



Depletion of ozone in
the plume of Mt. Etna

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Quantification of the depletion of ozone in the plume of Mount Etna

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Abstract

Volcanoes are an important source of inorganic halogen species into the atmosphere. Chemical processing of these species generates oxidised, highly reactive, halogen species which catalyse considerable O₃ destruction within volcanic plumes. A campaign of ground-based in situ O₃, SO₂ and meteorology measurements was undertaken at the summit of Mount Etna volcano in July–August 2012. At the same time, spectroscopic measurements were made of BrO and SO₂ columns in the plume downwind.

Depletions of O₃ were seen at all in-plume measurement locations, with average O₃ depletions ranging from 11–35 nmol mol⁻¹ (15–45 %). Atmospheric processing times of the plume were estimated to be between 1 and 4 min. A 1-D numerical model of early plume evolution was also used. It was found that in the early plume O₃ was destroyed at an approximately constant rate relative to an inert plume tracer. This is ascribed to reactive halogen chemistry, and the data suggests the majority of the reactive halogen that destroys O₃ in the early plume is generated within the crater, including a substantial proportion generated in a high-temperature “effective source region” immediately after emission. The model could approximately reproduce the main measured features of the O₃ chemistry. Model results show a strong dependence of the near-vent bromine chemistry on the presence or absence of volcanic NO_x emissions and suggest that near-vent O₃ measurements can be used as a qualitative indicator of NO_x emission.

1 Introduction

Volcanoes are known to be a major source of climatically important species, trace gases, and aerosol into the atmosphere, both through explosive eruptions and sustained quiescent degassing (e.g. von Glasow et al., 2009). The largest gaseous components of most eruptions are water, carbon dioxide and sulphur compounds, followed by hydrogen halides (Symonds et al., 1994). These volcanogenic halides are known

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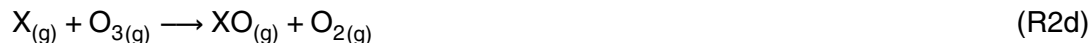
to present environmental hazards upon deposition to soils (e.g. Delmelle et al., 2003). Emissions of bromide, while weaker and less well studied than those of fluoride and chloride (Pyle and Mather, 2009), are of interest to atmospheric chemistry due to the conversion of HBr to very reactive O₃-depleting bromine species (Bobrowski et al., 2003, 2007; Gerlach, 2004; Oppenheimer et al., 2006; Bobrowski and Platt, 2007; von Glasow et al., 2009; Kern et al., 2009; Roberts et al., 2009, 2014; von Glasow, 2010; Kelly et al., 2013).

The bromine explosion is an autocatalytic chemical reaction cycle which is known to convert bromine from HBr to very reactive forms (Wennberg, 1999). It is considered to be the reason for detections of elevated BrO associated with depleted O₃ (e.g. von Glasow et al., 2009; Saiz-Lopez and von Glasow, 2012).



There is no equivalent “chlorine explosion” as HCl is less reactive than HBr (see von Glasow et al., 2009).

In the troposphere reactive halogen species catalyse O₃ destructive cycles (e.g. Saiz-Lopez and von Glasow, 2012) (X and Y are halogen atoms):



Reactive halogen chemistry and related O₃ depletion has been studied in detail in the polar and marine boundary layers and over salt lakes (see Saiz-Lopez and von Glasow, 2012, for an overview).

BrO is detectable through spectroscopy, and detection of elevated levels are used as an indicator for the occurrence of reactive bromine chemistry. BrO was first detected in a volcanic plume by Bobrowski et al. (2003), and has, to date, been detected in the plumes of about 20 different volcanoes. A good overview of ground-based measurements of BrO in volcanic plumes can be found in Boichu et al. (2011) and references therein. A systematic study of satellite data by Hörmann et al. (2012) greatly extended the dataset of known BrO events detected via satellite measurements.

In both satellite and ground-based studies, in-plume ratios of BrO to SO₂ have been found to be of the order of 10⁻⁵–several 10⁻⁴ once the plume has been transported a few km from the source (e.g. Bobrowski et al., 2007; Boichu et al., 2011; Hörmann et al., 2012). Measurements and modelling studies of in-plume BrO/SO₂ ratios have shown BrO to be either present at low levels or undetectable within 1 km of volcanic vents whilst BrO/SO₂ ratios of up to several 10⁻⁴ are measured a few km downwind of the same vent (e.g. Bobrowski et al., 2007; Kern et al., 2009). This suggests the formation of BrO is occurring within the time taken for this downwind transport. SO₂ is widely used as a tracer for volcanic emissions due to its high concentration in volcanic

plumes, low reactivity, and easily-detectable spectroscopic signal (McGonigle et al., 2004).

Volcanoes are known to emit other halogens (F, Cl, I). The HF molecule is expected to be too stable for any in-plume reactive F chemistry to occur (von Glasow et al., 2009), whilst the magnitudes of volcanic HI emissions are probably too low to have a significant effect on plume chemistry (Aiuppa et al., 2005a). Measurements of oxidised Cl in volcanic plumes are varied, having been observed at Sakurajima (Lee et al., 2005), Etna (Bobrowski et al., 2007; General et al., 2014), and Puyehue-Cordón Caulle (Theys et al., 2014). However a DOAS investigation by Kern et al. (2009) specifically looking for oxidised Cl did not detect any in the plume of Masaya volcano. It is unknown whether this reflects natural variability or measurement issues. See Roberts et al. (2009) for a discussion of reactive chlorine formation in volcanic plumes.

The conceptual model of halogen–O₃ chemistry within volcanic plumes is complicated by the very high temperatures of the plume immediately after emission and mixing with the atmosphere. Such high temperature mixtures are believed to reach or approach thermodynamic equilibrium (Symonds et al., 1994), resulting in the production of non-negligible quantities of oxidised halogen species which may begin the autocatalytic cycles described above (Gerlach, 2004; Bobrowski et al., 2007; Martin et al., 2009). Because of the hazards involved, this “effective source region” within the crater (Bobrowski et al., 2007) cannot be investigated directly. Instead, inventories of volcanic emission species are based mostly on samples of fumarole emissions or crater-rim measurements (Gerlach, 2004). Processes occurring in the effective source region are inferred from these measurements, theory, and measurements of the plume further downwind.

While BrO (and, with greater difficulty, OCIO) can be measured remotely using passive spectroscopic techniques, direct measurements of O₃ depletion within volcanic plumes have to be made in situ due to the large atmospheric O₃ column, and as a result the existing body of literature on the depletion of O₃ within volcanic plumes is small, see Table 1. Active DOAS O₃ measurement within volcanic plumes may be possible,

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but, to the authors' knowledge, no such measurements have been made at any volcano.

This study expands this small collection of O₃ observations. In addition, the O₃ depletion data collected are associated with simultaneous measurements of an inert plume tracer (SO₂). To the authors' knowledge, no prior dataset exists of simultaneous measurements of O₃ depletion and a tracer species within 1 km of volcanic vents. Wind speeds have also been measured, such that processing time can be determined for every datapoint. As in-plume halogen and O₃ chemistry are closely linked, from these data we can investigate both qualitatively and quantitatively the fast chemical processes occurring within the early plume.

2 Campaign and data processing

2.1 Location

The measurement campaign was conducted at Mount Etna volcano, Sicily, Italy (37.7° N, 15.0° E) with the majority of measurements being taken between 24 July and 2 August 2012. Mount Etna is an active stratovolcano with a peak elevation of about 3300 m. At the time of measurement the volcano was in a passively degassing phase with three active vents (North East, Voragine and Bocca Nuova) within our survey area. Small Strombolian eruptions and an inner-crateric lava flow were observed at Bocca Nuova but explosive ejecta only rarely surpassed the crater rim. Due to the vicinity of the Voragine and Bocca Nuova craters it was not possible to distinguish between their plumes. Therefore in this analysis we have considered them to be a single "Central craters" source.

Most of the measurements were taken near the crater rim at elevations significantly above the planetary boundary layer. Due to logistical constraints we took these measurements between 08:40 and 12:00 UTC (10:40–14:00 LT). The sky was cloud-free

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on all days of measurement. The ground-based remote sensing measurements of the plume were taken from locations further downwind with plume ages of up to 30 min.

On all days of near-crater measurements we took measurements at a fixed site that was upwind of all summit craters and at 1–3 sites in the plume at varying distances from the craters (Fig. 1). This was done to sample plumes at different processing times. Sampling times at the sites varied between 20 and 60 min (see Table 3).

The names given to the near-crater measurement sites in the figures and in Table 3 indicate the day on which the measurements were taken and the order in which they were measured. For example, site “d2-27” was the second downwind site measured on 27 July. All upwind measurements were taken at the same location. In Table 3 the upwind site datasets collected on each day have been treated separately. For example, “up-30” is the set of measurements taken at the upwind site on 30 July.

2.2 Instrumentation

O₃ mixing ratios were measured via UV adsorption with a 2B Technologies instrument, model 202. A particle filter was placed on the inlet to prevent aerosols from influencing data or damaging the instrument. Because of the overlap of the O₃ and SO₂ adsorption spectra (e.g. Vance et al., 2010) we also fitted the inlet with two SO₂ scrubbers in series to prevent interference in the O₃ measurements. The scrubbers were packed with Cr₂O₃-coated microfibre filter paper. We tested the endurance of the scrubbers prior to the campaign. Air with a SO₂ mixing ratio of 700 μmol mol⁻¹ was passed through the setup at a flow rate of 0.58 L min⁻¹. No SO₂-related signal could be detected on the O₃ monitor for 2.25 h, a removal of approximately 15 mg of SO₂. This greatly exceeds the expected SO₂ exposure of the scrubbers in the field.

New scrubbers and particulate filters were used daily. We calibrated the O₃ monitor and inlet set-up daily with a 2B Technologies model 306 O₃ calibration source. We determined a measurement error of ±3 nmol mol⁻¹ from the calibration results.

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We measured several gases' mixing ratios with a portable version of the the INGV-type Multi-component Gas Analyser System (MULTIGAS) (Aiuppa et al., 2011, 2012), though only the SO₂ measurements have been used in this analysis. The SO₂ measurement used an electrochemical sensor (0–200 μmol mol⁻¹; 3ST/F electrochemical sensor, City Technology Ltd.). A protective particulate filter was included on the instrument inlet. Data were recorded on an on-board data-logger and stored internally. The instrument's sensors and data-logger were housed in a water-proof box with a 1.2 L min⁻¹ pump and a 12 V battery. The sensors were calibrated before and after fieldwork with standard calibration gases; the instrument's accuracy and precision were determined to both be about 20 %. The MULTIGAS was not used for the first two days of the campaign (24 and 25 July).

Temperature, humidity and wind vector were measured with a Kestrel 4500 commercial weather station, mounted on a tripod. Prior to the campaign, the device's relative humidity measurement was calibrated with standardised salt solutions.

Each instrument recorded data at a different frequency. Table 2 shows the instruments' measurement intervals and precision errors.

At the measurement sites we set up the O₃ monitor and MULTIGAS on the same tripod, with the inlet tubes taped closely together. The weather station tripod was positioned within 5 m of the tripod supporting the in situ instruments. The locations of the sites were determined by hand-held GPS. The source of the plume at each downwind site was determined visually.

Remote sensing measurements of the downwind evolution of the volcanic plume with two Mini-MAXDOAS (Multi Axis Differential Optical Absorption Spectroscopy) instrument were carried out (see Bobrowski et al., 2007, for an instrument description). Scans approximately perpendicular to the plume axis were made at distances between 6 and 16.6 km from the craters, corresponding to plume ages between about 8 and 30 min.

Prior to the main campaign, additional measurements were taken at the crater rim of North East Crater and Bocca Nuova on 26 and 27 June 2012 to characterize the

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composition of the plume (Wittmer et al., 2014). Two different kinds of alkaline traps (Drechsler bottle, flow rate 2 L min^{-1} and Raschig tube, flow rate $4\text{--}5 \text{ L min}^{-1}$) filled with a 1 M NaOH solution were used to determine the concentrations of the acidic gases CO_2 , SO_2 , HCl, HBr and HI from the amounts of C, S, Cl, Br and I dissolved in the solution. After sampling the solutions were first neutralised with an ASRN 300, which is a membrane-based electrolytic device that is replacing sodium ions with hydronium ions. After neutralization hydrogen peroxide was added to the solution to oxidize all sulphur species in order to determine the total sulphur concentration. S and Cl were then analysed with Ion Chromatography, Br and I were analysed with Inductively Coupled Plasma mass spectrometry (ICP-MS) and the solved Carbon was analyzed by titration (Orion 960 Autochemistry System) (Wittmer et al., 2014).

2.3 Data processing

The instruments listed in Table 2 each had independent internal clocks which could only be roughly synchronised in the field. The MULTIGAS' internal clock does not record absolute time, but only time since the the device was switched on. In the field we turned the device on at the same time as the other instruments, however it is probable some desynchronisation of the data sets has occurred because of this. Inspection of the O_3 and SO_2 signal suggests that this desynchronisation may have been up to 25 s.

We used the upwind site data sets as reference values of the background air. For each downwind site, the O_3 concentration time-series was converted to a time-series of O_3 change (ΔO_3) using the average O_3 mixing ratio measured at the upwind reference site on that day.

As the collection frequency of the instruments differed, the data were binned into 120 s bins. Each 120 s bin therefore covered several measurements from each instrument and for each parameter a mean value was calculated. The use of 120 s bins reduced the precision error on the resulting data points. Additionally, the use of 120 s bins is expected to reduce the impact of any potential asynchronisation resulting from either the problem discussed above or from differing instrument response times.

Inspection of the signals (e.g. Fig. 2) showed clear anticorrelation between the O₃ and SO₂ mixing ratios.

SO₂ is used as the inert plume tracer, a measure of plume strength for the bin. Measured background levels of SO₂ were negligible in comparison to in-plume measurements and SO₂ is expected to be effectively chemically inert. For each 120 s measurement bin a ratio $\Delta O_3/SO_2$ (change in molecules O₃ per molecule inert plume tracer) was calculated, this is a measure of O₃ change that is attributable to chemical and not physical processes (a proof of this can be found in the Appendix).

Transport times between the craters and the downwind sites were determined from the distances between the sites and the vents, and the measured wind speeds. Uncertainty in the data-points for each bin was calculated from the known uncertainties in the instruments' measurements (Table 2). When calculating the uncertainty in the ΔO_3 values, the variance of the O₃ signal at the reference sites were considered, along with the expected instrument error.

The MAXDOAS data were evaluated for BrO and SO₂ with the WinDOAS V2.10 software package (van Roozendaal and Fayt, 2001) which uses a nonlinear least-square method (Stutz and Platt, 1996). A BrO/SO₂ ratio was calculated for each measurement day by a correlation plot of the daily data set. The plume ages at the point of measurement were calculated from the wind speed and lateral distance from the craters. In the absence of wind speed data at Etna, speeds from soundings taken at Trapani (37.91° N, 12.50° E, data from <http://weather.uwyo.edu/upperair/sounding.html>) were used. The 220 km distance between the location of the soundings and the volcano means that there is a relatively large and unquantifiable uncertainty in the calculated plume ages.

3 Results

An overview of the near-crater results from this campaign can be seen in Table 3. Calculated plume ages were found to be of the order 1–4 min.

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O₃ depletion of up to 45 % was observed at all seven downwind sites. SO₂ decreases with transport time (Fig. 3), as would be expected due to dilution. The low SO₂ mixing ratios at site d2-30 suggest this site was at the plume edge, this is consistent with visual observations of the plume. A plot of ΔO₃ against transport time (Fig. 4) shows no comparable trend as chemical destruction of O₃ and dilution with background air occur simultaneously.

In Fig. 5 Δ[O₃]/[SO₂] versus transport time is plotted. The linear trend is indicative of chemical destruction of O₃ occurring within the first few minutes of plume transport (see Appendix).

The data on Fig. 5 appear to fit a linear trend. This indicates, that as a ratio to the inert plume tracer, the rate of chemical O₃ destruction is constant within the first few minutes of plume evolution. In the expected chemical cycles (Reaction R2) the rate of O₃ destruction is dependant on the concentration of halogens in highly reactive (non-hydrogen halide) forms. Therefore a constant rate of reaction indicates that the ratio of these species to SO₂ is approximately constant during the first few minutes of plume evolution.

Depletion of O₃ occurred on 30 July even when the relative humidity was < 10 %. This is below the crystallisation point of any major aerosol component that would be expected to be present in the plume. It would therefore be expected that at such low humidities aqueous phase reactions (such as Reaction R1d) would occur at a much slower rate, preventing the bromine explosion from converting HBr to very reactive forms of bromine. No significant increase in humidity due to volcanic H₂O was observed at the crater rim. The possible impacts of a short-lived elevated humidity within the crater due to volcanogenic H₂O are considered with the “dry” model runs in Sect. 4 of this paper.

Data points from all measurement sites appear to approximately fit the same line-of-best fit on Fig. 5. This is despite the measurements spanning two separate days and these two days having very different circumstances. On 27 July the measurements were made in the plume of the North East crater, and on 30 July the measurements

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were made in the plume of the central craters. The different craters are known to exhibit differing emission compositions (Aiuppa et al., 2005a). In addition the relatively humidity on these two days was markedly different. It is unknown whether the cause of these two data sets' approximate alignment in Fig. 5 is due to mechanistic reasons relating to the “effective source region” (see below) or coincidence.

A linear line of best fit was calculated using Williamson-York Iterative Bivariate analysis (Cantrell, 2008), its gradient is $(-1.02 \pm 0.07) \times 10^{-4} \text{ s}^{-1}$. The r^2 value of this fit is 0.76. This linear trend can be interpreted as there being a rate of destruction of O_3 within the plume of approximately 10^{-4} molecules per molecule of SO_2 (the inert plume tracer) per second in the first few minutes of plume evolution. SO_2 is only used as a measure of plume intensity, SO_2 does not play a role in O_3 destruction.

Extrapolating the line-of-best-fit on Fig. 5 results in an intercept of the x axis of approximately -60 s . Assuming chemical O_3 destruction is not instantaneous in the plume, it would be expected that the line of best fit would pass through the origin. We determine that this offset is most likely the result of inaccuracy in the calculation of processing time. Firstly, the calculation assumes air is assumed to travel in a straight line between vent and sampling point, however the path length is likely to be greater than this due to turbulence, the topology of the mountain-top, and variation in wind direction. Second, the distances between vents and sampling points were calculated only from their lateral displacement and did not consider the time taken for vertical transport from the vent to the crater rim. From our visual observations of the plume, we estimate this vertical transport time is likely to have been of the order of a minute.

Table 4 lists the composition of volcanic volatiles. These figures are calculated from June 2012 measured values of SO_2 , HF, HCl, and HBr (Wittmer et al., 2014), as well as the MULTIGAS measurements of CO_2 and SO_2 made on the main campaign. As complete characterisation of the volcanic volatiles could not be made from the June 2012 measurements alone, the ratio of the gases to CO_2 were used in these calculations with absolute values of H_2O and CO_2 calculated from the values reported in (Aiuppa et al., 2005b). Additionally, H_2/SO_2 was taken from (Aiuppa et al., 2011), and

H₂S/SO₂ was calculated from the values reported in (Aiuppa et al., 2005b). These values were then normalised to ensure that the sum equals unity.

The remote sensing results are shown in Table 5, along with the correlation between the BrO and SO₂ columns and the estimated plume age (based upon distance from the crater and wind speed, see Sect. 2.3). The BrO/SO₂ column ratios are within the range typically measured both in the Etna plume (Bobrowski and Giuffrida, 2012) and volcanic plumes in general (Boichu et al., 2011; Hörmann et al., 2012).

4 Modelling study

We used a vertically resolved 1-D numerical model MISTRA to simulate the chemical evolution of the volcanic plume in the atmosphere and to test the model's performance against the data presented above. The model is the same as used in von Glasow (2010) with minor modifications. Based on previous work (Gerlach, 2004; Martin et al., 2006; von Glasow, 2010) we used the thermodynamic equilibrium model HSC (Roine, 2007) to calculate the composition of the mixture of volcanic volatiles and ambient air in the "effective source region" which is located in the crater where temperatures are high enough so that the assumption of immediate thermodynamic equilibrium is still valid but also enough ambient air has been entrained to oxidise the main volcanic reduced gases (mainly H₂S and H₂) which leads to a dramatic change in halogen speciation. Compared to von Glasow (2010) we used a higher ratio of volcanic volatiles : ambient air (95 : 5) which is as rich in volcanic volatiles as possible but already oxidised.

The model is run in Lagrangian mode, following the evolution of the plume downwind of the volcano and explicitly modelling the interaction of the plume with background air (see von Glasow, 2010).

The S and Br elemental ratios of the volcanic volatiles used in the HSC calculation are taken from the average values measured at the crater rim (Table 4, column "low Br/S") on 26 and 27 June 2012. We also did a second set of model runs initialised with a much higher Br/S ratio (Table 4, column "high Br/S") based on unpublished

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data from Alessandro Aiuppa. Table S1 in the Supplement gives the composition of the volcanic volatiles and the results of the HSC calculations used as input for the 1-D model.

The relative humidity varied significantly during the campaign (see Table 3), which is important as the bromine explosion is efficient in the presence of aqueous aerosol. The crystallisation humidity of sulphate particles is around 43 % (depending on contents of other salts see, e.g. Seinfeld and Pandis, 2006) which implies that on the days of this study when simultaneous SO₂ and O₃ measurements were made the aerosol will have contained only very small amounts of water and will not have been deliquesced. We therefore ran the model at three different settings regarding the aerosol:

1. “moist”: relative humidity 57 % (above sulphate crystallisation humidity), aerosol aqueous phase chemistry occurs throughout the plume,
2. “dry”: relative humidity 21 % (below sulphate crystallisation humidity), aerosol aqueous phase chemistry consequently disabled. Exception is the first 1 min, where water from the volcano elevates the humidity within the plume,
3. “noHet”: where all heterogeneous chemical reactions were deactivated.

Being remote from major sources of anthropogenic pollution and above the planetary boundary layer, the ambient NO_x levels at Etna are expected to be negligible compared to the amount of nitrogen oxides (NO_x) that thermodynamic models such as HSC predict would be formed in the effective source regions of volcanic vents. However Kaschka (2007) and Martin et al. (2012) discussed the problems associated with this, mainly that the time required to reach equilibrium for NO_x under the given temperatures in the effective source region is, by far, too long. The generation of NO_x could significantly perturb bromine chemistry due to the formation of BrNO₂ (see e.g. Fig. 2 in von Glasow, 2010). A detailed discussion of volcanic plume Br–NO_x chemistry, including a modelling study that includes additional BrNO₂ reactions, can be found in Roberts et al. (2014). For each of the three aerosol settings described above, two model runs

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were done – one with volcanic NO_x in the quantities predicted in the thermodynamic model and one with no volcanic NO_x . These six runs were performed for both of the plume initialisations shown in Table 4.

4.1 “Low Br/S” modelled plume

Model results are shown for the core of the plume which is most appropriate for the grounded plume measured in our campaign. Comparison of modelled and measured plume SO_2 mixing ratios, shown in Figs. 6 and 3 respectively, show the plumes to be of similar intensity. Differences in SO_2 mixing ratio between the six model runs are negligible. In order to approximately reproduce the measured SO_2 mixing ratios at the crater rim the “initial dilution” ratio of the HSC output with ambient air (see *Materials and Methods* in von Glasow, 2010) was set to a factor of $9\times$.

Figure 7 shows the modelled O_3 depletion in the six runs. Figure 8 shows this as a ratio to SO_2 mixing ratio (c.f. Figs. 4 and 5 respectively).

In comparison to the measured data where bromine chemistry at the craters can only be inferred from O_3 and SO_2 data, the modelled bromine chemistry can be investigated directly; Fig. 9 shows the speciation of bromine in the six different runs.

In all three runs with volcanic NO_x , the bromine almost entirely partitions to BrNO_2 . BrNO_2 does not contribute to O_3 depletion. As shown in Fig. 7, in these runs the net O_3 change is almost zero for all runs and is actually positive in the “noHet” and “dry” cases as a consequence of O_3 -generating NO_x chemistry.

The bromine explosion, as evidenced by conversion of HBr to other forms of bromine can be seen in the “moist” runs and has also occurred between 0 and 60 s of the “dry” run (where volcanic H_2O is modelled to increase the plume’s humidity). In the “noHet” runs and in the “dry” runs after the volcanic humidity increase has ended, the processes that convert HBr to other forms are effectively halted.

In all three NO_x -free runs O_3 is depleted. Reactive bromine is generated by the high-temperature processes of the effective source region in all three runs. In the “moist” case, and to a slightly reduced extent in the “dry” case, this is supplemented by the

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generation of reactive bromine species via the bromine explosion, to the extent that in the “moist” case the O₃ depletion is near 100 %. The consequences of these three runs’ differences in bromine chemistry can be seen on Fig. 8, where the $\Delta[\text{O}_3]/[\text{SO}_2]$ ratios diverge over the first few minutes.

5 A comparison of the O₃ depletion (Figs. 7 and 8) after 60 s for the “noHet” run with that for the “dry” and “moist” runs shows the comparative influence of different processes within the crater. The O₃ depletion in the “noHet” case must be due to reactive halogen generated in high temperature processes as heterogeneous reactions are required for low-temperature reactive bromine generation (the bromine explosion).
10 The additional O₃ depletion at 60 s in the “dry” and “moist” cases can therefore be attributed to the bromine released via the bromine explosion within the crater. As the plume moves away from the crater, the heterogeneous bromine explosion can only occur in the “moist” run so the increasing differences between the “moist” and “dry” runs are due to the continued bromine explosion in the “moist” run.

15 The model results can also be used to calculate column ratios of BrO and SO₂. Figure 10 shows these data over the first 60 min of plume evolution. This figure is also overlaid with the spectroscopic observations listed in Table 5. Due to logistical constraints we have concurrent near-crater and downwind data only for 27 July; this datapoint is highlighted on Fig. 10. As can also be seen in Fig. 9, only the “moist” runs maintain significant amounts of volcanic bromine as BrO and show column BrO/SO₂ ratios comparable with measurements. Also notable is the rise in the column ratio in the
20 “moist-withNO_x” run after a few minutes. After significant dilution of the plume has occurred the dominance of the BrNO₂ reservoir diminishes. Thus volcanic NO_x, if present, delays but does not prevent in-plume reactive bromine chemistry.

25 4.2 “High Br/S” modelled plume

The elemental emissions ratio of Etna is known to vary between craters and over time (Aiuppa et al., 2005a). Figure 11 shows the evolution of modelled ΔO_3 for the six runs where they have been initialised using the “high Br/S” ratios (see Table 4). Further

plots relating to these are shown in the Supplement of this paper (Figs. S1–S5). As for the runs described previously, in order to approximately reproduce the measured SO₂ mixing ratios at the crater rim (and those from the prior runs) an “initial dilution” ratio was again used, in these runs it was set to a factor of 15× dilution.

The increase in the amount of volcanic bromine has a significant impact on the chemistry. In the NO_x-free runs the reactive bromine generated by the effective source region is sufficient to destroy almost all of the O₃ within the plume and the plume chemistry is O₃-limited. As can be seen in Table S1 of the Supplement, the NO_x/S ratio is very similar for the “low Br/S” and “high Br/S” cases. As a consequence the Br/NO_x is very different, being 0.0875 in the “low Br/S” runs and 3.35 in the “high Br/S” runs. Whereas in the “low Br/S” runs with volcanic NO_x almost all reactive Br had partitioned to BrNO₂, in the corresponding “high Br/S” the partitioning of the reactive bromine to BrNO₂ is more moderate and a significant amount of reactive bromine in other forms remains. This results in moderate O₃ depletion in the early plume, with similar variation between the humidity cases as discussed above.

4.3 Comparison with measured data

This modelling study shows that the plume chemistry is highly sensitive to several factors: the presence of volcanic NO_x, the magnitude and composition of the primary volcanic emissions, and heterogeneous processes which are dependant on aerosol and humidity. Any comparison between the model results and the measurements must be made with caution. In particular:

- volcanic volatile Br/S ratios are known to vary considerably both over time and between Etna’s different craters (Aiuppa et al., 2005a). The composition of the volcanic volatiles used in the “low Br/S” modelling study was based on measurements which were taken a month prior to the O₃ and SO₂ measurements. It is unknown how the emissions may have changed in the intervening period, and

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comparing the results with the two different initialisations shows that variations in volatile composition can be very significant.

- Over the time that measurements were taken the magnitude and composition of the volcanic emissions may have varied significantly. This cannot be reproduced in the model.
- We focussed on model output from the plume core. However, the varying wind velocity at the measurement sites mean that sampling will have been from varying parts of the plume.

As such it is not possible to conclude definitively from the comparison of the measurement and modelling studies the exact chemical processes that were occurring within the plume at the time of the measurement campaign. Nevertheless, the modelling study shows that the reactive bromine generated in the effective-source region is sufficient to cause appreciable O₃ depletion within the early plume, however the effect is stronger and more sustained when further reactive bromine can be generated by the bromine explosion.

The model runs which are the best fit for the near-crater O₃ and SO₂ measurements are not the same runs which best match the BrO/SO₂ columns measured further downwind. This is a discrepancy which highlights the need for further investigation into plume chemistry and the relationship between in-plume bromine, NO_x and humidity.

5 Conclusions

In this study of chemical evolution in the plumes of Mount Etna during a passively degassing phase we have confirmed O₃ depletion to occur less than a few minutes after emission. This extends the limited dataset regarding volcanic O₃ depletion and is the first dataset to date based on ground-based data to include simultaneous measurements of O₃ and a plume tracer. The depletion process is ongoing over this time

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period, and the data suggests it occurred at an approximately constant rate. For the Etna craters measured in late July 2012, this rate was found to be a depletion of approximately 10^{-4} molecules of O_3 per molecule of SO_2 (the inert plume tracer) per second.

Substantial depletion of O_3 was observed within minutes after emission, and occurred at very low humidities at which the heterogeneous processes of the bromine explosion would be significantly slowed. On the basis of this, an approximately constant rate of O_3 depletion (as a ratio of the inert tracer), and analysis of our modelling study we conclude that most of the very reactive halogens that caused the observed O_3 depletion within the 1–4 min old plume were not a product of chemical cycling in the plume once it had emerged from the crater, but rather generated in effective source regions near the vents in high-temperature processes that ceased shortly after emission, and/or very fast low-temperature chemical processes within the crater. This is in agreement with the thermodynamic modelling studies of Gerlach (2004), Martin et al. (2009), and von Glasow (2010) which predict oxidised halogens being produced by high-temperature effective source regions in volcanoes. The in situ measurements in this study were taken at distances less than 500 m from the vents. Measurements of BrO/SO_2 at such distances tend to be low compared to those measured further downwind (Bobrowski et al., 2007; Boichu et al., 2011). That substantial O_3 depletion can occur in such regions suggests these low levels of reactive bromine (and possibly chlorine) species that are generated within the crater are sufficient to cause the O_3 depletion observed in this study.

We have also shown that further downwind, contemporaneous spectroscopic observation of the plume shows BrO/SO_2 columns are within the typical range that has been observed within volcanic plumes. Our near-crater measurements are therefore likely to be typical for Mount Etna in its passively degassing phase.

Results from our modelling study suggest that a significant factor influencing the bromine-ozone chemistry in the very early plume is the presence or absence of volcanic NO_x and, if it is present, its source strength relative to that of Br. The modelling

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study shows that volcanic NO_x would be expected to significantly retard early O_3 depletion and therefore plume O_3 and Br data could be compared to model output to yield information on NO_x within a plume. The measured data from this campaign are insufficient to definitively ascertain whether or not volcanic NO_x generation is occurring but it appears unlikely to be the case as near-crater O_3 depletion was observed whilst volcanic NO_x emissions suppressed such O_3 depletion in the modelling study. The modelling study also shows how variations in humidity, and the consequent variations in heterogeneous chemistry, may impact the plume chemistry in detectable ways. A comparison of the results from our three different humidity/heterogeneous chemistry cases gives an indication as to the extents that O_3 depletion can be ascribed to reactive halogens generated in high-temperature processes within the crater, low-temperature processes within the crater, and low temperature processes further downwind.

Appendix A: Proof that $\Delta\text{O}_3/\text{SO}_2$ is a measure of chemical change only

The following is a proof that $\Delta A/\Delta B$ cannot be changed by physical plume mixing processes, and thus any change observed in the ratio is the result of chemical change only.

Starting with a generic plume dispersal equation for a change in concentration due to mixing (von Glasow et al., 2003):

$$\begin{aligned} \left. \frac{dc}{dt} \right|_{\text{mix}} &= -\frac{1}{A_p} \frac{A_p}{dt} (c - c_{\text{bg}}) \\ &= -\omega (c - c_{\text{bg}}) \end{aligned}$$

Where A_p is the cross-sectional area of the plume, $\omega = \omega(t)$ is the mixing parameter, c and c_{bg} are the concentration of the species in the plume and the background air, respectively.

Discretising:

$$\left. \frac{\delta c}{\delta t} \right|_{\text{mix}} = -\omega(c - c_{\text{bg}})$$

Let c_i be the concentration of the species at time t_i :

$$c_2 = c_1 + \frac{\delta c}{\delta t} \delta t = c_1 - \omega(c_1 - c_{\text{bg}}) \delta t$$

We define:

$$\Delta c_i = c_i - c_{\text{bg}}$$

Therefore:

$$\begin{aligned} \Delta c_2 &= c_1 - \omega(c_1 - c_{\text{bg}}) \delta t - c_{\text{bg}} \\ &= \Delta c_1 - \Delta c_1 \omega \delta t = \Delta c_1 (1 - \omega \delta t) \end{aligned}$$

Taking the ratio of gas A and gas B

$$\frac{\Delta c_2^A}{\Delta c_2^B} = \frac{\Delta c_1^A (1 - \omega \delta t)}{\Delta c_1^B (1 - \omega \delta t)} = \frac{\Delta c_1^A}{\Delta c_1^B}$$

In the volcanic case as in this study, $A = \text{O}_3$ and $B = \text{SO}_2$. The concentration of SO_2 outside of the plume is negligible in comparison to in-plume measurements, $\text{SO}_{2\text{bg}} \approx 0$ thus $\Delta \text{SO}_2 = \text{SO}_2$ and $\Delta \text{O}_3 / \Delta \text{SO}_2 = \Delta \text{O}_3 / \text{SO}_2$. Therefore:

$$\frac{\Delta \text{O}_{3,1}}{\text{SO}_{2,1}} = \frac{\Delta \text{O}_{3,2}}{\text{SO}_{2,2}}$$

Therefore, if no chemical change in O_3 occurs between time 1 and time 2, the ratio remains unchanged.

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**Table 1.** Table of reported depletions of O₃ in tropospheric volcanic plumes.

Volcano	Measurement platform	Reference
Augustine	airborne	Vance et al. (2010)
Erebus	airborne	Oppenheimer et al. (2010) Boichu et al. (2011)
Etna	ground-based	Vance et al. (2010)
Eyjafjallajökull	airborne	Vance et al. (2010) Schumann et al. (2011)
St. Helens	airborne	Hobbs et al. (1982)
Redoubt	airborne	Kelly et al. (2013)
Sakurajima	ground-based	Lee et al. (2005)

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**Table 2.** Instruments used at the near crater sites.

Name	Parameter	Precision	Sampling interval
Kestel 4500	Temperature	$\pm 1\text{ }^{\circ}\text{C}$	30 s
	Humidity	$\pm 3\%$ RH	
	Wind speed	$\pm 3\%$ or $\pm 1\text{ m s}^{-1}$ (whichever larger)	
MULTIGAS	SO ₂	$\pm 20\%$	2 s
2B Technologies Model 202	O ₃	$\pm 3\text{ nmol mol}^{-1}$	10 s

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**Table 3.** Overview of results from Etna summit measurement campaign.

Site	Upwind/Downwind	Plume Source	Distance to source/m	Date	Time (UTC)	Average Values				
						Temp./°C	Humidity/%	[SO ₂] / μmol mol ⁻¹	[O ₃] / nmol mol ⁻¹	Δ[O ₃] / nmol mol ⁻¹
up-24	Upwind	–	–	24 Jul 2012	09:10–09:35	3	49	not measured	86	–
d1-24	Downwind	Central	300	24 Jul 2012	10:05–11:30	7	64	not measured	69	–18
up-25	Upwind	–	–	25 Jul 2012	11:05–11:30	7	63	not measured	83	–
d1-25	Downwind	Central	440	25 Jul 2012	09:52–10:30	11	60	not measured	58	–25
up-27	Upwind	–	–	27 Jul 2012	08:41–09:02	9	59	0	77	–
d1-27	Downwind	NEC	150	27 Jul 2012	09:26–10:16	11	49	34	46	–31
d2-27	Downwind	NEC	380	27 Jul 2012	10:34–11:06	13	42	11	50	–26
d3-27	Downwind	NEC	240	27 Jul 2012	11:20–11:50	13	34	17	41	–35
up-30	Upwind	–	–	30 Jul 2012	09:12–09:34	12	< 5	0	73	–
d1-30	Downwind	Central	240	30 Jul 2012	10:05–10:43	16	6	26	40	–32
d2-30	Downwind	Central	300	30 Jul 2012	11:07–11:41	15	5	9	62	–11

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Table 4. Fractional composition (by volume) of pure volcanic volatiles of Mt. Etna in June 2012 (“low Br/S”) and in 2005 (“high Br/S”). These compositions were used to initialise the HSC calculations (for results see Supplement Table S1). “High Br/S” refers to the plume composition used in von Glasow (2010).

Species	low Br/S	high Br/S
H ₂ O	8.75×10^{-1}	8.57×10^{-1}
CO ₂	9.76×10^{-2}	9.56×10^{-2}
SO ₂	1.63×10^{-2}	2.86×10^{-2}
H ₂ S	8.14×10^{-4}	1.43×10^{-3}
H ₂	2.11×10^{-4}	3.72×10^{-4}
HF	2.96×10^{-3}	2.20×10^{-3}
HCl	6.87×10^{-3}	1.43×10^{-2}
HBr	9.99×10^{-6}	7.04×10^{-5}

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Table 5. Spectroscopic measurements of the Mount Etna plume. These data are also plotted on Fig. 10. R^2 refers to the correlation of BrO and SO₂ within the measurements.

Date	BrO/SO ₂	R^2	Plume age (min)
24 Jul 2012	0.9×10^4	0.94	21
24 Jul 2012	0.7×10^4	0.80	12
25 Jul 2012	1.2×10^4	0.66	28
25 Jul 2012	1.3×10^4	0.52	18
26 Jul 2012	1.1×10^4	0.64	30
26 Jul 2012	1.0×10^4	0.90	16
27 Jul 2012	1.2×10^4	0.48	12
28 Jul 2012	0.8×10^4	0.47	15
28 Jul 2012	0.9×10^4	0.50	11
31 Jul 2012	0.6×10^4	0.72	17
2 Aug 2012	1.0×10^4	0.48	8

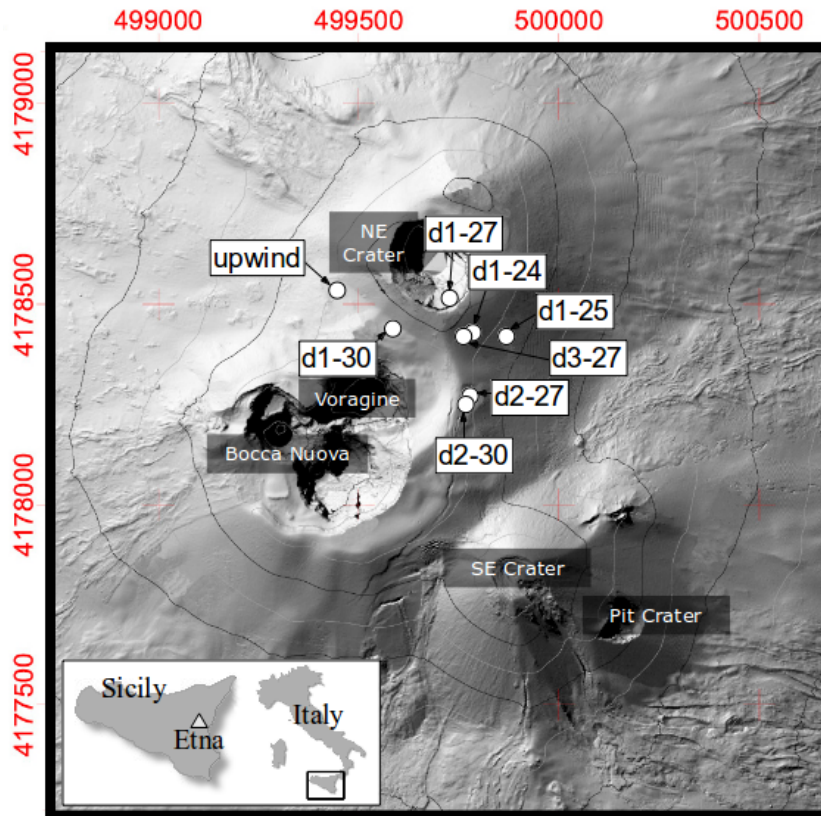


Figure 1. Map of the sampling sites and summit craters. Terrain from Neri et al. (2009). Coordinates are UTM Easting/Northing.

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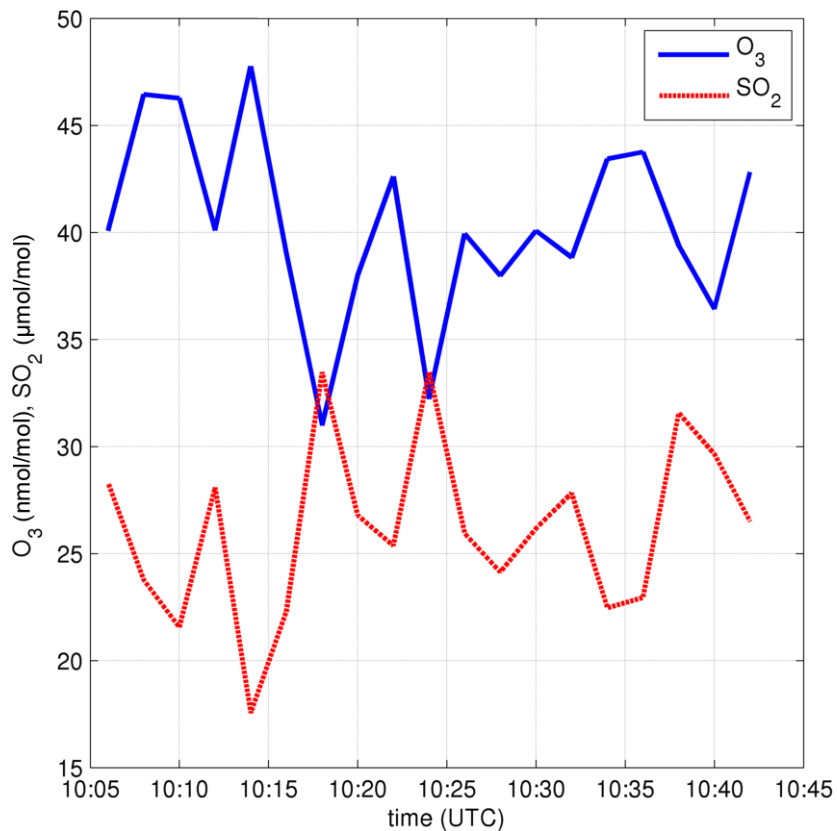


Figure 2. An example time series of measurements: O₃ and SO₂ mixing ratios measured in the plume at site d1-27. Data have been averaged into 120 s bins as described in the text.

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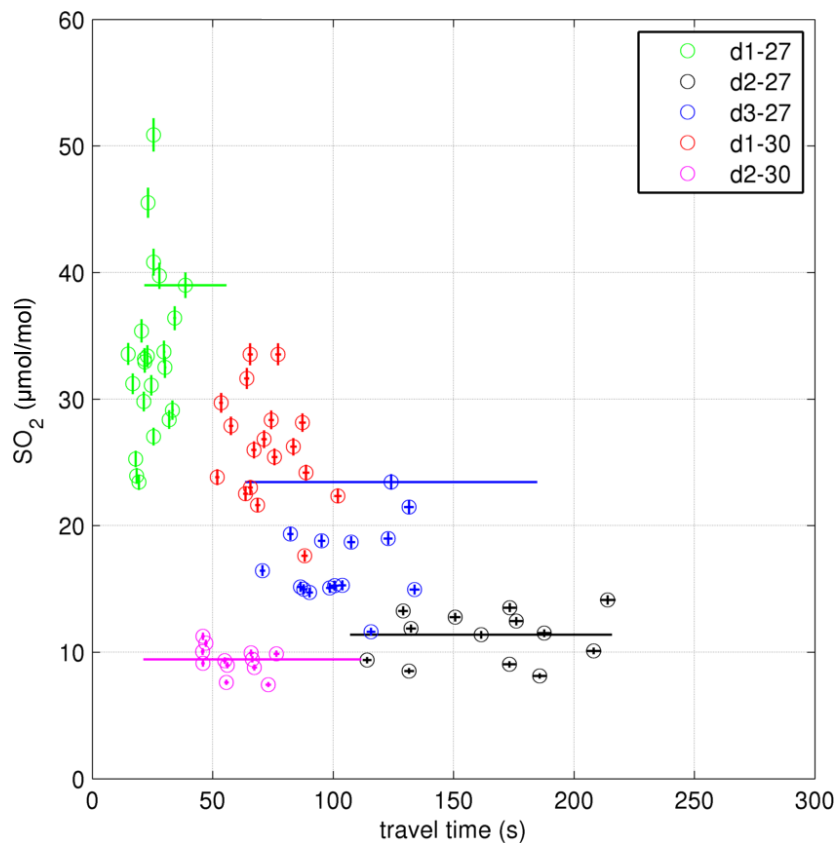


Figure 3. SO₂ mixing ratios against calculated processing time at the in-plume measurement sites. Error bars are one standard deviation, accounting for both variance in the values over the 120 s of each bin and known errors of the instruments.

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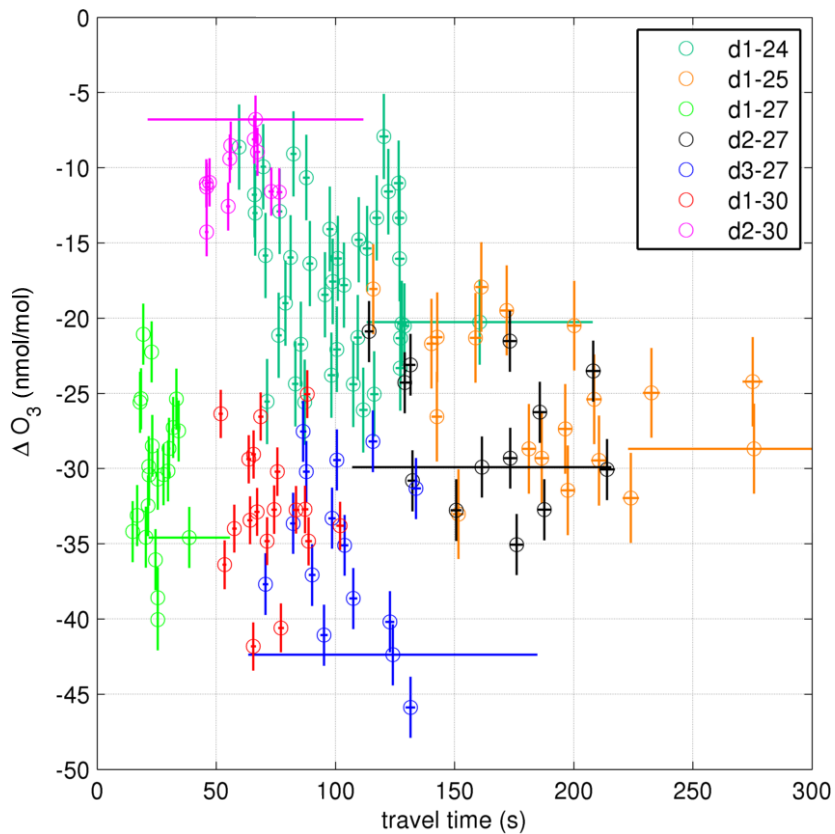


Figure 4. ΔO_3 against calculated processing time at the in-plume measurement sites. Error bars are one standard deviation, accounting for both variance in the values over the 120 s of each bin and known errors of the instruments.

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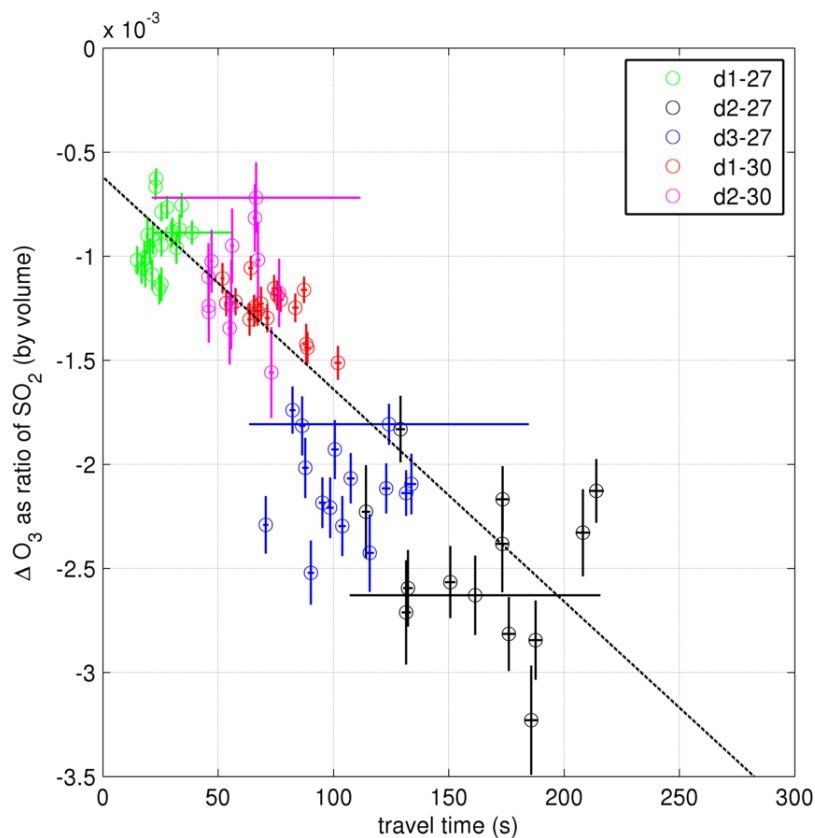


Figure 5. $\Delta O_3/SO_2$ against calculated processing time at the in-plume measurement sites. The gradient of the linear line of best fit is $-(1.02 \pm 0.07) \times 10^{-5} \text{ s}^{-1}$ and the y intercept is $(-6.2 \pm 0.5) \times 10^{-4}$. Error bars are one standard deviation, accounting for both variance in the values over the 120 s of each bin and known errors of the instruments.

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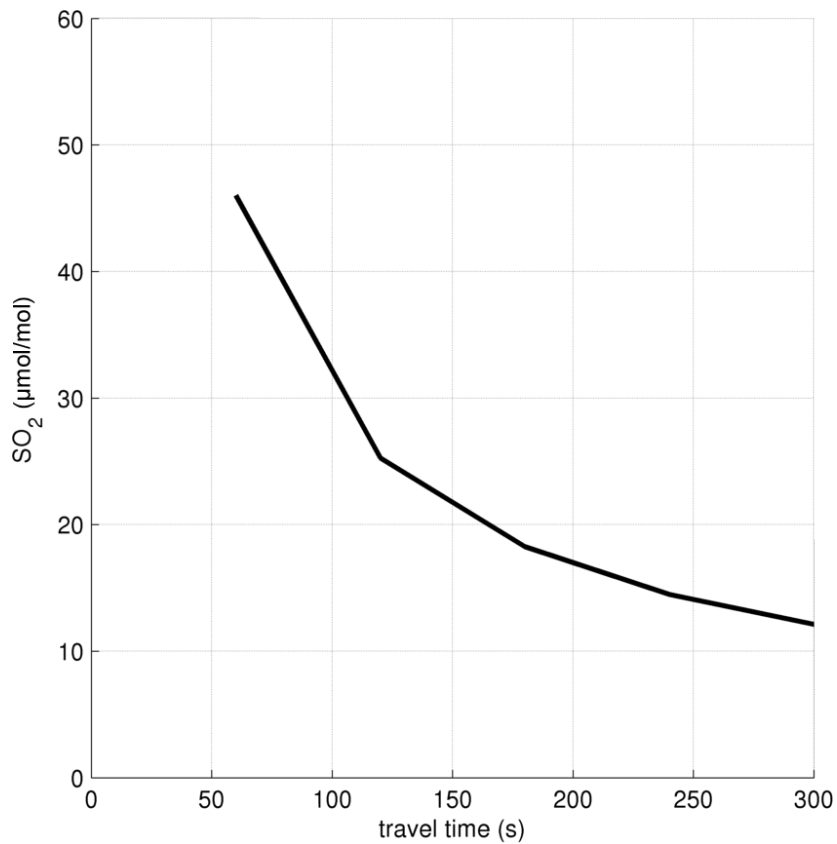


Figure 6. Modelled SO₂ mixing ratio in the plume core (“low Br/S” initialisation).

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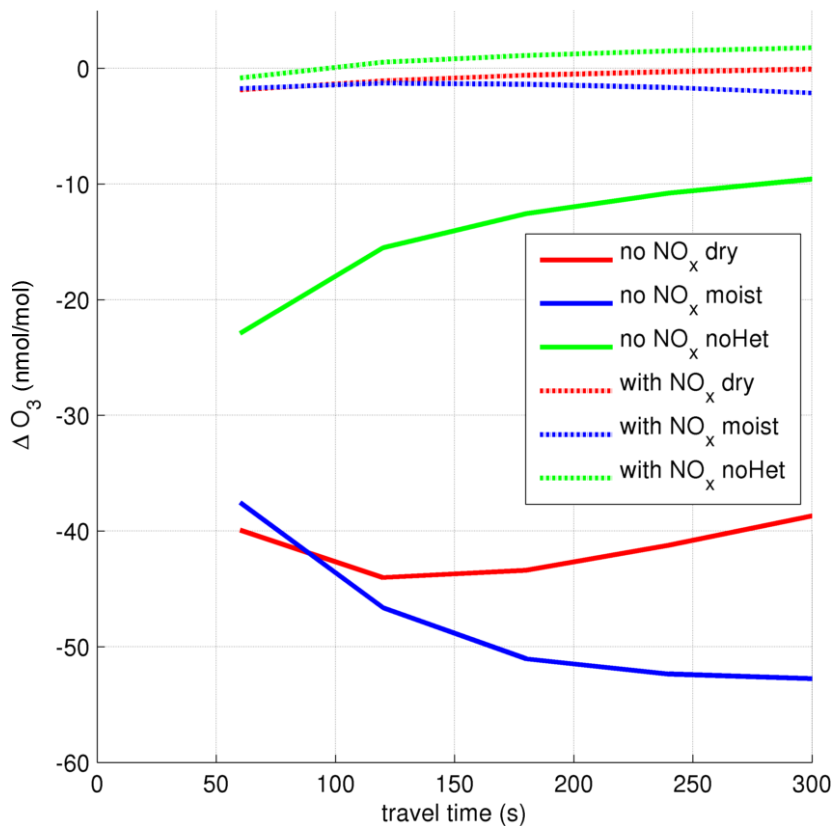


Figure 7. Evolution of ΔO_3 in the core of the plume for the six model scenarios discussed in the text (“low Br/S” initialisation).



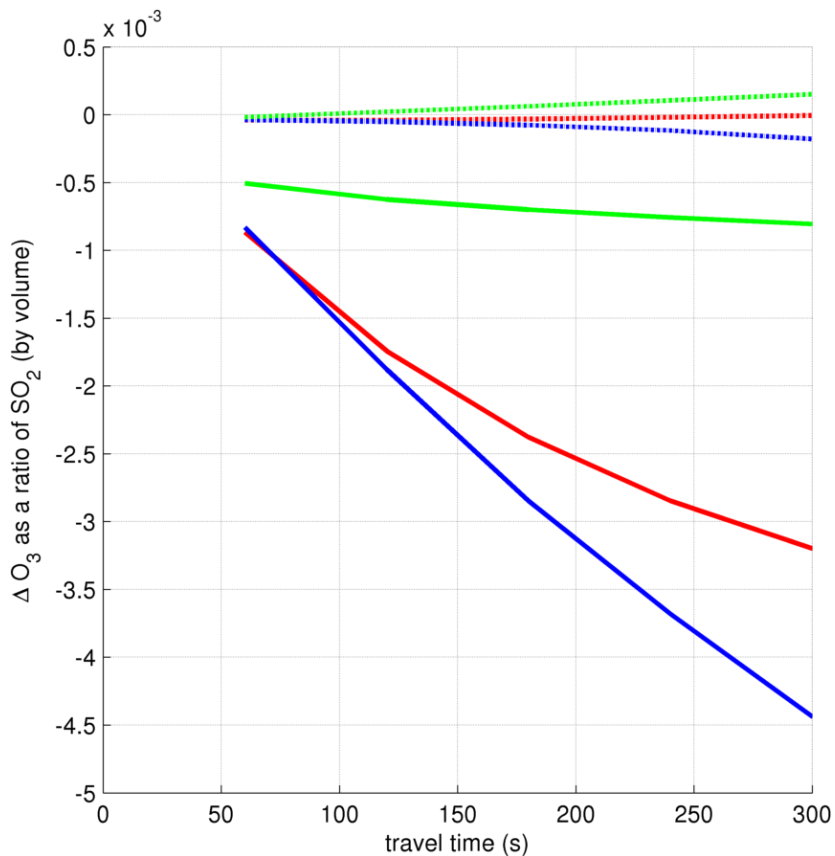


Figure 8. Evolution of $\Delta O_3/SO_2$ in the core of the plume for the six model scenarios discussed in the text (“low Br/S” initialisation). The colour code is the same as in Fig. 7.

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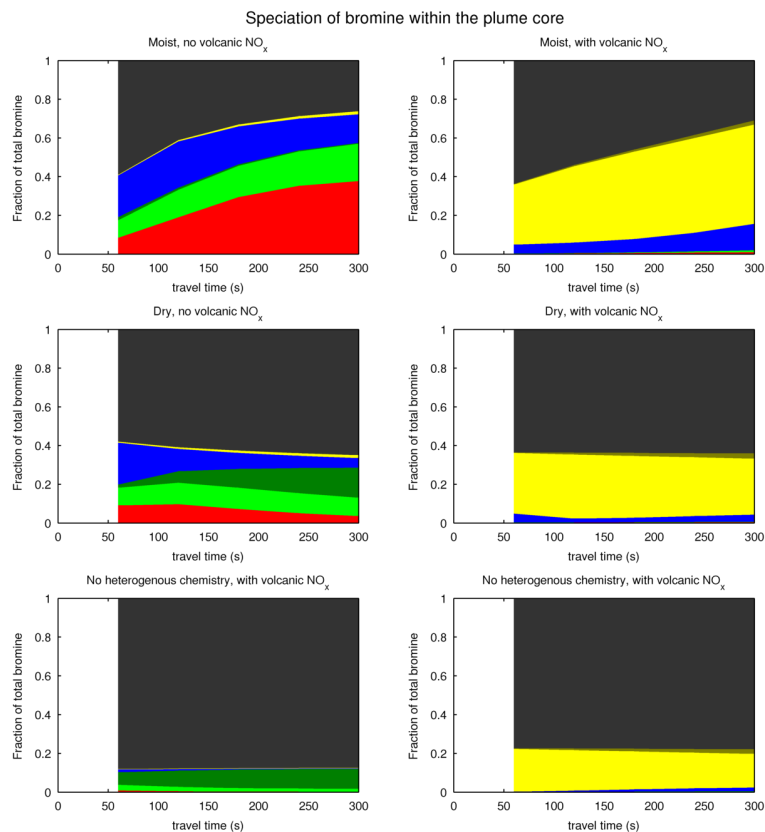


Figure 9. Speciation of bromine for the six model scenarios discussed in the text (“low Br/S” initialisation). Red – Br; Light Green – BrO; Dark Green – HOBr; Blue – Br_2 ; Yellow – BrNO_2 ; Grey – HBr.

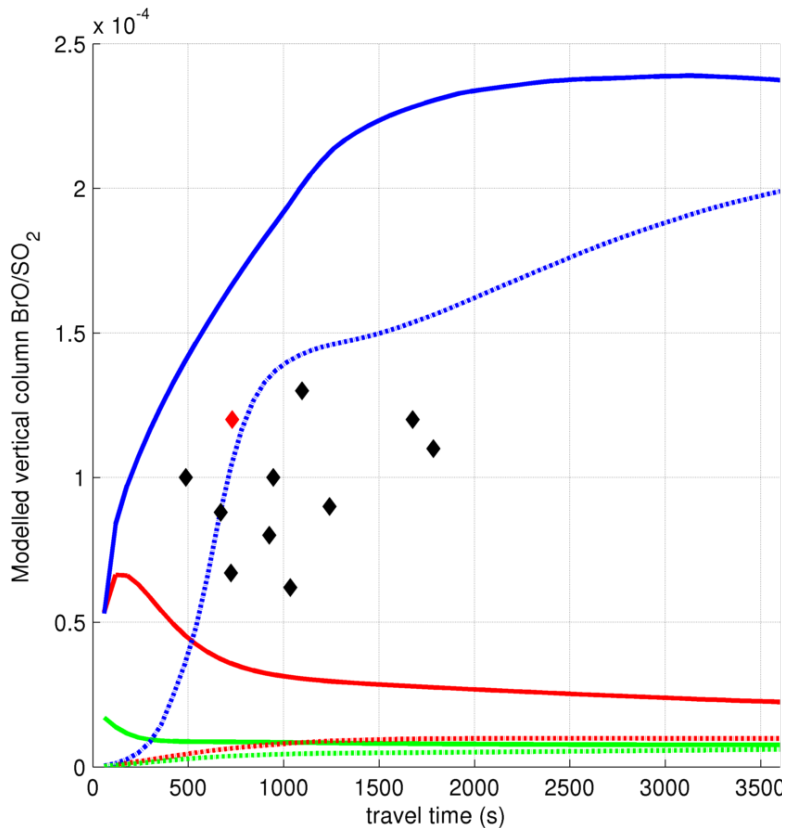


Figure 10. Evolution of vertical column BrO/SO₂ for the six model scenarios discussed in the text (“low Br/S” initialisation). The colour code is the same as in Fig. 7. The black diamonds represent the spectroscopic measurements listed in Table 5, the red diamond represents the 27 July 2012 measurement contemporaneous with near-crater measurements of both O₃ and SO₂.

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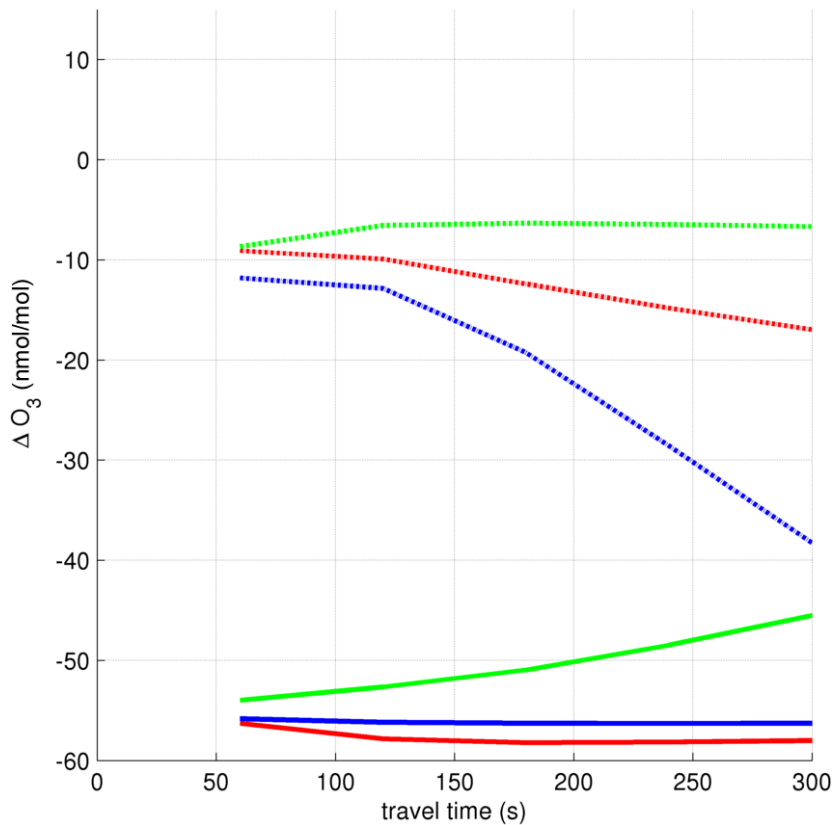


Figure 11. Evolution of ΔO_3 in the core of the plume for the six model scenarios discussed in the text using the “high Br/S” initialisation. The colour code is the same as in Fig. 7.

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