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Total Hg, methyl Hg and other toxic heavy metals in a northern Gulf of Mexico estuary: Louisiana Pontchartrain basin

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Total Hg, methyl Hg and other toxic heavy metals in a northern Gulf of Mexico estuary: Louisiana Pontchartrain basin

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Concentration of total Hg, methyl Hg, and other heavy metals were determined in sediment collected along a salinity gradient in a Louisiana Gulf Coast estuary. Surface sediment was collected at established coordinates (n = 292) along a salinity gradient covering Lake Maurepas, Lake Pontchartrain, Lake Borgne and the Chandeleur Sound located in the 12,170 km² Pontchartrain basin estuary southeastern coastal Louisiana. Lake Maurepas sediment with lower salinity contained higher levels of methyl Hg (0.80 μ g/kg) than Lake Pontchartrain (0.55 μ g/kg). Lake Maurepas sediment also had higher levels of total Hg (98.0 μ g/kg) as compared to Lake Pontchartrain (67.0 μ g/kg). Average total Hg content of Lake Borgne and the Chandeleur Sound sediment was 24.0 μ g/kg dry sediment and methyl Hg content averaged 0.21 μ g/kg dry sediment. Methyl Hg content of sediment was positively correlated with total Hg, organic matter and clay content of sediment. Methyl Hg was inversely correlated with salinity, sediment Eh and sand content. Total Hg and methyl Hg decreased with increase in salinity in the order of Lake Maurepas >Lake Pontchartrain>Lake Borgne/ the Chandeleur Sound. Lake Maurepas containing several times higher amount of methyl Hg in sediment as compared to Lake Pontchartrain and Lake Borgne and the Chandeleur Sound is an area that could serve as potential source of mercury to the aquatic food chain. Methyl Hg content of sediment in the estuary could be predicted by the equation: Methyl Hg = 0.11670–0.0625 x Salinity + 0.05349 × O.M. + 0.00513 × Total Hg - 0.00250 × Clay. Concentrations of other toxic heavy metals (Pb, Cd, Ni, Cu and Zn) in sediment were not elevated and was statistically correlated with sediment texture and iron and aluminum content of sediment.

Keywords: Heavy metals, Lake Marepas, Lake Pontchartrain, Lake Borge, the Chandeleur Sound, mercury.

Introduction

Many water bodies worldwide have elevated mercury levels in top predator fish that has prompted the issuance of advisories on fish consumption by various public health agencies. The main source of methyl Hg in humans is through fish consumption.^[1] Methyl Hg makes up 90% of the total Hg in fish.^[2] Methyl Hg is a neurotoxic compound that can easily biomagnify through the food web to humans. The compound has detrimental effect on pregnant women, children and harmful effect on other biota.^[1] Mercury contamination of fish in freshwater lakes and streams in Louisiana and elsewhere along the Gulf Coast is also a public health issue. There are many advisories from various public health agencies limiting consumption of fish.

Levels up to 3 mg/kg have been found in largemouth bass in some Louisiana lakes, which is considerably above the maximum permissible level (0.5 to 1 mg/kg) for edible fish tissue. Having mercury advisories issued for a number of lakes in Louisiana has resulted in a reduced interest in these lakes for sports fishing. Even though there are advisories, information on source and distribution of mercury in gulf fish is scarce. Therefore knowledge on distribution of mercury including methyl Hg in Gulf Coast estuaries is important. Source of mercury to the Northern Gulf of Mexico is lacking. Atmosphere fallout is believed to be the main contribution.^[3]

Mercury levels in the sediment and water column of lakes worldwide have increased since the advent of the industrial revolution. Mercury entering water bodies originates from

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local regional and global sources. The majority of Hg entering water bodies are from atmospheric source. A common source is the increased widespread on the fallout of elemental mercury that originates from incinerators, smelters and power plants. Research in the Florida Everglades and elsewhere has shown that uptake of mercury by fish can occur at low levels of mercury in the sediment and water column if proper biogeochemical conditions exist in the sediment. Several studies^[4] have shown that the total Hg input or concentration is frequently less important than the sediment conditions in controlling methyl Hg formation.

The accumulation of unacceptable concentrations of mercury in fish occurs largely as the result of bioaccumulation of methyl Hg up the food chain to the top predator fish,^[5] which are also the most desired species. Methyl Hg formed largely in the anaerobic sediments of lakes move up the food chain through several trophic levels. It is thought that the mercury source in fish is related to sediment Hg originating from the increase in atmosphere fallout of mercury during the past century as a result of coal burning and smelting operations and from runoff into the lakes from watersheds receiving this fallout mercury.

The microbially mediated processes of methylation and demethylation are influenced by sediment redox potential, pH, and microbial activity of the sediment water system. Aquatic environments with positive redox potential and low pH would favor Hg demethylation. The rate of biological methylation of added Hg in sediment is greater under reduced conditions as compared to oxidized conditions.^[6] It has been reported that 95% of mercury Hg in an estuarine sediment is attributable to anaerobic sulfate reducing bacteria such as *Desulfovibrio*.^[7,8] Researchers have also found that high salinity levels inhibited methylation while methylation increased when sulfate levels were low and concentrations of organic fermentation products were high.^[9] Methylation is reported to depend more on the organic content of sediment rather than sulfate concentration in pore water. ^[10] Bishop^[11] reported the present of H₂S would allow for the formation of HgS. The extremely low solubility of this compound could restrict methylation under these conditions.

Demethylation of methyl Hg (to HgO and methane) was found to occur at high redox potentials (+110 mV) in estuarine sediments.^[6,12] Therefore, demethylation would be an important transformation in the aerobic or moderately aerobic zone in sediment. The dynamics of methylation and demethylation of Hg in sediments may be the key factor in the flux of methyl Hg from bottom sediments to the overlying water column. When methyl Hg is released from anaerobic conditions through a zone of higher redox or aerobic conditions, the methyl Hg may be demethylated to elemental Hg, lowering the flux of methyl Hg to the water column. Since the size of this aerobic layer is dependent on the sediment oxygen demand (organic matter content), lake sediment with high organic matter content have very small aerobic zones, which would limit demethylation. is an area with development of oil exploration, refining, and petrochemical industries, which are potential source of heavy metals.^[15] Many researchers^[16,17] have reported that wetland systems act as sinks, removing toxic material such as heavy metals from contaminated water entering the system.

The objective of this study was to (1) determine methyl Hg, total Hg, and other heavy metals (Pb, Cd, Ni, Cu and Zn) content of sediment from water bodies in the Pontchartrain Basin estuary and (2) determine the relationship between methyl Hg, total Hg to salinity and sediment properties and the relationship among other heavy metals other than mercury.

Although there are no current advisories on consumption of fish from Lake Pontchartrain and Lake Maurepas, several of the streams draining into these lakes do have mercury advisories. Bayou Liberty in St. Tammany Parish has mercury advisory from its origin to Lake Pontchartrain. Blind River in St. John the Baptist Parish that drains into Lake Maurepas also has an advisory along its entire length (Louisiana Department of Environmental Quality).

Materials and methods

Sediment was collected along a grid sampling within the Pontchartrain Basin. Sediment samples were collected on 7.92 km sampling grid in Lake Maurepas, Lake Pontchartrain, Lake Borgne and the Chandeleur Sound. Transects of these location samples are shown in Figure 1. Using a global positioning system (GPS), sample sites were identified so that a map of the locations could be constructed.

Sediment sampling

The samples were collected from the surface 10-12 cm of sediment using a hand operated Peterson dredge. A sub sample of the sediment was placed in mercury free glass containers, sealed and placed on ice until transported to the laboratory for storage at 5°C. until the various analysis were carried out. The jars were completely filled to exclude air (oxygen) in order to prevent any oxidation reactions.

Analyses

Sediment samples were analyzed for total Hg, methyl Hg, total element or other heavy metals and various chemical and physical parameters (pH and redox potential) as described below. Total Hg, methyl Hg and element content including other heavy metals are based on oven-dry weight. The relationships between methyl Hg content and sediment properties were determined in order to obtain



Fig. 1. Arch view map showing sampling sites.

information on possible causes of methyl Hg formation in the lake sediment.

A sub sample of sediment was removed from each jar and used for the determination of total Hg, methyl Hg, other heavy metals, organic matter, salinity, and grain size. Then the sediment redox potential and the pH were measured using platinum electrodes and an Ag/AgCl reference electrode. Two replicate electrodes were inserted in the sediment and allowed to equilibrate for 6 hours before measurement. The pH was measured using a combination glass-reference electrode.

Surface water salinity and conductivity were taken at the same time the sediment samples were collected using a portable salinity/conductivity meter. Sediment particle size analysis and organic matter content was also determined in the sediment. Sediment particle size was determined using the sedigraph technique.^[18] Organic matter was determined by loss on ignition following acid treatment to remove carbonate.

Methyl Hg analysis

Methyl Hg analysis was performed using a GC-AFS system. An integrated gas chromatography – mercury atomic fluorescence spectrometer included a Hewlett-Packard model HP 6890 Series Plus gas chromatograph and coupled to a PSA Merlin Detector via a pyrolysis oven maintained at 810°C.

A fused silica analytical column with dimensions of $15 \text{ m} \times 0.53 \text{ mm}$ i.d. (Megabore) coated with a $1.5 \mu \text{m}$ film thickness of DB-1 (J&W Scientific) was used in the analysis. The column oven temperature was maintained at 50°C for 1.0 min, programmed at 30°C/min to 140°C, which was held for 3.0 min, then was programmed at 30°C/min to 250°C, which was held for 3.0 min. A split/splitless injector was used in the splitless mode and maintained at 200°C. The carrier gas flow was 4.0 mL/min of high purity argon and make-up gas flow was 120 mL/min of high purity argon.

The column eluate was passed through a pyrolyzer (Thermolyne Tube Furnace 21100) via deactivated fused silica tubing into a Merlin Mercury Fluorescence Detector System (AFS) Model 10.023 (P.S. Analytical) which was used for mercury detection. For the PSA Merlin Mercury Fluorescence Detector system, the sheath gas flow was 200 mL/min of argon. A real time chromatographic control and data acquisition system (Hewlett-Packard ChemStation) was interfaced with the GC and AFS detector system for the analysis.^[19] Quantitative methyl mercury analysis was obtained using a five-point (between 0.2 ppb and 10.0 ppb) calibration curve forced to zero (R = 0.999). Sample preparation was performed based on the method of Alli et al.^[20] and Cai et al.^[21–23]

Total Hg analysis

Total (organic and inorganic) Hg was measured by cold vapor technique based on EPA Method # 245.1, 245.5 and 7471A using a Mercury Instruments Analytical Technologies LabAnalyzer Model 254.

Determination of the total Hg concentration was based on the resonance absorption of the Hg atoms at a wavelength of 253.7 nm. Mercury contained in the sample is reduced to its elementary state by a reductant (tin-IIchloride). A stream of air, which is produced by a built-in membrane pump, strips the mercury from the sample and draws it into the optical cell. The concentration of mercury in the cell is determined by measuring light absorption at a wavelength of 253.7 nm. A built-in computer performs the quantitative evaluation of the response. In order to obtain an extremely stable baseline, the UV-light source is controlled by the reference beam method. In addition, the UV-detectors of the LabAnalyzer are thermostatically stabilized. Heating of the optical cell prevents decrease in sensitivity associated with water vapor. Thus the use of a desiccant, which shows some adsorption of mercury vapor, is avoided. Using this method, a stable and accurate calibration was obtained (R = 0.998).

Metal analysis (Total analysis)

Sediment were dried (100°C), ground, and thoroughly mixed prior to analysis. Sediment samples were digested using nitric-perchloric acid digestion procedures.^[24] The digested samples were diluted to volume and analyzed using Inductively Couple Argon Plasma spectrophotometer (ICAP). Analysis was calibrated against known standard of each metal. Data were compiled and statistical analyses performed using Microsoft Excel program available in Microsoft Professional 2000 on an IBM PC-AT.

Results and discussion

Total Hg and methyl Hg

The data in Tables 1, 2, and 3 shows average content of total Hg, methyl Hg, and sediment properties for water bodies samples. Total Hg and methyl Hg decreased with increase in salinity in the order of Lake Maurepas >Lake Pontchartrain > Lake Borgne/ the Chandeleur Sound. The measured decreases in methyl Hg with increase in salinity is supported by previous study reported in the literature.^[9,25] Salinity has a negative effect on methylation with lower levels of methyl Hg in estuaries and marine environment as compared to freshwater system.^[25] Methyl Hg may be reduced at high salinity because of the production of H₂S, which limit the availability of Hg²⁺through the formation of HgS.^[9]

Results identified no hot spots or elevated mercury levels in sediment at the sites sampled. Total Hg and methyl Hg

Table 1. Averages of sediment analysis parameters for Lake Maurepas (n = 27 samples).

		Average	Stdev	Maximum	Minimum
Salinity	(‰)	1.91	1.15	3.80	0.20
Conductivity	(mS/cm)	3.59	2.08	6.94	0.32
Methyl_Hg	$(\mu g/kg dry sed)$	0.80	0.49	2.33	0.21
Total_Hg	$(\mu g/kg dry sed)$	98	47	237	12
O.M.	(%)	4.60	5.93	32.77	0.30
Eh	(mv)	-163	83	30	-280
pН		7.2	0.3	7.8	6.3
Al	mg/kg dry sed)	24131	12561	44369	1530
As	mg/kg dry sed)	0.41	0.02	0.43	0.36
Ca	mg/kg dry sed)	9817	14199	58776	162
Cd	mg/kg dry sed)	0.262	0.014	0.280	0.230
Cu	mg/kg dry sed)	11.8	6.8	29.2	< 0.5
Fe	mg/kg dry sed)	17533	7790	28861	1598
Pb	mg/kg dry sed)	26	12	46	3
Mg	mg/kg dry sed)	5044	2681	8918	124
Mn	mg/kg dry sed)	730	445	1665	52
Ni	mg/kg dry sed)	13.88	6.93	24.30	0.70
Р	mg/kg dry sed)	285	228	1094	1
K	mg/kg dry sed)	4494	2468	8228	13
Se	mg/kg dry sed)	2.493	3.374	11.180	0.04
Na	mg/kg dry sed)	1903	1108	3958	99
S	mg/kg dry sed)	3583	2381	10066	89
Zn	mg/kg dry sed)	66	34	146	3
Sand	%	19.7	18.3	70.2	2.3
Clay	%	35.8	16.5	57.7	2.9
Silt	%	44.5	11.2	72.9	26.9

levels in the Ponchartrain Basin sediment especially in Lake Pontchartrain and Lake Borgne were lower than reported values by Louisiana Department of Environmental Quality for noncoastal interior water bodies, some of which have mercury advisory for fish consumption.

Lake Maurepas sediment with lower salinity contained higher levels of methyl Hg (0.80 μ g/kg) than Lake Pontchartrain (0.55 μ g/kg) (Tables 1 and 2). Lake Maurepas sediment also had higher levels of total Hg (98.0 μ g/kg) as compared to Lake Pontchartrian (67.0 μ g/kg) (Tables 1 and 2). Average total Hg content of Lake Borgne and the Chandeleur Sound sediment was 24.0 μ g/kg dry sediment (Table 3). Sediment methyl Hg content averaged 0.21 μ g/kg dry sediment for Lake Borgne and the Chandeleur Sound. Both total Hg and methyl Hg content of Lake Borgne and the Chandeleur Sound sediment located nearer the coast was lower than that measured in Lake Maurepas or Lake Pontchartrain. The total Hg levels were less than total Hg concentration in sediment of 6 Louisiana freshwater lakes (143 to 221 μ g/kg) where health advisories are in effect due to mercury level in fish.^[26] Correlation analyses of total Hg, methyl Hg to sediment properties (organic matter, particle size, salinity, etc.) are shown in Table 4.

Distribution of total Mg, methyl Hg, organic matter, and salinity in the lake sediments are shown in Figures 2, 3, 4,

Minimum

8.20

14.50

0.05

6

0.60

-240

6.0 2255

< 0.5

1952

< 0.5

1.0

2731

< 0.5 2086

68

3.63

162

616

1.065

1500

395

7

12.5

1.5

2.0

Table 2. Averages of sediment analysis parameters for Lake Pontchartrain (n = 147 samples).

Table 3. Averages of sediment analysis parameters for Lake Borgne and the Chandeleur Sound (n = 118 Samples).

		Average	Stdev	Maximum	Minimum			Average	Stdev	Maximum
Salinity	(‰)	2.95	1.49	5.00	0.10	Salinity	(‰)	21.27	10.96	37.41
Conductivity	(mS/cm)	5.38	2.65	9.84	0.11	Conduct	(mS/cm)	33.08	15.67	51.10
Methyl_Hg	$(\mu g/kg dry sed)$	0.55	0.38	2.60	0.15	Methyl_Hg	$(\mu g/kg dry sed)$	0.21	0.11	0.60
Total_Hg	$(\mu g/kg dry sed)$	67	31	177	11	Total_Hg	$(\mu g/kg dry sed)$	24	11	58
O.M.	(%)	3.45	2.06	18.18	0.08	O.M.	(%)	4.41	3.90	42.50
Eh	(mv)	-120	75	20	-260	Eh	(mv)	-32	120	330
pН		7.4	0.4	8.7	6.0	pН		7.3	0.3	7.9
Al	mg/kg dry sed)	28250	11685	51324	1805	Al	mg/kg dry sed)	17983	8475	44037
As	mg/kg dry sed)	0.40	0.02	0.43	0.35	As	mg/kg dry sed)	1.62	0.59	2.89
Ca	mg/kg dry sed)	7778	9048	60954	226	Ca	mg/kg dry sed)	10900	33212	284528
Cd	mg/kg dry sed)	0.254	0.025	0.280	< 0.5	Cd	mg/kg dry sed)	0.86	0.39	20.9
Cu	mg/kg dry sed)	14.0	6.7	31.5	< 0.5	Cu	mg/kg dry sed)	5.9	3.8	24.3
Fe	mg/kg dry sed)	20467	7383	34357	1780	Fe	mg/kg dry sed)	12002	4161	23620
Pb	mg/kg dry sed)	32	13	57	4	Pb	mg/kg dry sed)	7	3	17
Mg	mg/kg dry sed)	7434	3215	13509	355	Mg	mg/kg dry sed)	4764	1237	8549
Mn	mg/kg dry sed)	738	492	2866	55	Mn	mg/kg dry sed)	187	84	616
Ni	mg/kg dry sed)	17.99	7.27	34.00	1.20	Ni	mg/kg dry sed)	14.39	3.99	29.20
Р	mg/kg dry sed)	403	199	1157	1	Р	mg/kg dry sed)	329	54	431
K	mg/kg dry sed)	6566	2942	12547	105	K	mg/kg dry sed)	2356	1032	5878
Se	mg/kg dry sed)	2.627	3.235	17.881	0.04	Se	mg/kg dry sed)	2.764	1.130	8.640
Na	mg/kg dry sed)	2702	1629	6371	93	Na	mg/kg dry sed)	4700	3180	19375
S	mg/kg dry sed)	3745	2594	12926	76	S	mg/kg dry sed)	2079	3082	31156
Zn	mg/kg dry sed)	76	32	167	4	Zn	mg/kg dry sed)	35	23	253
Sand	%	13.0	15.9	92.4	0.9	Sand	%	57.9	23.9	94.8
Clay	%	42.3	14.0	64.3	1.1	Clay	%	15.4	9.5	48.3
Silt	%	45.3	11.5	78.3	10.6	Silt	%	26.8	16.9	65.5

and 5. Methyl Hg content of sediment was significantly correlated ($r = 0.648^{***}$) to total Hg content of sediment, organic matter content ($r = 0.349^{***}$) and salinity (r = -0.427^{***}). Total Hg and methyl Hg decreased with increase in salinity in the order of Lake Maurepas > Lake Pontchartrain > Lake Borgne/Chandeleur Sound (Figures 6 and 7). By comparison total and methyl Hg concentration in Florida Bay (n = 30) ranged from 3 to 100 ug/kg and from <0.1 to 0.318 ug/kg, respectively.^[27] The values are similar to level found in Lake Borgne and the Chandeleur Sound representing a similar coastal environment as Florida Bay.

Total Hg in sediment (Table 4) was inversely correlated to salinity (-0.584***) and conductivity (-0.597***), respectively, which indicated the sediment sites near the coast contained less total Hg than the water bodies in the upper basin (e.g., Lake Maurepas). Total Hg was correlated to organic matter (0.157**), silt (0.443***) and clay (0.644**) content of sediment. Total Hg was inversely correlated to sand content of sediment. Methyl Hg was also correlated with sediment Eh (-0.285^{***}) . Methyl Hg was also higher in sediment with higher organic matter, clay and silt content with correlation of 0.349***, 0.438*** and 0.321***, respectively. Methyl Hg was inversely related to sand content (-0.416^{***}) of sediment.

Other heavy metals and elemental content

The concentration of other heavy metals (Pb, Cd, Ni, Cu, and Zn) in sediment collected were not elevated and were within the normal range for the metal in sediment for other areas of coastal Louisiana^[15] (Tables 1, 2, and 3). Lead range from 26 ± 12 mg/kg in Lake Maurepas sediment to 7.0 ± 3.0 mg/kg in Lake Borgne and the Chandeleur Sound

Table 4. Correlation of total mercury and methyl mercury to various sediment properties (represent analysis of all data set, n = 292 total).

Variable	Methyl mercury	Total mercury
Methyl mercury	1.000	0.648***
Total mercury	0.648**	1.000
Salinity (ppt)	-0.427^{***}	-0.584^{***}
Conductivity	-0.442^{***}	-0.597^{***}
O.M.%	0.349***	0.157**
Sediment Eh	-0.285^{***}	-0.322^{***}
Sediment pH	-0.180^{**}	-0.166**
Sand%	-0.416^{***}	-0.599^{***}
Silt%	0.321***	0.443***
Clay%	0.438***	0.644***

**Denotes significance at 1% levels.

*** Denotes significance at 0.1% levels.



Fig. 2. Correlation between methyl Hg and total Hg concentrations.

sediment. Average cadmium level was less than 1 mg/kg in sediment from Lake Maurepas and Lake Pontchartrain, and Lake Borgne and the Chandeleur Sound. Average Nickel concentrations were 13.8 ± 6.93 , 17.99 ± 7.27 and 14.39 ± 3.99 mg/kg respectively for Lake Maurepas, Lake Pontchartrain, and Lake Borgne and the Chandeleur Sound sediment. Average copper concentration was 11.88 \pm 6.8 mg/kg, 14.0 ± 6.7 mg/kg, and 5.9 ± 3.8 , respectively, for Lake Maurepas, Lake Pontchartrain, and Lake Borgne and the Chandeleur Sound sediment. Average zinc concentration was 66.0 ± 34.0 mg/kg, 76 ± 32.0 mg/kg, and 35.0 ± 23.0 mg/kg, respectively, for Lake Maurepas, Lake Pontchartrain, and Lake Borgne and the Chandeleur Sound sediment.

Sediment texture likely affects mercury levels in several ways. A greater amount of mercury would be adsorbed on sediment containing high silt and clay content. High clay content sediment would also result in less oxygen diffusion



Fig. 3. Correlation between methyl mercury and organic matter content.

into the sediment as compared to coarse texture sandy sediment. This, in turn along with higher organic matter content, would support lower redox potential, which in turn supports condition for methylation.

Lake Maurepas contained several times higher levels of methyl Hg in sediment as compared to Lake Pontchartrain and Lake Borgne and the Chadeleur Sound. This was attributed to lower salinity and higher total Hg content in sediment. Results suggest Lake Maurepas sediment could serve as a potential source of mercury to the aquatic food chain and would need future monitoring (Fig. 7). Organic matter, which supports reducing condition or low redox potential, enhances both the sulfate reduction rate and mercury methylation rate.^[28,29] The combination of low salinity and organic matter to support reducing condition in Lake Maurepas sediment provide ideal sediment condition for methyl mercury production. Methyl mercury production has been positively correlated with organic matter content of sediment^[30] and inversely correlated with amount of sulfide in sediment.^[31] Sulfate-reducing bacteria can effectively





Fig. 5. Correlation between total mercury and salinity concentrations.

methylate mercury when sulfate is limiting (low salinity) and when other carbon sources (sediment organic matter) are available to be utilized in the absence of sulfate.^[7]

Although despite a vast body of literature, it is still difficult to predict environmental process regulating methyl Hg production in aquatic environment.^[32] Benoit et al.^[33] reported even though methylation is a function of Hg concentration, the range in methylation rate across a ecosystem is larger than the range in Hg deposition rates. This supports that factors in addition to Hg deposition play a major role in methyl Hg production and bioaccumulation in aquatic ecosystem. In this study using multiple regression analysis, the equation shown below was developed for predicting methyl Hg level in sediment within the Ponchartrain Basin estuary.

Methyl Hg =
$$0.11670 - 0.0625 \times \text{salinity} + 0.05349 \times 0.M. + 0.00513 \times \text{Total Hg} - 0.00250 \times \text{clay}$$

The main variable influencing methyl Hg content was salinity, organic matter and total Hg content of sediment. Salinity effect of methyl Hg in sediment likely reflected differences in sulfate content of sediment.

Sulfate is a particularly important factor controlling methylation. Sulfate reducing bacteria are important methylators of Hg in anaerobic sediments, and sulfate stimulates microbial Hg methylation at the typically low sulfate concentration prevailing in freshwater systems (e.g., Lake Maurepas). However at high sulfate levels methylation is inhibited due to sulfide formation, (sites near Gulf



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Fig. 6. Average total mercury concentrations in three lakes.



Fig. 7. Average methyl mercury concentrations in three lakes.

of Mexico). Recent studies have shown that the inhibitory effect of sulfide on Hg methylation is not only due to HgS precipitation, but also the result of sulfide lowering the availability of Hg for bacterial methylation by formation of less bioavailable charged Hg-S complex.^[32]

High organic content of sediment generally stimulate microbial activity and hence Hg methylation. Conversion rates of inorganic Hg to methyl Hg are generally much higher when sediments contain organic substances.^[34] Mercury methylation is generally favored under anaerobic conditions.

The measured metal concentrations in sediment collected from the Pontchartrain estuary were similar to results from a previous study along the Louisiana Coastal zone where concentration ranges found included: Al from 1.6 to 6.1%; Fe from 1.0 to 3.5%; Cu from 7.4 to 30.3 mg/kg^{-1} ; Zn from $51.5 \text{ to } 133 \text{ mg kg}^{-1}$; Cd from 2.3 to 9.7 mg kg^{-1} ; Pb from 46.9 to 193 mg kg⁻¹; Cr from 17.2 to 65.7 mg kg⁻¹; and Ni from 13.6 to 43.0 mg kg⁻¹.^[15] The concentration of metals determined in this study were also in the range of averaged concentrations of some trace metals in the mudflat sediment in the Mai Po and Inner Deep Bay Ramsar Site of Hong Kong, China.^[35] These data collected provides a base line for monitoring future metal inputs into the Pontchartrain Basin.

A common problem in assessing toxic metal contamination is determining whether concentrations in a particular area are elevated over "normal" baseline concentrations. This is difficult due to differences in sediment composition across the region. Soil and sediment substrates in wetland and coastal environments vary widely in their physical and chemical properties including their mineralogy and organic matter content.^[36] Differences in quantities of metal-bearing phases (e.g., clay mineral content, organic matter, Fe and Mn oxides) account for much of the heterogeneity. For these reasons, the total baseline concentrations can vary over a wide range making determination of local anthropogenic impact difficult.^[15] "Normal" baseline concentration is used to determine whether trace and toxic metals in a particular area are elevated. The use of ratios to compare metals with conservative elements (e.g., Al or Fe) has been demonstrated as a method of removing variability of sediment parameters between different sites.^[15] Normalization of heavy metal concentrations to Al is a method used for inter-site comparison and for identification of metal-contaminated sites by many workers such as in the Florida coastal region,^[37] in Florida and Georgia/South Carolina coastal regions,^[38] and in Louisiana coastal regions.^[15]

Regression analysis were performed on the metal data sets for the Pontchartrain Basin comparing concentrations of Al and Fe in sediment with the various metals. The regression of the trace and toxic metals to Al and Fe are shown next.

A strong relationship was found between Al and Cu(r = 0.900^{***}), Pb (r = 0.864^{***}), Ni (r = 0.936^{***}), As (r = 0.319^{***}), Cd (r = -0.129^{*}), Zn (r = 0.861^{***}), and Mn (r = 0.703^{***}) (see Figure 8 as example).

Al is a major constituent of aluminosilicate minerals that are important metal-bearing phases in coastal sediments.^[38] Strong correlations with Al in these sediments suggest that metals found in mineral sediment material rather than pollution as a source of metals in sediment from the water bodies sample. Metal/Al correlations remain significant despite likely repartitioning into various sediment phases (e.g., sulfide or Fe oxide phases) following deposition.^[15]

The above heavy metals (Pb, Cd, Ni, Cu, and Zn) were also statistical correlated with Fe content of the Lake sediment. Figure 9 shows typical relationship. The correlations (r values) for Pb, Cd, Ni, Cu and Zn were 0.921***, 0.287***, 0.928**, 0.931*** and 0.894***, respectively. The heavy metals were also correlated with clay content of sediment. The higher concentrations of these heavy metals were found in sediment with high clay content. Sandy sediment was



Fig. 8. Correlation between Al and Ni concentration in the sediment.



Fig. 9. Correlation between Fe and Ni concentration in the sediment.

inversely correlated with metal content, which contained lower amount of the metals. Results show that over-all there was little heavy metal pollution in sediment of the lakes. Results will serve as a baseline for future studies documenting metal pollution in the lakes.

Conclusions

- (i) There were no elevated levels of total Hg and other heavy metals in sediment in the Pontchartrain estuary.
- (ii) Sediment methyl Hg content was positively correlated with organic matter, total Hg and texture (clay or silt content of sediment).
- (iii) Methyl Hg content of sediment was inversely correlated with salinity and sediment Eh and sand content.
- (iv) Lake Maurepas had higher total Hg and methyl Hg levels in sediment as compared to Lake Pontchartrain and Lake Borgne and the Chandeleur Sound.
- (v) Total Hg and methyl Hg decreased with increase in salinity in the order of Lake Maurepas > Lake Pontchartrain > Lake Borgne and the Chandeleur Sound.
- (vi) Lake Maurepas due to low salinity, high organic matter content and high methyl Hg content in sediment is an area which could be a potential source of mercury to aquatic environment.

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References

- Campbell, L.M.; Balirwa, J.S.; Dixon, D.G.; Hecky, R.E. Biomagnification of mercury in fish from Thruston Bay, Napoleon Gulf, Lake Victoria (East Africa). Afri. J. Aqu. Sci. 2004, 29, 91–96.
- [2] Bloom, N.S. On the chemical form of mercury in edible fish and marine invertebrate tissue. Can. J. Fish. Aqu. Sci. 1992, 49, 1010– 1017.
- [3] National Science and Technology Council Committee on the Environmental and Natural Resources, N. *Methylmercury in the Gulf of Mexico: State of Knowledge and Research Needs*: National Science and Technology Council Committee, 2004.
- [4] Kelly, C.A.; Rudd, J.W.M.; St Louis, V.L.; Heyes, A. Is total mercury concentration a good predictor of methyl mercury concentration in aquatic system? Water Air Soil Poll. 1995, 80, 715–724.
- [5] Watras, C.J.; Back, R.C.; Halvorsen, S.; Hudson, R.J.M.; Morrison, K.A.; Wente, S.P. Bioacculation of mercury in pelagic freshwater food webs. The Sci. Total Environ. **1998**, *219* (2–3), 183–208.
- [6] DeLaune, R.D.; Jugsujinda, A.; Devai, I.; Patrick, W.H. Jr. Relationship of sediment redox condition to methyl mercury in surface sediment of Louisiana Lakes. J. Environ. Sci. Health Pt. A, 2004, 39, 1925–1935.
- [7] Compeau, G.C.; Bartha, R. Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. Appl. Environ. Microbiol. 1985, 50, 498–503.
- [8] Wiener, J.G.; Krabbenhoft, D.P.; Heinz, G.H.; Scheuhammer, A.M. Ecotoxicology of Mercury. In *Handbook of Ecotoxicology, second edition;* Hoffman, D.J.; Rattner, B.A.; Burton, Jr., G.A.Jr.; Cairns. Jr., J. Eds. Lewis Publishers: Boca Raton, FL, 2003; pp. 409– 463.
- [9] Compeau, G.C.; Bartha, R. Effect of salinity on mercury-methylatin activity of sulfate-reducing bacteria in estuarine sediments. Appl. Environ. Microbiol. 1987, 53, 261–265.
- [10] Pak, K.R.; Bartha, R. Mercury methylation and demethylation in anoxic lake sediments and by strickly anaerobic bacteria. Appl. Environ. Microbiol. **1988**, 64, 1013–1017.
- [11] Bishop, P.L. Biogenesis of methyl mercury in anaerobic pond sediment, University Microfilems, Ann Arbor, Michigan, 1972.
- [12] Compeau, G.C; Bartha, R. Methylation and demethylation of mercury under controlled redox, pH, and salinity conditions. Appl. Environ. Microbiol. 1984, 48, 1203–1207.
- [13] Bruland, K.W.; Bertine, K.; Koide, M.; Goldberg, E.D. History of metal pollution in Southern California coastal zone. Environ. Sci. Technol. 1974, 8, 425–432.

- [14] Grieg, R.A.; McGrath, R.A. Trace metals in sediments of Raritan Bay. Mar. Pollut. Bull. 1977, 8, 188–192.
- [15] Pardue, J.H.; DeLaune, R.D.; Patrick, W.H. Jr. Metal to aluminum correlation in Louisiana coastal wetlands: Identification of elevated metal concentrations. J. Environ. Qual. 1992, 21, 539– 545.
- [16] Walker, D.J.; Hurl, S. The reduction of heavy *metals* in a stormwater *wetland*. Ecological Engineering 2002, 18, 407–414.
- [17] Delfino, J.J. Revisiting heavy *metals* in the environment: using *wet-lands* for their removal. Ecol. Model. **2004**, *178*, 35–38.
- [18] Coakley, J.P.; Syvitski, J.P.M. Sedigraph technique: In, *Principles, methods, and application of particle size analysis*; Syvitski, J.M.P., Ed.,: Cambridge, Cambridge University Press, 1991, pp. 368.
- [19] Devai, I.;DeLaune, R.D.; Patrick, W.H. Jr.; Gambrell, R.P. Changes in methylmercury concentration during storage: Effect of temperature. Organic Geochemistry 2001, 32, 755–758.
- [20] Alli, A.; Jaffe, R.; Jones, R. Analysis of organomercury compounds in sediments by Capillary GC with atomic fluorescence detection. J. High Resol. Chromatogr. 1994, 17, 745–748.
- [21] Cai, Y.R.; Jaffe, A.; Alli, J.; Jones, R. Determination of organomercury compounds in aqueous samples by capillary gas chromatography — Atomic fluorescence spectrometry following solid phase extraction. Anal. Chim. Acta **1996**, *334*, 251–259.
- [22] Cai, R.; Jaffe, R.; Jones, R. Ethylmercury in the soils and sediments of the Florida Everglades. Environ. Sci. Technol. 1997a, 31, 302– 305.
- [23] Cai, Y.R.; Tang, G.; Jaffe, R.; Jones, R. Evaluation of some isolation methods for organomercury determination in soil and fish samples by capillary gas chromatography – Atomic fluorescence spectrometry. Inter. J. Environ. Anal. Chem. **1997b**, *68*, 331–345.
- [24] APHA. Standard Methods for the Examination of Water and Wastewater 19th ed. American Public Health Association, Washington, DC, 1995
- [25] Barkay, T.; Gillman, M; Turner, R.R. Effect of dissolved organic carbon and salinity on bioavailability of mercury. Appl. Environ. Microbiol. 1997,63, 4267–4271.
- [26] Gambrell, R.P.; DeLaune, R.D.; Patrick, W.H Jr.; Jugsujinda, A. Mercury distribution in sediment profile of six Louisiana Lakes. J. Environ. Sci. Health Pt. A 2001, 36, 661–678.
- [27] Rood, B.E.; Gotlgons, J.F.; Delfino, J.J.; Eark, C.D.; Crisman, T.L. Mercury accumulation trends in Florida Evergrade and Savanas marsh flooded soils. Biogeochemistry 1995, 80, 981– 990.

- [28] Lambertsson, L.; Nelsson, M. Organic material: The primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments. Environ. Sci. Technol. 6 2006, 40, 1822–1829.
- [29] King, J.K.; Kostka, J.E.; Frischer, M.E.; Saunders, F.M.; Jahnke, R.A. Sulfate-reducing bacteria methylate mercury at variable rates in pure culture and in marine sediments. Appl. Environ. Microbiol. 2001, 66, 2430–2437.
- [30] Benoit, J.M.; Gilmour, C.C.; Mason, R.P.; Riedel, G.S.; Riede, G.G. Behavior of mercury in the Patuxent River estuary. 1998, 40, 249– 265.
- [31] Gilmour, C.C.; Riedal, G.S.; Ederington, M.C.; Bell, J.T.; Benoit, M.; Gill, G.A. Methylmercury concentrations and production rates across a trophic gradient in the northern Evergrades. Biogeochemistry 1998, 44, 327–345.
- [32] Ullrich, S.M.; Tanton, T.W.; Abdrashitova, S.J. Mercury in aquatic environment: A review of factors affecting methylation, Crit. Rev. Environ. Sci. Technol. 2001, 31, 241–293.
- [33] Benoit, J.M.; Gilmour, C.C.; Heyes, A.; Mason, R.P.; Miller, C.L. Geochemical and biological controls and methyl mercury prediction and degradation in aquatic ecosystem. Biogeochemistry of Environmentally Important Trace Elements. ACS Symposium Series 2003, 83, 262–294.
- [34] Jackson, T.A. Methyl mercury levels in a polluted prairie river–lake system: seasonal and site-specific variations, and the dominant influence of trophic conditions. Can. J. Fish. Aquat. Sci. 1986, 43, 1873.
- [35] Man, K.W.; Zheng, J.S.; Leung, A.; Lam, P.L.; Paul, K.S.; Lam, M.H.W.; Yen, Y.F. Distribution and behavior of trace metals in the sediment and porewater of a tropical coastal wetland. Sci. Tot. Environ. 2004, 27, 295–314.
- [36] Feijtel, T.C.; DeLaune, R.D.; Patrick, W.H. Jr. Biogeochemical control on metal distribution and accumulation in Louisiana sediments. J. Environ. Qual 1988, 17, 88–94.
- [37] Schropp, S.J.; Lewis, F.G.; Windom, H.L.; Ryan, J.D.; Calder, F.D.; Burney, L.C. Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. Estuaries 1990, 13, 227–235.
- [38] Windom, H.L.; Schropp, S.J.; Calder, F.D.; Ryan, J.D.; Smith, R.G. Jr.; Burney, L.G.; Lewis, F.G.; Rawhson, C.H. Natural trace metal concentrations in estuarine and coastal marine sediment of the southeasthern United States. Environ. Sci. Technol. 1989, 23, 314– 320.