



Mercury isotope fractionation during the exchange of Hg between the atmosphere and land surfaces: implications for atmospheric Hg cycles

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Mercury (Hg) is a neurotoxic pollutant distributed globally via atmospheric transportation of elemental Hg (Hg(0)). Both anthropogenic and natural processes emit Hg to the atmosphere, where the later contributes up to approximately two thirds of the total emissions. Hg(II) in the Earth's surface can be reduced chemically and biologically, resulted subsequent re-emission of Hg(0) back to the atmosphere. The Hg(0) exhibits bi-directional exchange (i.e., deposition and/or emission) between the land surface and atmosphere. Soil is the largest terrestrial Hg reservoir and its interaction with the atmosphere influences the atmospheric Hg cycling largely. Hg(0) emission from the terrestrial surfaces soil has been postulated to carry a negative MDF and positive MIF in the global Hg biogeochemical models. However, to date, no experimental evidence support that the complex terrestrial soil Hg(0) emission in accordance with this hypothetical simplification.

We coupled the *in-situ* Hg(0) dynamic flux chamber measurement and stable Hg isotope analysis to report a first dataset on the Hg isotope fractionation during the exchange of Hg(0) between the atmosphere and 8 soils and 1 cinnabar surfaces. The effect of air-soil/cinnabar exchange shifted Hg(0) concentrations in the flux chamber [i.e., $(\text{Hg}(0)_{\text{chamber}} - \text{Hg}(0)_{\text{ambient}}) / \text{Hg}(0)_{\text{chamber}}$] by a factor of -0.29 – 0.90, corresponding to Hg(0) exchange fluxes ranging from -773 – 14457 ng m⁻² h⁻¹. Our results showed that the exchange of Hg(0) between the atmosphere and soil/cinnabar could lead to an enrichment of both light and heavy isotopes ($\delta^{202}\text{Hg}$ signatures) in Hg(0), as well as depletion or enrichment of odd isotopes ($\Delta^{199}\text{Hg}$ signatures). This highlighted that multiple processes controlled the land-atmosphere exchange of Hg(0) and affected Hg isotope fractionation. Using a conservative isotope mass balance model, we found urban soils Hg(0) emission exhibited large variations in both $\delta^{202}\text{Hg}$ (-3.04 to -0.34‰) and $\Delta^{199}\text{Hg}$ (-0.60 to 0.38‰), which might be controlled by the Hg isotopic signatures in soils and environmental factors. The isotope signatures of Hg(0) emitted from agricultural background soils ($\delta^{202}\text{Hg} = -1.31 \pm 1.09\text{‰}$, $\Delta^{199}\text{Hg} = -0.26 \pm 0.16\text{‰}$, 1σ , $n=15$) and Hg-enriched agricultural soils in Hg mining area ($\delta^{202}\text{Hg} = 0.51 \pm 1.09\text{‰}$, $\Delta^{199}\text{Hg} = -0.10 \pm 0.11\text{‰}$, 1σ , $n=12$) exhibited contrasting mass dependent fractionation (MDF). Photo-reduction of soil Hg(II) coordinated to sulfurless ligands likely dominated the MIF of Hg isotope during the exchange of Hg between the atmosphere and both urban and agricultural soils. While the positive shift of $\delta^{202}\text{Hg}$ in mining area suggested that other processes including sorption and oxidation

were also important in controlling MDF of Hg isotope during air/soil exchange. In a line with Hg-enriched agricultural soils, the forest soil emitted Hg(0) in Hg mining area enriched in heavy isotopes relative to the soil but depleted in odd isotopes. Hg(0) emission from cinnabar ore waste exhibited significant negative $\delta^{202}\text{Hg}$ (-2.21 to -1.67‰) but positive $\Delta^{199}\text{Hg}$ (0.17 to 0.38‰). Our results demonstrate complex Hg isotope fractionation during air-soil/cinnabar Hg(0) exchange resulted contrasting enrichment or depletion effects on the atmospheric Hg isotope compositions, thus have important implications for understanding the atmospheric Hg isotope signatures and modeling the global Hg cycling.