REPORT

Linking landscape development intensity within watersheds to methyl-mercury accumulation in river sediments

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Abstract An indicator of the disturbance of natural systems, the landscape development intensity (LDI) index, was used to assess the potential for land-use within watersheds to influence the production/accumulation of methyl-mercury (MeHg) in river sediments. Sediment samples were collected from locations impacted by well-identified land-use types within the Mobile-Alabama River Basin in Southeastern USA. The samples were analyzed for total-Hg (THg) and MeHg concentrations and the obtained values correlated to the calculated LDI indexes of the sampled watersheds to assess the impact of prevalent land use/land cover on MeHg accumulation in sediments. The results show that unlike THg, levels of MeHg found in sediments are impacted by the LDI indexes. Overall, certain combinations of land-use types within a given watershed appear to be more conducive to MeHg accumulation than others, therefore, pointing to the possibility of targeting land-use practices as potential means for reducing MeHg accumulation in sediments, and ultimately, fish contamination.

Keywords Watersheds · Ecological Disturbance index · LDI · Mercury

INTRODUCTION

Land at the surface of the Earth is being continually transformed by human activity (Vitousek et al. 1997), a process that is linked to human population growth and its associated needs. A great deal of attention has been paid to the relationship between land use on one hand, and the (i) quality of ecological communities (Crosbie and Chow-Fraser 1999; Galatowitsch et al. 2000), (ii) the biological

indicators of ecosystem health (Jones et al. 2001; Patil et al. 2001), and (iii) the development of a “classification system” for watersheds (Habersach 2000; Hawkins et al. 2000) on the other. These research efforts are stimulated by the continuously increasing anthropogenic pressure on natural resources and the resulting effects on biogeochemical cycles and ecological functions. While indicators of ecological disturbances are now commonly used to study the impact of rapid land-use transformations on different environmental compartments (Li et al. 2010; Carey et al. 2011; Oliver et al. 2011), research which addresses the response of mercury (Hg) accumulated in aquatic sediments in response to land changes and at a watershed scale is still lacking. Despite some preliminary studies on a watershed scale (Bonzongo and Lyons 2004; Balogh et al. 2005; Warner et al. 2005), the following pertinent questions on the long-term fate of Hg already present in soils/sediments remain unanswered. First, how can the dominant factors controlling the methylation of inorganic Hg already present in soil/sediment be identified and their effects quantified on a watershed scale? Second, in what ways the coupling of physical, chemical, and biological processes involved in Hg methylation occurs and how can these couplings be elucidated and quantified? Third, how can we predict the fate of Hg over the range of pertinent temporal and spatial scales, and how does land use evolve over time, and what approaches are useful in predicting the temporal evolution of land use and associated impacts on Hg fluxes and transformations?

With regard to Hg, Fig. 1 illustrates how both natural and anthropogenic “forcings” can hypothetically impact its biogeochemical cycle in aquatic systems, and how impacted systems could respond to such forcings. In theory, the effects of these forcings on the fate of pollutants such as Hg can be studied in isolation through simplified

Fig. 1 Natural and anthropogenic forcings driving the physicochemical and biological processes that define the cycle of Hg in aquatic systems. The resulting characteristics rates of Hg transformation and the extent of Hg bioavailability could be inferred from the concentrations of ambient total-Hg and methyl-Hg in different environmental compartments and measured bioaccumulation levels using data at the watershed scale

controlled laboratory experiments. However, in soils and sediments, several issues emerge that make laboratory predictions alone non-suitable, especially when the impact of the assessed perturbations can range from minutes (e.g., response to rain storm) to centuries (response to climate change). Ideally, a combination of temporal and spatial field observations to laboratory investigations should be sought to expect a better insight into the anticipated long-term response of natural systems to both natural and anthropogenic forcings.

One of the aspects of environmental cycling of Hg that remains poorly investigated is the potentially complex response of soil/sediment-Hg within watersheds to land use. This is illustrated by the rather limited number of papers dealing specifically with the impacts of land use on Hg cycling in aquatic systems (Balogh et al. 1998, 2005; Lacerda et al. 2004; Almeida et al. 2005; Roue-LeGall et al. 2005; Warner et al. 2005), as compared to the overwhelming published literature on environmental Hg biogeochemistry. It is, however, likely that the focus on

both the fate of Hg already in the watershed (i.e., *old Hg*) and the fraction newly introduced (e.g., *Hg inputs mimicked by spiking sediment slurries or sediment cores with Hg salt compounds*) could help better predict how these Hg pools would respond to natural and anthropogenic forcings over temporal and spatial scales.

In this study, we focus on how land use might impact Hg already present in aquatic sediments, and only a few aspects of the first question raised above are addressed here. We investigate the relationship between land-use type and Hg transformation/accumulation in sediment at a watershed scale by use of the landscape development intensity (LDI) index (Brown and Vivas 2005), and Hg data obtained from sediment samples collected from sites with well-identified dominant land use and land cover (LULC). This paper is written primarily to stimulate discussion and research focusing on land use, land-use change over time, and their long-term effects on environmental Hg cycling.

MATERIALS AND METHODS

Study site

The study site is the Mobile-Alabama River Basin (MARB), a large (110 000 km²), dynamic watershed with varied land use and geology in the Southeastern USA. It traverses four physiographic provinces: Appalachian Plateau, Valley and Ridge, Piedmont, and Coastal Plain (Fig. 2a). The major sub-basins are 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 m³ s⁻¹ and represents the fourth largest discharge from U.S. watersheds. Most of the land cover is forest (69 %), 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. Further details on the MARB can be found in our earlier publications (Bonzongo and Lyons 2004; Warner et al. 2005).

Sampling site selection, spatial analysis and LULC identification

Based on the US Geological Survey (USGS), LULC maps of the MARB and verification of dominant land uses by a combination of aerial photographs and ground truthing, triplicate surface sediment, and water samples were collected from selected sites with direct impact of identified land-use types (Fig. 2b; Table 1). Data obtained from this survey were used to identify Hg trends relative to LULC. Calculations and maps of LULC for the studied sub-basins within the MARB were completed using the National Land-Cover Data (NLCD) for

the southeast US obtained from the USGS. NLCD data were re-projected 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 EPA's stream reach files and 7.5-min digital elevation files for Alabama acquired from ChartTiff (Image Peak Corp.). LULC maps for each sub-basin were generated in ArcMap using the land-use grids and stream coverages. A LULC map of the MARB is shown in Fig. 2b. Information on geographical locations of studied sites (e.g., latitude and longitude) has been published elsewhere (Warner et al. 2005).

Sample collection and analysis

Sediments samples used in this study were collected from rivers and streams in the MARB. However, only samples from 28 sites (Table 1) out of the 52 sampled (Fig. 2a) were retained because they corresponded to well-identified and well-delineated LULC watersheds dominated by parameters known to impact MeHg production (e.g., mining, agriculture, wetlands, and forests). Triplicate surface sediment samples were collected from each site and analyzed following metal-free ultra-clean techniques and Hg detection by CV-AFS. Details on used sampling and analytical techniques can be found in several of our previous publications (e.g., Warner et al. 2003; Donkor et al. 2005, 2006; Warner et al. 2005). Briefly, sediment samples were collected from a small workboat using a Ponar grab sampler. Acid-cleaned rubber spatulas were used to remove the top 5 cm of sediment not in contact with the grab sampler. Sediment samples were then placed in acid-cleaned polyethylene jars. Total mercury (THg) concentrations in analyzed sediments were determined on ~1 g of freeze-dried material after sample digestion with a 7:3 (V/V) mixture of concentrated HNO₃/H₂SO₄. Although another set of the same samples were digested with HNO₃/H₂SO₄/HF mixture to account for the refractory Hg fraction, data obtained from the former method are used here because this study focused on the Hg fraction that could become bioavailable and methylated. Following the hot acid digestion, cooling at room temperature, and sample dilution with Nanopure[®] water, the SnCl₂-reduction technique was used and Hg was detected by CV-AFS. Unlike total-Hg concentrations, methyl-Hg concentrations in analyzed samples were determined using a method adapted from previous publications (Bloom 1989; Horvat et al. 1993). Briefly, about 1 g of freeze-dried sediment was digested with a 25 % KOH/methanol solution and sample distillation method avoided to minimize the artificial methylation artifact reported by other researchers (Horvat et al. 1993). Next, samples in loosely capped Teflon vials were placed in an oven at 45 °C

Fig. 2 Maps of the Mobile-Alabama River Basin (MARB), showing physiographic provinces, major rivers, and numbered sampled sites (Fig. 2a). The corresponding land use and land cover (LULC) map is shown in Fig. 2b (adapted from USGS 2002)

Table 1 Land-use classification, non-renewable empower density, and resulting LDI coefficients. When expressed in units of $\text{sej ha}^{-1} \text{ year}^{-1}$, the energy use per area per time is referred to as *empower density** and is calculated as average value for the different defined land-use categories (Adapted from Brown and Vivas 2005)

Land-use types	Non-renewable Empower Density (NED) in $\text{sej ha}^{-1} \text{ year}^{-1} (\times \text{E}14)$	Ln (NED)	LDI coefficients
Forest	5	1.63	1.58
Agriculture	1349	7.21	7.00
Wetland	0	–	1.00
Mine/coal bed methane	5211	8.56	8.32
Urban	16 150	9.69	9.42

The LDI coefficient is calculated as the normalized (on a scale of 1–10) natural log of the empower densities

overnight. Following the digestion step, samples were diluted, buffered with a 2 M sodium acetate solution (pH 5), and brought to a final known volume prior to analysis. An aliquot of the digestate was then ethylated in aqueous phase, GC-separated, thermo-decomposed, and detected by atomic fluorescence spectrometry (Bloom 1989). Analytical QA/QC criteria were met by the use of certified reference materials

(IAEA-405 and DORM-2 corresponding to sediment/soil and fish tissues, respectively). The percent recoveries on IAEA-405 averaged $98 \pm 7 \%$ for total-Hg ($n = 7$) and $91 \pm 4 \%$ for methyl-Hg ($n = 8$). For DORM-2 with certified values of $4.64 \pm 0.26 \text{ mg kg}^{-1}$ for THg and $4.47 \pm 0.32 \text{ mg MeHg as Hg/kg}$, recovered averaged values were 4.55 ± 0.16 ($n = 6$) and $4.38 \pm 0.09 \text{ mg kg}^{-1}$ ($n = 6$), respectively.

Ancillary water column data

Water overlying sediments were also collected from all sampled locations. Water samples for dissolved organic carbon (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 (Shimadzu TOC 5000). Water samples for dissolved nutrients were filtered through GF/F glass fiber filters and kept refrigerated until analysis in HCl-washed containers. 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. For total Kjeldahl nitrogen (TKN), collected water samples were preserved with sulfuric acid and analyzed by standard methods (APHA 1992). Sulfate samples were collected in distilled water-rinsed bottles, filtered (0.2 μm), and determined by ion chromatography as described in Welch et al. (1996). Finally, the pH of the different samples was measured on site using a calibrated portable pH meter (Accumet[®], Fisher Scientific).

Determination of the landscape development intensity (LDI) Index

The intensity of human-dominated land use in landscapes affects ecological processes in natural systems and could be a suitable metric for the disturbance gradient that results from increasing human use of landscapes (Brown and Vivas 2005). Using LULC data and a development intensity measure derived from energy use per unit area, the LDI index was calculated as proposed by Brown and Vivas (2005) and shown in Eq. 1.

$$\text{LDI}_{\text{total}} = \sum (\% \text{LU}_i \times \text{LDI}_i), \quad (1)$$

where $\text{LDI}_{\text{total}}$ is the LDI ranking for a given landscape unit; $\% \text{LU}_i$ is the percent of the total area of influence in land use i ; and LDI_i the landscape development intensity coefficient for land use i .

This method is based on the use of a GIS and compatible LULC digital data to determine the human development intensity, which is quantified as “emergy” use per unit area per time as described by Odum (1996). Briefly, *emergy* is the availability of energy of one kind that is used up in transformations directly and indirectly to make a product or service. The unit of emergy is the *emjoule*, a unit referring to the available energy consumed in transformations. For example, sunlight, fuel, electricity, and human service can be put on a common basis by expressing them all in the *emjoules* of solar energy that is required to produce each. In this case, the value is a unit of solar emergy expressed in *solar emjoules*, which is abbreviated *sej*. When expressed in units of $\text{sej ha}^{-1} \text{ year}^{-1}$, the emergy use per area per time is referred to as *empower density* and is calculated as average values for the different defined land-use categories (Brown and Vivas 2005). Finally, the LDI index is obtained as the normalized value of the natural log of the empower density on a scale of 1–10. LDI index values between 1 and 2 correspond to sub-basins that are nearly 100 % natural (e.g., open water bodies, natural forests, etc.). LDIs of 2–5 are representative of sub-basins that are dominated primarily by agriculture; and LDIs >5 indicate mining, industrial, and urban land uses (Brown and Vivas 2005). Table 1 gives the non-renewable empower densities obtained from Brown and Vivas (2005) and used to calculate LDI indexes for the various land-use types relevant to this study.

Statistical analyses

The LULC classification used in this study was determined using GIS. However, to make sure that water parameters confirmed the prevalence of a given land-use type with regard to factors affecting Hg methylation in aquatic systems, the Kruskal–Wallis test (SAS Institute, Inc. 1989), a one-way nonparametric analysis of variance was used to determine whether significant differences existed between water quality parameters measured on samples collected from two watersheds dominated by different land-use categories. For example, this test was used to identify significant differences between nutrient concentrations measured from agriculture dominated versus mining dominated watersheds.

RESULTS AND DISCUSSION

The calculated LDI indexes (see Eq. 1.) for the studied sub-basins in the MARB ranged from 1.11 to 7.37 (Table 2), suggesting the presence of (i) non to slightly impacted systems including open water bodies and natural forests, with $\text{LDI} \leq 2$, (ii) agriculture dominated systems with LDI index values ranging from >2 to 5; and (iii) systems impacted by mining, industrial, and urban land uses with LDI index values >5 (Brown and Vivas 2005).

The scattered plot obtained by correlating THg concentrations in sediments to the calculated LDI index values suggests that the distribution and levels of THg in the MARB sediments are not controlled by the identified dominant land uses (Fig. 3). Previous research in the MARB does point to atmospheric deposition as the main source of Hg, which results in a relatively uniform Hg deposition/input across the MARB (Bonzongo and Lyons 2004; Rypel et al. 2008).

In contrast, Fig. 4 shows that levels of MeHg accumulated in analyzed sediments do increase with increasing LDI index values, but in a non-linear manner. In fact, the observed trend of MeHg concentrations as a function of LDI index can be divided in two distinct portions shown as Fig. 4a, b. Overall, the trend shown in Fig. 4 is likely due to changes in the percentage of the different LULC present simultaneously in watersheds, and how in combination such changes in LULC favorably or negatively impact methyl-Hg accumulation. For instance, in forested wetland-dominated watersheds, the stimulation of microbial MeHg production would be fueled by the oxidation of abundant organic matter as microbial respiration of organic carbon leads to the development of anoxic conditions which in turn favors sulfate reduction by sulfate reducing bacteria (SRB). The latter are one of the prevalent microbial groups linked to Hg methylation in several published

Table 2 Sampling sites within the MARB (see Fig. 2a for locations), calculated LDI coefficients in decreasing order, percentage (%) land use and land cover (LULC), and average ($n = 3$) total (THg) and methyl (MeHg) mercury concentrations in ng Hg/g dry weight. Italicized rows correspond to watersheds with Landscape Development Intensity (LDI) index values >4 , and methyl-Hg concentrations <0.3 ng/g

Site # (Fig. 2a)	Sampling site ID	Land-use type	LDI coefficient	Sub-basin area (km ²)	%Land use/land cover (LULC)				Methyl- Hg (ng g ⁻¹)	Total-Hg (ng g ⁻¹)
					Agriculture	Wetland	Urban	Forest		
52	Big Beaver Creek	1, 4	7.37	5.6	48	0.0	43	0.0	1.18	7.37
21	Penachee Creek	1	5.68	44.4	75	8.0	0.2	14	0.57	11.8
47	Catoma Creek	1	5.38	958	68	2.5	1.6	27	0.86	5.38
<i>13</i>	<i>French Creek</i>	<i>1</i>	<i>4.83</i>	<i>37</i>	<i>61</i>	<i>7.6</i>	<i>1.0</i>	<i>24</i>	<i>0.07</i>	<i>82.7</i>
<i>41</i>	<i>Bogue Chitto Creek</i>	<i>1</i>	<i>4.39</i>	<i>940</i>	<i>53</i>	<i>11.7</i>	<i>0.6</i>	<i>33</i>	<i>0.29</i>	<i>4.39</i>
<i>17</i>	<i>Sawmill/Grain Silo</i>	<i>4</i>	<i>4.20</i>	<i>1.1</i>	<i>13</i>	<i>2.3</i>	<i>25</i>	<i>58</i>	<i>0.20</i>	<i>43.3</i>
<i>19</i>	<i>McConico Creek</i>	<i>1</i>	<i>4.09</i>	<i>68</i>	<i>48</i>	<i>12.5</i>	<i>0.1</i>	<i>38</i>	<i>0.19</i>	<i>73.3</i>
45	Pintalla Creek	1	3.76	685	41	7.3	0.5	48	2.29	3.76
27	Chickassaw Bogue	1	3.49	891	35	5.2	0.5	54	0.08	8.45
2	Locust Fork	1, M	3.28	3111	20	0.1	6.0	72	3.79	41.9
3	Mulberry Fork	1, M, C	2.84	6130	17	0.3	1.0	78	3.11	71.2
46	Autauga Creek	1	2.81	314	21	8.0	2.2	68	1.27	2.81
50	Bayou Sara	3	2.23	114	8.7	11.1	3.6	74	0.97	2.23
18	Spidel Creek	2	2.07	18.9	16	47.6	0.2	31	0.11	45.4
9	Minters Creek	3	2.05	83.3	8.7	4.5	0.9	83	1.27	42.2
10	Gabriel Creek	2	2.04	62.5	11	17.0	0.1	69	1.22	63.2
25	River Channel	3	2.01	2040	10	9.1	0.4	76	0.01	7.82
26	River confluence	3	2.01	2040	10	9.1	0.4	76	0.01	25.9
5	Yellow Creek	0, M	2.00	171	3.7	0.0	0.1	93	1.26	53.1
37	Turkey Creek	3	1.91	676	7.5	9.3	0.4	79	0.01	1.91
14	Backbone Creek	2	1.82	7	9.2	35.9	0	51	0.12	36.7
1	Sipsey Fork	0	1.77	477	3.7	0.1	0.2	94	1.14	8.90
42	Rum Creek	2	1.74	38	7.3	33.6	0	57	0.16	1.74
32	Bilbo/Bates Creek	3	1.71	432	3.9	6.6	0.4	84	0.08	29.4
28	Turkey Creek	3	1.66	144	3.0	7.0	0.2	87	1.19	59.0
38	Silver Creek	0	1.58	89	0.5	2.8	0	96	0.11	1.58
22	Lowrey's Lake	2	1.54	6.3	8.4	69.7	0	16	1.15	34.0
34	Smith Lake	2	1.11	12	1.9	80.9	0	10	0.06	1.11

0 Control “pristine” Forest, 1 agriculture, 2 wetland, 3 forest/agriculture/wetland, 4 urban, M mine, C coal bed methane

Fig. 3 Landscape development intensity (LDI) index versus total-Hg concentrations in surface sediments of the Mobile-Alabama River Basin (MARB)

studies (Gilmour et al. 1992; King et al. 2000; Drott et al. 2007; Shao et al. 2012). Also, wetlands have been identified as factories of MeHg production (St. Louis et al. 1994; Branfireun et al. 1999; Hall et al. 2008) and would likely behave as sources of both MeHg and DOC to rivers when present within watersheds. Measured DOC concentrations in waters of the MARB ranged from 2.55 to 10.36 mg C/L, and the results of the Kruskal–Wallis test indicated that waters within watershed dominated by forests and wetlands had significantly higher ($p < 0.05$) DOC concentrations than those impacted by other LULC types (data per site not shown). And such DOC inputs to the river could stimulate microbial respiration and Hg methylation within river’s sediments. Besides DOC from forested areas and riparian wetlands, mining activities release acidic waters and

Fig. 4 Relationship between the calculated watershed landscape development intensity (LDI) indexes and methyl-Hg concentrations determined in impacted surface sediments from the Mobile-Alabama River Basin (MARB). (a) LDI index <4.0. (b) LDI index >4.0

sulfate which can impact Hg methylation and accumulation in sediments (Ramial et al. 1985). In fact, mining in the MARB refers primarily to coal and coal bed methane mining activities resulting in waters with pH <7 (water pH measured on site in the MARB ranged from 5.5 to 8.5) and pollution with sulfate (measured dissolved sulfate concentrations ranged from 32 to 1100 μM). The Kruskal–Wallis test confirmed that watersheds with mining as prevalent activities had significantly higher ($p < 0.05$) concentrations of sulfate than the other identified land-use types. Although both sulfate and organic matter can stimulate microbial methylation of ionic Hg (Jeremiason et al. 2006), they also do have optimum values beyond which Hg methylation becomes limited due to reduced Hg bioavailability through both binding to organic ligands and precipitation as insoluble Hg sulfide minerals. Finally, agricultural and urban activities within the MARB could impact MeHg production/accumulation in sediments

through nutrient inputs as reported for other watersheds by Balogh et al. (2002, 2003). Nutrient addition stimulate primary production, ultimately leading to depletion of dissolved oxygen and development of anoxic conditions which can be favorable to Hg methylation as mentioned earlier in connection with microbial respiration of organic carbon. Measured concentrations of total nitrogen (TN) and dissolved nitrate ranged from 0.2 to 10 mg TN/L and from 0.03 to 8 mg $\text{N-NO}_3^-/\text{L}$, respectively. Concentrations of total phosphorus (TP) and dissolved orthophosphate ranged from 0.008 to 2.22 mg TP/L and 0.01 to 0.45 mg $\text{P-PO}_4^{3-}/\text{L}$; respectively. With regard to nutrients, the results of the Kruskal–Wallis test indicated that both agricultural and urban dominated watersheds had significantly higher ($p < 0.05$) concentrations of N and P than those dominated by other LULC types.

The above discussion shows how complex the process of accounting for factors controlling the accumulation of methyl-Hg in aquatic systems could be. Results presented here in Table 2 and Fig. 4 are intended for linking an indicator of ecological disturbance, the LDI index in this case, to the potential for methyl-Hg accumulation in sediments. First, the results presented in Table 2 show the proportions of each of the land-use types converted into LDI index values, and the corresponding levels of methyl-Hg accumulated in sediments. Figure 4 relates the determined LDI values to the corresponding methyl-Hg concentrations. For sediments collected from watersheds with LDI index values <4 (Fig. 4a), methyl-Hg levels varied from values at the analytical detection limit of used method ($\sim 0.01 \text{ ng g}^{-1}$) to the highest levels measured for the entire river basin. However, as the LDI index continues to increase to values ranging from 4.09 to 4.83 (see italicized values in Table 2, and drop line from Fig. 4a to b), its effect on levels of methyl-Hg accumulated in sediments becomes non-existent as the concentrations of accumulated methyl-Hg falls to values ranging from 0.07 to 0.29 ng g^{-1} . Finally, as the LDI coefficient reaches its highest calculated value (7.37), the concentration of methyl-Hg in sediments increases slightly to 1.18 ng g^{-1} .

The use of the LDI index in combination with levels of methyl-Hg accumulated in surface sediments suggests that knowledge of spatial distribution of LULC within a watershed can help predict the potential for methyl-Hg accumulation in aquatic sediments. Of interest in the above described trend (Fig. 4), there are specific combinations of different LULCs leading to nearly zero methyl-Hg accumulation, with LDI values ranging between 4.09 and 4.83 (see italicized cells of Table 2). In contrast to reports by Balogh et al. (2002, 2003) which focused on the aqueous phase, the introduction of N and P into rivers seems not to favor MeHg accumulation in sediments. It is likely that in these hydrodynamic systems, the bioavailable fraction of Hg would be removed from

solution through a combination of binding to cell membranes and incorporation into algal cells, a phenomenon which would result in bio-dilution of Hg (Chen and Folt 2005), and subsequent downstream export of Hg by planktonic biomass in free flowing rivers and streams. This could have negative implications for receiving downstream waters characterized by sluggish water flow (e.g., reservoirs, lakes). Overall, further studies are needed to investigate, preferentially under laboratory conditions, the effects of specific LULC proportions characteristic of watersheds on methyl-Hg production and accumulation.

The second observation is that as LULC changes, its impacts on Hg cycling changes as well. Therefore, over time, changes of LULC within watersheds should merit consideration in terms of potential impacts on aquatic Hg cycling. Accordingly, regulation of land-use practices that enhances the release/mobilization of Hg accumulated in soils/sediments and methyl-Hg production from inorganic Hg already present in sediments could be considered as a potential means for managing the issue of Hg bioaccumulation in aquatic biota, and ultimately, human exposure via fish based diets.

In conclusion, this preliminary effort tends to suggest that the combination of geochemical and GIS knowledge at a watershed scale can help forecast the impact of anthropogenic activities on at least one aspect of Hg cycling in aquatic systems. However, further studies are needed to fine tune the approach by identifying the end members (conditions for lowest and highest methyl-Hg accumulation) between which specific combinations of LULC would result in a clear gradient of responses.

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