Geophysical Research Abstracts
Vol. 20, EGU2018-8882-1, 2018
EGU General Assembly 2018

Bromine chemistry in the volcanic plume of Nevado del Ruiz, Colombia

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Halogens (X) released into the atmosphere by volcanoes are thought to be predominantly hydrogen halides (HX), which are thermodynamically favoured over other halogen species. However, once the plume begins to mix with ambient air, HX is converted to more reactive halogen species such as halogen oxides (XO, OXO). Halogen oxides, in particular bromine monoxide (BrO), can relatively easily be measured by remote sensing with Differential Optical Absorption Spectroscopy (DOAS).
Today, BrO together with SO_2, can be retrieved from spectra recorded by autonomous spectrometers installed around many volcanoes, resulting in long-term time series of BrO/SO_2. Because gas ratios often are related to volcanic activity (e.g. magma degassing depth), variations in BrO/SO_2 have been suggested to be an indicator for volcanic activity changes.
Current model and field studies point to BrO formation due to photochemical and multiphase reactions involving gas and particle phase chemistry of volcanic emissions mixed with the surrounding atmosphere. This means, that the BrO amount depends not only on volcanic activity but also on the plume age (formation time), as well as on the spatial position within the plume (e.g. through mixing with ambient atmosphere). For the interpretation of BrO data regarding volcanic activity, it is therefore essential to have a detailed understanding of the ongoing plume chemistry in order to infer total bromine emissions.
From October 10th to 13th 2017, we performed mobile DOAS measurements at the vicinity of Nevado del Ruiz volcano in Colombia, which is presently characterized by very strong gas emissions. Note that SO_2 is considered to be chemically inert in the atmosphere on the time scales of our observations. Our results confirm the expected increase of the BrO/SO_2 ratio in young plumes as a function of plume age, as well as a BrO/SO_2 decrease towards the centre of the plume. The latter observation is very pronounced for measurements close to the volcano (i.e. in younger plumes, a difference between centre and edge of the plume of ca. 20% - 40% is found), while hardly observable in older plumes. This might be induced by mixing and an indication of the importance of contributions from the ambient atmosphere (e.g. ozone). Besides comparing our data with existing model studies and former, similar datasets at other volcanoes, we propose improvements in the measurement strategy and technique (e.g. imaging techniques).