Simultaneous determination of mercury and organic carbon in sediment and soils using a direct mercury analyzer based on thermal decomposition–atomic absorption spectrophotometry

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HIGHLIGHTS

- A direct mercury analyzer was used to estimate total organic carbon.
- Mercury and organic carbon were measured in oxbow lake sediment cores.
- Temporal and spatial deposition of Hg in the Mississippi Delta were evaluated.

GRAPHICAL ABSTRACT

Comparison of LOI data obtained by a conventional method and by the DMA. The dark line represents a 1:1 ratio.
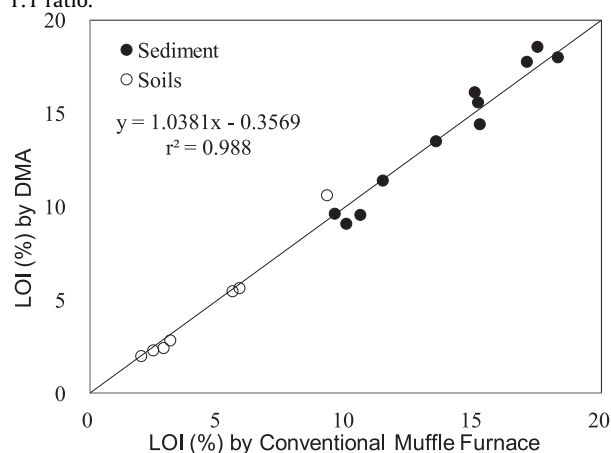
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ABSTRACT

The purpose of this work was to study the feasibility of using a direct mercury analyzer (DMA) to simultaneously determine mercury (Hg) and organic matter content in sediment and soils. Organic carbon was estimated by re-weighing the sample boats post analysis to obtain loss-on-ignition (LOI) data. The DMA-LOI results were statistically similar ($p < 0.05$) to the conventional muffle furnace approach. A regression equation was developed to convert DMA-LOI data to total organic carbon (TOC), which varied between 0.2% and 13.0%. Thus, mercury analyzers based on combustion can provide accurate estimates of organic carbon content in non-calcareous sediment and soils; however, weight gain from moisture (post-analysis), measurement uncertainty, and sample representativeness should all be taken into account. Sediment cores from seasonal wetland and open water areas from six oxbow lakes in the Mississippi River alluvial flood plain were analyzed. Wetland sediments generally had higher levels of Hg than open

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Mississippi River
Wetland

water areas owing to a greater fraction of fine particles and higher levels of organic matter. Annual loading of Hg in open water areas was estimated at 4.3, 13.4, 19.2, 20.7, 129, and 135 ng cm^{-2} yr^{-1} for Beasley, Roundaway, Hampton, Washington, Wolf and Sky Lakes, respectively. Generally, the interval with the highest Hg flux was dated to the 1960s and 1970s.

1. Introduction

Mercury is a global pollutant dispersed widely through the atmosphere. It enters lakes either directly through wet and dry deposition or via runoff from the lake's catchment. Within lakes, inorganic Hg can be converted to methyl-Hg via biotic and abiotic processes [1]. Sulfate reducing bacteria found in anoxic sediments play an important role in production of methyl-Hg in lakes [1]. Methyl-Hg readily accumulates in biological tissues and magnifies up the aquatic food chain. Lake sediments are complex deposits of inorganic and organic matter that also serve as a natural archive for Hg. Fluctuations of Hg levels in lake sediments have been used to study Hg deposition trends and have been linked to pollution and climate influences [2–5].

The Mississippi River alluvial flood plain, commonly known as the Mississippi Delta, is located in northwest Mississippi and is one of the most intensive agricultural areas in the United States, with primarily corn, cotton, rice, and soybean production. The region has numerous oxbow lakes that were once part of the main Mississippi River channel or its tributaries. The lakes tend to have high sedimentation rates, although recent erosion control measures have reduced sedimentation in some [6]. Sources of Hg in these particular lakes have not been investigated but generally they include direct deposition from the atmosphere and Hg delivered to the lake from its catchment [1–4]; the latter may include Hg released from the natural weathering of geologic materials and from the historical use of fungicides on agricultural fields. Mercury use in agriculture declined dramatically in the 1960s with publicity of several large-scale Hg poisonings, but, due to its persistence and particle-reactivity, Hg can be washed from fields and find its way into lakes where it can accumulate in sediments and potentially be converted to more bioavailable forms [16].

Organic matter is an important parameter that affects the distribution of trace elements, including Hg, in soils and aquatic sediments [7–10]. It can be found, for example, as surface coatings on inorganic materials or separate organic particles and debris [7]. Because of its complexity, organic matter is commonly measured indirectly as total organic carbon (TOC). TOC is determined by a number of methods but most commonly by quantifying CO_2 that is produced from samples by oxidation of organic carbon using combustion or chemicals. Because carbon can be also present as inorganic forms (e.g., carbonate minerals) it is important to eliminate or mathematically subtract its contribution from the total carbon results [11].

Because of its simplicity and low cost, weight loss-on-ignition (hereafter termed LOI) is commonly used as a predictor of TOC. In LOI analyses, soils and sediments are weighed before and after an ashing treatment [12]. Combustion temperatures in the literature vary from 375 to 800 °C, with 550 °C being commonly employed [11,13]. A conversion factor or regression equation is used to obtain the organic carbon value from the weight difference [11]. Because of the variation in natural organic matter, a single equation is inadequate, and accuracy is greatly improved when equations are individually developed for similar soil- and sediment-type [13].

When done carefully, LOI has been shown to yield precision comparable to TOC determined by elemental analyzers [14]. However, LOI and other combustion-based methods can overestimate the amount of organic matter due to: (1) release of hygroscopic and inter-crystalline water, (2) thermal breakdown of carbonates, (3) conversion of various hydroxyl groups to water vapor, and (4) release of CO_2 from carbon in the elemental state [14]. Samples containing carbonates can still yield accurate results if conditions are set to prevent thermal breakdown of the carbonate, but these can vary depending on particle size and other factors that are matrix dependent [14]. Thus LOI is best suited for soils and sediments low in carbonate and clay content.

Concentrations of Hg in soils and sediments are routinely determined using cold vapor atomic absorption or atomic fluorescence spectrometry. First, all the Hg in the sample is converted to Hg^{+2} through acid digestion. Next, it is reduced to Hg^0 using a reducing-agent such as tin(II) chloride and purged from solution. The Hg is then concentrated on a gold trap before being thermally desorbed into a spectrophotometer. Alternatively, direct mercury analyzers (DMA) use thermal decomposition–atomic absorption spectrometry (AAS) to directly measure concentrations of Hg in soils and sediments. These Hg analyzers integrate sample combustion, matrix removal and preconcentration of Hg by gold traps, and AAS. The instruments are popular because they improve analytical throughput, minimize reagent waste, and reduce potential for contamination. Thus, direct mercury analyzers have been used in a large number of studies for a wide variety of applications, including determining Hg in fish [15–17], waterfowl [18], and geological materials [19], to assess Hg emissions from coal-fired power plants [20], and to characterize mercury compounds by thermal desorption profiles [21]. Although DMA instruments use oxygen as a carrier gas and have a combustion furnace with programmable temperatures, we have not found any reports on its effectiveness for acquiring LOI data along with Hg concentrations. We hypothesize that the sample combustion occurring within the DMA during a Hg determination will be complete and sufficiently similar to that which takes place in conventional muffle furnaces, and thus should yield similar LOI data.

The aims of this study were to: (1) assess the capability and reliability of the DMA to simultaneously determine Hg and total organic carbon in soil and sediment, (2) investigate temporal and spatial patterns of Hg deposition in six oxbow lakes (Beasley, Hampton, Washington, Roundaway, Sky and Wolf) in the Mississippi Delta, (3) compare Hg levels in sediment from wetland and open water areas, and (4) examine the relationship between organic matter and Hg in the lakes.

2. Materials and methods

2.1. Study area

We studied six oxbow lakes (Beasley, Hampton, Washington, Roundaway, Sky and Wolf) in the Mississippi alluvial plain in northwestern Mississippi (Fig. 1). Locations, lake surface area, watershed area, and maximum depth of the cores are given in Table 1. The lakes are among many that were naturally created as the Mississippi River and its tributaries changed paths over the time, and they have been thoroughly described elsewhere [6,22]. Briefly, the lakes were subject to seasonal flooding by the Mississippi River until major levees were constructed starting in

the early 1900s. The region, once dominated by bottomland hardwoods and natural wetlands, now supports intensive agriculture [23]. Much of the remaining wetlands are associated with oxbow lakes. The watersheds for the six lakes in this study vary in size from about 9 to 118 km². The lakes are primarily used for recreation.

Beasley Lake, located in Sunflower County, was formed when a bend of the Big Sunflower River was isolated. Hampton Lake, located in Tallahatchie County, is furthest east from the Mississippi River. Lake Washington, located in Washington County, and Sky Lake in Humphreys County, are meander loops (once part of the contiguous Mississippi River), with Sky Lake being left behind from a much older river migration. Washington Lake is the largest lake in the study. Roundaway Lake is located in Coahoma County, Mississippi. It is the smallest lake in this study and has a relatively

high sedimentation rate. Wolf Lake is located in northern Yazoo and southern Humphreys Counties.

2.2. Sediment core collection and sample preparation

We collected sediment cores from both seasonal wetland and open water areas from the six lakes. Most cores were sampled using a vibracoring method which has been shown to extract relatively undisturbed samples of bottom sediments [24]. Core pipes were cut to match the length of the core upon removal from the lake bed, capped, and stored at 4 °C until processed. The compaction ratio caused by vibracoring, assumed to be linear with depth, was determined by dividing the depth of core-pipe penetration by the length of the sediment core. Except for the open water cores from Sky Lake and Washington Lake, the bulk
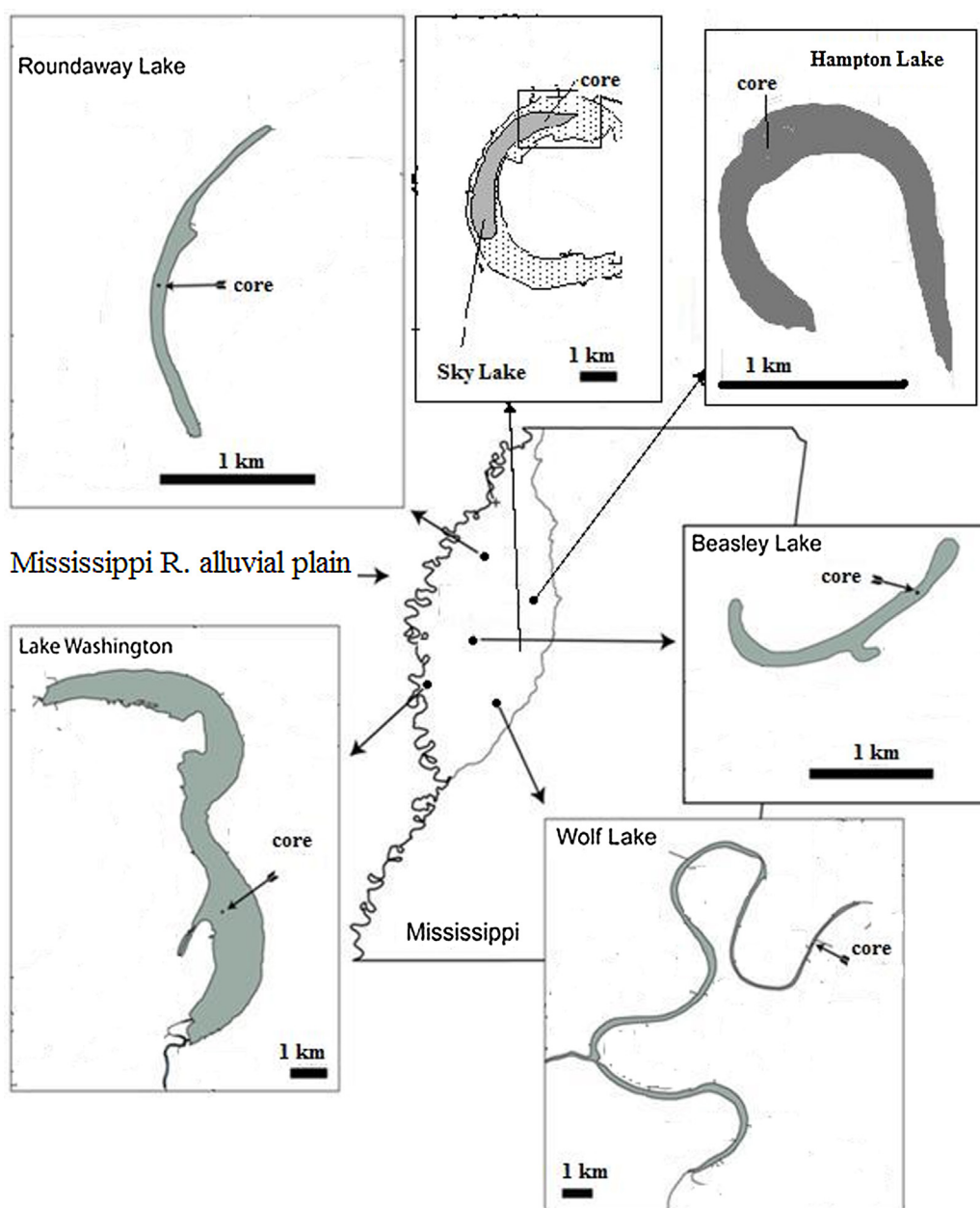

Fig. 1. Approximate locations and sizes of the six oxbow lakes investigated in this study. All are located in the Mississippi River alluvial floodplain, known as the "Delta" region of the state of Mississippi.

Table 1
Oxbow lake and sample information.

Lake	Latitude (°N)	Longitude (°W)	Surface[a] area (km²)	Watershed area (km²)	Core location	Core depth (cm)
Beasley	33.2408	90.432	0.25	9.2	Open water	97
					Wetland	58
Hampton	33.8436	90.2353	0.28	NA	Open water	333
					Wetland	134
Washington	33.0253	91.0246	12.6	110	Open water	126
					Wetland	211
Sky	33.2888	90.4985	0.14	18.6	Open water	136
					Wetland	14
Wolf	32.5563	90.2799	4.5	118	Open water	13
					Wetland	126
Roundaway	34.0125	90.3574	0.21	12.5	Open water	27
					Wetland	71

[a] Fluctuates with seasons and storm events.

density of the sediment gradually increased from the top of the core to the bottom, suggesting that the sediment was not disturbed post deposition. Individual 1-cm core increments were collected using a piston core extruder, except Sky Lake, which was cut length-wise and sliced on a table. Open water cores from Roundaway and Wolf Lakes, and from Sky Lake wetland were obtained by using an AMS sediment sampler outfitted with plastic liner (AMS, American Falls, Idaho). The sediment intervals were dried to a constant weight at 60 °C in an oven, crushed with a mortar and pestle, and sieved through mesh of 1-mm pore size. The dried sediment was stored at room temperature in labeled plastic bags in a closed box.

2.3. Sediment chronology and sedimentation rates

All lake sediment cores were age-dated except for the 3 cores collected by the AMS sediment sampler (open water cores from Roundaway and Wolf Lakes and from Sky Lake wetland). We determined sediment core chronology by conventional ^{210}Pb and ^{137}Cs age-dating as described in previous reports [6,22]. Briefly, ^{210}Pb and ^{137}Cs activities were determined from powdered, bulk sediment samples using standard radiochemical techniques [25,26]. Sedimentation rates were based on ^{210}Pb and assumed a constant rate of sediment accumulation and rate of atmospheric ^{210}Pb fallout over the period of interest. The ^{210}Pb decay rate constant of $0.0311 \, yr^{-1}$ was divided by the negative slope of the natural log of excess ^{210}Pb versus depth to arrive at sedimentation rates in $cm \, yr^{-1}$. Sedimentation rates were corrected for in-situ settling and for compression during sampling, but not for focusing because of the relatively small lake size and fetch, and the relatively uniform lake depths [6].

2.4. Soils

We also analyzed several different types of soils provided by the U.S. National Sedimentation Laboratory, including the Atwood, Bosket, Sharkey, and Clarion soil series. Briefly, Atwood consists of silt loam with moderate permeability; it was collected from the uplands of the Southern Mississippi Valley Silty Uplands Land Resource Area and its taxonomic class is fine-silty, mixed, semiactive, thermic Typic Paleudalfs. Bosket series is a fine sandy loam that is formed in loamy alluvium; it is found on terraces in the lower Mississippi River Valley and its taxonomic class is fine-loamy, mixed, active, thermic Mollic Hapludalfs. Sharkey is a clay soil that is poorly drained; it is found on flood plains and low terraces of the Mississippi River and its taxonomic class is very-fine, smectitic, thermic Chromic Epiaquerts. Clarion is from Iowa; its taxonomic classification is fine-loamy, mixed, superactive, mesic Typic Hapludoll.

2.5. Loss-on-ignition, thermal gravimetric analysis, and total organic carbon

We determined LOI using a muffle furnace (conventional approach) and by the DMA. For the former, we heated ~5 g of dried soil or sediment in ceramic crucibles for 16 h (overnight) at 550 °C. For the DMA, we used the same temperature (550 °C, decomposition temperature) and simply re-weighed the boat post-Hg analysis. Weights were taken immediately after the DMA analysis due to absorption of moisture from the atmosphere. As noted, the sediment was homogenized by crushing and sieving. From our experience this is sufficient to obtain a representative subsample at the 0.25 g level based on replicate ($n \geq 3$) measurements. The effect of different decomposition temperature and times is discussed below.

Because thermal breakdown of carbonates in sediment and soil can result in sample weight loss, we used thermal gravimetric analysis (TGA) to determine the potential contribution of inorganic carbon on LOI for our sample types. Thermograms were obtained for select samples with an EXSTAR 6000 (SII Nanotechnology Inc.). Temperature programming consisted of a ramp rate of $20 \, °C \, min^{-1}$ from 25 °C to 1000 °C.

To develop the relationship between LOI and organic matter, we determined TOC for a range of samples using a Vario Max CNS elemental analyzer (Elementa, Hanau, Germany). L-Glutamic acid was used for calibration and QC measurements.

2.6. Determination of mercury

We determined total-Hg in the sediment following US EPA Method 7473 using a direct mercury analyzer (DMA-80; Milestone Inc., Shelton, CT, USA) [27]. The method is based on thermal decomposition, amalgamation, and AAS. Briefly, about 0.25 g of dried sediment from each 1-cm core interval was weighed (to 0.1 mg) in nickel boats. The boats were placed into an autosampler which sequentially inserts them into the combustion tube of the instrument. There, the samples were heated with oxygen flowing over them at $\sim 200 \, mL \, min^{-1}$. The decomposition and combustion products were swept through a catalyst tube where oxidation was completed, and nitrogen and sulfur oxides and halogens were trapped. The remaining gases, including Hg^0, were carried to a gold amalgamator which selectively traps Hg. Later, the gold trap was rapidly heated releasing Hg vapor into the spectrophotometer. Absorbance, measured at 253.7 nm, is a function of Hg concentration.

In the current study, we operated the instrument with "decomposition" temperatures of 550 °C to match that of the conventional LOI method. Operating times for drying, combustion, and post-combustion flushing periods were 60, 180, and 45 s, respectively, for a total analysis time of <5 min per sample. The

DMA was calibrated using a sediment reference material (MESS-3) certified for 0.091 ± 0.009 mg kg^{-1} Hg. For quality control, a calibration check, duplicate and blank were run every 10 samples. Recoveries for SRM 1573a (tomato leaves) and SRM 1566b (oyster tissue), alternately used for calibration checks, were within 15% of the certified value. Relative percent difference for duplicates were <10%. Blanks consisting of empty Ni boats were negligible yielding <0.10 ng of Hg. The limit of detection (3 σ criteria) was estimated at ~0.02 ng, corresponding to 0.08 ng g^{-1} for a 250 mg sample.

2.7. Bulk density and particle size

We determined bulk density as dry mass divided by sample volume. The distribution of particle sizes was determined for select samples by sieve analysis using mesh sizes of 125 μm, 250 μm, 500 μm and 1000 μm.

2.8. Mercury flux calculations

We used flux calculations to estimate annual Hg pollutant loading to the lakes. Mercury flux was calculated as follows: Flux [ng cm^{-2} yr^{-1}] = Hg concentration [ng g^{-1}(dry sediment)] × Bulk Density [g cm^{-3}(dry sediment)] × Sedimentation Rate [cm yr^{-1}].

3. Results and discussion

3.1. Sample drying and loss of mercury

Sediment and soil are typically dried prior to chemical analysis to reduce variability associated with varying moisture contents and to make comparisons with literature data more applicable. Because of the volatility of Hg, we examined the effect of different drying temperatures on Hg release. We dried fresh (wet) sediment directly in the DMA at different temperatures (50 °C, 60 °C, 80 °C, and 100 °C) for 300 s, heating the amalgamator after the drying step to determine whether Hg was released in the process. We found negligible Hg (<0.001 absorbance units) released at 60 °C, but measurable amounts released 80 °C (~3% of the total-Hg) and higher temperatures. We also split select samples of sediment into two groups: one was allowed to air-dry in a laminar flow hood over a seven day period, the other was dried at 60 °C in an oven overnight. We found no significant ($p < 0.050$) difference for Hg between the two groups. Thus, samples in this study were either air-dried or oven-dried at 60 °C.

3.2. Decomposition temperature and time

We emphasize that both moisture and LOI are operationally dependent and thus obtained results are only valid for strictly specified conditions. For sediments and soils, LOI temperatures of 475–550 °C are generally considered optimal [28]. Although this is lower than the 650 °C typically used for the determination of Hg using the DMA, we found that operating the DMA at 550 °C yielded accurate Hg data for soil and sediment reference materials. Moreover, TGA thermograms of sediment collected in this study show that there is little if any inorganic carbon (carbonates) and that most of the carbon combusted before temperatures reached 550 °C (Fig. 2). Thus, to be consistent with the conventional LOI method we used 550 °C in the current study. For the sediment and soil, the first peak in the thermogram is associated with loss of moisture, while the second (and third) corresponds to loss of different types of organic matter.

To evaluate DMA decomposition time on both Hg and LOI, we split select samples into two groups: one was combusted at 550 °C for 180 s (the time recommended by Method 7473 based on the formula, decomposition time (s) = 0.4 s × weight (mg) + 100 s, and
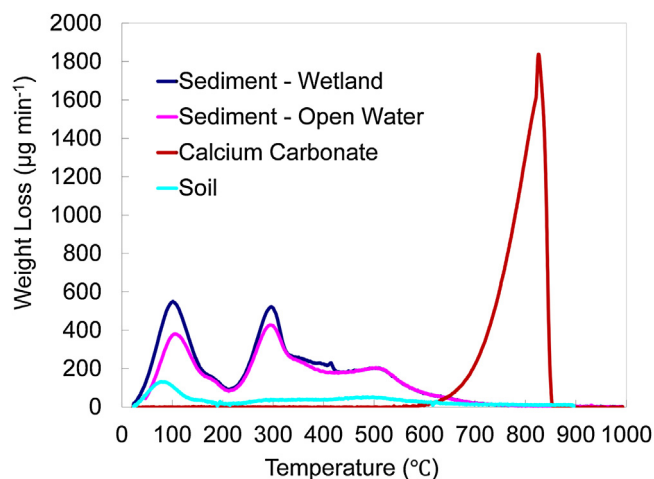

Fig. 2. TGA analysis of sediment (Beasley Lake), soil and CaCO$_3$ using oxygen as a purge gas. The largest peak is from calcium carbonate. The sediment samples mirror each other with wetland sediment giving a slightly higher weight loss for the first two peaks.
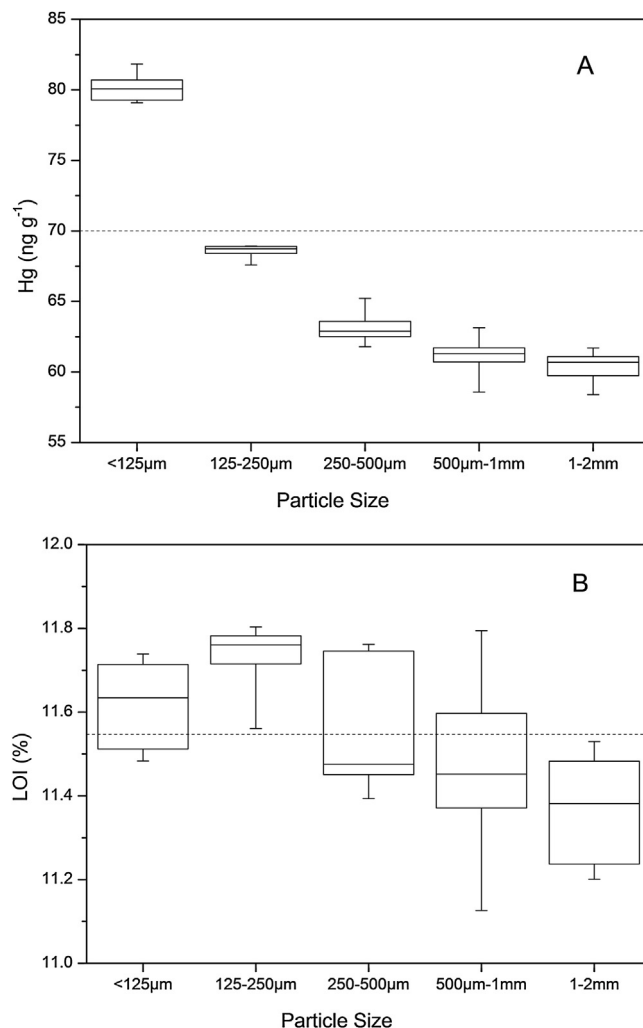

Fig. 3. Box plots displaying the relationship of sediment particle size with both total-Hg concentrations (A) and LOI determined by the DMA (B). The central horizontal line in the box marks the median value ($n = 6$); the ends of the box represents the lower quartile (25%) to the upper quartile (75%); lines extending outward to each end of fences represent 5th and 95th percentiles; the dashed line across the chart represents the mean value of all the size fractions.

the other for double the time. We found no significant ($p < 0.01$) difference between the groups for both Hg and LOI.

3.3. Effect of sediment particle size on LOI and Hg-levels

We analyzed different size fractions of sediment for LOI and total-Hg (Fig. 3). Compared to the larger sized fractions, smaller-sized particles had both higher levels of organic matter (as determined by LOI) and Hg concentrations. Several factors make smaller particles amenable to accumulating more Hg relative to larger particles, including greater overall surface area for adsorption of Hg, the finest fraction often contains more clay minerals, and organic coatings can increase the adsorption capacity [7]. The relationship between organic matter and Hg is further described below.

3.4. Conventional-LOI versus DMA-LOI

LOI was determined in sediment and soil containing a range of organic matter by a conventional method (550 °C, overnight) and by the DMA (550 °C decomposition temperature, 180 s). Despite the shorter analysis time, the DMA yielded results that were generally in good agreement with the conventional method (Fig. 4). For sediments, the difference was <10% in each case. Upon inspection it was observed that the DMA tends to underestimate (slightly) the LOI (mean difference −1.4%). Also, the variability (relative standard deviation) for replicate LOI analyses using the DMA was higher (mean 6.84%, range 3.70–9.97%) than the conventional approach (mean 2.44%, range 1.77–3.38%). Both of these observations are not surprising given the shorter analysis time and the smaller weights used for the DMA compared to the muffle furnace method.

An important factor that can introduce inaccuracies in LOI is weight gain from moisture subsequent to heating but before weighing. This could also possibly account for the slight negative bias observed for the DMA-LOI compared to the conventional-LOI. Thus, measurement uncertainty and sample representativeness are important factors that need to be taken into account.

In conventional-LOI, samples are typically cooled in a dessicator prior to weighing. This approach is not convenient for the DMA because it requires the operator to wait for the end of each analytical run to either re-weigh the boat immediately or to place it into a dessicator for later weighing. For DMA measurements, the amount of water the sediment can absorb from the air post-analysis can impact the LOI data (Fig. 5). For our samples, post-analysis weights became relatively consistent after about 5–10 min of cooling [A possible alternative to weighing boats immediately
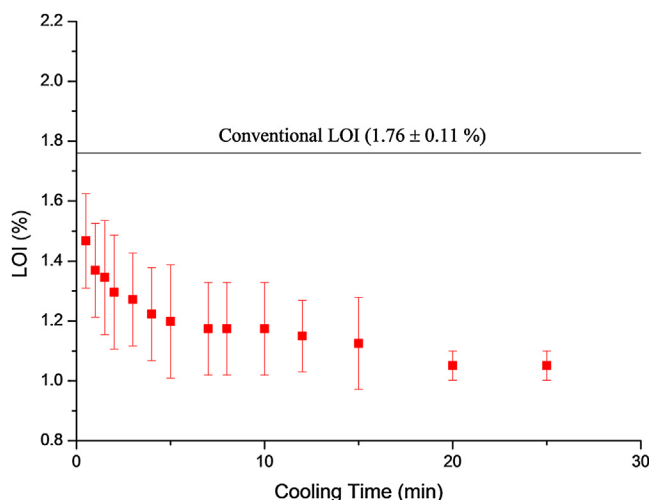

Fig. 5. LOI data related to cooling time in the open air after DMA analysis.

after each analysis is to let the system complete all analytical runs and then remove the autosampler tray and place it into an oven for drying. Once dried the sample tray can be placed into a dessicator box for cooling and subsequent boat weighing.]. Even when weighing immediately, there was a slight difference for LOI between the methods (1.48% by DMA versus 1.76% by the muffle furnace). This difference can potentially be remedied for non-calcareous samples by increasing the DMA decomposition temperature. The DMA-LOI approach as described herein provided a good estimate of total organic carbon for sediment from the studied lakes (see below).

3.5. Relating LOI with organic carbon

The relationship between LOI (determined by the DMA) and total carbon (determined by the elemental analyzer) resulted in an r^2 value of 0.98 ($n = 24$; $p < 0.01$) for the sediments, and the regression equation was: organic carbon = $0.0093(LOI)^2 + 0.1482$ $(LOI) − 0.2502$ (Fig. 6). As noted, inorganic carbon in the sediment was found to be negligible so the total carbon value reflects total organic carbon. Clearly, for sediment collected in this study (from oxbow lakes across the Mississippi Delta), LOI is a good estimator of organic carbon. Using this relationship, we estimated TOC for all the sediment samples. TOC ranged from 0.2% to 13.0%, and averaged between 0.7% and 6.5% for each core. Only Sky Lake had TOC values higher than 3.0%.
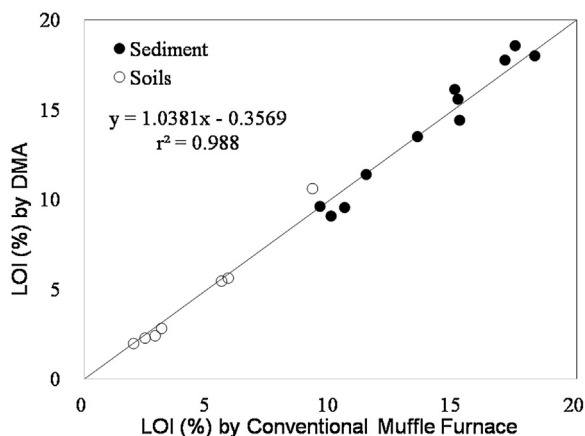

Fig. 4. Comparison of LOI data obtained by a conventional method and by the DMA. The dark line represents a 1:1 ratio.
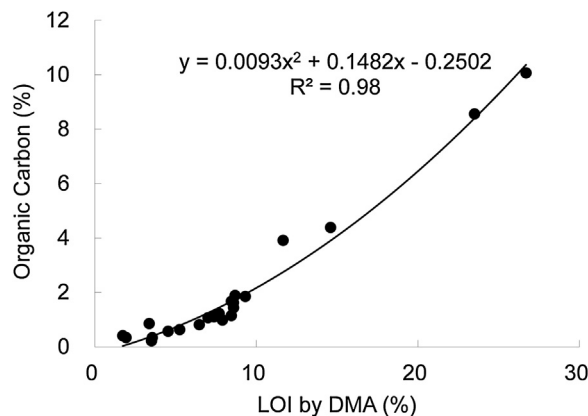

Fig. 6. The relationship between LOI and TOC for sediment from six oxbow lakes in the Mississippi Delta.

Table 2
Summary statistics for mercury and ancillary data in sediment from six oxbow lakes in the Mississippi Delta.

Lake	Core location	n	Bulk density (g cm⁻³)				Loss-on-ignition (%)				Mercury (ng g⁻¹, dry weight)				Mercury flux (ng cm⁻² yr⁻¹)[a]			
			Min	Max	Mean	1 SD	Min	Max	Mean	1 SD	Min	Max	Mean	1 SD	Min	Max	Mean	1 SD
Beasley	Open water	66	0.5	0.6	0.5	0.1	3.8	25.7	10.6	2.7	2.2	6	3.7	0.8	4.3	8.9	4.3	2.3
	Wetland	24	0.1/0.4	0.3/3.8	0.2/1.4	0.06/1.1	4.5	29.9	9	5.7	17.6	72.9	40.2	14.9	0.7/1.8	1.4/9.9	1.1/3.9	0.3/2.4
Hampton	Open water	111	0.4	0.6	0.4	0.1	7.4	20	11.6	3.8	5.2	31.1	9.9	3.6	7.1	42	19.2	6.7
	Wetland	59	0.7/1.1	0.9/1.6	0.8/1.5	0.13/0.1	0.8	21	4.8	2.5	5	97	63.4	20.8	6.2/0.7	6.3/14.7	6.2/9.2	0.03/3.1
Washington	Open water	25	0.4	1.6	1.2	0.3	1.3	12.9	6.5	3.8	15	104	50.4	22.2	9.3	30.6	20.7	6.7
	Wetland	38	0.1	1.7	0.6	0.3	1.2	18.6	8.6	3.2	19	133	81.5	22.0	8	87.7	26.1	14.1
Sky	Open water	28	0.7	1.6	1.3	0.2	3.5	30.6	18.8	8.5	2	61.7	32.4	20.9	0.7	48.5	13.4	10.9
	Wetland	14	0.4	0.7	0.5	0.1	11.7	21.6	14.6	3.04	94.5	153	127	23.3	51.9	129	96.9	23.7
Wolf	Open water	13	1.2	1.4	1.3	0.1	5.03	6.88	6.23	0.52	74.4	124	92.4	14.5	105	185	129	22.5
	Wetland	24	0.3	0.8	0.6	0.1	6.6	13.5	8.3	1.8	52.5	71.7	58.4	4.3	20.8	46.9	35.7	8.1
Roundaway	Open water	27	0.4	0.9	0.5	0.1	4.34	8.63	6.68	1.12	41.7	73.6	56.4	9.4	63.7	153	112	25.1
	Wetland	13	0.5	0.9	0.8	0.1	6.3	9.5	8.1	0.9	48.9	70.2	60.6	6	9.6	21.6	15	3.6

[a] Beasley and Hampton Lake wetlands exhibited two regions with distinct bulk densities and Hg fluxes; the upper is given in the numerator, the lower in the denominator.

3.6. Profiles of mercury and organic carbon in oxbow lake sediment cores

Summary statistics for bulk density, LOI, Hg concentrations and Hg deposition flux are given in Table 2 for open water and wetland samples from all six lakes. Beasley, Hampton, and Washington Lakes were selected for profiling Hg, bulk density and LOI with depth (time) in Fig. 7 because cores from open water and wetland areas in those lakes were well-characterized (dated). Due to high sedimentation rates within the lakes, the deepest portion of most of the open water cores dated to no earlier than about the 1920s (except for Washington and Sky Lake) (Fig. 7). Thus, these open water cores are not suitable for studying the history of Hg pollution encompassing pre-industrial levels. In contrast, the wetland cores (and Washington and Sky Lake open water cores) are estimated to go back several centuries (Fig. 7). For the Beasley Lake wetland core, there was a sharp rise in Hg around 1900. Data from Hampton Lake and Washington Lake wetlands also seem to show a similar
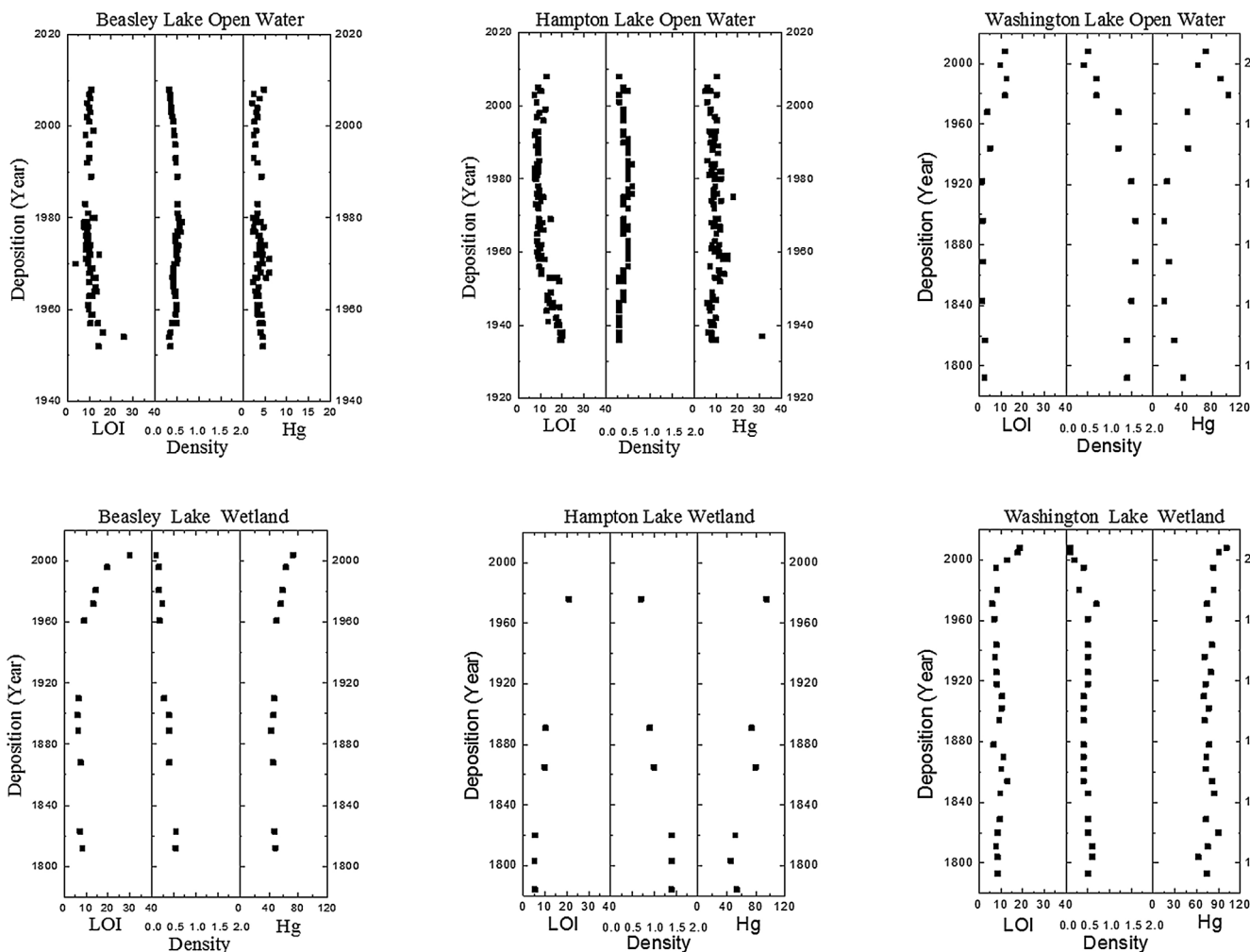

Fig. 7. Profiles of Hg (ng g⁻¹), bulk density (g cm⁻²) and LOI (%) in sediment cores from three oxbow lakes in the Mississippi Delta. Note: Hg concentration scale varies for each open water core.
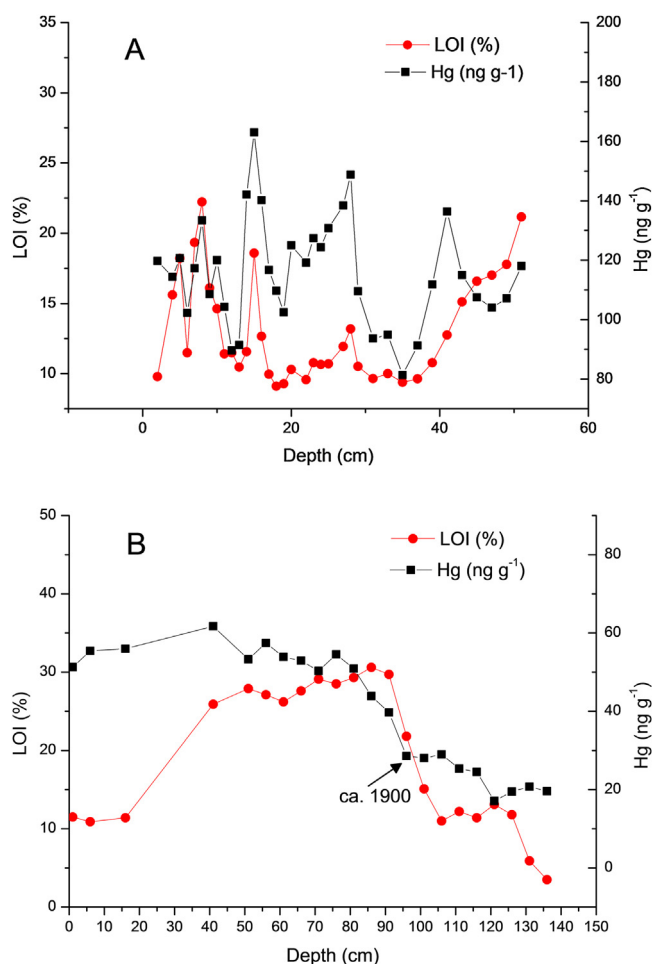
Fig. 8. The relationship between LOI and Hg with depth for sediment cores from Sky Lake wetland (A) and open water (B).

Organic matter plays an important role in controlling the distribution of Hg in soils and sediments by affecting physical and chemical processes [7–10]. Both particle size distribution and levels of organic matter influence Hg sorption to suspended sediments and thus Hg transport and retention in aquatic systems. There are several possible sources of organic matter in the sediment, including that derived from within the lake by primary productivity, and organic material transported in runoff from adjacent terrestrial areas. Silt and clay exposed through agriculture practices are particularly vulnerable to erosion, and these fine fractions not only have greater surface area for sorption of Hg ions but often contain higher levels of organic matter. Thus, Hg is preferentially transported by these fine materials in suspended sediments and deposited into lakes where it concentrates.

The distribution of Hg and organic carbon in sediment cores for several lakes is shown in Fig. 7. LOI values in Beasley Lake and Hampton Lake had similar profiles. Generally, the open water sediment had fairly uniform LOI values ($\sim$5–10%) with depth corresponding to $\sim$1960, with a slight increase (to $\sim$15%) at lower depths. In contrast, the wetland sediment for these same lakes, as well as Washington Lake, had slightly higher LOI values ($\sim$20–25%) for the top of the core and dramatic decreases with depth (in the first few centimeters) to 5–10%. In Sky Lake, LOI and Hg were correlated in the open water core ($r = 0.63$, $p = <0.05$) and, to a lesser extent, in the wetland core ($r = 0.32$, $p = 0.063$) (Fig. 8). Biological matter produced in the wetland is a plausible source for the high organic content in the top layers of the wetland sediment, whereas organic matter in the open water sediments may originate from catchment soils (mostly agricultural) transported via runoff. In addition, the size-distribution of suspended solids reaching the wetlands is believed to be skewed to the finer fractions due to deposition of the larger particles in the open water prior to movement into the wetland areas. Indeed, we found that wetland cores had higher fractions of fine particles ($<$125 μm) than open water cores (data not shown).

3.7. Recent trends in mercury flux to the lakes

Mercury flux data is summarized in Table 2. The variability in Hg loading to the lakes stems primarily from different sedimentation rates, reflecting land cover and erosion characteristics within the catchment. Given that the cores were divided into 1-cm intervals for analysis and that open water areas have relatively high sedimentation rates, the dated open water cores (Beasley, Hampton and Sky Lake) were most suitable for examining recent
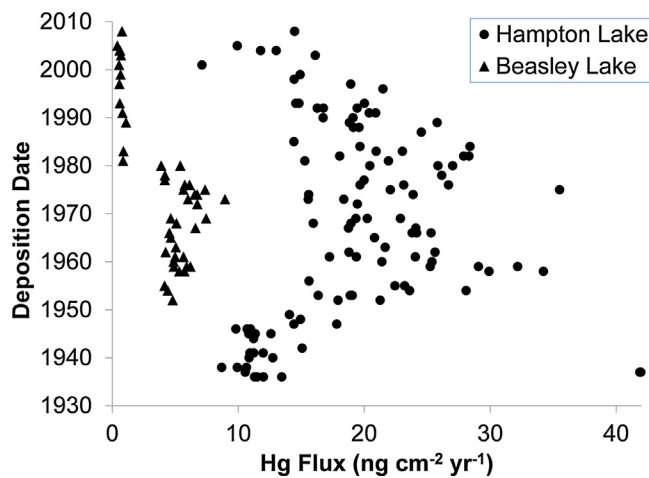
increase in Hg during the same period. For Sky Lake (open water core), there was also an increase in Hg starting around 1900; while not shown in Fig. 7, this can be seen in the lower portion of Fig. 8 where a depth $\sim$95 cm corresponds to $\sim$1900. Others have reported a similar 2 to 3 times increase in Hg deposition often starting during the mid-19th century [4,28]. Still other studies have shown increases in Hg in core sections pre-dating the industrial era, although these are often due to local or regional impacts such as metal refining in South America in the 15th century [29]. Less dramatic increases have been documented over even longer time scales; for example in a peat bog core dating back $\sim$2000 years [30].

Mercury concentrations in wetland sediments were generally higher than in open water sediments (Table 2). Mercury in the Beasley Lake wetland ranged from 17.6 to 72.9 ng g^{-1} (mean 40.2 ng g^{-1}), whereas the open water core ranged from 2.2 to 6.0 ng g^{-1} (mean 3.7 ng g^{-1}). Hampton and Washington Lakes also had higher levels of Hg in wetland sediment (63.4 and 81.5 ng g^{-1}, respectively) versus the open water sediment (9.9 and 50.4 ng g^{-1}, respectively). Sky Lake had substantially higher levels of Hg in the wetland sediment (mean 127 ng g^{-1}) compared to the open water sediment (mean 32 ng g^{-1}). Roundaway Lake had similar levels between the two sites (mean 60 and 56 ng g^{-1}). Only Wolf Lake had higher Hg levels in the open water core (mean 92 and 58 ng g^{-1}). The reason for the higher Hg levels in the wetland sediment compared to the open water sediment is likely related to differing particle size distributions and organic matter content.

Fig. 9. Recent changes in Hg flux to open water areas in two oxbow lakes in the Mississippi Delta.

(prior century) trends in Hg deposition. For Hampton Lake, the open water core corresponds to a deposition interval of ~1936–2008. The mean Hg flux for the lake was 19.2 ng cm^{-2} yr^{-1}, with the highest interval occurring during the 1960s (Fig. 9). There was also a spike in the Hg flux associated with an interval occurring in the early 1930s that may have been associated with the use of Hg-based fungicide/insecticides in agricultural practices in the watershed. Whereas it is possible that the sample was contaminated, it seems unlikely given the sample was processed the same as the others and no other samples were such outliers. For Beasley Lake, the deposition interval was divided into two parts (~1952–1980 and ~1981–2008) based on the addition of erosion control structures near the lake around 1980. The impact of the reduced sedimentation in the lake on Hg flux is evident (Fig. 9). Sky Lake's open water core (data not shown) exhibited a rise in mercury around 1900, with a mean Hg flux of 104 ng cm^{-2} yr^{-1} from ~1860 to 1900 and 353 ng cm^{-2} yr^{-1} from 1900 to 2006. Again, the decade with the highest interval was the 1970s.

4. Conclusions

In this work, we show that direct mercury analyzers based on combustion can be used to obtain LOI data comparable to conventional methodology. Thus, for many sediment and soil types, organic carbon can be determined simultaneously with mercury (on the exact same sample material), reducing analytical time and costs. We demonstrate application of the method by profiling Hg and organic matter in sediment cores from six different oxbow lakes, evaluating, for the first time, temporal deposition of Hg in the region. A regression equation was developed from LOI data for prediction of organic carbon for oxbow lake sediments from across the Mississippi Delta. Organic carbon and Hg content generally increased as particle size decreased. Erosion control structures placed near the lakes were effective at decreasing Hg flux to the lakes. Generally, Hg deposition fluxes to the lakes generally rose around 1900 and peaked in the 1960s or 1970s.

Acknowledgements

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