

EGU24-16447, updated on 18 Jul 2024

<https://doi.org/10.5194/egusphere-egu24-16447>

EGU General Assembly 2024

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## Assessment of the potential of high temperature halogen chemistry in volcanic plumes for the oxidation of mercury

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Volcanoes contribute as a natural source to the global emission of mercury into the atmosphere. The emission of mercury takes place mainly in the gas phase, predominately as elemental mercury. But, several observations show different degrees of mercury oxidation in early-stage volcanic plumes. During the first seconds of volcanic plume evolution, hot magmatic gases mix with the atmosphere and the in-mixture of atmospheric oxygen triggers fast oxidation processes. These change the chemical composition of the volcanic plume drastically and lead to the conversion of hydrogen halides (e.g. hydrogen bromide and hydrogen chloride) into reactive halogen species. These reactive halogen species are well known to interact with mercury and promote the oxidation of elemental mercury towards divalent gaseous mercury.

We present model studies investigating the first seconds of the evolution of a volcanic plume assessing the degree of mercury oxidation through reactive halogen chemistry. We utilize a new chemical box model that simulates chemical kinetics alongside cooling and dilution of the plume. The model is based on a chemical combustion mechanism coupled to an atmospheric chemistry mechanism, including sub-mechanisms for reactive halogens and mercury. It shows that high-temperature halogen chemistry can potentially cause an oxidation of mercury in the percent range depending on emission temperature and mixing scenario. We compare these model calculations to mercury speciation measurements performed in near-source plumes at Mt Etna and Vulcano island in August/September 2023, where we find a relative abundance of divalent mercury of 5% and 37%, respectively. As well as showing evidence for rapid mercury oxidation, the field-observations at Vulcano indicate the potential for subsequent plume processes to cause mercury reduction.

Model simulations in combination with field-measurements illustrate a complex behavior of volcanic mercury and halogens going from the hot emission to the cooled plume.

