the comments on the BrNO2-related chemistry. We are using the same chemical reaction mechanism as in von Glasow (2010). The uncertainties in trying to model the chemistry in volcanic plumes are very large and there is no point to repeat all sensitivity studies that other studies have done. Therefore we decided to cite Roberts et al. (2014) rather than to repeat their tests especially given that Roberts et al. found that "The impact of this scheme on Br speciation is rather modest" (p.11211) and that there are still large uncertainties in the mechanism that they used (p. 11211). We changed the text to make this clearer. We did not include a full discussion of NOx chemistry in volcanic plumes as large uncertainties remain and referred to two publications that give a good overview of this discussion. To alert the reader's attention to the potential ramifications of Roberts et al. (2014)'s findings , the following text has been added to the manuscript: "Use of their scheme would likely result in less bromine being present as BrNO2 and might lead to somewhat different O3 development."

(8-iii) Regarding comment on the HSC initialisation. The use of HSC is problematic as it appears to predict the composition of some volcanic volatiles reasonably well but not at all for others. All modelling studies of volcanic plumes face the same problem of how to initialise their model and all that we are aware of resort to using HSC with or without modifications of the HSC output. The references that we chose are relevant in the context of this paper and our discussion does not claim to be a full discussion of this subject. Neither Martin et al (2009) nor Roberts et al (2014) suggest a physical reason as to why the reduced gasses H2 and H2S should not be oxidised. We changed the discussion of the use of HSC. Clearly many open questions remain that are far beyond the scope of the current study. We have modified the assumption of the appropriateness of assuming immediate thermodynamic equilibrium in this case from

"valid" to "largely valid". We have added the following text to give qualification to our use of HSC, and to direct the reader's attention to relevant literature in this area: "Recent studies (e.g. Aiuppa et al., 2007; Martin et al., 2012) have shown that the assumption of thermodynamic equilibrium is incorrect for a number of compounds, especially for H2S and NOx which makes the use of an equilibrium model such as HSC problematic but it is still regarded to provide a better approximation of the composition of volcanic volatiles than not assuming any equilibration. See also related comments in Roberts et al. (2014)."

(9) Regarding the first 60 seconds of model data. The reviewer's statement that we do not simulate the early stages of the plume chemistry is incorrect. The plume is simulated directly after plume release. For technical reasons the first model output is 60 sec after plume release. The reasons for using the "initial dilution" are discussed in Bobrowski et al (2007) and von Glasow (2010). To clarify why there are no lines on the figures for 0-60 seconds, the following text has been added:

"The 0 - 60 seconds section of the following figures are not plotted as the first data output from the model occurs at 60 seconds after plume release."

To increase the ease of reproducing the model study, we have followed the reviewer's suggestion to include the wind speed and dispersal scheme in the text. Due to the "puff" nature of the model, defining single numbers for aerosol and gas emissions flux is not simple or necessarily useful. Instead readers are directed to von Glasow (2010) for a more thorough discussion of the model.

(10) As per the reviewer's suggestion, we have included a plot of the modelled columns of BrO and SO2, superimposed with the relevant measurements. For consistency, a corresponding plot with the alternative initialisation has been added to the supplemental material.

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