A National Pilot Study of Mercury Contamination of Aquatic Ecosystems along Multiple Gradients

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ABSTRACT

Mercury (Hg) contamination of aquatic ecosystems is a global problem. However, databases for Hg in environmental samples at regional-to-national scales are few, especially for multi-media sampling that include determination of methylmercury (MeHg). A national scale pilot study to examine relations of total Hg (Hg_T) and MeHg in water, sediment and fish was conducted in the summer and fall of 1998. Samples were collected at 106 sites from 21 basins across the United States, including Alaska and Hawaii. The data showed wide ranges in concentrations, which were expected given the diverse array of environmental settings, water chemistry, and Hg loading represented by these sites. Wetland density was the single most important basin-scale factor controlling MeHg production. At low concentrations, total Hg in sediment may also influence MeHg production, but at high total Hg concentrations (>1,000 nanograms per gram; ng/g) in sediment there was little evidence of increasing MeHg production with increasing total Hg. An atmospheric Hg accumulation index was developed for differentiating areas where atmospheric Hg deposition was the dominant Hg source from areas with significant on-site sources. Four study basins along the east coast of the United States had the greatest methylation efficiency, as reflected by the MeHg/HgT ratio in sediments. Nationwide, sub-basins characterized as mixed agriculture and forest cover types had the highest methylation efficiency, whereas areas affected by mining had the lowest efficiency. This study represents a first step toward a national assessment of Hg contamination of aquatic ecosystems in the United States, however, additional data are needed to improve our resolution of the factors controlling MeHg production and bioaccumulation.

INTRODUCTION

Methylmercury is the most toxic and widespread contaminant affecting our Nation's aquatic ecosystems. Methylmercury contamination has prompted steadily increasing numbers of fish-consumption advisories in 40 states, now accounting for more than eighty percent of all such advisories in the Nation (1,782 advisories for mercury of 2,196 total advisories nationwide; U.S. Environmental Protection Agency, 1998). Eleven states have statewide advisories for Hg in fish from lakes and/or rivers, and five have statewide advisories for coastal waters. In addition, some tribal representatives report that adherence to fish-consumption advisories has adversely affected the social, economic, and cultural well being of certain Native American tribes (for example, Wheatley

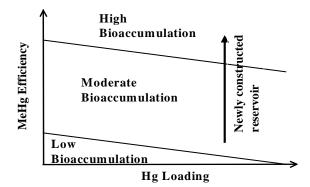
and others, 1997; Wheatley, 1997). Methylmercury readily crosses biological membranes, can accumulate to harmful concentrations in exposed organisms, and biomagnifies to concentrations of toxicological concern in aquatic food webs, posing a threat to humans (Grandjean and others, 1997) and an increasing, potentially severe threat to fish-eating wildlife (Heinz and Hoffman, 1998).

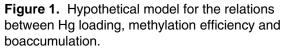
For most aquatic ecosystems, atmospheric deposition of inorganic Hg (about 0.3 to 30 micrograms per square meter per year; U.S. Environmental Protection Agency, 1997) is the primary source of contamination. Generally only a small fraction of this atmospheric Hg load to aquatic ecosystems exists as MeHg (Rudd, 1995). In addition, the masses of MeHg found in sedimentary and biological compartments of most aquatic ecosystems cannot be accounted for by direct inputs of MeHg (Branfireun and others, 1998), and mass effluxes of MeHg from watersheds generally far exceed total inputs (Hurley and others, 1995). The bridge between the seemingly incongruent observations that inorganic Hg is the dominant form released to the environment, and MeHg is the dominant form of Hg found in edible fish (Bloom, 1992; Wiener and Spry, 1996) is the process of methylation. It is generally accepted that in natural settings mercury methylation is mediated through microbial sulfate reduction (Gilmour, 1991). Over the past 10 years, a great deal of scientific attention has been placed on trying to better understand mercury methylation. Yet, a complete understanding of the factors controlling methylation has remained elusive.

Management and regulatory responses to the growing mercury problem have been greatly impeded by a lack of information from a wide range of locations and environmental settings on the sources, transport, biogeochemical transformations, biological exposure, and toxicological consequences of mercury in the environment. Although there is a growing body of literature on mercury in the environment, to date there has not been a coordinated effort using consistent sampling and analytical methods conducted at the national scale. This paper presents the initial results of a pilot study to evaluate whether trends in Hg accumulation and MeHg production can be identified at national or regional scales across the United States. The study was designed so that a range of factors known to affect contamination levels, such as Hg loading rates, Hg source types, water chemistry, and land use and cover, could be evaluated.

THE USGS NATIONAL MERCURY PILOT STUDY

The National Mercury Pilot Study was conducted though the collaborative efforts of the Toxic Substances Hydrology program and the National Water Quality Assessment (NAWQA) program of the U.S. Geological Survey (USGS). The overall objective of this study is to identify ecosystem characteristics that favor the production and bioaccumulation of MeHg. Ultimately, we would like to be able to construct predictive models indicating environments of most concern for MeHg contamination, such as that depicted in figure 1. Ecosystems that have low methylation efficiency may exhibit low or moderate bioaccumulation even under high Hg loads, such as the Poplar Creek watershed, near Oak Ridge, Tennessee (Turner and others, 1993). On the other hand, significant bioaccumulation of methylmercury can result even when very low Hg loading rates exist if methylation efficiency is high, such as low-pH lakes in northern Wisconsin (Wiener and others, 1990; Lamborg, and others, 1995). Other ecosystems, such as newly constructed reservoirs, may experience a





perturbation that increases methylation efficiency without increasing the mercury load (Bodaly and others, 1997). In this case, after flooding, the methylation efficiency of the reservoir would be expected to show a vertically upward trend across this conceptual model.

Regional and national scale fish surveys have been done in the past for mercury and other bioaccumulative contaminants. This is the only known study, however, in which national-scale, multi-media sampling (water, sediment, and fish) was conducted in concert with low-level Hg speciation analysis. Recent studies in Wisconsin have shown that several basin-scale factors influence the relative sensitivity of ecosystems to MeHg production (Hurley and others, 1995). These basin-scale factors include the relative abundance of wetlands (a site known to favor Hg methylation), soil types, and land use and cover. In Wisconsin, these factors serve as good predictors of mercury methylation efficiency, Hg and MeHg yields, and levels of MeHg in water. We caution that when viewed from a national perspective, however, the variation in atmospheric Hg-deposition rates across Wisconsin are small (U.S. Environmental Protection Agency, 1997), point-source contributions were presumably few and moderate in strength, geologic sources were negligible, and the range of ecosystem types were limited. Thus, we can not reliably transfer these results to a national scale.

Study Design

The major characteristics of this study were its (1) national scope, (2) emphasis on multimedia sample collection (water, sediment, and predator fish), (3) consistent use of trace metal clean sampling methods, and (4) low-level Hg and MeHg analytical procedures. By collecting and analyzing all three media, much more can be ascertained about controls of Hg and MeHg partitioning, accumulation, bioconcentration, and methylation efficiency across the vast diversity of sites that comprise our Nation's freshwater ecosystems.

The NAWQA program has scientists located throughout the United States who are trained in the procedures for the collection of water, sediment and biological samples; this greatly facilitated field efforts for this study. An additional benefit of conducting the pilot study at NAWQA study basins is the substantial amount of ancillary information available to strengthen the interpretations of the data generated via this study.

Sampling was conducted from June to October, 1998 at multiple locations (3 to 8) in each of 21 NAWQA study basins (figure 2, table 1) for a total of 106 sampling sites. Nationally, these basins spanned the dominant east-to-west mercury deposition gradient (figure 3) and represented a wide range of environmental settings. Individual study basin teams were asked to choose sites spanning gradients of wetland density, surface water pH, sulfate (SO₄), total organic carbon (TOC), and suspected or known Hg loading. In most cases, the sites sampled were streams, and every attempt was made to sample during baseflow conditions. Several of the chosen basins had known point sources of mercury from mining activity, and were representative of very high mercury loading conditions.

Abbrev.	Study Basin Name
ACAD	Acadian-Pontchartrain
ALMN	Allegheny and Monongahela Basins
COOK	Cook Inlet Basin
DELR	Delaware River Basin
GRSL	Great Salt Lake Basins
LINJ	Long Island and N. J. Coastal Drainages
LTEN	Lower Tennessee River Basin
MIAM	Great and Little Miami River Basins
MOBL	Mobile River and Tributaries
NECB	New England Coastal Basins
NROK	Northern Rockies Intermontane Basins
NVBR	Nevada Basin and Range
OAHU	Oahu Island
SACR	Sacramento Basin
SANA	Santa Ana Basin
SANT	Santee Basin and Coastal Drainages
SOFL	Southern Florida
TRIN	Trinity River Basin
UCOL	Upper Colorado River Basin
UIRB	Upper Illinois River Basin
YELL	Yellowstone Basin

 Table 1. NAWQA study basins from which samples were collected for this study.

Sampling Methods for Water, Sediment, and Fish

Aqueous Hg and MeHg samples were collected with trace-metal clean methods (Fitzgerald and Watras, 1989). All sample containers were Teflon (any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government), which had been rigorously cleaned in hot acid, partially filled with one percent HCl for storage, and then double bagged in Ziploc bags. Sampling crews wore plastic gloves, and executed clean-hands, dirty-hands techniques (Olson and DeWild, 1999) to remove the sample bottle from the two bags. Almost all of the sampling locations were streams, whereby grab samples were taken from the centroid of flow by submersing the bottle while wearing arm-length

gloves. Total-Hg (Hg_T) samples were acidified to one percent HCl by volume, while MeHg samples were immediately placed in a darkened cooler until they could be frozen.

Bed sediment samples were collected using the NAWQA program's trace-element sampling protocols (Shelton and Capel, 1994). Briefly, field personnel wore plastic gloves and used a clean Teflon or plastic scoop to collect the top few centimeters of sediment. Generally, samples were taken from multiple points (about 5 to 10) at each site, which were then pooled, homogenized, and then subsampled. A Teflon vial was used for the total Hg and MeHg subsample, while a second subsample was taken in a polypropylene vial and used for other analyses. Sediment samples were frozen as soon as possible.

Fish were collected by the most efficient means available, provided it did not jeopardize the specimen with regard to mercury contamination. Up to five individuals of a single, top-predator species were collected from each site. Field crews were asked to focus sampling efforts on largemouth bass of age 2-3 years, but in the absence of these fish to collect the most common predator species inhabiting the basin. If at all possible, the same species was collected from each sampling site within a study basin. Each fish was rinsed in stream water, measured for length and weight, placed in Ziploc bags, and frozen as soon as possible.

Anaytical Methods for Sediment and Water and Wetland Delineation

Details of the analytical procedures for Hg_{T} and MeHg in sediment and water are given in Olson and DeWild (1999) and Olson and others (1997). Samples collected for this study were shipped to the USGS Mercury Research Laboratory in Middleton, Wisconsin. Total mercury in aqueous samples was determined by cold vapor atomic fluorescence spectroscopy (CVAFS) following oxidation with BrCl at 50°C, reduction by SnCl₂, and purge and trap of the evolved Hg⁰ onto gold-coated glass bead columns. Total mercury in sediments was determined with the same procedure, but samples were predigested with nitric and sulfuric acids in sealed

Teflon bombs at 125°C. Methylmercury in sediment and water was analyzed with the distillation and aqueous phase ethylation method of Horvat et al. (1993), and detection by CVAFS. Analytical results for fish tissue samples were not available at the time of this paper, so the procedures are not given. Ancillary chemical parameters were determined by the following methods: pH was measured in the field with a calibrated probe; SO_4 by ion chromatography; DOC by a carbon analyzer that employs acidification and persulfate/UV oxidation; dry weight percent by drying wet sediment at 105°C; and loss on ignition (LOI) by heating dried sediment samples to 550°C.

A Geographic Information System (GIS) was used to quantify wetland areas within the study basins. Sampling locations for each study basin were plotted, and the sub-basin areas upstream of each point were delineated. Percent wetland area for each of the sub-basins was determined by overlaying a GIS coverage of the National Wetlands Inventory (Greg Allord, USGS, unpub. data, 1999).

RESULTS AND DISCUSSION

The study results are presented in three ways: across individual sites, among basins, and among site types.

All analytically determined parameters varied considerably within and among sites (table 2). This was expected given the extreme ranges in environmental settings (climate, geology, land use, and land cover), water chemistry, and Hg loading represented by this array of sampling sites. Generally, the Hg_{T} and MeHgconcentrations in water and sediment were similar to the range of values from other recent freshwater studies that employed clean sampling and low-level Hg analysis. Very high concentrations of Hg_{T} and MeHg in water and sediment observed at the mining affected sites created a highly skewed distribution of concentration data. As a result, the mean values were much larger than their respective median values (table 2).

Overall, stronger correlations were observed between sediment MeHg and the

ancillary data (wetland density, pH, DOC and SO_4) than for aqueous MeHg results. This was likely due to the more transient nature of surface water samples compared to sediment, which tends to integrate site conditions over longer periods of time. Of the ancillary measurements, the strongest correlation was between sediment MeHg and percent wetland in the sub-basin (figure 4). Previous studies of MeHg production in boreal ecosystems also concluded that wetland density greatly influenced MeHg production (St. Louis and others, 1994; Hurley and others, 1995).

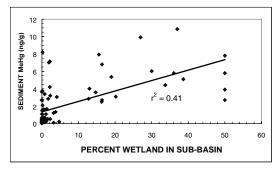


Figure 4. Sediment MeHg versus percent wetland in the sub-basins sampled during this study.

Similar positive correlations observed here suggest that these conclusions are valid over much broader geographical scales and ecosystem types. Sediment MeHg concentration also correlated positvely with LOI ($r^2 = 0.26$), which was used as a surrogate for organic carbon content of sediment. A subset of fifteen samples collected for this study and analyzed for organic carbon concentration showed a strong correlation with LOI ($r^2 = 0.97$). Negative correlations were observed between sediment MeHg and percent dry weight and surface water pH ($r^2 = 0.29$ and 0.15, respectively). The correlation results between MeHg and TOC was lower than expected $(r^2 = 0.18)$, given that other studies have observed much stronger relations between these variables (Hurley and others, 1998). A more detailed analyses of the TOC quality from these various study basins may help to unravel the complexities of Hg-carbon interactions. Our observations suggest that mercury methylation is greatest for sub-basins with significant wetland density, organic sediments, and with low surface water pH.

One of the difficulties in analyzing Hg data from such differing ecosystems is the considerable variation in the measurable factors controlling important processes, such as methylation. For example, when we excluded the sites with mining impacts, a strong, positive correlation was observed between sediment MeHg and SO₄. When we included the data from the sulfate-rich mining sites, a weak, negative correlation was observed. At very high sulfate levels, methylation of mercury may not be limited by the availability of sulfate, or methylation can be inhibited by the abundance of sulfide (a by product of sulfate reduction) (Gilmour and others, 1998).

One important question concerning Hg bioaccumulation in aquatic ecosystems is whether Hg load drives methylation. The averaged, LOI-adjusted Hg_T and MeHg data for the 21 study basins suggest that Hg load (as reflected by Hg_T accumulation in sediment) has a logarithmic effect on methylation (figure 5). Methymercury production appears proporational to Hg_T concentrations at low sediment Hg_T levels; but at high Hg_T levels little additional MeHg is produced with additional Hg_T.

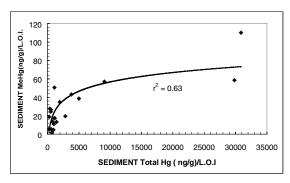


Figure 5. Average normalized (to LOI) sediment MeHg versus Hg_{τ} for the 21 basins sampled for this study.

This finding is consistent with mercury methylation experiments on sediments, where a reduced methylation response to loading was observed when concentrations of $Hg_T > 1,000$ ng/g were used (Rudd and others, 1983). The two data points on the high end of the curve in figure 5 had Hg_T concentrations of about 1,000 ng/g (before normalizing to LOI).

The importance of atmospheric deposition relative other Hg sources within each

study basin was assessed by normalizing sediment Hg_{T} concentrations to estimated current atmospheric deposition rates for each study basin and LOI. In essence, this calculation produces an index of atmospheric Hg accumulation (AHA). High AHA values would be diagnostic of study basins having Hg sources other than atmospheric deposition, and low index values would suggest the atmosphere is the dominant Hg source for the basin. The AHA values for all 21 study basins are shown in table 3. Those study basins with the six highest AHA indices were heavily contaminated with metals from mining. Interestingly, the next highest AHA index value is for the Oahu study basin, which has no known mining contamination sites. One likely Hg source for Hawaii is the Kilauea volcano. Volcanoes are known to emit gaseous Hg vapors; however, quantitative estimates of Hg emissions and their impacts are scarce. Although not a precise estimate, this analysis suggests Hg from Kilauea is depositing on Oahu Island at a rate similar to loading from areas where mining activity is pervasive. After the Oahu study basin, the next highest AHA value was for the Yellowstone study basin. One likely Hg source for this study basin is the numerous hot springs that are known to have high mercury concentrations (Rytuba, 1997). The remaining study basins all had AHA values that were notably lower. Many of these study basins were heavily urbanized, yet the AHA values suggested that the atmosphere was the dominant Hg source for these areas. It should be noted that several of these areas have relatively high Hg_{T} concentrations in sediment, such as the New England Coastal Basins, but that apparently most of this mercury can be accounted for by high atmospheric deposition rates. Ecosystem effects from pending legislation to reduce atmospheric mercury emissions would likely be most effective in such areas. The Southern Florida study basin, which had the lowest AHA value, provides a calibration point for this index, given that recent studies have demonstrated that atmospheric deposition is the dominant source of mercury to the Everglades (Guentzel and others, 1995).

Methylation efficiency is a critical factor affecting the susceptibility of ecosystems to bioaccumulation. Actual methylation rate estimates would be expensive to perform on a national basis, but the MeHg/Hg_T ratio in

sediments and water provides a reasonable predictor of methylation efficiency (Gilmour and others, 1998). Table 3 lists the average MeHg concentration in sediments and the average MeHg/Hg_T ratio for sediment and water for each study basin. Both of these measures identify the New England Coastal Basins, Santee Basin, Long Island and N. J. Coastal Drainages, and Southern Florida as systems having enhanced methylation efficiency. All of these areas have widespread advisories for high Hg concentrations in game fish.

Table 3.	Summary	/ data fo	r the 21	stud	/ basins.
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Site	Hg Atm.	AHA	Sed.	MeHg/Hg _T
Abbrev.	Dep. Rate	Index ²	MeHg	Ratio ³
	$(\mu/m^2/y)^1$		(ng/g)	
ACAD	4	170	0.17	0.05
ALMN	18	80	0.48	0.02
COOK	1	3,828	1.24	0.03
DELR	25	31	0.77	0.03
GRSL	2	4,533	2.45	0.01
LINJ	27.5	19	6.23	0.06
LTEN	7.5	146	0.65	0.01
MIAM	17	114	0.51	0.03
MOBL	8	126	0.24	0.02
NECB	27.5	182	7.28	0.09
NROK	1.5	20,584	3.52	0.02
NVBR	1	29,817	2.00	0.02
OAHU	1	963	1.10	0.01
SACR	1.5	1,891	0.91	0.01
SANA	2	188	2.30	0.05
SANT	7.5	35	3.60	0.11
SOFL	25	9	5.05	0.10
TRIN	5	114	0.28	0.01
UCOL	1	1,153	1.03	0.04
UIRB	10	110	0.99	0.06
YELL	1	545	1.04	0.04

¹Estimated from USEPA, 1997.

²Average Hg_T concentration observed for each study basin normalized to the atmospheric deposition rate and the average loss on ignition percentage of sediment. ³Average value for the MeHg/Hg_T ratio for sediment and water.

All of the study basins were heterogeneous with respect to land cover and use. For the purposes of this analysis, the sub-basins above each of the sampling sites were categorized into one of the five following broad classes: agriculture dominant (Ag); mixed agriculture and forest (A/F); background or reference site for the study basin (Bkg); current or abandoned mining activity near sampling site (Mine); and urban or industrial activity near sampling site (Urb) (table 2). Total and methyl mercury concentrations in sediment and water differ significantly among these broad categories (table 4).

Table 4. Summary data for Hg_{τ} and MeHg by land use/cover category.

Land				
use/cover (N) ¹	MeHg (ng/L)	Hg _⊤ (ng/L)	MeHg (ng/g)	Hg _⊤ (ng/g)
A/F (11)	0.48	5.59	2.73	34.07
Ag. (30)	0.15	10.76	1.20	73.34
Bkg (21)	0.13	3.43	2.10	104.9
Mine (14)	0.10	84.43	1.89	788.2
Urb. (30)	0.09	3.34	2.07	218.6

¹Land use/cover definitions are found in table 2, N is the number of sampling sites falling each categories.

Sub-basins with mining operations present had the highest Hg_T concentrations in sediment and water, but MeHg levels were relatively low. Interestingly, sub-basins described as mixed agriculture and forest had the lowest average Hg_T concentration in sediment, yet the highest MeHg levels in sediment and water. Thus, the mixed agriculture and forest land type had the highest methylation efficiency, whereas mining and urban areas had the lowest (figure 6).

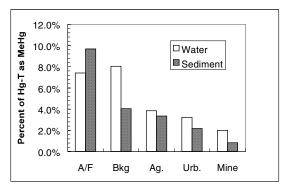


Figure 6. Average, normalized (to LOI) sediment MeHg versus Hg_{τ} for the 21subbasins sampled for this study.

SUMMARY

The concentrations of Hg_T and MeHg in sediment and water collected at 106 sites from 21 basins across the United States ranged widely. Variability in these data were expected, given the wide array of environmental settings, water chemistry, and Hg loading represented. Wetland density was found to be the most important basinscale factor controlling MeHg production. By normalizing the sediment Hg_{T} and MeHg data to LOI, a logarithmic relation between Hg_{T} and MeHg was revealed. Methylmercury production appears proportional to Hg_{T} concentrations at low sediment Hg_{τ} levels. At high Hg_{τ} levels (<1,000 ng/g), however, little additional MeHg was evidently produced with increasing Hg_T. By normalizing the sediment Hg_T concentrations to LOI and the estimated atmospheric deposition rate for each study basin, a useful index (AHA) for assessing areas where atmospheric deposition is the dominant Hg source was obtained. Surprisingly, this index indicated that a significant Hg source other than atmospheric deposition exists for the Oahu study basin. Volcanic activity was a likely source of mercury in this basin. The New England Coastal Basins, Santee Basin, Long Island and N.J. Coastal Drainage, and Southern Florida showed the greatest methylation efficiency as reflected by the MeHg/Hg_T ratio in sediments. That all of these sites had low AHA indices suggests that pending emission reductions might be especially effective in these areas. Sub-basins characterized as mixed agriculture and forested had the highest methylation efficiency, whereas areas affected by mining were the lowest. This study was designed as a "pilot" effort to test whether multi-media sampling for low-level Hg determinations could be effectively conducted. While the spatial coverage of sampling was good, the site density (106 sites nationally) is probably not adequate for making final conclusions about mercury contamination of aquatic ecosystems across the United States. More detailed sampling, including sampling for seasonal differences, across this same series of study basins is needed to provide a more thorough analysis of what controls Hg methylation, partitioning, and bioaccumulation at national scales.

ACKNOWLEDGMENTS

The authors are indebted to the NAWQA study-basin teams who participated in this study and demonstrated great diligence, commitment, and enthusiasm to the collection of the samples.

REFERENCES

- Bloom, N.S., 1992, On the chemical form of mercury in edible fish and marine invertebrate tissue: Canadian Journal of Fisheries and Aquatic Sciences, v. 49, pp. 1010-1017.
- Bodaly, R.A., St. Louis, V.L., Paterson, M.J.,
 Fudge, R.J.P., Hall, B.D., Rosenberg, D.M.,
 and Rudd, R.W.M., 1997, Bioaccumulation of
 mercury in the aquatic food chain in newly
 flooded areas, Sigel, A., and Sigel, H. eds.,
 Mercury and its Effects on Environment and
 Biology: Marcel Dekker, New York, pp. 259-287.
- Branfireun, B.A., Hilbert, D., and Roulet, N.T., 1998, Sinks and sources of methylmercury in a boreal catchment: Biogeochemistry, v. 41, pp. 277-291.
- Fitzgerald, W.F. and Watras, C.J., 1989, Mercury in surficial waters of rural Wisconsin lakes: Science of the Total Environment, v. 87/88, pp. 223-232
- Gilmour, C.C., Henry, E.A. and Mitchell, R., 1991, Sulfate stimulation of mercury methylation in freshwater sediments: Environmental Science and Technology, v. 26, pp. 2281-2287.
- Gilmour, C.C., G.S. Riedel, M.C. Ederlington, J.T. Bell, J.M. Benoit, G.A. Gill, and M.C. Stordal, 1998, Methylmercury concentrations and production rates across a trophic gradient in the Northern Everglades: Biogeochemistry, v. 40, pp. 326-346.
- Grandjean, P., P. Weihe, R.F. White, F. Debes, S. Araki, K. Yokoyama, K. Murata, N.
 Sorenson, R. Dahl, and P. Jorgensen, 1997, Cognitive deficit in 7-year-old children with prenatal exposure to methylmercury: Neurotoxicology and Teratology, v. 19, pp. 417-428.
- Guentzel, J.L., Landing, W.M., Gill, G.A., and Pollman, C.D., 1995, Atmospheric deposition

of mercury in Florida: Water, Air, and Soil Pollution, v. 80, pp. 393-402.

- Heinz, G.H., and Hoffman, D.J., 1998, Methylmercury chloride and selenomethionine interactions on health and reproduction in Mallards: Environmental Toxicology and Chemistry, v. 17, pp. 139-145.
- Horvat, M., Bloom, N.S. and Liang, L. 1993, Comparison of distillation with other current isolation methods for the determination of MeHg compounds in low level environmental samples. Part I. Sediment: Analytica Chemica Acta, v. 282, pp. 135-152.
- Hurley, J.P., Benoit, J.M., Babiarz, C.L., Shafer, M.M., Andren, A.W., Sullivan, J.R., Hammond, R., and Webb, D., 1995, Influences of watershed characteristics on mercury levels in Wisconsin rivers: Environmental Science and Technology, v. 29, pp. 1867-1875.
- Hurley, J.P., D.P. Krabbenhoft, L.B Cleckner,M.L. Olson, G. Aiken, and P.J. Rawlik, 1998,System controls on aqueous mercurydistribution in the northern Everglades:Biogeochemistry, v. 40, pp. 293-310.
- Lamborg, C.H., Fitzgerald, W.F., Vandal, G.M., and Rolfhus, K.R. 1995. Atmospheric mercury in northern Wisconsin: Sources and species. Water, Air and Soil Pollution, v. 80, pp. 189-198.
- Olson, M.L., L.B. Cleckner, J.P. Hurley, D.P. Krabbenhoft, and T.W. Heelan, 1997, Resolution of matrix effects on analysis of total and methyl mercury in aqueous samples from the Florida Everglades, Fresenius Journal of Analytical Chemistry, v. 358, pp. 392-396.
- Olson, M.L., and DeWild, J.F., 1999, Low-level techniques for the collection and speciesspecific analysis of low levels of mercury in water, sediment, and biota, Morganwalp, D.W., and Buxton, H.T., eds., 1999, U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999--Volume 2--Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey

Water-Resources Investigations Report 99-4018B, this volume.

Rudd, J.W.M. 1995. Sources of methylmercury to freshwater ecosystems: A review: Water, Air, and Soil Pollution, v. 80, pp. 697-713.

Rudd, J.W.M., M.A. Turner, A. Furutani, A. Swick and B.E. Townsend, 1983, A synthesis of recent research with a view towards mercury amelioration: Canadian Journal Fisheries Aquatic Sciences, v. 40, pp. 2206-2217.

Rytuba, J.J., Environmental geochemistry of mercury deposits in the Coast Range mercury belt, CA: USGS Open-File Report 97-496, 26 p.

Shelton, L.R., and Capel, P.D., 1994 (rev. 1996), Guidelines for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–458, 20 p.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, K.G., Bloom, N.S., and Flett, R. J. 1994. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems: Canadian Journal of Fisheries and Aquatic Sciences, v. 51, pp. 1065-1076.

Turner, R.R., Southworth, G.R., Bogle, M.A., Peterson, M.J., and Bloom, N.S., 1993, Availability of sediment-bound mercury for methylation and bioaccumulation in Upper East Fork Poplar Creek: Y/ER-108, Oak Ridge National Laboratory, Oak Ridge, TN, USA.

United States Environmental Protection Agency (USEPA), 1997, Mercury Study Report to Congress, United States Environmental Protection Agency, EPA-452-97-003 –010, Office of Air and Radiation, 1980 pp.

1998, Update: Listing of Fish and
 Wildlife Advisories: United States
 Environmental Protection Agency, LFWA
 Fact Sheet EPA-823-98-009, Office of Water,
 Washington, DC. 4 p.

Wheatley, B., S. Paradis, M. Lassonde, M.F. Giguere, and S. Tanguay, 1997, Exposure patterns and long term sequelae on adults and children in two Canadian indigenous communities exposed to methylmercury: Water, Air and Soil Pollution, v. 97, pp. 63-73

Wheatley, M., 1997, Social and cultural impacts of mercury pollution on aboriginal peoples in Canada: Water, Air and Soil Pollution, v. 97, pp. 85-90.

Wiener, J.G., Martini, R.E., Sheffy, T.B., and Glass, G.E., 1990, Factors influencing mercury concentrations in walleyes in northern Wisconsin lakes: Transactions of the American Fisheries Society, v. 119, pp. 862-870.

Wiener, J.G., and Spry, D.J., 1996, Toxicological Significance of Mercury in Freshwater Fish, Beyer, W.N., Heinz, G.H., and Redmon-Norwood, A.W. eds., Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations, Special Publication of the Society of Environmental Toxicology and Chemistry, Lewis Publishers, Boca Raton, Florida, USA, pp. 297-339.

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Table 2. Study basin names, type, percent wetland area of sub-basin, and analytical results from the	
sediment (dry weight) and water samples.[indicate no data, ng/L (nanograms per liter); ng/g (nanograms	
per gram); mg/L (milligrams per liter)]	

		rams pe				Water				-	
Study Basin	Site Name	Site ¹ type	% Wet- Land ²	MeHg (ng/L)	Hg _T (ng/L)	TOC (mg/L)	pН	SO ₄ (mg/L)	MeHg (ng/g)	Hg _T (ng/g)	LOI (%)
ACAD	Mermentau R. @ Mermentau	Urb.		0.09	1.11	8.9	7.5	3.6	0.06	157.0	7.8′
ACAD	Calcasieu River @ Kinder	A/F		0.15	3.68	5.2	6.8	3.7	0.05	1.9	0.20
ACAD	Bayou Boeuf	Urb.		0.05	1.66	8.6	8.9	21.06	0.10	53.5	5.93
ACAD	Turtle Bayou nr B. Penchant	Bkg.		0.03	1.03	8.6	7.4	29.07	0.41	83.6	32.4
ACAD	Bayou Lacassine	Ag.		0.46	1.61	11.1	6.7	3.03	0.26	88.1	10.0
ALMN	Youghiogheny R.	Mine	2	0.02	1.16	2.1	7.6	94	0.52	96.78	4.0
ALMN	Allegheny R. @ New Kensing.	Urb.	1	0.01	0.85	1.8	7.8	86	0.27	56.51	4.10
ALMN	Dunkard Crk. @ Shann.	Mine	0	0.04	0.64	2.6	7.5	195	0.15	12.8	4.2
ALMN	Tenmile Crk @ Amity	Bkg.	0	0.10	2.48	3.9	7.7	31	0.38	20.7	3.04
ALMN	Clarion River	Mine	1	0.09	8.09	4.2	7.4	39	1.08	76.5	2.8
COOK	Chester Creek	Urb.	0	0.02	2.96	3.8	8	28	0.38	109.9	3.2
COOK	SF Campbell Creek	Bkg.	0	0.02	2.50	1.6	7.8	9.3	0.67	200.0	2.8
COOK	Deshka River	Bkg.	39			8.4	6.8	0.2	5.10	21.0	4.0
COOK	Johnson R. abv Lateral Glacier	Bkg.	0	0.02	9.78	0.7	7.7	6.1	0.01	50.4	0.7
COOK	Costello Creek	Bkg.	0	0.02	4.97	0.7	8.1	41	0.04	169.1	3.4
DELR	Little Neshaminy Ck.	Ag.	0	0.10	4.08	4.9	7.8	39	0.38	40.1	3.0
DELR	Tulpehocken Creek	Ag.	1	0.09	2.14	2.7	7.9	28	0.57	45.8	6.4
DELR	Hay Creek nr Birdsboro, PA	Ag.	1	0.04	0.77	1.4	7.8	24	1.64	36.4	5.4
DELR	Manataway Creek	Urb.	0	0.06	1.37	3.3	8.7	17	1.08	62.8	8.8
DELR	Raccoon Ck. @ Swedesboro	Ag	5	0.05	1.11	2.9	7.3	21	0.20	33.9	4.4
GRSL	Cub River nr. Richmond, UT	Ag.	0	0.03	2.60	2.1	8.5	9.9	0.14	11.3	1.8
GRSL	Weber River nr. Coalville, UT	Mine	13	0.10	21.76	3.1	8.5	14.0	4.02	1041	7.1
GRSL	Jordan River @ Salt L. City, UT	Urb.	2	0.03	4.80	3.3	7.5	217.6	3.20	116.3	3.9
LINJ	Passaic River, Millington, NJ	Urb	37	0.24	2.72	5.5	6.9	15	2.67	89.8	15.
LINJ	Swan River	Urb	0	0.06	2.13	2.4	6	11	10.85	161.4	34.
LINJ	Muddy Run	Ag.	30	0.06	2.25	3.9	7.3	10	6.03	252.3	43.
LINJ	Great Egg @ Sicklerville	A/F	19	0.35	12.26	3.4	5.8	8.4	5.36	31.8	8.9
LTEN	Seqwatchie R. @ Whitnell, TN	A/F		0.01	1.38	1.4	7.6	6.7	0.18	10.4	2.3
LTEN	Buffalo River, Flatwoods, TN	Bkg.		0.01	1.45	0.9	7.2	6.1	0.64	47.7	2.8
LTEN	Indian Creek nr Madison, AL	Urb		0.03	3.40	1.6	7.2	7.2	1.14	66.4	6.1

Table 2. Site names, type and analytical results from the sediment and water samples— Continued

[-- indicate no data]

Study		Site ¹	%			Water		<i>a</i> -	Sediment				
Basin	Site Name	type	Wet- Land ²	MeHg (ng/L)	Hg _T (ng/L)	TOC (mg/L)	pН	SO ₄ (mg/L)	MeHg (ng/g)	Hg _T (ng/g)	LOI ² (%)		
MIAM	Stillwater R. on Springfield Rd	Ag.	1	0.05	2.10	3.3	7.6	56.87	0.17	34.0	1.04		
MIAM	Great Miami R.	Ag.	1	0.05	2.52	3.4	7.9	64.2	0.34	31.4	1.4		
MIAM	Mad R., Hwy 41, Springfield	Ag.	0	0.08	0.79	2.1	8.0	61.5	1.54	30.8	2.2		
MIAM	Holes Creek	Urb	0	0.05	1.10	2.5	7.8	37.23	0.26	10.5	1.0		
MIAM	Great Miami R., Hamilton, OH	Urb	1	0.19	3.00	5.0	8.4	73.5	0.67	87.2	2.3		
MIAM	Whitewater R. @ Nulltown, IN	Ag.	0	0.03	0.81	1.9	7.7	33.67	0.43	11.7	1.5		
MIAM	Little Miami R. @ Milford, OH	Urb.	0	0.05	1.57	3.5	8.3	49.3	0.45	9.2	1.1		
MIAM	EF L. Miami R., @ Williamsburg	Ag.	0	0.07	2.09	4.4	8.3	44.9	0.24	13.3	1.0		
MOBL	Shades Ck. @ Homewood, AL	Urb		0.04	1.31	2.6	8.2		0.17	15.2	1.4		
MOBL	Cahaba Valley Creek	Urb		0.02	0.97	1.7	6.7		0.31	34.8	3.5		
MOBL	Satilpa Ck.nr Coffeeville, AL	A/F		0.07	2.09	3.8	7.5		0.18	11.8	1.0		
MOBL	Chickasaw Creek	A/F		0.21	2.27	5.5	6.3		0.65	11.1	2.1		
MOBL	Alabama River @ Clairborne	Ag.		0.04	1.78	4.4	7.8		0.15	19.5	2.3		
MOBL	Coosa River @ Rome	Ag.		0.04	4.68	2.4	7.5		0.15	33.2	1.7		
MOBL	Tombigbee R. @ Coffeeville	Urb		0.04	2.74	4.3	7.9		0.06	26.3	2.8		
NECB	Stillwater River, Sterling, MA	Bkg.	2	0.25	0.53	2.1	6.6	10.9	7.02	72.9	17.4		
NECB NECB	Neponset R. @ Norwood, MA Ipswich R. nr S.	Urb Urb	16 27	0.28 0.44	4.40 2.72	6.6 7.0	6.6 6.6	7.9 15.6	7.93 9.91	2477 380.0	20.2 22.5		
NECB	Middleton, MA Saugus R. @	Urb	34	0.11	2.72	4.4	7	19.5	4.41	309.2	16.		
NECB	Saugus Iron. Aberjona River	Urb	2	0.08	9.11	4.0	6.5	24.4	7.14	1488	17.3		
UCOL	Red Mountain	Mine	0	0.02	1.68	0.4	3.3	484	0.13	107.2	6.4		
UCOL	Creek Dry Creek @	Ag.	1	0.15	6.05	3.9	8.2	467	1.68	37.4	3.8		
UCOL	Begonia Road Snake River @	Mine	0	0.02	0.48	1.3	6.7	46	0.28	56.2	7.4		
UCOL	Peru Creek French Gulch nr	Mine	0	0.02	0.64	1.4	7.8	63	0.21	113.2	5.7		
UCOL	Breckenridge Colorado River @	Bkg.	13	0.05	0.57	1.3	7.8	6.2	2.84	27.4	6.1		
NROK	Baker Gulch Flathead River @ Perma, MT	Ag.	1	0.01	1.14	1.7	8.1	2.7	0.18	19.2	1.6		
NROK	Clark Fork @ Turah Bridge	Mine	0	0.09	5.57	2.0	8.6	39.6	3.75	337.7	3.2		
NROK	Clark Fork@ St. Regis, MT	Ag.	1	0.02	1.53	1.5	8.1	12.8	3.39	41.4	1.8		
NROK	MF Flathead R. nr W. Glacier.	Bkg.	0	0.01	1.63	0.7	8.5	4.5	2.10	24.0	3.5		
NROK	S. Fork Coeur d'Alene	Mine	0	0.01	8.91	0.6	7.0	61	8.21	4517	5.7		
NVBR	Carson @ Dresslerville	Mine	0	0.16	3.42	1.5	8.3	24	2.73	66.2	5.5		

Study		Site ²	%			Water			Sediment			
Basin	Site Name	type	Wet- Land ²	MeHg	HgT	TOC	pН	SO ₄	MeHg (ng/g)	Hg_T	LOI^2	
NVBR	Carson @	Bkg.	0	(ng/L) 0.08	(ng/L) 4.74	(mg/L) 1.3	8.31	(mg/L) 	(ng/g) 0.55	(ng/g) 45.3	(%) 5.69	
NVBR	Markleeville Carson @ Deer Run Rd.	Ag.	3	0.68	31.08	6.9	8.1	52	1.21	78.4	1.73	
NVBR	Carson @ Fort Churchill	Mine	2	5.12	1106	4.7	8.2	77	4.20	4130	3.33	
NVBR	Carson @ Tarzan Rd.	Ag.	4	1.34	204.57	5.5	8.4	145	1.34	778.3	0.82	
OAHU	S. Fork Lake Wilson	Urb		0.12	1.93	3.3	6.8		1.18	300.2	17.02	
OAHU	Kawainui Canal	Bkg.		0.02	1.00	3.1	7.0		0.64	106.2	41.79	
OAHU	Ala Wai Canal	Urb		0.01	1.17	0.6	8		0.34	255.7	21.62	
OAHU	Nuuanu Reservoir	Ref		0.10	24.27	2.5	7.8		0.46	291.2	23.97	
OAHU	Waikele Stream	Ag.		0.01	1.27	0.8	7.2		3.55	186.0	15.95	
SACR	Bear River @ Hwy 70	Mine	0	0.24	17.82	3.5	7.4	5.6	0.55	176.8	2.89	
SACR	Putah Creek @ Davis	Mine	0	0.05	4.10	2.3	8	28	0.27	275.6	3.86	
SACR	Cottonwood Creek	Mine	0	0.03	1.02	1.5	8.5	10.8	0.36	26.3	2.61	
SACR SACR	Sacramento Slough Colusa Basin	Ag.	2 2	0.15 0.08	10.19 6.90	3.2 5.9	7.9 7.9	7.9 55.3	2.84 0.52	128.5 53.3	7.07 6.85	
SACK	Drain Santa Ana R. blw	Ag. Urb	2	0.08	14.67	4.8	7.9	105	1.47	45.6	5.77	
SANA	Prado Dam Mill Ck. @	Urb		0.08	2.99	6.9	10.0	53.8	1.47	30.3	7.75	
SANA	Chino-Cor. Rd. Santa Ana R. @	Urb		0.03	3.71	3.0	8.2	94.4	1.70	24.3	5.02	
SANA	Hamner Rd. Santa Ana R. @	Urb		0.05	2.28	2.3	8.1	87.6	3.42	27.3	5.81	
SANA	MWD Cross. S. Fork, Santa Ana River	Bkg.	0	0.02	0.61	0.6	7.7	1.4	3.65	28.8	17.22	
SANT	NF Edisto R. nr Fairview Cross	A/F	16	0.32	3.77	4.8	6.1	1.1	6.80	86.6	12.04	
SANT	NF Edisto River nr Branchville	A/F	16	1.48	9.41	3.8	6.4	2.9	2.50	6.1	15.46	
SANT	SF Edisto River @ Springfield	A/F	16	0.41		3.0	6.3		2.70	41.5	28.09	
SANT	SF Edisto River, Canaan	A/F	20	0.40	7.27	5.9	6.4	2.1	3.10	69.4	31.03	
SANT	Edisto River, Givhans	A/F	36	1.36	8.18	4.6	6.6	4	5.80	70.1	21.31	
SANT	Saluda River, Silverstreet, SC	Bkg.	0	0.09	1.05	2.9	7.1	5.5	0.70	23.9	6.67	
SOFL	WCA 2, site U3	Bkg.	50	0.61	3.50	24.0	7.5	25.6	2.70	194.0	91.00	
SOFL	WCA 2, site 2BS	Bkg.	50	0.45	2.10	18.0	6.9	10.2	3.90	234.0	90.00	
SOFL	WCA 3, site 3A15	Bkg.	50	0.50	1.90	16.0	7.1	0.5	7.80	288.0	92.00	
SOFL	Everglds. Natl. Pk., site TS7	Bkg.	50	0.20	2.38	12.0	6.8	0.5	5.80	145.0	90.00	
TRIN TRIN	Trinity River nr Crockett, TX Lake Livingston	Urb. Urb	0	0.02 0.02	6.50 1.34	5.8 6.0	7.5		0.28 0.20	30.6 45.2	4.42 7.59	
TRIN	White Rock Ck.	Urb.	0	0.02	1.34	6.0 4.9			0.20	45.2 8.6	1.59	
TRIN	White Rock Ck. Dallas, TX White Rock Lake,	Urb. Urb.	0	0.04	1.65	4.9 5.6	 7.9		0.14	8.0 55.4	6.24	
11/11/	Dallas	010.	U	0.02	1.24	5.0	1.7		0.52	55.4	0.24	

Table 2. Site names, type and analytical results from the sediment and water samples—Continued

 [-- indicate no data]

		0.1	%			Water			Sediment			
Study Basin	Site Name	Site ¹ type	Wet- Land ²	MeHg (ng/L)	Hg _T (ng/L)	TOC (mg/L)	рН	SO ₄ (mg/L)	MeHg (ng/g)	Hg _T (ng/g)	LOI ² (%)	
TRIN	Clear Crk. @ Sanger	Bkg.	0				8.0	55	0.23	5.9	2.18	
UIRB	Des Plaines River	Ag.	15	0.10	4.18	11.4	7.5	94	3.58	11.6	1.40	
UIRB	Nippersink Ck. bv Wonder L.	Ag.	0	0.04	1.42	3.5	7.8	64	0.08	8.7	2.30	
UIRB	Salt Creek @ W. Springs, IL	Urb	0	0.13	9.26	6.3	7.3	89	1.10	46.8	3.29	
UIRB	Pitner Ditch nr LaCrosse, IN	Ag.	0	0.03	0.27	3.1	7.8	89	0.09	9.1	1.66	
UIRB	Mukwanago R. @ Mukwanago	Ref	3	0.06	1.48	6.9	8.0		0.11	31.6	1.15	
YELL	Bighorn River nr. Kane	Ag.	1	0.13	3.89	3.7	8.4	170	0.60	16.3	2.09	
YELL	Bighorn Lake @ Hwy14A	Ag.	1	0.10	2.48	3.8	8.3	190	0.59	33.0	5.31	
YELL	Shoshone River	Ag.	0	0.13	5.31	4.2	8.1	240	0.53	11.1	1.83	
YELL	Tongue River	Ag.	4	0.06	1.87	3.4	8.5	94	3.05	27.7	8.23	
YELL	Yellowstone R. near Sidney	Ag.	1	0.15	4.07	2.9	8.6	110	0.45	18.7	2.14	
Summary	v Statistics											
Mean				0.15	16.6	4.15	5.3	55.5	1.87	211	11	
Median				0.06	2.28	3.4	7.7	28	0.62	46.3	4	
Std. Dev.				0.26	110.4	3.57		83.7	2.39	648	18	
Coeff. of Variat	tion			1.73	6.63	0.86		1.51	1.27	3.06	1.64	
Minimur	n			0.01	0.27	0.4	3.3	0.2	0.01	1.85	0.0	
Maximu	m			1.481	1106.7	24	10.09	484	10.851	4517	92	
N				104	103	105	104	84	106	106	105	

Table 2. Site names, type and analytical results from the sediment and water samples—Continued [-- indicate no data]

<u>N</u> 104 103 105 104 84 General site categories for the sampling locations within each study basin:

Ag. = agriculture dominant.

A/F = agriculture and forested mix.

Bkg. = Background or reference site.

Mine = Current or abandon mining activity near sampling site.

Urb. = Urban or industrial activity near sampling site.

²Percent of each sub-basin classified as wetland areas.

³Percent of dry sediment mass lost on ignition (LOI) after firing to 550°C for two hours.