

2011

Methylmercury in Mosquitoes: Impact of a Large Coal-fired Power Station in Central Ohio

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METHYLMERCURY IN MOSQUITOES: IMPACT OF A LARGE COAL-FIRED
POWER STATION IN CENTRAL OHIO

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

MATTHEW JOHN KONKLER
B.S., Muskingum University, 2008

2011
Wright State University

WRIGHT STATE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

September 19, 2011

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Matthew John Konkler ENTITLED Methylmercury in Mosquitoes: Impact of a Large Coal-Fired Power Station in Central Ohio BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Konkler, Matthew J. M.S., Department of Earth & Environmental Sciences, Wright State University, 2010. Methylmercury in Mosquitoes: Impact of a Large Coal-Fired Power Station in Central Ohio.

Emissions from coal-fired utilities are the major anthropogenic source of mercury (Hg) to the atmosphere. Because emitted Hg may be deposited near the source, there are concerns on levels of toxic monomethylmercury (MeHg) in local biota. We investigated the potential impact of a large Hg-emitting ($> 500 \text{ kg Hg y}^{-1}$) coal-fired power station on MeHg levels in mosquitoes near the Conesville power station in central Ohio.

Mosquitoes were sampled with CO₂-baited traps at 23 locations within a 60 km radius of the utility and at three reference sites distant from Hg combustion sources. MeHg in mosquitoes within a 30-km radius of the plant ($n = 12$) were comparable to those within a 30–60 km radius ($n = 11$) and the three control sites. This suggests that either little of the Hg emitted is deposited locally or near-source Hg deposition doesn't have a significant impact on MeHg in mosquitoes.

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Acknowledgments

I thank Mark Cohen for providing mercury emission data, Geraldine Nogaró for helpful manuscript reviews, Robbie Weller for help with sampling. Deepthi Nalluri and Dan Marsh assisted with sample preparation and analysis.

I. Introduction

Mercury (Hg) is a persistent and bioaccumulative toxin in the environment (Munthe et al., 2007). The primary toxicological concern related to Hg is accumulation in biota as the methylmercury (MeHg) species, which has deleterious health effects to wildlife (Scheuhammer et al., 2007) and humans (Grandjean, 2007; Mergler et al., 2007). Unlike complexes of inorganic mercury (Hg(II)), MeHg biomagnifies in food webs and concentrations increase with successive trophic transfers (Bloom, 1992; Watras and Bloom, 1992; Watras et al., 1998). This has resulted in humans and piscivorous wildlife being most susceptible to MeHg poisoning (Bloom, 1992; Mergler et al., 2007; Scheuhammer et al., 2007).

About two thirds of the Hg presently cycling in the environment is from anthropogenic sources (Fitzgerald et al., 2005; Fitzgerald and Lamborg, 2003; Mason et al., 1994), namely the combustion of fossil fuels (Pacyna et al., 2010). Coal-fired power plants are the largest anthropogenic source, accounting for about half of human Hg emissions (Pacyna et al., 2010). Coal-burning facilities emit Hg into the atmosphere in three major forms: elemental Hg (Hg^0), gaseous ionic Hg (reactive gaseous mercury or RGM), and particulate Hg (Hg_p ; Landis et al., 2002; Landis et al., 2004). Relative distributions of these three Hg species are variable and uncertain, although it is estimated that about 45% is as Hg^0 , 45% as RGM, and 10% as Hg_p (Pacyna et al., 2003). Differences in the speciation of emitted Hg species can influence the atmospheric residence time and transport. Of the three Hg species, Hg^0 has the longest atmospheric residence time of about a year (Lamborg et al., 2002), while RGM and Hg_p have residence times on the order of hours to days (Landis et al., 2002; Landis et al., 2004).

Hence, Hg^0 can be distributed globally, while RGM and Hg_p may be deposited within tens to hundreds of kilometers around a point source (Landis et al., 2002; Landis et al., 2004). Due to the brief atmospheric residence times of RGM and Hg_p , atmospheric Hg deposition may be increased near coal-fired power plants relative to fluxes at locations more distant from the source. Indeed, dry deposition of RGM can increase atmospheric fluxes by more than 50% near an emission source (Landis et al., 2004). Deposited Hg(II) can be readily methylated by microorganisms in water and aquatic sediments (Compeau and Bartha, 1985; Gilmour et al., 1992; Benoit et al., 2003), where the degree of MeHg production is influenced by Hg(II) availability and loadings (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2006; Fitzgerald et al., 2005). Studies in the northeast United States have suggested that increased levels of MeHg in biota are associated with proximity to local Hg emissions (Evers et al., 2007; Driscoll et al., 2007).

Recent research indicates a correlation between atmospheric Hg deposition and MeHg accumulation in aquatic food webs (Hammerschmidt and Fitzgerald, 2005, 2006b; Orihel et al, 2007; Harris et al., 2007). Such relationships suggest that if atmospheric Hg deposition were enhanced near an emission source, then one would expect a corresponding increase of MeHg in biota. It is poorly understood, however, to what degree 1) RGM and Hg_p emissions from coal-fired power plants increase atmospheric Hg deposition near the source, and 2) these fluxes affect the accumulation of MeHg in local biota. Hammerschmidt and Fitzgerald (2005) have suggested that adult mosquitoes (*Diptera: Culicidae*) may be useful bioindicators of atmospheric Hg deposition. Mosquitoes have aquatic life stages, including a larval phase during which they are suspected to accumulate most of their adult MeHg burden while feeding on

microorganisms and detritus (Merritt et al., 1992; Hammerschmidt and Fitzgerald, 2005), and they typically disperse to distances less than 10 km from their location of maturation to flying adults (Service, 1993). Accordingly, adult mosquitoes may be sensitive and site-specific biological indicators for examining the impact of near-source Hg deposition from coal-fired power plants on MeHg levels in local food webs.

II. Hypotheses

The objective of this research was to investigate the potential impact of Hg emissions from a coal-fired power plant on MeHg accumulation in nearby aquatic biota. This was investigated by examining MeHg levels in adult mosquitoes near a large coal-fired power plant in Conesville, Ohio. I hypothesize that 1) MeHg in mosquitoes would be elevated in the environs near the Conesville plant compared to reference locations and 2) mosquito MeHg will decrease with increasing distance from the facility, thereby reflecting differences in atmospheric Hg flux.

III. Methods

Mosquito Sampling. Adult female mosquitoes were sampled at 23 locations within a 60-km radius of the Conesville power plant in central Ohio between 17–24 July 2010, as well as three reference sites distant from known combustion sources of Hg (Figure 1). The Conesville utility was selected because, until recently, it was the largest Hg emitting coal-fired power plant in Ohio and among the top 15 in the United States, with over 600 kg of Hg emitted annually (personal communication, Dean Ponchak, Ohio Environmental Protection Agency). It also is distant (> 90 km) from other large Hg-emitting combustion sources. Mosquito sampling locations were focused around the

Conesville plant: 5 sites were within a 10-km radius, 7 between 10–30 km, and 11 between 30–60 km of the station. This sampling design was used to investigate 1) the potential areal extent of localized Hg deposition on MeHg bioaccumulation and 2) whether MeHg concentrations in mosquitoes vary with direction and distance from the Conesville station. The prevailing wind direction is 210° at the Zanesville, OH, airport (~ 40 km south of Conesville), with a mean wind speed of 8 km/h (Aug 2009–July 2010; NOAA, 2011). This suggests that Hg emissions from the plant travel predominately toward the northeast, which is where the relatively greatest degree of localized Hg deposition would be expected, if near-source deposition were to occur. All mosquito sampling locations were on wooded public lands, close to stagnant water, and in shaded damp environments. Rural central Ohio is characterized by forested and agricultural landscapes. Low-lying regions within these systems can trap and stagnate water, thereby providing suitable breeding conditions for mosquitoes. Mosquitoes also were sampled from three reference sites in southwest Ohio (Figure 1), which are characteristically similar to the sampling locations near Conesville but distant from large combustion source of Hg.

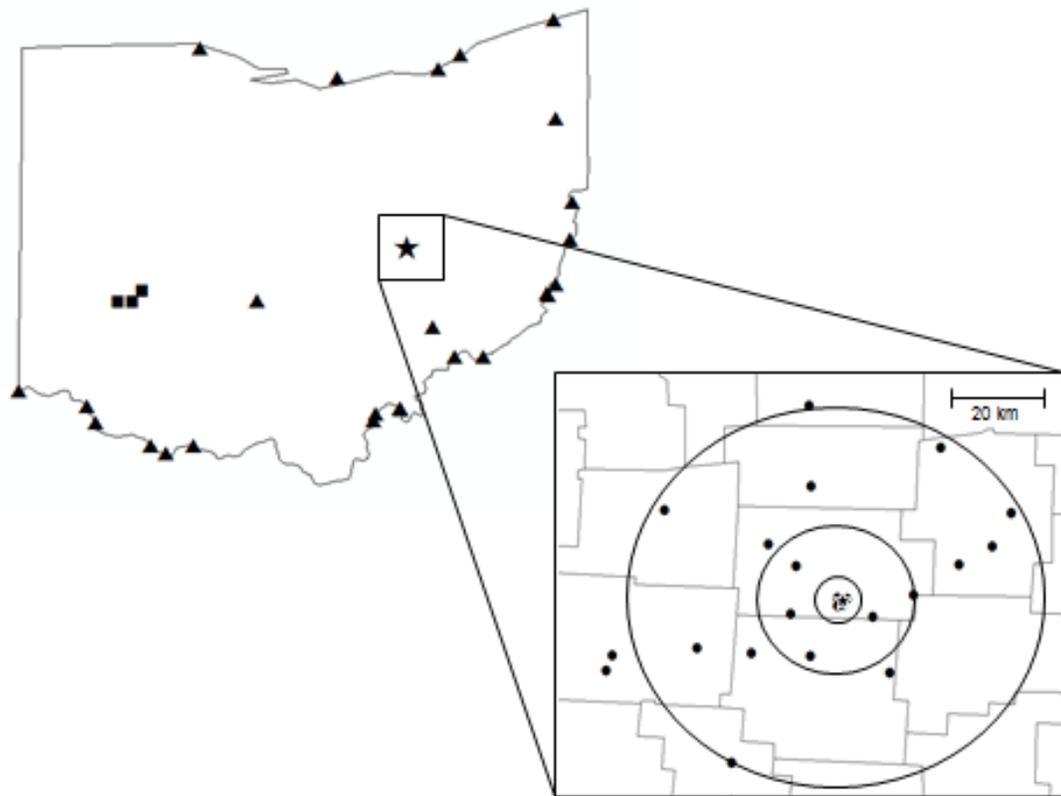


Figure 1. Mosquito sampling locations (filled circles) near the Conesville, Ohio, power station (star). Reference mosquito sampling locations are indicated with filled squares and other large-scale, coal burning facilities with filled triangles. Concentric circles around the power plant have 10-, 30-, and 60-km radii.

Host-seeking adult female mosquitoes were sampled with CO₂-baited traps that were set for 1–2 d prior to collection (Sudia and Chamberlain, 1962; Hammerschmidt and Fitzgerald, 2005). Mosquitoes were handled with trace-metal clean techniques, identified to genus level, and stored frozen (≤ -20 °C) until freeze drying. More than 90% of sampled mosquitoes were *Culex* sp.

Extraction and Analysis of MeHg and THg. Because a vast majority of the mosquitoes were of the same genus, samples were not divided to examine either genus- or species-level differences in Hg content, as done previously (Hammerschmidt and Fitzgerald, 2005). Subsamples (2–37 mg) of lyophilized, intact adult mosquitoes were weighed, counted, and digested with 3.5 mL of 4.57 M HNO₃ in a covered 60 °C water bath for 10–14 h (Hammerschmidt and Fitzgerald, 2005). This method of extraction releases MeHg and inorganic Hg from biological tissues into solution, and is effective with purge and trap techniques that derivatize MeHg with sodium tetraethylborate. MeHg in the digestates was measured by gas-chromatographic cold vapor atomic fluorescence spectrometry (CVAFS; Bloom, 1989; Tseng et al., 2004).

The accuracy of MeHg determinations was examined by analysis of 1) procedural blanks and calibration standards taken through the digestion and analysis process, 2) certified reference materials from the National Research Council of Canada (TORT-2 lobster hepatopancreas and DORM-3 fish protein), 3) analytical replicates, and 4) multiple subsamples of mosquitoes from the same collection. MeHg standards were calibrated versus a Hg(II) solution traceable to the U.S. National Institute of Standards and Technology (NIST). All analyses of the reference materials ($n = 12$ each of TORT-2

lobster hepatopancreas and DORM-3 fish protein) were within their certified ranges: mean measured concentrations of MeHg in TORT-2 were 156 ng/g (certified range = 139–165 ng g⁻¹) and 335 ng/g (certified range = 299–411 ng g⁻¹) in DORM-3. Analytical precision of MeHg determinations averaged 4.0% relative difference ($n = 28$). However, the agreement among multiple subsamples from the same collection averaged 30% relative standard deviation (RSD), which is considerably greater than the analytical precision and represents the heterogeneity of MeHg levels among mosquitoes in each sample (Hammerschmidt and Fitzgerald, 2005). Method detection limit (3σ) for MeHg was about 1 ng/g dry weight for a 10-mg subsample.

Digestates analyzed for MeHg also were used for determination of total Hg after treatment with a strong oxidant. Aliquots of digestates were diluted with reagent-grade water (nominal resistance > 18 M Ω -cm) and oxidized with bromine monochloride (BrCl; Hammerschmidt and Fitzgerald, 2005). Oxidized digestates were measured for total Hg by dual-gold (Au) amalgamation CVAFS (Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988). Total Hg analyses were calibrated with a Hg²⁺ solution traceable to the U.S. NIST. Recovery of known additions of Hg²⁺ from sample matrixes averaged 101% (range = 96–106%, $n = 8$) and, similar to MeHg in TORT-2 and DORM-3, all analyses of total Hg in these reference materials were within their certified ranges. The mean measured concentration of total Hg in TORT-2 was 267 ng/g dry weight ($n = 11$, certified range, 210–330 ng/g) and that in DORM-3 was 360 ng/g ($n = 11$, certified range, 322–442 ng/g). The analytical precision of total Hg determinations averaged 2.7% RSD and variability among subsamples from the same collection averaged 27% RSD, similar to

that for MeHg. Method detection limit (3σ) for total Hg was about 5 ng/g dry weight for a 10-mg subsample.

Trace Metal Analysis. Mosquitoes also were analyzed for three trace metals, nickel (Ni), lead (Pb), and vanadium (V), associated commonly with fossil fuel combustion. Aliquots of the digestates used for MeHg analysis were diluted with reagent-grade water, and Ni, Pb, and V were measured by inductively coupled plasma mass spectrometry (U.S. EPA, 2007). Analyses were calibrated with standards traceable to the U.S. NIST and accompanied by procedural blanks. Variability among subsamples from the same collection site averaged 30% RSD for Ni, 39% RSD for V, and 34% RSD for Pb, which is consistent with the variability observed for MeHg and total Hg. Method detection limits (3σ) were about 90 ng V/g, 65 ng Ni/g, and 10 ng Pb/g dry weight for a 10-mg subsample.

Statistical Analysis. Statistical analyses were conducted with commercially available software (Statistica 7) and without data transformation. Correlation analyses and one-way ANOVA were used to examine the effect of distance and direction from the power plant on MeHg and total metal concentrations in mosquitoes.

IV. Results and Discussion

Hg speciation in mosquitoes. Most of the Hg in mosquitoes was as MeHg (Figure 2). The average percentage of total Hg as MeHg (%MeHg) in sampled mosquitoes was $91 \pm 26\%$ (Figure 2), which is similar to ratios observed in other North American mosquitoes (mean = 92%; Hammerschmidt and Fitzgerald, 2005) and within the range of that in other aquatic invertebrates (Niamo, et al., 2000; Watras and Bloom,

1992; Tremblay, et al., 1998; Gorski, et al., 2003). The large fraction of total Hg as MeHg indicates that MeHg accumulates preferentially in mosquitoes compared to inorganic Hg complexes. The relatively high degree of variability in mosquito %MeHg is due largely to two samples that had the lowest MeHg concentrations and anomalously low %MeHg (Figure 2).

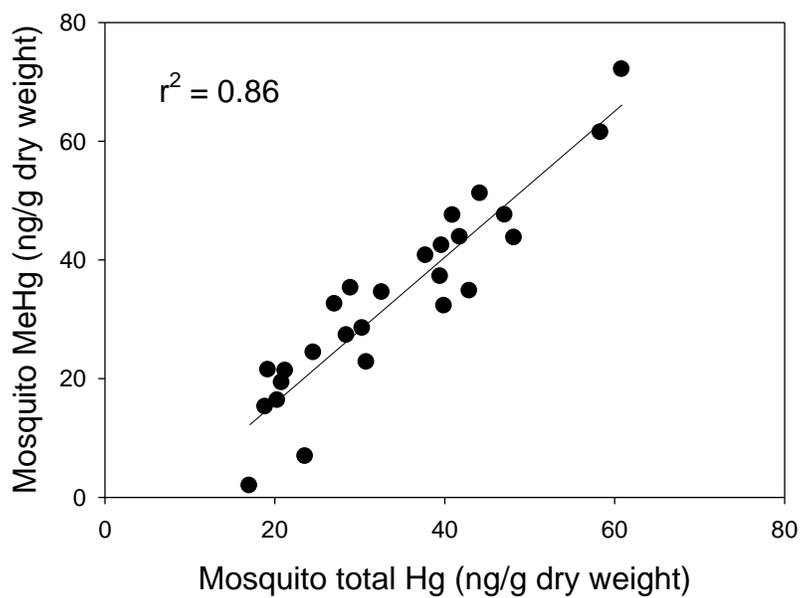


Figure 2. Relationship between MeHg and total Hg in adult mosquitoes sampled near the coal-fired power plant in Conesville, OH, and at three reference locations.

Mosquitoes can inhabit diverse aquatic ecosystems where they are exposed to varying biogeochemical factors that can affect MeHg production and accumulation. Sulfur chemistry, pH, organic matter, temperature, and larval diet/habits have all been linked to either Hg cycling and bioaccumulation by mosquitoes and other aquatic invertebrates (Hammerschmidt and Fitzgerald, 2005; Sackett et al., 2010). Mosquitoes also can disperse up to 40 km, which is species dependant and typically much less (≤ 10 km; Service, 1993), but demonstrates the geographical range one sampling location may encompass. Mosquitoes collected at a particular location, therefore, are an integrated sample of populations reared in diverse aquatic environments and exposed to various biogeochemical processes and loading of Hg. This natural variability is observed in the differences of MeHg concentrations among subsamples from a particular sampling location—the average variability was 30% RSD for MeHg and similar for the other metals. Differences among breeding habitats and food sources also may account for variation among subsamples, and MeHg concentrations can vary among mosquito species collected at the same location (Hammerschmidt and Fitzgerald, 2005). The duration of time spent in the larval life stage also may be important. These factors appear to be secondary compared to atmospheric Hg deposition when considering continental-scale variations of mosquito MeHg (Hammerschmidt and Fitzgerald, 2005).

Mosquitoes grow and develop during four aquatic larval stages referred to as instars, with each successive instar producing a larger larval mosquito. Mosquitoes do the majority of feeding as larvae, consuming plankton and detritus that also contain MeHg. The high percentage of total Hg as MeHg indicates that MeHg 1) accumulates

preferentially in mosquitoes relative to inorganic Hg complexes, and 2) biomagnifies during dietary trophic transfer to larval mosquitoes.

Distribution of MeHg in mosquitoes. MeHg in adult mosquitoes averaged 30 ± 17 ng/g dry weight and ranged from 2 to 72 ng/g among sampling locations near the Conesville power plant ($n = 23$ sites). These concentrations are within the range of those observed in adult mosquitoes at other North American locations (10–480 ng/g; Hammerschmidt and Fitzgerald, 2005, 2008). The mean concentration also is in relatively good agreement with that predicted from a linear relationship observed between mosquito MeHg and atmospheric Hg deposition. Among North American locations, mosquito MeHg (*MeHg*, ng/g dry weight) is related to wet atmospheric Hg deposition (*Hg*, $\mu\text{g}/\text{m}^2/\text{y}$; Hammerschmidt and Fitzgerald, 2005):

$$MeHg = -1.5 + 8.0[Hg] \quad (1)$$

Wet atmospheric fluxes of Hg near Conesville are estimated to be about $6.5 \mu\text{g}/\text{m}^2/\text{y}$, based on deposition measurements about 100 km south of the plant at the Athens (Ohio) Super Site in 2009 (MDN, 2011); annual deposition data for 2010 are incomplete. From this flux and eq. 1, mosquito MeHg levels would be predicted to average 51 ± 11 ng/g dry weight. The relatively good agreement between the mean measured MeHg level (30 ± 17 ng/g) and that predicted from wet atmospheric deposition suggests that MeHg bioaccumulation near the Conesville plant is not increased substantially relative to wet atmospheric Hg fluxes alone.

Mosquito MeHg was unrelated to distance from the Conesville power station (Figure 4). The mean concentration of MeHg in mosquitoes captured less than 10 km

from the station (29 ± 11 ng/g dry weight) was similar to the average levels in those 10–30 km (28 ± 17 ng/g) and 30–60 km from the plant (36 ± 18 ng/g; ANOVA, p -value = 0.6). MeHg levels in mosquitoes around Conesville are similar to those at three reference locations in southwest Ohio (mean = 41 ± 11 ng/g; ANOVA, p -value = 0.23). The absence of a decreasing trend of mosquito MeHg with increasing distance from the utility, in addition to comparability with the control sites, suggests that Hg emissions from the Conesville utility do not have a localized impact on MeHg levels in adult mosquitoes and, by extension, other aquatic organisms.

Concentrations of MeHg in mosquitoes also were unrelated to direction from the Conesville plant. The study area was divided into four quadrants, NE ($n = 7$), SE ($n = 2$), NW ($n = 6$), and SW ($n = 8$), to statistically evaluate the effect of direction on mosquito MeHg (Figures 3 & 4). The mean concentration of MeHg in captured mosquitoes was similar in each of the four quadrants (25 ± 13 ng/g dry weight in the NE quadrant, 41 ± 28 ng/g SE, 47 ± 22 ng/g NW, and 29 ± 10 ng/g SW; ANOVA, p -value = 0.26). The similarity of mosquito MeHg levels among quadrants, and especially the predominantly upwind (southwest) and downwind (northeast) quadrants, further suggests an absence of significant impact from the power station.

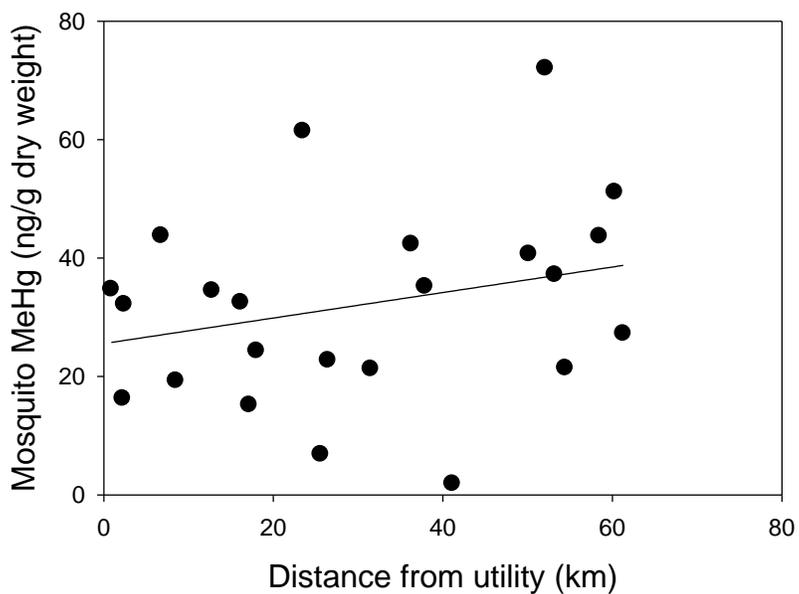


Figure 3. Variation of mosquito MeHg levels with distance from the Conesville, OH, power station (linear correlation p -value = 0.2; $n = 23$).

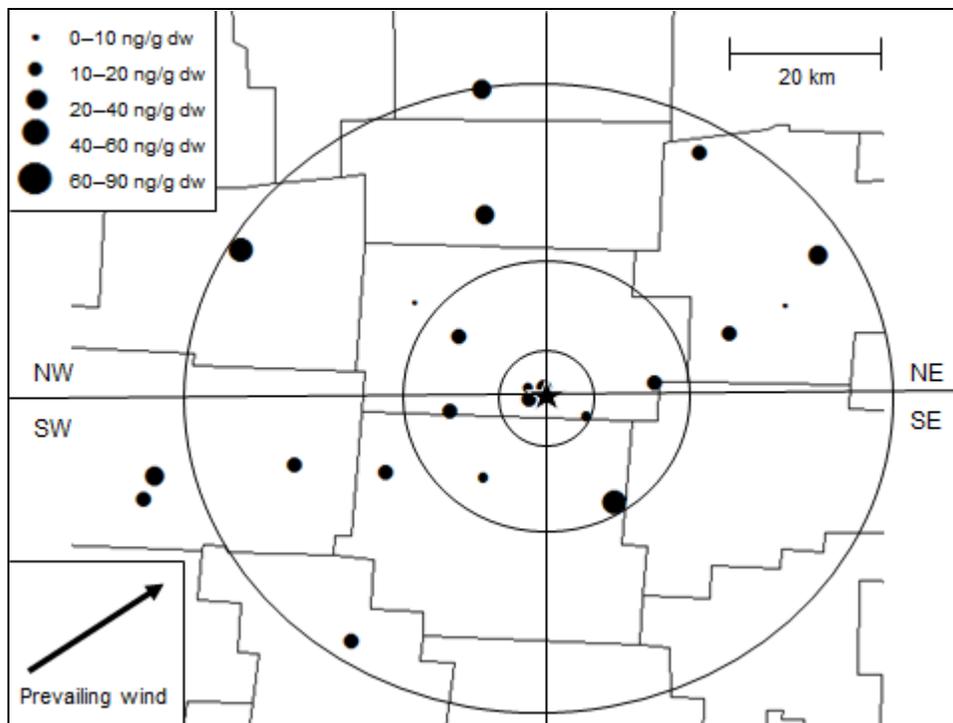


Figure 4. Spatial distribution of mosquito MeHg concentrations at locations around the Conesville, OH, power plant. Concentric circles around the power plant have 10-, 30-, and 60-km radii.

Loadings of inorganic Hg from atmospheric deposition and watershed inputs are a major control on MeHg production and bioaccumulation in aquatic ecosystems (Hammerschmidt and Fitzgerald, 2004, 2005, 2006a; Orihel et al., 2007; Harris et al., 2007). Inversely, MeHg levels in biota may be interpreted to reflect the relative degree of Hg loadings, with such an extension being most applicable within or among biogeochemically similar ecosystems and regions, such as the study area of this investigation. A lack of MeHg enrichment in mosquitoes near the Conesville utility suggests that either there is not enhanced Hg deposition near the plant, relative to geographically averaged wet atmospheric fluxes, or that localized deposition does not affect MeHg accumulation in resident biota.

The absence of detectable impact of the Conesville plant on mosquito MeHg is consistent with distributions of Ni, V, and Pb—three other metals associated commonly with fossil fuel combustion—in the same organisms. Concentrations of Ni (range =100–1100 ng/g dry weight), V (100–800 ng/g), and Pb (20–290 ng/g) in mosquitoes varied considerably among sampling locations and were not different from levels in mosquitoes at the reference sites (Ni = 400–600 ng/g; V = 410–700 ng/g; Pb = 43–100 ng/g). Moreover, concentrations of the three metals in mosquitoes were unrelated to either distance from the Conesville utility (p -values ≥ 0.24) or mosquito MeHg (p -values ≥ 0.59). These results suggest that potential emissions of Ni, V, and Pb from the Conesville power plant do not have a localized impact on levels of these metals in adult mosquitoes, which is comparable to observations for Hg and MeHg.

Studies with different biological indicators have found seemingly conflicting impacts of Hg emissions sources on Hg levels in biota near the source. Lichens (*Hypogymnia physodes*), for example, have been observed to have increased levels of Hg within one km of a chlor-alkali plant (Sensen and Rishardson, 2002), facilities that emit both Hg⁰ and RGM to the atmosphere (Landis et al., 2004; Wängberg et al., 2005). Similarly, total Hg in lichens (*Usnea* spp.) and water striders (*Aquarius remigis*) decreased with distance from a coal-fired power plant in New Brunswick, Canada, with the lichens having greatest concentrations within 10 km of the plant (Jardine et al., 2009). In contrast, concentrations of total Hg and MeHg in aquatic invertebrates (Belzile et al., 2005) and fish (Chen et al., 2001) have been found to be *lowest* in close proximity to a metal smelter and increase with distance away from it, a spatial distribution that also has been observed for total Hg in fish around coal-fired power plants (Anderson and Smith, 1977; Sackett et al., 2010).

One potential explanation for the differences in bioindicator Hg levels around emission sources is the antagonistic effect of selenium (Se) on Hg bioaccumulation. Se is posited to inhibit bioaccumulation of Hg species by, for example, reducing MeHg bioavailability and enhancing elimination from organisms (Bjerregaard et al., 1999; Chen et al., 2001; Khan and Wang, 2009). Many types of Hg emission sources, including both coal combustion and metal smelters, also commonly emit Se that is rapidly deposited to the near-source environment. This results in enriched concentrations of Se in sediments, biota, and water near the emission source that appear to attenuate the bioaccumulation of Hg species (Chen et al., 2001; Belzile et al., 2005; Sackett et al., 2010). Lichens, in contrast, may be less susceptible to the ameliorative effects of Se, especially near chlor-

alkali plants that do not emit substantial amounts of Se (Gibičar et al., 2009). Se was not measured in this assay; however, a group of four locations most immediately and predominantly downwind (east-northeast) of the plant have some of the lowest mosquito MeHg levels, which would be consistent with Se inhibition of MeHg bioaccumulation.

An absence of significantly enhanced atmospheric Hg deposition near the Conesville plant is the most obvious potential explanation for the lack of impact on mosquito MeHg concentrations. Indeed, mosquito MeHg levels near the plant 1) were in good agreement with a predictive relationship based on wet atmospheric Hg deposition alone, 2) were similar to those in mosquitoes at three reference sites, and 3) showed no consistent geographical distribution in the vicinity of the facility that would be indicative of a localized impact. The absence of an apparent impact at Conesville may be related to either 1) the stack heights or 2) the majority of emitted Hg being in the elemental form, which can be influenced by the type of coal burned and emission control technologies.

About 40% of Hg in coal that enters a coal-fired plant is captured with emission control technologies with the other 60% emitted to the atmosphere during combustion (Pavlish et al., 2003). These percentages are highly variable; Hg emitted from a coal-fired power plant can range from < 10% to about 90%, depending upon a combination of the types of coal and emission control technologies (Pavlish et al., 2003). Appalachian bituminous coal and western subbituminous coal account for about 75% of the coal burned in the United States and are responsible for about 80% of all Hg emissions in a coal-fired utility (Pavlish et al., 2003). This type of coal has relatively high levels of Hg, chlorine, sulfur and low concentrations of calcium resulting in higher levels of divalent

Hg (Hg II) emission (Pavlish et al., 2003), which is more readily captured with control technologies. Western subbituminous coal has significantly lower levels of Hg, chlorine, sulfur, and higher concentrations of calcium, resulting in increased emission of Hg⁰ (Pavlish, 2003). The Conesville power utility utilizes predominately bituminous and subbituminous coal (personal communication, Dean Ponchak, Ohio Environmental Protection Agency).

Emission control technologies can greatly determine how much and what species of Hg are emitted from a utility, but the type of coal utilized is also important. Cold electrostatic precipitator (ESP), for example, used to capture emission particulates, remove about 35% of Hg from bituminous coal emissions while only removing about 10% of Hg from lower grade lignite/bituminous coal emissions (Brown et al., 1999). This is predominately because the speciation of Hg in bituminous and lignite/bituminous coal is different and ESP's more efficiently remove Hg species generated from bituminous coal combustion (Brown et al., 1999). Three-fourths of coal-fired power plants nationwide have only particulate control devices, namely cold-side electrostatic precipitators (CS-ESP) but hot-side electrostatic precipitators (HS-ESP) or fabric filters are also prevalent (Pavlish et al., 2003). The average capture efficiency of mercury species by these three emission control technologies are about 27% (CS-ESP), 4% (HS-ESP), and 58% (fabric filters). However, the majority of the captured Hg species are largely in the gaseous or particulate Hg phase because ESP's are inefficient at capturing Hg⁰. Of the remaining Hg species not captured by emission control technologies about 47% (CS-ESP), 66% (HS-ESP), and 23% (fabric filters) are emitted from the plant and into the atmosphere in Hg⁰ form (EPRI, 2000).

Wet flue gas desulfurization (WFGD) units are installed on about 25% of coal-fired boilers nationwide. These units greatly reduce Hg emissions by removing ~ 90% of divalent Hg species during the combustion process (Pavlish et al., 2003; Streets et al., 2005). However, and similar to ESP's, emissions of Hg⁰ are not affected significantly by WFGD. While it has been suggested that the combination of ESP's and WFGD's may significantly reduce the levels of particulate and gaseous mercury emitted from a coal-fired utility, Hg⁰ emissions are still highly variable.

Hg speciation in a coal-fired power plant can be affected throughout the entire combustion process. Indeed boiler design, coal type and composition, heating and cooling rates, emission control devices, and operating practices can affect the speciation of mercury (Pavlish et al., 2003). However, recent studies have suggested that high levels of chlorine are the most significant factor determining mercury speciation during the combustion process (EPRI, 2000). High levels of chlorine are correlated with higher mercury oxidation levels which are more easily removed and sequestered during the combustion process. Furthermore, stack height is also important to consider: tall stacks release pollutants higher into the atmosphere, thus facilitating long range transport. Many coal-fired utilities built before 1988 were not under the same restrictions as today and therefore built tall stacks to limit near source pollution (Report to the Chairman, Subcommittee on Oversight, Committee on Environment and Public Works, U.S. Senate, 2011).

The Conesville utility has a total of six stacks, two of which were retired in 2006. The remaining four units all have ESP and WFGD scrubbers. ESP were installed and

have been operational since construction of each of the units (1970–1972). The largest unit at Conesville (800 MW) also has selective catalytic reduction (SCR), a relatively new technology designed to reduce nitrogen oxide emissions but also may further reduce Hg emissions (personal communication, Dean Ponchak, Ohio Environmental Protection Agency). The use of these control technologies may result in most of the Hg emitted from the Conesville plant being in the Hg^0 form, which would not tend to deposit locally because of its slow rate of reactivity in the atmosphere (Lamborg et al., 2002).

Furthermore, the Conesville utility has tall stacks, (~ 240 m; personal communication, Dean Ponchak, Ohio Environmental Protection Agency) which facilitates long-range transport and dispersion of Hg. This, combined with the type of coal burned and the emission control technologies installed at Conesville, may reduce the amount of particulate and RGM emitted. Therefore the data collected near the Conesville power utility suggests that Hg emissions may be predominately in the elemental form, and due to elemental Hg's long atmospheric residence time little near source deposition may occur.

Previous mosquito MeHg research investigating the link between atmospheric deposition and MeHg accumulation determined that MeHg accumulation in mosquitoes was related positively and linearly proportional to atmospheric Hg deposition (Figure 5). While the relationship between atmospheric Hg deposition and MeHg accumulation is limited by having few sampling locations, the extent to which coal-fired utilities affect local MeHg accumulation also is poorly understood. Measurements of MeHg in mosquitoes sampled near the Conesville power plant suggest that the facility does not

greatly impact levels of MeHg in local aquatic biota and this may result from limited near-source deposition of emitted Hg. Accordingly, these results imply that either 1) little of the Hg emitted from the utility is deposited locally, because the majority of emitted Hg from the Conesville power plant is presumed to be as Hg⁰ and can therefore be transported globally or 2) near-source deposition of Hg emissions from the plant does not have a significant impact on MeHg residues in mosquitoes and, by extension, potentially other organisms in the local food web.

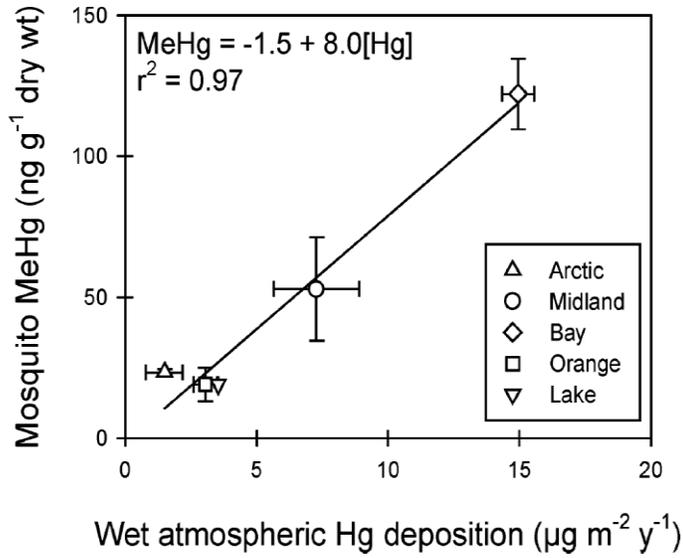


Figure 5. Mean level of MeHg in mosquitoes versus total Hg (± 1 SE) in wet deposition measured at representative North American locations (from Hammerschmidt & Fitzgerald, 2005).

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Table 1. Mosquito sampling locations around the Conesville power station and at three reference sites.

Sample ID	Date sampled	Site location	Distance from station (km)
Station 1	7/22/2010	N 39.7583 W 82.1965	54.5
Station 3	7/22/2010	N 40.0026	23.5
Station 4	7/22/2010	W 81.7376 N 40.0469	17.0
Station 5	7/13/2010	W 81.9688 N 40.6107	53.0
Station 6	7/13/2010	W 81.5899 N 40.7245	60.0
Station 7	7/13/2010	W 81.9714 N 40.5058	36.5
Station 8	7/13/2010	W 81.9663 N 40.0496	58.5
Station 9	7/23/2010	W 82.5420 N 40.3445	41.0
Station 10	7/14/2010	W 81.4409 N 40.4337	50.0
Station 11	7/23/2010	W 81.3856 N 40.1533	9.0
Station 12	7/23/2010	W 81.7875 N 40.2952	31.5
Station 13	7/15/2010	W 81.5374 N 40.2024	2.5
Station 14	7/15/2010	W 81.8618 N 40.2031	2.5
Station 15	7/15/2010	W 81.8902 N 40.1823	1.0
Station 16	7/23/2010	W 81.8884 N 40.2114	18.0
Station 17	7/15/2010	W 81.6694 N 40.1610	13.0
Station 18	7/15/2010	W 82.0256 N 40.0548	26.5
Station 19	7/15/2010	W 82.1382 N 40.0676	38.0
Station 20	7/24/2010	W 82.2968 N 40.2148	7.0
Station 21	7/24/2010	W 81.9477 N 40.2908	16.0
Station 22	7/24/2010	W 82.0086 N 40.3499	25.5
Station 23	7/24/2010	W 82.0892 N 40.4426	52.0
Station 24	7/25/2010	W 82.3898 N 40.0068	60.0
Reference - RWH	6/28/2010, 8/5/2010, 8/9/2010, 8/10/2010,	W 82.5586 N 39.8628	173.0
Reference - CMX	7/8/2010, 7/29/2010, 8/10/2010, 8/19/2010	W 83.8740 N 39.7804	182.0
Reference - WSU	6/7/2010, 6/17/2010, 8/10/2010, 8/11/2010	W 83.0583 N 39.7853	189.0
		W 83.9559	