



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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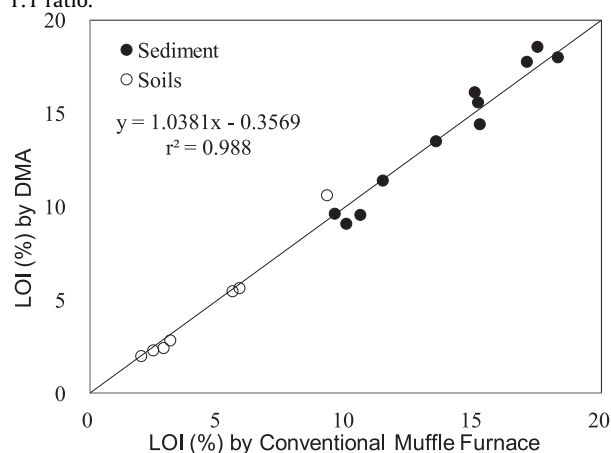
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HIGHLIGHTS

- 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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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.

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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 CO₂ 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 CO₂ 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 Hg⁰ 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

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