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# Reactive bromine chemistry in Mt. Etna's volcanic plume: the influence of total Br, high temperature processing, aerosol loading and plume-air mixing

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## Abstract

Volcanic emissions present a source of reactive halogens to the troposphere, through rapid plume chemistry that converts the emitted HBr to more reactive forms such as BrO. The nature of this process is poorly quantified, yet is of interest to understand volcanic impacts on the troposphere, and infer volcanic activity from volcanic gas measurements (i.e. BrO/SO<sub>2</sub> ratios). Recent observations from Etna report an initial increase and subsequent plateau or decline in BrO/SO<sub>2</sub> ratios with distance downwind.

We present daytime *PlumeChem* model simulations that reproduce and explain the reported trend in BrO/SO<sub>2</sub> at Etna including the initial rise and subsequent plateau.

Through suites of model simulations we also investigate the influences of volcanic aerosol loading, bromine emission, and plume-air mixing rate on the downwind plume chemistry. Emitted volcanic HBr is converted into reactive bromine by autocatalytic bromine chemistry cycles whose onset is accelerated by the model high-temperature initialisation. These rapid chemistry cycles also impact the reactive bromine speciation through inter-conversion of Br, Br<sub>2</sub>, BrO, BrONO<sub>2</sub>, BrCl, HOBr. Formation of BrNO<sub>2</sub> is also discussed. We predict a new evolution of Br-speciation in the plume, with BrO, Br<sub>2</sub>, Br and HBr as the main plume species in the near downwind plume whilst BrO, and HOBr are present in significant quantities further downwind (where BrONO<sub>2</sub> and BrCl also make up a minor fraction). The initial rise in BrO/SO<sub>2</sub> occurs as ozone is entrained into the plume whose reaction with Br promotes net formation of BrO. Aerosol has a modest impact on BrO/SO<sub>2</sub> near-downwind (< 6 km) at the relatively high loadings considered. The subsequent decline in BrO/SO<sub>2</sub> occurs as entrainment of oxidants HO<sub>2</sub> and NO<sub>2</sub> promotes net formation of HOBr and BrONO<sub>2</sub>, whilst the plume dispersion dilutes volcanic aerosol so slows the heterogeneous loss rates of these species. A higher volcanic aerosol loading enhances BrO/SO<sub>2</sub> in the (> 6 km) downwind plume.

Simulations assuming low/medium and high Etna bromine emissions scenarios show the bromine emission has a greater influence on BrO/SO<sub>2</sub> further downwind and a modest impact near downwind, and show either complete or partial conversion of

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HBr into reactive bromine, respectively, yielding BrO contents that reach up to ~ 50 % or ~ 20 % of total bromine (over a timescale of a few 10's of minutes).

Plume-air mixing (which in our model with fixed plume dimensions is inversely related to the volcanic emission flux) non-linearly impacts the downwind BrO/SO<sub>2</sub>. A slower rate of plume-air mixing (or greater volcanic emission flux) leads to lower BrO/SO<sub>2</sub> ratios near downwind, but also delays the subsequent decline in BrO/SO<sub>2</sub>, thus yields higher BrO/SO<sub>2</sub> ratios further downwind. We highlight the important role of plume chemistry models for the interpretation of observed changes in BrO/SO<sub>2</sub> during/prior to volcanic eruptions, as well as for quantifying volcanic plume impacts on atmospheric chemistry. Simulated plume impacts include ozone, HO<sub>x</sub> and NO<sub>x</sub> depletion, the latter converted into HNO<sub>3</sub>. Partial recovery of ozone concentrations occurs with distance downwind (as BrO concentrations decline), although cumulative ozone loss is ongoing over the 3 h simulations.

We suggest plume BrNO<sub>2</sub> may be less prevalent than previous model predictions. We highlight additional reactions for BrNO<sub>2</sub> (and alternative pathways via BrONO) which likely reduce in-plume BrNO<sub>2</sub> prevalence. We also highlight uncertainty in volcanic NO<sub>x</sub> emissions that might be lower than previously assumed (i.e., equilibrium NO<sub>x</sub>), due to the slow rate of N<sub>2</sub> oxidation. The atmospheric:magmatic gas ratio,  $V_A : V_M$ , in equilibrium model representations of the near vent plume is presently poorly defined. Using a revised equilibrium model methodology, lower  $V_A : V_M$  become suitable (e.g.  $V_A : V_M = 98 : 2, 95 : 5$ ), which also yield a lower estimate for volcanic NO<sub>x</sub>, although uncertainties to such equilibrium model representations of near-vent plume chemistry and especially NO<sub>x</sub> formation are emphasized.

## 1 Introduction

The discovery of volcanic BrO (Bobrowski et al., 2003), and its subsequent observation in many volcanic plumes globally (e.g. Oppenheimer et al., 2006; Bobrowski et al., 2007; Bobrowski and Platt, 2007; Kern et al., 2009; Bani et al., 2009; Louban

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et al., 2009; Theys et al., 2009; Boichu et al., 2011; Heue et al., 2011; Bobrowski and Giuffrida, 2012; Rix et al., 2012; Hörmann et al., 2013; Kelly et al., 2013; Lübcke et al., 2013), demonstrates the reactivity of volcanic halogen emissions in the troposphere. Notably, DOAS (Differential Optical Absorption Spectroscopy) measurements show BrO forms at 100's pptv to ppbv concentrations just minutes downwind, an order of magnitude higher than that found in the Arctic, where BrO episodes of up to 10's pptv cause significant ozone depletion and mercury deposition events (Simpson et al., 2007). Additionally, there is potential to use long-term BrO monitoring at volcanoes as an indicator of volcanic activity (Bobrowski and Giuffrida, 2012). Thus there is strong interest in developing models to simulate the formation of reactive bromine (and chlorine) in volcanic plumes, and to predict the downwind impacts from both quiescently degassing volcanoes and episodic eruptions to the troposphere. Studies to date have used equilibrium models to predict the high-temperature chemistry of the near vent plume, which is then used to initialise kinetic atmospheric chemistry models of the downwind reactive halogen chemistry (Bobrowski et al., 2007; Roberts et al., 2009; von Glasow, 2010; Kelly et al., 2013). See von Glasow et al. (2009) for an overview.

This study uses a purpose-built kinetic model, *PlumeChem* (Roberts et al., 2009), to investigate the volcanic plume reactive halogen chemistry, focusing here on bromine. We include a revised methodology (Martin et al., 2009) for equilibrium calculations used to represent the near-vent high-temperature chemistry, and discuss uncertainties in the use of thermodynamic equilibrium models. Below, we outline the progression of recent research on using equilibrium models for high-temperature near-vent plume chemistry and the development of kinetic models for volcanic plume reactive halogen (BrO) chemistry. We then describe the new findings of this study specifically regarding the in-plume reactive bromine evolution presented by the model, and to highlight uncertainties in model high-temperature initialisation and the influence of total bromine, aerosol and plume-air mixing on the plume chemistry.

## 1.1 Application of the HSC equilibrium model to the near-vent plume

HSC is a commercially-available model (Outokumpo, Finland) that predicts the thermodynamic equilibrium composition of a gas mixture at a defined temperature, pressure and atomic composition. Such models are used to represent the composition of the near-vent volcano plume (e.g. Gerlach, 2004; Martin et al., 2006), predicting a vast array ( $\geq 100$ ) of chemical species. An overview of the input and outputs to HSC is provided in Table 1. The atomic composition of the mixture is determined by combining magmatic (comprising of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$ ,  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{Hg}$ , typically at around  $800\text{--}1100^\circ\text{C}$ ) and air ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Ar}$ , typically around  $0\text{--}20^\circ\text{C}$ ) components. The magmatic gas composition varies between volcanoes and may be estimated from crater-rim measurements. It is also possible to predict the abundance of gases that are missing from measurements as the magmatic gas  $\text{H}_2\text{O}\text{--}\text{H}_2$ ,  $\text{CO}_2\text{--}\text{CO}$ ,  $\text{SO}_2\text{--}\text{H}_2\text{S}$  equilibria are functions of oxygen fugacity, pressure of degassing and temperature (e.g. Giggenbach, 1987). The resulting HSC output composition depends critically on the assumed ratio of air to magmatic gases in the near-vent plume,  $V_A : V_M$ . However, this ratio is poorly defined, an issue we examine further in this study.

The HSC output is then used to initialise low-temperature kinetic models (such as *PlumeChem*, Roberts et al., 2009, *MISTRA*, von Glasow, 2010) of the volcanic plume reactive halogen chemistry including formation of BrO. These models show that elevated radicals in the HSC output accelerate the onset of autocatalytic BrO chemistry, leading to very rapid BrO formation. BrO formation occurs more slowly in kinetic models that are not initialised with high temperature chemistry. For the interest of atmospheric modellers, we simplify the complex HSC output ( $\geq 100$  species) in Table 1, following Roberts et al. (2009) who identified impacts of  $\text{HO}_x$ ,  $\text{NO}_x$ ,  $\text{Br}_x$  and  $\text{Cl}_x$  on the downwind plume halogen chemistry. The key species are further identified to be OH, NO, Br, Cl and  $\text{Cl}_2$ , noting  $\text{NO}_2 \ll \text{NO}$  and  $\text{HO}_2 \ll \text{OH}$ ,  $\text{Br}_2 \ll \text{Br}$  in the HSC output. These species act to accelerate autocatalytic reactive bromine formation (see Fig. 4 of Roberts et al., 2009). High-temperature near-vent formation of  $\text{SO}_3$  (a precursor to

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H<sub>2</sub>SO<sub>4</sub>) also influences the volcanic plume halogen chemistry by providing a source of aerosol surface area.

However, the thermodynamic assumption behind equilibrium models such as HSC may not always be appropriate for volcanic plume applications: Martin et al. (2009) noted that the re-equilibration (i.e., oxidation) of H<sub>2</sub>S within HSC is in disagreement with the widespread observed presence of H<sub>2</sub>S in volcanic plumes (exception: Erebus), and suggested a revised operation of HSC in which H<sub>2</sub>S is removed prior to re-equilibration. Furthermore, recent measurements confirming volcanic H<sub>2</sub> (Aiuppa et al., 2011; Roberts et al., 2012) indicate this argument also applies to H<sub>2</sub>, as well as CO (although CO is typically present in very trace concentrations, with some exceptions e.g. Mt. Erebus, see e.g. Gerlach, 2004 for various collated compositions). Here, the influence of this revised methodology on HSC output is evaluated, and uncertainties on downwind BrO chemistry investigated, including the effect of the assumed near-vent plume atmospheric to magmatic gas ratio ( $V_A : V_M$ ).

## 1.2 Kinetic models of downwind volcanic plume reactive halogen chemistry

Atmospheric chemistry models have been developed in an effort to simulate the reactive halogen chemistry of volcanic plumes, explain observed BrO formation and predict impacts of this chemistry. To date, two models: *MISTRA* (that simulates an advected column of air) and *PlumeChem* (in an expanding box or multi-grid box modes) have been developed for this purpose. Initialisation of these models includes the high-temperature chemistry of the near-vent plume, as represented by HSC. Calculations by Oppenheimer et al. (2006) showed BrO formation to be too slow if high-temperature near-vent radical formation is ignored. Bobrowski et al. (2007) performed the first kinetic model simulations of volcanic plume reactive halogen chemistry, using a model initialised with HSC at  $V_A : V_M$  of 0 : 100, 15 : 85, 40 : 60 finding the 40 : 60 simulation yielded highest downwind BrO/SO<sub>2</sub>. Roberts et al. (2009) queried the use of such high  $V_A : V_M$  of 40 : 60 which yields rather high SO<sub>3</sub> : SO<sub>2</sub> ratios, that implies volcanic sulfate emissions would exceed volcanic SO<sub>2</sub>. Roberts et al. (2009) presented model

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simulations initialised with HSC at  $V_A : V_M$  of 10 : 90 that reproduced the rapid formation of BrO/SO<sub>2</sub> at a range of Arc (subduction zone) volcanoes for the first time (including Etna, Soufriere Hills, Villarrica), and suggested the higher BrO/SO<sub>2</sub> observed in the Soufriere Hills volcano plume may be fundamentally due to higher Br/S in the emission. A model study by von Glasow (2010) with simulations initialised at  $V_A : V_M$  of 15 : 85 demonstrated good agreement to both reported column abundances of SO<sub>2</sub> and BrO/SO<sub>2</sub> ratios downwind of Etna.

All of the abovementioned simulations (Bobrowski et al., 2007; Roberts et al., 2009; von Glasow, 2010) predict substantial in-plume depletion of oxidants, including ozone, although to varying extents, and predict contrasting plume halogen evolution. Roberts et al. (2009) also demonstrated conversion of NO<sub>x</sub> into nitric acid via BrONO<sub>2</sub>, and proposed this mechanism can explain reported elevated HNO<sub>3</sub> in volcano plumes. Von Glasow (2010) simulated the impacts of volcanic reactive halogen chemistry on mercury speciation predicting significant conversion to Hg<sup>II</sup> in the plume.

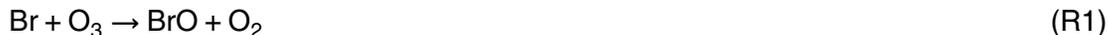
A number of observations of ozone abundance in volcanic plumes have recently been reported: Vance et al. (2010) observed ozone depletion in the Eyjafjallajökull plume, and at ground-level on Etna's flanks (by passive sampling). Schumann et al. (2012) presented multiple measurements of the downwind plume of Eyjafjallajökull that observed ozone depletion to variable degrees. There exist also observations of depleted ozone in Mt. St. Helen's plume (Hobbs et al., 1982) that are now believed to be likely due to BrO chemistry. A systematic instrumented aircraft investigation of ozone depletion in a volcano plume (where emissions are also quantified) is presented by Kelly et al. (2013), and compared to *PlumeChem* model simulations over 2 h of plume evolution, finding good spatial agreement in the modelled and observed ozone concentrations. However, Baker et al. (2010) did not detect an ozone depletion signal upon the (variable) background.

A number of modelling discrepancies exist. For example, the model studies of Roberts et al. (2009), von Glasow (2010), and Kelly et al. (2013), predict contrasting Br-speciation (and consequently contrast in predicted impacts on ozone and other





repeated cycling between BrO and Br (Reactions R1 and R2) causing rapid ozone loss (10's ppbv, i.e. loss is orders of magnitude larger than BrO concentration). Autocatalytic formation of BrO occurs through cycles involving reaction of BrO with oxidants, (HO<sub>2</sub>, NO<sub>2</sub>), (Reactions R3 and R4), aerosol-phase heterogeneous chemistry (Reactions R5 and R6) to release a halogen dimer, whose photolysis generates two halogen radicals (Reaction R7). Aqueous-phase equilibria (Wang et al., 1994) determine that the halogen dimer produced is Br<sub>2</sub>. Formation of reactive chlorine is promoted if aerosol becomes Br<sup>-</sup> depleted such that aqueous-phase equilibria begin to favour BrCl (Wang et al., 1994), as the product from (Reactions R5 and R6), which photolyses, to generate reactive chlorine (albeit not autocatalytic), and re-generating reactive bromine.



The background atmosphere chemistry scheme used here is identical to that of Roberts et al. (2009), assuming a somewhat polluted atmosphere. For the model simulations initialised around midday, background ozone is ~ 60 ppbv, HO<sub>x</sub> and NO<sub>x</sub> are around 0.17 ppbv and 30 pptv respectively, with an ambient temperature of 285 K and 60 % relative humidity (RH). The plume dispersion parameterisation used in this study is identical to that of Roberts et al. (2009), based on Pasquill-Gifford case 4, with a SO<sub>2</sub> gas flux of 10 kg s<sup>-1</sup> (unless otherwise stated) at a wind-speed of 10 m s<sup>-1</sup>. Volcanic aerosol loading in the model is investigated as part of the study, and for the majority of simulations is set to be a factor of 10 lower than that of Roberts et al. (2009), following the *PlumeChem* model set-up used in Kelly et al. (2013).

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aerosol surface area loading an order of magnitude lower ( $\sim 10^{-11} \mu\text{m}^2 \text{ molec SO}_2^{-1}$ ) than the “high” estimate. Further discussion on the aerosol surface area loading estimate is provided below.

Both the volcanic aerosol loading and volcanic bromine content influence the downwind BrO/SO<sub>2</sub> evolution, as discussed further in terms of the time-evolution of plume reactive bromine speciation in Sect. 3.5. Interestingly, whilst the volcanic aerosol and bromine content have a strong impact on the plateau in BrO/SO<sub>2</sub> far downwind (both in terms of value and when it is reached), Fig. 1b indicates that aerosol and bromine content exert a much more limited impact on BrO/SO<sub>2</sub> in the very young plume during the first  $\sim 8$  min ( $\sim 5$  km) of plume evolution, at least for the plume dispersion conditions simulated. For example, at 36 km downwind, the two contrasting aerosol loadings cause the model BrO/SO<sub>2</sub> to vary from  $4.2 \times 10^{-4}$  to  $1.4 \times 10^{-3}$  (“high” bromine scenario) and from  $2 \times 10^{-4}$  to  $4 \times 10^{-4}$  (“medium” bromine scenario), whereas at 6 km downwind all of these model runs predict BrO/SO<sub>2</sub> between  $2.5 \times 10^{-4}$  and  $4 \times 10^{-4}$ . This near-downwind similarity in BrO/SO<sub>2</sub> (despite varying Br<sub>tot</sub>/SO<sub>2</sub> as well as aerosol loading) is related to the role of oxidants in forming BrO, and differences in the proportion of HBr converted to reactive bromine. This model finding is consistent with the observations of Bobrowski and Giuffrida (2012) at 6 km downwind that showed BrO/SO<sub>2</sub> was independent of relative humidity (a key control on sulphate aerosol volume hence surface area). A model explanation (see Sect. 3.5) is that BrO/SO<sub>2</sub> ratios are primarily controlled by Br to BrO partitioning – itself a function of in-plume ozone concentrations – in this region where the plume is still relatively concentrated. In the relatively concentrated plume, reactive uptake of HOBr and BrONO<sub>2</sub> on volcanic aerosol is very rapid (exceeding photolytic loss pathways and their formation rates) thus ensures these species do not accumulate in this region of the plume. Aerosol surface area becomes a significant control on BrO : HOBr : BrONO<sub>2</sub> partitioning hence BrO/SO<sub>2</sub> in the more dilute dispersed plume downwind where HOBr and BrONO<sub>2</sub> can begin to accumulate.

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In general, a higher  $\text{Br}_{\text{tot}}/\text{SO}_2$  in the emission leads to greater  $\text{BrO}/\text{SO}_2$  far downwind. This is in accordance with the proposed role of  $\text{Br}/\text{S}$  in the emission to explain order of magnitude variation in  $\text{BrO}/\text{SO}_2$  ratios across Arc volcanoes (Roberts et al., 2009). A higher aerosol loading promotes the conversion of  $\text{HBr}$  into reactive forms, and the occurrence of reactive bromine as  $\text{BrO}$  in the far downwind plume but has limited impact on  $\text{BrO}/\text{SO}_2$  levels near to source, as mentioned above. Notably, the simulation with both “high” bromine and the larger aerosol estimate predicts  $\text{BrO}/\text{SO}_2$  that exceeds reported observations far downwind, and does not reproduce the plateau in  $\text{BrO}/\text{SO}_2$  beyond  $\sim 5$  km downwind of Etna summit recently reported by Bobrowski and Giuffrida (2012). We acknowledge the Etna bromine emission may vary with time therefore use both medium and high bromine emission scenarios alongside a low  $\text{Br}$  scenario in the further model simulations of this study (shown by gray and red lines). However, for the high bromine scenario, only the simulation with “medium” aerosol surface area loading appears consistent with the  $\text{BrO}/\text{SO}_2$  observations by Bobrowski and Giuffrida (2012). The “medium” aerosol surface area loading is considered as likely being more representative and this estimate,  $\sim 10^{-11} \mu\text{m}^2 \text{ molec SO}_2^{-1}$ , is used in all further model simulations of this study. Further justification is given below.

As mentioned above, few estimates of volcanic aerosol surface area loading exist, particularly in ash-poor plumes, and the available aerosol measurements are not always reported in the context of plume strength (e.g as indicated by a plume “tracer” or quasi-tracer such as  $\text{SO}_2$ ). For Etna plume, Watson and Oppenheimer (2000) report sun-photometer measurements of plume particles, from which a total particle mass flux of between  $4.5$  and  $8.0 \text{ kgs}^{-1}$  is derived. Assuming their end-member densities of sulphate ( $1.67 \times 10^3 \text{ kg m}^{-3}$ ) or water ( $1 \times 10^3 \text{ kg m}^{-3}$ ) yields volume fluxes of  $(2.7\text{--}4.8) \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$  or  $(4.5\text{--}8.0) \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$ , which, using the reported mean effective radius,  $R_{\text{eff}} = 0.83 \mu\text{m}$ , yields a surface area flux range between  $550$  and  $1650 \text{ m}^2 \text{ s}^{-1}$ . Concurrent  $\text{SO}_2$  fluxes are not reported, but the assumption of an Etna  $\text{SO}_2$  flux of on the order of thousand of tonnes per day ( $11.6 \text{ kgs}^{-1}$ ) results in a surface area to  $\text{SO}_2$  ratio of  $5 \times 10^{-12}\text{--}1.5 \times 10^{-11} \mu\text{m}^2 \text{ molec}^{-1} \text{ SO}_2$ . This estimate is consistent with

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our “medium” aerosol loading (although a wider range of values can be obtained if  $R_{\text{eff}}$  is allowed to vary). However, even though Watson and Oppenheimer (2006) report  $R_{\text{eff}}$  values from their sun-photometer measurements, it must be emphasized that the data actually indicate a substantial (majority) proportion of volcanic aerosol surface area to be contributed by particles with radii beyond their reported measurement range (see their Fig. 6b in particular) at either  $\geq 5 \mu\text{m}$  or  $\leq 0.1 \mu\text{m}$  respectively.

Spinetti and Buongiorno (2007) report airborne multispectral image observations, from which an aerosol effective radius of  $\sim 1 \mu\text{m}$  is derived for quiescent degassing conditions. Martin et al. (2008) and Allen et al. (2006) report in-situ measurements of Etna aerosol, although in the absence of concurrent in-situ measurements of  $\text{SO}_2$  it is challenging to derive a value for the total particle surface area loading from these data. We supply the following rough calculation of total aerosol surface area assuming particles of one radius size only. Based on reported sulphate :  $\text{SO}_2$  molar ratio of 1 : 100 (Martin et al., 2008), and an estimated sulphate aerosol particle size of  $\sim 1 \mu\text{m}$  radius in the Etna Voragine crater emission (i.e. yielding individual particle volume of  $\sim 4.2 \mu\text{m}^3 \text{particle}^{-1}$ ), combined with an estimated total sulphate aerosol volume from E-AIM yielding  $\sim 5 \times 10^{-5} \text{cm}^3 \text{m}^{-3}$  in a plume containing 0.01 ppmv sulphate (280 K, 50 % RH) i.e. for 1 ppmv ( $\sim 10^{13} \text{molec cm}^{-3}$ )  $\text{SO}_2$  (see Roberts et al., 2014), a particle number concentration of  $10^7 \text{m}^{-3}$  can be calculated, yielding a total particle surface area of  $\sim 10^{-11} \mu\text{m}^2 \text{molec SO}_2$ . Ongoing work is attempting to refine these estimates of the volcanic surface area loading using new in-situ size-resolved aerosol measurement data. Nevertheless the available evidence points towards the aerosol surface area loading for Etna to be significantly lower (an order of magnitude) than the  $\sim 10^{-10} \mu\text{m}^2 \text{molec SO}_2$  estimate of Roberts et al. (2009). This “medium” aerosol loading (per molecule  $\text{SO}_2$ ) estimate was also assumed in *PlumeChem* simulations of Redoubt volcano plume (Kelly et al., 2013) that found good agreement between the observed and modelled BrO-mediated plume ozone depletion.

### 3.3 Thermodynamic modelling of near-vent volcanic plumes

An important model parameter in the *PlumeChem* model initialisation is the use of output from thermodynamic model HSC to represent the composition of the high-temperature near-vent plume. From the vast HSC output (> 100 species) we identify NO, OH, Cl and Br and Cl<sub>2</sub> as key species that act to accelerate the onset of autocatalytic BrO formation in the downwind plume, with SO<sub>3</sub> important as a precursor to volcanic H<sub>2</sub>SO<sub>4</sub> aerosol. Further, the observed presence of H<sub>2</sub>S and H<sub>2</sub> in volcanic plumes leads us to a revised HSC methodology (see Martin et al., 2009). Figure 2 compares the key species in the HSC output for the near-vent plume of Etna (“medium” Br scenario), using the standard HSC methodology, in which (a) H<sub>2</sub> and H<sub>2</sub>S re-equilibrate, and (b) the modified method whereby H<sub>2</sub>S and H<sub>2</sub> do not re-equilibrate. NO, OH, Cl and Br and Cl<sub>2</sub> gas mixing ratios are shown for V<sub>A</sub> : V<sub>M</sub> ranging from 0 : 100 to 15 : 85, where V<sub>A</sub> : V<sub>M</sub> is the ratio of air to magmatic gases in the near-vent plume (with V<sub>A</sub> : V<sub>M</sub> plotted as a fraction in Fig. 2), with the HSC temperature varied according to the mixture of magmatic (1050 °C) and ambient (20 °C) temperatures.

In general, higher mixing ratios of these species occur at higher V<sub>A</sub> : V<sub>M</sub>, with a corresponding decrease in HBr, and other “parent” species unless they are in excess. However, the trend is not linear. NO concentrations are particularly enhanced at high V<sub>A</sub> : V<sub>M</sub>, reflecting the dissociation and partial oxidation of N<sub>2</sub> that originates from the background atmosphere. However, we highlight uncertainties in such near-vent plume NO<sub>x</sub> production, as discussed in Sect. 3.6.2. The greater proportion of air relative to magmatic gases at high V<sub>A</sub> : V<sub>M</sub> is also accompanied by a lower temperature, which alters the balance between Cl<sub>2</sub> and Cl radicals (Br<sub>2</sub> remains low over the whole V<sub>A</sub> : V<sub>M</sub> range). Of particular note is a step increase in radical concentrations in Fig. 2a (in which H<sub>2</sub> and H<sub>2</sub>S re-equilibrate). This is the so-called compositional discontinuity (C.D.) (Gerlach, 2004), which occurs at around V<sub>A</sub> : V<sub>M</sub> ~ 0.02 for Etna’s magmatic composition. At the C.D., the reduced magmatic gases (H<sub>2</sub>S, H<sub>2</sub>, CO, etc.) are essentially fully oxidised (SO<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>), thus addition of further oxidant (increasing V<sub>A</sub>/V<sub>M</sub>) causes a step

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increase in the concentrations of other oxidised species and radicals. However, in the revised HSC methodology (in which  $\text{H}_2$  and  $\text{H}_2\text{S}$  do not re-equilibrate) the C.D. has shifted to low  $V_A : V_M$ , as first shown by Martin et al. (2009). Indeed, it may no longer be relevant to talk of a C.D. at all, as an increase in radicals occurs immediately as  $V_A : V_M$  is increased; this is because the composition of the mixture is no longer buffered by magmatic  $\text{H}_2/\text{H}_2\text{O}$  and  $\text{H}_2\text{S}/\text{SO}_2$  ratios. Notably, the new method for operating HSC also changes the composition of the HSC output, particularly at low  $V_A : V_M$ .

### 3.4 Effect of $V_A : V_M$ in HSC on the predicted downwind BrO formation

We now investigate how the assumed  $V_A : V_M$  in HSC (using the revised methodology) impacts the downwind volcanic plume reactive halogen chemistry. A suite of 1 h simulations predicting downwind BrO/ $\text{SO}_2$  evolution are shown in Fig. 3, and compared to reported BrO/ $\text{SO}_2$  ratios from Oppenheimer et al. (2006) and Bobrowski et al. (2007). Model runs using HSC initialisations (2 : 98 and 5 : 95) are highlighted in red.

In Fig. 3 the *PlumeChem* model is initialised using HSC operated at a range of  $V_A : V_M$  varying from 0 : 100, 1 : 99, 2 : 98, 5 : 95, 10 : 90 to 15 : 85 for six different model scenarios: (a) “medium” bromine emission with a chemistry scheme that excludes  $\text{BrNO}_2$ , (b) “medium” bromine emission with a chemistry scheme that includes  $\text{BrNO}_2$ , (c) “high” bromine emission with a chemistry scheme that excludes  $\text{BrNO}_2$ , (d) “high” bromine emission with a chemistry scheme that includes  $\text{BrNO}_2$ , (e) “low” bromine emission with a chemistry scheme that excludes  $\text{BrNO}_2$ , (f) “low” bromine emission with a chemistry scheme that includes  $\text{BrNO}_2$ . The corresponding variation in BrO/ $\text{SO}_2$  in each plot indicates that the assumed  $V_A : V_M$  has a significant, and rather complex impact on the downwind chemistry.

Nevertheless, some generalizations can be made: all model runs initialised using HSC with  $V_A : V_M$  of 0 : 100 (i.e. with no air mixed into the near-vent plume) under-predict BrO/ $\text{SO}_2$  ratios compared to the observations. Inclusion of some air is needed to generate sufficient radicals in the near-vent magmatic-air mixture to significantly accelerate the onset of autocatalytic BrO formation in order that BrO/ $\text{SO}_2$  rises to  $10^{-4}$

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over a timescale of minutes downwind. This has also previously been shown (e.g. Bobrowski et al., 2007; Roberts et al., 2009, von Glasow, 2010) using atmospheric chemistry models. For this reason, previous studies have chosen to initialise atmospheric chemistry models with HSC output using  $V_A : V_M > 0 : 100$ . However, the choice of  $V_A : V_M$  in HSC calculations of the near-vent plume is rather poorly defined, and mostly motivated by the need for  $V_A : V_M$  to exceed the so-called “compositional discontinuity”, e.g. Bobrowski et al. (2007) used  $V_A : V_M = 40 : 60$ , Roberts et al. (2009) suggested lower  $V_A : V_M = 10 : 90$  (as the 40 : 60 initialisation converts too much  $\text{SO}_2$  to sulfate), and Von Glasow (2010) used  $V_A : V_M = 15 : 85$ . Given the revised location of the compositional discontinuity outlined above in Fig. 2, here we suggest an even lower  $V_A : V_M$ , e.g.  $V_A : V_M = 2 : 98$  or  $V_A : V_M = 5 : 95$  as still suitable. The BrO/ $\text{SO}_2$  evolution for these  $V_A : V_M$  is highlighted (in red) in Fig. 3, demonstrating generally good agreement to the reported observations, particularly when  $\text{BrNO}_2$  is not included in the model chemistry scheme (further discussion on  $\text{BrNO}_2$  is given in Sect. 3.6). Lowering the assumed  $V_A : V_M$  in HSC yields a lower  $\text{SO}_3/\text{SO}_2$  ratio, and lowers the volcanic  $\text{NO}_x$  source, see Fig. 3. As  $\text{SO}_3$  is a direct precursor to  $\text{H}_2\text{SO}_4$  the  $\text{SO}_3/\text{SO}_2$  ratio in the emission exerts a primary control on the sulphate/ $\text{SO}_2$  in the volcanic emission. The lower  $V_A : V_M$  proposed here yields  $\text{SO}_3/\text{SO}_2 \sim 0.01$ , in reasonable agreement to sulphate :  $\text{SO}_2$  molar ratios reported at Etna Voragine crater emission ( $\sim 0.017$ ) and slightly lower than that of the Etna north-east crater emission ( $\sim 0.05$ ), whose aerosol emission may also have included a volcanic ash component (see Martin et al., 2008). The lower volcanic  $\text{NO}_x$  emission at lower  $V_A : V_M$  is also consistent with our discussion of uncertainties in volcanic  $\text{NO}_x$  emissions (Sect. 3.6.2).

Figure 3 also highlights the impact of formation of  $\text{BrNO}_2$ . For the medium and low bromine scenarios with the chemistry scheme that includes  $\text{BrNO}_2$  the model tends to underestimate the near downwind formation of BrO relative to the observed BrO/ $\text{SO}_2$  ratios at Etna (particularly for HSC initialisations at high  $V_A : V_M$ ), Fig. 3b. Conversely, the same simulations performed without  $\text{BrNO}_2$  in the model chemistry scheme are able to reproduce the reported rapid and immediate rise in downwind BrO/ $\text{SO}_2$ ,

Fig. 3a. We now evaluate more carefully the plume Br-speciation, the volcanic  $\text{NO}_x$  emission and the chemical fate of  $\text{BrNO}_2$  in volcanic plumes.

### 3.5 Speciation of reactive bromine in Etna plume and implications for observations of volcanic BrO

The time evolution of reactive bromine speciation is illustrated in Fig. 4 for simulations initialised using HSC at  $V_A : V_M = 5 : 95$  and with varying bromine content (Medium, High, or Low corresponding to  $\text{Br}_{\text{tot}}/\text{SO}_2$  of  $7.4 \times 10^{-4}$ ,  $2.4 \times 10^{-3}$ , and  $4.8 \times 10^{-4} \text{ mol mol}^{-1}$  respectively) and inclusion/exclusion of  $\text{BrNO}_2$ . A number of interesting features are identified:

- The proportion of reactive bromine as BrO rises rapidly in the first few minutes, but then stabilises or declines further downwind.
- HBr is fully converted to reactive bromine in the “medium” and “low” bromine simulations but only partially converted in the “high” bromine simulations. The extent of HBr conversion also depends on other factors as discussed below.
- BrO is formed in the plume at up to 40–50 % (“medium” and “low” Br emission scenario) or 10–20 % (high Br emission scenario) of total bromine. This difference is related to the extent of HBr conversion, as BrO reaches a similar maximum fraction ( $\sim 50\%$ ) of reactive bromine in the three simulations.
- An increase in plume BrCl occurs when HBr concentrations are depleted, which is due to the aqueous-phase equilibria producing significant BrCl instead of just  $\text{Br}_2$ .
- HOBr and  $\text{BrONO}_2$  are present in all simulations, and represent an increasing proportion of reactive bromine as the plume disperses downwind, whilst the proportion of BrO declines.

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- When  $\text{BrNO}_2$  is included in the model chemistry scheme, it is rapidly formed near to the source as a significant proportion (20–30 %) of total bromine. The proportion of reactive bromine as  $\text{BrNO}_2$  subsequently declines with distance or time downwind.
- When  $\text{BrNO}_2$  is included in the model chemistry scheme, the proportion of reactive bromine as  $\text{Br}_2$  and  $\text{Br}$  is lower near to source and formation of  $\text{BrO}$  is delayed for the “medium” and “low” Br emission’ scenarios.

The observed and modelled trend in  $\text{BrO}/\text{SO}_2$  shown in Figs. 1 and 3 is thus explained as follows:  $\text{HBr}$  is converted into reactive forms by autocatalytic bromine chemistry cycles involving volcanic aerosol, entrained atmospheric oxidants, sunlight and which are accelerated by radical species present in the high-temperature initialisation. The initial rise in  $\text{BrO}/\text{SO}_2$  primarily reflects trends in reactive bromine speciation; entrainment of background air containing ozone into the plume, promotes greater partitioning to  $\text{BrO}$  via the reaction  $\text{Br} + \text{O}_3$ . Plume-air mixing is thus an important control on  $\text{BrO}/\text{SO}_2$ , because the dilution of volcanic components and entrainment of air alter the balance between  $\text{Br}$  and  $\text{BrO}$ , e.g. by reducing the rate of  $\text{BrO}$  loss by the self-reaction  $\text{BrO} + \text{BrO}$  (to form  $2\text{Br}$  or  $\text{Br}_2$ ) relative to the formation of  $\text{BrO}$  by  $\text{Br} + \text{O}_3$ . The subsequent decline or plateau in  $\text{BrO}/\text{SO}_2$  occurs due to net conversion of reactive bromine from  $\text{BrO}$  in the forms  $\text{HOBr}$  (and to a lesser extent  $\text{BrONO}_2$ ) in the downwind, dispersed plume. These species are formed at an accelerated rate in the downwind plume as it disperses and entrains background air containing oxidants ( $\text{HO}_2$ ,  $\text{NO}_2$ ) which react with  $\text{BrO}$ . Further, the heterogeneous loss pathways for these species are slowed in the dispersed downwind plume where volcanic aerosol is diluted. The heterogeneous reactions of  $\text{HOBr}$  and  $\text{BrONO}_2$  with aerosol present a more rapid loss pathway than photolysis in the aerosol-rich environment of a volcanic plume. As the plume disperses and dilutes further downwind, net accumulation of  $\text{HOBr}$  (and  $\text{BrONO}_2$ ) occurs whilst  $\text{BrO}$  declines (as a fraction of  $\text{Br}_{\text{tot}}$ ), although it is emphasized that plume chemistry cycling between these species is ongoing throughout the simulation and is very rapid.

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reactive bromine). Roberts et al. (2009) suggested order of magnitude differences in  $\text{BrO}/\text{SO}_2$  between Soufriere Hills volcano ( $\text{BrO}/\text{SO}_2 \sim 10^{-3}$ ) and other Arc volcanoes like Etna ( $\text{BrO}/\text{SO}_2 \sim 10^{-4}$ ) could be attributed to order of magnitude differences in the ratio of total bromine to  $\text{SO}_2$  in their emissions. However, the non-linear relationship between BrO and emitted HBr, as identified in Figs. 4 and 5 for small-scale bromine variations, presents a complexity to efforts to quantify volcanic bromine emissions using DOAS observations of plume  $\text{BrO}/\text{SO}_2$  ratios within volcano monitoring programmes, and to modelling efforts to quantify impacts from volcanic halogen emissions to the troposphere. Further understanding of the extent to which volcanic bromine is rapidly converted into reactive forms in the near-downwind plume is needed as part of efforts to evaluate global impacts from volcanic halogen degassing. Further studies of the wider model parameter space can contribute to this aim, although more observations are also needed to constrain model uncertainty.

### 3.6 Uncertainties in plume chemistry regarding formation of $\text{BrNO}_2$

We now focus attention on the  $\text{BrNO}_2$  in volcanic plumes (first suggested by von Glasow, 2010), and highlight uncertainties in its in-plume prevalence. Simulations that include  $\text{BrNO}_2$  exhibit a delay in the rise in  $\text{BrO}/\text{SO}_2$  compared to observations such as Oppenheimer et al. (2006) for the “medium bromine emission scenario”, and particularly when initialised at high  $V_A : V_M$ , see Fig. 3. This is problematic, because the known reaction rate constant for the  $\text{Br} + \text{NO}_2$  reaction does suggest the rate of reaction should exceed photolytic loss leading to a significant partitioning of reactive bromine as  $\text{BrNO}_2$  in the young plume, as proposed by von Glasow (2010). Furthermore, observations elsewhere e.g. Masaya, Nicaragua, have (separately) identified elevated concentrations of both the reactants  $\text{NO}_2$  (Mather et al., 2004a) and BrO (Kern et al., 2009) at that volcano crater-rim. Figure 4b and d further illustrates how formation of  $\text{BrNO}_2$  from Br and  $\text{NO}_2$  is very rapid in the near-source plume, enabling  $\text{BrNO}_2$  to reach up to 20–30% of total bromine. As the plume subsequently disperses, the proportion of reactive bromine as  $\text{BrNO}_2$  declines as its photolytic loss begins to exceed its formation rate

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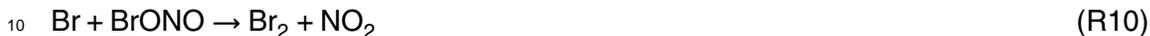
in the more dilute plume. This trend in BrNO<sub>2</sub> is broadly similar to that predicted by von Glasow (2010). However, as mentioned above, the discrepancy in Fig. 3 between the “medium” and “low” bromine emissions scenario model runs that include BrNO<sub>2</sub> and reported observations of BrO/SO<sub>2</sub> is problematic. We suggest firstly that BrNO<sub>2</sub> prevalence is likely lower than the model predicts due to occurrence of additional and alternative reaction pathways. Secondly we highlight uncertainty surrounding volcanic NO<sub>x</sub> emissions (which may be lower than previously assumed) as a further cause of uncertainty in BrNO<sub>2</sub>.

**3.6.1 Alternative Br + NO<sub>2</sub> products and additional BrNO<sub>2</sub> loss pathways**

Prior to considering the chemistry BrNO<sub>2</sub>, we highlight the contrasting example of BrONO<sub>2</sub>, which is included in all the simulations of this study. The rate of formation of BrONO<sub>2</sub> in the volcanic plume is rapid, especially in the near-downwind concentrated plume where BrO and NO<sub>2</sub> abundances are high. However, BrONO<sub>2</sub> is simulated to undergo a heterogeneous loss pathway on volcanic aerosol ( $\tau \sim$  s to 10 min further downwind) and loss via gaseous reaction with Br ( $\tau \sim$  s to 10 min further downwind), as well as a photolytic loss ( $\sim$  10's min). The fast loss pathways ensure that BrONO<sub>2</sub> does not accumulate to a large extent in the near downwind plume environment, occurring as small fraction of total bromine in the downwind dispersed plume (where Br and aerosol are diluted).

In contrast, the simulations of BrNO<sub>2</sub> by von Glasow (2010) and in Fig. 4b, d, and f predict rapid near-downwind formation of BrNO<sub>2</sub>, but include photolysis of BrNO<sub>2</sub> as the only loss mechanism (timescale  $\sim$  few min, von Glasow, 2010). We suggest BrNO<sub>2</sub> life-time hence its near source formation might be reduced by additional loss mechanisms (e.g. Reactions R13–R15): BrNO<sub>2</sub> may react with Br to produce Br<sub>2</sub> and NO<sub>2</sub> (Reaction R13) or with NO to form BrNO and NO<sub>2</sub> (Reaction R14), with BrNO reacting with Br to produce Br<sub>2</sub> and NO (Reaction R15), Bröske and Zabel (1998). Furthermore, Orlando and Burkholder (2000) and Bröske and Zabel (1998) find that the reaction of Br with NO<sub>2</sub> results primarily in an alternative product BrONO (Reaction R9)

that is likely shorter-lived in terms of chemistry (see Reactions R10–R12) as well as thermal decomposition. According to Bröske and Zabel (1998), and references therein, reaction of Br with NO<sub>2</sub> produces BrNO<sub>2</sub> only as a minor product (8 %) (Reaction R8), with BrONO as the major product (92 %) (Reaction R9). The latter undergoes rapid thermal decomposition (Reaction R12),  $\tau \sim 1$  s, thus is much shorter lived compared to BrNO<sub>2</sub>. BrONO can also react with Br to form Br<sub>2</sub> and NO<sub>2</sub> (Reaction R10), or with NO<sub>2</sub> to form BrNO<sub>2</sub> and NO<sub>2</sub> (Reaction R11).



Evaluation of the net impact of these reactions requires further investigation through numerical modelling. Nevertheless, the likely net effect is for much less BrNO<sub>2</sub> to be formed in the plume. The reaction Br + NO<sub>2</sub> primarily forms the less stable BrONO which will undergo fast thermal dissociation. The lifetime of any BrNO<sub>2</sub> (or BrONO) that is formed is likely shortened by the additional chemistry (Reactions R8–R15). Consequently a lower in-plume prevalence of BrNO<sub>2</sub> or BrONO is expected. We also note (data not shown) that in-plume ozone depletion predicted by the simulations that include BrNO<sub>2</sub> is generally lower than that predicted by the simulations that exclude BrNO<sub>2</sub> (see Fig. 7). For example, for the medium Br scenario, a maximum of  $\sim 16$  ppbv in-situ depletion is predicted which seems rather modest compared to reported observations of ozone loss at Etna (Vance et al., 2010), whilst the “medium Br” simulation

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without  $\text{BrNO}_2$  predicts loss of 30 ppbv, see Fig. 7). Below, we highlight further uncertainty in Etna  $\text{BrNO}_2$  chemistry arises from uncertainty in the volcanic  $\text{NO}_x$  emission.

### 3.6.2 Uncertainty in volcanic $\text{NO}_x$ emissions

It is emphasized that the rapid initial formation of  $\text{BrNO}_2$  is critically dependent on the high-temperature volcanic source of  $\text{NO}_2$  and Br, thus is subject to uncertainties in the near vent plume composition (represented by HSC). It is possible that volcanic  $\text{NO}_x$  emissions may be lower than previously assumed using the HSC thermodynamic equilibrium model, thereby further limiting the rate of formation of  $\text{BrNO}_2$ . We suggest that formation of  $\text{NO}_x$  via thermal  $\text{N}_2$  dissociation is likely kinetics (rather than thermodynamics) limited in the near-vent plume, given the very high bond-strength of  $\text{N}_2$  ( $945 \text{ kJ mol}^{-1}$ ). Thus near-vent formation of NO is likely limited due to the short ( $\sim 10$ 's seconds) timescales involved as the near-vent plume disperses and thereby cools. Under these conditions, formation of large quantities of volcanic  $\text{NO}_x$  as predicted by HSC assuming thermodynamic equilibrium for high  $V_A : V_M$  may not necessarily be valid. Indeed, this has recently been shown using a high-T kinetic model across a range of assumed  $V_A : V_M$  (Martin et al., 2012), who speculated other  $\text{NO}_x$  production pathways must instead occur to generate volcanic  $\text{NO}_x$ .

Here, we alternatively suggest that  $\text{NO}_x$  emissions from non lava-lake quiescently degassing (i.e. non-explosive) volcanoes such as Etna may simply be lower than previously assumed from HSC studies. We also emphasize that  $\text{HNO}_3$  (or nitrate) can be rapidly (on a seconds-minutes time-scale) formed within the plume from available  $\text{NO}_x$ , through formation of  $\text{BrONO}_2$  and its heterogeneous reactive uptake on aerosol. This low-temperature oxidation of  $\text{NO}_x$  to  $\text{HNO}_3$  was demonstrated by plume chemistry modelling of Roberts et al. (2009) and proposed as a mechanism for volcanic  $\text{HNO}_3$ , although was not considered in the study of Martin et al. (2012). Importantly, elevated "volcanic"  $\text{HNO}_3$  produced by this mechanism can originate either from  $\text{NO}_x$  of volcanic origin, and/or from  $\text{NO}_x$  from background air entrained into the plume. Furthermore, acidification of nitrate aerosol from background air entrained into the plume can

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also lead to gas partitioning therefore enhance the “volcanic”  $\text{HNO}_{3(\text{g})}$  signature. This acid-displacement of  $\text{HNO}_{3(\text{g})}$  by  $\text{H}_2\text{SO}_{4(\text{aq})}$  has been observed by Satsumabayashi et al. (2004). The observations collated by Martin et al. (2012) require consideration in the context of these two mechanisms. For Etna in particular the reported  $\text{HNO}_3/\text{SO}_2$  ratios are somewhat inconsistent and show large variability ( $-2.3 \times 10^{-4}$ ,  $7.8 \times 10^{-6}$ ,  $4.2 \times 10^{-3}$ ), which in itself might be indicative of a role of plume chemistry processing. Further investigation of the reported  $\text{HNO}_3/\text{SO}_2$  ratios as a function of plume concentration and background  $\text{NO}_x$  (and nitrate aerosol) is required to ascertain to what extent volcanic  $\text{HNO}_3$  measurements reflect a volcanic  $\text{NO}_x$  emission under different volcanic degassing scenarios.

### 3.7 Influence of plume-air mixing (volcanic gas flux) on BrO formation and ozone depletion

Here we investigate the role of plume-air mixing on the (low-temperature) halogen chemistry evolution of the downwind plume. This is achieved by keeping the plume dimensions constant, but increasing the volcanic gas and aerosol emission (by a factor of  $\times 5$  and  $\times 10$ ). For a constant specified volcanic plume dimensions (and emission composition), an increased volcanic emission results in a relatively slower rate of plume-air mixing, hence a lower oxidant:bromine ratio, but with volcanic components sustained at higher concentrations in the downwind plume. In a real plume environment, a change in degassing rate will likely also alter the plume dimensions somewhat, but a higher degassing rate will nevertheless generally lead to stronger, more concentrated plumes.

Simulations of 3 h duration (equivalent to 108 km downwind assuming  $10 \text{ ms}^{-1}$  wind-speed) with volcanic gas and aerosol emission increased from the basic run to  $\times 5$  and  $\times 10$  are shown in Fig. 6, for both the “medium” and “high” bromine emission scenarios. Results are shown for HSC initialisation at  $V_A : V_M = 5 : 95$ , and  $\text{BrNO}_2$  is excluded from the plume chemistry according to discussion above, and the volcanic  $\text{NO}_x$  emission from HSC is assumed although abovementioned uncertainties are acknowledged. The rate of plume-air mixing (inversely proportional to volcanic emission flux in the model)

has a linear impact on in-plume  $\text{SO}_2$  as expected, but a non-linear effect on the plume chemistry and impacts.

In particular, the greater volcanic emission (lower plume-air mixing) leads to a later onset and slower decline in  $\text{BrO}/\text{SO}_2$ . Far downwind ( $> 2$  h for specific simulation conditions), high  $\text{BrO}/\text{SO}_2$  is sustained for longer in plumes with high gas flux (low rate of plume-air mixing). Conversely, in the near downwind (several 10's of mins), plumes with lowest gas flux exhibit the fastest initial rise and highest  $\text{BrO}/\text{SO}_2$  ratios. This non-linear effect of the volcanic emission flux (inversely related to plume-air mixing) on volcanic  $\text{BrO}_2/\text{SO}_2$  can be explained as follows: a more rapid entrainment of oxidants in the low gas flux plumes leads to a high  $\text{BrO}/\text{SO}_2$  ratio due to more rapid initial rate of  $\text{BrO}$  formation via  $\text{Br} + \text{O}_3$  and slower  $\text{BrO}$  loss via the self-reaction (due to the greater rate of dilution of plume components). The subsequent decline in  $\text{BrO}/\text{SO}_2$  occurs as  $\text{BrO}$  is converted into reservoirs  $\text{HOBr}$  and  $\text{BrONO}_2$ . The onset and magnitude of this decline is greatest for plumes with a high rate of plume-air mixing (low gas flux) due to the entrainment of air containing  $\text{HO}_x$  and  $\text{NO}_x$  (promoting  $\text{HOBr}$  and  $\text{BrONO}_2$  formation) and dilution of volcanic aerosol (slowing  $\text{HOBr}$  and  $\text{BrONO}_2$  heterogeneous loss rates).

Ozone,  $\text{HO}_x$  and  $\text{NO}_x$  are depleted in the downwind plume, Fig. 7. For  $\text{HO}_x$  and  $\text{NO}_x$  the HSC initialisations used assumed a volcanic source of these species (elevated in-plume concentrations relative to background values of around 30 pptv and 0.17 ppbv for  $\text{HO}_x$  and  $\text{NO}_x$  respectively), which then become depleted downwind due to plume chemistry.  $\text{NO}_x$  is converted into  $\text{HNO}_3$  by  $\text{BrONO}_2$  chemistry, such that in-plume  $\text{HNO}_3$  is elevated above background. Ozone depletion in the plume reaches a maximum depletion around 10 min downwind, coincident with the highest in-situ  $\text{BrO}$  abundances that reach  $\sim 1$  ppbv (Fig. 6). For the base run, the maximum local ozone depletion is 30 or 45 ppbv for the medium and high bromine emission scenarios respectively. Greater in-plume ozone loss occurs at higher emissions flux (lower plume-air mixing), however for these runs the maximum ozone loss is constrained by the fact it cannot exceed  $\sim 60$  ppbv (the background ozone concentration). Thereafter ozone

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concentrations begin to recover as the plume disperses (Fig. 7), entraining background air, and BrO concentrations decline (Fig. 6), albeit at a slower rate than the SO<sub>2</sub> plume tracer. Ozone recovery is greater for the base run than the higher volcanic flux cases due to both physical and chemical consequences of enhanced plume-air mixing. Thus presence of a detectable ozone depletion signature at distances far downwind depends on the emission flux and plume-dispersion. It is emphasized, however, that ozone depleting BrO chemistry is in fact ongoing despite the in-plume ozone trend towards recovery, as shown by the continuing negative trend in the area-integrated ozone loss. Thus Fig. 7 indicates that the plume atmospheric impacts extend beyond the one to 3 h simulations presented in this study. Simulations over the lifetime of volcanic plumes under different volcanological and meteorological conditions are therefore required to quantify the global tropospheric impact from volcanic halogen emissions.

### 3.8 Implications for interpretation of volcanic BrO observations

We emphasize the complex role of plume chemistry in the interpretation of volcano flank DOAS measurements of BrO/SO<sub>2</sub>. Bobrowski and Giuffrida (2012) recently reported variation in BrO/SO<sub>2</sub> ratios at Etna related to the onset of eruption activity, for example with increasing BrO/SO<sub>2</sub> shortly prior to an eruptive event, and lower BrO/SO<sub>2</sub> during the eruption event, according to DOAS measurements 6 km downwind from the summit. These observations have been interpreted in the context of variable bromine and SO<sub>2</sub> emissions, related to subsurface magmatic processes. Lübcke et al. (2013) identified a decrease in BrO/SO<sub>2</sub> observed using a DOAS instrument prior to an eruption event at Nevado del Ruiz, Colombia (in a period whilst SO<sub>2</sub> emissions were increasing). However, we emphasize that a variation in plume BrO/SO<sub>2</sub> can also result from differences in the plume chemistry for varying volcanic emission flux magnitudes. Figure 6 shows that changes in volcanic gas flux (for a fixed plume dimension) can yield substantial changes in plume BrO/SO<sub>2</sub> ratio, even for a fixed Br<sub>tot</sub>:SO<sub>2</sub> ratio in the emission. In the near-downwind plume, a key control on BrO formation is the entrainment of oxidants, therefore an increase in volcanic emission flux



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wind-speed and the plume dimensions) as the plume disperses, which dilutes the volcanic components but entrains oxidants. These exert non-linear influences on the plume reactive bromine formation from emitted HBr and its speciation through interconversion of BrO, Br, Br<sub>2</sub>, BrCl, HOBr, BrONO<sub>2</sub>. Radicals in the high-temperature model initialisation (Br, Cl, NO<sub>x</sub>, HO<sub>x</sub>) act to accelerate the onset of the autocatalytic reactive bromine formation. The representation of high-temperature plume environment using thermodynamic models such as HSC is highlighted as a major area of model uncertainty, particularly regarding choice of atmospheric:magmatic gas ratio ( $V_A : V_M$ ) and the volcanic NO<sub>x</sub> emission. Also highlighted are uncertainties in the in-plume prevalence of BrNO<sub>2</sub>.

Available observational datasets only partially constrain the volcano plume chemistry model parameter space. Few simultaneous observations exist to both constrain plume conditions and quantify BrO formation and plume impacts e.g. on ozone under specific volcanological and meteorological conditions. Extremely few observations are available to constrain the near-vent plume composition. The study has shown that more than one model solution can exist that reproduces reported volcanic plume BrO/SO<sub>2</sub>. Whilst acknowledging these limitations, we summarize the following recommendations based on the parameter space investigated in this study:

The volcanic aerosol loading at Etna is likely significantly lower than that suggested by Roberts et al. (2009), and the simulations here found  $\sim 10^{-11} \mu\text{m}^2 \text{ molec SO}_2^{-1}$  to be suitable. Volcanic aerosol becomes an important control on BrO as the plume disperses downwind but seems to have a more modest influence on the BrO/SO<sub>2</sub> ratio closer to source, where the rate of plume-air mixing has a stronger control. Further in-situ measurements alongside SO<sub>2</sub> are needed to better constrain the aerosol surface area:SO<sub>2</sub> ratio, and future studies should also consider uncertainties in the kinetics of the heterogeneous chemistry on volcanic aerosol as recently highlighted by Roberts et al. (2014).

For the volcanic bromine emission, we presented simulations using the average Br/S ratio for NEC crater reported from filter-pack measurements by Aiuppa et al. (2005),

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$\text{Br}_{\text{tot}}/\text{SO}_2 = 7.4 \times 10^{-4}$ , a higher bromine emission,  $\text{Br}_{\text{tot}}/\text{SO}_2 = 2.4 \times 10^{-3}$ , as used by von Glasow (2010), as well as a lower  $\text{Br}_{\text{tot}}/\text{SO}_2 = 4.8 \times 10^{-4}$  corresponding to a measurement of Oppenheimer et al. (2006). Bromine emissions from volcanoes may exhibit variability with time (see Aiuppa et al., 2005, and a later study by Martin et al. (2008) reported a higher bromine emission ( $10^{-2}$ ). Likely the variability in measured  $\text{Br}/\text{S}$  reflects a combination of varying volcanic conditions and measurement error. Nevertheless, near-downwind  $\text{BrO}/\text{SO}_2$  ratios for the modelled “medium” and “high” bromine emission scenarios were found to be similar, whilst a proportionally greater conversion of emitted HBr into reactive bromine forms was simulated for the low and medium Br compared to the high Br scenarios. In other words, the extent to which volcanic emissions of HBr are converted to reactive forms is non-linearly dependent on the degassing scenario. This finding is important for future efforts to predict BrO-mediated atmospheric impacts arising from volcanic halogen degassing.

The model parameterisation for plume-air mixing used in this study (10 kgs<sup>-1</sup> SO<sub>2</sub>, 10 ms<sup>-1</sup> and Pasquill-Gifford case D dispersion) provides a plausible dispersion scheme for Etna, and broadly reproduces the reported SO<sub>2</sub> column abundance downwind, although the model simulations are not fully constrained by available observational data. Improved quantification of plume width, depth, gas flux and wind-speed (simultaneous to the plume chemistry measurements) are needed, which might be provided by aircraft observations, as has been recently demonstrated in the model-observation study of Redoubt eruption plume, Kelly et al. (2013). Here we showed that the rate of plume-air mixing (related to plume size and the volcanic emission flux) has a strong non-linear impact on  $\text{BrO}/\text{SO}_2$  ratios in the downwind plume, with implications for the interpretation of volcanic plume  $\text{BrO}/\text{SO}_2$  ratios as described above

When  $\text{BrNO}_2$  is included in the model (following von Glasow, 2010) it acts as a reservoir for reactive bromine, causing a delay in the downwind rise in  $\text{BrO}/\text{SO}_2$  that appears inconsistent with observations under the model conditions simulated. We suggest volcanic plume  $\text{BrNO}_2$  is likely less prevalent than previously assumed, highlighting additional chemical pathways for  $\text{BrNO}_2$  and alternative pathways via BrONO in the plume.

Formation of  $\text{BrNO}_2$  is also dependent on the volcanic  $\text{NO}_x$  emission, which is rather uncertain.

We emphasize the uncertainties in the use of thermodynamic models such as HSC to represent the high-temperature near-vent plume composition. A new HSC methodology that does not allow  $\text{H}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{S}$  to oxidise yields plausible initialisations using lower atmospheric : magmatic gas ratio,  $V_A : V_M$  (e.g. 5 : 95 or 2 : 98 compared to 10 : 90, 15 : 85, 40 : 60) and also predicts lower volcanic  $\text{NO}_x$ . Alternatively higher  $V_A : V_M$  ratios (e.g. 10 : 90) might still be used although very high  $V_A : V_M$  can cause excessive  $\text{SO}_2$  conversion to  $\text{SO}_3$  (relative to reported volcanic sulphate :  $\text{SO}_2$  observations, see Roberts et al., 2009). High  $V_A : V_M$  also yields higher equilibrium  $\text{NO}_x$  concentrations in HSC (via thermal dissociation of air- $\text{N}_2$ ) even though this process is believed to be kinetics limited in the near-vent plume. Given the limitations of using a thermodynamic equilibrium model to represent kinetic processes in the near-vent plume chemistry, the development of high-temperature kinetic models is to be encouraged.

## 4 Conclusion

We present a *PlumeChem* model study of the reactive halogen chemistry of Mt. Etna volcano plume that reproduces the recently reported trends in  $\text{BrO}/\text{SO}_2$ ; namely a rapid increase in the near-downwind followed by stability or decline in the far-downwind. A new in-plume evolution of Br-speciation is predicted:  $\text{BrO}$ ,  $\text{Br}_2$ ,  $\text{Br}$  and  $\text{HBr}$  are the main plume species in the near downwind plume whilst  $\text{BrO}$ ,  $\text{HOBr}$  (and  $\text{BrONO}_2$ ) are present in significant quantities further downwind. Emitted volcanic  $\text{HBr}$  is converted into reactive bromine by autocatalytic bromine chemistry cycles whose onset is accelerated by the model high-temperature initialisation. The initial rise in  $\text{BrO}/\text{SO}_2$  is primarily due to entrainment of ozone through plume dispersion that promotes  $\text{BrO}$  formation from  $\text{Br}$  radicals. A subsequent decline or plateau in  $\text{BrO}/\text{SO}_2$  occurs upon plume dispersion, which both dilutes the volcanic aerosol (slowing  $\text{HOBr}$  and  $\text{BrONO}_2$  heterogeneous loss rates) and entrains  $\text{HO}_2$  and  $\text{NO}_2$  from the background

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atmosphere (promoting their formation from BrO). This promotes net accumulation of reservoirs HOBr and BrONO<sub>2</sub> and a reduction in BrO in the dispersed downwind plume. Thus the model can explain the reported BrO/SO<sub>2</sub> trend at Etna.

We demonstrate the role of plume chemistry models to interpret volcanic BrO/SO<sub>2</sub> observations as well as quantify atmospheric impacts on HO<sub>x</sub>, NO<sub>x</sub>, HNO<sub>3</sub> and ozone. A number of volcanological and meteorological factors can influence plume BrO/SO<sub>2</sub> ratios, and we illustrate simulations with contrasting total bromine content, volcanic aerosol loading, and rate of plume-air mixing (inversely related to volcanic emission flux in the model). BrO contents reach up to 20% and ~50% of total bromine (over a timescale of a few 10's of minutes), for the high and medium/low bromine emission scenarios, respectively. The latter agrees well with observations that report BrO (at 3–5 min downwind) can reach up to 40% of the total bromine emission at Etna (Oppenheimer et al., 2006).

Partial (up to ~50%) or complete (100%) conversion of HBr to reactive forms is predicted over the 1 h simulations, depending on bromine content (high or medium/low, respectively) as well as other the plume conditions (e.g. aerosol, dispersion, HSC initialisation). Simulations using the two volcanic aerosol loadings significantly differ in the downwind plume chemistry but result in a similar initial rise in BrO/SO<sub>2</sub> near-downwind (up to 6 km), a finding that is in agreement with the reported low RH dependence of BrO/SO<sub>2</sub> (Bobrowski et al., 2007). The influence of plume-air mixing is illustrated through simulations with a fixed plume dimension but varying volcanic emission flux. A higher emission flux hence relative decrease in rate of in plume-air mixing causes a slower rise in BrO/SO<sub>2</sub> in the near downwind plume (< 40 min) and a slower and delayed onset of the decrease in BrO/SO<sub>2</sub> in the far downwind plume (> 2 h, for the volcanic conditions simulated). This simulated dependence of BrO/SO<sub>2</sub> on volcanic emission flux is particularly relevant for the interpretation of changes in BrO/SO<sub>2</sub> during/prior to eruptive events (e.g. Bobrowski and Giuffrida, 2012).

Model uncertainties are also highlighted, particularly regarding BrNO<sub>2</sub>, volcanic NO<sub>x</sub> and the high-temperature model initialisation. Simulations excluding BrNO<sub>2</sub> reproduced

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the observed rapid formation of BrO (within minutes), whereas the rise in BrO/SO<sub>2</sub> was delayed in simulations that included BrNO<sub>2</sub>, with lesser ozone depletion. We suggest possible additional BrNO<sub>2</sub> loss reactions and alternative Br+NO<sub>2</sub> chemical pathways. It is also possible that NO<sub>x</sub> emissions from passively degassing (non lava lake) volcanoes might be lower than previously assumed (i.e., equilibrium NO<sub>x</sub>), due to the slow rate of N<sub>2</sub> oxidation. The use of thermodynamic equilibrium models to initialise atmospheric chemistry models is highlighted as a major area of uncertainty in modelled downwind plume BrO/SO<sub>2</sub>. The atmospheric:magmatic gas ratio,  $V_A : V_M$ , in equilibrium model representations of the near vent plume is presently poorly defined. We show that using a revised equilibrium model methodology, lower  $V_A : V_M$  become suitable (e.g.  $V_A : V_M = 98 : 2, 95 : 5$ ), which also yield a lower estimate for volcanic NO<sub>x</sub>. However, not all species may be under equilibrium control. Development of high-temperature kinetic models is encouraged for progress in this area, as well as further coordinated field observations, given the range of parameters that influence volcanic BrO as highlighted by this study, combined with further model sensitivity studies.

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## References

Afe, O. T., Richter, A., Sierk, B., Wittrock, F., and Burrows, J. P.: BrO emission from volcanoes: A survey using GOME and SCIAMACHY measurements, *Geophys. Res. Lett.*, 31, L24113, doi:10.1029/2004GL020994, 2004.

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Aiuppa, A., Federico, C., Franco, A., Giudice, G., Gurrieri, S., Inguaggiato, S., Liuzzo, M., McGonigle, A. J. S., and Valenza, M.: Emission of bromine and iodine from Mount Etna volcano, *Geochem. Geophys. Geos.*, 6, Q08008, doi:10.1029/2005GC000965, 2005.

Aiuppa, A., Shinohara, H., Tamburello, G., Giudice, G., Liuzzo, M., and Moretti, R.: Hydrogen in the gas plume of an open-vent volcano, Mount Etna, Italy, *J. Geophys. Res.*, 116, B10204, doi:10.1029/2011JB008461, 2011.

Bagnato, E., Aiuppa, A., Parello, F., Calabrese, S., D'Alessandro, W., Mather, T. A., McGonigle, A. J. S., Pyle, D. M., and Wangberg, I.: Degassing of gaseous (elemental and reactive) and particulate mercury from Mount Etna volcano (Southern Italy), *Atmos. Environ.*, 41, 7377–7388, 2007.

Bani, P., Oppenheimer, C., Tsanev, V. I., Carn, S. A., Cronin, S. J., Crimp, R., Calkins, J. A., Charley, D., Lardy, M., and Roberts, T. J.: Surge in sulphur and halogen degassing from Ambrym volcano, Vanuatu, *B. Volcanol.*, 71, 1159–1168, doi:10.1007/s00445-009-0293-7, 2009.

Bobrowski, N. and Giuffrida, G.: Bromine monoxide / sulphur dioxide ratios in relation to volcanological observations at Mt. Etna 2006–2009, *Solid Earth*, 3, 433–445, doi:10.5194/se-3-433-2012, 2012.

Bobrowski, N. and Platt, U.: SO<sub>2</sub>/BrO ratios studied in five volcanic plumes, *J. Volcanol. Geoth. Res.*, 166, 147–160, doi:10.1016/j.jvolgeores.2007.07.003, 2007.

Bobrowski, N., Honniger, G., Galle, B., and Platt, U.: Detection of bromine monoxide in a volcanic plume, *Nature*, 423, 273–276, doi:10.1038/nature01625, 2003.

Bobrowski, N., von Glasow, R., Aiuppa, A., Inguaggiato, S., Louban, I., Ibrahim, O. W., and Platt, U.: Reactive halogen chemistry in volcanic plumes, *J. Geophys. Res.*, 112, D06311, doi:10.1029/2006JD007206, 2007.

Boichu, M., Oppenheimer, C., Roberts, T. J., Tsanev, V., and Kyle, P. R.: On bromine, nitrogen oxides and ozone depletion in the tropospheric plume of Erebus volcano (Antarctica), *Atmos. Environ.*, 45, 3856–3866, 2011.

Bröske, R. and Zabel, F.: Kinetics of the gas-phase reaction of BrNO<sub>2</sub> with NO, *J. Phys. Chem. A*, 102, 8626–8631, 1998.

Edmonds, M., Pyle, D. M., and Oppenheimer, C.: HCl emissions at Soufriere Hills volcano, Montserrat, West Indies, during a second phase of dome building: November 1999 to October 2000, *B. Volcanol.*, 64, 21–30, 2002.

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Frenzel, A., Scheer, V., Sikorski, R., George, C., Behnke, W., and Zetzsch, C.: Heterogeneous interconversion reactions of  $\text{BrNO}_2$ ,  $\text{ClNO}_2$ ,  $\text{Br}_2$ , and  $\text{Cl}_2$ , *J. Phys. Chem. A*, 102, 1329–1337, 1998.

Gerlach, T. M.: Volcanic sources of tropospheric ozone-depleting trace gases, *Geochem. Geophys. Geosy.*, 5, Q09007, doi:10.1029/2004GC000747, 2004.

Giggenbach, W. F.: Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand, *Appl. Geochem.*, 2, 143–161, 1987.

Heue, K.-P., Brenninkmeijer, C. A. M., Baker, A. K., Rauthe-Schöch, A., Walter, D., Wagner, T., Hörmann, C., Sihler, H., Dix, B., Frieß, U., Platt, U., Martinsson, B. G., van Velthoven, P. F. J., Zahn, A., and Ebinghaus, R.:  $\text{SO}_2$  and BrO observation in the plume of the Eyjafjallajökull volcano 2010: CARIBIC and GOME-2 retrievals, *Atmos. Chem. Phys.*, 11, 2973–2989, doi:10.5194/acp-11-2973-2011, 2011.

Hobbs, P. V., Tuell, J. P., Hegg, D. A., Radke, L. F., and Eltgroth, M. W.: Particles and gases in the emissions from the 1980–1981 volcanic eruptions of Mt. St. Helens, *J. Geophys. Res.*, 87, 11062–11086, 1982.

Hörmann, C., Sihler, H., Bobrowski, N., Beirle, S., Penning de Vries, M., Platt, U., and Wagner, T.: Systematic investigation of bromine monoxide in volcanic plumes from space by using the GOME-2 instrument, *Atmos. Chem. Phys.*, 13, 4749–4781, doi:10.5194/acp-13-4749-2013, 2013.

Kelly, P. J., Kern, C., Roberts, T. J., Lopez, T., Werner, C., and Aiuppa, A.: Rapid chemical evolution of tropospheric volcanic emissions from Redoubt Volcano, Alaska, based on observations of ozone and halogen-containing gases, *J. Volcanol. Geoth. Res.*, 259, 317–333, 2013.

Kern, C., Sihler, H., Vogel, L., Rivera, C., Herrera, M., and Platt, U.: Halogen oxide measurements at Masaya Volcano, Nicaragua using active long path differential optical absorption spectroscopy, *B. Volcanol.*, 71, 659–670, 2009.

Louban, I., Bobrowski, N., Rouwet, D., Inguaggiato, S., and Platt, U.: Imaging DOAS for volcanological applications, *B. Volcanol.*, 71, 753–765, 2009.

Lübcke, P., Bobrowski, N., Arellano, S., Galle, B., Garzón, G., Vogel, L., and Platt, U.: BrO/ $\text{SO}_2$  molar ratios from scanning DOAS measurements in the NOVAC network, *Solid Earth Discuss.*, 5, 1845–1870, doi:10.5194/sed-5-1845-2013, 2013.

Martin, R. S., Mather, T. A., and Pyle, D. M.: High-temperature mixtures of magmatic and atmospheric gases, *Geochem. Geophys. Geosy.*, 7, Q04006, doi:10.1029/2005GC001186, 2006.

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- Martin, R. S., Roberts, T. J., Mather, T. A., and Pyle, D. M.: The implications of H<sub>2</sub>S and H<sub>2</sub> stability in high-T mixtures of magmatic and atmospheric gases for the production of oxidized trace species (e.g., BrO and NO<sub>x</sub>), *Chem. Geol.*, 263, 143–150, 2009.
- Martin, R. S., Mather, T. A., Pyle, D. M., Power, M. Allen, A. G., Aiuppa, A., Horwell, C. J., and Ward, E. P. W.: Composition-resolved size distributions of volcanic aerosols in the Mt. Etna plumes, *J. Geophys. Res.*, 113, D17211, doi:10.1029/2007JD009648, 2008.
- Mather, T. A., Pyle, D. M., and Allen, A. G.: Volcanic source for fixed nitrogen in the early Earth's atmosphere, *Geology*, 32, 905–908, doi:10.1130/G20679.1, 2004a.
- Mather, T. A., Tsanev, V. I., Pyle, D. M., McGonigle, A. J. S., Oppenheimer, C., and Allen, A. G.: Characterization and evolution of tropospheric plumes from Lascar and Villarrica volcanoes, Chile. *J. Geophys. Res.*, 109, D21303, doi:10.1029/2004JD004934, 2004b.
- Mather, T. A., McCabe, J. R., Rai, V. K., Thiemens, M. H., Pyle, D. M., Heaton, T. H. E., Sloane, H. J., and Fern, G. R.: Oxygen and sulfur isotopic composition of volcanic sulfate aerosol at the point of emission, *J. Geophys. Res.*, 111, D18205, doi:10.1029/2005JD006584, 2006.
- Metrich, N. and Rutherford, M. J.: Low pressure crystallization paths of H<sub>2</sub>O-saturated basaltic-hawaiitic melts from Mt. Etna: implications for open-system degassing of basaltic volcanoes, *Geochim. Cosmochim. Ac.*, 62, 1195–1205, 1998.
- Oppenheimer, C., Tsanev, V. I., Braban, C. F., Cox, R. A., Adams, J. W., Aiuppa, A., Bobrowski, N., Delmelle, P., Barclay, J., and McGonigle, A. J. S.: BrO formation in volcanic plumes, *Geochim. Cosmochim. Ac.*, 70, 2935–2941, 2006.
- Oppenheimer, C., Kyle, P. Eisele, F., Crawford, J., Huey, G., Tanner, D., Saewung, K., Mauldin, L., Blake, D., Beyersdorf, A., Buhr, M., and Davis, D.: Atmospheric chemistry of an Antarctic volcanic plume, *J. Geophys. Res.*, 115, D04303, doi:10.1029/2009JD011910, 2010.
- Orlando, J. J. and Burkholder, J. B.: Identification of BrONO as the major product in the gas-phase reaction of Br with NO<sub>2</sub>, *J. Phys. Chem. A*, 104, 2048–2053, doi:10.1021/jp993713g, 2000.
- Orlando, J. J. and Tyndall, G. S.: Rate coefficients for the thermal decomposition of BrONO<sub>2</sub> and the heat of formation of BrONO<sub>2</sub>, *J. Phys. Chem.*, 100, 19398–19405, 1996.
- Rix, M., Valks, P. Hao, N., Loyola, D., Schlager, H. Huntrieser, H., Flemming, J., Koehler, U., Schumann, U., and Inness, A.: Volcanic SO<sub>2</sub>, BrO and plume height estimations using

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GOME-2 satellite measurements during the eruption of Eyjafjallajökull in May 2010, *J. Geophys. Res.*, 117, D00U19, doi:10.1029/2011JD016718, 2012.

Roberts, T. J., Braban, C. F., Martin, R. S., Oppenheimer, C., Adams, J. W., Cox, R. A., Jones, R. L., and Griffiths, P. T.: Modelling reactive halogen formation and ozone depletion in volcanic plumes, *Chem. Geol.*, 263, 151–163, 2009.

Roberts, T. J., Braban, C. F., Martin, R. S., Oppenheimer, C., Dawson, D. H., Griffiths, P. T. G., Cox, R. A., Saffell, J. R. and Jones, R. L.: Electrochemical sensing of volcanic plumes, *Chem. Geol.*, 332–333, 74–91, 2012.

Roberts, T. J., Jourdain, L., Griffiths, P. T., and Pirre, M.: Re-evaluating the reactive uptake of HOBr in the troposphere with implications for the marine boundary layer and volcanic plumes, *Atmos. Chem. Phys. Discuss.*, 14, 2717–2771, doi:10.5194/acpd-14-2717-2014, 2014.

Schumann, U., Weinzierl, B., Reitebuch, O., Schlager, H., Minikin, A., Forster, C., Baumann, R., Sailer, T., Graf, K., Mannstein, H., Voigt, C., Rahm, S., Simmet, R., Scheibe, M., Lichtenstern, M., Stock, P., Rüba, H., Schäuble, D., Tafferner, A., Rautenhaus, M., Gerz, T., Ziereis, H., Krautstrunk, M., Mallaun, C., Gayet, J.-F., Lieke, K., Kandler, K., Ebert, M., Weinbruch, S., Stohl, A., Gasteiger, J., Groß, S., Freudenthaler, V., Wiegner, M., Ansmann, A., Tesche, M., Olafsson, H., and Sturm, K.: Airborne observations of the Eyjafjalla volcano ash cloud over Europe during air space closure in April and May 2010, *Atmos. Chem. Phys.*, 11, 2245–2279, doi:10.5194/acp-11-2245-2011, 2011.

Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., Frieß, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., and Wolff, E.: Halogens and their role in polar boundary-layer ozone depletion, *Atmos. Chem. Phys.*, 7, 4375–4418, doi:10.5194/acp-7-4375-2007, 2007.

Theys, N., Van Roozendaal, M., Dils, B., Hendrick, F., Hao, N., and De Mazièrem, M.: First satellite detection of volcanic bromine monoxide emission after the Kasatochi eruption, *Geophys. Res. Lett.*, 36, L03809, doi:10.1029/2008GL036552, 2009.

Vance, A., McGonigle, A. J. S., Aiuppa, A., Stith, J. L., Turnbull, K., and von Glasow, R.: Ozone depletion in tropospheric volcanic plumes, *Geophys. Res. Lett.*, 37, L22802, doi:10.1029/2010GL044997, 2010.

Von Glasow, R.: Atmospheric Chemistry in Volcanic Plumes, *P. Natl. Acad. Sci. USA*, 107, 6594–6599, 2010.

Von Glasow, R., Bobrowski, N., and Kern, C.: The effects of volcanic eruptions on atmospheric chemistry, *Chem. Geol.*, 263, 131–142, 2009.

5 Wang, T. X., Kelley, M. D., Cooper, J. N., Beckwith, R. C., and Margerum, D. W.: Equilibrium, kinetic and UV-spectral characteristics of aqueous bromine chloride, bromine and chlorine species, *Inorg. Chem.*, 33, 5872–5878, 1994.

ACPD

14, 5445–5494, 2014

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**Table 1.** Thermodynamic modelling of the high temperature near vent plume using HSC: overview of inputs and outputs.

HSC Input: Chemical	Comments
H <sub>2</sub> O, CO <sub>2</sub> , SO <sub>2</sub>	Major Volcanic Gases
HF, HCl, HBr, HI	Halogen Emissions
H <sub>2</sub> S, CO, H <sub>2</sub>	Reduced Gases
Hg	Trace Metals
N <sub>2</sub> , O <sub>2</sub> , Ar	Air
HSC Input: Physical	
V <sub>A</sub> : V <sub>M</sub>	Atmospheric : Magmatic Gas Ratio
Temperature	Magmatic and Ambient Temperature
HSC Output:	
Full Matrix of Species	*
Key Reactive Species in Output:	
NO, OH, Cl, Br, Cl <sub>2</sub>	Species that act to kick-start BrO chemistry
SO <sub>3</sub>	Direct precursor to H <sub>2</sub> SO <sub>4</sub> (Sulfate)
Major Volcanic Gases in Output:	
SO <sub>2</sub> , HCl, HBr, CO <sub>2</sub> , H <sub>2</sub> O	Present in plume and in HSC output
H <sub>2</sub> S, H <sub>2</sub> , CO	Present in plume but missing in HSC output

\* Full Matrix of Species typically included in HSC output: H<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>, HCl, O<sub>2</sub>, H<sub>2</sub>S, CO, Ar, S<sub>2</sub>, SO<sub>3</sub>, SO, NO, HBr, COS, HS, OH, Cl, Br, S<sub>2</sub>O, H<sub>2</sub>S<sub>2</sub>, Cl<sub>2</sub>, I, HOCl, S<sub>3</sub>, HI, HF, H, H<sub>2</sub>SO<sub>4</sub>, BrCl, NO<sub>2</sub>, S, ClO, O, HO<sub>2</sub>, Br<sub>2</sub>, HIO, H<sub>2</sub>O<sub>2</sub>, HNO<sub>2</sub>, SOCl, ICl, HCOOH, CS<sub>2</sub>, BrO, S<sub>2</sub>Cl, N<sub>2</sub>O, NOCl, HSO<sub>3</sub>Cl, IBr, SCl, S<sub>4</sub>, IO, NOBr, COOH, HNO, NH<sub>3</sub>, ClOO, S<sub>5</sub>, SCl<sub>2</sub>, CH<sub>4</sub>, HNO<sub>3</sub>, HCO, BrOO, CS, OClO, O<sub>3</sub>, I<sub>2</sub>, ClO<sub>2</sub>, SBr<sub>2</sub>, HCICO, SOCl<sub>2</sub>, ClClO, ClOCl, NOI, NO<sub>2</sub>Cl, SO<sub>2</sub>Cl<sub>2</sub>, SOF, IOO, HSO<sub>3</sub>F, ClOCl, SN, COCl, NO<sub>3</sub>, S<sub>2</sub>Cl<sub>2</sub>, OBrO, S<sub>6</sub>, F, NBr, HOCN, HNCO, BrOBr, CH<sub>3</sub>, ClF, HCN, COCl<sub>2</sub>, N<sub>2</sub>O<sub>2</sub>, BrF, NH<sub>2</sub>, OIO, IF, N, BrBrO, S<sub>2</sub>Br<sub>2</sub>, NOF, IIO, N<sub>2</sub>O<sub>3</sub>, NH<sub>2</sub>OH, SO<sub>2</sub>ClF, SF

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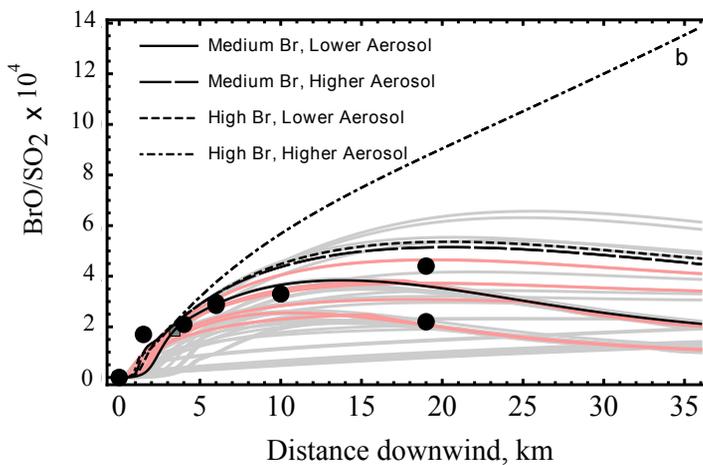
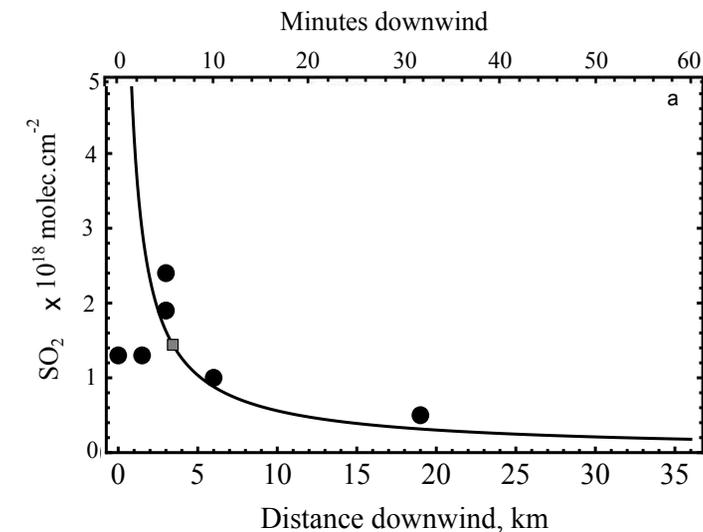
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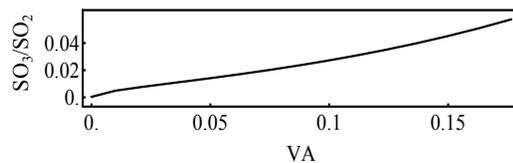
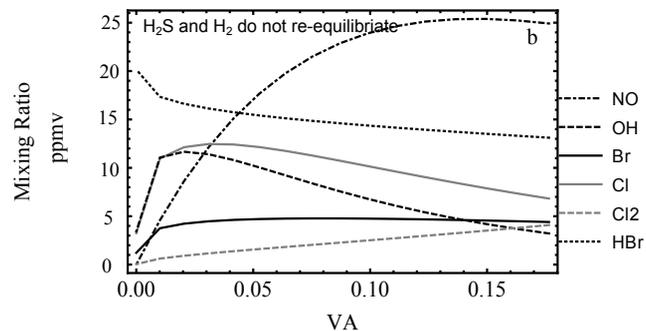
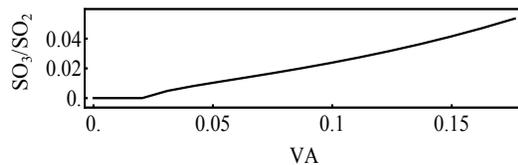
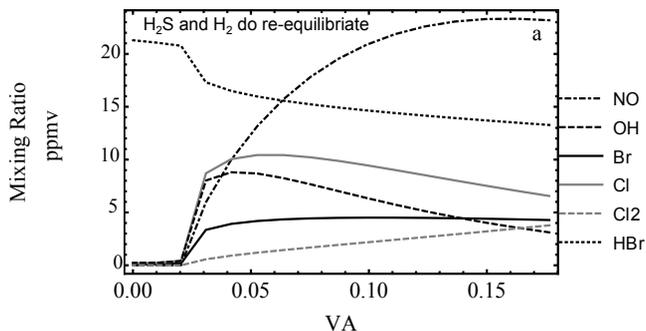
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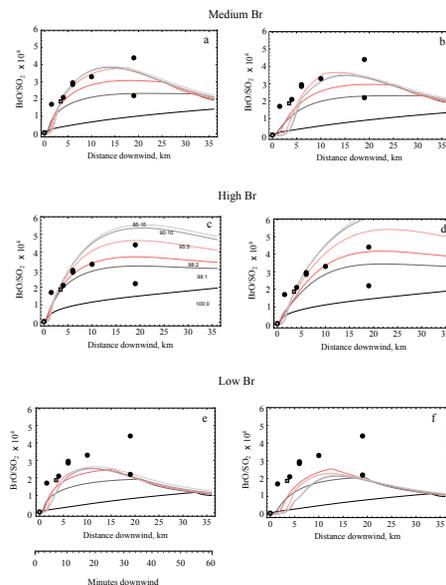
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**Fig. 3.** Impact of variations in the representation of the near-vent plume on the downwind BrO/SO<sub>2</sub> evolution simulated over 1 h. Suites of *PlumeChem* model simulations, each model run initialised with HSC output assuming varying atmospheric : magmatic gas ratio in the near-vent plume;  $V_A : V_M$  (0 : 100, 1 : 99, 2 : 98, 5 : 95, 10 : 90, 15 : 85). The bromine emission scenario is also varied: **(a)** and **(b)** use a “medium”  $Br_{tot}/SO_2$  of  $7.4 \times 10^{-4}$ , which corresponds to the average measured Br/S molar ratio at Etna (Aiuppa et al., 2005), **(c)** and **(d)** use a high  $Br_{tot}/SO_2$  of  $2.4 \times 10^{-3}$ , which corresponds to that used in the model study by von Glasow (2010). **(e)** and **(f)** use a low  $Br_{tot}/SO_2$  of  $4.8 \times 10^{-4}$  reported from a filter-pack measurement of Oppenheimer et al. (2006). The model chemistry is also varied to include **(b, d, f)** or exclude **(a, c, e)** formation of BrNO<sub>2</sub>. The simulations are compared to BrO/SO<sub>2</sub> ratios reported by Oppenheimer et al. (2006), and Bobrowski et al. (2007); grey and black disks respectively.

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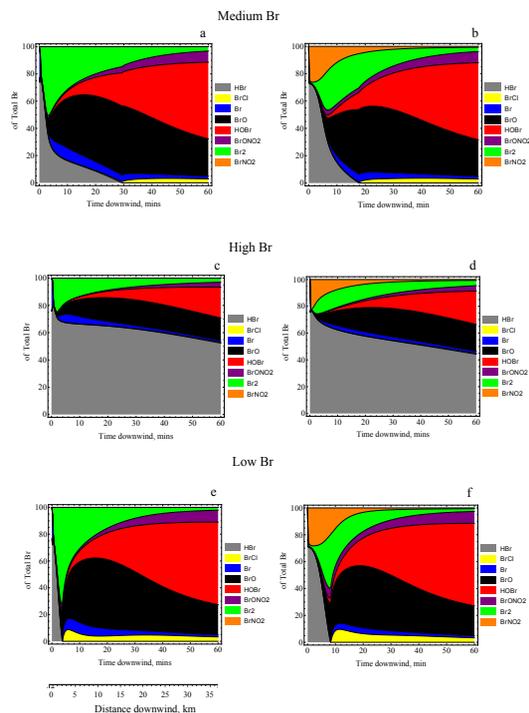
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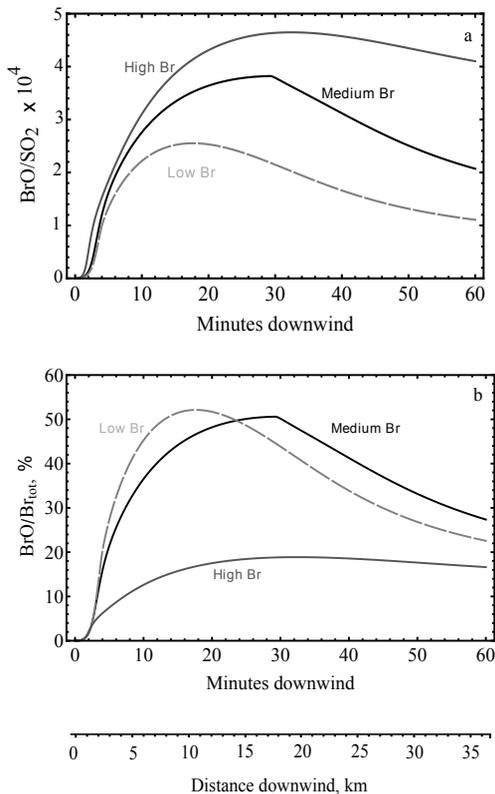
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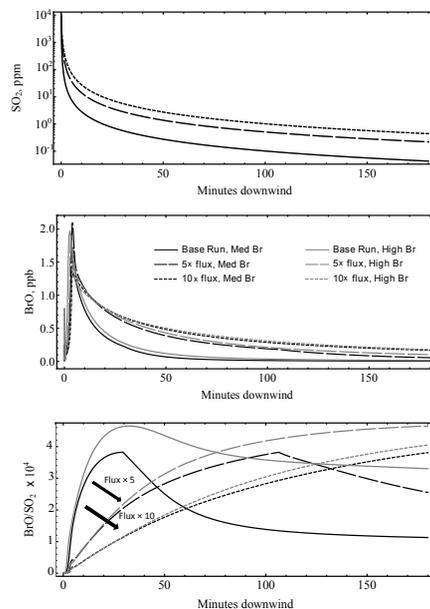
**Fig. 4.** Upper: Bromine speciation as predicted by the *PlumeChem* model. Simulations assume **(a)** “medium”  $\text{Br}_{\text{tot}}/\text{SO}_2$  of  $7.4 \times 10^{-4}$  with formation of  $\text{BrNO}_2$  excluded from the model chemistry scheme, **(b)** “medium”  $\text{Br}_{\text{tot}}/\text{SO}_2$  with formation of  $\text{BrNO}_2$  from Br and volcanic  $\text{NO}_x$  included, **(c)** high  $\text{Br}_{\text{tot}}/\text{SO}_2$  of  $2.4 \times 10^{-3}$ , excluding plume  $\text{BrNO}_2$  formation, **(d)** high  $\text{Br}_{\text{tot}}/\text{SO}_2$  of  $2.4 \times 10^{-3}$ , including plume  $\text{BrNO}_2$  formation. **(e)** low  $\text{Br}_{\text{tot}}/\text{SO}_2$  of  $4.8 \times 10^{-4}$ , excluding plume  $\text{BrNO}_2$  formation, **(f)** low  $\text{Br}_{\text{tot}}/\text{SO}_2$  of  $4.8 \times 10^{-4}$ , including plume  $\text{BrNO}_2$  formation. All simulations are initialised using HSC output at  $V_A : V_M$  of 5 : 95, with volcanic aerosol loading of  $10^{-11} \mu\text{m}^2 \text{ molec}^{-1} \text{ SO}_2$ , with plume dispersion parameterisation as stated in the text.



**Fig. 5.** Predicted  $\text{BrO}/\text{SO}_2$  and  $\text{BrO}/\text{Br}_{\text{tot}}$  ratios over 1 h simulations for three different bromine emission scenarios considered for Mt. Etna. The “medium” ( $\text{Br}_{\text{tot}}/\text{SO}_2 = 7.4 \times 10^{-4}$ ) and “high” bromine ( $\text{Br}_{\text{tot}}/\text{SO}_2 = 2.4 \times 10^{-3}$ ) emission scenarios are shown alongside the lower bromine emission scenario of  $\text{Br}_{\text{tot}}/\text{SO}_2 = 4.8 \times 10^{-4}$ , corresponding to the observations of Oppenheimer et al. (2006). Model chemistry scheme excludes  $\text{BrNO}_2$  in these simulations, i.e. corresponds to speciation shown in Fig. 4a, c and e.

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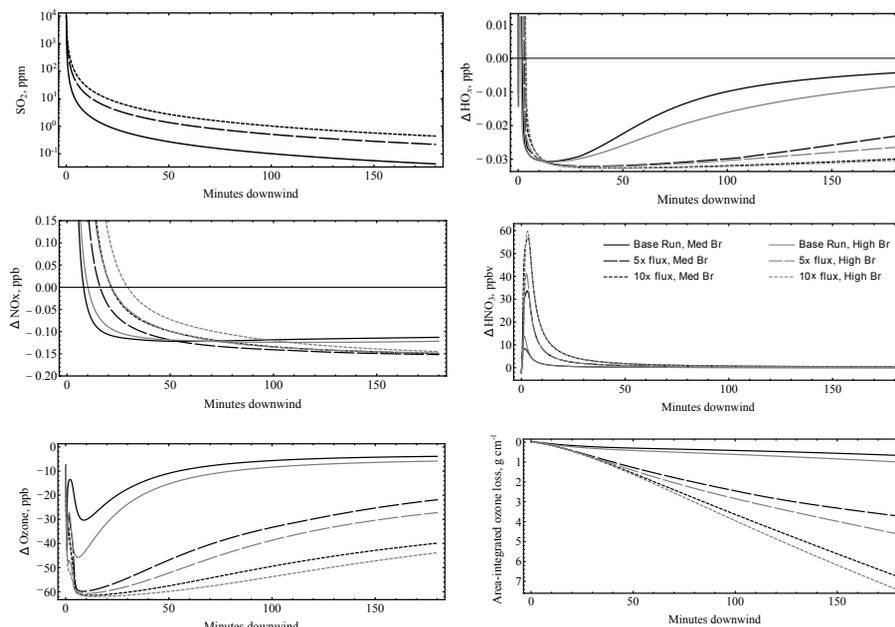


**Fig. 6.** Simulated plume chemistry over 3 h of plume evolution with varying volcanic emission flux. The effect of varying the rate of plume-air mixing is illustrated by simulations with varying (total) volcanic emission fluxes (baseline run, and with volcanic gas+aerosol emissions flux  $\times 5$  and  $\times 10$ , shown by full-, long-dashed and short-dashed lines, respectively), whilst keeping the same plume dimensions (based on Pasquill-Gifford case D, at  $10 \text{ ms}^{-1}$  windspeed). Thus a greater volcanic emission flux denotes a slower rate of plume-air mixing. Simulations with medium and high bromine emission scenarios with HSC initialisations using  $V_A : V_M$  of 5 : 95 are presented. All model runs assume a volcanic aerosol loading of  $10^{-11} \mu\text{m}^2 \text{ molec}^{-1} \text{ SO}_2$ , formation of  $\text{BrNO}_2$  excluded from the chemistry scheme, (upper) in-plume  $\text{SO}_2$  concentration, (middle)  $\text{BrO}$  concentration, (lower)  $\text{BrO}/\text{SO}_2$  ratios. Plume  $\text{SO}_2$  and  $\text{BrO}$  (to a lesser extent) abundances increase with greater volcanic emission flux, in contrast to the  $\text{BrO}/\text{SO}_2$  that shows more complex behaviour. A decrease in near-downwind  $\text{BrO}/\text{SO}_2$  with increasing volcanic emission flux is highlighted by arrows.

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**Fig. 7.** Simulated impact of plume BrO chemistry on atmospheric oxidants, shown for the model scenarios of Fig. 6. Depletion of oxidants and formation of  $\text{NO}_y$  is shown through the plume – background concentration difference for  $\text{HO}_x$  ( $\text{OH} + \text{HO}_2$ ),  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ),  $\text{HNO}_3$ , and ozone, as well as the area-integrated ozone loss across the 3 h simulation.