

Changing Climate and Sea Level Alter Hg Mobility at Lake Tulane, Florida, U.S.

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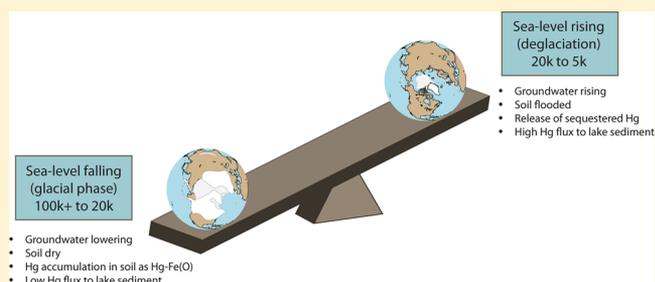
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S Supporting Information

ABSTRACT: Between 45 000 cal years BP and the beginning of the Holocene, the accumulation rate for Hg in sediments of Lake Tulane, Florida ranged from ≈ 2 to $10 \mu\text{g m}^{-2} \text{yr}^{-1}$, compared with $53 \mu\text{g Hg m}^{-2} \text{yr}^{-1}$ in the 1985–1990 period of anthropogenic input. The locality experienced regional draw-down of the water table during the Wisconsin glaciation, which lowered global sea level by nearly 130 m. Natural atmospheric deposition of Hg to the surrounding area resulted in long-term (ca. 100 000 years) sequestration of this atmospheric flux of Hg, primarily by adsorption in the oxic Al- and Fe-hydroxide-rich sandy subsoil.

Global sea level rise during deglaciation led to a rising regional water table, flooding the oxidized soils surrounding Tulane. Iron and adsorbed Hg were mobilized by reductive dissolution and transported by groundwater flow to Lake Tulane and ultimately to the accumulating sediment. The accumulation rate of Hg (and Fe) increased rapidly about 16 000 cal years BP, peaked at nearly $60 \mu\text{g Hg m}^{-2} \text{yr}^{-1}$ ca. 13 000–14 000 cal years BP, declined sharply during the Younger Dryas, and then increased sharply to a second $60 \mu\text{g Hg m}^{-2} \text{yr}^{-1}$ peak about 5000 cal years BP. Thereafter, it declined nearly to background by 900 cal years BP. In similar geologic situations, rapid modern sea level rise will initiate this process globally, and may mobilize large accumulations of Hg and lesser amounts of As, and other redox sensitive metals to groundwater and surface water.



INTRODUCTION

Human activities, including smelting of ores, burning of forests and organic soils, and combustion of fossil fuels have introduced large amounts of mercury (Hg) into the environment during the past few thousand years, and especially in the 20th century. The upper levels of lake and peat sediment cores indicate that fluxes of $20\text{--}40 \mu\text{g m}^{-2} \text{yr}^{-1}$ and higher have been common during the past century.^{1–4} And yet, human activities are not the only sources of Hg entering these systems. Management and regulation of Hg and other toxic substances thus require accurate information about the rates and variability of natural processes involving Hg in the environment.

Long-term sediment records from peatlands and lakes in widely separated geographic areas have revealed that preindustrial (background) levels of Hg deposition were consistently above zero. In fact, the background fluxes have generally been in the range of $1\text{--}3 \mu\text{g m}^{-2} \text{yr}^{-1}$, with occasional episodes of higher inputs, resulting from natural processes. For example, Roos-Barraclough and colleagues report background Hg fluxes between 0.3 and $8.0 \mu\text{g m}^{-2} \text{yr}^{-1}$ in three peat cores from Switzerland.^{3,5} A similar study at Caribou Bog, Maine showed an average background accumulation rate of 1.7 ± 1.3

$\mu\text{g m}^{-2} \text{yr}^{-1}$ in ombrotrophic peat, and $3.1 \pm 2.3 \mu\text{g m}^{-2} \text{yr}^{-1}$ in samples of minerotrophic peat.⁴ A slightly higher range of background fluxes occurs in Holocene sediments of Elk Lake in northwestern Minnesota, with periods of Hg fluxes above $20 \mu\text{g m}^{-2} \text{yr}^{-1}$ during times when forest changed to prairie in the mid-Holocene, apparently causing Hg to be leached to the lake during oxidation of organic forest soils.⁶ Lake sediments from northern Brazil reveal preindustrial fluxes of approximately $2 \mu\text{g m}^{-2} \text{yr}^{-1}$ during the past 30 000 years.⁷ A recent review by Biester et al. discussed other archives.⁸

What are the sources and mechanisms of natural variability in Hg deposition in the preindustrial world? The influences of altered groundwater levels and variation in water flux on Hg mobility are well documented in the literature (see ref 9 for an overview). Commonly, in boreal forests, increased runoff is associated with elevated dissolved organic carbon (DOC), an important carrier of dissolved ionic and methylated Hg.

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However, this type of variability is short-lived, being seasonal at the longest. Long-term trends of increasing or decreasing runoff can affect retention of Hg by watershed soils. By altering the groundwater hydrology, changing the water budget, and warming the soil, forestry practices may increase the export of total dissolved Hg and methyl Hg.¹⁰ This process is also relatively short-lived, lasting perhaps 5–10 years at most. Inundation of organic soils (as in reservoir construction) releases Hg to the overlying water with effects lasting up to 10 years. Interestingly, *draining* of organic soils also increases the export of total (dissolved plus particulate) and dissolved Hg, the latter apparently as the result of oxidation of organic matter and leaching of DOC–Hg complexes.¹¹ Oxidation by fire leads to volatilization of Hg from organic soils, reducing the export of both forms of Hg for periods in excess of decades.¹² All of these processes add variability to loss of Hg from watersheds and possible variability in the delivery rate to lakes. Many in-lake processes are discussed in ref 13.

Lake Tulane, which lies in a region of central Florida, has become an important research site far south of the limits of Quaternary glaciations. Its 60 000+ year-old sediment profile reveals that the region has undergone repeated major climate fluctuations between cool-dry and warm-wet conditions during last half of the most recent ice age as well as during the Holocene interglacial.¹⁴ The wet/dry fluctuations at the site have a striking temporal correspondence to phenomena in the North Atlantic known as Heinrich events, which involved massive fluxes of icebergs from Hudson Bay and elsewhere into the seas south of Greenland. Those times of cold in the North Atlantic correspond precisely to times of warm, moist climate in central Florida, when precipitation was dominated by summertime convective storms, as is the case today.

An additional major environmental change during glacial periods involved sea-level. Sea-level lowers as terrestrial ice sheets build. At the Last Glacial Maximum (LGM), approximately 26 500–19 000 cal years BP (henceforth years BP), eustatic sea level had lowered ~130 m.¹⁵ A secondary effect is the altered shape of the Earth's geoid in response to changes in ice loading in some areas, sediment loading in others, and reduced water loading in still others (isostatic sea-level change).¹⁶ The unique sea-level history of the Florida region for the past 20 000 years is discussed in refs 17 and 18.

Lowered sea-level would have influenced groundwater table elevations in Florida in two ways. First, at the LGM, the shoreline was farther seaward, particularly to the west along the Gulf of Mexico. The effect of sea level lowered by up to 130 m would dominate and cause a lower groundwater table in the interior of Florida. Because of the hydraulic connectivity in Florida, including karstic interconnected lakes and a sheet of overlying sand, response time of the groundwater table should be relatively rapid. The absolute lowering of the water table would be a function of climate plus lowered sea level, but certainly would not approach 130 m.

Over the past 40 years, paleoecological investigation of lake-sediment records in the Florida by W. A. Watts, E. C. Grimm, G. L. Jacobson, and colleagues has shown that most lakes were dry for extended times during the last glacial period (indicated by hiatuses in sedimentation). Many of these lakes currently have water depths exceeding 10 m, and therefore some combination of climate change (temperature and water budget) and sea level effects must have exceeded 10 m of groundwater table lowering. In fact, Lake Tulane is the only known Florida lake to have persisted through the LGM, having contained

water continuously for at least the past 60 000 years. The core from Grimm et al.'s study¹⁴ was taken in 23 m of water. Sediment dated at 10 000, 15 000, 20 000, and 30 000 years BP occurs at depths (below present water surface) of 27.3, 29.8, 31.4, and 34.2 m.¹⁴ Thus, with continuous sedimentation, groundwater table lowering could not have exceeded 32 m over the last 20 000 years. Cores taken at different water depths have shown large fluctuations in lake-level. At nearby Buck Lake, which is currently 18 m deep, sedimentation was interrupted until about 9000 years BP (Grimm and Jacobson, unpublished data); assuming 0.5 mm of sediment per year, the lowering of the groundwater table must have been in excess of 22 m below present. These two lakes, taken together, suggest a water table lowering of 22–32 m. Similarly, Lake Annie (south of Lake Tulane) resumed sedimentation at 13 000 years BP, after a hiatus of at least 20 000 years.¹⁹

Together, the current water depth of 23 m and accumulated sediment of 17+ m in the north basin provide a basis to estimate maximum groundwater lowering during the Wisconsinan glaciation, which reached maximum extent about 22 000 years ago, and corresponded to a eustatic sea level lowering of about 130 m. Since then, eustatic sea level has risen at an average rate of 5.9 mm yr⁻¹, less rapidly over the last 10 000 years.¹⁷ If Lake Tulane were nearly dry at 60 000 years BP, then the water table would have to rise, on average, about 3 mm per year to account for new sediment and the current water depth. This rate is approximately 50% of the rate of sea level rise over the same period. Since 22 000 years BP, the groundwater table must have risen an average of approximately 1.5 mm per year, or about 25% as fast as sea level. Groundwater table depression since 60 000 years BP is therefore constrained to between 32 and 22 m below the present (36 m asl). These arguments assume that subsidence within the karst lakes has not occurred since continuous sedimentation started.

Adams et al. proposed a model to explain the stranding of shoreline features in northern Florida because of isostatic uplift due to karstification.²⁰ Their model assumed a paleo-sea-level history,²¹ precipitation,²² and effective weathering rates to remove mass from the Florida peninsula. They calculated an isostatic uplift rate, unadjusted for ET and platform loading by water, ranging from 0.02 mm yr⁻¹ (interglacial) to 0.05 mm yr⁻¹ (glacial). The uplift from karstification must be incorporated into the groundwater response but is clearly a small fraction of the total assessment of Lake Tulane's history. The process is important over periods longer than one glacial cycle because its effects are cumulative.

Additional isostatic adjustment from loading and unloading of 60 m of water on the Florida platform would result in about 20 m of additional variability in the land elevation, not small compared to the effect on the groundwater from rising sea level. In summary, we do not know the precise allotment of impact of eustatic sea level and isostasy on groundwater, at Tulane. However, rising eustatic sea level and platform loading by water from rising sea level are additive. These isostatic factors would increase the local sea level increase to perhaps as much as 150 m. Thus, sea level rise over the last 22 000 years has translated into 22–32 m of groundwater table rise at Lake Tulane, approximately 100 km from the coast of Florida, and 200 km from the LGM coastline on the exposed continental shelf. Most of the rapid addition of glacial meltwater to the world's oceans had been completed by about 10 000 years ago, when sea-level curves for the Gulf of Mexico region reached around -10 m relative to present conditions.

The large hydrologic changes in central Florida make that region ideal for evaluating the influence of sea level on Hg transport and deposition over the past 45 000 years. During that period, changes in climate involved differences in atmospheric circulation and in local hydrologic and biological conditions. Thus, sediments from Lake Tulane provide an opportunity to evaluate possible differences in pathways by which Hg entered the lake under a wide range of climates, vegetation, and hydrology.

MATERIALS AND METHODS

Lake Tulane (27°35' N, 81° 30' W) lies within the town of Avon Park on the Lake Wales Ridge in central Florida, at an elevation of 36 m above sea level (m a.s.l.). The 36 ha lake is one of many sinkhole (karst) lakes formed by dissolution of Eocene limestone, under a landscape covered by thick sands of the Pliocene Cypresshead Formation. Data extending from 1995 to 2011 ($n > 100$) indicate that total P in the lake ranges from 2 to 17 $\mu\text{g L}^{-1}$, and the secchi depth ranges from 3 to 9 m. Tulane is a clear-water lake (www.hillsborough.wateratlas.usf.edu). The lake level is controlled by the groundwater surface in those sands. Regional flow at the lake is southerly.²³ Inputs of Hg would have been from the atmosphere or groundwater, with little or no surface runoff into the lake.

The sediment core used for this study of Hg was the same core TFG collected by Grimm, Jacobson, and colleagues for the work described in refs 14,24 and 25). The core site was located in the approximate center of the north basin of the lake at a water depth of 22.37 m. The core had been intensively studied for physical and biological (pollen and macrofossil) contents; 55 AMS radiocarbon dates were used to develop a chronology for the profile. Thus, the Hg stratigraphy is placed within a well-documented framework of environmental change.

For the results presented here, we have applied a new age model based on the IntCal09 calibration curve,²⁶ which covers the entire radiocarbon time scale. The age model¹⁴ was based on the IntCal04 calibration curve²⁷ for ^{14}C ages < 20 000 years BP and the Fairbanks0805 curve²⁸ for older ages. For the new chronology, we used the Bayesian age-modeling software "Bacon",²⁹ which models the accumulation process using an autoregressive time series. For interpolated ages, Bacon produces 95% highest posterior density (HPD) intervals (essentially 95% confidence intervals) as well as maximum a posteriori (MAP) estimators of the HPD modes. The MAP estimators provide point ages for sample depths, which could be used for stratigraphic diagrams and calculation of flux rates; however, the sample-to-sample differences (in years) between adjacent MAP estimators is unrealistically variable, especially considering that Bacon is assuming some consistency in accumulation rate. Therefore, the MAP estimators were smoothed with a locally weighted scatter plot smoothing (LOWESS) model³⁰ using a 1000 year window. The new chronology does not differ significantly from that used in the 2006 paper,¹⁴ and because the sample levels for Hg and the other stratigraphic analyses are still the same, there is no material effect on interpretations. Ages older than ca. 45 000 years BP are extrapolated using Heinrich event surrogate signals in the core.¹⁴ We calculate fluxes only for the period 1000–45 000 years BP.

Loss-on-ignition of samples at 4 cm intervals at 500 °C was carried out to estimate organic content. Original data and methods are in ref 14

We analyzed 156 subsamples at approximately 10 cm intervals from 63 cm below the sediment surface to the bottom of the approximately 17 m long core. The sediment between 0 and 63 cm was disturbed by the coring process and was discarded. Analyses yielded a temporal resolution of about 350 years. For Hg, samples were dried at 40 °C. Approximately 0.4 g of dry sediment was microwaved with 8 mL of optima ultrapure HNO_3 plus 2 mL of optima ultrapure HCl. We then added potassium permanganate (5 mL of 5% by weight of reagent in 100 mL of DI) plus potassium persulfate (8 mL of 5% solution by weight of reagent in 100 mL of DI), and finally hydroxylamine hydrochloride (10 mL of 24% by weight of reagents in 100 mL of DI), and then brought the solution to 100 mL with DI (U.S. EPA Method 245.6). We included duplicate samples, laboratory reagent blanks and spiked blanks, and replicate measurements to produce the data used herein. The SRM was MESS-3. Mercury was determined on a Perkin-Elmer flow injection mercury system (FIMS) model 400.

Iron (Fe), aluminum (Al), and titanium (Ti) (reported here), and a suite of other metals were determined by Inductively coupled plasma emission spectrometry (ICP-40) in the Tampa, Florida research laboratory of the U.S. Geological Survey.

RESULTS

The concentration of Hg in the Tulane sediments varies by at least a factor of 5 within the core (Figure 1). The patterns can be separated into the portions of the core representing sediments older than about 12 500 years BP and those from the Late-Glacial and Holocene. For most of the core (age >12 500 y), Hg variability is strongly and positively correlated with sedimentary organic matter (Figure 2b). This relationship is not surprising, as Hg complexes strongly with particulate

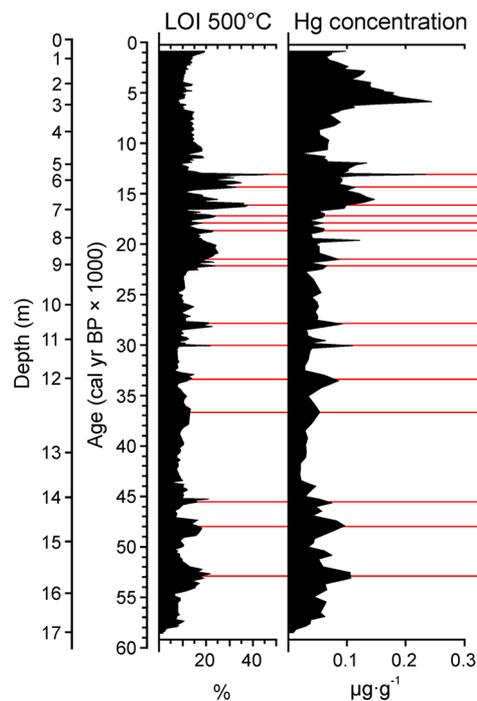


Figure 1. Loss-on-ignition (LOI) and Hg concentration in sediment from Lake Tulane, Florida as a function of sediment depth and calendar age. Red horizontal bars indicate coincident peaks for LOI and Hg.

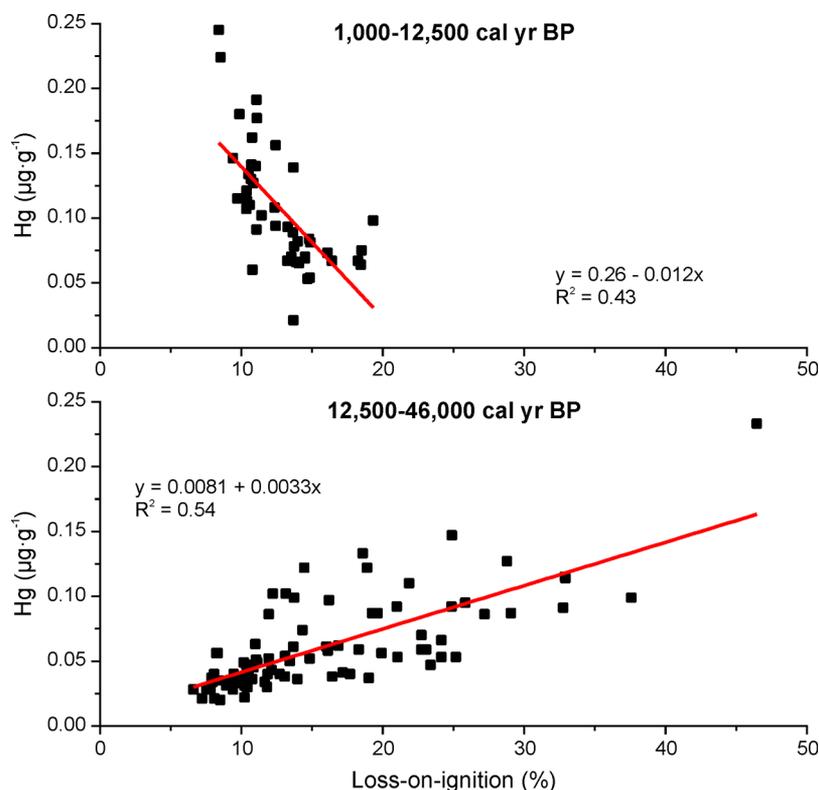


Figure 2. The relationship between LOI and Hg concentration in sediment from Lake Tulane, Florida for (a) sediment ca. 900 to 12 500 years old and (b) sediment >12 500 years old.

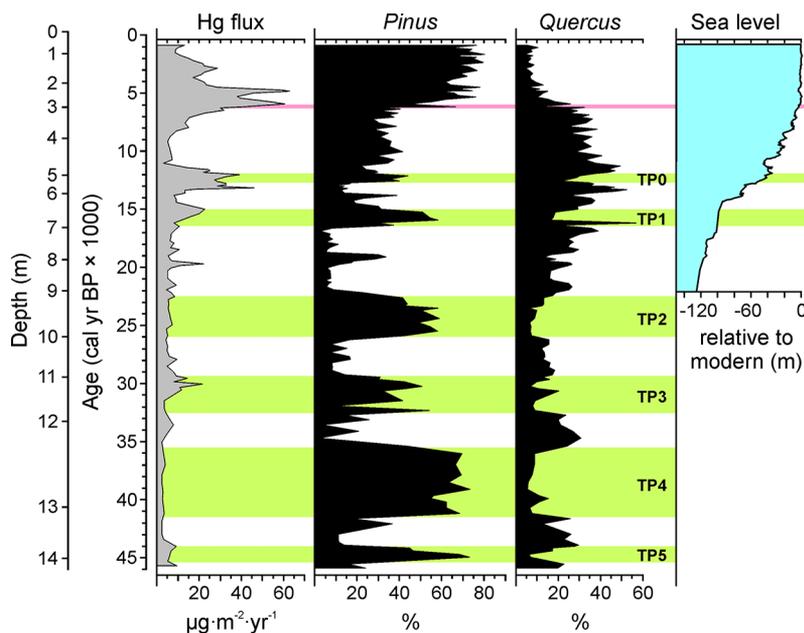


Figure 3. Lake Tulane Hg flux in relation to organic matter and selected plant taxa over the last 60 000 years. Horizontal green bars indicate Tulane *Pinus* periods (TP0 through TP6), which correspond to YD and Heinrich Events H1 through H6.¹⁴ Sea level in the Gulf of Mexico since 25 000 years BP is based on ref 17.

organic matter in oxidized natural settings. Below sediment depth 530 cm, almost all peaks in Hg concentration coincide with peaks in organic matter. The variability is modest, with most Hg and organic peaks only about twice the intervening low values. However, organic matter is generally higher during dry phases, and the major peaks in organic matter occur during dry phases. These peaks generally coincide with high

concentrations of plant macrofossils, particularly of submerged aquatic, emergent aquatic, and damp-ground species. The highest LOI values and largest concentrations of plant macrofossils date to the LGM, between Heinrich events 2 and 1, and to the Late-Glacial, between Heinrich 1 and the Younger Dryas.¹⁴ Thus, high organic matter corresponds with an abundance of aquatic macrophytes, which grow in shallow

water or on damp ground. The modern steep-sided, deep-water lake has little habitat for aquatic macrophytes. Aquatic macrophyte populations and organic matter production were greater when the lake was shallower and shoreline was closer to the coring site, and were greatest during LGM, when sea level was lowest, and presumably lake-level was at its lowest level. The fluctuations in Hg and organic matter do not appear to be closely coupled with the major wet/dry shifts in terrestrial vegetation and climate. That is, episodes of increased organic sedimentation do not appear to be systematically associated with the Tulane pine peaks and Heinrich events described in ref 14.

In contrast, the correlation between Hg and organic matter is strongly negative in sediments deposited since 12 500 years BP. Figures 1 and 2a indicate that there is less variation in LOI during the last 12 500 years, and a strong long-lasting peak in Hg concentration, unrelated to LOI. During this period, Hg concentrations reach the highest values in the entire 60 000 year profile, peaking in sediments dated to around 6000 years BP (Figure 1).

Accumulation rates for Hg, mass, and LOI occur concurrently at about 45 000, 30 000, 20 000, 12 500, and 5000 years BP (Figure 3, Supporting Information (SI) Figure S1). Mass and LOI rates increase over background ranges up to a factor of about 3×. The magnitude of the Hg peak is up to 7×. Thus, a significant fraction of the increase in Hg flux is associated with higher sedimentation, which in turn is associated with transitions to *Pinus* vegetation and more precipitation. The higher sedimentation is interpreted to be linked to a fairly rapid rise in lake level, causing shore erosion and greater deposition in the deeper parts of the lake. The question remains, where did the extra Hg originate? It is unlikely to be from shallow water sediment. Thus we attribute the increase in Hg to groundwater inundation of soils, with additional scavenging of Hg from the lake water column by additional organic matter.

The sediment chemistry is dominated by SiO₂. The four major metals, as oxides, are Al (up to 10%), Fe (<2%), Ca (<1%), Ti (<1%), and Mg (<0.1%). The total of these five, as oxides, is <15%, and as low as about 5%. The trace metals are very dilute. The ICP measurements at the time of analysis did not yield useful data for metals that might be interesting to compare to Hg. An example is As, which in soils would be largely sorbed as arsenate, AsO₄. Arsenic was everywhere in the core <10 mg kg⁻¹. Similarly, PO₄ values are too close to analytical detection limits for meaningful interpretation. All major elements generally decline upward until about 10 000 years BP, and then increase to 1000 years BP as a consequence of variable biogenic silica or quartz (we measured neither), relative to other metals, with the obvious dramatic exception of Hg. Co-variation of the metals occurs despite a 3-fold variation in the mass accumulation rate.

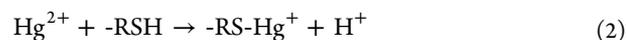
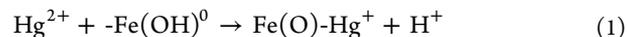
DISCUSSION

The apparent decoupling of Hg and organic matter in the upper part of the Lake Tulane core suggests either that some aspect(s) of Hg delivery during the Holocene differed from what had been in effect for the older segments of the core, or that the flux of Hg increased dramatically prior to and within the Holocene. Grimm et al.'s research found that several of the early times dominated by *Pinus* at Tulane had conditions that most resemble those of the late Holocene (the most recent 5000 years).¹⁴ That is, the times of Tulane *Pinus* peaks 4, 5, and

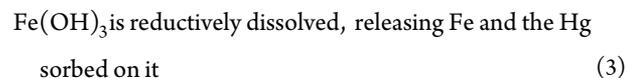
6 were most similar in the entire core to the upper 5000 years, suggesting frequent convection-driven rainfall in summer. If this interpretation is correct, then simply the occurrence of climate and vegetation similar to that of today did not produce an unusual flux of Hg to the Tulane sediments (Figure 3).

Many studies have identified variables that relate to the mobility of Hg in terrestrial (refs 9, 31, and 32) and aquatic systems.¹³ They include watershed:lake area ratios, % wetlands, concentration of DOC, organic matter quality, catchment history (including atmospheric loading of Hg, and changing water level in lakes), lake productivity, and the aerobic state of the water body. The effects of variations in hydrology are well understood for surface water, and include variations in DOC and thus export of Hg. However, water table as an important variable in mobility is well-documented only for artificial impoundments.

We hypothesize that rising groundwater level, in response to rising sea level and isostasy, is linked to Hg mobilization from soils, transport to Lake Tulane via groundwater flow, and deposition in sediment. The concentration of Hg in well-drained soil profiles is commonly highest in O horizons, but normalized to carbon (C) is higher in the Bh or Bs horizons, and the mass of Hg is by far largest in the mineral-rich, C-poor B horizon.^{9,31,32} Hg accumulations in tropical soils may greatly exceed those in temperate and boreal soil profiles, as a consequence of a greater period of accumulation and more advanced pedogenesis, with more secondary Al and Fe hydroxides.³² Wasserman et al.³³ suggested that mobilization of Hg in the Amazonian Basin may have been the consequence of particulate erosion, coupled with reductive dissolution of Fe-rich oxisols following flooding.^{33,34} These Al and Fe hydroxides out-compete DOC–Hg complexes for the Hg in downward moving soil water.³⁵ As groundwater solutions descend, the DOC ligands for Hg, Al, and Fe are metabolized, organic acidity is reduced (and pH is increased), and Fe and Al are precipitated as amorphous hydroxides, providing sorption sites for Hg. In a regime of stable and low groundwater level in the Tulane hydrologic setting, Hg in atmospheric deposition directly on the lake would be largely sequestered by solid organic matter and be incorporated into the sediment record. Any Hg deposited to the terrestrial vegetation or land surface would be partially retained in complex with soil organic matter or with secondary ferric oxy-hydroxide (FeOOH or Fe(OH)₃) and possibly Al(OH)₃.



The input and output of Hg to groundwater should reach a quasi-steady state, with little retention in the soil after exchange sites become saturated. Delivery of Hg to the lake via subsurface flow would approach steady state. With a declining groundwater table, retention in the soil column should increase as more soil becomes aerobic and secondary Fe phases become distributed to greater depth. However, in a regime of rising water table, previously aerobic soils would be inundated incrementally upward. Two hypotheses are proposed for such a regime.



Production of NH_4^+ under anaerobic conditions could cause displacement of Hg from the organic matter, or more likely from Fe and Al phases (4)

Both hypotheses 3 and 4 increase dissolved Hg which is then available for transport to the lake. Sequestration of Hg to the sediment could be either through forming complexes with autochthonous particulate organic matter or adsorption on precipitated $\text{Fe}(\text{OH})_3$, produced by oxidation of Fe^{2+} in emerging groundwater (the reverse of hypothesis 3). The LOI in mid-Holocene Tulane sediment varies little, whereas Fe increases relative to Al (Figure 4) and Hg increases even more.

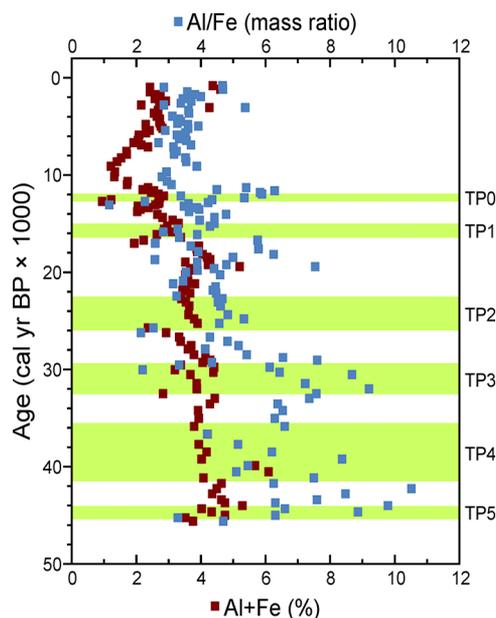


Figure 4. Mass ratio of Al/Fe and $\sum(\text{Al} + \text{Fe})$ in sediment from Lake Tulane, Florida.

This suggests that neither the organic matter nor the secondary Fe were saturated with respect to exchangeable Hg prior to the increase in Hg sedimentation. Thus, Hg availability, and not solid substrate, limited the Hg accumulation rate in sediment.

The concentration of Fe in the sediment through the Holocene reached a minimum about 4000–5000 years BP. However, Fe concentration was primarily driven by variations in the SiO_2 concentration, which ranged from 80 to 95%, with Fe and Al being the first and second most abundant metal (SI Figure 2). The concentration of SiO_2 reached a maximum at the time Fe reached a minimum (along with Al, Ti, and other rock-forming elements; SI Figure 2). If Fe mobilized from soil were reoxidized and precipitated in the lake,

Fe in the sediment should be enhanced relative to Al, whose mobility is not redox sensitive. Figure 4 shows that this was the case during the last 15 000 years. The rising groundwater would have mobilized Hg that had been deposited from the atmosphere and fixed in the soil over perhaps the last 80 000 to 100 000 years. The accumulated Hg was then released in about 15 000 years. Interestingly, the second maximum apparent flux of Hg to the sediment occurs centered on about 5000 years BP. At that time, sea level was less than 3–5 m below the present value. We interpret this to mean that

much of the mobilized Hg was derived from the upper few meters of the soil profile.

The second of the dramatic peaks of the accumulation rate of Hg (ca. 13 000 and 5000 years BP, Figure 3) is slightly before the sharp increase in *Pinus* pollen, which lags a few hundred years. The *Pinus* rise is interpreted as a change in water regime, with increasing warmth and higher summer precipitation. If correct, the result would be an acceleration of the rise in regional water table, creating conditions for increased reductive dissolution of secondary Fe (and release of Hg). The soil, nearly at its present groundwater state, apparently was then rapidly depleted of stored Hg.

Does this understanding of the process of Hg release during the rising groundwater surface associated with rising sea level have utility for interpreting Hg profiles in sediments from lakes in other regions with variable water balance? The answer would depend on the setting and especially the degree to which the site is linked to sea level. Holocene water levels in localities as diverse as the northern Great Plains to Maine have fluctuated by as much as 6–8 m as a result of variations in climate and vegetation.^{36–39} The first two studies document a connection between variable flow in a stream and the water levels in nearby lakes on a transect across a Minnesota sand plain. But those studies, and the ones in Maine, all involve sites that are in glaciated regions (hence have soils only 12 000–15 000 years old), and far from the influence of rising sea level. Thus, even if the rather large upward movement of groundwater surfaces during the Holocene had released some Hg (in the manner postulated for Lake Tulane), the quantity of the metal accumulated in the oxidized soils would have been limited to that deposited in a few thousand years.

The Florida peninsula, on the other hand, would have had Hg accumulating for at least 80 000–100 000 years. That process could have begun once global sea level started falling. The classic oxygen isotope records,⁴⁰ which represent sea level and ice volume, indicate that onset of ice accumulation leading into the most recent ice age would have been well underway by 100 000 years ago, initiating the long period of accumulation of Hg–organic and Hg– $\text{Fe}(\text{OH})_3$ complexes. In other words, whether driven by large changes in sea level or by a combination of other factors influencing regional water table, the key determinant in whether a large release of Hg would follow a rising water surface would be the length of time during which the Hg would be accumulating, and the cumulative amount available to release when anoxic conditions returned.

The flux of Hg to Lake Tulane sediment (Figure 3) has varied substantially through time. From 45 000 to about 15 000 years BP, the flux varied between <2 to about $10 \mu\text{g m}^{-2} \text{yr}^{-1}$. It then increased to a peak of about $45 \mu\text{g m}^{-2} \text{yr}^{-1}$, concurrent with the peak in concentration (Figure 1), declined coincident with the Younger Dryas, increased rapidly to a peak of about $60 \mu\text{g m}^{-2} \text{yr}^{-1}$ about 5000 years BP, and has since declined to about $10 \mu\text{g m}^{-2} \text{yr}^{-1}$ by 900 years BP, still substantially above pre-Holocene values. We interpret the minimum during the Younger Dryas to the slowing, by about 80%, of sea level rise.⁴¹ This would allow less soil to be inundated per unit time and also allow for depletion of the Hg reservoir in the anerobic soil profile. The pre-15 000 years BP Hg accumulation rate is larger than the early Holocene rate at Caribou Bog, Maine ($1.3 \mu\text{g m}^{-2} \text{yr}^{-1}$)⁴ when that site was a very shallow lake and the sediment was minerotrophic. Postglacial and early Holocene Hg fluxes to sediment of Sargent Mountain Pond, Maine ranged from 1 to $3 \mu\text{g m}^{-2} \text{yr}^{-1}$.⁴² Background atmospheric wet

deposition in Maine must have been less than at Tulane, because these northeastern lakes had watersheds contributing Hg to the lake.

Unfortunately we do not have sediment for the last 1000 years at Tulane. Mercury accumulation rates in Everglade Florida lakes, to the south, average $53 \mu\text{g m}^{-2} \text{yr}^{-1}$ for post-1985 sediment, with a range from 23 to $141 \mu\text{g m}^{-2} \text{yr}^{-1}$ ($n = 18$).⁴³ For the late 19th century, deposition in these same lakes was about 20% of the late 20th century, presumably as a consequence of increasing atmospheric anthropogenic pollution. Tulane averaged about $20 \mu\text{g m}^{-2} \text{yr}^{-1}$ during the Holocene, and averaged about $6 \mu\text{g m}^{-2} \text{yr}^{-1}$ between 20 000 and 40 000 years BP. Between 6000 and 4000 years BP, Tulane averaged $40 \mu\text{g m}^{-2} \text{yr}^{-1}$. Thus, the mid-Holocene peak was similar in value to mid-1980s pollution. Tulane is a relatively steep-sided lake and likely there is some sediment focusing and thus an exaggeration of the atmospheric deposition rate. Thus, we suggest that background Hg atmospheric deposition in central Florida was <2 to $10 \mu\text{g m}^{-2} \text{yr}^{-1}$ prior to 20 000 years BP. Interestingly, in 2010 atmospheric wet deposition of Hg to peninsular Florida was about $15 \mu\text{g m}^{-2} \text{yr}^{-1}$,⁴⁴ primarily in the summer. It is not known whether this total is dominated by anthropogenic pollution, but our study suggests that to be the case, and at least four times background values.

An alternative hypothesis is that higher flux of Hg from the upper atmosphere in the past caused the variation in Hg concentration and flux recorded in the sediment. Puerto Rico currently receives about $28 \mu\text{g Hg m}^{-2} \text{yr}^{-1}$ in precipitation,⁴⁵ more than twice the wet loading in Florida (SI Figure 3). With no point sources, this high flux is attributed to scavenging from the upper troposphere and lower stratosphere, largely in convective storms similar to those that occur in Florida today. The high values may be enhanced by the greater topographic relief in Puerto Rico (1000 m versus 100 m), and almost certainly they were not so high in the preindustrial period. However, if the same process led to Hg transport from the upper atmosphere during prehistoric convective storms in Florida, then Hg should be high whenever *Pinus* vegetation dominates. That is clearly not the case (Figure 3).

The processes identified here for Hg in Lake Tulane are likely to occur in other regions of the world in coming decades. Mercury mobility will be particularly pronounced where soil Hg has accumulated for a long period, and where the groundwater table beneath these soils is tied to nearby sea level, which may well rise by a meter or more in the 21st century. The transition from unsaturated to saturated soils should result in the mobilization of any redox-sensitive elements, including Fe, Mn, and Co, and elements that may complex with them, such as Hg (this paper), some rare earth elements, and elements that form oxyanions such as As (arsenate/arsenite; e.g., Bangladesh), and Cr (chromate/chromite).

Policy initiatives designed to lower emission of Hg to the atmosphere and lower Hg in the environment will be judged effective only to the extent that they acknowledge the natural variability of Hg in the environment caused by multiple factors, including changing groundwater table. The latter may be driven by rising sea level, changes in land use or land cover, or changing precipitation and evapotranspiration, all of which are linked to climate change.

■ ASSOCIATED CONTENT

📄 Supporting Information

We include time series data for mass accumulation rate, and loss-on-ignition (“organic matter”) accumulation rate and concentration (SI Figure 1); concentration of Ti, Fe, Al, and Hg, and mass ratios of Hg:Ti and Hg:Al (SI Figure 2); and yearly cumulative Hg deposition for western Florida for four different years (SI Figure 3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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