



Mercury emissions and stable isotopic compositions at Vulcano Island (Italy)

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Mercury (Hg) is a heavy metal of great concern due to both its extreme mobility and biotoxicity. Many aspects of the biogeochemical cycle of Hg are still poorly known and substantial uncertainties affect estimations of Hg fluxes released by both human and volcanic activities. Volcanic Hg emissions are 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 volcano 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 signature and species transformations.

Fumarolic gases with outlet temperatures in the range 272-460°C were condensed using quartz tubes connected to an acetone cooler for total Hg (Hg_(t)) analysis. Particulate (Hg_(p)) and gaseous elemental mercury, (Hg⁰ or GEM), were sampled using glass fibre filters and gold traps respectively. Cold vapour – multi collector ICP-MS was used for all isotopic analysis. 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]. The total variation in δ²⁰²Hg ranges from 0.01‰, to -1.74‰, relative to the NIST SRM 3133 Hg standard. No significant isotopic fractionation has been found between the lava source (δ²⁰²Hg = -0.46‰, ±0.36, 2SD) and Hg_(t) in the condensed fumarolic gas (δ²⁰²Hg = -0.74‰, ±0.23, 2SD). Substantial fractionation was observed within the plume between Hg_(p) (δ²⁰²Hg = 0.11‰, ±0.18, 2SD) and residual Hg⁰ (δ²⁰²Hg of

-1.74‰, ±0.36, 2SD). This suggests an enrichment of Hg^0 in the lighter isotopes concurrent with an enrichment of the heavier isotopes in the condensed $\text{Hg}_{(p)}$. A similar gas-particle isotope fractionation process was recently 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