

Report for 2003KY18B: Occurrence and Distribution of Mercury in Mammoth Cave National Park - Phase II

- Conference Proceedings:
 - Berryman, Gretchen E., Sreedevi Dawadi, and Cathleen J. Webb, 2004, Occurrence and distribution of mercury in Mammoth Cave National Park, in Proceedings of the Kentucky Water Resources Annual Symposium, Kentucky Water Resources Research Institute, Lexington, Kentucky, 71-72.

Report Follows

Problem and Research Objectives

Atmospheric deposition of mercury from power plants is currently of great concern throughout the country and is slated for increased regulation in the future. Coal-fired power plants were the largest unregulated source of mercury emissions in the United States prior to 2005, accounting for one-third of all anthropogenic mercury releases to the atmosphere. There are 18 existing coal-burning power plants in Kentucky and 6 proposed constructions or expansions in the Commonwealth of Kentucky since October 1999 to meet a growing national demand for electricity. A significant increase in atmospheric deposition of mercury at Mammoth Cave National Park (MCNP) is anticipated. Addition of more mercury emission sources in the region will increase the probability that MCNP may be impacted by a larger geographical distribution of coal-fired power plants. Kentucky's power plants generate approximately nine x 10⁹ kg of ash per year. The Peabody Thoroughbred Power Plant is one of the proposed new power plants and is slated for construction at a site 74 km west of MCNP. If built, this plant will be the fourth largest emitter of mercury in Kentucky and is expected to emit over 190 kg of mercury, over 6 x 10⁶ kg /year of NO_x (maximum 30-day rolling average of 0.08 lbs/MMBTU) and 11 x 10⁶ kg/year of SO_x (maximum 0.167 lbs/MMBTU per each unit based on a 30-day rolling average and maximum 24-hour block average of 0.410 lbs/MMBTU) per the final Kentucky Division for Air Quality permit dated October 11, 2002. There is little current data that can be used to predict the potential impact on MCNP and the karst ecosystem. Determination of mercury levels in MCNP and the factors that affect mercury levels and distribution is critical.

The specific objectives of this research project are to: (1) establish the extent, occurrence, distribution, and speciation of mercury in groundwater, surface water and sediments in Mammoth Cave National Park, including storm events, (2) examine the bioaccumulation and ecological impacts of mercury in surface, subsurface, and aquatic organisms at the Park, (3) investigate the fate and transport characteristics of mercury in a karst aquifer system, and (4) determine the TMDL of mercury at the Park.

Methodology

Approximately 60 mL samples of unfiltered water were transported to Materials Characterization Center, Western Kentucky University for total Hg analysis. Sample preparation included transferring 30 mL of the sample to a 50 mL container and adding 7.5 mL of 33% v/v HCl and 1 mL 0.1N KBr/KBrO₃. Samples were then diluted to 50 mL with ultra-high DI water. The concentration of mercury in water samples was determined by PS Analytical fluorescence spectrometry.

Sediment samples of 25-30 grams were oven-dried for 24 hours to remove excess water. The samples were then homogenized and prepared for analysis by drying the homogenized samples in a 105°C oven overnight. A 1.000 g sample was transferred to a sample tube and 1.0 mL water and 3 to 4 aluminum oxide anti-bump granules were added. Approximately 12 mL 33% HCl and 4 mL 70% HNO₃ (aqua regia) were run down the side of the tube carefully. The sample was heated at 140°C for 20 minutes, followed by an addition of 5 mL of water. The sample was then gently refluxed for an additional 10 minutes. After heating, it was diluted with water to 100 mL and filtered using Whatman 541 filter paper. Finally, 10 mL of the filtered aqua regia extract was pipetted and diluted with water to 100 mL and analyzed for total mercury.

Water and sediment samples were digested using EPA methods 245.1 and 245.5. The concentrations of total mercury were analyzed by EPA method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Absorption Spectrometry (CVAAS). This method consists of three essential steps: oxidation of Hg species to reactive mercury (Hg^{2+}), reduction of Hg^{2+} to elemental mercury (Hg^0), and detection of Hg^0 by CVAAS.

Principal Findings and Significance

Mercury concentrations in upstream and downstream water sample locations sampled monthly from July 2002 through February 2005 are shown in Figure 1. Mercury levels are evenly distributed throughout the upstream and downstream portions of the river. Mercury levels in water are low (5-13 ppt) since mercury preferentially binds to sediments and organic matter. Samples taken from Buffalo Spring Creek (BSBC) and Big Spring (BSBS) sites showed higher levels of Hg in water. Statistical analysis using unpaired t-test was performed to determine the p value. Analysis compared mercury levels at all the sampling sites and indicated that the p values are greater than 0.05. Therefore, variations in mercury concentrations at all the sampling sites are statistically insignificant.

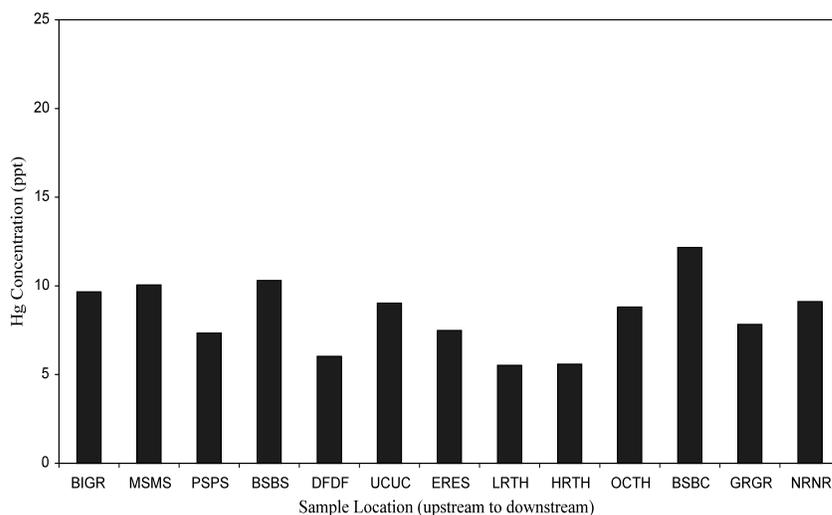


Figure 1. The average mercury concentration in each water sample location sampled monthly from July 2002-February 2005.

The sediments were collected seasonally as weather and river water levels permitted. Over the sampling period, the average mercury concentration at all of the sample sites ranged from 15-70 ppb. A rough correlation was observed between mercury levels in the water and mercury in the sediment. The sample location BSBC had the highest levels of mercury in both water and sediment. Mercury levels in sediments varied more widely from location to location than in water and are on the average 33,987 times higher.

To date, biological samples have been collected from freshwater drum, large mouth bass, *M. Salmoides*, Asiatic clam, *Cirbicula fluminea*, mayflies and bats. The concentrations of Hg are shown in Table 1. The 0.6 ppm Hg level found in the muscle of the Large Mouth Bass illustrates the potential threat of bioaccumulation of mercury in the food chain. The 0.233 ppm Hg concentration in the muscle of the freshwater Drum demonstrates biomagnification because

these fish are long-lived bottom feeders. Observed levels of mercury in fish and clam samples are comparable to values observed in other studies.

Sample Name	May Flies	Drum Liver	Drum Muscle	Large Mouth Bass Liver	Large Mouth Bass Muscle	Asiatic Clam
Hg (mg/kg) ppm	0.0025	0.2030	0.2330	0.2300	0.6000	0.0520

Table 1. Mercury concentrations in biological samples collected at the Park.

Hair samples from adult male bats of five different species captured at Long Cave, MCNP were analyzed for mercury (Table 2). These species have bioaccumulated significant levels of mercury with *Pipistrellus subflavus* having the highest Hg concentration. Mercury in the range of 3-4 ppm was detected in hair samples from two endangered mammals, Gray bat (*Myotis grisescens*) and Indiana bat (*Myotis sodalis*).

Species (<i>Scientific Name</i>)	Sample Composition (Adult Males)	Hg (ppm)
Indiana Bat (<i>Myotis sodalis</i>)	6	3.82
Gray Bat (<i>Myotis grisescens</i>)	5	4.20
Big Brown Bat (<i>Eptesicus fuscus</i>)	9	5.00
Eastern Pipistrelle (<i>Pipistrellus subflavus</i>)	8	6.60
Little Brown Bat (<i>Myotis lucifugus</i>)	7	4.90
Little Brown Bat (<i>Myotis lucifugus</i>) (Duplicate)	7	4.10

Table 2. Mercury concentrations in the fur of adult male bats of 5 different species.

Batch tests were performed to determine if limestone sequesters mercury and acts as a potential sink for mercury removal. Two sizes of Kentucky limestone (< 0.5 mm and 1-2 mm) were examined to see if limestone is efficient in removing mercury. Samples of the limestone were placed in labeled round-bottom flasks. Blanks with 100 mL of de-ionized water also were prepared. Batch experiments were conducted with 50 ppt inorganic mercury. The initial pH of the standard mercury solution was adjusted to 8 using sodium hydroxide. All samples were secured to a wrist shaker and agitated for 48 hours. The samples were allowed to settle for 30 minutes. The final solutions were filtered with a 0.45 μm filter. The pH and conductivity of the final solutions were measured. Standard, blank and duplicate samples were run for each batch test for QA-QC. The samples were analyzed for total mercury. The results showed that varying amounts of limestone of two different sizes removed 97% of mercury. Therefore, it can be concluded that limestone indeed has the potential to act as a major sink for inorganic Hg.