

Total mercury and methylmercury in Louisiana fresh, brackish and salt marsh

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TOTAL MERCURY AND METHYLMERCURY IN LOUISIANA FRESH, BRACKISH AND SALT MARSH

Problem and Research Objectives:

Mercury contamination of lakes and streams has taken on new importance worldwide since it was discovered several decades ago that inorganic mercury compounds can undergo methylation in sediments under proper anaerobic conditions with a resulting increase in solubility, mobility and bioaccumulation in the food chain (Jernolov and Lann, 1971). Many waterbodies worldwide have evaluated mercury levels in top predator fish that has prompted the issuance of advisories on fish consumption by various public health agencies. Lakes and waterbodies in the southern U.S. including Louisiana have been impacted by mercury contamination. Recent finding of elevated mercury concentrations in fish and wildlife from fresh water lakes throughout much of the Southern United States including Louisiana has caused great concern for person for whom fish are significant part of their diet and for pregnant women and nursing mothers. Levels of up to 3 ppm have been found in largemouth bass in some lakes, which is considerably above the maximum permissible level (1 ppm) for edible fish tissue. The Louisiana Department of Health and the Department of Environmental Quality have issued mercury advisories for a number of lakes in the state with the results that the desirability of these lakes for fishing has decreased. This proposal describes a study of the conditions in Louisiana marshes that govern the formation and accumulation of methylmercury, the form of mercury that bioaccumulates in the food chain.

Mercury contamination of fish in Louisiana wetlands has become a serious water quality problem with advisories on consumption of fish issued for several areas in the state. The accumulation of unacceptable concentrations of mercury in fish is thought to occur largely as the result of bioaccumulation of methylmercury up the food chain to the top predator fish, which are also the most desired species. Methylmercury is thought to form largely in the anaerobic sediments and then move up through several trophic levels. Information is needed on the historical accumulation of mercury and production of methyl Hg in Louisiana coastal marsh habitats, which serve as nursery ground for aquatic fish species and other organisms.

The over-all research objective was to determine the historical patterns of mercury deposition, rates of accumulation, sources, and distribution of mercury in the Louisiana coastal marsh environment. The study quantifies the amount of methylmercury in Louisiana coastal marsh, which serve as nursery ground for fish and other aquatic species. Due to high organic matter contents of marsh or wetland soil, there likely be greater amount of methylmercury.

Methodology

In this study was determined the accumulation and distribution of mercury and methylmercury in profile of Louisiana Mississippi River deltaic plain fresh water and salt

marsh soils and in surface soil of wetland sites surrounding Lake Pontchartrain and Lake Maurepas. Profile distribution of mercury and methylmercury. Cores (15 cm diameter X 50 cm length) were taken from Louisiana Barataria Basin freshwater marsh, and salt marsh was determined. Salinity level in freshwater marsh was less than 1 ‰. In the salt water marsh salinity was in range of 10 to 14 ‰ (Hatton et al., 1983). The cores were sectioned into 3 cm increments. The sections were air-dried and bulk density determined. Sedimentation or vertical accretion rates were calculated from the peak ^{137}Cs concentration measured in the marsh profile, which corresponded to 1963, the year of ^{137}Cs fallout, and 1954, the first year of significant ^{137}Cs fallout (DeLaune et al., 1978). In addition we collected surface soil from 33 wetland sites surrounding Lake Pontchartrain and Lake Maurepas.

Total mercury was extracted from individual sections using a hydrochloric-nitric acid mixture. Total (organic and inorganic) mercury Hg was measured by cold vapor technique based on EPA Method # 245.1 and 245.5 and 7471A using an Instruments Analytical Technologies LabAnalyzer Model 254. Basis for determination of the mercury concentration is 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 reductant (tin(II)-chloride). 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. In this cell the concentration of mercury is determined by measuring light absorption at a wavelength of 253.7 nm. A built-in computer performs the quantitative evaluation of the results. In order to get an extremely stable baseline, the UV-light source is controlled by the reference beam method. In addition to that, the UV-detectors of the LabAnalyzer are thermostatically stabilized. Heating of the optical cell prevents sensitivity for water vapor. Thus the use of a desiccant, which always shows adsorption of mercury vapor, is avoided. Using this method a stable and accurate calibration will be obtained ($R=0.998$). Continuous calibration check will be maintained over the time of the project and recorded.

MeHg 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 m x 0.53 mm i.d. (Megabore) coated with a 1.5 μm film thickness of DB-1 (J&W Scientific) will be used in the analysis. The column oven temperature will be maintained at 50 C for 1.0 min, programmed at 30 C/min. to 140 C, which will be held for 3.0 min. A split/splitless injector was used in the splitless mode and maintained at 200 C. The carrier gas flow will be 4.0 mL/min. of high purity argon and make-up gas flow was 120 mL/min. of high purity argon. The column eluate will be passed through a pyrolyzer (P.S. Analytical)-positioned inside the oven of the gas chromatograph-via a deactivated fused silica tubing into a Merlin Mercury Fluorescence Detector System (AFS) Model 10.023 (P.S. Analytical) which will be used for mercury detection. For the PSA Merlin Mercury Fluorescence.

Detector system, the sheath gas flow will be 200 mL/min. of argon (Alli et al., 1994; Cai et al. 1996). A real time chromatographic control and data acquisition system (Hewlett-Packard ChemStation) interfaced with the GC and AFS detector system will be used for the analysis. Quantitative MeHg analysis will be obtained using a five-point (between 0.2 ppb and 10.0 ppb) calibration curve forced to zero ($R=0.999$) generated using standard solutions which were prepared by dissolving appropriate amounts of MeHgCl powder in methanol and then subsequently diluting it with methylene chloride to achieve the required concentrations. Sample preparation will be performed based on the method of Alli and co-workers (1994) and Cai and co-workers (1996,1997a, 1997b). Continuous calibration check will be maintained over the time of the project and will be recorded appropriately.

Principal Findings:

The salt marsh soil had higher bulk density than fresh marsh soil. Average bulk density (0-30 cm) of fresh marsh was 0.07 g cm^{-3} compared to 0.25 g cm^{-3} for salt marsh. The higher bulk density value for salt marsh reflects a greater amount of sediment input onto the vertically accreting marsh soil profile. Due to rapid subsidence Louisiana coastal marshes vertically accrete through organic matter and mineral sediment accumulation to keep pace with water level increases (Hatton et al. 1983). ^{137}Cs activity of fresh and salt marsh showed accretion rates for 0.90 and 0.75 cm yr^{-1} , respectively. The freshwater marsh soil on a dry weight basis contained more methylmercury and total mercury than the salt marsh soil (Table 1). Average total mercury content in the soil profile was $140 \mu\text{g kg}^{-1}$ dry soil for freshwater marsh and $80 \mu\text{g kg}^{-1}$ dry soil for the salt marsh (Figure 1). Average methylmercury content was $4.2 \mu\text{g kg}^{-1}$ dry soil and $1.33 \mu\text{g kg}^{-1}$ dry soil, respectively for the freshwater and salt marsh (to depth 30 cm) (Figure 2).

Due to greater bulk density the salt marsh soil contained more total mercury per unit area ($\mu\text{g m}^{-2}$, 30 cm depth) than the fresh marsh (Table 2). On a volume basis average methylmercury content was approximately the same for the fresh marsh and salt marsh. Due to greater sediment input as reflected in the higher bulk density mercury accumulation was greater in salt marsh as compared to the fresh marsh. Along a salinity gradient extending inland from the Louisiana coast, sediment input decreases going from salt to freshwater marsh (Hatton et al., 1983). Methylmercury represented a larger percentage of total mercury content in fresh marsh soils as compared to the salt marsh soils (3 percent versus 1.7 percent). The results show that coastal marshes, which serve as nursery ground for fish species, contained considerable greater amount of methylmercury in the soil profile than reported data for bottom sediment from Louisiana stream and water bodies.

Results when expressed on a dry soil weight basis support greater methylation in freshwater marsh as compared to higher salinity salt marsh soil. However, when expressed on a volume basis the amount of methylmercury in the soil profile is the same. In the salt marsh, sediment input is a greater mercury source than for freshwater marsh soil where mercury input is primary from atmosphere source.

This profile study of Barataria Basin salt and freshwater marsh clearly shows that the amount of mercury present in Louisiana marsh soil differ when results are expressed on a dry weight basis as compared to the amount of mercury/methylmercury on a per unit volume basis. For determining potential source and availability to the aquatic environment additional studies should include diffusion flux studies of mercury release to the overlying water.

Table:1 Total and methylmercury content of fresh marsh and salt marsh at 30 cm depth (data based on soil bulk density)

Site	Bulk Density (g cm ⁻³)	Total Hg (µg)	Methyl Hg (µg)
Fresh Marsh	0.07	2,929	87
Salt Marsh	0.25	5,340	91

Table:2 Total and methylmercury content of fresh marsh and salt marsh at 30 cm depth.

Site	Total Hg (µg kg ⁻¹)	Methyl Hg (µg kg ⁻¹)	% Methyl Hg
Fresh Marsh	140	4.19	3.0
Salt Marsh	80	1.34	1.7

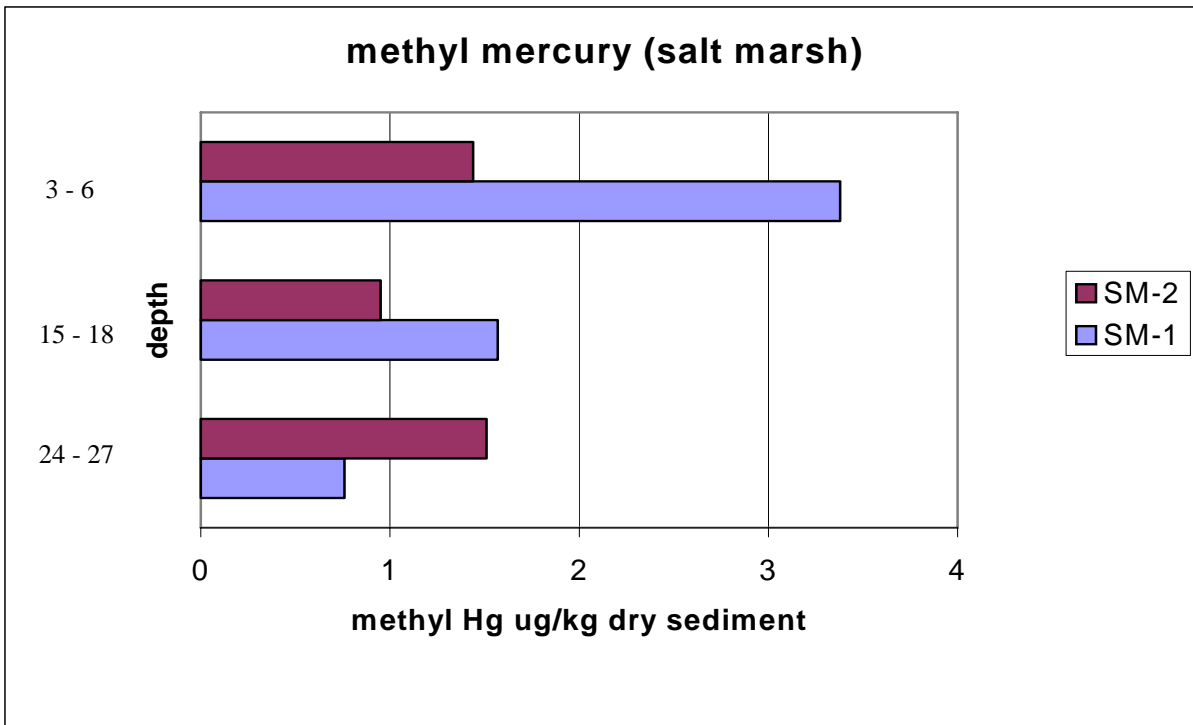
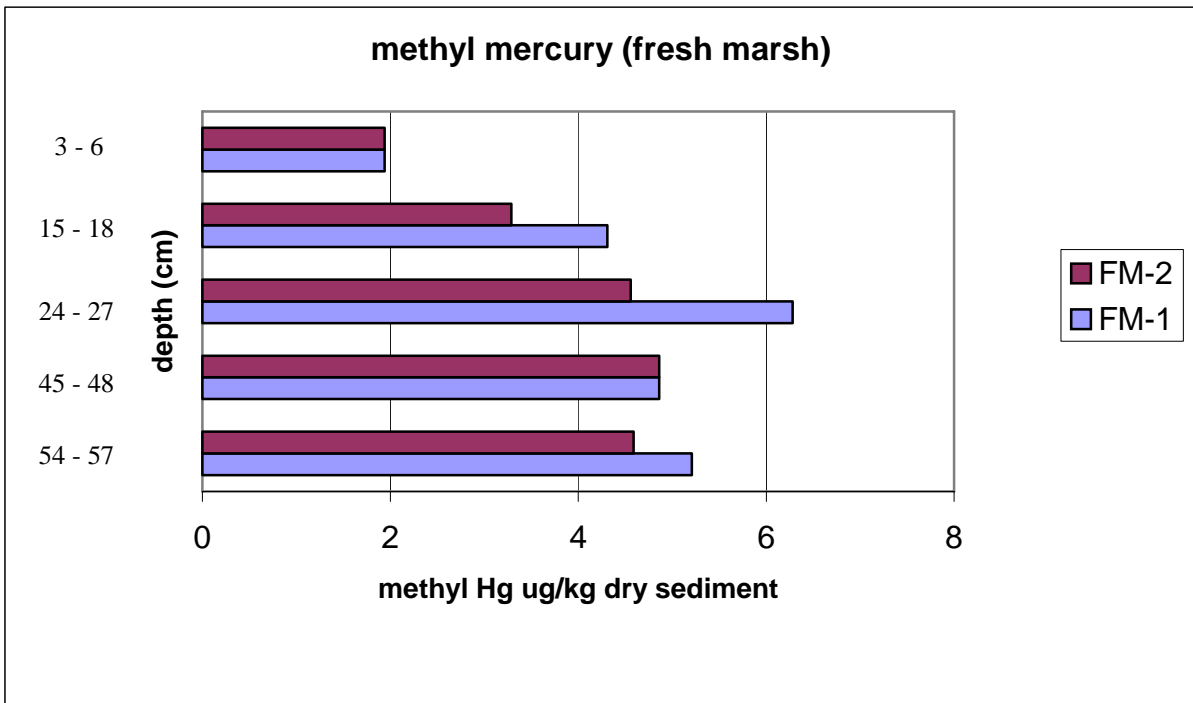


Figure 1. Profile distribution of methylmercury in freshwater and salt marsh soil.

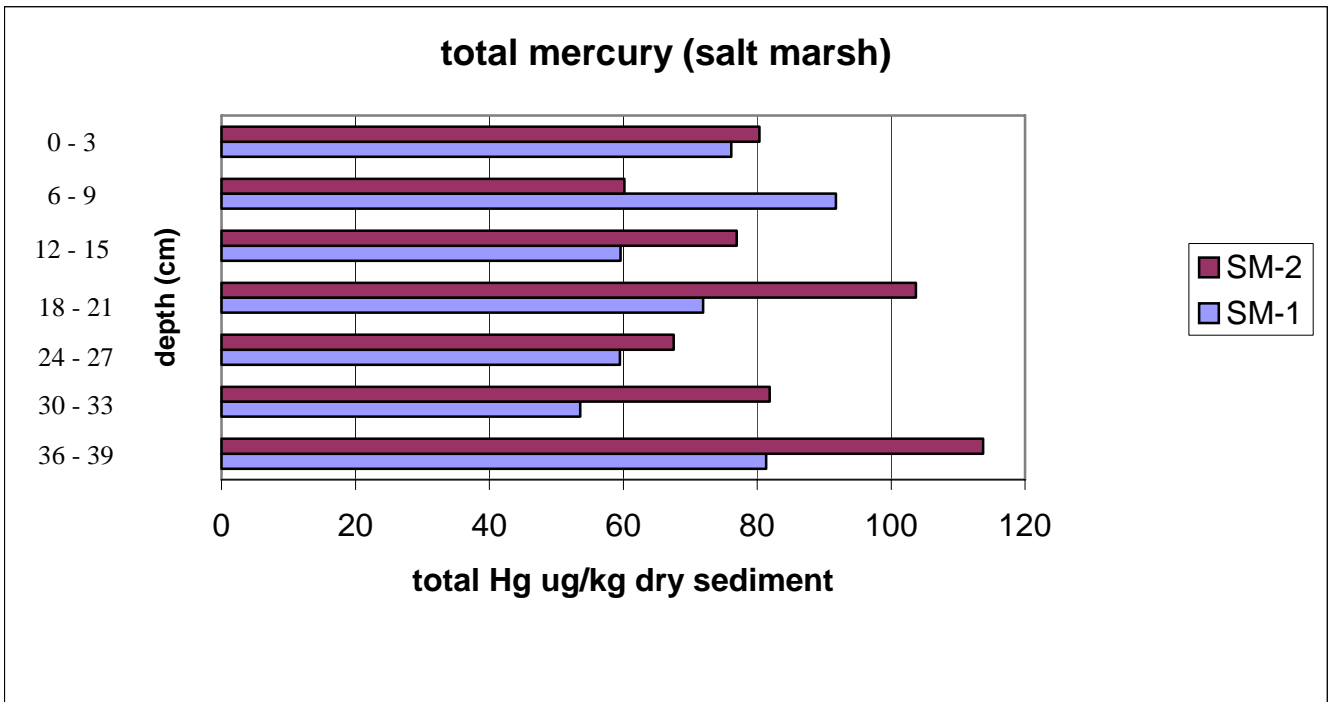
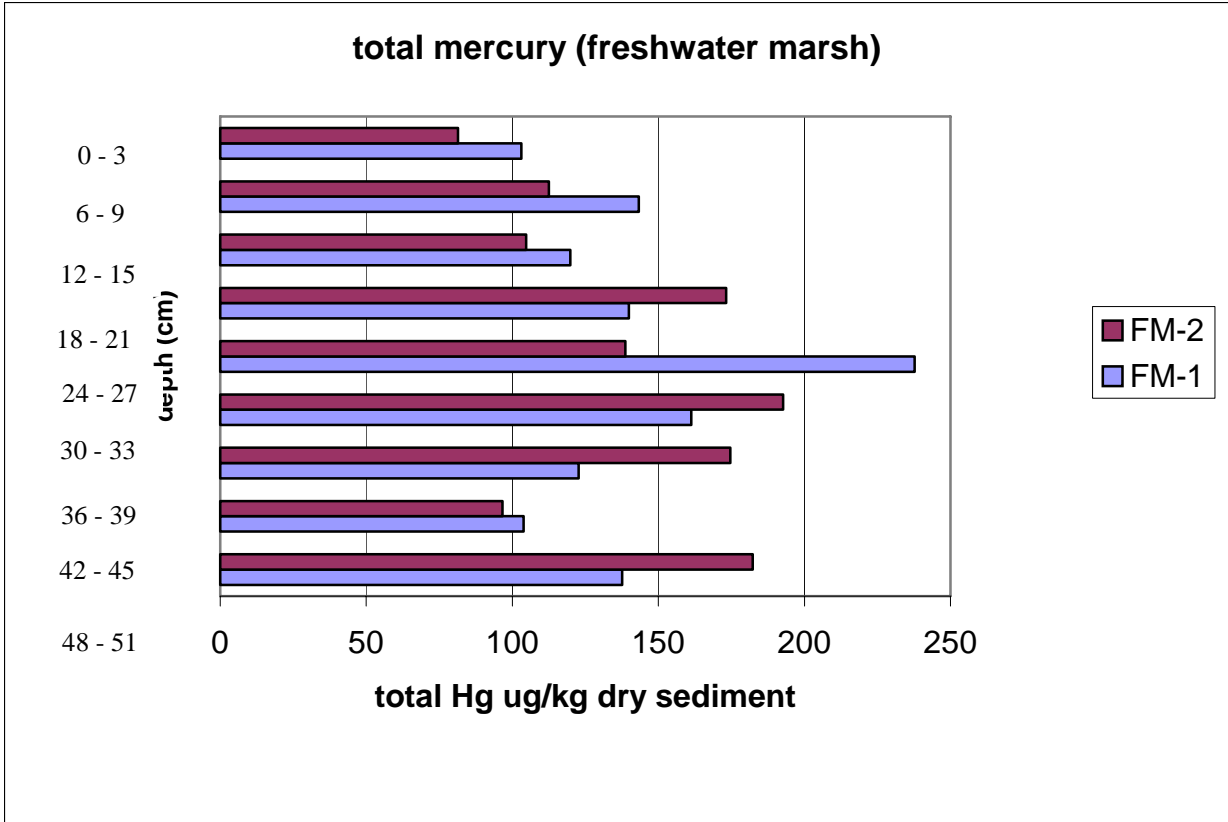


Figure 2. Profile distribution of total mercury in freshwater marsh and salt marsh soil.

Pontchartrain Basin Wetland Soil Mercury Data

In addition to the detailed profile study, we measured mercury and methylmercury in surface soil of wetland in the Pontchartrain Basin (33 sites bordering Lake Pontchartrain and Lake Maurepas). The locations and mercury levels in the soil are shown in Table 3. Total mercury level ranged from 8.72 to 138.63 ug/Kg soil methyl mercury ranged from 0.09 to 11.37 ug/Kg soil. Average total mercury and methylmercury values for all sites were 63.15(± 26.83) and 1.59 (± 2.48) respectively.

Measured total mercury and methylmercury in Lake Maurepas and Lake Pontchartrain bottom sediment, (project funded by Lake Pontchartrain Basin Foundation), water bodies which the wetland sites from which soil samples border were:

Lake Maurepas:

Total mercury	-	96.8 ug/Kg
Methylmercury	-	1.09 ug/Kg

Lake Pontchartrain

Total mercury	-	67.4 ug/Kg
Methylmercury	-	.49 ug/Kg

This study of mercury level in wetland surrounding the lakes shows that average methylmercury level in the wetland soil were higher in methylmercury than in bottom sediment in the 2 lakes.

Table 3: Mercury and Methylmercury in wetland soil of Pontchartrain Basin					
Lab#	Sample #	Methyl Mercury	Total Mercury	Latitude	Longitude
		Concentration	Concentration		
		ug/kg dry soil (Avg.)	ug/kg dry soil (Avg.)		
PW1		9.36	138.63	N30.31473	W90.41686
PW2		3.62	63.99	N30.28833	W90.39570
PW3		2.92	53.57	N30.28435	W90.36783
PW4		4.26	59.1	N30.29673	W90.33965
PW5		0.34	47.61	N30.29212	W90.31012
PW6		0.76	57.56	N30.30024	W90.34131
PW7		0.21	49.28	N30.30868	W90.35997
PW8		0.17	41.08	N30.31705	W90.39400
PW9		1.67	86.97	N30.32033	W90.41124
PW10		1.06	74.77	N30.26127	W90.69801
PW11		0.35	50.92	N30.29499	W90.61769
PW12		11.37	68.45	N30.13232	W90.71968
PW13		1.25	110.72	N30.10162	W90.42351
PW14		0.09	71.6	N30.07257	W90.39888
PW15		1.06	99.75	N30.06175	W90.41294
PW16		1.35	49.21	N30.02862	W90.39872
PW17		2.04	119.66	N30.05758	W90.37202
PW18		0.08	82.71	N29.98110	W89.94591
PW19		0.13	58.78	N29.97367	W89.94879
PW20		0.65	71.37	N30.11148	W89.89828
PW21		0.91	35.49	N30.12396	W89.86537
PW22		0.49	54.94	N30.15306	W89.85902
PW23		1.09	55.19	N30.22644	W89.82135
PW24		0.11	54.35	N30.1945	W89.75497
PW25		0.36	18.99	N30.17612	W89.72909
PW26		1.15	41.59	N30.14642	W89.7444
PW27		1.21	53.97	N30.27568	W89.91184
PW28		1.36	57.81	N30.26254	W89.9563
PW29		0.29	40.79	N30.27462	W89.95499
PW30		0.49	8.72	N30.34643	W90.05631
PW31		1.23	90.87	N30.35317	W90.06215
PW32		0.22	51.43	N30.40146	W90.15191
PW33		0.69	64.1	N30.44339	W90.33902
Average		1.59 (± 2.48)	63.15(± 26.83)		

The wetland soil on dry weight basis sediment contained approximately 1.5 times more methylmercury as found in Lake Maurepas and 3 times the amount found in Lake Pontchartrain sediment.

These results suggest that there is greater potential for methylmercury formation in wetland soils as compared to bottom sediment. This could be attributed to higher organic matter content in wetland soil, which would support more reducing conditions conducive to mercury methylation. The ratio of totalmercury to methylmercury (40:1) for the wetland sites was considerably lower than the ratio for Lake Maurepas (89:1) and Lake Pontchartrain (138:1). These ratios suggest a greater percentage of the mercury in the wetland soil is being methylated as compared to mercury in bottom sediment of the two lakes.