



Distribution of mercury species and mercury isotope ratios in soils and river suspended matter of a mercury mining area

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Mercury (Hg) undergoes Hg species transformations in the environment that can be further altered, e.g., during Hg mining activities. So far, Hg isotope ratios (δ -values and Δ -values) have been used as tracers to distinguish Hg contamination sources. Although, it is unclear whether anthropogenic Hg species released are isotopically different from the Hg source of contamination. We investigated the well-documented cinnabar (Hg sulphide) mine area in Idrija (Slovenia). Sediments are loaded with mining-residues (cinnabar and calcines), whereas soils contain Hg bound to natural organic matter (NOM-Hg) related to atmospheric Hg deposition. Hg is released from sediments and soils, and is transported as suspended matter (SM) in the Idrijca river to the Gulf of Trieste (GT) in Italy. Previously, high $\delta^{202}\text{Hg}$ values in the GT have been related to cinnabar, and more negative $\delta^{202}\text{Hg}$ values have been associated with the Adriatic Sea background, neglecting the influence of NOM-Hg in the Hg isotopic composition. We determined Hg isotope ratios in river SM, sediments and soils from the Idrijca-catchment, and interpreted them together with Hg species to decipher variability of Hg isotopic composition related to the distribution of Hg species in different grain-size fractions (0.45-90 μm). Speciation measurements reveal that fine fractions (0.45-20 μm) are dominated by NOM-Hg, while larger fractions contain more mining-residues. $\delta^{202}\text{Hg}$ values of SM (0.45-20 μm) collected from tributaries corresponded to those found in soils ranging from -2.58 to 0.19‰ and from -2.27 to -0.88‰ respectively. More negative $\delta^{202}\text{Hg}$ values were related to higher proportions of NOM-Hg, which are predominant in soils and SM. Rain events increase SM loads in the river mainly due to resuspension of coarse grain-size fractions of bottom sediments bearing larger proportions of cinnabar and calcines, which leads to more positive $\delta^{202}\text{Hg}$ values. The large-magnitude of variation of $\delta^{202}\text{Hg}$ and the small-magnitude of variation of $\Delta^{199}\text{Hg}$ (-0.37 to 0.09‰) were related with fractionation during ore roasting. Soil samples with high NOM-Hg content show more negative $\delta^{202}\text{Hg}$ values and the largest variation of $\Delta^{199}\text{Hg}$ compared to samples dominated by cinnabar. Similar to previous studies, we related high positive $\delta^{202}\text{Hg}$ values in the GT to the occurrence of cinnabar, although more negative $\delta^{202}\text{Hg}$ values were rather linked to distant sedimentation of soil derived NOM-Hg than to sedimentation of autochthonous marine material. In comparison with the proportions of NOM-Hg, the occurrence of cinnabar and calcines led to larger variation of $\delta^{202}\text{Hg}$ values, which was explained by ore processing and natural processes that likely produce large variation in the Hg isotopic composition. Consequently, prediction of Hg isotopic composition and differentiation of Hg sources may result challenging. Our study reveals that Hg isotope ratios rather indicate different Hg species, and are not necessarily symptomatic for Hg pollution sources. Combining Hg isotope measurements with solid phase Hg speciation provides a better understanding of Hg isotope ratios and distinguishes isotopic fingerprints of Hg sources from Hg species and related Hg species transformation processes.