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$_2$ ratios). Recent observations from Etna report an initial increase and subsequent plateau or decline in BrO/SO$_2$ ratios with distance downwind.

We present daytime PlumeChem model simulations that reproduce and explain the reported trend in BrO/SO$_2$ at Etna including the initial rise and subsequent plateau. Suites of model simulations 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$_2$, BrO, BrONO$_2$, BrCl, HOBr.

We predict a new evolution of Br-speciation in the plume. BrO, Br$_2$, Br and HBr are the main plume species near downwind whilst BrO and HOBr are present further downwind (where BrONO$_2$ and BrCl also make up a minor fraction). BrNO$_2$ is predicted to be only a relatively minor plume component.

The initial rise in BrO/SO$_2$ 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$_2$ near-downwind (< ~6 km, ~10 min) at the relatively high loadings considered. The subsequent decline in BrO/SO$_2$ occurs as entrainment of oxidants HO$_2$ and NO$_2$ promotes net formation of HOBr and BrONO$_2$, whilst the plume dispersion dilutes volcanic aerosol so slows the heterogeneous loss rates of these species. A higher volcanic aerosol loading enhances BrO/SO$_2$ in the (> 6km) downwind plume.

Simulations assuming low/medium and high Etna bromine emissions scenarios show the bromine emission has a greater influence on BrO/SO$_2$ further downwind and a modest impact near downwind, and show either complete or partial conversion of 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 non-linearly impacts the downwind BrO/SO₂, as shown by simulations with varying plume dispersion, wind-speed and volcanic emission flux. Greater volcanic emission flux leads to lower BrO/SO₂ ratios near downwind, but also delays the subsequent decline in BrO/SO₂, thus yields higher BrO/SO₂ ratios further downwind. We highlight the important role of plume chemistry models for the interpretation of observed changes in BrO/SO₂ during/prior to volcanic eruptions, as well as for quantifying volcanic plume impacts on atmospheric chemistry. Simulated plume impacts include ozone, HOₓ and NOₓ depletion, the latter converted into HNO₃. Partial recovery of ozone occurs with distance downwind, although cumulative ozone loss is ongoing over the three hour simulations.
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., 2007a;b, Kern et al., 2009, Bani et al., 2009, Louban 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. Volcanoes release H$_2$O, CO$_2$ and SO$_2$, but also a range of hydrogen halides to the atmosphere including HF, HCl, and HBr (in descending order of abundance in the emission, see e.g. Aiuppa et al. 2005). HF is too strong an acid for reactive halogen cycling, but for HBr and HCl, observational evidence shows these are not simply just washed-out from the atmosphere, but can undergo transformation into reactive halogen species. Notably, DOAS (Differential Optical Absorption Spectroscopy) measurements show BrO forms at 100’s pmol/mol to nmol/mol mixing ratios just minutes downwind, an order of magnitude higher than that found in the Arctic, where BrO episodes of up to 10’s pmol/mol 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 usually use 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., 2007a, 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 in a case study for Mt Etna. 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 chemical 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 (≥100) of
chemical species. An overview of the input and outputs to HSC is provided in Table 1. The
chemical composition of the mixture is determined by combining magmatic (comprising of
H2O, CO2, CO, SO2, H2S, H2, HF, HCl, HBr, HI, Hg, typically at around 800-1100°C) and air
(N2, O2, Ar, typically around 0-20°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
H2O-H2, CO2-CO, SO2-H2S 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, Kelly et al., 2013, MISTRA, Bobrowski et al., 2007a, 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 (≥100 species) in
Table 1, following Roberts et al. (2009) who identified impacts of HO_x, NO_x, Br_x and Cl_x on
the downwind plume halogen chemistry. The key species are further identified to be OH, NO,
Br, Cl and Cl2, noting NO2 << NO and HO2 << OH, Br2 << Br in the HSC output. These
species act to accelerate autocatalytic reactive bromine formation (see Figure 4 of Roberts et
al., 2009). High-temperature near-vent formation of SO3 (a precursor to H2SO4) 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 near-complete re-equilibration (i.e., oxidation) of H$_2$S within HSC is in disagreement with the widespread observed presence of H$_2$S in volcanic plumes (exception: Erebus), and suggested a revised operation of HSC in which H$_2$S is removed prior to re-equilibration. Furthermore, recent measurements confirming volcanic H$_2$ (Aiuppa et al., 2011, Roberts et al., 2012) indicate this argument also applies to H$_2$, as well as CO (although CO is typically present in low concentrations, with some exceptions e.g. Mt. Erebus. See e.g. Gerlach, 2004 for various collated emission compositions. Uncertainties and limitations in the use of HSC to represent the near-vent plume composition are discussed further in this study in the context of downwind BrO chemistry.

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 reactive volcanic halogens on atmospheric chemistry. To date, two models: MISTRA (that simulates an advected column of air, Bobrowski et al., 2007a) and PlumeChem (in an expanding box or multi-grid box modes, Roberts et al., 2009) 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. (2007a) performed the first MISTRA 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$_2$. Roberts et al., (2009) queried the use of such high $V_A:V_M$ of 40:60 which yields rather high SO$_3$:SO$_2$ ratios, that implies volcanic sulfate emissions would exceed volcanic SO$_2$. Roberts et al. (2009) presented model simulations initialised with HSC at $V_A:V_M$ of 10:90 that reproduced the rapid formation of BrO/SO$_2$ at a range of Arc (subduction zone) volcanoes for the first time (including Etna, Soufriere Hills, Villarrica), and suggested the higher BrO/SO$_2$ 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$_2$ and BrO/SO$_2$ ratios downwind of Etna.

All of the abovementioned simulations (Bobrowski et al., 2007a, 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$_x$ into nitric acid via BrONO$_2$, and proposed this mechanism to explain reported elevated HNO$_3$ in volcano plumes. Von Glasow (2010) simulated the impacts of volcanic reactive halogen chemistry on mercury speciation predicting significant conversion to Hg$^{II}$ 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 Eyjafjallajokull 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. Ozone depletion of up to ~35 % was reported in an aircraft study of Mt Erebus plume in Antarctica (Oppenheimer et al., 2010), where BrO has also been observed (Boichu et al., 2011). 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 hours of plume evolution, finding good spatial agreement in the modelled and observed ozone mixing ratios. At higher altitudes, ozone depletion in a volcanic plume is reported in the UTLS (upper troposphere, lower stratosphere) region observed by Rose et al. (2006), and investigated and attributed to reactive halogen chemistry by Millard et al. (2006).

However, ozone depletion has not been universally observed: Baker et al. (2010) did not detect an ozone depletion signal relative to the (somewhat variable) background level during an aircraft transect through Eyjafjallajökull plume. An instrumented aircraft study found no evidence for O$_3$ depletion in the plume of Nevado del Huila (Colombia) and found ozone levels 70-80 % of ambient in the plume of Tungurahua, (Ecuador), which could not be conclusively attributed to BrO chemistry (Carn et al., 2011).
A number of modelling discrepancies also exist. For example, the model studies of Roberts et al. (2009), von Glasow (2010), and Kelly et al. (2013), predict contrasting Br-speciation and contrast in predicted impacts on ozone and other oxidants. These may reflect differences in the model representations and modelling uncertainties or demonstrate volcano-specific differences in the plume chemistry. Navigating the vast model parameter space of volcanic plume chemistry is challenging due to the non-linear controls on the plume chemistry of multiple inter-dependent parameters including volcanic aerosol, rate of horizontal dispersion, rate of vertical dispersion, wind-speed, volcanic gas flux, bromine in the emission, and high-temperature radical formation. Limited observational datasets are available to compare to the models, and the available data do not fully constrain the high- and low-temperature plume chemistry. To provide further insight, this study presents new PlumeChem model simulations to compare to recently reported trends in BrO/SO₂ ratios, and illustrates several of the major controls and uncertainties in the reactive halogen chemistry of volcanic plumes.
2. Methods

2.1 HSC: equilibrium modelling of near-vent plume chemistry

The use of HSC for calculating the composition of the near-vent plume is described by Gerlach (2004) and Martin et al. (2006). This study uses HSC thermodynamic model version 7.1, and applying the modifications which were proposed by Martin et al. (2009). A simple background atmosphere of N₂ (78 %), O₂ (21 %) and Ar (1%) is assumed for the HSC calculations. The magmatic composition used for Etna follows that of Bagnato et al. (2007), with gas mixing ratios for H₂O, CO₂, SO₂, H₂, HCl, H₂S, CO, of 0.86, 9.6·10⁻², 2.9·10⁻², 5·10⁻³, 1.4·10⁻², 1.5·10⁻³ and 3.5·10⁻⁴ respectively. Hg and CO are excluded for the purposes of this study due to their low abundances in the volcanic emission. The bromine content as HBr, was set to be either medium, high or low: ‘Medium’ bromine (molar mixing ratio of 2.16·10⁻⁵, equivalent to a total bromine to SO₂ ratio (Br₉₀/SO₂) in the emission of 7.4·10⁻⁴) corresponds to the average Br/S molar ratio at Etna NEC crater determined from filter-pack measurements over 2004, Aiuppa et al. (2005). ‘High’ bromine (mixing ratio of 7.03·10⁻⁵, equivalent to Br₉₀/SO₂ in the emission of 2.4·10⁻³) corresponds to that assumed in a previous model study of Etna (von Glasow, 2010), and is in the upper range (within one standard deviation) of the observations of Aiuppa et al. (2005). Simulations are also performed at a ‘lower’ Br₉₀/SO₂ = 4.8·10⁻⁴ which corresponds to a filterpack Br/S measurement at Voragine crater reported by Oppenheimer et al. (2006). These are summarized in Table 2.

The magmatic temperature is set to 1050 °C in order to match that prescribed by von Glasow (2010), although we note Metrich and Rutherford (1998) estimated Etna magmatic temperature to be 1100°C. For the near-vent plume mixture input to HSC, ambient air temperature was set to 20°C. This is somewhat high considering Etna’s elevation (3 km), but this has a minor influence on the HSC output (especially considering 50 °C difference in the magmatic temperature estimates outlined above). For the actual PlumeChem atmospheric chemistry model runs, the atmospheric temperature was a more realistic 285 K. The equilibrium composition was calculated for standard operation of HSC (in which H₂ and H₂S are allowed to re-equilibrate) and in a revised (Martin et al., 2009) operation of HSC (in which H₂ and H₂S are replaced by inert Ar such that they do not re-equilibrate). The HSC calculations were performed over 16 different Vₐ:Vₘ ranging from 0:100 to 15:85.

2.2 PlumeChem: kinetic model of downwind BrO chemistry
The *PlumeChem* model simulates the reactive halogen chemistry of volcanic plume, as described by Roberts et al. (2009). It can be run in single-box (Roberts et al., 2009) or multi-box (Kelly et al. 2013) modes. Here we used the single-box that expands as a background atmosphere is entrained into it, representing dispersion of the plume as it is advected downwind. *PlumeChem* includes a background atmospheric chemistry scheme and bromine and chlorine reactive halogen chemistry, including photolysis, gas-phase and heterogeneous (gas-aerosol) phase reactions. Autocatalytic formation of BrO occurs through cycles involving reaction of BrO with oxidants, (HO₂, NO₂), (R1,2), aerosol-phase heterogeneous chemistry (R3,4) to release a halogen dimer, whose photolysis generates two halogen radicals (R5), which may react with ozone (R6) to form BrO. The heterogeneous reactive uptake of HOBr and BrONO₂ on volcanic aerosol are thus key drivers of reactive halogen formation. Within the volcanic aerosol, aqueous-phase equilibria (Wang et al. 1994) control the nature of the product, which is Br₂ for a typical volcanic plume composition, thereby enabling autocatalytic formation of reactive bromine. Once aerosol Br⁺(aq) becomes depleted (as consequence of the BrO formation cycles), BrCl becomes a significant product from the heterogeneous reactions (R3,R4), leading to non-autocatalytic formation of reactive chlorine. Repeated cycling around R1-R6 can cause substantial ozone loss (orders of magnitude greater than the BrO mixing ratio). Repeated cycling between BrO and Br (R6, R7) further enhances ozone loss in concentrated plume environments.

**R1** \[ BrO + HO₂ \rightarrow HOBr + O₂ \]

**R2** \[ BrO + NO₂ \rightarrow BrONO₂ \]

**R3** \[ HOBr + H⁺(aq) + Br⁻(aq) \rightarrow Br₂(aq→g) + H₂O \]

**R4** \[ BrONO₂ + H₂O(aq) \rightarrow HOBr + HNO₃ \]

**R5** \[ Br₂ \rightarrow 2Br \]

**R6** \[ Br + O₃ \rightarrow BrO + O₂ \]

**R7** \[ BrO + BrO \rightarrow 2Br + O₂ \]
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 nmol/mol, NOx and HOx are around 0.17 nmol/mol and 30 pmol/mol respectively, with an ambient temperature of 285 K and 60% relative humidity (RH). Plume dispersion is defined according to Pasquill-Gifford dispersion schemes (see Supplementary Material). The base run plume dispersion parameterisation used in this study is identical to that of Roberts et al., (2009), based on Pasquill-Gifford case D, with a SO2 gas flux of 10 kg/s at a wind-speed of 10 m/s. The influence of variations in wind-speed (3-15 m/s), volcanic emission flux (10-20 kg/s SO2) and dispersion rates (Pasquill-Gifford case B,C,D) on downwind BrO/SO2 ratios are also shown, as well as simulations with much greater volcanic emission flux (5× or 10× the base run). Volcanic aerosol loading in the model is investigated as part of the study, and for the majority of simulations is set to be 10^{-11} μm^2 molec.SO2^{-1}, a factor of 10 lower than that of Roberts et al. (2009), following the PlumeChem model set-up used in Kelly et al. (2013).

The reaction of Br with BrONO2 to form Br2 + NO3 (Orlando and Tyndall, 1996) was added to PlumeChem model in this study. This reaction influences the overall rate of HBr conversion into reactive bromine as follows: as a sink for BrONO2 it slows the conversion of HBr into reactive bromine as less BrONO2 undergoes heterogeneous uptake (which converts HBr into Br2 via HOBr). However, as a sink for Br it slows the conversion of reactive bromine back into HBr from the reaction Br + HCHO. Under a high volcanic aerosol loading the former dominates, whilst the latter is more important at lower aerosol loadings. It is noted that this reaction is neither included in the IUPAC Kinetics nor JPL Data evaluation databases, thus is not necessarily included ‘as standard’ in all atmospheric models of reactive halogen chemistry.

BrNO2 was suggested by von Glasow (2010) to be an important reservoir for Br in the near-downwind plume, based on assumed formation of BrNO2 from volcanic NOx and Br radicals at a rate that exceeds BrNO2 loss via photolysis. Formation of BrNO2 was not included in previous PlumeChem model studies (Roberts et al., 2009, Kelly et al., 2013). Here, the fate of the products (BrNO2 but also BrONO) from reaction of Br + NO2 are investigated in more detail to evaluate the potential of BrNO2 to influence the plume chemistry.

3. Results
3.1 Model SO$_2$ column abundance, and variability in simulated BrO/SO$_2$

The formation of volcanic BrO is typically reported relative to SO$_2$, which, given slow in-plume oxidation, acts as a plume tracer on the observation time-scales (typically minutes to hours). Therefore, prior to comparing PlumeChem model output to the observed BrO/SO$_2$, a comparison is made between the simulated and reported SO$_2$ column abundances. Figure 1a shows slant SO$_2$ column abundance in Mt Etna’s plume over 2004-2005, reported from DOAS (Differential Optical Absorption Spectroscopy) observations from Oppenheimer et al., (2006) and Bobrowski et al. (2007a). The data show a general decline with distance downwind, with the exception of two very near source measurements, which may have been underestimated in the very strong near-source plume, see discussion by Kern et al. (2012) and Bobrowski and Guiffrida (2012) for improved SO$_2$ evaluation. Also shown in Figure 1a is the model downwind plume SO$_2$ column abundance calculated for the plume in the vertical. The decline in modelled SO$_2$ column abundance with distance (or time) downwind is largely due to dispersion, given the slow rate of in-plume SO$_2$ oxidation. The rate of dispersion depends on plume depth, width, gas flux and wind-speed during each DOAS measurement, which are not fully constrained by available observations. Nevertheless, the broad agreement between model and observations indicates a suitable model parameterisation of plume-air mixing in the base run. This supports the use of further simulations to investigate the plume halogen chemistry using this plume-air mixing parameterisation scenario, for comparison to reported BrO/SO$_2$ observations.

Figure 1b shows formation of BrO (relative to plume tracer SO$_2$) for a range of model simulations presented later in this study, all using this same plume-air mixing parameterisation, but where the other parameters (volcanic aerosol loading, total plume bromine, initialisation using thermodynamic model output) are varied. Clearly, these variables can have a strong influence on the downwind plume halogen chemistry. Also shown are BrO/SO$_2$ ratios reported by Oppenheimer et al. (2006) and the observed trend in (mean) BrO/SO$_2$ with distance downwind reported by Bobrowski et al., (2007). Several, but not all of the model simulations in Figure 1b conform to the BrO/SO$_2$ observations, . Indeed simulations whose initialisations assume no plume-air mixing at high-temperature typically underestimate downwind BrO/SO$_2$ (see section 3.3 for further discussion). The remaining model runs demonstrate broad agreement to the BrO/SO$_2$ measurements and provide an
explanation for the observed rise and subsequent plateau or decline in BrO/SO$_2$ with distance downwind reported by Bobrowski and Giuffrida (2012).

In order to provide further insight into the factors controlling volcano plume reactive halogen chemistry, we investigate here the influence of the abovementioned variables, and particularly uncertainties regarding the initialisation by HSC. To do so, suitable values for the volcanic bromine and aerosol loading are first identified, as outlined below.

3.2. The effect of aerosol and bromine content on downwind BrO/SO$_2$

Highlighted in black in Figure 1b are four model runs that assume the ‘medium’ and ‘high’ bromine (Br$_{tot}$/SO$_2$) emission scenarios (see Table 2), and two contrasting aerosol surface area loadings; namely ‘high’ aerosol estimated as $\sim 10^{-10}$ $\mu$m$^2$ molec.SO$_2^{-1}$ following Roberts et al. (2009), and the ‘medium’ aerosol estimate, which is an order of magnitude lower, $10^{-11}$ $\mu$m$^2$ molec.SO$_2^{-1}$ as was used by Kelly et al. (2013). Both the volcanic aerosol loading and volcanic bromine content influence the downwind BrO/SO$_2$ evolution, as.

In general, a higher Br$_{tot}$/SO$_2$ in the emission leads to greater BrO/SO$_2$ far downwind. This is in accordance with the proposed role of Br/S in the emission to explain order of magnitude variation in BrO/SO$_2$ ratios across Arc volcanoes (Roberts et al., 2009). A higher aerosol loading promotes the conversion of HBr into reactive forms, and promotes the occurrence of reactive bromine as BrO in the far downwind plume to its role in the heterogeneous reactive uptake of HOBr and BrONO$_2$. Interestingly, whilst the volcanic aerosol and bromine content have a strong impact on the plateau in BrO/SO$_2$ far downwind (both in terms of value and when it is reached), Figure 1b indicates that aerosol and bromine content exert a much more limited impact on BrO/SO$_2$ in the very young plume during the first $\sim 8$ mins ($\sim 5$ 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$_2$ to vary from 4.2$\cdot 10^{-4}$ to 1.4$\cdot 10^{-3}$ (‘high’ bromine scenario) and from 2$\cdot 10^{-4}$ to 4$\cdot 10^{-4}$ (‘medium’ bromine scenario), whereas at 6 km downwind all of these model runs predict BrO/SO$_2$ between 2.5$\cdot 10^{-4}$ and 4$\cdot 10^{-4}$. This near-downwind similarity in BrO/SO$_2$ (despite varying Br$_{tot}$/SO$_2$ 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 predicted near-downwind independence of BrO/SO$_2$ on aerosol loading is consistent with the observations of
Bobrowski and Giuffrida (2012) at 6 km downwind that showed BrO/SO₂ was independent of relative humidity (a key control on sulphate aerosol volume hence surface area). A model explanation (see Section 3.4 for further discussion) is that near-downwind BrO/SO₂ ratios are primarily controlled by Br to BrO partitioning—itself a function of in-plume ozone mixing ratio—in this region where the plume is still relatively concentrated. See section 3.4 for details of the plume reactive bromine speciation and section 3.6 for further discussion on the plume impacts on atmospheric ozone.

Notably, the simulation with both ‘high’ bromine and the larger aerosol estimate predicts BrO/SO₂ that exceeds reported observations far downwind, and does not reproduce the plateau in BrO/SO₂ beyond ~ 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 Br scenario in the further model simulations of this study. However, for the high bromine scenario, only the simulation with ‘medium’ aerosol surface area loading appears consistent with the BrO/SO₂ observations by Bobrowski and Giuffrida (2012). The ‘medium’ aerosol surface area loading is considered as likely being more representative and this estimate, ~10⁻¹¹ μm² molec.SO₂⁻¹, is used in all further model simulations of this study. Further discussion on estimates of the aerosol surface area loading is provided in Supplementary Material.

3.3. The high-temperature near-vent plume - a source of model uncertainty

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. Figure 2 compares the key species in the HSC output (Table 1) for the near-vent plume of Etna (‘medium’ Br scenario), using the standard HSC methodology, in which (a) H₂ and H₂S re-equilibrate, and (b) the modified method (Martin et al., 2009) whereby H₂S and H₂ do not re-equilibrate. NO, OH, Cl and Br and Cl₂ gas mixing ratios are shown for Vₐ:Vₘ ranging from 0:100 to 15:85, where Vₐ:Vₘ is the ratio of air to magmatic gases in the near-vent plume (plotted as a fraction in Figure 2), with the HSC temperature varied according to the mixture of magmatic (1050 °C) and ambient (20 °C) temperatures.

Of note is a step increase in radical mixing ratios in Figure 2a (in which H₂ and H₂S re-equilibrate). This is the so-called compositional discontinuity, C.D., (Gerlach, 2004), which
occurs at around $V_A:V_M \sim 0.02$ for Etna’s magmatic composition. At the C.D., the reduced magmatic gases (H$_2$S, H$_2$, CO, etc) are essentially fully oxidised (SO$_2$, H$_2$O, CO$_2$), thus addition of further oxidant (increasing $V_A/V_M$) yields increases in the mixing ratios of the radicals (Br, Cl, NO, OH). As $V_A:V_M$ increases further, the greater proportion of air relative to magmatic gases yields a lower HSC temperature, leading to slight declines or a plateau in the mixing ratios of NO and OH, and altering the balance between Cl$_2$ and Cl radicals (Br$_2$ remains low over the whole $V_A:V_M$ range). Formation of Br with increasing $V_A:V_M$ also leads to a corresponding decrease in its ‘parent’ or ‘source’ species HBr (note other ‘parent’ species e.g. HCl, H$_2$O are in excess relative to Cl and OH). However, in the revised HSC methodology (in which H$_2$ and H$_2$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 H$_2$/H$_2$O and H$_2$S/SO$_2$ ratios.

The fact that certain species need to be ‘protected’ from re-equilibration within presents a major limitation to the use of thermodynamic models to represent near-vent plume, as neither the choice of $V_A:V_M$, nor the protection of certain species (but not others) are fully justified on a physical basis. It is likely that some processes may be kinetics limited thus poorly described by thermodynamic models. Studies suggest this is indeed the case for formation of NO$_x$ from background N$_2$ entrained into the plume (Martin et al. 2012), due to the high bond-strength for N$_2$ (945 kJ/mol). Nevertheless, some evidence for the high-temperature formation of radicals in the near-vent plume, for example in the presence of crater-rim sulphate at SO$_4^{2-}$/SO$_2 \sim 1:100$ (e.g. Mather et al., 2003, Martin et al., 2008), from which near-vent SO$_3$ production might be inferred. Further, a volcanic source of HO$_x$ is suggested by plume H$_2$O$_2$ observations of Carn et al. (2011), a source of HO$_x$ and NO$_x$ is suggested by observations of HO$_2$NO$_2$ at Erebus (Oppenheimer et al. 2010), and elevated NO and NO$_2$ in plumes of Masaya (Mather et al. 2004) and Mt St Helens (see Martin et al., 2012 and references therein). Given abovementioned kinetic limitations to near-vent NO$_x$ production from entrained background air, these results imply the need for alternative explanations for NO$_x$ at volcanoes where it has been reported, and raise the possibility that volcano NO$_x$ emissions at other volcanoes (e.g. Etna) might be lower than predicted by HSC.

A representation of high-temperature radical formation in the near-vent plume is, however, necessary for the initialisation of atmospheric chemistry models of downwind BrO chemistry.
The HSC model output is thus used for this purpose, despite above-mentioned limitations.

Figure 3 shows 1 hr \textit{PlumeChem} model simulations for the three bromine emission scenarios (low, medium, high), initialised using HSC operated at a range of $V_A:V_M$ varying from 0:100, 2:98, 5:95, 10:90 to 15:85, compared to reported BrO/\text{SO}_2 ratios from Oppenheimer et al. (2006) and Bobrowksi et al. (2007). Simulations initialised 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, as has been shown previously (e.g. Bobrowski et al., 2007, Roberts et al., 2009, von Glasow, 2010) using atmospheric chemistry models. This is due to the low radical content at $V_A:V_M = 0:100$ as shown in Figure 2). Previous studies therefore chose HSC initialisations using $V_A:V_M > 0:100$, e.g. Roberts et al. (2009) suggested $V_A:V_M = 10:90$, Von Glasow (2010) suggested $V_A:V_M = 15:85$. Given the revised location of the compositional discontinuity outlined above in Figure 2, even lower $V_A:V_M$ e.g. $V_A:V_M = 2:98$ or $V_A:V_M = 5:95$ (shown in red) can become suitable. Further progress will require more sophisticated models to be developed e.g. to include full kinetic representations of chemical and mixing processes.

Nevertheless, an interesting feature of Figure 3 is that whilst choice of HSC initialisation affects the 1 hr downwind plume BrO/\text{SO}_2 strongly, the model runs show a degree of convergence towards the end of the model run (particularly for low/medium Br cases). Understanding the < 1 hr plume chemistry is, however, important for interpretation of flank volcano BrO/\text{SO}_2 observations, and is investigated further with simulations initialised using HSC with $V_A:V_M = 5:95$.

3.4. Speciation of reactive bromine in Etna plume and implications for observations of volcanic BrO

The evolution of reactive bromine speciation is also illustrated in Figure 3 for the three bromine emission scenarios, with simulations initialised using HSC at $V_A:V_M = 5:95$. A number of interesting features are identified:

- BrO/Br$_{tot}$ 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.
• 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
(∼50%) of reactive bromine in the three simulations.

• An increase in plume BrCl occurs when HBr becomes depleted, which is due to the
aqueous-phase equilibria producing substantial BrCl in place of Br₂.

• HOBr and BrONO₂ are present in all simulations, and represent an increasing
proportion of reactive bromine as the plume disperses downwind, whilst the
proportion of BrO declines.

The observed and modelled trend in BrO/SO₂ shown in Figure 1 and 3 is thus explained as
follows: HBr is converted into reactive forms by autocatalytic bromine chemistry cycles
involving volcanic aerosol, entrained atmospheric oxidants and sunlight. The HBr conversion
is accelerated by radical species present in the high-temperature initialisation. The initial rise
in BrO/SO₂ primarily reflects trends in reactive bromine speciation; entrainment of
background air containing ozone into the plume, promotes greater partitioning to BrO via the
reaction Br + O₃. Plume-air mixing is thus an important control on BrO/SO₂, because the
dilution of volcanic components and entrainment of air alter the balance between Br and BrO,
e.g. by reducing the rate of BrO loss by the self-reaction BrO + BrO (to form 2Br or Br₂), R7,
relative to the formation of BrO by Br⁺+O₃, R6. The subsequent decline or plateau in BrO/SO₂
occurs due to net conversion of reactive bromine from BrO to HOBr and BrONO₂ in the
downwind plume (R1, R2). These species are formed at an accelerated rate in the downwind
plume as it disperses and entrains background air containing oxidants (HO₂, NO₂) which
react with 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
HOBr and BrONO₂ 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 HOBr (and BrONO₂) occurs whilst BrO declines (as a
fraction of Br_{tot}), although it is emphasized that plume chemistry cycling between these
species is ongoing throughout the simulation and is very rapid.

This predicted reactive bromine evolution is somewhat similar to that of Roberts et al. (2009)
but contrasts to the one hour simulations of von Glasow (2010) that did not predict the in-
plume presence of HOBr and BrONO₂. The higher proportion of total bromine as BrO in the
‘medium’ and ‘low’ Br emission scenarios (40-50 %) compared to the ‘high’ Br emission scenario (10-20 %) is related to the extent (complete and partial, respectively) of HBr conversion into reactive bromine species. This dependence of the HBr conversion on Brtot/SO2 in the emission may to some extent explain differences between the model studies of Roberts et al. (2009) and von Glasow (2010) that predicted complete and partial in-plume conversion of HBr into reactive bromine, respectively.

Predicted BrO/SO2 and BrO/Brtot trends for the three Br emission scenarios (initialised with VA:VM = 5:95) are shown in Figure 4. The ‘low’ Br emission scenario simulation can be compared to observations by Oppenheimer et al. (2006) who reported (using DOAS) BrO/SO2 ratios reached ~2 × 10^-4 within 3-4 minutes downwind of Etna summit, and used filter-packs to quantify the emitted Brtot/SO2 to be 4.8·10^-4, i.e. implying a BrO/Brtot of ~40 %. For the ‘low’ Br model run initialised at Brtot/SO2 = 4.8·10^-4, which predicts complete conversion of HBr into reactive forms over 4 minutes, BrO/SO2 rises to 10^-4 within 4 minutes, reaching a maximum of 2.5·10^-4 at about 18 minutes downwind (i.e. earlier than the ‘medium’ and ‘high’ bromine cases of this study) afterwhich BrO/SO2 declines, Figure 4a. BrO/Brtot reaches 25 % within 4 minutes, and 40 % by about 8 minutes (Figure 4b), thus converging towards the observations of Oppenheimer et al. (2006): the agreement is relatively good considering the predicted BrO/Brtot can also be affected by other model parameters kept constant here e.g. in HSC initialisation, rate of plume-air mixing, aerosol loading, whilst observations of BrO/Brtot are subject to measurement uncertainties e.g. in filterpack Br/S, DOAS measurement of BrO/SO2.

The non-linearity of HBr conversion to BrO shown in Figure 4 yields the following implications for volcanology: BrO/SO2 ratios for these simulations (initialised at VA:VM = 5:95) reach maxima of 3.6·10^-4 and 4.6·10^-4 and 2.5·10^-4 for the medium, high and low Br scenarios respectively in the downwind plume. Thus, whilst the modelled bromine emission has varied by a factor of three between the ‘medium’ and ‘high’ bromine scenarios, the simulated BrO/SO2 ratio has varied by less than 30 %. This result for small-scale bromine variations contrasts to the earlier PlumeChem simulations (Roberts et al., 2009) that suggested order of magnitude differences in BrO/SO2 between Souffrière Hills volcano (BrO/SO2 ~10^-3) and other Arc volcanoes like Etna (BrO/SO2 ~10^-4) could be attributed to order of magnitude differences in the ratio of total bromine to SO2 in their emissions. However, the non-linear relationship between BrO and emitted HBr, as identified in Figure 4
for small-scale bromine variations, presents a complexity to efforts to quantify volcanic bromine emissions using DOAS observations of plume BrO/SO$_2$ ratios within volcano monitoring programmes, and to modelling efforts to quantify impacts from volcanic halogen emissions to the troposphere. Nevertheless, DOAS observations (e.g. Bobrowski et al. 2003; 2007b) do suggest a positive correlation between BrO/SO$_2$ and volcanic HBr emissions. For Soufrière Hills volcano, where high Br/S in the emission was proposed to lead to high plume BrO/SO$_2$, further aspects to consider include the low altitude emission where ambient humidity and background aerosol might be high, potentially promoting both BrO chemistry and SO$_2$ oxidation rates.

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. Overall, the model suggests HBr conversion into reactive bromine depends on a balance between the autocatalytic “bromine explosion” cycles in the near-downwind plume (accelerated by radicals produced in the high-temperature near-vent plume), and the conversion of reactive bromine back into HBr (e.g. via the reaction Br + HCHO).

3.5 Low in-plume prevalence of BrNO$_2$

Formation of BrNO$_2$ from Br + NO$_2$ was excluded from the 1hr simulations presented in Figure 3 and 4. However, the plume chemistry modelling study of von Glasow (2010) predicted high in-plume prevalence of BrNO$_2$, due to reaction of Br with NO$_2$, given high Br and NO$_x$ mixing ratios are assumed in the (HSC) model initialisation. In the Etna simulations of von Glasow (2010) formation of BrNO$_2$ exceeds its photolytic loss rate in the young plume, leading to a significant partitioning (> 30 %) of plume bromine as BrNO$_2$. To further evaluate this model difference, a similar two-reaction scheme for BrNO$_2$ was introduced into the PlumeChem model, with BrNO$_2$ the assumed (sole) product of the reaction Br + NO$_2$. With this two-reaction scheme, model runs for the three bromine scenarios also show rapid formation of BrNO$_2$, Figure 5 (acd). The in-plume BrNO$_2$ prevalence (< 30 % of plume bromine declining to just a few percent after 30 minutes), is still somewhat less than that of von Glasow (2010), and model differences remain in Br-speciation regarding presence of HOBr and BrONO$_2$, potentially due to differences between the models’ aerosol loading or...
dispersion schemes. Figure 5 (acd) highlights that the rapid formation of BrNO2 in these model runs causes a slight delay to the formation of BrO downwind compared to the standard model runs of Figure 3.

However, we do not recommend use of the two-reaction BrNO2 scheme, because the chemistry is in fact more complex. Firstly, the reaction Br + NO2 primarily produces BrONO (~92%) rather than BrNO2 (~8%), Bröske and Zabel (1998), Orlando and Burkholder (2000). Secondly, BrONO undergoes a more rapid thermal dissociation (τ ~ 1 s at room temperature), and photolytic loss (τ ~ seconds) than BrNO2, Burkholder and Orlando (2000). BrONO and BrNO2 also react with NO2 (Bröske and Zabel, 1998). BrONO (and possibly also BrNO2) also react with Br radicals. The reactions are summarized in Table 3. PlumeChem simulations using a more detailed reaction scheme for BrNO2-BrONO-BrNO, incorporating the quantified reactions of Table 3, are illustrated in Figure 5 (bdf). With this revised BrNO2-BrONO-BrNO model scheme, these species account for only < 12 % of reactive bromine (with BrONO and BrNO at only < 1%). The impact of this scheme on Br-speciation is rather modest but some differences can be seen in comparison to the ‘standard’ simulations of Figure 3; for example a slightly faster rate of HBr conversion to reactive bromine. However, this more detailed reaction scheme is itself limited in that it does not include reaction of BrNO2 with Br (rate constant unknown), and assumes the two possible BrONO photolysis pathways occur equally (as products are unknown). Further, the scheme does not include potential heterogeneous reactions relevant for BrNO2. Heterogeneous reactive uptake of N2O5 might produce BrNO2 or ClNO2, however, these products might react further within the aerosol to form Br2 or BrCl (Frenzel et al. 1998). Proper investigation of such heterogeneous chemistry on volcanic aerosol would require detailed consideration of the underlying rate constants for all the aqueous-phase reactions (e.g. in a manner similar to that recently attempted for HOBr reactive uptake, Roberts et al., 2014). In addition to uncertainty in the model chemistry, the model findings are also subject to uncertainty in the HSC initialisation (which determines the volcanic Br and NO2 radical source), see Section 3.3. Nevertheless, the more detailed reaction BrNO2-BrONO-BrNO scheme findings suggest the influence of BrNO2 on the plume chemistry is much lower than that proposed by von Glasow (2010). Further simulations of this study therefore do not include BrNO2.

3.6 Influence of plume-air mixing 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. A first study investigates small variations as might be expected on a day-to-day basis at Etna. A second study investigates how large variations in the volcanic emission flux (e.g. due to an eruption) influence the plume chemistry, albeit within the limitations of an idealised model scenario.

3.6.1 Influence of plume dispersion parameters, volcanic emission flux and wind-speed on BrO/SO2

As already discussed in Section 3.4, BrO formation is initially promoted by the entrainment of background air (containing ozone, HOx and NOx), due to the balance between the reaction Br + O3 (R6) and the self-reaction of BrO (R7), but as the plume becomes more diluted the entrainment of air acts to reduce BrO/SO2 due to the reaction of BrO with HO2 and NO2 (R1, R2). Thus, the proportion of background air that has been entrained into the plume acts as a key control on BrO/SO2. In the single-box Gaussian plume dispersion model used here, the extent of mixing of the background air into the plume is controlled by the Pasquill-Gifford dispersion parameters as a function of distance downwind, and whose choice depends on atmospheric turbulence (a function of wind-speed and atmospheric stability). Further, for a given dispersion parameterisation, the extent of mixing depends inversely on the volcanic emission flux, and also depends on wind-speed (through dilution along the plume). Here the effects of these three variables are illustrated for a range of plausible volcanic and meteorological conditions at Etna.

For the base run simulations (Figure 3-4), a Pasquill-Gifford (PG) dispersion case D was used, that is for a relatively neutral atmosphere, with a wind-speed of 10 m/s and volcanic gas flux of 10 kg/s SO2 (with the emission of all other volcanic gas and aerosol components scaled accordingly). This SO2 flux estimate is close to the ~13 kg/s reported by McGonigle et al. (2005) for 30 July 2004. The model 10 kg/s SO2 flux is, however, a somewhat low representation for Mt Etna during 2004-5 in general. Aiuppa et al. (2005) report gas flux data that show summer-time variations between 800-2000, equivalent to 9-23 kg/s SO2, with even greater SO2 flux during eruption periods. Burton et al. (2005) report 7-day average SO2 fluxes of 1000-2500 t/d (12-25 kg/s). To illustrate the influence of variation gas flux and plume dispersion, simulations were also performed at 20 kg/s SO2 flux, and for a range of dispersion and wind-speed cases. Cases C and B are introduced for more unstable atmospheric
conditions involving enhanced plume-air mixing, which occur more readily at lower wind-speed (< 6 m/s), see Supplementary Material.

Simulations performed at wind-speeds of 10 m/s (case D and C), 15 m/s (case D and C), 5 m/s (case D and C), and 3 m/s (case C and B) are shown in Figure 6 (a ‘medium’ bromine scenario is assumed for all these simulations, with $V_A:V_M = 5:95$ in the initialisation). The model runs illustrate how plume-air mixing may cause variation in the downwind BrO/SO$_2$.

The variation is of a similar magnitude to that identified in the model runs with the three bromine scenarios, Figure 4 (which themselves encompass only a portion of the reported variability in Br/S in the emission, see Aiuppa et al., 2005). The model runs suggest that a combination of variations in plume-air mixing and bromine emission could provide – at least theoretically – a variability in BrO/SO$_2$ similar to the observed variability in BrO/SO$_2$ ($5 \times 10^{-5}$ - $3.9 \times 10^{-4}$) reported by Bobrowski and Guiffrida (2012) at 6 km downwind. Variability in the volcanic aerosol emission could potentially add further to this.

Plume dispersion causes a transition between the two chemical regimes outlined above and an intermediate maximum in BrO/SO$_2$. The magnitude and location of the downwind maximum in BrO/SO$_2$ depends on the extent of plume-air mixing, as determined by the gas flux, rate of dispersion and wind-speed, as well as on the volcanic aerosol loading and bromine content, and the HSC initialisation. Variations in background atmospheric composition (e.g. ozone, HO$_x$, NO$_x$, aerosol) could further modify the results. Finally, if applying these results to volcanoes elsewhere, the summit altitude is also a relevant consideration, as the greater atmospheric density at lower altitude will yield a higher in-plume ratio of background oxidants to bromine, for a given volcanic SO$_2$ flux.

Nevertheless, large increases in the volcanic emission flux tend to maintain for longer the more ‘concentrated’ regime where BrO/SO$_2$ is limited by the balance between R6 and R7, as discussed further below.

### 3.6.2 Effect of a large increase in volcanic flux on BrO/SO$_2$

The sensitivity study is continued for high emission scenarios by keeping the plume dispersion case and bromine emission scenario constant (case D, ‘medium’ Br$_{tot}$/SO$_2$), but increasing the volcanic gas and aerosol emission (by a factor of × 5 and × 10 of the base run 10 kg/s SO$_2$ flux). Such an increased volcanic emission maintains higher concentrations of
volcanic gases thus reduces the extent of plume-air mixing, hence entrainment of background oxidants into the plume. We caution that in a real volcanic environment, such a large change in degassing rate may also be accompanied by a change in composition of the volcanic emission (including halogen content or aerosol loading) or act to alter the plume dimensions somewhat (e.g. by the dynamics of explosive eruptions). The model results here focus solely on the effect of (substantially) enhanced gas flux with all other variables held constant.

Simulations of three hours duration (equivalent to 108 km downwind plume propagation assuming 10 m/s windspeed) with volcanic emission flux increased from the base run to ×5 and ×10 are shown in Figure 7, for both the ‘medium’ and ‘high’ bromine emission scenarios (initialised with HSC using $V_A/V_M = 5:95$). The enhanced volcanic emission flux linearly enhances in-plume SO$_2$ abundance, as expected, but exerts a non-linear effect on the plume chemistry and impacts.

In particular, the greater volcanic emission (lower plume-air mixing) leads to a slower rise, and a later onset and slower decline in BrO/SO$_2$. At distances far downwind (> 2 hr for the specific simulation conditions), high BrO/SO$_2$ is sustained for longer in plumes with high gas flux. Conversely, in the near downwind (several 10’s of mins), plumes with lowest gas flux exhibit the fastest initial rise and highest BrO/SO$_2$ ratios. As described above, these model findings are readily explained by the model chemistry that partitions reactive bromine between Br and BrO (during the initial rise), and BrO, and HOBr, BrONO$_2$ (during the subsequent decline) as the plume disperses. The onset and magnitude of the decline is greatest for low flux plumes that are more dilute and where a higher proportion of background air has been mixed into the plume. Conversely, high flux thus more concentrated plumes have a slower initial increase in BrO/SO$_2$, with a delayed maximum. In the relatively near-downwind plume (0-30 minutes), the model predicts lower BrO/SO$_2$ at greater volcanic gas fluxes, as shown by the arrows in Figure 6. Implications for the interpretation of volcano plume observations are discussed in Section 3.7.

### Atmospheric impacts of volcanic reactive halogen chemistry

BrO chemistry causes ozone, HO$_x$ and NO$_x$ to become depleted in the downwind plume, Figure 8. For HO$_x$ and NO$_x$ the near-downwind plume abundances are initially elevated as the HSC initialisations used assumed a volcanic source of these species (Figure 2), but
become depleted within a few to 10’s minutes downwind. The maximum depletion reaches is
near 100 % and > 70 % depletion relative to background values of around 30 pptv and 0.17
ppbv for HOx and NOx respectively. HOx is converted into H2O(l) via HOBr chemistry (R1,
R3). HOx abundances are also reduced by the gas-phase reaction of OH with SO2, and by
ozone depletion in the plume (see below). The volcanic NOx source is converted into HNO3
by BrONO2 chemistry (R2, R4), causing a rapid increase in-plume HNO3, particularly in the
concentrated near-downwind plume, where HNO3 reaches up to 60 nmol/mol (exceeding the
background NOy of ~6 nmol/mol). This mechanism was proposed by Roberts et al. (2009) as
an explanation for observations of high HNO3 in volcanic plumes. See collated observations
by Martin et al. (2012) reporting plume HNO3/NOy that can reach up to 10⁻¹. For Etna in
particular, reported crater-rim HNO3/NOy ratios are somewhat inconsistent and show large
variability (⁻²·³⁻⁴, 7.8⁻¹⁰⁻⁶, 4.2⁻¹⁻³), which in itself might be indicative of a role of plume
chemistry processing. Recently Voigt et al. (2014) also observed elevated HNO3 in the
downwind Etna plume, with HNO3 as the dominant form of NOy. Importantly, elevated
‘volcanic’ HNO3 produced by the BrONO2 mechanism can originate from both NOx of
volcanic origin, and from NOx from background air entrained into the plume. As
consequence, the in-plume NOx declines from initially elevated abundance (due to the
assumed high temperature volcanic NOx source) to become depleted relative to the
background abundance downwind. Finally, it is noted that simple acidification of nitrate
aerosol from background air entrained into the plume could also lead to gas partitioning
therefore enhance the ‘volcanic’ HNO3(g) signature. Such acid-displacement of HNO3(g) by
H2SO4(aq) has been observed by Satsumabayashi et al. (2004). The observations of volcanic
HNO3 collated by Martin et al. (2012) and Voigt et al. (2014) thus require consideration in
the context of these two mechanisms.

Ozone is also depleted in the plume and reaches a maximum depletion (up to 100%) around
10 minutes downwind, coincident with the highest in-situ BrO abundances that reach ~ 1
nmol/mol (Figure 7). For the base run, the maximum plume ozone depletion is 30 or 45
nmol/mol for the medium and high bromine emission scenarios respectively. Greater in-
plume ozone loss occurs at higher emissions flux (lower relative plume-air mixing), however
for these runs the maximum ozone loss is constrained by the fact it cannot exceed ~60
nmol/mol (the background ozone mixing ratio). Thereafter ozone begins to recover as the
plume disperses (Figure 8), entraining background air, and BrO declines (Figure 7), albeit at a slower rate than the SO$_2$ 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. Further, the single box simulations presented here that predict the downwind trend do not simulate the ozone distribution across the plume cross-section. Ozone loss is typically greater in the plume centre than near the edges, see for example the spatially resolved model simulations for Redoubt plume that assumes similar Gaussian plume dispersion (Kelly et al. 2013). The single-box simulations should be interpreted in this context, e.g. a predicted loss of 45 nmol/mol implies greater loss at the plume centre (likely close to 60 nmol/mol or 100%) declining to near-ambient ozone at the plume edges. For example spatially resolved model simulations for Redoubt plume predicted greater loss in the plume centre than the edges (Kelly et al. 2013). The ozone mixing ratio starts to increase when the entrainment of ambient air containing O$_3$ is faster than the local O$_3$ destruction. Nevertheless, ongoing occurrence of ozone depleting BrO chemistry is demonstrated by the continuing negative trend in the cumulative ozone loss: the ozone difference (plume-background) integrated across the plume cross-sectional area declines along the 3 hr simulations to reach ~1, 4, and 7 g/cm$^2$ for the three flux scenarios (SO$_2$ flux = 10, 50, 100 kg/s) respectively with greater ozone loss for the high Br compared to the medium Br scenario, as expected. These Lagrangian simulations of plume ‘puff’ ozone evolution over 3 hr can also be viewed in a Eularian context: the 3 hr impact of continuous volcano emissions is calculated by integrating the cross-sectional impact (g/cm$^2$) over the distance downwind. This yields ozone losses of $35\cdot10^3$ ($38\cdot10^3$), $26\cdot10^3$ ($23\cdot10^3$), and $6\cdot10^3$ ($4\cdot10^3$) kg for the $\times10$ flux, $\times5$ flux and base run (10 kg/s SO$_2$ flux) scenarios respectively the assuming the medium Br scenario (numbers in brackets refer to high Br scenario). Whilst there is some linearity in ozone loss per Br emitted (e.g. in comparing the base run to $\times5$ flux cases), the constraint that ozone loss cannot exceed 100% of the background abundance introduces some non-linearity for the $\times10$ flux case, thereby reducing its overall ozone loss. Note that the plume cross-sectional area after 3 hrs is $\pi\cdot\sqrt{2}\cdot\sigma_h\cdot\sqrt{2}\cdot\sigma_z = 2\cdot\pi\cdot4470\cdot485 = 1.4\cdot10^7$ m$^2$. The volcanic plume cone thus resides within a cylinder of volume $1.4\cdot10^7\cdot108\cdot10^3 = 1.5\cdot10^{12}$ m$^3$, containing approx. 110$\cdot10^3$ kg ozone.

Figure 8 indicates that the plume atmospheric impacts extend beyond the one to three hour 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.

3.7 Implications for modelling and observations of volcanic BrO

The parameter space governing volcanic plume reactive halogen chemistry is vast, and is not fully constrained by available observations. Of particular importance in controlling the reactive bromine formation and downwind plume bromine speciation are: \( \text{Br}_\text{tot}/\text{SO}_2 \) in the emission, the volcanic aerosol loading, and the extent of background air mixing into the plume (itself a function of the plume dispersion parameterisation, volcanic emission flux and wind-speed). These factors exert non-linear influences on the conversion of emitted HBr into plume reactive bromine, and its speciation through interconversion of BrO, Br, Br_2, BrCl, HOBr, BrONO_2.

The onset of the autocatalytic reactive bromine formation is also accelerated in the model by radicals in the high-temperature model initialisation (Br, Cl, NO_x, HO_x). A major area of uncertainty is, however, the representation of this high-temperature near-vent plume environment using thermodynamic models such as HSC. Development of high-temperature kinetic models of the near-vent plume is encouraged for progress in this area.

Further uncertainty to the downwind plume chemistry is contributed by uncertainty in the volcanic bromine emission, and in aerosol surface area, that sustains halogen cycling downwind. Crater-rim filter-pack measurements (e.g. Aiuppa et al., 2005) provide estimates of volcanic Br/S emissions for model initialisation (see Table 2) but also highlight temporal variability in this parameter. The volcanic aerosol emission is poorly constrained by observations at Etna, and from volcanoes globally. A surface area loading of \(~10^{-11} \, \mu\text{m}^2\) molec SO_2^{-1}, i.e. an order of magnitude lower than that used by Roberts et al. (2009) yields simulated (0-20 km) downwind BrO/SO_2 more consistent with that observed in the Etna plume. Volcanic aerosol has a small influence on BrO/SO_2 ratio near source, but is an important control in the more dispersed plume downwind. Uncertainties in the volcanic aerosol emission magnitude, and its size distribution (which for sulfate varies as a function temperature and humidity) thus contribute to uncertainties in models of the plume halogen chemistry. Plume aerosol may be augmented by in-plume oxidation of volcanic SO_2 to H_2SO_4, and the entrainment and acidification of background aerosol may also promote
halogen cycling. Future model evaluation of volcanic reactive halogen impacts in the wider
troposphere will require development of regional and global models, with detailed treatment
of aerosol processes as well as plume dispersion (shown to be a key control on the downwind
chemistry). An improved quantification of the kinetics of HOBr reactive uptake on volcanic
aerosol is also needed according to Roberts et al. (2014). Global models may need to include
a representation of the sub-grid scale volcanic plume processes, particularly as this study
highlighted how the proportion of emitted HBr converted into reactive forms is non-linearly
dependent on the degassing scenario.

We emphasize the complex role of plume chemistry in the interpretation of volcano flank
DOAS measurements of BrO/SO2. Bobrowski and Giuffrida (2012) recently reported
variation in BrO/SO2 ratios at Etna related to the onset of eruption activity, for example with
increasing BrO/SO2 shortly prior to an eruptive event, and lower BrO/SO2 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 SO2 emissions,
related to subsurface magmatic processes. Lübcke et al. (2013) identified a decrease in
BrO/SO2 observed using a DOAS instrument prior to an eruption event at Nevado del Ruiz,
Colombia (in a period whilst SO2 emissions were increasing). However, we emphasize that a
variation in plume BrO/SO2 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/SO2 ratio, even for
a fixed Brtot:SO2 ratio in the emission. In the near-downwind plume, a key control on BrO
formation is the entrainment of oxidants. A substantial increase in volcanic emission flux
leads to greater plume strength and reduced ratio of background oxidants to bromine in the
model. Thus, on the <60 min timescale of volcano flank DOAS observations, a substantially
enhanced rate of volcanic degassing generally leads to lower plume BrO/SO2 ratios in more
concentrated plumes. Potentially, the variations in BrO/SO2 identified by Bobrowski and
Giuffrida (2012), and Lübcke et al. (2013) may result from a combination of volcanological
and plume chemistry factors. This example highlights the complexity surrounding
interpretation of volcanic BrO and shows the role of plume chemistry modelling in the effort
to use volcanic BrO observations to monitor and predict volcanic activity.
We also highlight that the plume chemical evolution causes a decline in BrO/SO₂ ratios in the dispersed plume further downwind through net conversion of BrO into reservoirs such as HOBr and BrONO₂. This plume chemical evolution acts to reduce the BrO column abundance, contributing additional limitations to its possible detection in dispersed plumes, and is the model explanation for the plateau in BrO/SO₂ downwind of Etna reported by Bobrowski and Guiffrida (2012). Detection of volcanic BrO by satellite is primarily constrained to large volcanic emissions (Theys et al., 2009, Rix et al. 2012, Hörmann et al., 2013). Smaller volcanic emissions that generate high but localised BrO at lower altitudes are less readily detected particularly due to dilution effects across the satellite measurement pixel (Afe et al., 2004). The modelled plume chemical evolution adds to this limitation for satellite detection of BrO in dispersed volcanic plumes (even at higher resolution). Importantly, however, the model Br-speciation shows that a declining trend in BrO abundance as the volcanic plume disperses does not preclude the occurrence of continued in-plume reactive bromine chemistry as predicted by the model.

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 BrO/SO₂; 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: BrO Br₂, Br and HBr are the main plume species in the near downwind plume whilst BrO, HOBr (and BrONO₂, BrCl) are present in significant quantities further downwind. An evaluation of the (quantifiable) chemistry surrounding BrNO₂ suggests a rather low prevalence in volcanic plumes, although uncertainties in model chemistry and initialisation are highlighted.

Emitted volcanic 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 BrO/SO₂ is primarily due to entrainment of ozone through plume dispersion that promotes BrO formation from Br radicals. A subsequent decline or plateau in BrO/SO₂ occurs upon plume dispersion, which both dilutes the volcanic aerosol (slowing HOBr and BrONO₂ heterogeneous loss rates) and entrains HO₂ and NO₂ from the background atmosphere (promoting HOBr and BrONO₂ formation from BrO). This promotes net accumulation of reservoirs HOBr and BrONO₂ and a reduction in BrO in the dispersed downwind plume.
Thus the model can explain the reported BrO/SO$_2$ trend at Etna. We demonstrate the role of plume chemistry models to interpret volcanic BrO/SO$_2$ observations as well as quantify atmospheric impacts on HO$_x$, NO$_x$, HNO$_3$ and ozone. A number of volcanological and meteorological factors can influence plume BrO/SO$_2$ ratios, and we illustrate simulations with contrasting total bromine content and volcanic aerosol loading. The influence of plume-air mixing is shown by simulations with varying dispersion rate, as well as wind-speed and volcanic gas flux.

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 one hour simulations, depending on bromine content (high, medium or 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$_2$ near-downwind (up to 6 km), a finding that is in agreement with the reported low relative humidity dependence of BrO/SO$_2$ (Bobrowski and Giuffrida, 2012).

Simulations with a fixed dispersion rate but enhanced volcanic emission flux are presented. For higher emission fluxes, the stronger plume and reduced ratio of background oxidants:bromine causes a slower rise in BrO/SO$_2$ in the near downwind plume (< 40 min) and a slower and delayed onset of the decrease in BrO/SO$_2$ in the far downwind plume (> 2 hr, for the volcanic conditions simulated). This simulated dependence of BrO/SO$_2$ on volcanic emission flux (albeit in an idealised model scenario) is particularly relevant towards the interpretation of changes in BrO/SO$_2$ during/prior to eruptive events (e.g. Bobrowski and Giuffrida, 2012, Lübcke et al., 2013).

Impacts of the plume halogen chemistry include downwind depletion of HO$_x$, NO$_x$ and ozone, and formation of HNO$_3$. Partial recovery of ozone is predicted, particularly for low gas flux emissions. However cumulative impacts on ozone are ongoing over the 3 h simulations.
**Acknowledgements**

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Table 1. Thermodynamic modelling of the high temperature near vent plume using HSC:

Overview of Inputs and Outputs.

<table>
<thead>
<tr>
<th>HSC Input: Chemical</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O, CO₂, SO₂</td>
<td>Major Volcanic Gases</td>
</tr>
<tr>
<td>HF, HCl, HBr, HI</td>
<td>Halogen Emissions</td>
</tr>
<tr>
<td>H₂S, CO, H₂</td>
<td>Reduced Gases</td>
</tr>
<tr>
<td>Hg</td>
<td>Trace Metals</td>
</tr>
<tr>
<td>N₂, O₂, Ar</td>
<td>Air</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HSC Input: Physical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vₐ/Vₘ</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
</tbody>
</table>

HSC Output:

- Full Matrix of Species (* see footnote)

Key Reactive Species in Output:

- NO, OH, Cl, Br, Cl₂: Species that act to kick-start BrO chemistry
- SO₃: Sulfur trioxide: direct precursor to sulphuric acid H₂SO₄ (or SO₄²⁻: Sulfate)

Major Volcanic Gases in Output:

- SO₂, HCl, HBr, CO₂, H₂O: Present in plume & in HSC output
- H₂S, H₂, CO: Present in plume but missing in HSC output

* Full Matrix of Species typically included in HSC output:

H₂O, N₂, CO₂, SO₂, H₂, HCl, O₂, H₂S, CO, Ar, S₂, SO₃, SO, NO, HBr, COS, HS, OH, Cl, Br,
S₂O, H₂S₂, Cl₂, I, HOCl, S₃, HI, HF, H, H₂SO₄, BrCl, NO₂, S, ClO, O, HO₂, Br₂, HIO, H₂O₂,
HNO₂, SOCl, ICl, HCOOH, CS₂, BrO, S₂Cl, N₂O, NOCl, HSO₃Cl, IBr, SCI, S₄, IO, NOBr,
COOH, HNO, NH₃, ClOO, S₅, Cl₂, CH₄, HNO₃, HCO, BrOO, CS, OCIO, O₃, I₂, ClO₂,
SBr₂, HCICO, SOCl₂, ClClO, ClOCl, NOI, NO₂Cl, SO₂Cl₂, SOF, IOO, HSO₃F, ClOCl, SN,
COCl, NO₃, S₂Cl₂, OBrO, S₆, F, NBr, HOCN, HNCO, BrOBr, CH₃, CIF, HCN, COCl₂,
N₂O₂, BrF, NH₂, OIO, IF, N, BrBrO, S₂Br₂, NOF, IIO, N₂O₃, NH₂OH, SO₂ClF, SF
Table 2. Parameters varied in *PlumeChem* sensitivity studies

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSC ( V_A : V_M )</td>
<td>0:100</td>
</tr>
<tr>
<td></td>
<td>8:92</td>
</tr>
<tr>
<td></td>
<td>5:95</td>
</tr>
<tr>
<td></td>
<td>10:90</td>
</tr>
<tr>
<td></td>
<td>15:85</td>
</tr>
<tr>
<td>Aerosol Loading: ( \mu m^2 / \text{molec SO}_2 )</td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>( 10^{-10} )</td>
</tr>
<tr>
<td>Medium</td>
<td>( 10^{-11} )</td>
</tr>
<tr>
<td>( \text{Br}_{50}/\text{SO}_2 ): molar ratio</td>
<td></td>
</tr>
<tr>
<td>Medium</td>
<td>( 7.4 \cdot 10^{-4} )</td>
</tr>
<tr>
<td>High</td>
<td>( 2.4 \cdot 10^{-3} )</td>
</tr>
<tr>
<td>Low</td>
<td>( 4.8 \cdot 10^{-4} )</td>
</tr>
<tr>
<td>Gas Flux kg/s SO(_2) (small variations)</td>
<td>10, 20</td>
</tr>
<tr>
<td>Gas Flux kg/s SO(_2) (large variations)</td>
<td>10, 50, 100</td>
</tr>
<tr>
<td>Wind-speed, m/s</td>
<td>3, 5, 10, 15</td>
</tr>
<tr>
<td>Dispersion</td>
<td>B, C, D</td>
</tr>
<tr>
<td>Pasquill-Gifford cases</td>
<td></td>
</tr>
</tbody>
</table>
Table 3. List of gas-phase and photolytic reactions related to formation of BrNO₂, BrONO and BrNO. Reactions listed are used in the -BrONO-BrNO scheme. The 2-reaction BrNO₂ scheme assumes BrNO₂ as the sole product from both Br + NO₂ reactions and photolysis of BrNO₂ as the only loss pathway. See text for discussion of possible additional heterogeneous pathways.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>at 285 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Br} + \text{NO}_2 \rightarrow \text{BrNO}_2 )</td>
<td>( ~3.8 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
<td>Brökse et al., 1998</td>
</tr>
<tr>
<td>( \text{Br} + \text{NO}_2 \rightarrow \text{BrONO} )</td>
<td>( ~4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
<td>Brökse et al., 1998</td>
</tr>
<tr>
<td>( \text{BrONO} + \text{Br} \rightarrow \text{Br}_2 + \text{NO}_2 )</td>
<td>( 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
<td>Mellouki et al. 1989</td>
</tr>
<tr>
<td>( \text{BrONO} + \text{NO}_2 \rightarrow \text{BrNO}_2 + \text{NO}_2 )</td>
<td>( ~2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} ) (uncertain)</td>
<td>Brökse et al., 1998</td>
</tr>
<tr>
<td>( \text{BrONO} \rightarrow \text{BrNO}_2 )</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>( \text{BrNO}_2 + \text{Br} \rightarrow \text{Br}_2 + \text{NO}_2 )</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>( \text{BrNO}_2 + \text{NO} \rightarrow \text{BrNO} + \text{NO}_2 )</td>
<td>( 2.3 \times 10^{-12} \text{ Exp}[-17.8/RT] \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} )</td>
<td>Brökse et al., 1998</td>
</tr>
<tr>
<td>( \text{BrNO}_2 + \text{NO} \rightarrow \text{BrNO} + \text{NO}_2 )</td>
<td>unknown, larger than BrNO₂ equivalent</td>
<td></td>
</tr>
<tr>
<td>( \text{BrNO} + \text{Br} \rightarrow \text{Br}_2 + \text{NO} )</td>
<td>( 3.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
<td>Hippler et al. 1978</td>
</tr>
<tr>
<td>( \text{BrNO}_2 \rightarrow \text{Br} + \text{NO}_2 )</td>
<td>( \leq 4.0 \times 10^{-4} \text{ s}^{-1} ) or ( 6.4 \times 10^{-5} \text{ s}^{-1} )</td>
<td>Brökse et al., 1998</td>
</tr>
<tr>
<td>( 2\text{BrNO}_2 \rightarrow \text{Br}_2 + 2\text{NO}_2 )</td>
<td>Unknown (slow)</td>
<td></td>
</tr>
<tr>
<td>( \text{BrONO} \xrightarrow{hv} \text{Br} + \text{NO}_2 )</td>
<td>( \tau \sim \text{s} ) (products unknown)</td>
<td>Burkholder and Orlando, 2000</td>
</tr>
<tr>
<td>( \text{BrONO} \xrightarrow{hv} \text{BrO} + \text{NO} )</td>
<td>( \tau \sim \text{min} )</td>
<td>Scheffler et al. 1997</td>
</tr>
<tr>
<td>( \text{BrNO}_2 \xrightarrow{hv} \text{Br} + \text{NO}_2 )</td>
<td>( \tau \sim \text{min} )</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. *PlumeChem* simulations illustrating (a) predicted SO$_2$ column abundance in the downwind plume (black line) according to the model dispersion parameterisation, (b) simulated downwind BrO/SO$_2$ ratios for model runs using this dispersion parameterisation but where: bromine in the emission (Br$_{tot}$/SO$_2$), volcanic aerosol loading, and the high-temperature initialisation are varied. The simulations are compared to DOAS SO$_2$ column abundances and (mean) BrO/SO$_2$ ratios reported by Oppenheimer et al., (2006), and Bobrowski et al., (2007a), gray squares and black disks, respectively. Simulations with
varying aerosol emission (for two bromine scenarios) are highlighted in black. Simulations
assuming medium aerosol loading and varying bromine emission (for a range of plausible
high-temperature model initialisations) are shown in red, orange and purple for medium, high
and low Br emission scenarios, respectively. Simulations assuming no plume-air mixing in
the high-temperature initialisation (VA:VM = 0:100) are shown in grey.
Figure 2. Mixing ratio ($10^{-6}$ mol/mol) of key species (NO, OH, Br, Cl, Cl₂) in the HSC output as a function of $V_A/V_M$, the assumed magmatic: atmospheric gas ratio in the near-vent plume, ranging from 0 (0.00:1.00) to 0.18 (0.15:0.85). SO₃:SO₂ ratios (that prescribe the volcanic sulfate/SO₂ emission) in the HSC output are also shown. (a) Standard operation of HSC in which volcanic H₂S and H₂ are allowed to re-equilibrate, yielding near-zero mixing ratios of these gases in the HSC output. (b) A revised operation of HSC (Martin et al., 2009) in which volcanic H₂S and H₂ are removed (and temporarily replaced by inert Ar) such that they do not re-equilibrate within HSC.
Figure 3. Left: Simulated 1 hr evolution of plume BrO/SO$_2$ for the three bromine emission scenarios, with varying atmospheric:magmatic gas ratio $V_A:V_M$ (0:100, 5:95, 10:90, 15:85) in the high-temperature initialisation. Also shown are observed BrO/SO$_2$ ratios reported by Oppenheimer et al., (2006), and Bobrowski et al., (2007a); grey and black disks respectively,
Figure 4. Predicted evolution in BrO/\text{SO}_2 (top) and BrO/Br_{tot} ratios (bottom) over 1 hr for the three different bromine emission scenarios. Model runs correspond to those shown in Figure 3 assuming VA:VM = 5:95 for the high-temperature initialisation.
Figure 5. Br-speciation in model runs that also include formation of BrNO₂, shown for the three bromine emission scenarios. Simulations incorporate BrNO₂ using a 2-reaction scheme.
(a,c,e) or a 12-reaction scheme including BrNO₂, BrONO and BrNO (b,d,f). See text for details.
Figure 6. Simulated BrO/\text{SO}_2 over 1 h for the medium bromine emission, predicted for two emission flux scenarios (10 or 20 kg/s), and for a range of wind-speeds (3, 5, 10, 15 m/s), and Pasquill-Gifford dispersion schemes (B, C, D). See text for details of the combinations. Model runs are compared to observations from Bobrowski et al. (2007) and Oppenheimer et al. (2006), shown as black circles and grey squares, respectively.
Simulated plume SO₂, BrO and BrO/SO₂ over 3 hours for the medium and high bromine emission scenarios, and with varying volcanic emission flux (baseline run, and with volcanic gas+aerosol emissions flux × 5 and × 10, shown by full-, long-dashed and short-dashed lines, respectively), whilst keeping the same plume dispersion parameterisation, wind-speed and
initialisation (see text for model details and interpretation). Arrows highlight the reduction in near-downwind BrO/ SO$_2$ predicted at greater volcanic emission flux.
Figure 8.

Simulated impact of plume BrO chemistry on atmospheric oxidants, shown for the model scenarios of Figure 7. Depletion of oxidants and formation of NOy is shown through the difference in plume–background mixing ratio for HOx (OH+HO2), NOx (NO+NO2), HNO3, and ozone. Cumulative ozone loss is also calculated across the 3 hour simulations.