Diel variation of stable isotope ratios record photoreduction of PM2.5-bound mercury

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Mercury (Hg) bound to fine aerosols ($PM_{2.5}$-Hg) is subject to complex transport, gas-particle partitioning, and transformation processes. $PM_{2.5}$-Hg may undergo photoreduction that causes isotopic fractionation and obscured the initial isotopic signatures, rendering the source tracing more difficult. In this study, we quantified Hg isotopic compositions of 56 $PM_{2.5}$ samples collected between Sept. 15th and Oct. 16th, 2015 in Beijing, China, with 26 collected during the daytime (between 8:00 a.m. and 6:30 p.m.) and 30 sampled at night (between 7:00 p.m. and 7:30 a.m.). The results showed ranges of both δ^{202}Hg (from −1.49‰ to 0.55‰) and Δ^{199}Hg (from −0.53‰ to 1.04‰), and statistically significant ($p < 0.05$, *t*-test) diel variation with more positive Δ^{199}Hg value in daytime (mean = 0.26 ± 0.40‰ 1SD) than nighttime (mean = 0.04 ± 0.22‰) samples. Geochemical characteristics of our samples and the air mass back trajectories ($PM_{2.5}$ source related) showed that this diurnal variation is not caused by either source contribution nor the change of weather conditions, but more likely by the photochemical reduction of divalent Hg that has been observed in homogeneous environments, as confirmed by the strong correlations of Δ^{199}Hg versus (i) Δ^{201}Hg (positive, slope = 1.1), (ii) δ^{202}Hg (positive, slope = 1.15), (iii) concentration of Hg in $PM_{2.5}$ (negative), (iv) sunshine durations (positive), and (v) ozone concentrations (positive) observed for consecutive day-night sample pairs with similar air mass back trajectories. The results of this study suggest that photoreduction of Hg bound to (fine) particles may contribute to gaseous elemental Hg of the atmosphere. Such contribution may be taken into account in future studies of biogeochemical cycling of Hg at local or regional scale.