SUPPORTING INFORMATION

TEMPORAL VARIATION IN SPATIAL SOURCES OF DISCHARGE IN A LARGE WATERSHED

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Mercury Loading to Rivers

Because of direct impacts to human health, mercury has been heavily studied in aquatic ecosystems, and cycling of this biotoxin is generally well understood. For example, industrial processes and the burning of fossil fuels are known to mobilize mercury, which is then introduced to watersheds through wet and dry atmospheric deposition [1]. Mercury adhered to soil particles enters aquatic ecosystems through soil erosion, resulting in non-point source loading of particulate mercury phases to watersheds; total mercury loads in rivers is commonly dominated by these particulate phases [2]. Bacteria in soils and sediments convert mercury to an organic form, methylmercury, that is of primary toxicological concern because it is efficiently bioaccumulated and biomagnified through the food web to fish and shellfish that are potentially consumed by humans [3]. Land cover type strongly influences both particulate and organic mercury loading to aquatic ecosystems. For example, agricultural lands are primary sources of particulate mercury phases and methylization of mercury occurs readily in wetlands [4, 5]. Hence, if source areas of contaminated runoff and their underlying land covers were delineated, a new method for the general mechanistic study of contaminant loading to rivers would result.

The Fox River watershed is the largest contributor of mercury to Lake Michigan, the watershed been a focal point in the study of mercury cycling in relation to land cover, and non-point source particulate loading dominates the mercury inputs [5-11]. It is also a watershed for which resource shed calculations and detailed land cover data were available. This study considered non-point source mercury loading in the entire Fox River watershed and encompassed catchments analyzed independently in previous mercury loading studies (i.e., 5-9). The results of the present study indicate that the mouth of the Fox River (i.e., the receptor) is most comparable to the "integrator" sites, i.e. sites in rivers draining watersheds of diverse land covers (e.g., site IN3 in Figure S1), as opposed to sample sites in rivers draining watersheds dominated by one or two land cover types [10].

Consistent with Babiarz et al. [9], who previously demonstrated that discharge alone does not fully explain differential mercury loading to rivers, the land covers within source areas did not explain the differential mercury concentrations measured during the two discharge events. Most of the total mercury measured in 1994 and 1995 was in the particulate phase (79% and 98%, respectively). Therefore, our results do not alter previous conclusions that the very high total mercury concentration recorded during the 1994 discharge event was likely due to re-suspension of contaminated sediments [10]. Moreover, while limnological parameters and nutrient concentrations were almost identical on both dates, Polychlorinated Biphenyl (PCB) concentration was much greater in 1994, consistent with greater sediment resuspension. Sediment re-suspension confounds analyses of source area and land cover influences on material loading to rivers. Mercury in this system exemplified this phenomenon and illustrated a limitation of the approach that should be avoided in the future. If materials are patchily distributed in river sediments, re-suspension of materials at high concentrations and the resulting influence on limnological measurements made downstream may be unpredictable. Moreover, resource shed calculations currently delineate sources of water. New terms should be added to the model to account for the physical (e.g., settling) and biogeochemical transformations that occur while materials are in transport. Analysis of the Fox River watershed, for example, would be greatly improved by such additions due to the presence of a complex system of lakes.

Table S1. Land Cover Classification Used in Fox River (WI, USA) Analysis [a,b]

class	sub class	WISCLAND numeric code
Agriculture*		110
	Herbaceous/Field Crops	111
	Row Crops	112
	Corn	113
	Other Row Crops	118
	Forage Crops	124
Deciduous Forest (Broad-leaved)*		175
	Aspen	176
	Oak	177
	Northern Pin Oak	179
	Red Oak	180
	Maple	183
	Sugar Maple	185
	Mixed / Other	187
Grassland*	Timothy, rye, pasture, idle, CRP, grass and volunteer	150
Wetland		210
	Emergent* / Wet meadow	211
	Floating Aquatic Herbaceous Vegetation	212
	Lowland Shrub*	217
	Lowland Shrub - Broad-leaved Deciduous	218
	Lowland Shrub - Broad-leaved Evergreen	219
	Lowland Shrub – Needle-leaved	220
	Forested*	222
	Forested - Broad-leaved Deciduous	223
	Forested – Coniferous	229
	Forested – Mixed Deciduous / Coniferous	234
	Cranberry Bog	148
Coniferous Forest*		161
	Jack Pine	162
	Red Pine	163
	White Spruce	166
	Mixed/Other Coniferous	173
Open Water*		200
Urban / Developed*		100
	High Intensity	101
	Low Intensity	104
	Golf Course	105
Barren*		240
Shrubland*		250

[a] Source: Wisconsin Initiative for Statewide Cooperation on Landscape Analysis and Data (WISCLAND)

[b] Land cover types denoted by an asterisk were identified in analysis. Lowland shrub and Forested wetlands included listed subcategories.

Table S2. Limnological parameters, nutrients, and contaminants measured at the mouth of the Fox River, WS, USA.[a]

	unit	20-Jul-94	21-Aug-95
Temperature	°C	24.4	25.5
pH		8.5	8.6
Conductivity	uS/cm	351	348
Dissolved O2	mg/l	7.7	8.2
Dissolved Organic Carbon	mg/l	8.4	
Particulate Organic Carbon	mg/l	3.0	3.4
Alkalinity-tot as CaCO3	mg/l	148	162
CL-	mg/l	17.5	16.8
NH3	mg/l	0.054	0.005
NO2+NO3	mg/l	0.084	0.026
Dissolved P	mg/l	0.012	0.049
Total P	mg/l	0.145	0.168
Particulate P (total-dissolved)	mg/l	0.133	0.119
SO4	mg/l	18.5	
SiO2	mg/l	2.3	2.1
Solids	mg/l	41.0	39.0
TKN	mg/l	1.27	1.47
PCB-Total	ng/l	24.8	15.1
Atrazine	ng/l		61.1
DEA	ng/l		46.9
DIA	ng/l		22.4

a. Source: Lake Michigan Mass Balance study (http://www.epa.gov/glnpo/lmmb/).

Figure S1. Study area map. The Fox River Watershed (black lines, Wisconsin, USA) showing the Wolf, Lake Winnebago, Upper Fox, and Lower Fox catchments. Blue circles are sites sampled previously by Hurley et al. [11]. WF = wetland and forest, AF = agriculture and forest, IN = integrator. The Fox River drains into Green Bay at the city of Green Bay, WI (open circle).

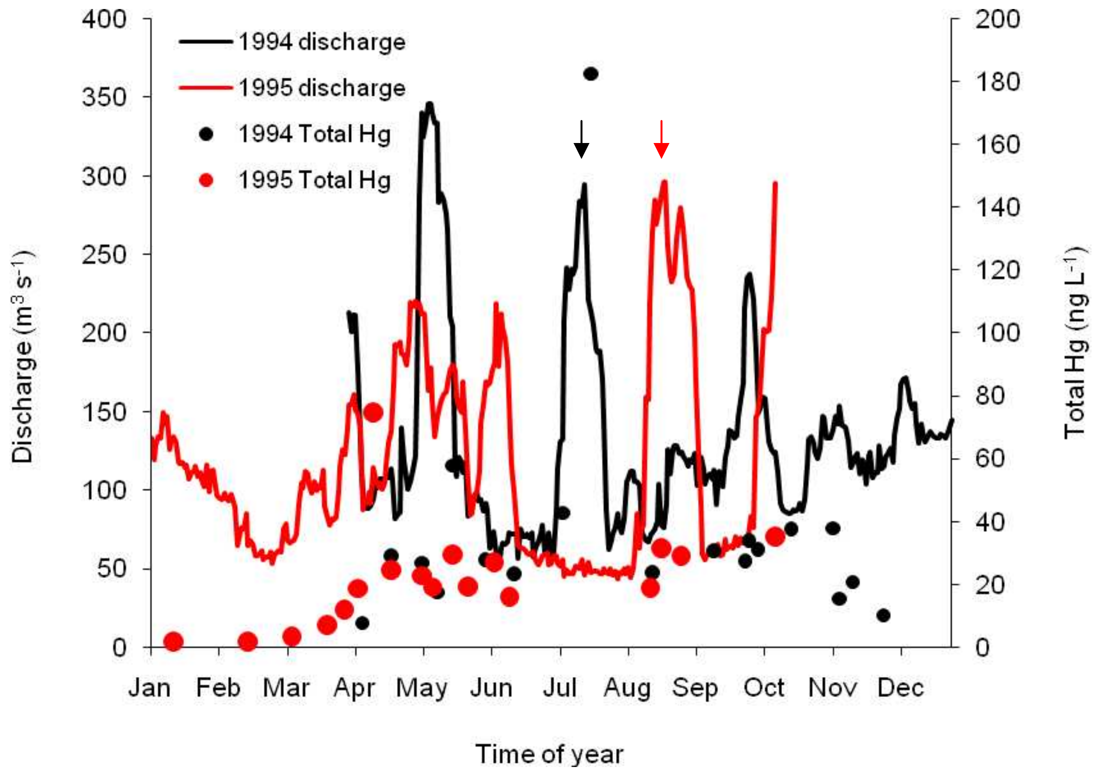
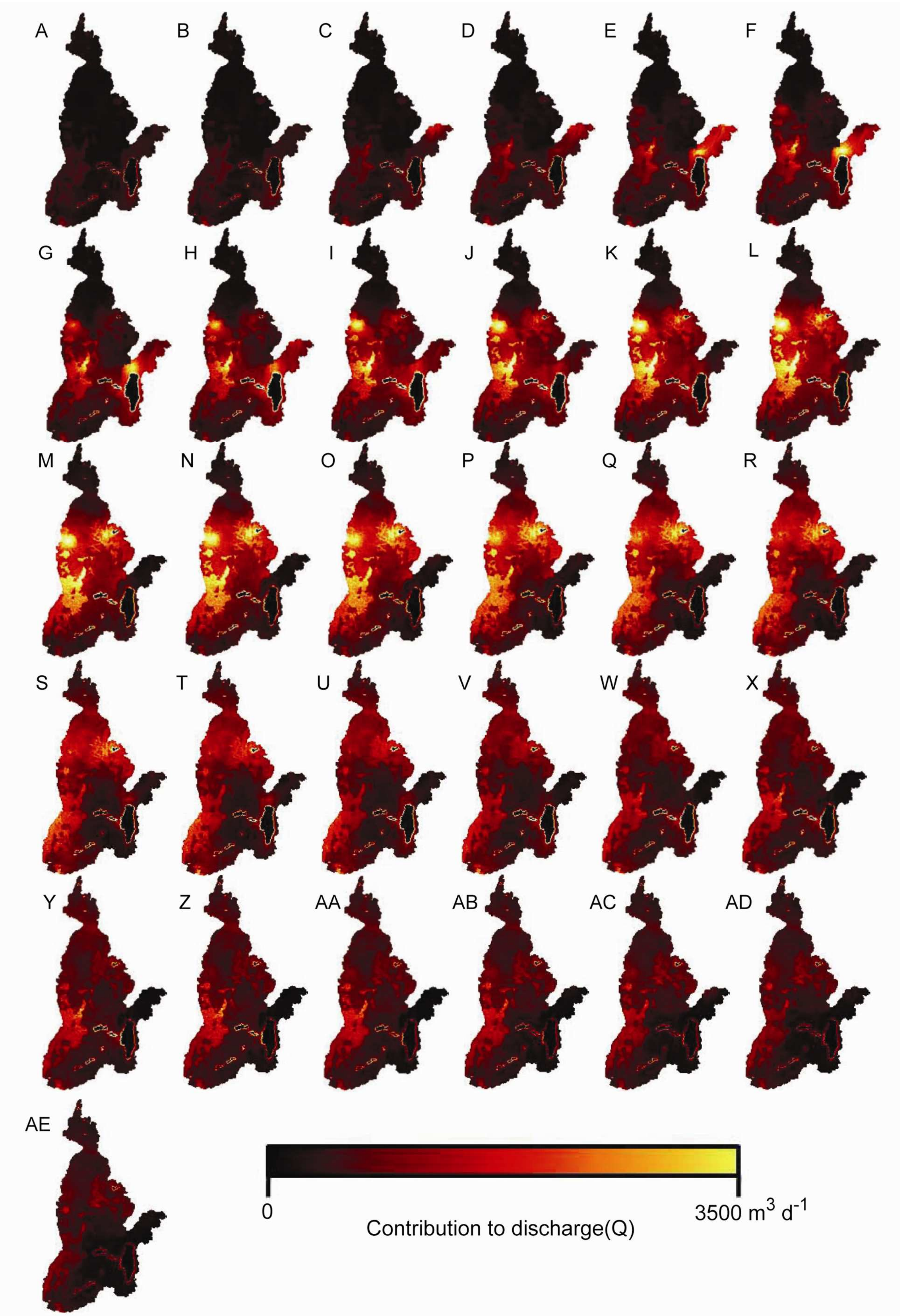


Figure S2. Fox River (WI, USA) hydrograph and total unfiltered mercury concentration for 1994 and 1995 [modified from [8] using data supplied by J. Hurley]. Hydrographs of the 1994 and 1995 Fox River discharge are overlaid to illustrate the similar temporal timing, discharge volume, and duration of the two analyzed discharge events. The 1994 event (black arrow) occurred 2 July 1994 to 29 July 1994, with a total mercury concentration of 182.6 ng L^{-1} measured on 20 July. The 1995 event (red arrow) began 13 August 1995 and ended 9 September 1995, with a total mercury concentration of 31.6 ng L^{-1} observed on 21 August. Mercury data were derived from composite water samples taken at multiple depths [3].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Contribution to discharge(Q)

Figure S3. Resource sheds for water exiting the Fox River watershed at Green Bay (WI, USA) during a discharge event beginning in August 1995 and ending in September 1995. Source areas (type II resource sheds with a 31-day lookback period) for water exiting the river mouth over the course of a day are shown, beginning with (A) 10 August 1995 and ending with (AE) 9 September 1995.

Movie S1. Resource sheds for water exiting the mouth of the Fox River (WI, USA) on July 20, 1994. Each frame in this sequence is a type II resource shed. With each frame, the length of the lookback period increases by one day (up to the maximum 31 days). Note that most of the change seen in the spatial configuration of the source area is seen during the middle of the sequence, as illustrated in Figure S3. Contribution to total discharge is shown increasing from black to red to yellow.

Movie S2. Resource sheds for water exiting the mouth of the Fox River (WI, USA) over the course of a July 1994 discharge event. Each frame of this sequence is a complete type II resource shed (using a 31-day lookback period) for one day of the discharge event. Note that most of the contribution to total discharge, shown increasing from black to red to yellow, occurs during the middle of the event, consistent with the hydrograph shown in Figure S2.

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