MAX-DOAS measurements of OClO and BrO profiles in the volcanic plume of Mt. Etna, Italy (09/2012, 09/2013)

Implications on the chemistry of reactive halogens in volcanic plumes

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I Motivation and Introduction

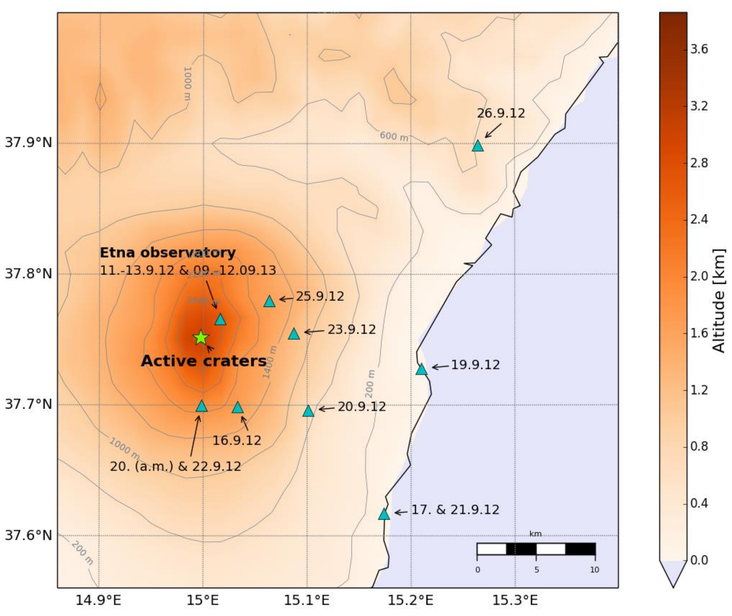
The spatial and temporal evolution of the oxidised halogen compounds OClO and BrO was studied in the volcanic plume of Mt. Etna (Italy) using the MAX-DOAS method[i,11]. In volcanic plumes, OClO is most likely formed via the reaction of BrO with ClO. The latter two species are formed from the initially emitted hydrogen halides HCl and HBr[1,3]. The formation process of BrO is well studied and most likely driven by a reaction mechanism often referred to as "bromine explosion" including a net destruction of atmospheric O_3.[2] The formation of ClO (from HCl) is rather less effective and the detailed mechanism of chlorine activation in volcanic plumes however, only poorly understood[9].

Slant column densities (SCDs[ii]) of BrO and OClO were measured as well as SO_2-SCDs using a standard DOAS fitting routine[4]. The chemical evolution of BrO and OClO was studied analyzing the $OClO/SO_2$ and BrO/SO_2 ratios at different times of the day (temporal variations) and different positions (spatial variations) in the plume. Here, SO_2 was treated as conservative plume tracer having a comparatively long lifetime of hours up to days[10]. We present results of MAX-DOAS measurements performed in September 2012 and September 2013.

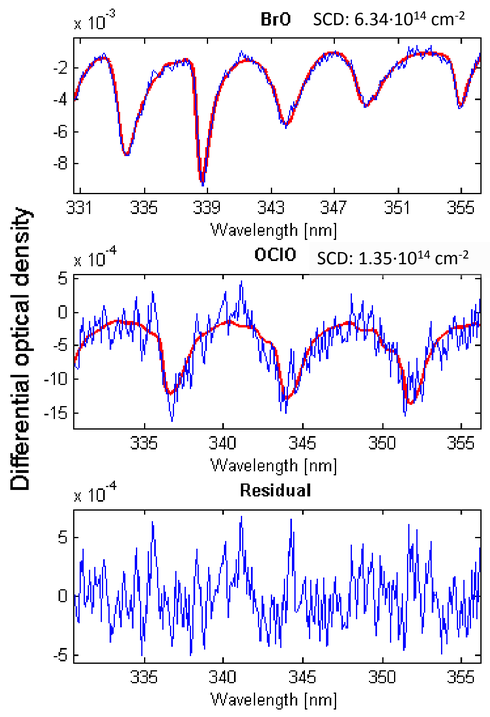
[i] Multi-AXis-Differential-Optical-Absorption-Spectroscopy

[ii] Integral of the concentration profile of measured species along the optical path of the analysed light

II Location and DOAS fit example



Measurement locations

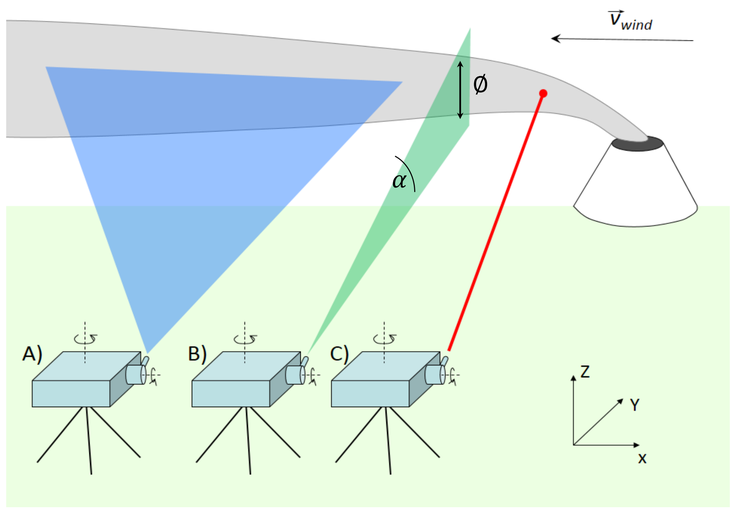


Exemplary DOAS fit result of OClO and BrO

Additionally included absorbers: SO_2, O_3, O_4,CH_2O,NO_2 and two Ring spectra[9]

III Measurement Scenarios

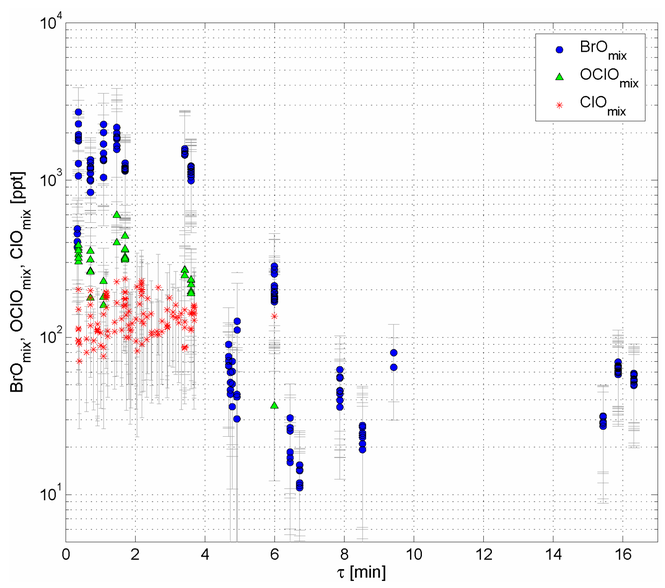
- **A) Plume Evolution Scan:** Study the chemical variability as a function of the plume age τ.
- **B) Plume Cross Section Scan:** i) Study variations between plume center and edge. ii) Estimation of plume diameter (Ø)
- **C) Point measurement:** Analysis of temporal variations



IV Mixing ratios of BrO, OClO and ClO

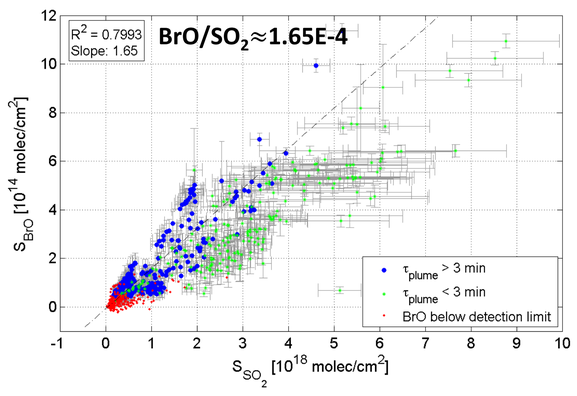
ClO concentrations were estimated from the BrO and OClO SCDs assuming chemical equilibrium between formation and destruction of OClO.

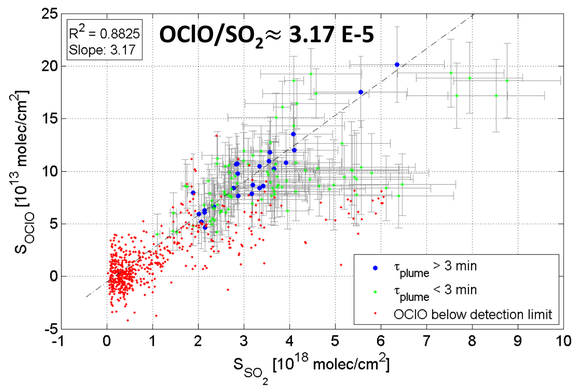
Mean BrO and OClO concentrations in the plume were estimated from the retrieved SCDs assuming a circular plume cross section (see section III).



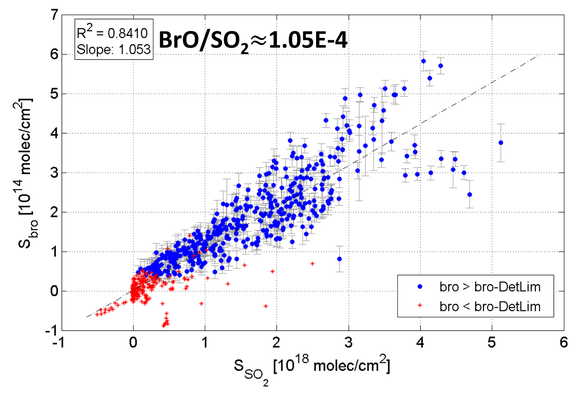
V Average BrO/SO_2 and $OClO/SO_2$ ratios

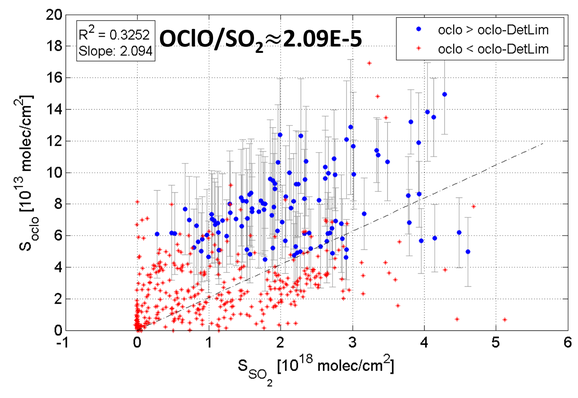
Data 2012 (11-26/09/2012)



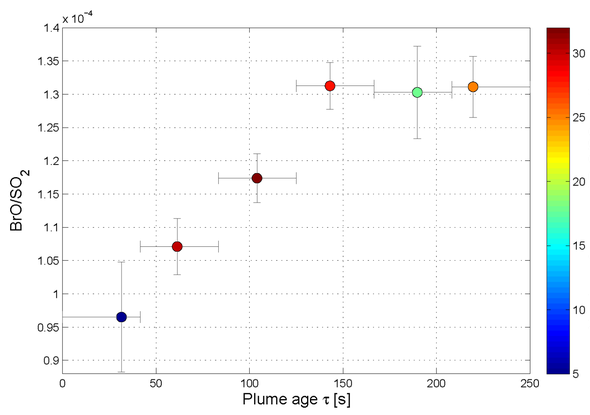


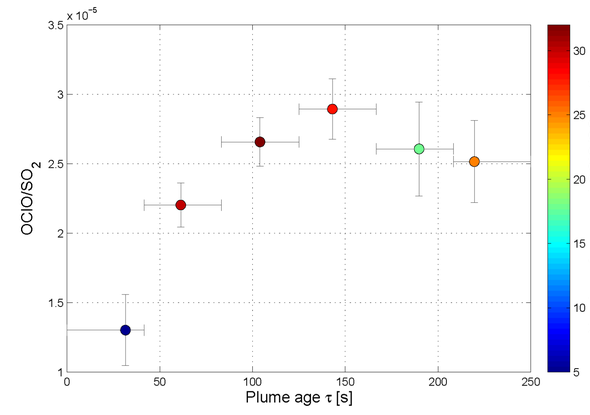
First Results 2013 (Etna observatory, 09-12/09/2013)





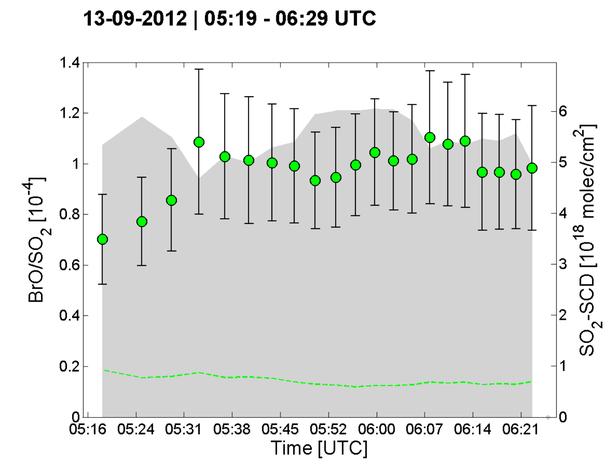
VI The young plume formation of BrO and OClO

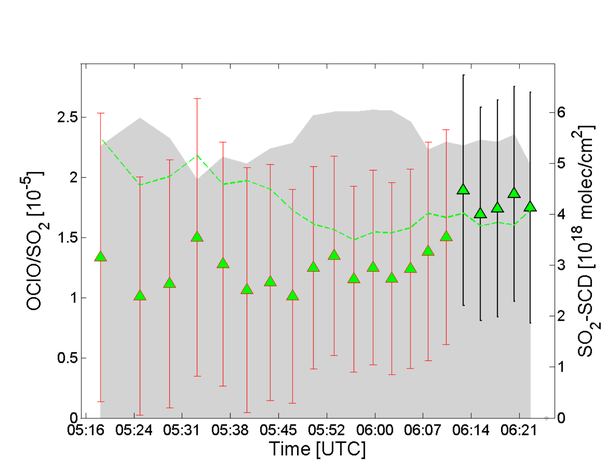




Both BrO/SO_2 and $OClO/SO_2$ showed a marked increase in the first two minutes downwind and a levelling off at larger plume ages. This observation was associated to the formation of these species from the initially emitted species (HCl and HBr). The average formation duration (τ_0) was found to be 142s for both species.

VII Early morning formation of BrO (and OClO)





A point measurement (see section II), performed in the early morning (05:20 - 06:20 UTC, sunrise: 04:40 UTC, Fig. 4) showed an increasing BrO/SO_2-ratio between 05:20 and 05:30 stabilising afterwards. The corresponding $OClO/SO_2$ ratios show indications of a similar trend stabilising about 40 min later (around 06:10 UTC). We associated this observation to the photochemistry involved in the formation of oxidised halogens (see section I).

VIII Chlorine atom concentrations and potential of CH_4 depletion in the plume

Cl atom concentrations in the plume could be estimated from the rate of increase of OClO and BrO in the young plume (i.e. the formation duration (τ_0) of both species in the young plume, see section VI). Together with the determined ClO and OClO concentrations (section IV), these values were used to estimate Cl atom concentrations using the following formula: $[Cl] = \frac{[ClO]+[OClO]}{\tau_0 \times [O_3] \times k_{Cl+O_3}}$ with $k_{Cl+O_3} = 1.2 \times 10^{-11} cm^3 s^{-1}$[12]. We found values between 5.1 × 10^6cm^{-3} (at 40 ppb O_3) and 2.1 × 10^8cm^{-3} (at 1 ppb O_3). Based on that, a potential – chlorine induced – depletion of tropospheric methane (CH_4) in the plume was investigated ($\tau_{CH_4} = \frac{1}{[Cl] \times k_{Cl+CH_4}}, k_{Cl+CH_4} = 1.0 \times 10^{-13} cm^3 s^{-1}$)[12]. We found CH_4 lifetimes between 13 h (at 1 ppb O3) and 23 days (at 40 ppb O3), thus a potential depletion of atmospheric CH_4 was assessed to be negligible for the plume of Mt. Etna during the prevailing plume conditions in September 2012.

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