Supporting Information

Mercury Isotopic Evidence for Distinct Mercury Sources in Coal from the Illinois Basin

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Supporting Information Includes: *2197 words (including all captions and references), 2 figures, & 2 tables.*

1. Experimental Section

Coal samples were collected from active mines in the Illinois Basin, also known as the Eastern Interior Basin. The Illinois Basin contains some of the most important coal resources in the United States (Hatch and Affolter, 2002; Korose and Elrick, 2010). This Paleozoic sedimentary basin is an elliptical intracratonic basin (Buschbach and Kolata, 1991) that covers 155,000 km^2 (60,000 mi^2) in Illinois, Western Indiana and Western Kentucky (Fig. 1).
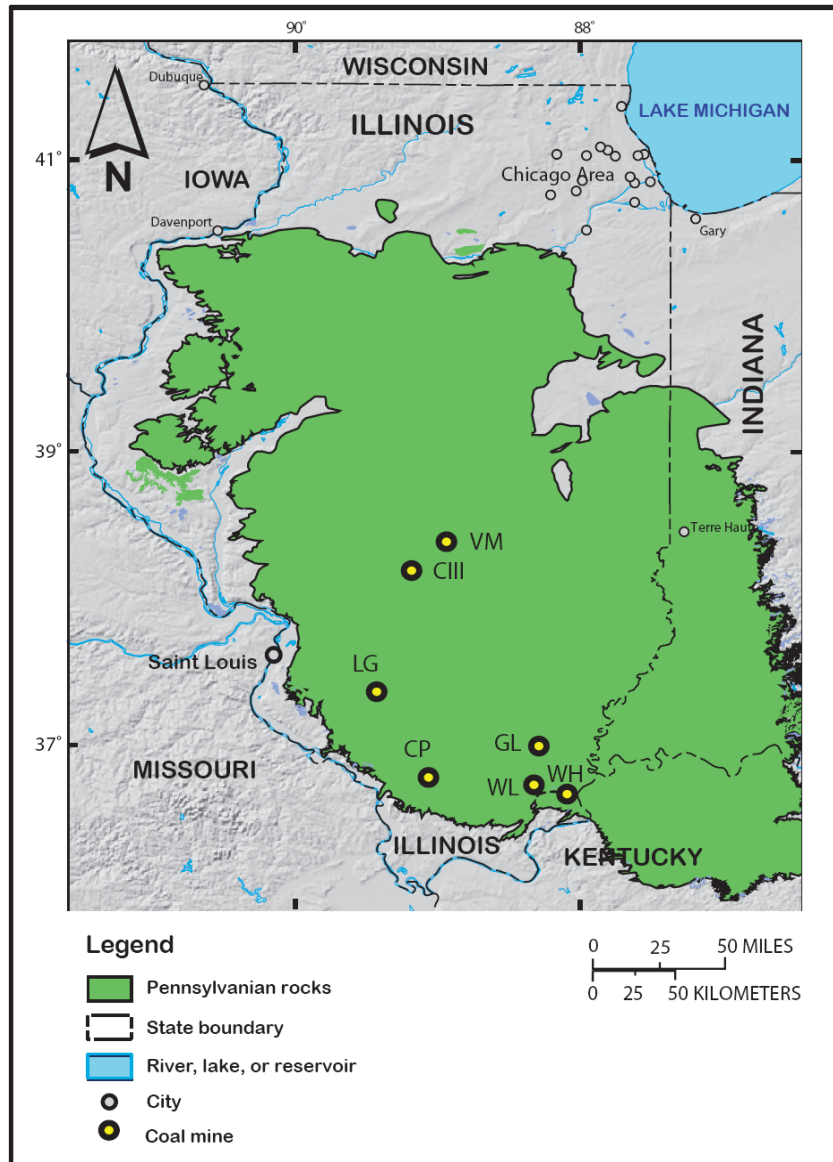
Figure SI-1: Location map showing mines where coal samples were collected. Names of the mines were abbreviated as follows: VM, Viper; CIII, Crown III; LG, Lively Grove; CP, Creek Paum; GL, Galatia; WL, Willow Lake; WH, Wildcat Hills. Also indicated is the extent of Pennsylvanian-age coal-bearing strata in the Illinois Basin.

The basin contains a nearly continuous record of deposition from the Cambrian through the Pennsylvanian (Kolata and Nelson, 1991). The Paleozoic sedimentary sequence disconformably overlies Precambrian granite and rhyolite, dated between 1,420 and 1,500 Ma. The Paleozoic sedimentary sequence is dominated by carbonate rocks and, to a lesser extent, by sandstone, shale, siltstone, and coal. All of the significant coal of the Illinois Basin is found in Pennsylvanian rocks (Fig. 2). To date, about 20 coal seams have been mined in Illinois (Korose and Elrick, 2010).

N.A. Series	U.S.M.C. Series	Formation	Coal Member or Bed
Middle Pensylvanian	Desmoinesian	Shelburn Fm.	
			Danville (No. 7)
			Jamestown
		Carbondale Fm.	Herrin (No. 6)
			Springfield (No. 5)
			Houchin Creek (No. 4)
			Colchester (No. 2)
	Atokan	Spoon Fm.	Mount Rorah
			Murphysboro
			Rock Island (No. 1)

Figure SI- 2: Stratigraphic column for Middle Pennsylvanian strata in the Illinois Coal Field, showing major coal members in Illinois. The position of major coal beds is largely derived from Greb et al. (1992). U.S.M.C. = United States Mid-Continent; N.A. = North America. (From N.A. Series; U.S.M.C.)

The coals in Illinois are dominantly high volatile C to A bituminous rank, and calorific values range from about 11,000 Btu/lb (moist, mineral-matter-free) in the northwestern part of the coalfield to about 15,000 Btu/lb in the southeastern part of the state. The increase in rank follows a dominant regional pattern from the northwest to the southeastern part of the coalfield (Rowan et al., 2002; Korose and Elrick, 2010). The regional distribution of the rank has partially been attributed to advective heat transport through the basin as a consequence of tectonic activity and regional fluid flow (Cluff and Byrnes, 1991; Rowan et al., 2002). The ash content of Illinois coals is highly variable with average values of ~10% (Korose and Elrick, 2010). Sulfur content of Illinois coal is frequently related to the depositional environment (Price and Sheih, 1979). Data computed from a large number of channel samples for the two principal coals mined in Illinois show that the average pyrite content (weight % low temperature ash) for Springfield coal of 3.9% (0.5 – 18.0%) is higher than the average pyrite content for Herrin coal of 3.4% (1.0 – 11.6%) (Korose and Elrick, 2010).

For this study, we collected coal samples from the following coal seams: Herrin No. 6 and Springfield No. 5 of Carbondale Formation and Murphysboro and Mt. Rorah of Spoon Formation. The Herrin, Springfield, Murphysboro and Mt. Rorah Coals are all highly volatile C and B bituminous coals. The coal samples from Viper, Crown-III, and Lively Grove mines are high volatile C bituminous and the coal samples from Creek Paum, Galatia, Wildcat Hills, and Willow Lake mines are high volatile B bituminous (Korose and Elrick, 2010). No high volatile A bituminous coal samples were analyzed in this study.

Each of the coals exhibits mean ash yields of 9%-12% and mean sulfur contents of 2%-5% (Lefticariu et al., 2009). Each of the coals is dominated by vitrinite macerals (generally more than 80%), but some compositional differences are noted within and among coals (Lefticariu et al., 2009). The two largest producers in the Illinois Basin are the Herrin and Springfield Coals (Korose and Elrick, 2010). Natural outcrops of the Herrin and Springfield Coals are practically non-existent, so our sampling was restricted to underground active mines. The Murphysboro and Mt. Rorah Coals are generally thin (< 1 m) and are mined in southern Illinois in open pit mines.

Hg Concentration Analysis by AAS

Hg concentrations in coal samples were determined by atomic absorption spectroscopy (wavelength = 253.7 nm) on Sn(II)-reduced solutions using a Nippon Instruments MA-2000 Hg analyzer, following combustion and recovery of Hg into 24 gram permanganate traps (1% $KMNO_4$, 1.8M purged H_2SO_4) using an offline combustion apparatus (Biswas et al. 2008). AAS concentrations were obtained using a calibration range of 0-20 ng Hg g^{-1} (0.25 ng Hg g^{-1} detection limit) with most samples falling within the mid-range of the calibration curve (r^2 = 0.999). Analyses of NIST SRM 3133 Hg standard solutions during each run agreed with certified values to within ± 5%. Samples were independently run for Hg concentration twice, first after combustion into 24 gram permanganate traps, and again following purge and trap transfer from 24 gram traps into 10 gram permanganate traps. Typical Hg loss on purge and trap transfer was ~10% during early stages of this study, and < 5% during later stages, based on results of multiple runs of NIST 1632c bituminous coal reference material combusted with each batch of coal samples. Total processing yields for NIST 1632c bituminous coal ranged from 91-99%.

An offline combustion and trapping procedure similar to that employed by Biswas et al. (2008) was used to liberate and quantitatively capture Hg from coal organic matrices and from pyrite mineral separates. Decomposition and volatilization was accomplished by step heating in a two-stage furnace configuration (2 Lindberg Blue M furnaces in series) using custom-made quartz glass furnace tubes following modifications from Biswas et al. (2008). Hg was released over a temperature range of 25-550 degrees C (5 hour schedule) in a pure oxygen (Hg-clean) atmosphere in the first-stage furnace, and combustion products further dissociated in a secondary combustion furnace at 1000 degrees C. Hg was trapped in an oxidizing solution of 1% $KMnO_4$/1.8 M H_2SO_4 through a custom-made quartz-glass

sparger tube and trap assembly attached to the end of furnace tube. Outlet tubing was heated to ensure that no H_2O condensation was formed within the combustion apparatus during the combustion procedure, which could have affected Hg recovery.

Prior to combustion, approximately 2 to 2.5 g samples of crushed and purified coal were weighed into Hg-clean ceramic boat crucibles (furnace blanked at 800 °C), interlayered with sodium carbonate and alumina (furnace blanked at 800 °C), and loaded into the 1st-stage end of the combustion unit. During combustion, samples were reduced to a reddish-brown oxidized sinter using a pure oxygen flux of 15 mL min^{-1}, with a secondary flow (all Au-trap filtered Hg-clean O_2) of 10 mL min^{-1} introduced at the decomposition furnace to enhance organic decomposition. For all combustion runs, Hg^{2+} in the 1% $KMnO_4$ sparger residues, plus any visible organic residue remaining on sparger tips, was recombined with the sample by rinsing using a dilute reducing hydroxylamine solution (1.5% w/v).

Procedural blanks, sample replicates, and the NIST SRM 1632c coal reference standard were all analysed over the course of this study. Procedural blanks for Hg were typically 15 pg Hg g^{-1} in a 24 gram trap (360 pg Hg) per combustion run. Most of the Hg blank was accumulated from the low-Hg stock permanganate (Alpha Aesar). Coal samples had Hg concentration ranges of 27 to 370 ng Hg g^{-1} with total Hg processed per sample being typically in the 100-300 ng range, approximately 300-1000x measured blank levels. Other materials combusted included pyrite, which ranged in concentration from 3500 to 7600 ng (n = 2), and a carbonaceous shale (420 ppb Hg). NIST SRM 1634c (bituminous coal) was combusted six times to monitor yields and reproducibility for Hg concentrations and Hg isotopic composition over the course of the study.

MC-ICP-MS Hg Isotopic Analysis

Prior to mass spectrometry, the post-transfer 10 g permanganate trap solutions were completely neutralized with a 30% (w/v) concentrated hydroxylamine solution and analyzed by AAS for Hg concentrations to determine post-transfer yield and to quantify concentrations for matching NIST SRM-3133 bracketing standards during isotopic analysis. Hg isotopic compositions were determined on a Nu Instruments MC-ICP-MS by continuous flow cold vapor generation using $Sn(II)Cl_2$ as the reductant. An internal thallium standard (NIST SRM 997) and standard-sample-standard bracketing (NIST SRM-3133) were used for correcting the instrumental mass bias. The SRM-3133 bracketing standard and external standard (Almaden) were matched to within ± 10% of sample Hg concentrations. All solutions were prepared with identical matrix compositions (neutralized 1% $KMnO_4$/1.8M H_2SO_4). For this study, samples and standards were prepared and run at 5ng Hg g^{-1}. An Aridus desolvating nebulizer (CETAC) was used to introduce the Tl internal spike as an aerosol to the Hg vapor after Sn(II)-reduction of the sample.

Mass spectrometry was carried out using a faraday cup configuration on the Nu Plasma multi-collector ICP-MS that simultaneously monitors masses 206 (Pb), 205 (Tl), 204, 203 (Tl), 202, 201, 200, 199, 198 and 196, with on-peak zero corrections applied and potential ^{204}Pb interference on ^{204}Hg

corrected by monitoring ^{206}Pb. Pb mass interferences on Hg were below detection throughout the study. Hg isotopic variations are reported in delta notation in units of permil (‰) referenced to the NIST SRM-3133 Hg standard (Blum and Bergquist, 2007). For even-numbered isotopes we report values for mass dependent fractionation (MDF) as δ^{202}Hg. For odd-numbered isotopes (^{199}Hg and ^{201}Hg), where measured isotope ratios in many of the samples analysed deviate from mass dependence, we also derive a value for mass independent fractionation (MIF) from the predicted mass-dependent values based on δ^{202}Hg, using a kinetic mass-dependent fractionation law (Bergquist and Blum, 2007). We report MIF as Δ^{xxx}Hg, which is the permil difference between the measured values of δ^{199}Hg and δ^{201}Hg and those predicted from δ^{202}Hg based on mass dependence.

Reporting Analytical Uncertainty

Long-term external reproducibility of Hg isotopic analyses by this method was estimated from the in-house Hg isotopic standard UM-Almaden (Blum and Bergquist, 2007), which was analysed multiple times during each isotope run. A typical analytical session consisted of five runs of the Almaden Hg isotopic standard plus NIST SRM-3133 bracketing standard and six samples. Samples (unknowns) were typically run twice per analytical session. The 2SD uncertainty for Almaden during eight analytical sessions was as follows: δ^{202}Hg = −0.57‰ ± 0.10‰ (2SD, $n = 40$), Δ^{201}Hg = −0.04‰ ± 0.07‰ (2SD, $n = 40$), and Δ^{199}Hg = −0.02‰ ± 0.08‰ (2SD, $n = 40$). These values represent the most conservative estimate of external analytical uncertainty for Hg isotopic ratios over the course of this study. Six separate combustions of NIST SRM 1632c bituminous coal yielded a mean δ^{202}Hg value of −1.86‰ ± 0.10‰ (2SD, $n = 6$), Δ^{201}Hg = −0.03‰ ± 0.04‰ (2SD, $n = 6$) and Δ^{199}Hg = −0.04‰ ± 0.02‰ (2SD, $n = 6$).

MDF is expressed as:
$$\delta^{XXX}Hg = ([(^{XXX}Hg/^{198}Hg)_{unknown}/(^{XXX}Hg/^{198}Hg)_{SRM3133}] - 1)*1000$$

MIF is expressed as:
$$\Delta^{201}Hg = 1000*([\ln((\delta^{201}Hg/1000) + 1)] - 0.752*[\ln((\delta^{202}Hg/1000) + 1)])$$
$$\Delta^{199}Hg = 1000*([\ln((\delta^{199}Hg/1000) + 1)] - 0.252*[\ln((\delta^{202}Hg/1000) + 1)])$$

Which can be approximated as (for small delta values):
$$\Delta^{201}Hg \approx \delta^{201}Hg - (\delta^{202}Hg * 0.752)$$
$$\Delta^{199}Hg \approx \delta^{199}Hg - (\delta^{202}Hg * 0.252)$$

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Table SI-S1. Sample information, Hg concentration, and Hg isotopic composition of coal samples from Illinois Basin.

Sample	Mine	Coal seam	Sample location	Sample type	Hg (ppb)	δ^{202}Hg (‰)	2SD	Δ^{201}Hg (‰)	2SD	Δ^{199}Hg (‰)	2SD	n
H6-WH1t	Wildcat Hills	Herrin	1/3 bench (top)	coal	31.8	-1.46	0.04	-0.22	0.06	-0.18	0.08	2
H6-WH2m	Wildcat Hills	Herrin	2/3 bench (middle)	coal	27.6	-1.55	0.06	-0.15	0.06	-0.17	0.12	2
H6-WH3m	Wildcat Hills	Herrin	3/3 bench (bottom)	coal	155.1	-1.17		-0.13		-0.16		1
H6-LV3m	Lively Grove	Herrin	2/3 bench (middle)	coal	53.6	-1.16	0.02	-0.14	0.06	-0.12	0.02	2
H6-LV3m*	Lively Grove	Herrin	2/3 bench (middle)	coal	49.7	-1.13	0.04	-0.12	0.02	-0.10	0.02	2
H6-B1t	Galitia	Herrin	1/3 bench (top)	coal	63.6	-1.89	0.08	-0.13	0.06	-0.16	0.06	2
H6-B2m	Galitia	Herrin	2/3 bench (middle)	coal	420.4	-1.27	0.06	-0.09	0.06	-0.04	0.02	2
H6-B2m*	Galitia	Herrin	2/3 bench (middle)	coal	411	-1.26	0.18	-0.05	0.10	-0.07	0.08	2
H6-B3b	Galitia	Herrin	3/3 bench (bottom)	coal	93.5	-1.74	0.04	-0.12	0.04	-0.12	0.02	2
H6-G1t	Galitia	Herrin	1/3 bench (top)	coal	46.4	-1.51	0.02	-0.06	0.02	-0.02	0.02	2
H6-G2m	Galitia	Herrin	2/3 bench (middle)	coal	76.1	-2.16	0.10	-0.10	0.00	-0.10	0.02	2
H6-G3b	Galitia	Herrin	3/3 bench (bottom)	coal	188.3	-1.44	0.04	-0.06	0.04	-0.05	0.08	2
H6-C3t	Crown III	Herrin	1/3 bench (top)	coal	65.5	-1.91	0.06	-0.14	0.04	-0.17	0.08	2
H6-C3m	Crown III	Herrin	2/3 bench (middle)	coal	39.8	-1.58	0.10	-0.18	0.02	-0.23	0.06	2
H6-C3b	Crown III	Herrin	3/3 bench (bottom)	coal	41.1	-1.57	0.04	-0.21	0.04	-0.19	0.06	2
H6-WH1t pyrite	Wildcat Hills	Herrin	1/3 bench (top)	pyrite	3479.2	-0.14	0.08	-0.02	0.06	-0.05	0.08	3
H6-WH1t pyrite*	Wildcat Hills	Herrin	1/3 bench (top)	pyrite	3031.0	-0.14	0.10	-0.03	0.02	-0.01	0.06	3
SF5-WL1t	Willow Lake	Springfield	1/3 bench (top)	coal	93	-1.59	0.02	-0.02	0.04	0.02	0.06	2
SF5-WL1t*	Willow Lake	Springfield	1/3 bench (top)	coal	89.6	-1.51	0.10	0.02	0.04	0.03	0.06	2
SF5-WL1m	Willow Lake	Springfield	2/3 bench (middle)	coal	238.7	-1.87	0.00	0.00	0.02	0.02	0.04	2
SF5-V1t	Viper	Springfield	1/3 bench (top)	coal	98.1	-1.21	0.12	-0.02	0.02	0.00	0.14	2
SF5-V2m	Viper	Springfield	2/3 bench (middle)	coal	89.4	-0.96	0.16	0.04	0.02	0.00	0.00	2
SF5-V3b	Viper	Springfield	3/3 bench (bottom)	coal	121.4	-0.75	0.00	-0.01	0.00	-0.01	0.10	2
SF-V2m pyrite	Viper	Springfield	2/3 bench (middle)	pyrite	7600.7	-0.05	0.02	0.01	0.04	0.04	0.02	2
MB-CP1t	Crown Paum	Murphysboro	1/3 bench (top)	coal	74.2	-2.68	0.02	0.01	0.10	-0.01	0.12	2
MB-CP2m	Crown Paum	Murphysboro	2/3 bench (middle)	coal	97.1	-2.46	0.18	-0.04	0.04	-0.02	0.00	2
MB-CP3b	Crown Paum	Murphysboro	3/3 bench (bottom)	coal	87.8	-1.91	0.10	-0.05	0.10	0.00	0.00	2
MTR-CP1t	Crown Paum	Mt. Rorah	1/4 bench (top)	coal	172.4	-1.81	0.12	-0.06	0.10	-0.11	0.12	2
MTR-CP2m	Crown Paum	Mt. Rorah	2/4 bench (middle)	coal	370.9	-1.54	0.24	-0.03	0.02	-0.04	0.00	2
MTR-CP3m	Crown Paum	Mt. Rorah	3/4 bench (middle)	coal	50.5	-2.10	0.02	-0.04	0.10	-0.07	0.08	2
MTR-CP4b	Crown Paum	Mt. Rorah	4/4 bench (bottom)	coal	62.1	-1.80	0.00	-0.09	0.14	-0.15	0.02	2

*: Replicate analysis

2 SD uncertainties based on n=2 measurements within the same analytical session (except for n = 3 for pyrites) for each sample. Uncertainty on Hg concentrations estimated at +/- 5%.

Long-term analytical uncertainty of Hg isotopic measurements based on reproducibility of Almaden isotopic standard: +/- 0.10‰ for δ^{202}Hg (2SD), +/- 0.07‰ for Δ^{201}Hg (2SD), and 0.08‰ for Δ^{199}Hg (2SD).

Table SI-S2: Hg isotopic composition of NIST 1632c coal Hg standard by MC-ICP-MS at the University of Michigan, with Hg yield estimates for six separate combustions.

Standard	δ202/198 Hg (‰)	Δ^{201}Hg (‰)	Δ^{199}Hg (‰)	ppb Hg conc.	% yield	certified ppb
NIST1632c_(5/04/10)_5ppb	-1.80	-0.03	-0.03	92.80	0.989	93.80
NIST1632c_(4/12/10)_5ppb	-1.82	-0.05	-0.04	93.20	0.994	93.80
NIST1632c_(3/17/10)_5ppb	-1.83	-0.03	-0.04	88.50	0.943	93.80
NIST1632c_(01/3/10)_5ppb	-1.94	-0.06	-0.03	81.00	0.864	93.80
NIST1632c_(08/12/09)_4.7 ppb	-1.89	-0.01	-0.03	89.35	0.953	93.80
NIST1632c_(07/10/09)_5ppb	-1.82	-0.01	-0.05	85.20	0.908	93.80
NIST1632c: average of 6	**-1.86**	**-0.03**	**-0.04**	**87.45**	**0.93**	93.80
NIST1632c: 1SD	**0.05**	**0.02**	**0.01**	**4.59**	**0.05**	
NIST1632c: 2SD	**0.11**	**0.04**	**0.02**	**9.19**	**0.10**	

Note: Hg isotopic values for each combustion of NIST 1632c represent the pooled average of three (n = 3) analyses acquired over the course of one analytical session by MC-ICP-MS.