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Seasonal influences on partitioning and transport of total and methylmercury in rivers from contrasting watersheds

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Abstract. Seven Wisconsin rivers with contrasting, relatively homogeneous watershed composition were selected to assess the factors controlling mercury transport. Together, these watersheds allow comparisons of wetland, forest, urban and agricultural land-uses. Each site was sampled nine times between September 1993 and September 1994 to establish seasonal signatures and transport processes of total mercury (Hg_T) and methylmercury (MeHg). Our results clearly show that land use and land cover strongly influence mercury transport processes. Under base-flow conditions, unfiltered MeHg yield varies by a factor of sixteen (12–195 mg km^{-2} d^{-1}), and increases with the fraction of wetland area in the watershed. Elevated mercury yields during high flow are particle-phase associated in agricultural sites, but filtered-phase associated in wetland sites. Methylmercury represented less than 5% of total mercury mobilized during the spring thaw across all watersheds. Autumn MeHg yield was generally 11–15% of Hg_T in wetland influenced watersheds, though a maximum of 51% was observed. In some cases, single high-flow events may dominate the annual export of mercury from a watershed. For example, one high-flow event on the agricultural Rattlesnake Creek had the largest Hg_T and MeHg yield in the study (107 and 2.32 mg km^{-2} d^{-1}, respectively). The mass of mercury transported downstream by this single event was an order of magnitude larger than the eight other (non-event) sampling dates combined. These results underscore the importance of watershed characteristics and seasonal events on the fate of mercury in fresh water rivers.

Abbreviations: DOC: Dissolved Organic Carbon; MeHg: Methylmercury; NEY: Non-event Yield, SPM: Suspended Particulate Matter; Hg_T: Total Mercury

Introduction

Transport of mercury in rivers is dependent on many factors, including: physical characteristics of watersheds (for example, land cover, soil type

and erosion), biogeochemical controls (associations with dissolved organic carbon [DOC], ionic strength influences), and seasonal dynamics (storm events, temperature extremes, snow melt). A thorough understanding of the relationships between these factors would provide efficient and effective tools for management of these water resources. Additionally, identification of controlling transport processes may provide an important link to understanding the terrestrial component of the global mercury cycle.

Partitioning to particles affects the transport efficiency of mercury in a river. Soils are the primary sequestering agent for atmospherically deposited mercury (Lindquist et al. 1991; Mason et al. 1994), and soils in the Upper Midwest of the United States have been shown to be enriched in total mercury (Hg_T) due to local and regional deposition (Nater & Grigal 1992). Characteristics of individual watersheds may play an important role in the remobilization of this mercury pool. Land use and land cover effects on mercury mobilization are important, because trace metals can undergo many transformations in the watershed that affect bioavailability in the associated river. Factors controlling these transformations in speciation and concentration can include pH, flow, DOC, suspended particulate matter (SPM), colloids, ionic strength, and dissolved oxygen.

Many studies have linked land-use and land-cover to net loadings downstream. For example, wetlands have been a net source of methylmercury (MeHg) for lakes in a Canadian Boreal forest (St. Louis et al. 1994, 1996). Branfireun et al. (1996) noted a three-fold increase in MeHg concentration as a stream passed through a Precambrian Shield peatland. Erosion of organic soils and downstream transport of particle bound Hg_T has been noted in agricultural watersheds of Wisconsin and Minnesota (Balogh et al. 1997; Hurley et al. 1995). Seventy-nine percent of Hg_T was associated with the particulate phase in the agricultural and urban influenced Sacramento River, California (Gill & Bruland 1990).

Seasonal dynamics also play an important role in mercury transport. In the Upper Midwest, the spring snow melt provides a substantial portion of the annual riverine water budget. Frozen soils limit the infiltration pathway for runoff, and may produce a source water of unique composition compared with high flow events later in the year (Balogh et al. 1997; Hurley et al. 1996). Storm water runoff that flushes pore waters from wetlands or soils can increase loadings of mercury to a river, especially following dry periods (Grondin et al. 1995; Zillioux et al. 1993). In late summer and autumn elevated mercury concentrations have been observed in heavily stained rivers (Mierle & Ingram 1991).

Previous work in Wisconsin has established that mercury concentrations in unimpacteded rivers are low compared with studies not using clean technique

(less than 10 ng L^{-1} base flow; less than 50 ng L^{-1} high flow), and show variability across the state (Babiarz & Andren 1995). The influence of watershed characteristics on concentration and downstream transport mechanisms was introduced by Hurley et al. (1995). Elevated fluxes of DOC-correlated Hg_T were associated with the filtered phase in forested-wetland zones, but particulate-associated in agricultural areas. Methylmercury yield was highest in forested-wetland sites and was positively correlated to wetland composition (percent of surface area). These transport mechanisms are similar to those observed in the Canadian Shield (Kelly et al. 1995).

This study examines seasonal and stream discharge effects on downstream transport of mercury. The streams drain watersheds consisting of wetland, forest, agricultural, and urban land uses, and are a representative subset of our previous work (Babiarz & Andren 1995; Hurley et al. 1995; Shafer et al. 1997). Unique to this phase of the study, streams were sampled once every 6–8 weeks to (1) assess seasonal trends that could not be established within the two-point sampling regime of previous studies; (2) refine watershed yield calculations to include particle-partitioning changes with flow rate; and (3), refine our description of watershed controls on riverine mercury concentration. These goals augment the watershed-based stewardship of our natural resources.

Methods

Seven sites were selected as representative indicators of common Wisconsin land-use patterns: Wetland and Forest mix, Agricultural and Forest mix, Agricultural only, and Urban (Figure 1, Table 1). In choosing a subset of previously studied sites, we maintained a contiguous data base, and assured a representative distribution of land use patterns (Babiarz & Andren 1995; Hurley et al. 1995). A Geographical Information System was used to determine and quantify watershed characteristics. Sampling of contrasting sites within a land-use classification enabled comparison of major study variables: DOC, SPM and ionic strength.

Each river was sampled nine times during 1993 and 1994 to detail the watershed effects on seasonal response and yield. All sampling for mercury followed strict trace-metal clean protocol (Gill & Fitzgerald 1985; Nriagu et al. 1993; Patterson & Settle 1976). Unfiltered water was collected for Hg_T, MeHg and SPM analysis. Particles were collected in-line on quartz-fiber filters in Teflon® housings (Hurley et al. 1994; Mason & Sullivan 1997). Filters had a 0.7 μm nominal pore size (2 μm used with water) and were ashed at 700 °C. We typically passed one to three liters of water through a filter for particle collection. All filters were analyzed for Hg_T. Filters analyzed

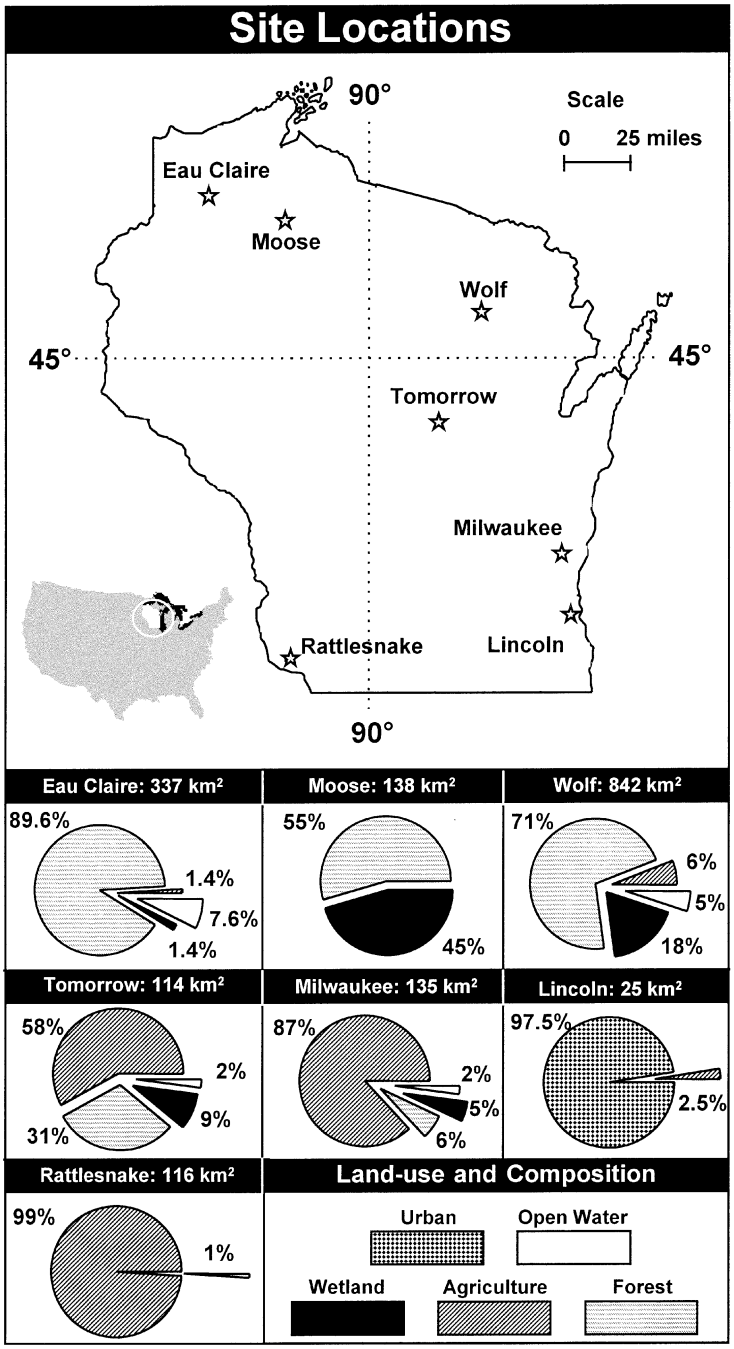

Figure 1. Land use, land composition and location of the seven study sites. Total catchment surface area above the sampling site is indicated next to the river name. The 1% wedge on Rattlesnake Creek is Open Water. Land use percentages not plotted include: 0.03% Urban (Wolf, Eau Claire, Tomorrow), and 0.6% Barren (Milwaukee). Study locations are indicated as stars.

Table 1. River location and flow characteristics.

	Rivers	Flow in cfs					Record	Location	
		Annual		Percentile			(years)	Latitude	Longitude
		Mean	Medium	10th	50th	90th			
Increasing agricultural	Moose	53.9	51.0	103	53.1	14.6	*	46°01′13″	90°58′50″
↓	Wolf	528	455	785	370	240	30	45°20′10″	88°53′23″
	Tomorrow	32.3	31.6	58	35	21	1	44°31′33″	89°20′23″
↑	Milwaukee	47.4	35.4	110	31	15	1	43°33′44″	88°03′08″
Increasing wetland	Rattlesnake	39.6	24.4	41	16	7.8	7	42°46′30″	90°55′23″
(Forest)	Eau Claire	85.1	87.1	102	85	70	*	46°13′25″	91°43′57″
(Urban)	Lincoln	5.8	8.5	31	4.1	2.1	1	43°05′51″	87°58′19″

Flow data from the United States Geological Survey (USGS) Water Data Reports WI-93-1 and WI-94-1, Madison, WI. * River not gauged: Flow measurements taken at time of sampling only.

for MeHg came from dates when the unfiltered MeHg concentration was at least 1% of the unfiltered Hg_T concentration. Past experience indicated that the majority of MeHg could be in the filtered phase, so analytical emphasis was placed on dates with the highest unfiltered MeHg concentration. For both Hg_T and MeHg, the filtered fraction was calculated by difference.

Total mercury and methylmercury analysis followed standard protocols (Bloom 1989; Bloom & Crecelius 1983; Horvat et al. 1993; Liang et al. 1994). Briefly, Hg_T samples were digested with a BrCl oxidizing solution, reduced with tin(II) chloride, concentrated onto gold traps and quantified using Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS). Methylmercury samples were distilled to remove matrix interferences, ethylated using sodium tetraethylborate, and concentrated onto Carbotrap® columns. Typical distillation volumes were approximately 120 mL. An isothermal gas chromatographic separation (eluting Hg°, $C_2H_5HgCH_3$, and $(C_2H_5)_2Hg$) was used before pyrolitic conversion to elemental mercury for detection by CVAFS.

Analytical detection limits were calculated as three times the standard deviation of the combined variance of each method. The combined variance includes contributions from added reagents, purge blanks, and distillations (MeHg only). The relative contribution from each source varies with each batch of samples analyzed. The maximum detection limits for Hg_T and MeHg were 0.13 ng L^{-1} and 0.03 ng L^{-1} respectively (typical sample aliquots were 160 mL (Hg_T) and 120 mL (MeHg)). Filter blanks, expressed as a percentage of the mercury in the particulate sample averaged 21.5% (σ = 13.5%) for Hg_T and 16.5% (σ = 10.5%) for MeHg. Two batches of filters were contaminated by poorly rinsed filter holders, extended storage, or both. The data from these filters were omitted.

Suspended particulate matter (SPM) was determined by filtering a known aliquot of water (usually 100 mL) through a tared 0.4 μm, 47 mm (diameter) polycarbonate track-etched filter. Dissolved organic carbon (DOC) samples were filtered through Whatman GF/F filters in an all-glass filtration unit (nominal pore size 0.7 μm). The use of a different pore size for Mercury, SPM and DOC results from two factors: (1) acid and temperature compatibility requirements on materials used for clean technique, and (2) the need to compare SPM data with the studies of other researchers. Although the difference is small compared with the wide range of particles in the water column ($>$5 orders of magnitude), we limit our data comparisons to those researchers who use the same methodology. Carbon was determined on a Shimadzu Model TOC5000 high-temperature combustion carbon analyzer. Temperature, dissolved oxygen, pH, and specific conductance were determined with a multiprobe instrument (Hydrolab-H_2O).

Stream discharge was measured using standard United States Geological Survey flow measurement protocols (USGS 1963). Wadable stream flows were determined with a pygmy or AA (Price) current meter. Stream discharge data from larger rivers were taken from USGS gauging stations. Four of the sites were both gauged and wadable, allowing us to compare and calibrate these methods.

For the purposes of data analysis, each sampling date was sorted into one of three categories: base flow, medium flow or event flow. Long term discharge records (USGS 1994, 1995), were used to determine flow-rate limits for each category based on percentile ranking. The base-flow maximum limit was defined as the flow rate that is exceeded by 90% of the historical record. The event-flow minimum rate is exceeded by only 10% of the record. Medium flow comprises the range between these extremes.

Statistical analysis was performed with the aid of Minitab version 9.0 for Windows and SAS version 6.11 for Unix. To describe our sampling scheme, we employed a randomized complete block design with subsampling. The data was "blocked" by river to account for watershed effects. Flow regime was the "treatment." Subsamples for each treatment and block came from separate (independent) trips to the river that fell within the given flow regime. Rankit and residual plots were used to confirm that the data comes from a normal distribution. In some cases, the limited sample size makes this assumption difficult to confirm, but for inference about the mean, the ANOVA and *t*-test procedures we used are fairly robust to departures from normality. All statistical tests were performed using a significance level of $\alpha = 0.05$.

Results and discussion

Unfiltered Hg_T levels ranged from 0.3 to 45.9 ng L^{-1} with a mean and median of 4.74 and 2.60 ng L^{-1}, respectively (Table 2). Unfiltered MeHg ranged from non-detectable (less than 0.01 ng L^{-1}) to 1.80 ng L^{-1}. Omitting non-detectable values, the unfiltered MeHg mean and median concentration was 0.25 and 0.11 ng L^{-1}, respectively. For both Hg_T and MeHg, the median was roughly half the magnitude of the mean, indicating a skewed distribution heavily influenced by a few high values. High concentrations are a result of storm events, or biogeochemical factors in watersheds, or both. Across all watersheds, unfiltered MeHg concentrations rarely exceeded 6% of unfiltered Hg_T (remaining below 0.2 ng L^{-1} except in areas influenced by wetlands, or during storm events). July and August were the only months when MeHg concentrations were above detection limits in all watersheds – a seasonal trend indicative of temperature and microbial controls on methylation.

Table 2. Unfiltered total mercury and methylmercury concentrations in rivers during the study period.

		Sept. 93	Nov. 93	Jan. 94	Mar. 94	Apr. 94	May 94	July 94	Aug. 94	Sept. 94	**Mean**	**St dev**	**Median**	Non-event Mean	Non-event LSD
Unfilterd Hg_T (ng L^{-1})															
Increasing agricultural	Moose	6.70	11.10	3.39	4.10	***8.70***	8.74	12.38	9.23	***8.14***	**8.05**	**2.95**	**8.70**	7.95	Z
↓	Wolf	***4.51***	1.46	1.17	4.82	2.55	2.19	2.73	2.35	***4.72***	**2.94**	**1.40**	**2.55**	2.47	X, Y
	Tomorrow	***3.65***	1.51	1.15	7.15	1.91	1.34	1.84	12.86	1.46	**3.65**	**3.94**	**1.84**	3.65	X, Y
↑	Milwaukee	***7.89***	—[a]—	1.23	***5.90***	2.27	3.65	7.28	7.57	2.20	**4.75**	**2.72**	**4.78**	4.03	X, Y
Increasing wetland	Rattlesnake	1.09	1.83	0.98	1.91	2.88	2.30	***45.9***	2.60	2.26	**6.86**	**14.6**	**2.26**	1.98	Y
(Forest)	Eau Claire	0.60	1.22	0.26	1.14	***1.13***	1.26	0.73	3.52	***1.05***	**1.21**	**0.93**	**1.13**	1.25	Y
(Urban)	Lincoln	4.82	—[a]—	4.24	14.73	2.69	1.61	9.93	6.49	2.01	**5.82**	**4.51**	**4.53**	5.82	X, Z
Unfiliterd MeHg (ng L^{-1})															
Increasing agricultural	Moose	0.75	1.77	0.51	0.08	***0.09***	0.26	1.28	0.76	***0.68***	**0.69**	**0.56**	**0.68**	0.77	A
↓	Wolf	***0.29***	0.75	0.13	0.12	0.12	0.08	0.12	0.12	***0.59***	**0.26**	**0.24**	**0.12**	0.21	B
	Tomorrow	***0.22***	0.08	<0.01	0.08	0.06	0.08	0.20	0.05	0.12	**0.11**	**0.06**	**0.08**	0.10	B
↑	Milwaukee	***0.18***	0.08	<0.01	***0.10***	0.06	0.12	0.10	0.07	0.16	**0.11**	**0.04**	**0.10**	0.10	B
Increasing wetland	Rattlesnake	<0.02	<0.03	<0.01	0.04	<0.02	0.11	***1.00***	0.12	<0.02	**0.32**	**0.46**	**0.11**	0.09	B
(Forest)	Eau Claire	<0.02	0.06	<0.01	<0.03	***<0.02***	<0.03	0.05	0.06	***0.02***	**0.05**	**0.02**	**0.92**	0.06	B
(Urban)	Lincoln	<0.02	<0.02	<0.01	0.04	0.01	<0.02	0.05	0.01	0.08	**0.04**	**0.03**	**0.04**	0.04	B

Values below the limit (indicated as "less than") are not included in the calculation of the mean, standard deviation, or median. High flow events set in bold italic. Rivers with the same symbol in the Non-event Least Significant Difference (LSD) column are not significantly different from each other at $\alpha = 0.05$. [a] Samples lost after collection.

These concentration ranges are in line with those reported in an earlier study (Hurley et al. 1995) with a two-point sampling schedule (Fall and Spring). Median unfiltered Hg_T concentrations are essentially identical (2.62 ng L^{-1} Hurley). The mean is 30% higher than that reported for base flow conditions (3.46 ng L^{-1} Hurley), a result of the 10 high flow data points in the current study average. The non-event mean for the current study, however, is quite comparable (3.50 ng L^{-1}). The agreement between these summary statistics strengthens our confidence that a representative subset of rivers was selected for the current study. Hurley et al. examined the role of selected water-chemistry variables and land-cover classes on Hg concentrations but did not explore seasonal and flow rate trends in depth. In the following discussion, we highlight seasonal trends within a framework of high flow effects on particle partitioning and transport of mercury.

Watershed influence on high flow concentrations

Mercury concentrations at high flow are dependent on watershed composition. In agricultural areas that are hydrologically responsive (poor infiltration, steep slope), erosional soils create a short-duration, efficient vector for downstream transport of mercury. On Rattlesnake Creek, for example, the mass of mercury transported down stream during a single event (July 1994) was an order of magnitude larger than the eight other (non-event) sampling dates combined. Compared with the average non-event unfiltered concentration, Hg_T increased by a factor of 20 and MeHg by a factor of 11. Ancillary parameters also changed dramatically (Table 3) with a seventy-fold increase in SPM (1005 mg L^{-1}) and a three-fold increase in DOC concentration and flow rate (9 mg L^{-1}; 110 m^3 sec^{-1}, respectively). This finding underscores the importance of event-based sampling within responsive watersheds. Balogh and coworkers (1997) also noted elevated storm-event Hg_T and SPM concentrations, at agricultural sites on the Minnesota River. Storm erosion of soils was the source of the mercury.

Mercury levels in other watersheds, such as wetlands, are less responsive to high flow. For example, event and non-event averaged concentrations on the Moose River are quite similar (Table 2). Accurate calculation of annual loading may depend more on frequent flow measurements than on frequent metals sampling.

To confirm that high flow alone is not a master variable for elevated mercury concentration, we compared the ten storm event samples (in bold italic on Table 2) to the remaining non-event data. Lincoln Creek was omitted due to a lack of data at high flow. If high flow was the only variable for elevated mercury concentration across all watersheds, we would expect a significant difference between the average event and non-event concentra-

Table 3. Ancillary parameters.

Ancillary parameters		Sept. 93	Nov. 93	Jan. 94	Mar. 94	Apr. 94	May 94	July 94	Aug. 94	Sept. 94	**Mean**	**St dev**	**Median**
SPM (mg L^{-1})													
Increasing agricultural	Moose	2.52	4.14	3.74	4.08	***5.90***	4.70	11.4	12.1	***7.20***	**6.19**	**3.41**	**4.70**
↓	Wolf	***10.9***	3.82	4.12	17.7	8.00	5.01	3.09	2.10	***6.96***	**6.86**	**4.90**	**5.01**
	Tomorrow	***4.0***	2.19	4.80	13.2	4.62	2.91	7.90	1.69	1.99	**4.81**	**3.69**	**4.02**
↑	Milwaukee	***31.4***	11.8	10.2	***9.91***	4.09	24.3	42.2	27.7	10.4	**19.1**	**12.7**	**11.8**
Increasing wetland	Rattlesnake	14.6	7.94	16.7	14.3	2.70	21.2	***1005***	20.5	22.5	**125**	**330**	**16.7**
(Forest)	Eau Claire	1.28	1.46	0.91	1.63	***1.94***	2.87	3.16	2.48	***1.70***	**1.94**	**0.75**	**1.70**
(Urban)	Lincoln	5.20	3.19	73.7	13.9	3.65	5.26	8.56	6.96	5.03	**13.9**	**22.6**	**5.26**
DOC (mg L^{-1})													
Increasing agricultural	Moose	19.2	25.6	14.4	8.52	***15.4***	23.0	41.1	37.7	***37.3***	**24.7**	**11.6**	**23.0**
↓	Wolf	***15.6***	7.83	4.94	4.82	5.22	4.16	10.9	7.40	***15.8***	**8.51**	**4.56**	**7.40**
	Tomorrow	***14.2***	4.75	1.81	4.77	5.55	7.19	8.34	3.19	4.45	**6.03**	**3.64**	**4.77**
↑	Milwaukee	***17.6***	6.71	4.05	***9.76***	7.05	3.38	5.15	5.18	5.01	**7.10**	**4.36**	**5.18**
Increasing wetland	Rattlesnake	2.41	3.20	1.48	2.39	4.95	2.32	***9.30***	4.72	2.07	**3.65**	**2.43**	**2.41**
(Forest)	Eau Claire	2.36	3.26	2.34	2.57	***2.29***	2.11	2.53	2.54	***2.59***	**2.51**	**0.32**	**2.53**
(Urban)	Lincoln	4.49	5.15	6.48	5.79	4.13	2.87	7.87	2.94	3.86	**4.84**	**1.66**	**4.49**
Conductivity (ms cm^{-1})													
Increasing agricultural	Moose	0.054	0.041	0.083	0.107	***0.033***	0.032	0.039	0.058	***0.032***	**0.053**	**0.026**	**0.041**
↓	Wolf	***0.093***	0.150	0.121	0.199	0.157	0.143	0.152	0.193	***0.126***	**0.148**	**0.034**	**0.150**
	Tomorrow	***0.306***	0.370	0.406	0.356	0.336	0.381	0.406	0.504	0.414	**0.388**	**0.56**	**0.381**
↑	Milwaukee	***0.619***	0.701	0.704	***0.442***	0.620	0.693	0.702	0.842	0.738	**0.673**	**0.109**	**0.701**
Increasing wetland	Rattlesnake	0.708	0.710	0.716	0.675	0.637	0.704	***0.365***	0.830	0.755	**0.678**	**0.129**	**0.708**
(Forest)	Eau Claire	0.116	0.114	0.120	0.146	***0.117***	0.121	0.119	0.138	***0.124***	**0.124**	**0.011**	**0.120**
(Urban)	Lincoln	0.536	0.738	1.370	1.550	1.470	1.109	0.483	1.061	0.717	**1.004**	**0.404**	**1.061**

High flow events are set in bold italic.

tions. Statistical tests provide no evidence that the cross-watershed mean concentrations between events and non-events are different. The event and non-event mean concentrations for Hg_T were 9.2 and 3.5 ng L^{-1} respectively; $p = 0.25$. The event and the non-event average for MeHg was 0.32 ng L^{-1} and 0.26 ng L^{-1} (omitting non-detectable values); $p = 0.40$. The high p-value results from large variances about each mean, and suggests additional influences on concentration beyond magnitude of flow (watershed characteristics, for example).

Under non-event flow there are statistical differences between watersheds. Using a protected least significant difference approach, we compared the non-event mean Hg_T and MeHg concentrations (and variances) between each river. For both Hg_T and MeHg, the means were *not* statistically equivalent with each other ($p = 0.001$). The non-event means in Table 2 must be separated by more than 3.2 ng L^{-1} (Hg_T) or 0.37 ng L^{-1} (MeHg) to be significantly different. The Moose River, a largely wetland-influenced site, had the largest non-event mean Hg_T and MeHg concentrations. It was also the only river to have a non-event mean MeHg concentration significantly different from all others in the study. The agricultural Rattlesnake Creek had the least variable non-event concentration across the year ($\sigma = 0.67$ ng L^{-1}).

One way these watersheds differ is in the quantity and character of the particulate matter. The extent to which mercury binds to colloids, DOC or SPM may determine the downstream transport efficiency of mercury. For example, 74% ($\sigma = 12\%$) of unfiltered Hg_T exists in the filtered phase in the Moose River, but in Rattlesnake Creek, 42% ($\sigma = 27\%$) of Hg_T is filter-phase associated. On the basis of particle settling, one might expect a longer water column residence time for mercury associated with DOC in the filtered phase.

Although the association of DOC with Hg_T has been documented (Andren & Harriss 1975; Mierle & Ingram 1991), the strength of the correlation varies with site and season – possibly due to changes in chemical character. When filtered mercury concentration was regressed against DOC within each river, the fits were poor (p-value ≥ 0.061) – a likely result of a narrow range in DOC concentration and small sample size. When the data is combined across all watersheds (Figure 2), much of the mercury concentration increase can be accounted for by DOC. Both Hg_T and MeHg regressions had a p-value of zero and relatively strong coefficients of determination (Hg_T $r^2 = 0.41$, MeHg $r^2 = 0.61$). A test for discordant data suggests the Hg_T point at 11.8 ng L^{-1} is an outlier (Bonferroni corrected p-value = 0.000). Discarding this point, the Hg_T regression increased to $r^2 = 0.72$). Although the strong correlation suggests an association, mercury in the filtered phase need not be bound to DOC. Unfortunately, the filtration techniques used in this study preclude the direct examination of the role of colloids.

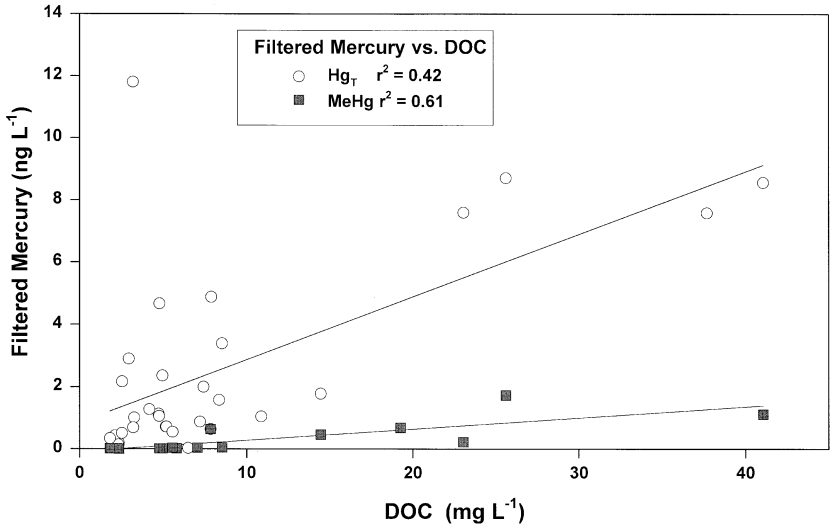

Figure 2. Plot of filtered Hg_T and filtered MeHg versus DOC across all watersheds and seasons. High flow events have been omitted to remove possible bias. The *p*-value for overall fit to the regression was zero for both Hg_T and MeHg.

Particle partitioning of mercury

The partitioning of mercury to particles can have a strong influence on the bioavailability and export of mercury from a watershed. The relative concentration of particles, the binding affinity of particles for mercury, and the abundance and strength of dissolved ligands, affects the quantity and efficiency in which mercury is transported downstream.

Across all watersheds, Hg_T concentrations on particles ranged from 27.4 to 627 ng g^{-1} with a mean, median and standard deviation of 302, 242, and 187 ng g^{-1}, respectively. The agricultural Rattlesnake Creek had the lowest and least variable concentrations (mean = 107, σ = 63.7 ng g^{-1}). Wetland-containing sites had mean concentrations that were not statistically different than agricultural sites (mean = 333, σ = 176 ng g^{-1} and mean = 231, σ = 202 ng g^{-1}, respectively). Methylmercury particulate concentrations range from 0.23 to 29.6 ng g^{-1} across all watersheds (mean = 8.5, median = 6.6, σ = 7.6 ng g^{-1}). Agricultural sites have the lowest concentrations, $<$6 ng g^{-1} (mean = 3.9, σ = 2.0 ng g^{-1}). Wetland influenced sites range from 2.4 to 29.6 ng g^{-1} (mean = 12.9, σ = 9.9 ng g^{-1}).

Our trends in particle concentration generally agree with particle and sediment concentrations reported elsewhere. Other researchers have found total mercury concentrations on mineral soils in the range of 22 to 50 ng g^{-1} (Balogh et al. 1997; Nater & Grigal 1992). Lake sediments have been

found to range from 34 to 753 ng g^{-1} (Long et al. 1996; Sorenson et al. 1990). Total Mercury content of SPM in lakes ranged from 10 to 1100 ng g^{-1} (Hurley et al. 1994; Mason & Sullivan 1997). Methylmercury particulate concentrations range from 3.8 to 370 ng g^{-1} with a median near 40 ng g^{-1} (Hurley et al. 1994; Mason & Sullivan 1997). The median concentration may be more representative of oxygenated river systems since the upper limit is influenced by particles from oxygen-depleted hypolimnetic lake waters.

The affinity of a given compound for the particulate phase is described by the distribution coefficient K_d defined as:

$$K_d = \frac{C_p}{C_f} \quad (L\ kg^{-1}) \tag{1}$$

Where, C_p is the particulate mercury concentration in ng kg^{-1}, and C_f is the filtered mercury concentration in ng L^{-1}. Higher K_d's suggest stronger affinity for the particulate phase.

Log K_ds for Hg_T and MeHg range from 2.8 to 5.5, and 2.9 to 5.8, respectively. The lowest Log K_ds for both Hg_T and MeHg were from the storm event at the agriculturally dominated Rattlesnake Creek. Without this data point, the magnitude of this log-scale range decreased by 50%. Both mercury species have similar median values across all sites (4.9 and 4.6 for Hg_T and MeHg respectively). Our partition coefficients compare well with other studies. Log K_d for Hg_T in Lake Michigan tributaries ranged from 5.0 to 6.9 (Hurley et al. 1996). In Wisconsin lakes, Log K_d ranged from 4.5 to 5.7 (Hurley et al. 1994). An open water Lake Michigan study found Log K_d to range from 5.5 to 5.8 for Hg_T, with a Log K_d for MeHg of 5.7 (Mason & Sullivan 1997).

When Log K_d is regressed against SPM for each of the rivers, the slope is either negative or statistically equivalent to zero. The former case suggests greater partitioning to the particulate phase at low particle concentrations. This could also be an indication of colloids in these watersheds. Colloidal particles can pass through our filters and artificially decrease the partition coefficient – an artifact known as the "particle concentration effect" (Benoit et al. 1994). The present work in our laboratory investigates mercury–colloidal interactions and their influence on our estimates of Log K_ds.

In Figure 3, we plot Log K_d versus SPM for (1) all seven sites, (2) the three predominantly agricultural sites (Rattlesnake, Milwaukee, Tomorrow) and (3) the three predominantly wetland sites (Moose, Wolf, Tomorrow). The Tomorrow River appears in both plots because it is an "integrator" site, meaning it contains significant contributions from more than one type of land use. If the Tomorrow is excluded from the regression, there is very little change in the coefficient of determination for the wetland sites (Hg_T $r^2 = 0.55$; MeHg $r^2 = 0.04$). However, excluding the Tomorrow from the agricultural grouping

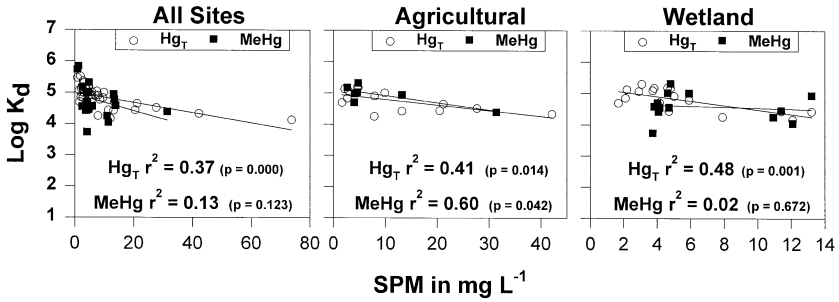

Figure 3. Log K_d vs. SPM for Hg_T and MeHg across (1) all seven sites, (2) agricultural sites (Rattlesnake, Milwaukee, Tomorrow), and (3) wetland sites (Moose, Wolf, Tomorrow). Data for the July storm event on the agricultural Rattlesnake Creek is omitted (Log K_d = 2.9, SPM 1005) because the point highly influences the slope.

has dramatic effects (Hg_T r^2 = 0.79; MeHg r^2 = 0.97). Interpretation of this strong correlation in agricultural zones is difficult. Because there are few data points with high SPM, the available data is very influential on the slope. If the correlation is valid, however, it would suggest particle partitioning of MeHg is important in agricultural zones but not in wetlands.

Watershed mercury yields

Another useful tool for comparing mercury transport among different watershed types is watershed yield. This statistic normalizes concentration to volumetric flow, and catchment surface area:

$$\text{Yield} = \frac{C * F}{A} \quad (\text{mg km}^{-2}\ \text{d}^{-1}) \tag{2}$$

where C is concentration in mg L^{-1}, F is volumetric flow in L d^{-1}, and A is the surface area of the contributing catchment upstream of the sampling point in km^{-2}. Since our data represent nine dates across an entire year and flow is evaluated on an average daily basis, we report these values in units of mg km^{-2} d^{-1}.

Effects of flow and season on yield

Flow and seasonal effects on yields of Hg_T and MeHg vary greatly among watersheds (Figure 4). The Upper Eau Claire River has the smallest variance in yield, and is relatively unresponsive to high flow. Soils in the Eau Claire watershed are very sandy and permeable, so hydrologic events are subdued. Our sampling site is within a predominantly forested watershed and is located 12 km downstream from the outlet of Lake Eau Claire. Contributions of water

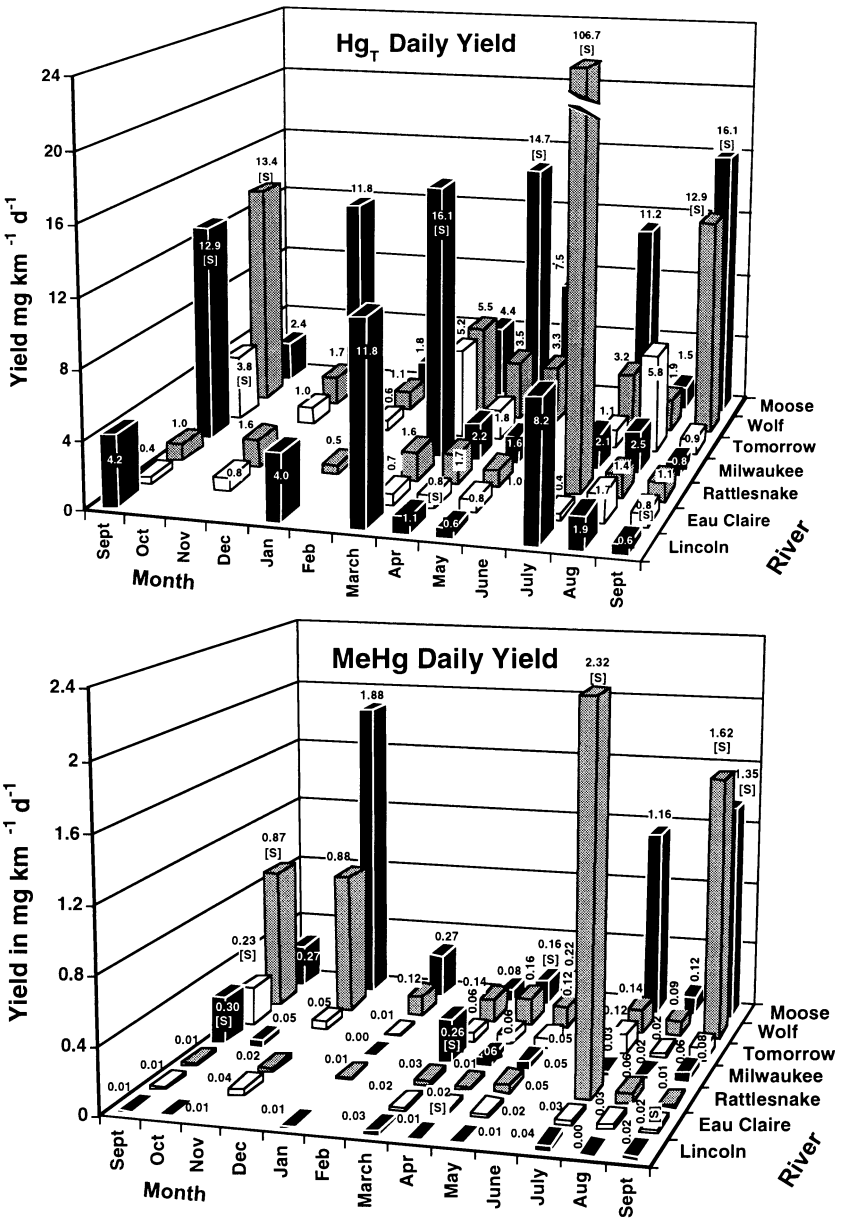

Figure 4. Plot of daily watershed yield vs. month. High flow events are indicated by the symbol "[S]." Note the ten-fold expansion of the MeHg y-axis. Each datum is from a single sample and should not be interpreted as an average for the entire month. Yield for the Eau Claire River in January 1994 could not be calculated because ice on the river prevented flow measurements. Total mercury yield for October 1993 is not available because the samples were lost. Methylmercury yields on dates where the unfiltered MeHg concentration was below the detection limit (see Table 2) are maximum estimates.

cycled through lakes may temper watershed influences (Babiarz & Andren 1995; Hurley et al. 1995; St. Louis et al. 1994, 1996).

Lincoln Creek, an urban watershed, was not sampled under high flow conditions. Nonetheless, Hg_T yield is erratic during the year, presumably due to anthropogenic influence. The highest unfiltered Hg_T yield occurred during an early spring melt. In contrast, MeHg yields remained low during the spring melt period for all rivers (including Lincoln). This suggests non-methyl forms of mercury are the primary species mobilized during the melt. Atmospherically-derived contaminants may become frozen in urban snow pack and ice until flushed by the spring thaw – a regular event in the annual cycle of temperate rivers.

Non-event mercury yields (combined base flow and medium flow) from agricultural sites are quite similar to the non-event mercury yield (NEY) for the forested Eau Claire River system. Mean and median NEYs are in the range of 1–2 mg km^{-2} d^{-1} Hg_T, 0.02–0.06 mg km^{-2} d^{-1} MeHg. Agricultural sites are very responsive to high flow. Since NEY is often less than 15% of event yield, frequent or large magnitude events (or both), could account for a substantial portion of the annual export of mercury. For example, the largest MeHg yield recorded in this study occurred during a July 1994 storm event on the agricultural Rattlesnake Creek. This is especially notable since high MeHg yields are more commonly associated with wetland zones.

Maximum Hg_T NEY increases with percent wetland composition: 1.7 (Rattlesnake), 2.4 (Milwaukee), 5.8 (Tomorrow), 5.5 (Wolf), and 11.8 (Moose). This trend is also consistent for MeHg: 0.06 (Rattlesnake and Milwaukee), 0.12 (Tomorrow), 0.88 (Wolf), and 1.88 (Moose). Watersheds with large wetland contributions (the Moose and Wolf) exhibit strong seasonal fluctuations in unfiltered MeHg yield. In addition to elevated yield during the spring thaw, events in autumn are important. This fall increase was also observed for Hg_T by Mierle & Ingram (1991). These observations may suggest flushing of MeHg built up during the warm summer months. July and August were the only two months when MeHg was above detection limit for all the rivers, an indication of temperature or microbial dependence on methylation. Methylmercury yield commonly reaches 11–15% of Hg_T yield during the fall at wetland influenced sites. During low flow in early November 1993, MeHg in the Wolf River accounted for 51% of Hg_T.

Particle partitioning and yields

Particle partitioning is an important component of mercury yields and appears to change with flow conditions. Figure 5 presents average Hg_T and MeHg yields against three flow regimes (base, medium, event). Under base flow conditions, unfiltered Hg_T yields are roughly equivalent across all watersheds.

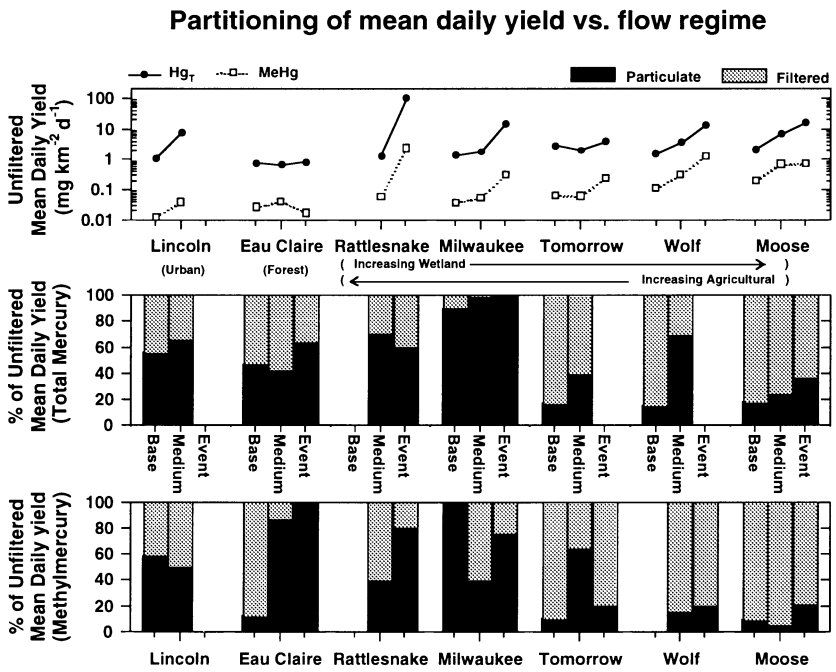

Figure 5. Plot of partitioning of the mean daily yield across three flow regimes (low, medium, and high). The top graph plots the mean daily yield for unfiltered Hg_T, and unfiltered MeHg. The bottom graphs plot the percent of the mean unfiltered-mercury daily yield as the particulate, and filtered phase. Lincoln Creek was not sampled during event flow. Rattlesnake Creek was not sampled during base flow. Omitted data on the Tomorrow and Wolf Rivers is due to one or more of the following: (1) freezing temperatures preventing filtration of the sample, (2) filters were compromised, and (3) filters were misplaced before analysis.

However, unfiltered MeHg yields vary by at least a factor of ten among different watershed types. Methylmercury yields increase with percent-wetland composition in the watershed under non-event flow. A regression to test this observation had r^2 values of 0.99, 0.97, and 0.01 for base, medium and event flow, respectively. All *p*-values for over-all fit of the regression were equal to zero. None of the analogous regressions Hg_Twere significant (*p*-value = 0.21).

Both unfiltered Hg_T and MeHg yield generally increase with increasing flow. Since yield and flow are proportional, riverine mercury concentrations would have to drop significantly if yield did not follow this trend. The lower MeHg yield at high flow on the Eau Claire river is probably due to a dilutional effect of epilimnetic waters influencing this site. Compared with other sites, the Eau Claire and the Tomorrow rivers have a relatively flat response of yield across all three flow regimes. We attribute this to lake effects on the Eau Claire and mixed watershed composition on the Tomorrow.

Wetland influenced sites have an approximate log-linear increase in yield across base, medium and event flows. The additional mercury is predominately associated with the filtered phase. In contrast, agricultural sites have sharp increases in yield between medium flow and event flow, which is undoubtedly a result of soil erosion.

The effects of flow on partitioning of mercury to the dissolved or filtered phase have some watershed dependency. For example, the distribution of Hg_T is relatively constant across flow regimes within Rattlesnake Creek and the Milwaukee River, the Eau Claire River, and Lincoln Creek (agricultural, forest and urban watersheds, respectively). The remaining integrator and wetland sites show much more variability. In contrast, the MeHg distribution between these phases has less variability within the wetland and urban sites than the agricultural or forest sites.

Conclusions

Selection of relatively homogeneous watersheds representing common land-use patterns – coupled with the use of clean techniques – has enabled resolution of factors influencing the mobility of Hg_T and MeHg in rivers. Results from this phase of the study have shown seasonal responses and high-flow effects on watershed mercury yield. Because our sampling sites were a representative subset of those studied in Hurley et al. (1995), we can augment previous findings. Together, all of this information helps predict the general behavior of mercury in unmonitored watersheds that have similar characteristics, and may result in more accurate management and regulation.

Observations from this study that refine previous findings include the following. (1) Particle-partitioning of mercury changes with river discharge. Agricultural sites are very responsive to high flow and require event based sampling to ensure accurate estimates of annual loadings. This corroborates earlier observations of particle mediated transport agricultural areas and filtered phase transport in wetland areas. (2) Unfiltered MeHg yield varies by more than an order of magnitude across all watersheds. Previous observations only reported filtered MeHg. (3) In strongly wetland-influenced rivers, MeHg as a fraction of Hg_T increases from $\sim$1% to more than 15% as the season progresses into the fall. The summer rise in MeHg concentrations above detection limits in all watersheds, supports previous suppositions about the source of this fall increase – namely, the flushing of late summer pore waters. (4) Under non-event flow, the average unfiltered MeHg yield for each river varies with percent wetland contribution ($r^2 \sim 0.98$). (5) The spring thaw mobilizes largely non-methyl forms of mercury.

The implication of this work for water resource management is that accurate modeling of the fate of mercury from effluents ought to begin with a watershed-level framework. "Background" mercury levels in rivers vary by watershed type. The behavior of mercury, once discharged, may vary greatly depending on the quantity and character of particulate matter and dissolved organic carbon. Discharge permits that are issued based on "background" criteria must consider the watershed surrounding the receiving water.

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