**Supporting Information**

**Experimental methods**

About 0.5 g of ground sample was digested (95 °C, 1 hour) in a 5 mL aqua regia (HCl:HNO3 = 3:1, v:v). Certified reference materials (NIST-2711, n=3; MESS-2, n=3) were prepared in the same way as the sample. Based on the measured THg (Table S1), the digest solutions were diluted to 0.5 and 1 ng mL-1 for most of the samples; For samples WSV504BSN and WSV549BVM, the digest solutions were diluted to 0.3 ng mL-1. NIST SRM 997 Tl standard solutions with Tl concentration of 20 ng g-1 were prepared by 0.12M HCl. All sample solutions have acid concentrations of < 20%. Duplicate UM-Almadén solutions with 10% aqua regia were prepared into 0.3 (n=3), 0.5 (n=3) and 1.0 (n=3) ng mL-1 Hg, to match the Hg concentrations of the sample solutions. NIST SRM 3133 was prepared in aqua regia solutions, the concentrations of Hg and aqua regia were adjusted to within 10% of other Hg solutions. SnCl2 (3%, w/v) was prepared in 10% (v/v) HCl. Acids (HCl and HNO3) used in this study were of suprapure grades (certified ACS Plus, Fisher Scientific). The 18.2-ΩM-grade water used for the preparation of reagents and solutions was provided by a Milli-Q water purification system (Millipore, Bedford, USA).

Hg isotopic measurements were performed on a Neptune Plus MC-ICP-MS housed at the University of Wisconsin-Madison’s State Laboratory of Hygiene. The instrument was equipped with a gas-liquid phase separator and an Apex-Q desolvation unit (Elemental Scientific Inc., USA) for Hg and thallium (Tl) introduction, respectively. Briefly, stannous chloride (SnCl2) was continually pumped along with Hg solutions onto a frosted glass phase separator, producing gaseous elemental Hg(0) which was mixed with the dry Tl aerosol generated by the Apex-Q nebulizer, before being introduced into the plasma. The Apex-Q nebulizer was set in the free flow-mode using the “sample” gas of the MC-ICP-MS, and the glass phase separator was flushed with the “additional” gas of the instrument. NIST SRM 997 Tl standard (205Tl/203Tl = 2.38714) was used as an internal standard for simultaneous instrumental mass bias correction of Hg. Seven of the nine faraday cups, L3, L2, L1, C, H1, H2 and H3, were used to monitor the 198Hg, 199Hg, 200Hg, 201Hg, 202Hg, 203Tl and 205Tl isotopes, respectively. The gains of the amplifier associated with each Faraday collector were calibrated for efficiency on a daily basis. Instrument parameters (e.g., Ar gas flows, torch settings, and lens system) were tuned for a maximum ion intensity of Hg and Tl in standard solutions. Operating conditions and instrumentation of this study are summarized in Table S2. Data was acquired using 3 block of 60 cycles, monitoring all isotopes for 2.097 s per cycle. An initial uptake of sample solution of 3 min to ensure stable signals before measurements started. Between samples, the glass phase separator was rinsed using 0.8 M HNO3 for 6 minutes until the signal intensity returned to background level. The signals for 202Hg and 205Tl were <0.02 V for acid blanks. The sensitivity for 201Hg during Hg isotope analysis is estimated to be 0.65 V per ng mL-1 Hg, and the intensities of 205Tl for 20 ng mL-1 Tl standard solution during all analysis range from 3.7 to 3.9 V. THg in acid digests was also monitored by MC-ICP-MS using 202Hg signals, which showed that the recoveries of Hg in acid digests were >93%.

A standard-sample-standard bracketing approach was used to compare relative per mil (‰) deviation (using the δ notation) of all our measurements to NIST SRM 3133, as suggested by Blum and Bergquist (2007):

δxxxHg(‰) = {(xxxHg/198Hgsample)/(xxxHg/198HgNIST 3133)－1}×1000 (1)

The concentrations of Hg and acid in the bracketing NIST SRM 3133 solutions were within 10% of that of the UM-Almadén. Hg-MIF is reported in Δ notation (ΔxxxHg, deviation from mass dependency in units of permil, ‰) and is the difference between the measured ΔxxxHg and the theoretically predicted ΔxxxHg value using the following formula:

ΔxxxHg ≈ δxxxHg - δ202Hg\*β (2)

where β is equal to 0.252 for 199Hg, 0.5024 for 200Hg, and 0.752 for 201Hg, respectively (Blum and Bergquist, 2007).

UM-Almadén solutions with different concentration of Hg were measured in every 10 samples. Data uncertainties reported in this study reflect the larger values of either the external precision of the replication of the UM-Almadén or the measurement uncertainty of standard reference materials. The overall average and uncertainty of all UM-Almadén measurements (δ202Hg: -0.52 ± 0.09‰; Δ199Hg: -0.01 ± 0.05‰; Δ200Hg: 0.00 ± 0.03‰; Δ201Hg: 0.00 ± 0.05‰, 2σ, n=9) agreed well with previous studies (Blum and Bergquist, 2007). No static differences in Hg isotopic compositions were observed for UM-Almadén with different Hg concentrations (Table S3). Measurements of replicate digests of NIST-2711 (δ202Hg: -0.13±0.11‰; Δ199Hg: -0.16±0.09‰; Δ200Hg: -0.02 ± 0.03‰; Δ201Hg: -0.16 ± 0.04‰, 2σ, n = 3) and MESS-1 (δ202Hg -1.85±0.10‰; Δ199Hg 0.01±0.06‰; Δ200Hg: 0.01 ± 0.03‰; Δ201Hg 0.02±0.05‰; 2σ, n=3) also agreed well with previous studies (Biswas et al., 2008; Donovan et al., 2013;Yin et al., 2014).

**References**

Biswas A, Blum JD, Bergquist BA, et al. 2008. Natural mercury isotope variation in coal deposits and organic soils. Environ Sci Technol 42(22): 8303-8309.

Donovan PM, Blum JD, Yee D, et al. 2013. An isotopic record of mercury in San Francisco Bay sediment. Chem Geol 349: 87-98.

Yin R, Feng X, Chen J. 2014. Mercury stable isotopic compositions in coals from major coal producing fields in China and their geochemical and environmental implications. Environ Sci Technol 48(10): 5565-5574.

Blum JD, Bergquist BA. 2007. Reporting of variations in the natural isotopic composition of mercury. Anal Bioanal Chem 388(2): 353-359.