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Airborne I-DOAS measurements at Mt. Etna: BrO and OClO evolution in the plume

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ABSTRACT

Spatial distributions of bromine monoxide (BrO), chlorine dioxide (OClO) and sulfur dioxide (SO_2) were determined in the volcanic emissions of Mt. Etna on 8th and 9th of July 2011 by Airborne Imaging Differential Optical Absorption Spectroscopy (AI-DOAS). Slant column densities (SCDs in units of molec/cm^2) of up to 4.2×10^{14} for BrO, 1.5×10^{14} for OClO and 4.6×10^{18} for SO_2 were detected. Assuming SO_2 to be a stable tracer to overcome dilution effects, measurements of BrO/SO_2 and OClO/SO_2 ratios from distances of 1–19 km to the summit crater region were used to investigate the evolution of BrO and OClO within corresponding plume ages of 2–34 min. Along the centerline of the plume relatively constant BrO/SO_2 ratios of 1.4×10^{-4} and 2.0×10^{-4} were detected on 8th and 9th of July 2011, respectively. Furthermore the BrO/SO_2 ratio was investigated along several cross-sections of the volcanic plume. On both days significant increases by a factor of 2–3 in the BrO/SO_2 ratio from the center to the edge of the plume were seen. From simultaneous measurements of BrO and OClO the mixing ratios of ClO could be inferred to range from about 80 to 300 ppt. In addition, decreases in the BrO/SO_2 ratio with time could be observed by measurements three to four hours before the culmination of a paroxysm at Mt. Etna on 9th July 2011.

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1. Introduction

Shape and position of emission plumes can often easily be identified by eye due to their high aerosol content (dust or condensing water vapor). However, not always sufficient condensation takes place to actually make a plume visible and the distribution of gases in the plume may also differ from the aerosol distribution. Thus, visual observations can merely give a very limited insight to the chemical processes in volcanic emissions. The detailed understanding of these processes requires a spatially resolved measurement of the involved gases, but for gases other than SO_2 only a limited number of investigations showing the spatial distributions of emitted or secondary formed volcanic gases have been carried out so far (e. g. Bobrowski et al., 2007; Louban et al., 2009; Lee et al., 2010; Stremme et al., 2012). In this paper, we describe airborne imaging UV-spectroscopic measurements using scattered sunlight as a light source. Differential optical absorption spectroscopy (DOAS; Platt and Stutz, 2008) is used to evaluate the data. DOAS is based on the Beer–Lambert law and uses the characteristic narrow band absorption of electromagnetic radiation by gas molecules along the light path in the open atmosphere. The DOAS technique relies on high resolution (typ. <1 nm) spectral information within a wavelength interval of several tens of nanometer. The Imaging DOAS (I-DOAS) technique, in contrast to the SO_2 camera (e. g. Mori and Burton, 2006; Bluth et al., 2007), permits the retrieval of two-dimensional distributions of several trace gases simultaneously in addition to SO_2. Since SO_2 has a typical lifetime of several days in the atmosphere (e. g. Oppenheimer et al., 1998; von Glasow et al., 2009), it can be used as a tracer for the dilution of volcanic gases. It therefore allows, for example, to study the evolution of reactive species like BrO and OClO in the volcanic emissions, where the observed plume ages are usually of the order of minutes to hours.

The I-DOAS technique combines the advantages of conventional DOAS, with its high spectral information, and the SO_2-camera, which offers a good spatial resolution but little spectral information. Drawbacks of the I-DOAS technique in comparison to the SO_2 camera might be the higher complexity of hard and software as well as the fact that it takes longer to acquire a full image of the plume. Imaging of an object generally produces a two-dimensional dataset of spatial information, i. e. each picture element of an image (pixel) corresponds to a defined solid angle of space. In the case of I-DOAS measurements a third dimension of data is added: the high resolved spectral information within each pixel. Therefore, imaging spectroscopic instruments require both, imaging and dispersive optical components. A detailed characterization of the I-DOAS principle is given in e. g. Lohberger et al. (2004) and General et al. (2014). The latter also includes a detailed description of the here

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applied I-DOAS instrument, thus only a brief technical description is given in the following (Section 3). In this work we are focusing on results obtained from measurements at the Mt. Etna volcano in July 2011 to investigate in particular the chemical evolution of BrO and OClO in the plume.

2. BrO and OClO chemistry in volcanic plumes

Volcanoes release high amounts of water vapor, followed by CO_2, SO_2, H_2S and HCl (e. g. Carroll and Holloway, 1994). Further emitted compounds in much lower abundances include CS_2, COS, CO, HF, HBr and a number of volatile metal chlorides as well as heavy metals like mercury (Buat-Ménard and Arnold, 1978; Carroll and Holloway, 1994; Hinkley et al., 1999). Beside gases also aerosols are highly abundant in volcanic plumes and due to the high amount of water vapor often condensation takes place, providing even more surface for heterogeneous reactions. Volcanic halogen emissions are thought to be degassed predominantly as hydrogen halides (see e. g. Carroll and Holloway, 1994), which should be thermodynamically favored over other halogen species as equilibrium model data suggest (e. g. Gerlach, 2004). However, measurements and laboratory kinetic data show that the transformation – at least of HBr to other bromine molecules – can be relatively fast. Already at the crater rim volcanic gases are usually diluted with the surrounding atmosphere by factors of more than 1000. As a result of model studies, von Glasow (2010) found that the contribution of HBr to total bromine can already fall below 50% at plume ages <2 min.

The BrO/SO_2 ratio in plumes generally increases with distance from the emission source (e. g. Oppenheimer et al., 2006; Bobrowski et al., 2007; von Glasow, 2010), indicating a chemical production of BrO in the volcanic plume. New enhanced data sets (e. g. Vogel, 2011; Bobrowski and Giuffrida, 2012; Platt and Bobrowski, submitted for publication) show that after an initial increase the BrO/SO_2 ratio reaches a quasi-equilibrium state for a certain – still to be determined – period of time.

2.1. Bromine chemistry

The formation of BrO in volcanic plumes is currently explained by an autocatalytic photo-chemical reaction cycle (the so-called "bromine explosion" mechanism, see Platt and Lehrer (1997)), which was first proposed for polar regions and involves multi-phase chemistry. An essential step for the "bromine explosion" mechanism is the uptake of gas phase HOBr and HBr into aerosol particles:

$$HOBr_{(g)} \rightarrow HOBr_{(aq)} \quad (1a)$$

$$HBr_{(g)} \rightarrow HBr_{(aq)} \quad (1b)$$

$$HBr_{(g)} \rightarrow Br^-_{(aq)} + H^+_{(aq)} \quad (1c)$$

Followed by the acid catalyzed reaction (2) in the aqueous phase:

$$HOBr_{(g)} + Br^-_{(aq)} + H^+_{(aq)} \rightarrow Br_{2(g)} + H_2O. \quad (2)$$

As soon as Br_2 is released to the gas phase, it is rapidly photolyzed during the day:

$$Br_2 + h\upsilon \rightarrow 2Br. \quad (3)$$

The thus generated Br radicals react with O_3, forming BrO:

$$Br + O_3 \rightarrow BrO + O_2. \quad (4)$$

The resulting high amounts of BrO in the plume can lead to rapid ozone destruction via self-reaction:

$$BrO + BrO \rightarrow 2Br + O_2 \quad (5a)$$

$$BrO + BrO \rightarrow Br_2 + O_2. \quad (5b)$$

The key ozone destruction steps in the reaction scheme above are reactions (5a), (5b) and (4). Moreover, the reaction of BrO with hydrogen peroxy radicals leads to the formation of HOBr:

$$BrO + HO_2 \rightarrow HOBr + O_2 \quad (6)$$

which can then react according to reactions (1a), (2), (3) and (4), closing the bromine explosion cycle. The atmospheric oxidants O_3 and HO_2 are required for the above described chemical mechanism. Thermodynamical model studies show that HO_2 may additionally be formed in the effective source region (Bobrowski et al., 2007) with mixing ratios >10 ppb (e. g. Gerlach, 2004; von Glasow, 2010). Because O_3 is neither emitted from the volcano nor produced in the plume, it will be mixed into the plume while it expands into the ambient atmosphere. Therefore, oxidation of halogenides should be more effective at the plume edge, resulting in a BrO enhancement in the exteriors of the plume. This has already been shown by Bobrowski et al. (2007) and Louban et al. (2009), and is again observed in the measurements presented in this article.

2.2. Chlorine chemistry

The chemistry of chlorine is quite different from that of bromine in some important regards: no "chlorine explosion" is expected nor could it be observed in the field as the reactions (2), (5a) and (5b) are slower for chlorine than for bromine and as chlorine reacts with hydrocarbons like methane, which is highly abundant in the atmosphere. Most of the emitted HCl either stays as HCl in the gas phase or is taken up into aerosol and cloud particles. This difference in the reactivity of hydrogen halides also leads to modeled decreases in HBr/SO_2 downwind of volcanoes, whereas the HCl/SO_2 ratio seems to stay fairly constant (e. g. Horrocks et al., 2003; Voigt et al., 2013). On the other hand, changes in HCl/SO_2 ratios were already detected by Burton et al. (2001) and Mather et al. (2003) in condensing plumes, but might be only the consequence of extreme conditions (RH >80%, Martin et al. (2012)).

To date, only few investigations of chlorine oxides (ClO, OClO) and Cl_2 have been carried out at volcanoes — e. g. at Mt. Sakurajima, Japan (Lee et al., 2005), at Mt. Etna, Italy (Bobrowski et al., 2007; Gliß, 2013) and at the Tolbachik volcanic complex, Russia (Zelenski and Taran, 2012). The measurements presented in this article are thus one of the first to show the spatially resolved distribution of OClO within volcanic emissions. The predominant source of OClO in volcanic plumes is thought to be the following reaction:

$$BrO + ClO \rightarrow OClO + Br. \quad (7)$$

Reaction (7) is much faster than the further possible production of OClO from ClO and ozone or from the ClO self reaction (Sander et al., 2006). However, reaction (7) has two further pathways:

$$BrO + ClO \rightarrow ClOO + Br \quad (8a)$$

$$BrO + ClO \rightarrow BrCl + O_2. \quad (8b)$$

The distribution of the reaction products thereby depends on the temperature, showing similar reaction rates for reactions (7) and (8a) at 300 K and a much lower reaction rate for reaction (8b). During daytime the main sink for OClO is its photolytic destruction:

$$OClO + h\upsilon \rightarrow ClO + O. \quad (9)$$

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