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Bromine Speciation in volcanic emissions of Guagua Pichincha and Sierra Negra (Galapagos), Ecuador

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Since volcanic emissions are driven by subsurface processes, their relative and total composition gives insights in volcanoes' interior. During the 13^{th} Field Workshop of the Commission on the Chemistry of Volcanic Gases (CCVG) in Ecuador alkaline traps and diffusion denuders were collected from two volcanoes, both providing fumarolic degassing caused by different geological settings. On 1^{st} October 2017 close to the active dome inside the caldera and slightly below the caldera rim of Guagua Pichincha, Ecuador (subduction) measurements were conducted under non–ideal meteorological conditions (very high humidity). On 6^{th} October 2017 fumarolic gas emissions were sampled from the upper fumarole of Volcan de Azufre in the crater of Sierra Negra volcano, Galapagos (hotspot). Within the large amounts of gas emissions, volcanoes release significant amounts of halogens into the atmosphere. Model and field studies presume HBr as major initially emitted bromine species and assume a rapid conversion due to photochemical and multiphase reactions involving the gas and particle phase of volcanic emissions (that might differ with geological settings) mixed with the surrounding atmosphere. The understanding of chemical reactions inside volcanic emissions is essential in order to use observed parameters for the calculation of the primary emitted gases, which might be used as a monitoring parameter. Lately, decreasing BrO/SO_2-ratios, measured by UV spectrometers, have been interpreted in connection with increasing volcanic activity prior to eruptions.

With the aim of enlightening bromine speciation in volcanic emissions, *in situ* methods have been developed that take advantage of specific properties of the species of interest. Total bromine emissions are thought to be represented by acidic bromine species, which can be determined by alkaline traps. Gas diffusion denuder retain selected gaseous species dependent on derivatization with organic coatings. Here, two coatings, 1,3,5-Trimethoxybenzene and 5,6-Epoxy-5,6-dihydro-1,10-phenanthroline, were applied for the analysis of reactive bromine species (Br_2, BrCl, HOBr) and hydrogen bromide (HBr), respectively. Alkaline samples resulted in $9x10^{-4}$ in the crater and $12x10^{-4}$ at the rim of Guagua Pichincha for total bromine to sulfur ratios and $3x10^{-4}$ in Sierra Negra's emissions. The detailed bromine speciation received by denuder samples will be compared between the two volcanic systems and discussed.