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Effect of watershed parameters on mercury distribution in different environmental compartments in the Mobile Alabama River Basin, USA

Kimberly A. Warner[a], Jean-Claude J. Bonzongo[b,*], Eric E. Roden[a], G. Milton Ward[a], Adrian C. Green[c], Indrajeet Chaubey[d], W. Berry Lyons[c], D. Albrey Arrington[a]

[a]*Department of Biological Sciences, The University of Alabama, Tuscaloosa, AL 35487, USA*
[b]*Department of Environmental Engineering Sciences, P.O. Box 116450, University of Florida, Gainesville, FL 32611, USA*
[c]*Byrd Polar Research Center, The Ohio State University, 1090 Carmack Road, Columbus, OH 43210, USA*
[d]*Department of Biological and Agricultural Engineering, University of Arkansas, Fayetteville, AR 72701, USA*

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Abstract

Total mercury (THg) and mono-methylmercury (MeHg) levels in water, sediment, and largemouth bass (LMB) (*Micropterus salmoides*) were investigated at 52 sites draining contrasting land use/land cover and habitat types within the Mobile Alabama River Basin (MARB). Aqueous THg was positively associated with iron-rich suspended particles and highest in catchments impacted by agriculture. Sediment THg was positively associated with sediment organic mater and iron content, with the highest levels observed in smaller catchments influenced by wetlands, followed by those impacted by agriculture or mixed forest, agriculture, and wetlands. The lowest sediment THg levels were observed in main river channels, except for reaches impacted by coal mining. Sediment MeHg levels were a positive function of sediment THg and organic matter and aqueous nutrient levels. The highest levels occurred in agricultural catchments and those impacted by elevated sulfate levels associated with coal mining. Aqueous MeHg concentrations in main river channels were as high as those in smaller catchments impacted by agriculture or wetlands, suggesting these areas were sources to rivers. Elevated Hg levels in some LMB were observed across all types of land use and land cover, but factors such as shallow water depth, larger wetland catchment surface area, low aqueous potassium levels, and higher Chl a concentrations were associated with higher Hg burdens, particularly in the Coastal Plain province. It is suggested that the observed large variability in LMB Hg burdens is linked to fish displacement by anglers, differences in food web structure, and sediment biogeochemistry, with surficial sediment iron oxides buffering the flux of MeHg from sediments to deeper water pelagic food webs.
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Keywords: Watershed; Land use–land cover; Riverine ecosystems; Mercury; Methylmercury; Hg bioaccumulation

* Corresponding author. Tel.: +1 352 392 7604; fax: +1 352 392 3076.
E-mail address: bonzongo@ufl.edu (J.-C.J. Bonzongo).

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1. Introduction

The bioaccumulation of mercury (Hg) and particularly mono-methylmercury (MeHg) in predatory fish from many inland waters is a serious health concern to humans and wildlife. While the risks of Hg contamination of different environmental compartments are relatively well known, significant gaps remain in our knowledge and understanding of Hg cycling and fate within watersheds, as well as its effects on ecosystem functions. Much of our current knowledge of Hg dynamics and fate in inland waters is based on studies in lacustrine systems, and published information on Hg in these systems abounds in the literature. In riverine systems, most studies have focused primarily on those with a history of Hg point-source contamination (e.g., Lacerda et al., 1991; Bonzongo et al., 1996, 2002; Appleton, 1999; Hines et al., 2000; Lechler et al., 2000; Maurice-Bourgoin et al., 2000; Mol et al., 2001; Roulet et al., 2001) while studies on Hg dynamics in rivers and watersheds with no known point sources remain quite limited. Based on current knowledge, inorganic Hg entering aquatic systems, regardless of source, must first be converted to MeHg prior to bioaccumulation (Gilmour and Henry, 1991) and sulfate reducing bacteria (SRB), residing in anoxic sedimentary environments, have been identified as one of the principal methylators of inorganic Hg (Compeau and Bartha, 1985; Gilmour et al., 1992; King et al., 2000). Thus, it is important to understand environmental factors, which favor the activity of SRB in different aquatic systems (e.g., sulfate levels and locations promoting the accumulation of fine, organic-rich anoxic sediments). In addition, watershed characteristics, including the presence of wetlands, agricultural land use, nutrient loading leading to algal blooms, and altered flow regimes leading to accumulation of fine sediment (Hurley et al., 1995; Rudd, 1995; St. Louis et al., 1996; Balogh et al., 1998, 2003; Chen et al., 2000; Cooper and Gillespie, 2001; Lawson et al., 2001) are known to affect the environmental fate and cycling of Hg. However, more information is needed on the linkages between regional/catchment-scale environmental conditions and reach-scale processes that influence MeHg production and bioaccumulation.

The riverine system on which we focused this study, the Mobile Alabama River Basin (MARB), is a large watershed, geologically and physiographically diverse with a mixture of land use and land cover (LULC) types. Another aspect of the MARB is the presence of iron-rich clastic sediments which distinguishes it from the carbonate-rich Everglades, the currently most studied aquatic system in southeastern USA (e.g., Vaithiyanathan et al., 1996; Cleckner et al., 1998, 1999; Gilmour et al., 1998; Hurley et al., 1998; Marvin-DiPasquale and Oremland, 1998; Cai et al., 1999; Khan and Tansel, 2000; Krabbenhoft et al., 2000). An earlier report of aqueous Hg levels across physiographic provinces of the MARB (Bonzongo and Lyons, 2004) suggested that throughout most of the basin, Hg inputs were from non-point sources, primarily atmospheric deposition to both water and land, with subsequent runoff from land to aquatic systems due to land use within watersheds. The observed differences in aqueous Hg speciation at different sites within the MARB, were attributed to site-specific conditions. Thus, landscape-scale conditions that influence the variable production of MeHg might be expected, in addition to variation in trophic structure, to result in differential bioaccumulation of MeHg in predatory fish, such as largemouth bass (LMB).

The goal of this study was to address hypotheses centered on watershed-scale environmental conditions and settings in the MARB that would create conditions in river and stream channels favoring methylation of Hg in sedimentary environments. Several hypotheses underpinned our observation-based investigation. First, nutrient loading from certain land-use activities and increased sedimentation above water impoundments were expected to lead to conditions favorable for MeHg production. Second, increased sulfate loading from mining and other energy resource operations was identified as a potential stimulant of MeHg production. Third, abundant wetlands within the MARB were expected to contribute to MeHg loads downstream and in fish. Finally, we hypothesized that fish tissue levels of MeHg would be related to MeHg water levels and net rates of MeHg production in sediments, as reflected by sediment MeHg levels, as observed in a recent nation-wide study (Brumbaugh et al., 2001). The specific objectives of this study were therefore: (1) to determine levels and speciation of Hg in water, sediment, and predatory fish (LMB) samples collected from rivers

and streams in the MARB; and (2) to investigate the linkage among LULC, particularly the presence of wetlands, and those hydrological and biogeochemical conditions that may enhance MeHg production and bioaccumulation. We focused primarily on the Coastal Plain physiographic province of the MARB, where aqueous MeHg:THg ratios were known to be relatively high (Bonzongo and Lyons, 2004), but also examined sites impacted by coal mining and coal-bed methane extraction (with associated elevated sulfate levels) in the Appalachian Plateau physiographic province.

2. Materials and methods

2.1. Site description

The MARB (Fig. 1) is a large (110,000 km^2), dynamic watershed with varied land use and geology. Approximately two-thirds of the MARB is contained in the state of Alabama. It traverses four physiographic provinces: Appalachian Plateau, Valley and Ridge, Piedmont, and Coastal Plain. The major sub-basins included in this study were the Black Warrior, Upper and Lower Tombigbee, Alabama, and Mobile, the latter of which drains into Mobile Bay. Average annual surface water discharge to Mobile Bay is 1760 m^3 s^{-1}, and represents the fourth largest discharge from U.S. watersheds. Most of the land cover is forest (60%), and most of the forested land is privately owned and subject to harvesting. Agriculture (26%), urban (3%), wetlands, streams, and reservoirs (11%) comprise the remaining LULC (USGS, 2002). The Black Warrior headwaters are located in the Appalachian Plateau where nearly all past and present coal mining sites and coal bed methane operations in the MARB are located (USGS, 2002), which contribute elevated sulfate loads. In addition, the Hg content of Alabama coals (range<0.003–1.3 mg Kg^{-1}) is elevated above the national mean in several areas (USGS, 1999).Wetlands surround most streams and rivers below the fall line in the Coastal Plain province. Nearly all rivers are impounded in some way, with numerous navigational locks and dams and/or hydroelectric dams. The dams produce a series of pools, which function as reservoirs, on impounded rivers, which are popular with recreational anglers.

2.2. Spatial analysis and LULC identifications.

Calculations of percent LULC and maps of LULC for four major sub-basins within the MARB (Black Warrior, Upper Tombigbee, Lower Tombigbee, and Alabama River) and for 27 sub-basins were completed using National Land Cover Data (NLCD) for the southeast US obtained from the USGS (Vogelmann et al., 2001). NLCD data were reprojected as Albers Conical Equal Area initially to match existing data. Re-projected NLCD data were extracted to correspond to delineated catchments. Percent land use by category was calculated from tabulated spreadsheet data. Delineations of catchment boundaries were made using Arcview and ArcGIS software. Digital elevation models were developed for each basin using Environmental Protection Agency stream reach files and 7.5-min digital elevation files for Alabama acquired from ChartTiff (Image Peak Berthoud, CO). LULC maps were generated in ArcMap using the land use grids and stream coverages.

2.3. Site selection

The study was conducted in two phases. Sites selected across the MARB in Phase 1 were based on presumptive impact factors such as dam influence, proximity to wetlands, agriculture, forested land cover, and open river reaches. For Phase 1, 52 sites were selected for collection of fish, water, and sediment samples (Table 1; Fig. 1). Twenty-seven of these sites were tributary streams, creeks, or sloughs draining smaller catchments primarily influenced by one of the above listed potential impact factors. Sampling sites associated with these 27 sub-basins were assigned an impact factor based on the following LULC criteria. Sites designated as impacted by "wetlands" or by "agriculture" had >15% LULC in that category and minor impact by LULC other than forest. Sub-basins designated as "mixed forest, agriculture, and wetland" were comprised of ≤10% each agriculture and wetlands with the remainder forested land cover. "Forested" sites contained >93% forest land cover. The remaining sites were located on mainstem river reaches or upstream of dams. Data obtained from Phase 1 were used to identify Hg trends relative to LULC and other site parameters at a broad spatial scale. The second phase of our study was intentionally

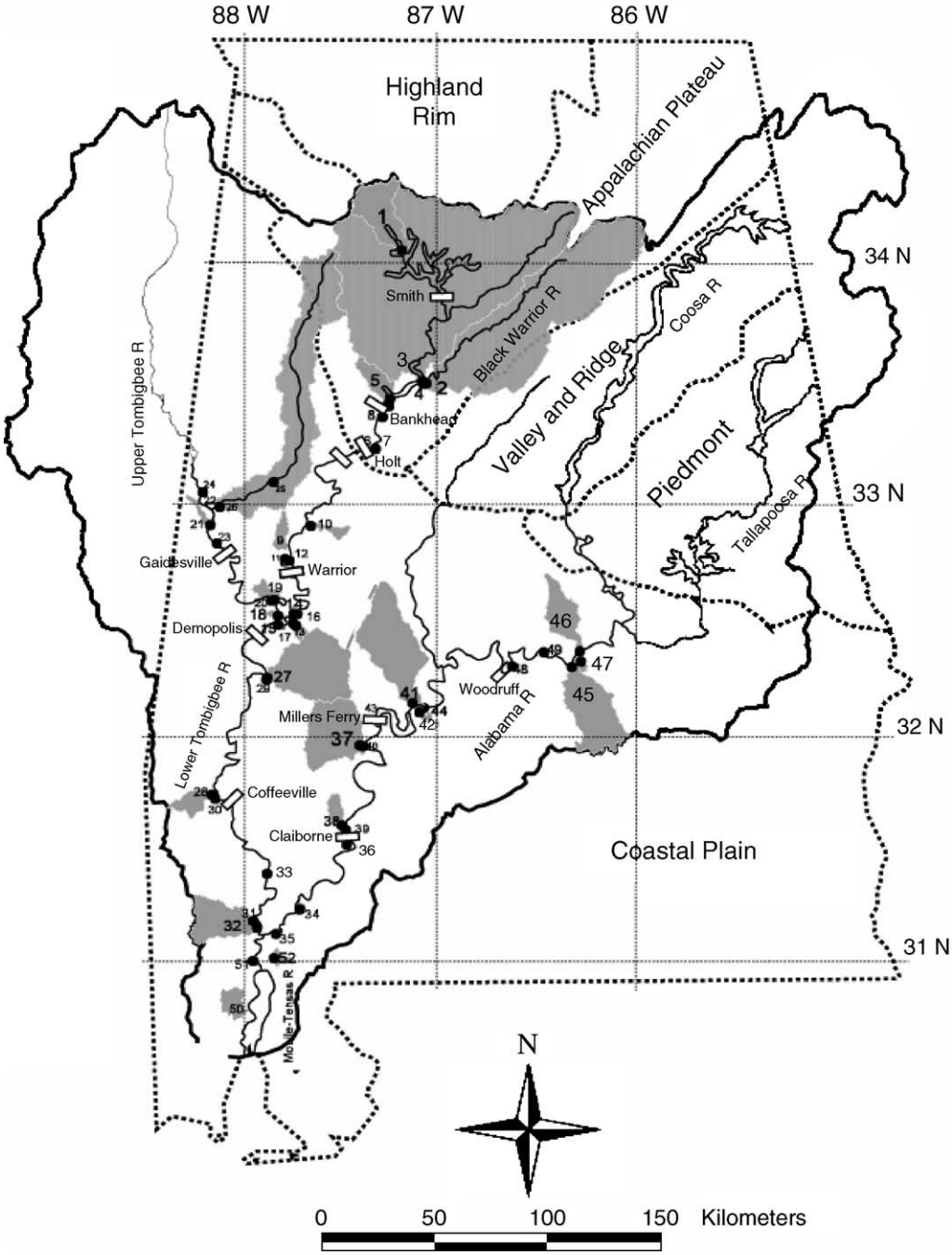

Fig. 1. The Mobile Alabama River Basin (MARB), showing physiographic provinces and major rivers, numbered sites, and named dams and associated pools sampled in Alabama.

Table 1
Site locations and percent land use/land cover in sub-watersheds

Site #	River basin[a]	Pool	Name	LONG (DMS deg)	LAT (DMS deg)	IF[b]	Area km^2	% Land use/land cover ag	Wetland	Urban	Forest
1	BW	Smith	Sipsey Fork	−87 17 55.32	34 07 11.64	0	477	3.7	0.1	0.2	94.2
2	BW		Locust Fork	−87 10 44.76	33 33 04.32	1, M	3110	20.3	0.1	6.0	71.7
3	BW		Mulberry Fork	−87 11 52.44	33 33 43.92	1, M, C	6130	17.1	0.3	1.0	77.8
4	BW	Bankhead	River channel	−87 11 45.6	33 33 02.16	6, M					
5	BW	Bankhead	Yellow Creek	−87 21 10.80	33 29 07.44	0, M	171	3.7	0.0	0.1	93.1
6	BW	Holt	Holt dam	−87 25 26.76	33 15 47.16	5, C					
7	BW	Holt	River channel	−87 23 04.92	33 24 27.00	6, C					
8	BW	Holt	River channel	−87 23 17.88	33 24 31.32	6, C					
9	BW	Warrior	Minters Creek	−87 50 54.60	32 51 08.28	3	83.3	8.7	4.5	0.9	82.9
10	BW	Warrior	Gabriel Creek	−87 43 02.28	32 56 27.60	2	62.5	11.2	17.0	0.1	68.5
11	BW	Warrior	River channel	−87 49 04.08	32 49 45.84	6					
12	BW	Warrior	Warrior dam	−87 49 32.88	32 47 35.16	5					
13	BW	Demopolis	French Creek	−87 48 21.24	32 31 38.28	1	37.0	61.1	7.6	1.0	24.0
14	BW	Demopolis	Backbone Creek	−87 48 14.40	32 33 54.72	2	7.1	9.2	35.9	0.0	51.4
15	LT	Demopolis	Demopolis dam	−87 51 12.60	32 30 56.88	5					
16	BW	Demopolis	River channel	−87 47 15.72	32 34 32.52	6					
17	LT	Demopolis	Sawmill and Grain Silo	−87 51 08.28	32 30 41.04	4	1.1	13.4	2.3	24.7	58.2
18	UT	Demopolis	Spidel Creek	−87 52 34.68	32 33 24.12	2	18.9	15.7	47.6	0.2	30.7
19	UT	Demopolis	McConico Creek	−87 53 26.52	32 37 22.44	1	68.2	47.7	12.5	0.1	38.2
20	UT	Demopolis	River channel	−87 53 43.08	32 37 00.48	6					
21	UT	Gainesville	Penachee Creek	−88 12 05.04	32 56 31.56	1	44.4	75.3	8.0	0.2	14.4
22	UT	Gainesville	Lowrey's Lake	−88 13 09.48	33 01 49.08	2	6.3	8.4	69.7	0.0	15.6
23	UT	Gainesville	Gainesville dam	−88 09 34.92	32 51 21.24	5					
24	UT	Gainesville	River channel	−88 14 20.76	33 04 48.36	6					
25	SR	Gainesville	River channel	−87 54 12.60	33 07 37.56	3	2040.1	10.0	9.1	0.4	75.5
26	SR	Gainesville	Near confluence	−88 09 28.08	33 01 14.16	3	2040.1	10.0	9.1	0.4	75.5
27	LT	Coffeeville	Chickasaw Bogue Creek	−87 55 26.40	32 17 29.40	1	891.2	35.2	5.2	0.5	53.5
28	LT	Coffeeville	Turkey Creek	−88 10 41.88	31 47 27.96	3	143.8	3.0	7.0	0.2	86.5
29	LT	Coffeeville	River channel	−88 08 42.72	31 46 12.00	6					
30	LT	Coffeeville	Coffeeville dam	−88 09 55.80	31 47 12.84	5					
31	LT	Coffeeville	River channel	−87 58 46.92	31 15 18.00	6					
32	LT		Bilbo/Bates Creek	−87 57 40.68	31 13 27.84	3	431.6	3.9	6.6	0.4	84.0
33	LT		River channel	−87 55 05.52	31 27 22.68	6					
34	AR		Smith Lake	−87 45 48.60	31 18 23.40	2	11.9	1.9	80.9	0.0	10.3
35	AR		River channel	−87 52 27.84	31 18 23.40	6					
36	AR		River channel	−87 32 53.88	31 36 00.00	6					
37	AR	Claiborne	Turkey Creek	−87 29 22.20	32 00 22.32	3	675.9	7.5	9.3	0.4	79.2
38	AR	Claiborne	Silver Creek	−87 34 15.60	31 39 49.32	0	88.6	0.5	2.8	0.0	95.9
39	AR	Claiborne	Claiborne dam	−87 33 10.08	31 37 45.12	5					
40	AR	Claiborne	River channel	−87 28 25.68	32 00 09.36	6					
41	AR	Millers Ferry	Bogue Chitto Creek	−87 13 58.44	32 10 47.28	1	940.3	52.7	11.7	0.6	33.0
42	AR	Millers Ferry	Rum Creek	−87 12 30.96	32 08 56.04	2	38.2	7.3	33.6	0.0	56.5
43	AR	Millers Ferry	Millers Ferry dam	−87 24 23.76	32 07 12.00	5					
44	AR	Millers Ferry	River channel	−87 11 23.28	32 09 59.76	6					
45	AR	Woodruff	Pintlalla Creek	−86 29 40.20	32 20 28.68	1	685.4	41.2	7.3	0.5	47.8
46	AR	Woodruff	Autauga Creek	−86 27 24.48	32 24 28.80	1	314.4	20.8	8.0	2.2	67.6
47	AR	Woodruff	Catoma Creek	−86 27 04.32	32 21 49.32	1	958.6	68.3	2.5	1.6	26.9

(continued on next page)

Table 1 (*continued*)

Site #	River basin[a]	Pool	Name	LONG (DMS deg)	LAT (DMS deg)	IF[b]	Area km^2	% Land use/land cover ag	Wetland	Urban	Forest
48	AR	Woodruff	Robert Henry dam	−86 45 46.44	32 20 57.48	5					
49	AR	Woodruff	River channel	−86 37 31.44	32 24 16.20	6					
50	MR		Bayou Sara	−88 01 57.36	30 50 47.04	3	114.6	8.7	11.1	3.6	74.1
51	MR		River channel	−87 58 18.12	31 05 02.40	6					
52	TR		Big Beaver Creek	−87 52 57.36	31 05 46.32	2	44.1	5.6	48.1	0.0	42.5

[a] BW: Black Warrior; UT: Upper Tombigbee; LT: Lower Tombigbee; SR: Sipsey; AR: Alabama; MR: Mobile; TR: Tensaw.
[b] Impact factor (IF): 0: forest; 1: agriculture; 2: wetland; 3: forest/ag/wetland; 4: urban; 5: dam; 6: river; M: mine; C: coal bed methane.

designed to constrain some of the variability associated with the distribution of Hg species at the MARB scale and to investigate these linkages within a single recreational pool near the city of Demopolis, Alabama. Investigations at a smaller scale allowed us to test our hypotheses related to biogeochemical controls on MeHg production and bioaccumulation at sites with contrasting LULC. The Demopolis Pool is located in the Coastal Plain and is formed by a navigational lock and dam on the Lower Tombigbee, about 3 river miles downstream of the confluence of the Black Warrior and Upper Tombigbee Rivers (Fig. 1). A fuller description of the Demopolis Pool sites can be found in an earlier publication (Warner et al., 2003).

2.4. Survey components

The Phase 1 survey of Hg distributions and ancillary data at 52 sites was conducted during 1999 and 2000 for fish samples, and from March through September 2000 for water and sediment samples. From each site the following data were collected: latitude and longitude; water temperature, pH, and dissolved oxygen; water samples for Hg speciation, nutrients, major cations and anions, iron, dissolved organic carbon (DOC), and total suspended solids (TSS); surficial sediment samples for Hg speciation, water content, organic matter content, total reactive iron, and total reduced sulfur; and LMB of two size classes (305 to <457 mm and ≥457 mm total length).

In Phase 2, four sites with contrasting LULC within the Demopolis pool were re-sampled from August to October 2001. At each of these four sites, 6 LMB (305 to <457 mm and ≥457 mm total length), water, and sediment (core) samples were collected for the determination of constituents measured in Phase 1. In addition, trophic position of LMB was assessed at each site through the determination of $\delta^{15}N$ in LMB tissues (Post, 2002).

2.5. Sampling methods

Water and sediment samples were collected from a small workboat. Water samples for Hg analyses were collected in acid pre-cleaned Teflon® bottles with gloved hands, using ultra-clean free-metal sampling protocol. Water samples for other analyses were collected in bottles pre-cleaned in a manner appropriate for the intended analysis method. During Phase 1 of the study, three replicate sediment samples were collected from each site, using a Ponar grab sampler. Acid-cleaned rubber spatulas were then used to remove the top 5 cm of sediment not in contact with the grab sampler. Sediment samples for Hg speciation were placed in acid-cleaned polyethylene jars. Sediments for TRS, FeT, and water content determinations were placed in 0.5 L glass jars filled to capacity and capped. In Phase 2 of the study, sediment was collected as cores (Warner et al., 2003). In all cases, samples were stored on ice until transported back to the laboratory. For Phase 1, 30% of fish samples were collected from bass fishing club tournaments in 1999 and 2000. Electro-shocking provided the remainder of the fish samples collected in 2000 (Phase 1) and 2001 (Phase 2). In the field, LMB were measured soon after capture and labeled, placed in polyethylene bags, temporarily stored on ice until returning to the laboratory where they were weighed, and then frozen at −20 °C until analyzed.

2.6. Sample analysis

2.6.1. Mercury analysis

Details on procedures used for the analysis of THg and MeHg have been described in several of our previous publications (e.g., Bonzongo et al., 1996, 2002; Lyons et al., 1999; Hines et al., 2000; Warner et al., 2003; Bonzongo and Lyons, 2004). Therefore, only a brief description is provided here. For water samples, the determination of THg followed USEPA method 1631, using bromine mono-chloride oxidation, $SnCl_2$-reduction, and detection by CV-AFS. THg in solid samples (i.e., sediment and fish tissues) were determined on ~1 g of freeze-dried material after sample digestion with a 7:3 (V/V) mixture of HNO_3/H_2SO_4, $SnCl_2$-reduction, and detection by CV-AFS. Fish data are expressed in wet mass units and sediment data in dry mass units. Analytical QA/QC criteria were met by running sample duplicates, reagent blanks, liquid standard solutions, spike/recovery, and certified reference materials (DORM-2 and IAEA-405 for fish and sediment samples, respectively). In addition, split samples from 23 separate fish were analyzed by both our laboratory and an independent lab using the above described method and the EPA standard method #245.6 (USEPA, 2000), respectively. The relative percent difference in Hg concentration between the two methods averaged less than 4%.

2.6.2. Ancillary water quality measurements

Dissolved oxygen (DO) and temperature were measured on site using a calibrated field probe (YSI95 DO Microelectrode Array). Ambient surface water pH was determined on site using a calibrated portable pH meter (Accumet®, Fisher Scientific). Water samples for DOC were collected and processed in sulfuric acid cleaned polyethylene bottles and apparatus, filtered through combusted GF/F glass fiber filters, acidified to pH 2 with Optima HCl, and held at 5 °C until analysis for non-purgable organic carbon by a TOC analyzer (Shimadzu TOC 5000). Water samples for dissolved nutrients were collected and processed with HCl-washed containers, filtered through GF/F glass fiber filters, and held at 5 °C until analysis. Nutrients were measured by flow injection analysis colorimetry (Zellweger Analytics, Lachat Instruments) by the following QuickChem® standard methods: Nitrite and Nitrate: 10-107-04-1-B; Ammonium (low flow phenolate method): 10-107-06-1-F; orthophosphate: 10-115-01-1-B. Total P (acid persulfate digestion method): 10-115-01-1-F. Total Kjeldahl Nitrogen (TKN) water samples, preserved in sulfuric acid, and total suspended solids (TSS) were analyzed by standard methods (APHA, 1992). Total water column iron (Fe_T) (dissolved and particle bound) was determined colorimetrically on unfiltered acidified samples using a Shimadzu UV-1201 spectrophotometer, using the ferrozine method (Murray et al., 1978). Chloride and sulfate samples were collected in distilled water-rinsed bottles, filtered (0.2 μm), and measured by ion chromatography (Dionex Model DX100). Water samples for major anion determination were collected in pre-washed polyethylene bottles, filtered through 0.4 μm polycarbonate filters, and analyzed by ion chromatography as described in Welch et al. (1996).

2.6.3. Ancillary sediment measurements

Bulk surficial sediment from the Phase 1 survey and sediment cores from Phase 2 were processed inside an anaerobic chamber. Total reduced sulfur (TRS) was determined by the single step Cr-reduction technique of Fossing and Jorgensen (1989). Total crystalline Fe (TFe) was determined by citrate/dithionate extraction method (Canfield, 1989). Sediment organic matter (loss on ignition or LOI) was determined by difference in weight of dried and combusted (500 °C) sediment material. Porosity was determined by dividing sediment water volume, obtained from difference in wet and dry weight, by the volume of sediment, obtained using a sediment dry weight density of 2.5 g mL^{-1}.

2.6.4. Determination of N stable isotope ratios in LMB tissue

Approximately 2 g of thawed, boneless, skinless dorsal muscle was prepared for stable isotopic analysis. Tissue preparation follows Arrington and Winemiller (2002) for frozen muscle tissue. Briefly, in order to prepare for isotopic analysis, muscle samples were dried at 60 °C for approximately 48 h, ground to a fine powder using a mortar and pestle, and 1.00±0.1 mg of tissue was loaded into tin capsules. Samples were then sent to University of Georgia's Stable

Isotope Laboratory in the Institute of Ecology for determination of nitrogen stable isotopic ratios. These values are reported using δ (delta) notation where

$$\delta^{15}\mathrm{N} = \left(\left[\frac{R_{\text{sample}}}{R_{\text{standard}}}\right] - 1\right) \times 1000$$

and R is $^{15}\mathrm{N}$:$^{14}\mathrm{N}$. Working standards were bovine (n=4, δ^{15}N=7.51, S.D.=0.06‰) and popular (n=4, δ^{15}N=−2.21, S.D.=0.15‰).

3. Results and discussion

3.1. Mercury in different environmental compartments of the MARB

The distributions of Hg species across water, sediment, and LMB follow the expected trends, with both THg and MeHg concentrations increasing from aqueous to sediment phases to fish (Table 2).

3.1.1. Water and sediment

Concentrations of THg in non-filtered water samples collected during Phase 1 of this study spanned only one order of magnitude, and about 54% of the analyzed samples had concentrations <1.0 ng L^{-1}. Our measured THg values remain within the range of concentrations reported by others for the southeastern USA (e.g., Mastrine et al., 1999; Bonzongo and Lyons, 2004; Paller et al., 2004). Concentrations of MeHg, determined on non-filtered samples ranged from values below our analytical detection limit (~0.03 ng L^{-1}) to 1.5 ng L^{-1}, with about 17% of analyzed samples containing THg and MeHg concentrations <1 ng L^{-1}. These MeHg concentrations compare quite well with ranges reported from streams and rivers draining watersheds with no known Hg point sources (<0.02–1.5 ng L^{-1}) (e.g., Lawson and Mason, 2001; Balogh et al., 2003, 2004; Paller et al., 2004). Nevertheless, they are still of concern due to the ability of the highly toxic MeHg to bioaccumulate and biomagnify in aquatic food chains.

THg concentrations determined on non-sieved sediments ranged from 3 to ~104 ng g^{-1}, whereas measured sediment MeHg values ranged from value below our analytical detection limit (~0.01 ng g^{-1}) to 3.79 ng g^{-1}. When expressed as fraction of total concentrations, MeHg represented up to ~13% of THg. Finally, none of the measured THg concentrations in surface sediments of the MARB exceeded the US-EPA quality guideline of 200 ng g^{-1}.

3.1.2. LMB

A total of 96 fish samples were collected from 51 out of 52 sites in Phase 1 (Table 2). Mercury concentrations in LMB sampled in Phase 1 spanned 2 orders of magnitude, ranging from 0.02 to 2.8 mg Kg^{-1} on a wet weight basis. Mean and median LMB concentrations were 0.45 and 0.32 mg Kg^{-1}, respectively, with the mean close to that of the National Mercury Survey (0.39 mg Kg^{-1}) reported for AL LMB, and exactly matching the mean for all national LMB collected during the USEPA National Survey (USEPA, 1999). Twelve percent of fish had Hg concentrations ≥1 mg Kg^{-1}, the level at which consumption advisories are posted in Alabama. Thirty percent were ≥0.5 mg Kg^{-1}, while the average LMB Hg concentrations were ≥0.5 mg Kg^{-1} at 21 (i.e., 41%) of the sites. Finally, calculated average bioconcentration factor of $10^{5.6}$ for THg and ~10^{6} for MeHg was consistent with published values for piscivorous fish (Bloom, 1992; Meili, 1997).

Large variability in Hg concentration was often observed between LMB caught at any one site (coefficients of variation ranged from 7–135%, mean=68%). Furthermore, at 43% of the sites where at least 2 fish were sampled, Hg concentration was higher in the smaller of the two fish. As such, we found no relationship between LMB size and Hg burden within any major pool, river basin, or in the watershed as whole. At the scale of the individual site, the finding of higher Hg concentrations in many smaller fish was unexpected, as bioaccumulation of Hg generally increases with fish size (i.e., age), all other environmental factors held constant. At larger scales (i.e., pool, river sub-basin or the entire MARB) this lack of relationship between LMB size and Hg burden was not entirely unexpected since we hypothesized that Hg burdens in fish would vary as a function of site specific LULC and hydrological conditions. LMB were assumed to have a small home range and thus would be good indicators of site-specific conditions in our study. Most of the LMB sampled from smaller creeks were caught within 0.5–3 miles of the creek mouth and many from the main river channel were caught near littoral zones with proximal access

Table 2
Phase 1 mercury species concentrations in MARB water, sediment, and largemouth bass (LMB)

Site #	THg	MeHg	THg	MeHg	THg	*n*
	Water (ng L^{-1})		Sediment (ng g^{-1} dw)		LMB (mgKg^{-1} wet) mean (range)	
1	2.15	0.14	8.90	1.14	0.98 (0.59–1.36)	2
2	0.85	0.03	41.9	3.79	0.11	1
3	0.75	0.29	71.2	3.11	0.60 (0.32–0.87)	2
4	1.27	0.03	103	1.93	0.08	1
5	0.57	0.03	53.0	1.26	0.10 (0.07–0.12)	2
6	0.59	0.03	47.0	0.62	0.09 (0.05–0.14)	2
7	2.23	0.03	32.9	0.60	0.24 (0.05–0.44)	2
8	0.43	0.03			0.13	1
9	0.9	0.03	42.2	1.27	0.13 (0.08–0.17)	2
10	0.72	0.39	63.2	1.22	0.92 (0.60–1.24)	2
11	0.63	0.81	4.83	0.26	0.11 (0.04–0.18)	2
12	0.61	0.03	27.9	0.11	0.51 (0.03–0.92)	3
13	0.21	0.04	82.7	0.07	0.36 (0.18–0.55)	2
14	0.65	0.16	36.7	0.12	0.22 (0.13–0.32)	2
15	0.29	0.03	17.5	0.02	1.56 (0.34–2.8)	2
16	0.73	0.03	10.5	0.16	0.59 (0.18–1.1)	3
17	2.11	0.21	43.3	0.20	0.60 (0.41–0.79)	2
18	1.09	0.18	45.4	0.11	0.71 (0.32–1.1)	2
19	1.60	0.03	73.2	0.19	0.74 (0.49–1.0)	2
20	1.15	0.24	9.21	0.16	0.29 (0.15–0.43)	2
21	1.65	0.10	11.8	0.57	0.27 (0.18–0.35)	2
22	0.73	0.02	34.0	1.15	0.26 (0.24–0.27)	2
23	1.00	0.09	6.75	0.11	0.53 (0.41–0.65)	2
24	1.06	0.77	17.5	0.03	0.41 (0.10–0.72)	2
25	2.36	0.11	7.82	0.01		0
26	0.83	0.24	25.9	0.01	0.60 (0.40–0.79)	2
27	0.94	0.03	8.45	0.08	0.46 (0.10–0.82)	2
28	0.75	0.01	59.0	1.19	0.66 (0.36–0.95)	2
29	0.40	0.24	8.79	0.30	0.08 (0.06–0.11)	2
30	1.00	0.17	20.7	0.38	0.34 (0.16–0.51)	2
31	2.38	0.03	22.1	0.04	0.17	1
32	3.78	0.15	29.3	0.08	0.59 (0.31–0.86)	2
33	1.16	1.11	13.4	0.26	0.28 (0.11–0.44)	2
34	0.66	0.92	101	0.06	0.20 (0.14–0.26)	2
35	0.81	0.31	3.84	0.01	0.28 (0.15–0.44)	2
36	0.46	0.03	3.12	0.01	0.95 (0.44–1.5)	2
37	2.27	0.49	8.11	0.10	0.04	1
38	0.83	0.03	29.1	0.11	1.3 (0.06–2.5)	2
39	0.5	0.48	9.01	0.02	0.28 (0.17–0.40)	2
40	0.22	0.03	12.8	0.03	0.34	1
41	1.35	1.47	24.8	0.29	0.79	2
42	0.64	0.55	57.6	0.16	0.86 (0.12–1.6)	2
43	0.81	0.03	19.4	0.06	0.10 (0.10–0.11)	2
44	0.9	0.03	31.3	0.57	0.62 (0.10–1.14)	2
45	2.06	0.09	24.9	2.29	0.18 (0.18–0.29)	2
46	1.30	0.08	78.5	1.27	0.63 (0.49–0.77)	2
47	1.25	0.09	20.6	0.86	0.34 (0.08–0.61)	2
48	0.22	0.36	23.2	0.73	0.05	1
49	1.14	0.03	22.2	0.28	0.02	1
50	1.14	0.54	61.3	0.97	0.14 (0.05–0.22)	2
51	1.15	0.03	11.5	0.43	0.27 (0.22–0.32)	2

(continued on next page)

Table 2 (*continued*)

Site #	THg	MeHg	THg	MeHg	THg	*n*
	Water (ng L^{-1})		Sediment (ng g^{-1} dw)		LMB (mgKg^{-1} wet) mean (range)	
52	1.02	0.03	26.7	1.18	0.58 (0.34–0.82)	2
Min	0.2	0.0	3.1	0.0	0.02	
Max	3.8	1.5	104	3.8	2.77	
Mean	1.1	0.2	32.3	0.6	0.45	
Median	0.9	0.1	24.9	0.3	0.32	
N	52	52	152	152	96	

MeHg values of 0.03 ng L^{-1}(water) and 0.01 ng g^{-1} (sediment) indicate analytical detection limits.

to numerous creek and slough openings. Radio-tagging of LMB in a recent study in one of the MARB pools showed that some LMB moved from smaller creeks to the main stem, into other creeks, and others were displaced by anglers (Maceina and Slipke, 2004). Relocation of LMB by anglers may also be significant in many MARB pools, for example, one MARB pool, Demopolis, hosted approximately 45 bass tournaments involving over 2700 anglers in one year (J. Haffner, Alabama Department of Conservation and Natural Resources, personal communication). In a striped bass radio tagging study in the ~8000 ha Smith Lake, roughly half of 22 tagged individuals was captured by anglers (Moss et al., 2004). Angler transport of LMB, observed locally and in other systems (Richardson-Heft et al., 2000), coupled with the practice of release of widely-caught LMB at a single location at bass tournament weigh-ins, is likely a factor in the highly variable Hg burdens from any given site.

3.2. Influence of water quality and sediment parameters on Hg concentrations and speciation

Hg distribution in water, sediment and fish were analyzed as a function of ancillary water and sediment parameters using simple and multiple linear regression models on data collected during Phase 1 of this study (JMP software, SAS Institute). Statistically significant results ($p<0.05$) are presented in Table 3. A statistically significant relationship was found between aqueous THg and TSS and between THg and aqueous total iron (Fe_T), when 2 outliers were excluded. Excluding these same outliers improved the regression between Fe_T and TSS (data not shown), suggesting that iron-rich particles were more strongly associated with aqueous THg, as found previously in southeastern US waters (Mastrine et al., 1999). In fact, in systems devoid of main point sources of Hg, the geology, hydrology, climate, and land use characteristics of the watershed tend to determine the degree to which Hg is transferred from land to surface waters, and a strong correlation is usually observed between THg and TSS concentrations (Balogh et al., 1998, 2003). While published data on the Hg content of native Alabama soils are lacking, a study in west central Alabama soils found an average total Hg content of 0.052 mg Kg^{-1} (range 0.014–0.092; n=9) in urban surface soils (M. Gabriel and D. Williamson, University of Alabama, unpublished data). The similarity of these values to our sediment data, plus those reported for south Alabama soils (mean THg=0.041 mg Kg^{-1}, range <0.02–0.13 mg Kg^{-1}) (USGS National Chemical Survey Database), support the suggested THg transport mechanism from land to MARB surface waters.

In contrast, no significant relationship was found between MeHg and TSS in the MARB surface waters.

Table 3
Statistical relationships between Hg distributions and MARB ancillary variables at the MARB-wide scale

Independent variable	Dependant variable (s)	Slope (±)	r^2	p
THg water	Fe_T water	+	0.28	<0.0001
	TSS (exclude 2 outliers)	+	0.44	<0.0001
THg sediment	LOI, Fe_T sediment	+	0.65	<0.0001
MeHg sediment	LOI, NO_3+NO_2	+	0.51	<0.0001
Log_{10} MeHg sediment	Log_{10} THg-sediment	+	0.23	0.0004
Hg LMB, mean	pH, DO	–	0.14	0.025
	K	–	0.23	0.0005
	K, DO, pH	–	0.29	0.0012

The concentrations of DOC measured during this study ranged from 2.55 to 10.36 mg C L^{-1}, with the highest values in samples from the Coastal Plain Region. However, no significant relationship was found between DOC and any of the Hg fractions. Positive correlations between Hg and DOC are often expected in cases where Hg is primarily derived from wetlands and soils (Wallaschlager et al., 1996), while aqueous systems receiving Hg primarily from direct atmospheric deposition on water surfaces tend to show a rather poor relationship between Hg and DOC (Ravichandran, 2004). In both cases, however, significant differences can be expected in the reactivity of DOC with Hg depending on the structural and chemical characteristics of DOC (Babiarz et al., 2001). This is because the binding of Hg to DOC under natural conditions is driven primarily by the presence of functional thiol-group containing organic molecules (Haitzer et al., 2002) and the presence of other competing ions in the water (Ravichandran, 2004), which vary with aquatic systems.

The amount of THg in sediment was a significant function of both sediment organic matter content (loss on ignition or LOI) and sediment iron (Table 3). Both of these latter parameters are associated with fine-grained particles, which accumulate in quiescent areas. Sediment MeHg was a weak, but significant function of sediment THg, indicating that Hg loading is one important factor governing MeHg production, as is generally seen worldwide (Benoit et al., 2003).

The amount of sediment organic matter and aqueous nitrate and nitrite explained over 50% of the variability in sediment MeHg at the MARB scale. Testing relationships between sediment MeHg levels and nutrients separately in the major recreational pools (n=4–7) showed that total P was a strong significant positive function ($p<0.05$) of sediment MeHg in the Warrior Pool (r^2=0.92) and in the Demopolis Pool in 2001 (r^2=0.86), but only weakly in 2000 (r^2=0.26). Conversely, TKN was positively associated with sediment MeHg in the 2000 Demopolis Pool samples (r^2=0.54), as well as in the Coffeeville (r^2=0.92) and Claiborne (r^2=0.91) pools. Although these relationships are significant, and likely indicative of influential factors affecting MeHg production (see below), the small sample size limits the power of these tests.

Fish Hg levels were a weak negative function of water pH, DO, and potassium, which together explained 29% of the variability in fish Hg burdens (Table 3). The pH of MARB waters sampled ranged from 6–8.5, with only 2 pools averaging less than 7. A stronger negative relationship between fish Hg levels and pH would be expected had we sampled more acidic waters, as is frequently observed (Lange et al., 1993 and references therein). The negative relationship with DO suggests that LMB residing in still water, organic-enriched habitats are slightly more prone to higher MeHg bioaccumulation. The negative relationship with aqueous K may indicate that K is behaving as a nutrient, in that decreased levels of potassium have been observed in areas of stimulated primary production (Mickle and Wetzel, 1978; Barko, 1982).

3.3. Effect of LULC and hypothesized impact factors on Hg species

The highest THg concentrations in sediments were observed in smaller catchments and tributaries impacted by wetlands, agriculture, or a combination (Fig. 2a). Sediment THg concentrations were generally lower at river channel and dam sites, except those impacted by coal mining or coal bed methane extraction. In contrast, aqueous THg concentrations were lower in smaller catchments impacted by wetlands relative to other LULC types (Fig. 2b), suggesting that wetlands have a greater capacity to retain particle-laden Hg. The highest concentrations of sediment MeHg were found in tributaries draining mining impacted sites in the Appalachian region and in certain smaller catchments impacted by agriculture and/or wetlands (Fig. 2c). Whereas sediment MeHg levels were generally lower in river channel and dam sites (Fig. 2c), aqueous MeHg concentrations in some river channels were as elevated as those from smaller catchments impacted by agricultural and wetland LULC (Fig. 4d). Together these results suggest that smaller catchments may be sources of MeHg to the main river channel. Given the small sample size and great variability in Hg burdens among LMB pairs at any given site, we did not observe any unambiguous trends with our projected impact factors (Fig. 2e) or with % LULC and LMB Hg levels collected during Phase 1. However, some variability associated with certain impact factors could be explained by other variables (see below).

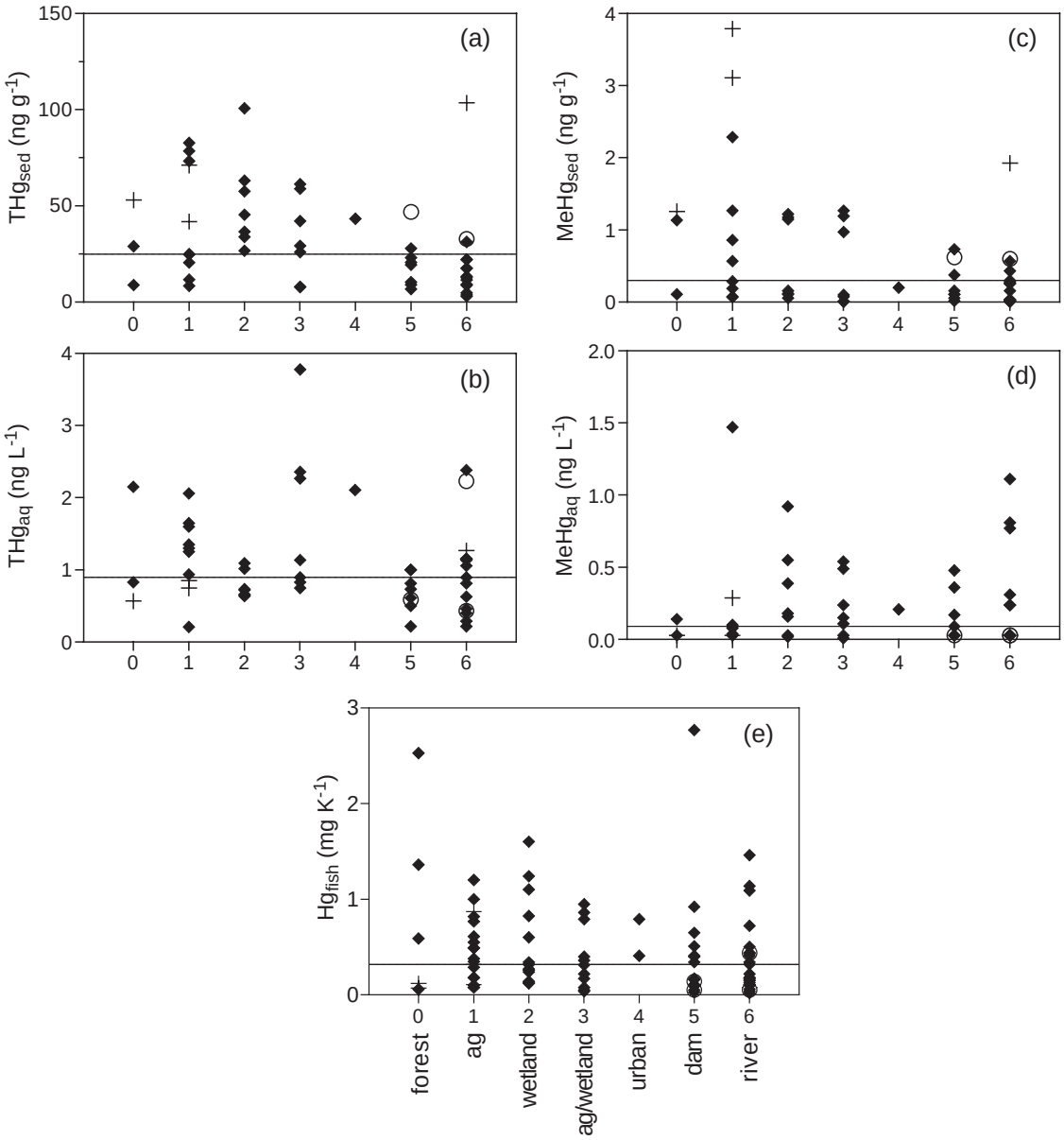

Fig. 2. Distribution of Hg species at sites segregated by proposed impact factors. THg concentration in (a) sediment and (b) water; MeHg concentration in (c) sediment and (d) water; THg concentration in individual LMB from survey (e)—symbols in panels (a) and (c) are the mean of 3 replicates. Crosses (+) denote sites additionally impacted by mining and circles (○) by coal bed methane production. Horizontal lines indicated median values for each data set.

3.3.1. Wetlands

Previous studies have found significant positive relationships between the % wetland area in watersheds and (a) MeHg fluxes (see Grigal, 2002) and (b) LMB Hg bioaccumulation (Brumbaugh et al., 2001). In this study, we did not measure MeHg fluxes. However, we did observe an efficient retention of particle-bound Hg in sampling sites affected by wetlands (Fig. 2a) and this retention was accompanied by low aqueous THg concentrations

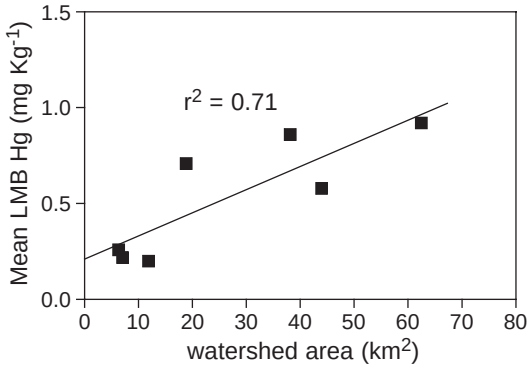

Fig. 3. Site-averaged LMB Hg burden (n=1–3) as a function of surface area for only those watersheds impacted by wetlands.

(Fig. 2b), but elevated aqueous MeHg (Fig. 2c). Sites designated as being impacted by wetlands in this study (% wetland area in sub-watershed=17–80; mean=48, Table 1), ranged from two small oxbow lakes with ill-defined watershed boundaries, but high % wetland (site #s 22 and 34, Table 1), to small creek watersheds whose majority LULC, aside from forest, was wetland. Although we found no positive relationship between % wetland area and LMB Hg burdens at these sites, we did observe a positive relationship between LMB Hg burden and watershed surface area for these wetland impacted sites (Fig. 3). In a study of southeastern depression wetlands, Snodgrass et al. (2000) found that those with larger surface areas were associated with more frequent flooding and drying cycles and were correlated with higher fish Hg burdens. The authors speculated that these hydrological cycles enhance release of bound Hg species thereby increasing their bioavailability to a greater extent than do smaller wetlands experiencing permanent flooding.

3.3.2. Dams and water depth

We hypothesized that dams, through their ability to concentrate fine particles, would be favorable areas for MeHg production and bioaccumulation. Contrary to our hypothesis, not all dams were particularly efficient in accumulating sediment MeHg (Fig. 2c), particularly above the fall line. However, dams affect many upstream creeks by restricting water flow and delivery of fine particles to the main river channel. Note that the retention of fine particles and organic matter in many of these creeks was associated with elevated sediment THg and MeHg levels (Fig. 2a,c; Table 3).

Hg levels also varied considerably among LMB sampled above the eight different dams in our study (Fig. 2e). However, when the depth of water above the dams was considered, we found that mean LMB Hg levels were inversely related to water depth above most dams, with the exception of one (Demopolis, see below) (Fig. 4a). Similarly, the Hg concentration averaged across all LMB from any one pool was a weakly significant negative function of the average depth of the pool (p=0.054) (Fig. 4b). The observation that fish residing in shallower water environments tended to have higher Hg concentrations may reflect more favorable habitats for MeHg production in shallower, warmer waters and a closer coupling

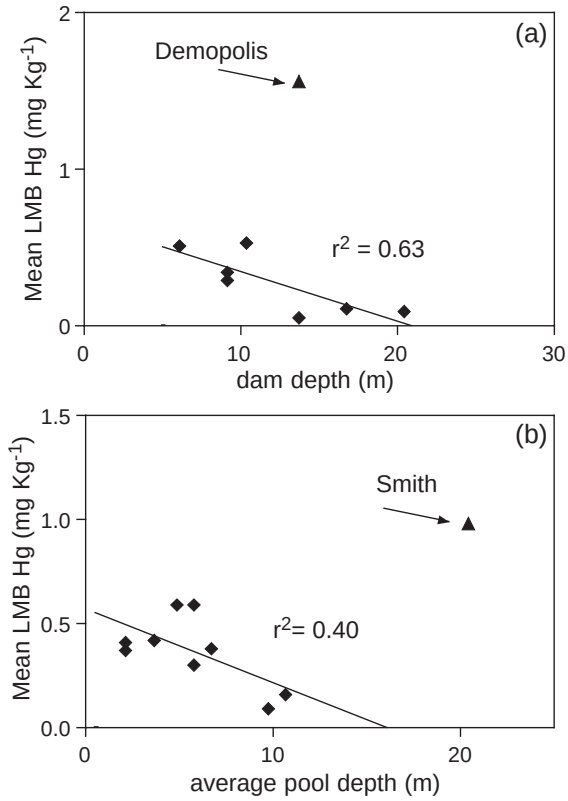

Fig. 4. Site-averaged LMB Hg burden (n=1–3) from (a) sites immediately upstream of a dam as a function of water depth and (b) pool-averaged LMB Hg burden (n=2–38, see Table 4) as a function of average pool depth.

between these benthic processes (e.g., MeHg production) and pelagic MeHg uptake than would occur in deeper pools, as observed in other systems (see Snodgrass et al., 2000; Bloom et al., 2004).

3.3.3. Effect of nutrients and pool trophic status

Increased organic matter production, via stimulation of primary production by nutrients, and subsequent deposition to sediments was one factor we hypothesized would stimulate sediment MeHg production. The significant contribution of sediment organic matter (LOI) to sediment MeHg levels supports this supposition (Table 3), as do observations of elevated sediment MeHg levels in agricultural impacted sites (Fig. 2c). The apparent stimulatory effect of nitrate on sediment MeHg levels is more difficult to explain, since P is generally the nutrient limiting primary production in most fresh water systems. ADEM water quality data from 1992–2000 were analyzed for major recreational pools in the Black Warrior, Lower Tombigbee, and Alabama rivers, where N and/or P was shown to be positively related to sediment MeHg levels. Using combined averages from 1992–2000, Chlorophyll a (Chl a) levels were positively associated with soluble reactive-P (r^2=0.41; p=0.034) and weakly positive with NO_3+NO_2 (r^2=0.26; p=0.10). There was also a strong positive relationship between TSS and total-P (r^2=0.87), showing that particles entering MARB waters are potentially transporting not only Hg, but also nutrients stimulating primary production. Land use and land cover surrounding streams in the MARB were found to be an important determinant of nutrient loads (Chaubey et al., 2001; USGS, 2003), thus providing a link between LULC and MeHg production. The connection between aqueous P and TSS suggests that land use practices that enhance sediment erosion may also contribute to MeHg production. For example, row crop land use was found to have the highest loads of TSS concentration among land use categories examined in a recent MARB study (USGS, 2003), with 3–8 tons soil acre^{-1} eroded by water annually from this type of land use in Alabama (NRCS, 1997).

The effect of pool trophic status on pool-averaged LMB Hg concentrations was assessed using both data from this study and those provided by the Alabama Department of Environmental Management (ADEM) from their 1990–2002 monitoring efforts (Table 4). Each ADEM sample was a composite of skinless fillets from 6 individuals (330–457 mm size class, with all individuals within 75% of the mean size) per site. A weak negative relationship was observed (r^2=0.32; p=0.085) when pool-averaged bass Hg concentrations from the Phase 1 survey of this study were regressed with Chl a data averages for each pool. This relationship was only significant if the 2 fish caught from the Sipsey Fork tributary (site #1, Tables 1 and 2) to Smith Lake were included. Smith Lake is the only oligotrophic pool sampled in our data set (Chl a=4 μg L^{-1}), while the remaining pools would be defined as meso- to eutrophic (Chl a=8–16 μg L^{-1}). A stronger positive trend between Chl a and LMB Hg levels was observed for meso- to eutrophic pools (excluding Demopolis) within the ADEM data set, presented in Fig. 5. The differences between the ADEM and this study may stem from the fact that the ADEM's LMB samples were restricted to the main river channel, and thus more reflective of the pelagic pool productivity status, whereas this study's samples included shallow creeks and sloughs in averages. The trophic status of lakes and reservoirs has previously been found to affect MeHg bioaccumulation and biomagnification in aquatic food webs (Lange et al., 1993; Kidd et al., 1999; Cizdziel et al., 2002), with oligotrophic systems tending toward higher Hg concentrations in predatory fish and their prey than in eutrophic systems. This may result from greater bloom dilution of algal MeHg and decreased MeHg

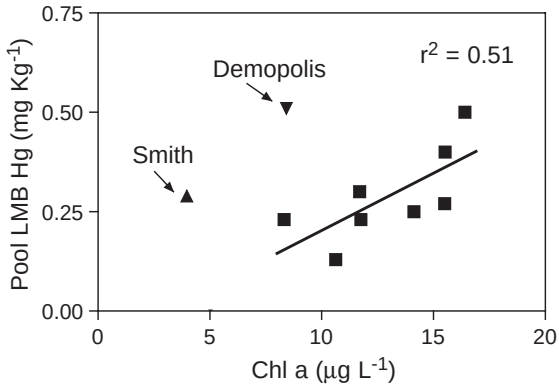

Fig. 5. Pool-averaged LMB Hg concentration in composite samples from the ADEM data set (see Table 4), as a function of average pool Chl a concentration.

trophic transfer (Pickhardt et al., 2002) and/or biodilution of MeHg in predatory fish due to more rapid growth rates in eutrophic systems (Allen et al., 1999). However, data from Alabama's recreational pools do not appear to follow the same trends and may point to a number of other competing factors (see below) that govern Hg bioaccumulation in shallow engineered/impounded southeastern river systems.

3.3.4. Sulfate

One of our hypotheses concerned elevated sulfate levels stimulating MeHg production and hence, bioaccumulation. Sulfate concentrations in the MARB freshwaters ranged from 32–1100 μM, with the highest levels found in the Black Warrior tributaries impacted by mining and other resource extractions. These inputs into the Black Warrior affect Bankhead and Holt pools, with the latter receiving additional sulfate inputs from coal bed methane production (Fig. 6b). Sulfate levels remain elevated downstream below the fall line in the Warrior, Demopolis, and Coffeeville pools, with the latter two Lower Tombigbee pools receiving sulfate loads from the tributary Black Warrior (Figs. 1 and 6b). In general, there were no relationships between aqueous sulfate or total reduced sulfur sediment levels and MeHg levels in sediment, water, or fish when analyzing data from all sites. However, the highest sediment MeHg levels found in the Phase 1 survey were from sites impacted by coal mines and associated elevated sulfate loading (Fig. 2c), lending some support to our hypothesis, although elevated sediment THg levels at these same sites (Fig. 2a) could also be a contributing factor. Many Alabama coals are rich in pyrite and associated trace elements, including Hg (USGS, 1999), which help explain these findings. However, neither water nor fish sampled at those sites had particularly high methyl- or total-Hg levels (Table 2), suggesting that MeHg flux from sediments was transported downstream. At a larger scale, there were also no clear relationships between mean river sulfate levels and Hg burdens in pool-averaged LMB (Fig. 6). In light of this last finding, it is interesting to note that a recent national study found a strong negative relationship between sulfate levels and LMB Hg bioaccumulation (Brumbaugh et al., 2001).

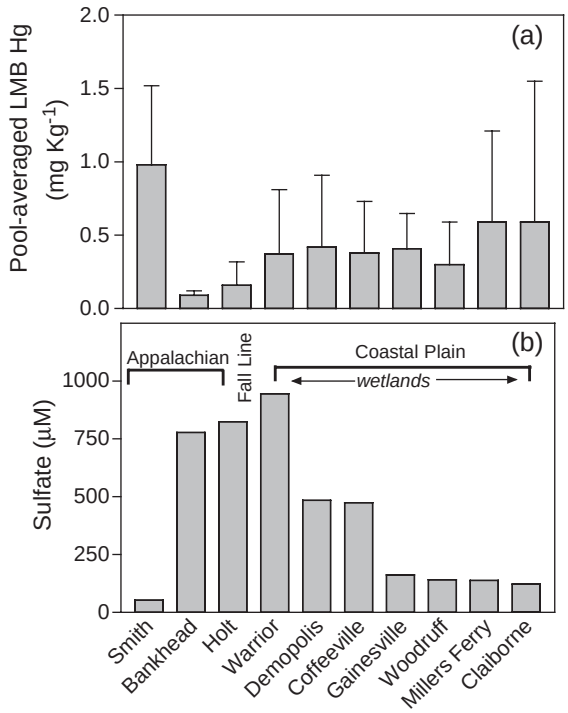

Fig. 6. Pool-averaged LMB Hg burden (a) and average sulfate concentration in main stem of river from pools sampled (b).

Sulfate levels in many areas of the MARB are within the range found to stimulate MeHg production in some freshwaters, while the presence of abundant iron may limit pore water sulfide to levels non-inhibitory to Hg methylation at higher sulfate levels (see Benoit et al., 2003 for further discussion). On the other hand, experimental results from the MARB suggest that (1) sulfate may not stimulate MeHg production if more energetic electron acceptors, such as iron oxides are present, and (2) sulfate is not required for Hg methylation to proceed (Warner et al., 2003). Thus, the effect of sulfate on MeHg production and propagated effects on bioaccumulation in dynamic iron-rich river systems is not straightforward and is in need of further investigation.

3.4. Geographic trends in bioaccumulation

The mean concentration of Hg in the recreational pool-averaged LMB (UA, Table 4) was assessed for other geographic trends, aside from sulfate (Fig. 6a). Excluding Smith pool, fish Hg levels in the deeper Appalachian pools (Bankhead and Holt) were relatively low. This may be due to a combination of

Table 4
Mean Hg concentration for largemouth bass collected from recreational pools in the MARB in the UA (this study) and ADEM monitoring data from 1990–2002

River basin	Pool	Mean pool depth (m)	Mean (range) UA LMB Hg (ppm)	N^a	Mean (range) ADEM LMB Hg (ppm)	N^b
BW	Smith	20.4	0.98 (0.59–1.36)	2	0.29 (<0.10–0.39)	3
	Bankhead	9.8	0.09 (0.07–0.12)	3	0.27 (<0.10–0.50)	4
	Holt	10.7	0.16 (0.05–0.44)	5	0.23 (0.10–0.36)	5
	Warrior	2.1	0.37 (0.04–1.24)	9	0.23 (0.15–0.31)	4
LT	Demopolis	3.7	0.42 (0.11–2.77)	32	0.50 (0.3–0–0.7)	6
	Coffeeville	6.7	0.41 (0.06–0.95)	10	0.30 (0.10–0.50)	2
UT	Gainesville	2.1	0.38 (0.10–0.72)	8	0.25 (0.16–0.40)	4
AL	Woodruff	5.8	0.59 (0.02–0.77)	6	0.40 (0.20–0.50)	3
	Claiborne	4.9	0.30 (0.06–2.53)	8	0.13 (0.10–0.22)	3
	Millers Ferry	5.8	0.59 (0.10–1.6)	8	0.50 (0.50)	2

See Table 1 for river basin names.
[a] N number of individuals.
[b] N number of composite samples of 6 individuals.

factors, such as increased water depth, less accumulation of fine particles behind dams, and lack of wetlands. Smith pool, in the Appalachian province, was the only deep, oligotrophic pool sampled and also had the lowest pH and alkalinity, factors found to influence Hg burdens in Florida lake LMB (Lange et al., 1993). Analysis of more pools outside the Coastal Plain would be needed to fully assess factors affecting Hg bioaccumulation in these types of systems. Below the fall line in the Coastal Plain, LMB Hg concentrations increase and become more variable, fine particles begin to settle out and wetland area surrounding the rivers becomes prominent. At the shallow Demopolis Pool, at the confluence of the Upper Tombigbee and Black Warrior, elevated sulfate levels in combination with drainage from prominent wetlands and agricultural inputs from the Upper Tombigbee likely provide a combination of factors favorable for MeHg bioaccumulation, which prompted more in-depth study (see below). Other factors, such as the prevalence of high viral loads in LMB (Maceina and Slipke, 2004) or other anthropogenic influences from area industry may help explain why the Demopolis pool often did not follow the same trends as other Coastal Plain LMB pool populations with regard to pool trophic status and depth of dams (e.g., see Figs. 3 and 6a). Much of the variability in LMB Hg concentration in the remaining pools from the Coastal Plain province may be reasonably explained by some of the other factors explored above, such as water depth, pool trophic status, and/or the prevalence of wetlands. In general, Hg contamination of LMB increases in the southern part of the MARB watershed, near the Mobile/Tensaw delta. These areas and other southern black water streams outside the MARB are where nearly all of Alabama's inland fish consumption advisories for Hg (at a level of 1 mg Kg^{-1} wet weight) are currently posted (Alabama Department of Public Health).

3.5. Biogeochemical and LULC links to bioaccumulation: Phase 2 Demopolis field study

Potential links between sediment biogeochemical conditions, LULC, and Hg levels in LMB were investigated in an integrated study at 4 sites in the Demopolis pool: dam (# 15), open river (# 16), agricultural creek (#13), and wetland impacted creek (# 18) (Table 1). The first three sites were the same used in the experiments and field study described more fully in Warner et al. (2003). Based on our project hypotheses, we posited that microbial Hg transformation activities and sediment MeHg levels, and hence bioaccumulation in fish, would be lowest in the open river segment and greater at the other impacted sites.

Concentrations of both THg and MeHg in sediments at the Demopolis sites increased in the following order of impacts: open river<dam<agriculture<wetland (Fig. 7a). Aqueous THg levels were higher in creek sites, but similar at the dam and open river sites, whereas aqueous MeHg levels were

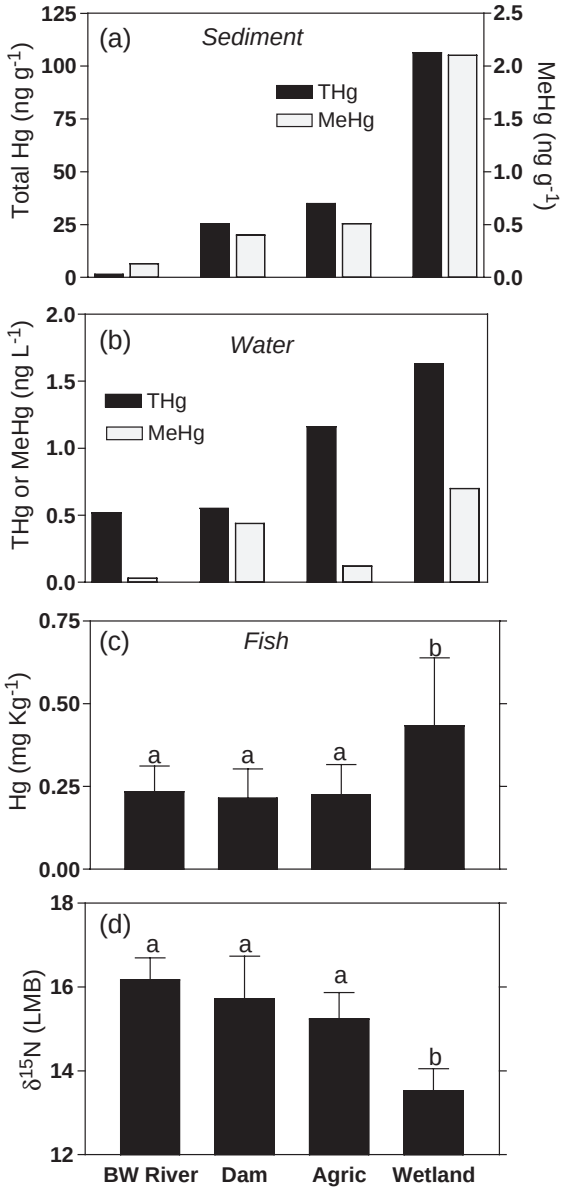

Fig. 7. THg and MeHg concentration in (a) sediment, (b) water, and (c) LMB at Demopolis sites. Average $\delta^{15}N$ ratios of LMB from different sites (d). Error bars in panels (c) and (d) denote one S.D. of the mean (n=6). Different letters above bars in panels (c) and (d) indicate significant difference in means (SNK test, p<0.05).

highest at the wetland and dam sites, and progressively lower at the agriculture and open river sites (Fig. 7b). Comparing mean fish Hg concentrations among sites (analyzed by ANOVA followed by Student Newman Keuls (SNK) test, JMP software, SAS Institute), only the wetland site was found to be significantly different from the other three sites (SNK test, p<0.05) (Fig. 7c).

Fish collected from the Demopolis sites were also analyzed for $\delta^{15}N$ (Fig. 7d). Since these data were not normalized to a common primary consumer, they cannot be used to rigorously assign the trophic position of LMB caught at different sites (Post, 2002). However, what is clear from the data is that all of the LMB obtained from the wetland-impacted site had consistently and significantly lower $\delta^{15}N$ values (SNK test, p<0.05), while values for fish taken from the other sites tended to be considerably higher. These limited data suggest that the wetland site may be functioning as a distinct food web module (separate from main channel), and that LMB from the wetland creek forage primarily from this module. If normalization of the $\delta^{15}N$ data support that the wetland creek LMB were at a lower trophic position than fish caught at the other sites, then these wetland fish with highest Hg burdens could be feeding from a more benthic or detrital-based food web.

The importance of sediment biogeochemical settings on potential rates of Hg methylation and MeHg degradation at the agricultural creek, dam, and river sites have been presented elsewhere (Warner et al., 2003). Although Hg transformation studies were not conducted at the wetland site, these sediments appeared to support a mix of iron reducing and sulfate reducing terminal electron accepting conditions in the surface sediments. The former microbial process was found to generally suppress MeHg production, but not degradation in other Demopolis pool sediments (Warner et al., 2003). The results of Warner et al. (2003) suggested that the presence of an iron-oxide surface sediment layer should decrease the flux of MeHg into the water column, thus mitigating MeHg biomagnification through pelagic food webs. If, however, LMB from the wetland site are feeding primarily from a benthic based food web, the "protective" effect of a surficial sediment iron oxide cap may do little to prevent uptake and trophic transfer of MeHg directly from sediment infauna. Clearly, more detailed studies are required to directly test these suppositions. Nevertheless, we believe that the iron-oxide hypothesis may help explain the LMB with low concentrations of Hg obtained in this study (i.e., those feeding from pelagic food webs in deeper

water habitats), while differential feeding habits and fish behavior/mobility likely account for finding LMB with very high Hg concentrations in close proximity (i.e., those likely feeding from benthic food webs in shallow, productive habitats).

3.6. Relationships among MeHg levels in water, sediment, and fish

While a number of environmental, ecological, and trophic factors govern MeHg bioaccumulation in different aquatic systems, based on first principles, areas with high MeHg sediment production or concentration would be expected to have higher MeHg water levels, and hence, higher transfer to biota, at least in relatively stable aquatic systems. Thus, a key hypothesis of this study was that fish tissue levels of MeHg are related to MeHg water and/or sediment levels. The positive correlations found between LMB Hg levels and both sediment and aqueous MeHg concentration in a nationwide survey of 20 USA watersheds, including the MARB, lend support to this reasoning (Brumbaugh et al., 2001). However, we found no such significant relationships in this data set and it is not known if the positive relationships observed in the nationwide study were observed locally in the MARB watershed, since only 7 LMB were sampled (Brumbaugh et al., 2001). The MARB possesses one of the higher stream flows of the watersheds sampled in Brumbaugh et al. (2001) and the dynamic nature of this river system may help explain our observed lack of correspondence. In free flowing river sections of the MARB, MeHg fluxing out of sediments would be transported downstream and therefore would not be expected to be correlated with ambient water MeHg levels. As the numerous navigational locks and dams in the MARB are not normally used for flood control, large amounts of fine sediment and water are transported during the frequent storms and associated flooding, which are characteristic of this semi-tropical area. As navigational boat traffic moves along the waterways, opening and closing of the locks, result in flushing of water from surrounding creeks, followed by backflow of water into creeks as water levels equilibrate with lock operation. The differential movement of both water and sediment in this dynamic system thus argues against local connection between MeHg sediment production and water levels for many areas and times of the year. Added to these dynamics are the angler-based and natural movements of LMB and their prey, into and out of our predefined impact areas. This type of behavior, together with unknown trophic dynamics, can account for the lack of clear relationships between levels of MeHg in fish, water, and sediment at across our study sites. In addition, more research on LMB behavior and biogeochemical links to trophodynamics are needed to explain the high variability in LMB Hg burdens observed in this study. Nevertheless, our results highlight a number of watershed and biogeochemical variables likely to be important to MeHg production and bioaccumulation in the MARB and other similar riverine ecosystems in the southeast USA. Lastly, this work suggests that watershed management strategies that strive to reduce particle erosion and nutrient runoff into the MARB waters would be beneficial in reducing wildlife and human exposure to Hg.

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