

MERCURY STABLE ISOTOPE COMPOSITIONS IN AIRBORNE PARTICULATE MATTERS IN AMBIENT AIR OF CHINA

Xinbin Feng¹, X.W. Fu¹, Y. Xu², J.E. Sonke², L. Ming³, X-D. Li³

¹*State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China.*

²*Observatoire Midi-Pyrénées, Laboratoire Géosciences Environnement Toulouse, CNRS/IRD/Université de Toulouse, Toulouse, France*

³*Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hong Kong, China*

fengxinbin@vip.skleg.cn

Keywords: Mercury, PM_{2.5}, mercury isotope, Source attribution

Introduction

Since the development of highly precise multi-collectors inductively coupled plasma mass spectrometry (MC-ICPMS), signatures in Hg isotopes have been deployed for pollutant source apportionment in samples from various environmental compartments (i.e. Feng et al., 2010). Significant mass dependent fractionations (MDF) of Hg isotopes has been reported during methylation, de-methylation, abiotic photochemical reduction, abiotic chemical reduction, biotic reduction, and physical processes including evaporation, volatilization, absorption, leaching and diffusion. Interestingly, recent studies also demonstrated mass independent fractionation (MIF) for both odd (e.g. ¹⁹⁹Hg and ²⁰¹Hg) and even (e.g. ²⁰⁰Hg, ²⁰⁴Hg) isotopes. Each fractionation process imparts a diagnostic pattern of isotopic variation, and consequently Hg isotope ratios provide key clues for understanding the possible sources and pathways on mercury transportation and transformation. Source attribution of atmospheric Hg is plausibly provided since the isotopic compositions of primary emission sources are significantly different from each other and from the background. In this paper, we collected airborne particulate matters (PM) at both urban and remote sites in China to investigate the sources of Hg of PM and the possible pathway of particulate bounded Hg formation in ambient air.

Methods

Fine airborne particulate matters (PM_{2.5}) were collected weekly using quartz fibre filters at four remote sites in China, which were located at Mt. Waliguan (northwestern China), Mt. Ailao (southwestern China), Mt. Changbai (northeastern China) and Huaniao Island (East China Sea). For accurate Hg isotope measurement by MC-ICP-MS, the sensitivity of our instrument requires introduction of the analyte in excess of 1 ng ml⁻¹ solution.

The sampled quartz filters were processed using a double-stage tube furnace following novel methodology (Fu et al. 2014). Accordingly, two tube furnaces (Thermo Scientific) were placed in close proximity. A sample was induced in a small quartz tube (100 mm length, 19 mm inner diameter, 20 mm outer diameter) and heated from room temperature to 1000 °C within 4 hours in the first tube furnace. High purity oxygen was introduced as carrier gas promoting complete oxidation of organics in the sample and transfer of resulting Hg⁰ into the second tube furnace. A bubbler filled with 10 mL KMnO₄ acid trapping solution (Zheng et al. 2007) was connected at the exit of the tube-furnace assembly to entirely oxidize and capture Hg from exhaust. Trapping solutions were subsequently diluted to 20 mL in order to control the acid concentration under 20% and kept in dark bottles prior to Hg concentration and isotope measurements.

Results

The averaged mercury (Hg) concentrations in PM_{2.5} at the studied sites ranged from 18.9 to 46.1 $\mu\text{g m}^{-3}$, which are 2-5 times greater than that observed from the North America and Europe. We identified that long-range transport from industrial and urbanized areas in eastern, northern, southwestern, northwestern China played a primary role in distribution of Hg in PM_{2.5} in remote areas of China. Hg in PM_{2.5} overall displayed negative $\delta^{202}\text{Hg}$ values ranging from -2.5‰ to -0.30‰. The negative $\delta^{202}\text{Hg}$ values were partly attributed to direct emission of PM_{2.5} from anthropogenic sources, as most previous studies suggested that PM_{2.5} Hg released from coal fired power plants were characterized by negative $\delta^{202}\text{Hg}$ values. Also, Hg isotopes fractionation during atmospheric transformation including oxidation of Hg^0 in the atmosphere followed by gas-particle partitioning could also induce negative shift in PM_{2.5} $\delta^{202}\text{Hg}$ values. We also observed significant mass independent fractionation (MIF) in PM_{2.5} with $\Delta^{199}\text{Hg}$ values ranging from -0.20‰ to 1.17‰. The PM_{2.5} $\Delta^{199}\text{Hg}$ values were significantly anti-correlated with PM_{2.5} Hg concentrations. As most of high PM_{2.5} Hg samples were directly related to anthropogenic Hg emission in mainland China, we suggest that PM_{2.5} released from anthropogenic sources of China were characterized by $\Delta^{199}\text{Hg}$ values near zero. This conclusion is consistent with previous studies which showed that MIF signatures in world coal and during coal combustion were all close to zero. On the other hand, atmospheric processes including oxidation of Hg^0 and photo reduction of PM_{2.5} Hg are thought to drive isotopic composition of PM_{2.5} Hg toward high positive $\Delta^{199}\text{Hg}$ values. This may explain the high positive $\Delta^{199}\text{Hg}$ values in low PM_{2.5} Hg samples.

Conclusion

We found that PBM $\Delta^{199}\text{Hg}$ at remote areas are significantly different the urban sites, with positive $\Delta^{199}\text{Hg}$ at remote sites and $\Delta^{199}\text{Hg}$ near zero at urban sites. We demonstrated that Hg isotope signatures can be used to trace the source of Hg in PM. We observed that atmospheric transformations of Hg species lead to the positive PBM $\Delta^{199}\text{Hg}$. We also observed MIF of Hg^{200} also occurs in the marine boundary layers.

References

- Feng, X., et al. (2010). Tracing mercury contamination sources in sediments using mercury isotope compositions. *Environ. Sci. Technol.* 44, 3363-3368.
- Fu, X., Heimbuerger, L-E; Sonke, J E., (2014). Collection of atmospheric gaseous mercury for stable isotope analysis using iodine-and chlorine-impregnated activated carbon traps. *J. Anal. Ato. Spectrom.* 29, 841-852.
- Zheng, W., et al. (2007). Mercury isotope fractionation during volatilization of Hg^0 from solution into the gas phase. *J. Anal. Ato. Spectrom.* 22, 1097-1104.