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Elemental and isotopic budget of volcanic mercury (Hg) at Vulcano Island (Italy)

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The most recent global 3D model of atmospheric mercury (GEOS-Chem), including a coupled ocean model, neglects volcanic Hg emissions due to uncertainties therein. Volcanic Hg degassing is estimated to be in the range 112-700 Mg.yr^{-1}, and may thus represent 12-78% of natural emissions and approximately 4-23% of total global emissions. There is therefore a continuing need for precise estimates of the volcanic Hg budget. Vulcano (Aeolian Islands, Italy) is a passively degassing hydrovolcanic complex which is often used as a natural laboratory for methodological developments. Volcanic fluids have been sampled to explore the use of Hg stable isotopes to address volcanic Hg budget, signature and species transformation.

Fumarolic gases with outlet temperatures in the range 272-460˚C were condensed for total Hg ($Hg_{(t)}$) analysis. Particulate ($Hg_{(p)}$) and gaseous elemental mercury ($Hg^0_{(g)}$), were sampled in the plume using glass fibre filters and gold traps respectively. The calculated $Hg_{(t)}$ fluxes based on plume $Hg_{(t)}/S_{(t)}$ ratios range from 2.0 to 3.6 kg.y^{-1}and are consistent with published values [1,2]. Soils fluxes were also sampled using the Au-Hg amalgamation technique using a dynamic flux chamber. These fluxes are low and range from 0.03 to 0.45 ng.m^{-2}.h^{-1} at sites of relatively high soil CO_2 degassing.

Cold vapour – multi collector ICP-MS was used for all isotopic analysis. Hg isotopic compositions are expressed as δ^{202}Hg values relative to the NIST 3133 Hg standard in per mil. δ^{202}Hg values are slightly different between the collected gases of each fumarole. This allows deciphering two groups: fumarole FA (δ^{202}Hg = -0.26‰)

vs. F0 (δ^{202}Hg = -0.79‰), F5 (δ^{202}Hg = -1.09‰) and F11 (δ^{202}Hg = -0.79‰) (2SD uncertainties are ±0.23‰). Substantial fractionation was observed within the plume between $Hg_{(p)}$ (δ^{202}Hg = 0.11‰±0.18, 2SD) and residual Hg^0 (δ^{202}Hg = -1.74‰±0.36, 2SD). This suggests a gas-particle fractionation, already reported by our group for Zn in Merapi volcanic gases.

[1] Ferrara et al. (2000) The Science of the Total Environment, 115-121; [2] Aiuppa et al. (2007) Geophysical research Letters, vol. 34, L21307