

Heavy Metal Accumulation in Hot Water Tanks in a Region Experiencing Coal Waste Pollution and Comparison Between Regional Water Systems

Andrew Wigginton · Stephanie McSpirit ·
C. Dewayne Sims

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Abstract In 2000, a coal slurry impoundment failure in Martin County, Kentucky, caused concerns about contaminants entering municipal water supplies. Water samples taken from impacted and reference area hot water tanks often exceeded US EPA drinking water guidelines. Concentrations of As, Cd, Cr, Cu, Fe, Mn, and Pb had maxima of 119; 51.9; 154; 170,000; 976,000; 8,710; and 12,700 µg/L, respectively. Significantly different metal accumulation between counties indicated this procedure's utility for assessing long-term municipal water quality. Correlations between metal concentrations were strong and consistent for As, Ba, Cd, Cr, Co, and Fe indicating that some metals accumulate proportionally with others.

Keywords Coal slurry · Heavy metals · Drinking water · Correlations between metal concentrations

In 2000, a coal waste impoundment breach in Martin County, KY, USA released over 300 million gallons of coal sludge and black water into area creeks and eastern KY waterways. Local residents were unsatisfied with

environmental impact assessments submitted by state agencies and private companies as they were conducted by research firms under subcontract with the responsible coal company (McSpirit et al. 2006).

In 2005, through efforts by area citizens and the KY State Environmental Quality Commission, an act was passed by the Kentucky General Assembly to release \$150,000 of the natural resource damage settlement for an independent assessment of the long-term impacts of sludge spill on the public water system with citizen oversight (Kentucky Legislature 2005. Conference Budget Report HB 267. <http://www.lrc.ky.gov/budget/05rs/50f.pdf>).

Hot water tanks may indicate previous contamination from the water supply. Since sediment and precipitates accumulate in the tanks from the moment of installation, they may indicate what metals were distributed with the water supply. Stout and Papillo (Well water quality in the vicinity of a coal slurry impoundment near Williamson, West Virginia. Prepared in response to: Questions from citizens attending the 15 January 2004 training session of the Coal Impoundment Location and Warning System, Delbarton, WV. Wheeling Jesuit University, Wheeling, WV, USA) found that iron and lead were concentrated in a hot water heater 1,179 times and 11.75 times higher than the source well water, respectively. Arsenic was not detected in the source water, but concentrated to 150 µg/L in the hot water tank, 15 times greater than the US EPA drinking water standard (2003).

Uranium accumulated in hot water tanks from long-term, naturally occurring sources in well water in South Carolina, USA. Concentrations of this metal were lower in water passing through hot water tanks than in source water, indicating that the metal was being stored in the tanks. However, when the source water was remediated reducing uranium concentrations, levels in water passing

A. Wigginton (✉)
Department of Biology, University of Kentucky,
101 T.H. Morgan Building, Lexington, KY 40506, USA
e-mail: ajwigg0@uky.edu

S. McSpirit
Department of Anthropology, Sociology, and Social Work,
Eastern Kentucky University, 108 Keith Building, Richmond,
KY 40475, USA

C. D. Sims
Gateway Area Development District, University of Kentucky,
110 Lake Park Dr, Morehead, KY 40351, USA

through hot water tanks were higher than in the source water, indicating uranium remobilization (DeVol and Woodruff 2004).

The purpose of our research was to examine whether there had been any long-term human health exposures to heavy metal pollutants derived from coal slurry releases via the county public water supply. Hot water tanks were sampled as they were expected to integrate metal availability in source water over time. These tanks also were assessed as a means of comparing long-term water quality between public water systems.

Materials and Methods

Metals were selected for analysis based on their prevalence in coal slurry. They included mercury, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese and selenium (Booth et al. 1999; Goodarzi 2002; Huggins 2002; Wagner and Hlatshwayo 2005). Calcium also was analyzed because high calcium levels may accompany high levels of heavy metals (Stout, Ben. 4 January 2006. Email correspondence).

Members of Supporting Appalachia's Vital Environment (SAVE), a local environmental organization, helped recruit potential participants into our study. In addition to single-family homes, hot water tanks from stores, schools, government buildings, and other establishments were tested. Fifty-five samples were taken in Martin County during September and October 2005. Additional samples were collected from Somerset, Pulaski County, KY, USA ($n = 30$) in October 2005 and Berea, Madison County, KY, USA ($n = 33$) during December 2005. These were selected as reference locales based upon the ease of sampling, similarity in size of the three counties' water treatment plants, and a desire to represent typical communities in Eastern Kentucky. To assess whether the metal observed to accumulate in hot water tanks resulted from unusually high levels of metal in the source water, 16 additional samples were taken from the cold-water tap of some Martin County participants.

In Martin County, sample collection was conducted by teams consisting of one to three Eastern Kentucky University (EKU) personnel and one member of SAVE or another local resident to act as guide/community liaison. Participants were provided with an informational sheet describing the study and a request for a signature of consent. Information was collected about the hot water tank, regarding water usage, flushing of tank, age of home (or establishment), and years in residence. Global Positioning System (GPS) coordinates were also recorded. Full anonymity and confidentiality of households and other establishments was maintained for all data obtained.

New polyethylene (PE) bottles were used to collect samples directly from the drain valve of water heaters or cold water taps. After collection, sample bottles were placed in plastic, resealable bags and kept on ice until they were acidified using trace metal grade nitric acid (HNO_3 ; US EPA 2005). Chain of custody forms were maintained by all parties handling sample bottles. Most sample analysis was conducted by Severn Trent Laboratories (STL), St Louis, Missouri, USA, a National Environmental Laboratory Accreditation Program (NELAP) certified analytical laboratory using US EPA (2005) standard methods for inductively coupled plasma with mass spectrometry (ICP-MS) analysis for most metals (Method 6020) and cold vapor atomic absorption spectrometry (CVAAS) to measure mercury (Method 7470A). Some additional Hg samples were analyzed at the Environmental Research and Training Laboratory (ERTL) at the University of Kentucky using CVAAS methods developed by the American Public Health Association (APHA 2000). The 16 cold tap water samples were analyzed at the Ecotoxicology and Environmental Assessment Laboratory (EEAL), also at the University of Kentucky, using methods developed by the APHA (2000).

Basic descriptive statistics were calculated for each metal. These included: identification of median and maximum values, and calculation of the mean and standard error. Additionally, one-way analysis of variance (ANOVA) was run to detect differences between metal concentrations in the three counties. If a difference was detected, Scheffe's test was used to assess its significance. As some measurements for certain metals were below the reporting limit (BRL), a modification of US EPA methods were used in analysis (1996). For each metal, except Hg, ANOVAs and Scheffe's tests were conducted twice, once with BRLs set to half of the reporting limit (RL) and again with the BRLs set to zero. This was done to ensure that the significance of results was neither under, nor over estimated. The concentrations of each metal were regressed against the concentrations for every other metal to determine if any of them may accumulate together.

Results and Discussion

Results for median, maximum, and mean metal concentrations with standard error and percentage of samples from each county exceeding US EPA limits such as maximum contaminant levels (MCL), action levels (AL) or non-enforceable secondary water standards, are reported in Table 1 (US EPA 2003). Reporting limits varied from 0.2 $\mu\text{g/L}$ for Hg to 6,250 $\mu\text{g/L}$ for Ca (Table 2). No US EPA limits have been established for either Ca or Co. Barium, Hg and Se did not exceed US. EPA limits in

Table 1 Number of samples taken (n), median, mean, and maximum metal concentrations ($\mu\text{g/L}$) with standard error (SE) and percentage of samples over US EPA limits (OL) for each metal tested in each county

Metal	County	N	Median	Mean	Maximum	SE	OL
As 10 $\mu\text{g/L}^a$	Martin	55	5.00	6.11	32.8	0.718	10%
	Pulaski	30	5.00	20.0	119	5.61	30%
	Madison	33	5.00	9.92	58.9	2.20	18%
Ba 2 mg/L^a	Martin	55	89.2	137	909	19.6	0%
	Pulaski	30	50.7	105	731	25.9	0%
	Madison	33	33.0	123	649	32	0%
Ca none ^b	Martin	55	53,700	79,600	1,050,000	19,300	n/a
	Pulaski	30	26,500	42,700	197,000	8,160	n/a
	Madison	33	46,900	114,000	714,000	29,000	n/a
Cd 5 $\mu\text{g/L}^a$	Martin	55	0.250	1.49	51.9	0.941	3%
	Pulaski	30	0.570	2.51	31.7	1.09	13%
	Madison	33	0.280	0.919	9.20	0.34	3%
Co none ^b	Martin	55	6.70	32.0	341	8.35	n/a
	Pulaski	30	4.65	33.5	354	13.7	n/a
	Madison	33	4.30	10.1	49.3	2.21	n/a
Cr 100 $\mu\text{g/L}^a$	Martin	55	7.60	13.1	50.0	1.88	0%
	Pulaski	30	7.50	18.6	134	4.87	3%
	Madison	33	13.6	15.4	50.1	1.78	0%
Cu 1.3 mg/L^c	Martin	55	307	4,600	116,000	2,300	16%
	Pulaski	30	4,530	27,700	141,000	34,100	77%
	Madison	33	1,170	16,800	170,000	7,220	42%
Fe 300 $\mu\text{g/L}^d$	Martin	56	1,360	21,400	713,000	13,400	78%
	Pulaski	30	10,900	79,600	976,000	34,100	87%
	Madison	33	1,270	5,530	42,800	1,930	64%
Hg 2 $\mu\text{g/L}^a$	Martin	52	0.00	0.007	0.370	0.007	0%
	Pulaski	11	0.00	0.080	0.430	0.041	0%
	Madison	33	0.00	0.003	0.065	0.000	0%
Mn 50 $\mu\text{g/L}^d$	Martin	55	267	1,030	7,010	234	62%
	Pulaski	30	317	1,490	8,710	423	86%
	Madison	33	140	336	5,110	153	73%
Pb 15 $\mu\text{g/L}^c$	Martin	55	27.7	123	1,910	46.2	77%
	Pulaski	30	320	1,610	12,700	582	86%
	Madison	33	42.4	337	2,240	102	70%
Se 50 $\mu\text{g/L}^a$	Martin	54	2.50	2.09	2.50	0.086	0%
	Pulaski	30	2.50	2.42	3.30	0.071	0%
	Madison	33	2.50	1.88	2.50	0.131	0%

^a US EPA Maximum Contaminant Level (MCL)^b No US EPA standards have been established for this element^c US EPA Action Level (AL)^d US EPA non-enforceable secondary drinking water standard

samples from any county. More than 60% of Fe, Mn, and Pb samples from all counties exceeded US EPA guidelines (Table 1). In fact, levels of Pb averaged 8.24, 22.5, and 108 times the U.S. EPA AL in Martin, Madison and Pulaski Counties, respectively. Copper and Ca also tended to accumulate at high levels. A few As and Cd samples from

each county exceeded US EPA MCLs, and one Cr sample from Pulaski County exceeded the MCL.

Average concentrations of several metals varied significantly between counties (Table 2). ANOVA and Scheffe's test indicated that As, Ca, Fe, Mn, and Pb average values were significantly higher ($p \leq 0.05$) in Pulaski County than

Table 2 Comparison of average metal concentrations in hot water tanks from Madison (Mad), Martin (Mar), and Pulaski (Pul) counties using ANOVA and Scheffe's test

Metal	ANOVA		Scheffe's test	
	BRL = 1/2	BRL = 0	BRL = 1/2	BRL = 0
As	$p = 0.002$	$p = 0.001$	Pul > Mar	Pul > Mar
Ba	$p = 0.668$	$p = 0.668$	No difference	No difference
Ca	$p = 0.097$	$p = 0.097$	No difference	No difference
Cd	$p = 0.539$	$p = 0.553$	No difference	No difference
Cr	$p = 0.382$	$p = 0.006$	No difference	Pul > Mar
Co	$p = 0.166$	$p = 0.168$	No difference	No difference
Cu	$p = 0.006$	$p = 0.006$	Pul > Mar	Pul > Mar
Fe	$p = 0.030$	$p = 0.030$	Pul > Mar	Pul > Mar
Hg	Not done	$p = 0.001$	Not done	Pul > Mar and Mad
Mn	$p = 0.031$	$p = 0.031$	Pul > Mad	Pul > Mad
Pb	$p < 0.001$	$p < 0.001$	Pul > Mar and Mad	Pul > Mar and Mad
Se	$p = 0.003$	$p = 0.966$	No difference	Pul > Mad

All tests were done twice, once with below reporting limit (BRL) values set to zero and once with BRL values set to half the reporting limit
Reporting limit: As = 10 µg/L; Ba = 5.0–62.5 µg/L; Ca = 500–6,250 µg/L; Cd = 0.5 µg/L; Cr = 10–100 µg/L; Co, Mn, Se = 5.0–50 µg/L; Fe = 3.0–500 µg/L; Hg = 0.2–0.5 µg/L; Pb = 3.0–37.5 µg/L

Scheffe's test indicates significant differences in average metal concentration between counties at $p \leq 0.05$

Table 3 Correlations found between the accumulations of various metals from public water systems ($n = 124$)

Metal	County		
	Martin	Pulaski	Madison
As	Ba, Co, Cu, Pb	Ba, Cr, Cu	Ba, Cd, Cu, Cr, Co, Fe
Ba	As, Ca, Cr, Mn	As, Ca, Cr, Cu	As, Cd, Ca, Cr, Co, Fe
Cd	Co, Cu, Fe, Pb, Mn	Co, Fe, Pb, Se	As, Ba, Cr, Co, Fe
Ca	Ba, Mn	Ba	As, Ba, Cu
Cr	Ba, Co, Mn	As, Ba, Co, Cu	As, Ba, Cd, Co, Fe
Co	As, Cd, Cr, Cu, Fe, Pb, Mn	Cd, Cr, Cu, Pb	As, Ba, Cd, Cr, Fe
Cu	As, Cd, Co, Fe, Pb, Mn	As, Ba, Cr, Co	Ca, Mn
Fe	Cd, Co, Cu, Pb, Mn	Cd, Pb, Mn, Se	As, Ba, Cd, Cr, Co
Pb	As, Cd, Co, Cu, Fe, Mn	Cd, Co, Fe	–
Mn	Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb	Fe	Cu
Se	–	Cd, Fe	–

Italics indicates that the metals indicated correlate in two counties, while bold indicates correlation in all three counties

Martin and/or Madison Counties when BRL values were set to zero and when set to half the RL. These tests also indicated that Cr, Hg, and Se average values were significantly higher ($p \leq 0.05$) in Pulaski County compared to Martin and/or Madison Counties when BRL values were set to zero.

Correlations between accumulated metal levels were especially strong and consistent for As, Ba, Cd, Cr, Co, and Fe (Table 3). In fact, these metals possessed significant Pearson correlation coefficients ($p < 0.05$) across all three county data sets. Similar relationships have been noted by others for various metals in groundwater (Bundschuh et al. 2004; Silliman et al. 2007). Given these correlations, if local communities or environmental groups use inexpensive, single indicator test kits to monitor ground water, they may

infer the possible presence of a broad suite of elements from the occurrence of a few particular metals. This may allow them to decide where and when more expensive, definitive analytical testing should be conducted.

High concentrations of several metals of human health concern were measured in many hot water tanks. However, no clear relationship was observed between accumulation in the hot water tank and metal available in the source water, as sampled from the cold-water tap. Samples taken from 16 locations' cold water taps, the point in the home upon which US EPA MCLs were based, did not show any metal concentrations above their respective MCLs (US EPA 2003). These included several locations with high levels of As or Pb accumulation in the hot water tank. It

seems that either hot water tanks are able to concentrate metals from source water very effectively [e.g., from levels below the MCL to levels well above the MCL as noted by Stout and Papillo (Well water quality in the vicinity of a coal slurry impoundment near Williamson, West Virginia. 2004)] or the source water formerly contained more metals. County water treatment plant annual reports do not indicate any high levels of metal contamination in the past.

Additionally, some of the accumulated Cu, Fe, and Pb could be derived from public water distribution system pipes or on-site plumbing rather than source water.

It is obvious that hot water tanks sometimes accumulated considerable quantities of heavy metals. In general, Pulaski County possessed a larger proportion of hot water tanks with higher quantities of metals. For 10 of the 12 metals analyzed, Pulaski County had the highest mean values, up to 8 of which were significantly (Table 2; Scheffe's test, $p < 0.05$) higher than Martin and/or Madison Counties, perhaps indicating that Pulaski County had lower quality source water than Martin County. Madison County may have possessed the best water quality source water as average values for 7 of 12 metals were higher in Martin County than Madison County. The only metal that was higher in Madison County than either Main or Pulaski Counties was Ca, the most benign metal studied. These results also indicate that sampling hot water tanks may provide a convenient way to compare the long-term quality of the water produced by different treatment plants. Assuming that sample groups are comparable, a water system that deposits fewer impurities into the hot water tanks of its customers has likely been producing higher quality water over a long period of time.

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