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Mercury concentrations in wetlands associated with coal-fired power plants

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Abstract There have been contradictory reports of the relative proportion of mercury from coal-fired power plants that deposits locally. Our objective was to determine any local effect of coal-fired power plants on total mercury concentrations in wetland sediment and tadpole samples. Four power plants and 45 wetlands were selected for study. Total mercury concentrations were determined in 75 sediment samples (range: 8–82 ng/g dry weight) and 100 bullfrog (*Lithobates catesbeiana*) and green frog (*Lithobates clamitans*) tadpoles (range: 5–318 ng/g wet weight). Tadpole and sediment total mercury did not significantly vary by power plant or distance from the plant. Only one power plant had a significantly greater concentration of total mercury in sediment downwind compared to upwind wetlands. A similar (but non-significant) trend was found for tadpole total mercury surrounding the same plant. Tadpole total mercury was negatively correlated with both tadpole weight and total length. Tadpole and sediment total mercury concentrations were not significantly correlated with one another. The results of the current study suggest that coal-fired power plants are not significantly affecting mercury concentrations in surrounding wetlands.

Keywords Mercury · Wetlands · Tadpoles · Coal-fired power plants

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Introduction

Mercury is a toxic trace element, and the methylated (MeHg) form is known to cause adverse effects to wildlife and aquatic organisms. Methylmercury can have neurotoxic, immunotoxic, and developmental effects on birds and mammals; and top consumers may be at elevated risk due to biomagnifications of MeHg through the food web. However, the effects of MeHg on reptiles and amphibians have not been well studied (Wolfe et al. 1998).

Wetlands are sites of active MeHg production and are a large source of MeHg in freshwater (St. Louis et al. 1994). Specifically, wetlands are mercury sinks in which inorganic mercury is methylated, and after a disturbance (e.g., flooding), can release mercury to the surrounding watershed (Zillioux et al. 1993). Sediment is the main reservoir for mercury in freshwater ecosystems (Ullrich et al. 2001), therefore sediment analysis can be an efficient way to monitor mercury in aquatic ecosystems (Vogel and Chovanec 1992).

Amphibians can be used as bioindicators because they often live in aquatic and terrestrial habitats, are numerous and readily available, and are easy to work with in lab and field settings (Burger and Snodgrass 2001). Larval amphibian exposure to mercury has been studied more extensively than adult exposure (Boening 2000; Gerstenberger and Pearson 2002). Tadpoles are susceptible to mercury exposure (Chang et al. 1974) and provide an important link in pollution biomagnification (Unrine et al. 2007). Amphibians absorb contaminants dissolved in aquatic systems through their skin, making them especially susceptible to chemical contamination (Smith et al. 2007). Tadpoles also ingest sediment while foraging, exposing them to contaminants to which organisms in the water column are not exposed. *Rana pipiens* tadpoles experience

mortality at MeHg concentrations of 50 μg/L or higher (Chang et al. 1974). Tadpoles exposed to these concentrations developed symptoms of mercury poisoning including irritative movements, abnormal swimming postures, and difficulty breathing. Inorganic mercury toxicity can vary among larval amphibian species, with LC_{50} values ranging from as low as 1.3 up to 100 μg/L (Birge et al. 1979; De Zwart and Sloof 1987; Khangarot and Ray 1987; Khangarot et al. 1985). This variability in mercury toxicity is likely a product of species differences, rather than inter-laboratory differences. Many of the values reported in the range of 1.3–100 μg/L come from a single source (Birge et al. 1979) and encompass the extremes and median values.

Total mercury concentrations (THg) in tadpoles collected in the field, vary by location. Southern leopard frog (*Rana sphenocephala*) tadpoles captured in wetlands near the Savannah River in South Carolina all had THg concentrations below the 0.2 ng/g (ww) detection limit (Burger and Snodgrass 2001). Unrine et al. (2005) collected leopard frog tadpoles from different wetlands in the same general area as Burger and Snodgrass (2001), and reported that tadpole (minus gut content) THg concentrations ranged from 99 to 308 ng/g (dw). Bank et al. (2007) reported THg concentrations (wet weight) of 19.1 ng/g for bullfrog (*Lithobates catesbeiana*) and 25.1 ng/g for green frog (*Lithobates clamitans*) tadpoles collected in Acadia National Park, Maine. Tadpoles (multiple species) collected from a historically polluted site in Texas had concentrations below a 500 ng/g detection limit (Clark et al. 1998). A metals-polluted delta in Greece contained *Rana ridibunda* tadpoles with THg concentrations ranging from below detection limits to 560 ng/g (Goutner and Furness 1997). Hylid tadpoles collected from the same location had THg concentrations that ranged from 560 to 1,490 ng/g (dw).

Coal-fired power plants (CFPPs) are the largest single source of Hg^{2+} released into the environment (Keeler et al. 2006; Nichols 1997). Coal-fired power plants release mercury in three primary forms: elemental (Hg^0), inorganic (Hg^{2+}), and particulate (Hg^p). The extended lifetime of elemental mercury (Hg^0) in the atmosphere has created elevated levels of mercury even in areas free of anthropogenic sources of mercury (Fitzgerald et al. 1998). Although most mercury emissions deposit far from the source, local deposition occurs. Studies reporting the proportion of mercury deposited at local, regional, and global scales have produced conflicting results (e.g., Keeler et al. 2006; Seigneur et al. 2003). A global modeling study of power plant emissions found that Hg^{2+} is deposited quickly, whereas Hg^0 has a longer lifespan (i.e., time until deposition) in the atmosphere (Dastoor and Larocque 2004).

The objectives of the current study were to measure total mercury in wetlands associated with CFPPs and identify potential differences between upwind and downwind deposition. We hypothesized that THg concentration in downwind wetlands would increase with increasing distance from the plants studied.

Materials and methods

Study sites

Four CFPPs in southern Illinois were selected for this study: Baldwin, Newton, Joppa and Southern Illinois Power Cooperative (SIPC) plants (Table 1). The US Fish and Wildlife Service's National Wetlands Inventory (USFWS 2009) was used to identify wetlands upwind and downwind of the CFPPs. Twelve wetlands were selected, on average, for each plant ($n = 45$). Three wetlands were upwind and within 5 km of the plant, and the remaining nine wetlands were divided into groups of three each, with one group located 3–5, 8–10, and 13–15 km downwind of the plant. The wetlands used in this study were primarily man-made farm ponds, which were semi-permanent and dried for short periods or during periods of drought. Natural wetlands ($n = 3$) also were used when they were available at the selected distances and large enough to contain individual tadpoles with enough mass for mercury analysis. Prevailing wind direction was determined for each CFPP from data collected by the National Climatic Data Center (1998). Average mercury emissions from each plant were taken from the Environmental Protection Agency's Toxics Release Inventory (USEPA 2008).

Sample collection

During May and June of 2007, three sediment samples of approximately 100 g each were collected from each wetland. A 5 cm stainless steel core auger was inserted in the sediment within 1 m of the shoreline, and at a 0–20° angle to prevent spillage of the sample. Sampling locations were selected using a random numbers generator (i.e., bootstrap) to obtain random distances to sample along the shoreline after approaching the wetland (e.g., between 5 and 20 m). With each sediment sample collected, temperature (±0.01°C) was measured in overlying water (≤0.5 m) using field thermometers. Once overlying detritus was removed from sediment samples using a stainless steel spatula, sediments were placed into glass jars and transported on ice to the Cooperative Wildlife Research Laboratory, Southern Illinois University, Carbondale and stored at −20°C. In the laboratory, oxidation-reduction potential (redox) and pH were determined for each sediment sample. Redox potential

Table 1 Mercury emitted from coal-fired power plants in southern Illinois during May and June 2007

Power plant	Owner	Location	Coordinates	Mercury emitted (kg/year)	Prevailing wind direction
Baldwin	Dynegy midwest, Inc.	Randolph co., Il	38°12′9.0″N 89°51′20.0″W	200	WNW
Joppa	Electric energy, Inc.	Massac co., Il	37°12′34.0″N 88°51′31.0″W	140	S
Newton	Ameren corporation	Jasper co., Il	38°56′13.0″N 88°16′40.0″W	140	S
SIPC	Southern Illinois electric company	Williamson co., Il	37°12′34.0″N 88°51′31.0″W	26	S

Emissions are an average of 2000–2006 reported emissions (USEPA 2008). Prevailing wind direction is from the National Climatic Data Center (1998)

was ascertained with a redox probe (Oakton ORP tester, Fisher Scientific, Pittsburgh, Pennsylvania, USA). The pH of a sample was deduced by drying an aliquot of the sediment sample overnight at 60°C, and then mixing with distilled/deionized water in a 1:1 solution. The solution was vigorously stirred by hand four times within 30 min and allowed to settle for 1 h at which time pH was determined using pH testing strips (EMD Chemicals Inc., Gibbstown, New Jersey, USA).

At each pond, tadpoles were captured opportunistically with dipnets in shallow water near the shore. It was rare that tadpoles were found at the location of randomized sediment samples, so in the case of larger ponds, tadpoles were occasionally collected a significant distance away from sediment sampling sites (e.g., >5 m). Tadpoles were identified to species and age was determined as Gosner stage (Gosner 1960). Either bullfrog (*Lithobates catesbeiana*) or green frog (*Lithobates clamitans*) tadpoles were collected from each pond when available. Mass (±0.1 g) and total length (±0.1 mm) was measured for each tadpole, followed by euthanasia with tricaine methanesulfonate (MS-222, 450 mg/L; Sigma–Aldrich, St. Louis, Missouri, USA). Following euthanasia, tadpoles were placed in a Whirl-pak container (Nasco Sampling Products Inc., Fort Atkinson, Wisconsin, USA) and transported on ice to the laboratory.

Chemical analysis

Sediment samples were taken to the Illinois Sustainable Technology Center (1 Hazelwood Dr, Champaign Illinois, 61820) for mercury analysis. Sediment samples were analyzed following EPA method 3051A (USEPA 2007). All sediment samples were dried in a fume hood at room temperature for 1–3 days until a constant weight was achieved. About 10 mL of double distilled HNO_3 and 1 mL of 30% (w/v) H_20_2 were added to a 0.250 g aliquot sediment sample. The sample was then placed in a microwave (Ethos EX microwave extraction labstation, Milestone Inc., Sheldon, Connecticut, USA) and heated for 10 min at 170°C and 30 m at 180°C. Samples were removed from the microwave after the temperature was allowed to cool to 32°C. Samples were then filtered with ashless filter paper to remove any particulates in the digested sample. The filter was placed in a funnel and, after samples were added, the filter was rinsed three times with 10% HNO_3, and three times with distilled/deionized water. After filtration the sample was diluted to 50 mL and separated into two 25 mL subsamples. About 250 μL of trace-metal grade HCl and 250 μL of BrCl solution were added to both subsamples, and each was diluted to 50 mL. To remove oxidizers, 250 μL of hydroxylamine was added to subsamples immediately prior to analysis. Subsamples were analyzed using a PSA Millennium Merlin cold vapor atomic fluorescence spectrometer (CVAFS) mercury analyzer (P.S. Analytical Inc, Deerfield Beach, Florida, USA). The average of the two subsamples was used as the concentration of the sample.

Tadpole samples were either homogenized or digested whole. Whole tadpole analysis was performed to confirm that homogenizing tadpoles did not disrupt (THg) concentrations during analysis. An aliquot of homogenate (0.2–0.4 g), or a whole tadpole, was digested with 4 mL of concentrated nitric acid in a 60°C water bath. The sample was diluted with 2 mL of 1% HCl, mercury was oxidized to the Hg^{2+} form with 15 mL $KMnO_4$ and 8 mL $K_2S_2O_8$, and 6 mL of NaCl–NH_2OH–HCl was added to remove oxidizers. Samples were analyzed using a Hydra AF CVAFS mercury analyzer (Teledyne-Leeman labs, Hudson, New Hampshire, USA), following EPA method 245.7 (USEPA 2005).

Quality control

Laboratory reagent blanks, laboratory fortified blanks, and replicate samples were analyzed with every batch of 20

samples. Batches were re-analyzed if laboratory fortified blanks exceeded ±20% of their expected values. A quad study was performed on the tadpole tissue matrix. Eight 0.5 g aliquots of a homogenized sample were digested and analyzed, and four aliquots were spiked with 0.05 g of 300 µg/L mercury standard. Mercury content was measured and the percent recovery was calculated by subtracting the concentration of the unspiked samples from the spiked samples. A matrix spike and a Montana Soil Standard Reference Material 2710 (certified value = 32 µg/g, National Institute of Technology, Cuyahoga Falls, Ohio, USA) were analyzed with each sediment batch. The method detection limit was 1 µg/L for both sediment and tadpole THg.

Statistical analysis

Statistical analyses were performed using SAS version 9.1 (SAS Institute Cary, North Carolina, USA) with significance set at $\alpha = 0.05$. Normality of THg concentrations was tested using a Shapiro-Wilks test. Data that were not normally distributed were log transformed and reanalyzed. Pond means were used for all analyses to avoid problems associated with pseudoreplication. An analysis of covariance was used to test spatial distributions of sediment and tadpole mercury, with distance from the plant representing the independent variable, and power plants used as covariates. Differences in THg among distances for each plant were determined using a one-way analysis of variance. Pearson Correlation matrices were used to evaluate relationships between mercury concentrations and characteristic variables (e.g., tadpole total length, sediment pH). To correct for the number of comparisons made in correlation matrices, a Bonferroni corrected α was calculated for sediment and tadpole variables by dividing $\alpha = 0.05$ by the number of correlations in the matrix. Correlation was also used to analyze the relationship between THg in sediment layers and tadpoles. All means are reported with ±1 SE.

Results

Sediment

A total of 95 sediment samples were collected from 45 ponds (Table 2). Sampling locations in some ponds contained an organic/detritus layer too deep to obtain a core sediment sample with the auger. A total of 75 sediment samples were analyzed for THg. Each pond ($n = 38$) had at least one sediment sample analyzed and each pond in which tadpoles were collected had multiple sediment samples analyzed if multiple sediment samples were collected from that pond. Water temperature at sampling locations ranged from 22.3 to 38.2°C (mean = 29.75 ± 0.6°C), pH ranged from 4.5 to 6.5 (mean = 5.33 ± 0.01), and redox potential ranged from −21.9 mV to +158.4 mV (mean = 78.7 ± 5.8 mV).

The mean sediment THg concentration was 36.7 ± 1.9 ng/g dry weight (dw) and ranged from 8 to 82 ng/g dw. The correlation matrix for sediment samples contained 15 variables, so the Bonferroni corrected $\alpha = 0.003$. Sediment THg concentrations were not correlated with pH ($r = -0.19$, $p = 0.16$), temperature of overlying water ($r = -0.22$, $p = 0.14$), wetland area ($r = 0.08$, $p = 0.65$), or CFPP mercury emissions ($r = 0.38$, $p = 0.61$). Sediment THg concentrations were not associated with redox potential ($r = 0.23$, $p = 0.07$), but redox potential was positively correlated with pH ($r = -0.85$, $p < 0.001$). Sediment THg did not vary by sediment texture ($F_{6, 65} = 0.97$, $p = 0.45$).

Overall sediment THg concentrations did not vary by power plant ($F_{3, 37} = 2.05$, $p = 0.13$) or distance from the CFPP ($F_{1, 37} = 0.91$, $p = 0.35$), and there was no interaction between plant and distance ($F_{3, 37} = 0.87$, $p = 0.47$, Fig. 1). Because samples sizes were small, and THg did not vary by distance from the plant, all ponds downwind were pooled and compared to upwind ponds for all power plants. Evaluation of sediment THg concentrations at each CFPP indicated that concentrations in downwind wetlands did not differ from concentrations in upwind wetlands at the Baldwin, Joppa, or SIPC power plants (all $p > 0.31$, Fig. 2). However, THg was significantly greater in sediments downwind from Newton power plant compared to upwind sediments ($F_{1, 7} = 11.4$, $p = 0.02$, Fig. 2).

Tadpoles

A total of 72 bullfrog and 86 green frog tadpoles were collected from 29 wetlands (Table 2). A minimum of three tadpoles were taken from most ponds ($n = 27$), there were two ponds in which <3 tadpoles were found and captured. Of the 158 tadpoles collected, 100 were analyzed for THg (≤5 tadpoles per pond). Of these, 71 were homogenized, and 29 were digested as whole tadpoles. Tadpoles ranged from Gosner stage 25–41 (20.2–138.6 mm total length) and from 0.06 to 35.1 g wet weight (ww). Only three bullfrog tadpoles had weights >5 g and one had a total length >100 mm. Seven green frog tadpoles were >5 g, five of which had a total length >100 mm. Six bullfrogs (12% of 49) and 19 green frogs (36.5% of 52) were greater than Gosner stage 25, the rest of the tadpoles were Gosner stage 25.

Bullfrog THg concentrations ranged from 16 to 197 ng/g ww with a mean of 56.8 ± 6.6 ng/g for homogenized tadpoles, and ranged from 13 to 318 ng/g ww with a mean of 86.5 ± 24.8 ng/g for whole tadpoles. Green frog THg concentrations ranged from 5 to 157 ng/g ww with a mean of 46.5 ± 5.9 ng/g for homogenized tadpoles, and ranged

Table 2 Number of sediment samples and tadpoles, and water temperature (°C) and pH from ponds sampled around four coal-fired power plants during May and June 2007

CFPP	Distance	Pond #	Sediment samples	Mean temperature	Mean pH	Green frog	Bullfrog
Baldwin	3–5 km up	1	1	28.3	5.9	4	1
		2	3	25.1	5.3	6	–[a]
		3	1	–	5.6	–	–
	3–5 km down	1	3	25.4	5.6	–	–
		2	3	26.4	5.5	5	–
		3	2	25.5	6	–	–
	8–10 km down	1	–	25.2	–	3	4
		2	3	25.7	5.8	–	3
		3	–	24.8	–	–	–
	13–15 km down	1	1	–	–	–	–
		2	1	–	6.8	–	–
		3	2	–	5	6	–
SIPC	3–5 km up	1	1	23.6	4.5	–	–
		2	2	30.5	4.8	7	–
		3	1	30.8	4.7	–	–
	3–5 km down	1	2	30.9	5	4	–
		2	3	33.6	5.6	–	5
		3	2	25.5	6.5	–	–
	8–10 km down	1	1	33.1	4.8	–	7
		2	2	31	5.1	–	8
		3	3	33.6	5.3	–	5
	13–15 km down	1	3	27.4	5.6	4	–
		2	3	28.6	5.5	–	–
		3	1	27.2	4.5	6	–
Joppa	3–5 km up	1	–	25.1	–	–	–
		2	3	33	6	–	–
	3–5 km down	1	3	30.8	5.1	–	5
		2	2	34.3	5.2	3	–
		3	1	31.6	4.4	–	–
	8–10 km down	1	2	28.2	4.6	1	4
		2	–	31.6	–	–	–
		3	2	37	5	–	–
	13–15 km down	1	–	23	–	–	–
		2	2	29.9	5.8	–	1
		3	1	32.2	6.2	–	–
Newton	3–5 km up	1	3	30.5	6.2	6	–
		2	1	34.1	4.5	2	–
	3–5 km down	1	3	33	4.8	–	6
		2	–	33.3	–	–	–
	8–10 km down	1	2	31.9	4.8	–	6
		2	1	30.5	4.9	–	–
		3	1	28.6	4.5	–	–
	13–15 km down	1	1	22.8	5.2	–	–
		2	1	–	–	–	–
		3	2	27.5	6.5	4	–

[a] None collected

from 12.3 to 66.0 ng/g ww with a mean of 28.2 ± 3.7 ng/g for whole tadpoles. Percent moisture was determined for 49 of 100 bullfrog and green frog tadpoles and ranged from 66 to 91% with a mean of 83.1 ± 0.7. Total mercury (dw) for the 49 tadpoles analyzed for percent moisture ranged from 93 to 1,155 (ng/g) with a mean of 312 ± 29.7 (ng/g dw).

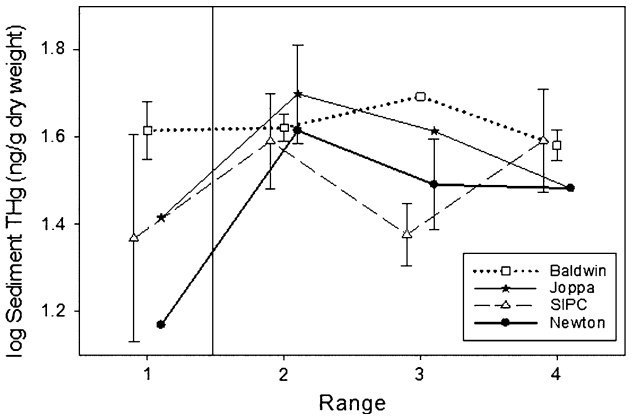

Fig. 1 Total mercury concentrations (ng/g dw ± SE) in sediments collected from ponds surrounding Baldwin, Newton, Joppa, and SIPC power plants in Illinois, May and June 2007. Range 1 = 3–5 km upwind, 2 = 3–5 km downwind, 3 = 8–10 km downwind, and 4 = 13–15 km downwind. Points without *error bars* indicate a range in which <3 ponds were analyzed for THg. The *vertical line* represents a graphical location of the CFPP

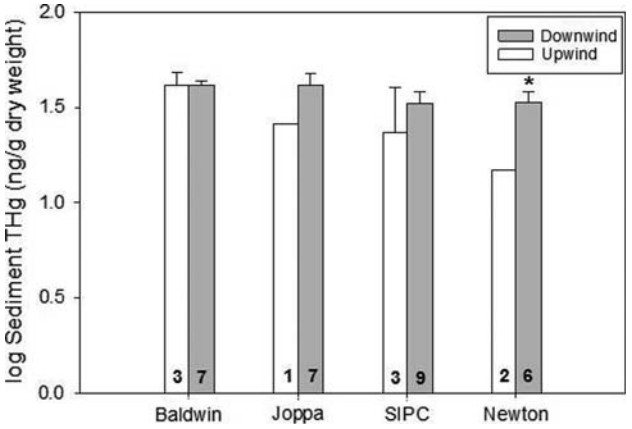

Fig. 2 Mean THg concentrations (ng/g dw ± SE) measured in sediment samples collected downwind and upwind from power plants in Illinois, May and June 2007. An *asterisk* indicates a significant difference from upwind wetlands ($\alpha = 0.05$). *Numbers* indicate the number of ponds analyzed for each group

Percent moisture could not be calculated for all tadpoles because some were analyzed whole, and there was not enough tissue available from some homogenized tadpoles for this measurement.

Mercury concentrations in whole and homogenized tadpoles did not differ in bullfrogs ($F_{1,46} = 0.76$, $p = 0.39$) or green frogs ($F_{1,49} = 2.24$, $p = 0.14$) therefore, whole and homogenized tadpoles were combined for statistical analysis. Bullfrog tadpoles had significantly higher THg concentrations than green frog tadpoles ($p = 0.004$). However, when species were split into groups by length (<50, 50–100, and >100 mm) and the groups were used as a covariate, no significant difference occurred between species ($p = 0.689$) and they were combined for further statistical analysis. Mass ($r = -0.39$, $p < 0.001$) and length ($r = -0.47$, $p < 0.001$) were significantly negatively correlated with tadpole THg; Gosner stage ($r = -0.25$, $p = 0.012$) tadpoles were marginally negatively correlated with THg (Bonferroni corrected $\alpha = 0.008$). Mass, length, and Gosner stage were strongly positively correlated with each other (all $r > 0.59$, all $p < 0.001$). There was no significant correlation between THg concentration in sediment and tadpoles overall ($r = 0.02$, $p = 0.93$), or when power plants were evaluated separately ($p > 0.13$).

Overall tadpole THg concentrations did not vary by power plant ($F_{3,21} = 2.28$, $p = 0.13$) or distance from the CFPP ($F_{1,21} = 1.18$, $p = 0.35$), and there was no interaction between plant and distance ($F_{3,21} = 1.74$, $p = 0.47$, Fig. 3). Due to small sample sizes for each pond and because THg concentrations in tadpoles did not vary by distance, data from ponds downwind were combined and compared to data from ponds upwind. Over all plants, there were no significant differences between upwind and downwind ponds ($p > 0.12$, Fig. 4).

Quality control

Laboratory-fortified spikes had a mean percent recovery of 104.2 ± 5.1 and 84 ± 3.6 for tadpoles and sediment, respectively. Replicate samples had a mean relative percent difference of 22.3 ± 12.4 for tadpoles, and 16.8 ± 7.1 for sediment. Mercury recovered from laboratory reagent blanks (0–5 ng/g for tadpoles, 1.6–7.2 ng/g for sediment) was subtracted from tadpole and sediment concentrations.

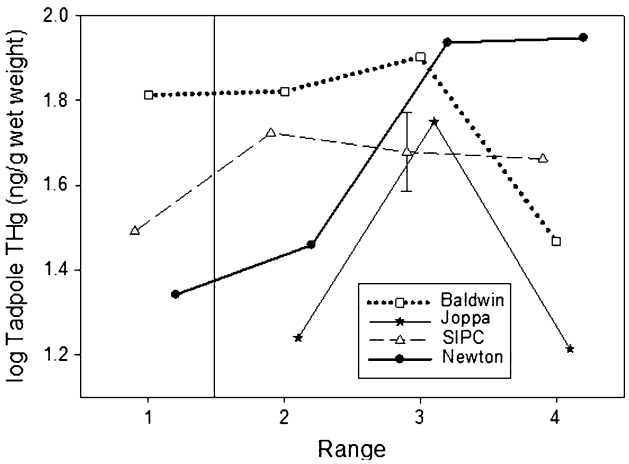

Fig. 3 Total mercury concentrations (ng/g ww ± SE) in tadpoles collected from wetlands surrounding Baldwin, Newton, Joppa, and SIPC power plants in Illinois, May and June 2007. Range 1 = 3–5 km upwind, 2 = 3–5 km downwind, 3 = 8–10 km downwind, and 4 = 13–15 km downwind. Points without *error bars* indicate a range in which <3 ponds were analyzed for THg. The *vertical line* represents a graphical location of the CFPP

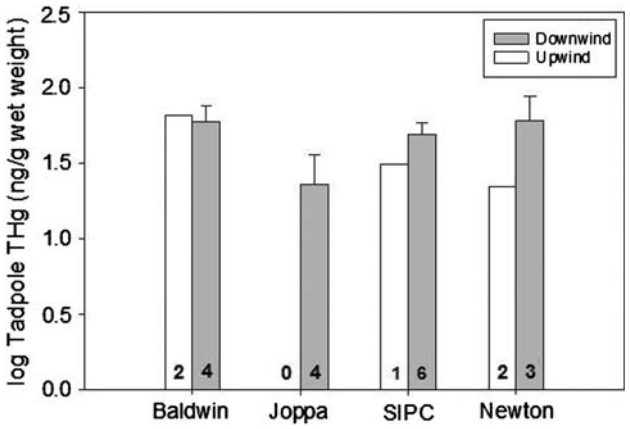

Fig. 4 Mean THg concentrations (ng/g dw ± SE) measured in tadpole samples collected downwind and upwind from power plants in Illinois, May and June 2007. *Numbers* indicate the number of ponds analyzed for each group. The zero for upwind wetlands at Joppa indicates that no tadpoles were captured in ponds upwind of Joppa power plant

The mean percent recovery in the matrix spikes was 105.7 ± 0.3 for tadpoles and 96 ± 6.9 for sediment spikes. The mean recovery of the Montana Soil Standard Reference material was 84% ± 4.5.

Discussion

Newton power plant was the only CFPP in which significantly greater sediment concentrations of THg were measured downwind of the plant compared to upwind; however, tadpoles collected from downwind sites did not have significantly greater THg concentrations compared to those collected from upwind sites for any of the CFPPs studied. In the current study, THg in sediment and tadpoles does not appear to be affected by either power plant mercury output or distance for the Baldwin, Joppa, and SIPC CFPPs. In the current study, tadpole THg concentrations were not significantly correlated with sediment THg and did not vary by power plant or distance from the plant. All sediment and tadpole THg concentrations were below sediment quality guidelines (0.18 μg/g for Hg, MacDonald et al. 2000) and limits of concern (500 ng/g THg ww) established by Health Canada (2007), respectively. However, Unrine et al. (2004) reported that southern leopard frogs with THg body burdens of 200–400 ng/g (dw) had longer tail reabsorption times, increased mortality, and a high incidence of malformation (50–60%). Correcting for dw, 32 of the 49 tadpoles analyzed for percent moisture in the current study would have body burdens (ranging from 200 to 1154 ng/g) similar to (and above) that reported by Unrine et al. (2004) to be associated with adverse effects. In the current study, it was not possible to evaluate these factors, except that no malformations were observed.

Sediment mercury

Sediment mercury concentrations in the current study (8.1–80.2 ng/g dw) are in the range of previously reported mercury concentrations for sediments and soils in the United States (US). Mercury from lakes throughout the US ranged from 30 to 330 ng/g (Menounou and Presley 2003; Huggett et al. 2001; Cooper and Gillespie 2001; Sorensen et al. 1990; He et al. 2007) and varied greatly across regions. No previously published studies of mercury content in wetlands or ponds in Illinois were found. A study of Illinois soils reported an average of 33 ng/g THg in samples taken throughout the state (Dreher and Follmer 2004), and Anderson and Smith (1977) reported a mean sediment THg concentration of 49 ng/g in Lake Sangchris surrounding the Kincaid power plant in Illinois. Both of these results are similar to the mean (36.7 ng/g dw) measured in sediments collected from ponds in the current study.

Tadpole mercury

Tadpole mercury concentrations differed from previous reports of mercury concentrations in tadpoles. Bank et al. (2007) reported lower THg concentrations in green (25.1 ng/g ww) and bullfrog (19.1 ng/g ww) tadpoles in Acadia National Park than the means for both species in the current study. Burger and Snodgrass (2001) reported that all tadpoles collected from three reference and one remediated pond on the Savannah River in western South Carolina had THg concentrations below the 0.200 ng/g detection limit. That study was performed in three ponds considered "reference" with no past history of contamination and in 1 remediated pond. Interestingly, southern leopard frog tadpoles collected from the same area (but different wetlands) averaged 184 ng/g dw THg (MeHg + Hg^{2+}) in the carcass and 1,275 ng/g in the gut contents that were removed prior to carcass analysis (Unrine et al. 2005). If the data from both tissues were combined, the mean (1,459 ng/g dw) would be much greater than the mean (312 ng/g dw) and the largest concentration (1,154 ng/g dw) of THg measured in tadpoles in the current study for which dry weight concentrations could be determined (49 of 100).

There have been conflicting reports of correlations between mercury and body size variables in amphibians. In the current study, tadpole THg concentrations were negatively correlated with body mass and length. Similarly, Burger and Snodgrass (2001) reported either no relationship or a negative relationship between tail/body THg concentration ratios and tadpole body weight. Total

mercury concentrations in northern two-lined salamanders (*Eurycea bislineata bislineata*) were either not correlated or negatively correlated with body size characteristics (Bank et al. 2005). Tissue THg from adult bullfrogs collected from a wetland in Nevada were also not correlated with size or length (Gerstenberger and Pearson 2002). In contrast, Bank et al. (2007) reported positive correlations between total length, snout-vent length, and tail length with whole body THg concentrations. However, the variability in length reported by Bank et al. (2007) was lower than in the current study, in which there was a large variation in tadpole length, weight, and Gosner stage. Many of the larger tadpoles in the current study were also in later Gosner stages (37–41). Tadpoles may change their feeding habits as they approach metamorphosis, and may stop eating entirely. This could cause a decrease in body burden as mercury stored in the individual is metabolized. In addition, during metamorphosis, tail reabsorption may cause stored mercury to be metabolized and excreted from the body. Both of these scenarios could account for the negative relationship determined between tadpole THg and body size variables (length, weight, and Gosner stage).

There were no significant differences in THg concentrations between size-adjusted bullfrog and green frog tadpoles in the current study. Very little is known regarding tadpole feeding ecology (Altig et al. 2007), and bullfrog and green frog tadpoles are no exception. However, considering that both bullfrog and green frog tadpoles would belong to the same feeding guild outlined by Altig (1989), and because they are so closely related, it is likely that they are feeding on similar items, which may explain the lack of significant difference observed in Hg concentrations between these two species.

Mercury patterns around CFPPs

The results of the current study are similar to previous studies that reported no relationship between distance from a power plant and the concentration of mercury found in soils or aquatic organisms. Anderson and Smith (1977) reported that THg sediment concentrations in Lake Sangchris near the Kincaid power plant in central Illinois were 37 ng/g prior to plant operation and 49 ng/g 6–7 years after plant operation. However, particulate matter deposition (μg Hg/g dust) did not differ between upwind (4.8 km, 0.65 μg Hg/g) and downwind (4.8 km, 0.71 μg Hg/g; 9.6 km, 0.75 μg Hg/g) sites. In addition, largemouth bass (*Micropterus salmoides*) collected from Lake Sangchris had lower mercury concentrations (mean = 0.07 mg/kg) than fish from Decatur, Otter, and Shelbyville lakes (means = 0.16, 0.24, and 0.56 mg/kg, respectively) >40 km away from the plant.

Crockett and Kinnison (1979) investigated mercury concentrations in soil surrounding a large CFPP in northeast Arizona. They reported that soil THg concentrations did not differ significantly in any direction up to 30 km from the plant. Similarly, Wangen and Williams (1978) analyzed soils downwind of a CFPP for multiple trace elements (including mercury) and found that chemical concentrations did not increase as a function of distance for all chemicals tested. However, Dreher and Follmer (2004) reported increased concentrations of THg in surface soil samples (mean 33 ± 20 μg/kg soil) collected throughout the state of Illinois, in comparison to THg concentrations in the C horizon of the soil core ("background concentrations", 20 ± 9 ng/g). The authors reported contradictory results for soil samples located near CFPPs. Out of 101 soil cores collected throughout Illinois, seven samples located within 50 km of CFPPs contained elevated mercury concentrations (>2× background concentrations); however, in nine different soil samples located near CFPPs, the authors reported no elevated concentrations of mercury.

Seigneur et al. (2003) reported that local deposition contributed 11–21% of the THg deposited in three locations in New York, while sources throughout the contiguous United States contributed 25–49%, and natural sources contributed 16–24%. The authors stated that comparing their results to reported deposition from the Mercury Deposition Network suggests that local and regional deposition is currently overestimated. This differs from a study of mercury sources in Ohio, in which the authors conclude that mercury deposition is dominated by local and regional sources of coal combustion (Keeler et al. 2006). The uncertainty associated with deposition models includes the lack of adequate data regarding: plume chemistry, deposition rates, kinetic data, and lack of deterministic product identification in the atmosphere (Lin et al. 2006). The local/regional/global impact of mercury may be specific to regions, as opposed to having a general pattern.

Many physical and biological factors can affect mercury cycling, methylation, and bioavailability. Organic matter, both in sediments and in the water column, will strongly affect mercury bioavailability. In sediments, Hg^{2+} and MeHg will be attracted to organic material (humic material) decreasing bioavailability to organisms (Hudson et al. 1994). Oxidation-reduction and pH conditions will affect Hg-humic complexes either releasing or storing metals depending on conditions. Metal sulfide complexes occur in sediments that are saturated with sulfides, and complexing with sulfides renders mercury unavailable for methylation (Du Laing et al. 2009). Low pH levels tend to facilitate the release of mercury from sediments, thus increasing bioavailability to organisms (Duarte et al. 1991). Many of the ponds in the current study had very low pH levels (<6.0) which may result in mercury being released from the sediment; however, no significant correlation between THg in sediment and pH was found. Mercury emissions from

soils can be very high (Rinklebe et al. 2009) and wetlands that are dry for much of the year, may emit Hg at a significant rate. Many of the ponds used in the current study were inundated for most of the year and were unlikely to lose an appreciable concentration of Hg due to emission.

Just as with cycling and bioavailability, several factors affect Hg methylation rates. Ullrich et al. (2001) provide an extensive review of this subject, and emphasized the importance of the following factors in methylation rates: species of microorganisms present, temperature, pH, percent of organic matter, redox conditions, and presence of sulfides. Sulfate-reducing bacteria are one of the primary sources of biotic mercury methylation in aquatic systems (Berman and Bartha 1986). Abiotic methylation does occur, but at a much lower frequency than biotic methylation. It has also been reported that mercury methylation increases with temperature and peaks in the summer when temperatures are highest (Hintelmann and Wilken 1995). As for pH, there are many possible routes for pH to affect mercury methylation rates, most of which result in indirect effects, including: low pH resulting in the release of heavy metals from sediments making them more available for organic and biological interactions, a positive correlation between pH and volatilization of Hg^0 lowering Hg^{2+} concentrations available for methylation, and low pH may increase sulfate concentrations which stimulates MeHg production (Ullrich et al. 2001). Similarly, concentrations of MeHg are greater in sediments with greater organic matter content and moisture, which is likely due to increased methylation rates from microbial activity (Davis et al. 1997), and methylation of mercury is greatest under anaerobic conditions (Compeau and Bartha 1985) largely because sulfate-reducing bacteria are anaerobic. It is important to note that redox conditions, pH, and organic matter will all significantly interact with each other, affecting mercury methylation.

Conclusions

With the exception of sediment concentrations associated with the Newton power plant, sediment and tadpole THg concentrations were not significantly greater in ponds located downwind compared to upwind of CFPPs studied, and no sediment or tadpole samples exceeded concentrations of concern (MacDonald et al. 2000; Health Canada 2007). This suggests that except for the Newton plant, CFPPs are not significantly affecting local mercury concentrations, which is consistent with results of previous studies (Crockett and Kinnison 1979; Pinkney et al. 1997). However, if wet weight data are converted to dry weight, 65% of the 49 tadpoles analyzed in the current study for percent moisture had body burdens equivalent to THg concentrations that caused increased mortality, malformations, and increased time to tail reabsorption in southern leopard frogs (Unrine et al. 2004). Tadpole THg concentrations were not significantly correlated with sediment THg, which is similar to the result reported previously for tadpoles and sediment collected from Acadia National Park, Maine (Bank et al. 2007). Little is known regarding how tadpoles acquire mercury (e.g., water, sediment, food), and additional research in toxicokinetics and toxicdynamics is needed. In addition, reports of tadpole MeHg:THg are few, and even less is known about amphibian metabolism and breakdown of MeHg. Finally, in some cases, sediment sampling sites and tadpole locations were far apart in large ponds. Sediment THg concentrations varied greatly within some ponds (e.g., 10–55 ng/g in a single pond) so it is possible that sediment THg concentrations were different in areas where tadpoles were collected. Given a randomized sediment sampling regime, this potential confounding factor cannot be resolved, and could contribute to a lack of correlation between tadpole and sediment THg.

There are potentially many confounding factors in determining the relationship between CFPPs and mercury contamination, including deposition of mercury from CFPPs located outside of the study area, municipal waste incineration, and oil refineries (Dreher and Follmer 2004). It is likely that prevailing wind direction alone may not be sufficient in determining the fate of inorganic mercury or particulate mercury from plumes. Similarly, there are many variables that affect the fate and bioavailability of mercury in aquatic systems (Ullrich et al. 2001). Future studies should integrate deposition variables with methylation characteristics and bioavailability to acquire a more complete understanding of mercury pollution from source to sinks, and to determine the impact of local, regional, and global sources of mercury.

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