Concentrations and isotope compositions of particle-bound mercury in a severe haze episode in Tianjin, China

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Haze episodes often lead to atmospheric Hg pollution because the elevated concentration of particles could enhance the adsorption of regionally emitted Hg$^{2+}$ and the catalytic oxidation of gaseous Hg$^0$, which directly influences the transport and fate of atmospheric Hg. Thus particle-bound Hg (PBM) does not necessarily reflect primary anthropogenic emission, but could also reflect atmospheric transformations of Hg. To further reveal the sources and processes of PBM under severe haze conditions, total suspended particles (TSP), PM$_{10}$, and PM$_{2.5}$ samples were simultaneously collected during day and night respectively in Tianjin, Northern China from January 8th to 15th, 2019, when the highest daily average concentration of TSP was up to 600 μg/m$^3$. Hg concentrations and isotopic compositions were analyzed, together with other geochemical parameters and meteorological data. For all samples, the total Hg concentration increased when haze pollution aggravated, ranging from 0.42 μg/g to 3.83 μg/g, and more than three-quarters of PBM existed in the particle size range less than 2.5 μm. Most samples display significantly negative mass dependent fractionation, positive mass independent fractionation (MIF) for odd mass isotopes (Δ$^{199}$Hg), and slightly positive MIF for even mass isotopes (Δ$^{200}$Hg). Among them, Δ$^{199}$Hg of Hg$_{PM2.5}$ and Hg$_{TSP}$ show diurnal variation, which is generally consistent with those day and night PM$_{2.5}$ samples reported by Huang et al. [1]. The difference is that our samples show the highest Δ$^{199}$Hg when haze pollution peaked. The Hg isotope results in our particulate samples suggest that there were likely multiple sources of PBM with variable contributions, including coal combustion, smelting, cement production and biomass burning. Furthermore, our data also suggest that PBM has undergone photoreduction to different extents after emission from primary sources during this severe haze episode. However, the mechanism of PBM photoreduction under haze conditions is still investigation.