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Trace elements and heavy metals in the Grand Bay National Estuarine Reserve in the northern Gulf of Mexico

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Abstract

The objectives of this study are to investigate distribution of trace elements and heavy metals in the salt marsh and wetland soil and biogeochemical processes in the Grand Bay National Estuarine Research Reserve of the northern Gulf of Mexico. The results show that Hg, Cd and to some extent, As and Pb have been significantly accumulated in soils. The strongest correlations were found between concentrations of Ni and total organic matter contents. The correlations decreased in the order: Ni > Cr > Sr > Co > Zn, Cd > Cu > Cs. Strong correlations were also observed between total P and concentrations of Ni, Co, Cr, Sr, Zn, Cu, and Cd. This may be related to the P spilling accident in 2005 in the Bangs Lake site. Lead isotopic ratios in soils matched well those of North American coals, indicating the contribution of Pb through atmospheric fallout from coal power plants.

Keywords

Environmental impact; Estuarine chemistry; Trace elements; Biogeochemical process; Lead isotopes; Grand Bay Reserve

1. Introduction

Anthropogenic activities lead to the release of a significant amount of heavy metals and trace elements into estuaries from agricultural fields, residential areas, septic tanks, industrial discharges, and other point sources by rivers and creeks. Estuaries are known areas of inflow plagued with extreme physico-chemical changes that are the direct result of

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tidal variations (de Vallejuelo et al., 2014). Sediment, soil, water and organic material in these areas may contain significantly higher levels of heavy metals and trace elements. Partly due to large quantities of dissolved organic complexes and particulate matter, heavy metals are translocated for great distances and end up in the sediments of estuaries, thus reflecting in the relatively high levels of these elements in numerous estuarine organisms and in sediments (Ip et al., 2007). This produces a detrimental effect on the biogeochemical cycling and biochemical balance in estuaries. The major inputs of heavy metals and trace elements to estuaries are from riverine, atmospheric, and anthropogenic sources. Therefore, the environmental fate of heavy metals and trace elements such as Pb, Cd, Hg, and As in estuaries is of great concern (Adriano, 2001), specifically those originating in or around industrial centers, dumps, and former mine sites near estuaries.

The physical behavior of an estuary is a major factor in the transport and transformation of heavy metals and trace elements. Since estuaries are governed by the tidal and river flow from the sea, various salt mixing zones, and physicochemical parameters, the biogeochemical processes of trace elements and heavy metals could be drastically affected. These processes include: precipitation and co-precipitation, flocculation and net sedimentation, desorption and adsorption, immobilization and solubilization, re-suspension of subsequent metals and transformation. The results may yield complex distribution patterns, which may differ from one estuary to another.

The Grand Bay National Estuarine Research Reserve (Grand Bay NERR) (approximately 18,000 acres) is located in the Gulf of Mexico, along the southeastern corner of Mississippi in Jackson County. This reserve contains a variety of wetland habitats, both tidal and non-tidal, such as pine savannas, salt marshes, saltpans, bays and bayous, as well as terrestrial habitats that are unique to the coastal zone, such as maritime forests (Peterson et al., 2007). The Grand Bay NERR is an important ecosystem because of the biodiversity of habitats. These habitats support many important species of fish and wildlife. Commercially and recreationally important species of finfish and shellfish such as brown shrimp, speckled trout and oysters abound in the region. Sea turtles, bottlenose dolphin and, on occasion, manatees can be found in the deeper waters of the reserve. Many species of carnivorous plants and orchids can be found in the higher savanna habitats. The Grand Bay NERR is a representative of the Louisianan biogeographic region and is in the Mississippi Deltaic subregion (Peterson et al., 2007).

In 2005, a local fertilizer company accidentally released 17.5 million gallons of waste water containing phosphorus (P) from retaining ponds into Bangs lakes (BL) in the Grand Bay Reserve, resulting in approximately 8 hectares of tidal marsh and 77 hectares of upland devastation (Peterson et al., 2007). Bangs Lake is an estuary of the Grand Bay Reserve of approximately 0.87 sq. mi. and its wetland is dominated by grass vegetation rooted in salt marsh soils comprised of an environmental matrix of biological and chemical interactions. The pH of the lake was drastically decreased and the PO_4 concentration was 144 μM (4.7 ppm), then has declined (Peterson et al., 2007). However, after 7 years of the accident, it is essential to re-assess the environmental effects of this P spilling accident on the biogeochemistry of trace elements and heavy metals of the reserve.

To date, a systematic study on the biogeochemistry of trace elements and heavy metals in the Grand Bay Reserve has not been conducted. Such a study would not only provide a solid scientific understanding of the biogeochemical processes controlling major biogeochemical cycling of these elements in the region, but would also secure sea food safety in large areas of the Gulf of Mexico. The objectives of this study are to investigate distribution of trace elements and heavy metals and major biogeochemical processes controlling their fate and transport in the Grand Bay National Reserve and to re-assess the environmental impacts of the 2005 P spill by ascertaining its long-term effects on the biogeochemistry of trace elements and heavy metals in the estuaries.

2. Materials and methods

2.1. Site description and field sampling

One hundred and twenty (120) samples were collected from four sites within the estuary in the summer of 2012: Bayou Heron (BH), Bayou Cumbest (BC), Crooked Bayou (CB), and Bangs Lake (BL) (Fig. 1). The Grand Bay National Estuarine Research Reserve (NERR) in the Gulf of Mexico is within a humid-temperate, nearly subtropical region with average annual rainfall of 184.4 cm between 1947 and 2003 (Peterson et al., 2007). The Grand NERR encompasses about 7446 hectares and consists of open water estuarine areas, muddy intertidal areas, a wide variety of marsh types, extensive and non-vegetated salt flats or pannes, and non-tidal areas (Peterson et al., 2007). The non-tidal areas include wet pine savanna, coastal bayhead and cypress swamps, freshwater marshes and maritime forests. There is also a 1.5–2.0 km wide marshy swampy wetland zone that separates the Grand Bay NERR shoreline from uplands that are underlain by Pliocene-age alluvial sandy-muddy soil – which is composed of gravelly Citronelle formation representing most of land surface in southern Mississippi (Otvos, 1990, 1997, 2000).

In general, Crooked Bayou is dominated by *Juncus* marsh and large vegetated shell midden. Bayou Cumbest is the site with soft sediments and unconsolidated oyster shell reefs. Bayou Heron is composed of a bottom type of soft muddy sediment that serves as a transition to a habitat of maritime slash pine flatwoods/savanna. Bangs Lake (BL) is more surrounded by industry and has extensive algal blooms in its shallow enclosed waters due to high P levels.

The geographical location of the sampling points were marked using a Garmin GPS. The samples were collected using a stainless steel soil testing probe at a depth of about 20 cm. The collected samples were packed in polyethylene bags and labeled before performing laboratory geochemical analysis. The packed samples were air dried in the greenhouse and homogenized using an agate mortar. The air-dried samples were then sieved through a 125 μ m mesh.

2.2. Soil characterization

The determination of the concentration of the total organic carbon and nitrogen in the samples was performed with a Shimadzu TOC analyzer. Soil texture and particle size analyses were conducted using the hydrometer method (Klute, 1986). Free Fe oxides were analyzed by the citrate–bicarbonate dithionite method (Sparks, 1996). Fe and Mn in solution

were determined with inductively coupled plasma optical emission spectroscopy (ICP–OES).

2.3. Trace element and heavy metal extraction and measurement

A Hot Block digestion method was employed to perform the tests of the total metal/metalloid contents in the estuarine soil samples (USEPA method 3050B). About 1 g of the soil was digested with a mixture of H₂O₂ (30%) and HNO₃ (concentrated). The samples were heated to 95 ± 5 °C (hot block) to reflux for 10–15 min without boiling. This solution was analyzed for trace elements and heavy metals using both inductively-coupled plasma–optical emission spectrometry (ICP–OES) (Perkin Elmer OPTIMA 3300 DV model) and inductively-coupled plasma mass spectrometry (ICP–MS) (Varian 820-MS ICP Mass Spectrometer). The ICP–OES was used for the analyses of Cu, Pb, Zn, Cr, Cd Ni, Fe, and Mn. The ICP–MS was used for the analyses of As, P, Hg, and Pb isotopes in all extracts. Multi-elements standards were made to the following concentrations: 0.02, 0.05, 0.1, 0.5, 1, and 2 mg/L for all elements except for Fe and Mn which was up to 5 mg/L for ICP–OES, while for ICP–MS, 0.02, 0.05, 0.1, 0.5 mg/L of P, As, Hg, and Pb isotopes were used.

The separate five independent standard solutions were prepared with concentrations from 0.05 mg/L to 2.0 mg/L and run as the samples for four times in order to check the accuracy and precision of ICP–OES. Independent standard solutions resulted in average 100.7–113.0% recoveries of Cd, Ni, Zn, Cr, Pb, Cu, Fe, and Mn at the concentrations from 0.1 mg/L to 2.0 mg/L and 90.5–120% average recoveries for the concentration at 0.05 mg/L. The relative errors among four repeated running were 0.1–10% for standard solutions with concentrations of 0.1–2.0 mg/L and 2–20% for standard solutions at 0.02 mg/L. Similar QA/QC procedures were also used for ICP–MS.

3. Results and discussion

3.1. Characterization of estuarial soils

The estuary soils are characterized by a majority of silt (54%) and sandy fractions, with relatively high organic matter (3.82% on an average) (Table 1). The silt contents ranged from 28% to 96% with 19% coefficient of variation (CV) and the sand particles ranged from 3.6% to 72% with 25% CV. Total organic matter contents varied from 0.52% to 10.2% with an average of 3.82% and a standard deviation of 2.1%. Organic N contents were in the range of 0.02–0.46% with an average of 0.11 ± 0.10%. The estuarine samples contained low amounts of iron and manganese oxide. Iron oxides averaged 0.16 ± 0.11% and Mn oxides were in the range of 0–0.012% with an average of 0.0006 ± 0.001%.

Iron and Mn oxides were relatively depleted compared to other upland soils. This may be related to the frequent changes of redox potentials and the leaching out of the soil where Fe and Mn oxides were reduced and became soluble in the sea water. Under saturated emergent regime, redox potential rapidly decreased. With a decrease in pE (redox potential, oxidation/reduction potential), iron and Mn were reduced from iron oxides such as amorphous and crystalline oxides into soluble and exchangeable iron, possible formation of carbonate (CARB) in the upland soils occurred with 2.4–11.2% Fe oxides and 0.03–0.06% Mn oxides (Han and Banin, 1996; Han et al., 2002b). Walna et al. (2010) reported that even in surface

layers of nutrient-poor forest soil (2% of Fe oxides and 0.03% Mn oxides), larger amounts of exchangeable and acid-extractable iron and manganese were found than those in deeper layers (47% of Fe oxides and 0.05% of Mn oxides). At reducing conditions, Fe/Mn oxide reduction serves as a major driving force for redistributing trace elements and heavy metals in soils (Han and Banin, 1996). Grybos et al. (2007) reported that reducing conditions in wetlands lead to the release of many trace elements into soil solutions by a factor of 20–25 which was concomitant with reductive dissolution of soil Fe-oxyhydroxide reduction as well as with strong dissolved organic matter release. Han and Banin (2003) also observed that saturated incubation of arid soils release significant native trace elements including Co, Cu, Zn, Ni, Pb, and As as the soluble and exchangeable form.

3.2. Spatial distribution of trace elements and heavy metals in the Grand Bay reserve

The heavy metal and trace element concentrations in the samples from the Grand Bay reserve are presented in Figs. 2 and 3. Concentrations of trace elements followed the order: Pb > Sr > Cr > As > Zn > Cu, Ni > Cd, Se > Hg > Cs > Co. Large spatial variations were found for As, Zn, Hg and Co with CV% > 100%, the rest of elements varied around 50%. This indicates that trace elements in the Grand Bay Reserve may be contributed from various sources and controlled by different biogeochemical processes. Often, solid phase components govern the dissolved levels of trace elements via sorption–desorption and dissolution–precipitation reactions (Han, 2007).

Compared to the global scale, ratios of concentrations of these elements in Grand Bay to the concentrations in worldwide soils and the global lithosphere (Han et al., 2002a; 2003) were calculated (Fig. 4). It was found that Hg and Cd seemed to be strongly polluted by anthropogenic processes. Ratios of Hg and Cd in the Grand Bay reserve over the global lithosphere were in the range of 20–40 and the ratios of Hg over global soils were also above 30.

The comparison of the trace elements and heavy metals among four sites (CB, BC, BH and BL) revealed that most of the samples from the Bangs Lake (BL) site in the Grand Bay reserve contained high concentrations of Cr, Sr, As, Zn, Cu, Ni, Cd, and Co. All these elements were significantly higher in the BL site than the rest of three sites (Fig. 5). This may be related to overall higher industrial activities especially anthropogenic P spilling in 2005. This will be discussed in detail below. Additionally, the levels of Pb and As were higher in BC than the rest of three sites and Hg (3 mg/kg⁻¹) was significantly higher in BH sites.

The Crooked Bayou (CB) site, dominated by *Juncus* marsh plants, showed concentrations of these trace elements in the order of Pb > Cr > Sr > As > Zn > Cu > Ni. Both Bayou Heron (BH) site and Bayou Cumbest (BC) site had similar concentrations of these elements (Pb > Cr > Sr > Zn > Ni > As and Pb > As > Sr > Cr > Zn > Cu > Ni for the BH and BC sites, respectively). Salinity in the BH site tends to decrease rapidly when rain events occur at the site or within the watershed. BC site is over soft sediments with unconsolidated oyster shell reefs. Lastly, Bangs Lake (BL) was characterized by the decreasing order of the concentrations of elements from Sr to Ni (Sr > Cr > Zn > As > Cu > Ni) and has experienced extensive algal blooms in its shallow enclosed waters, due to high P levels.

Slightly higher values were observed in the Bangs Lake [30°21.426'N, 88°27.774'W], which is a more industrial area of the estuary (Pb 20 mg/kg), Cr (48 mg/kg), Sr (74 mg/kg⁻¹), As (39 mg/kg⁻¹), Zn (43 mg/kg⁻¹), Cu (18 mg/kg⁻¹), Ni (17 mg/kg). Cd and Ni concentration levels were the lowest in the northern part of the estuary in Crooked Bayou and Bayou Heron (e.g. Cd 2–3 mg/kg⁻¹ and Cs 1 mg/kg⁻¹). The current concentrations of these elements were similar to the concentrations observed from Holocene peat soils in Philippine (Christanis et al., 1998).

3.3. Effect of bioaccumulation processes on accumulations of trace elements and heavy metals

Bioaccumulation processes play an important role in the accumulation of trace elements and nutrients in soils. Trace elements and heavy metals were taken up by wetlands and marsh plants either via active uptake as nutrients such as Zn and Cu or passive uptake as non-essential elements (such as Cd, Ni, Cr, As etc) from seawaters and soil. Some trace elements such as Cs and Sr behavior similarly as nutrients K and Ca, respectively, which may compete uptake by plants with respective nutrients. After death, trace elements and heavy metals have been accumulated in the original soils with the decomposition of these biomass residues and transformation and formation of soil humic materials. The current study shows strong correlations between concentrations of heavy metals/trace elements/phosphorus and organic matter content (Ni Cr, Sr, Zn, Co, Cd, Cu, and P) (Fig. 6). The strongest correlations were found for Ni while the weakest one for As. All these trace elements showed significant correlations with soil organic matter (at 0.01 probability level). The correlations between the organic matter content and element concentrations decreased as follows: Ni (r^{***} : 0.82, n : 126) > Cr (r^{***} : 0.76), Sr (r^{***} : 0.75) > Co (r^{***} : 0.72) > Zn (r^{***} : 0.66), Cd (r^{***} : 0.65) > Cu (r^{***} : 0.62) > Cs (r^{***} : 0.35) > As (r^{**} : 0.25). This may be related to the fact that Cr, Co, Zn, and Cu are essential micronutrients of plants and microbes. On the other hand, Cd, Ni, Cr, and Sr showed strong correlations with organic matter even though they are not essential nutrients. This implies these elements either had strong tendency to be accumulated by plants and microbes (Han et al., 1990) and/or the direct sorption of these elements onto the surface of soil organic matter (SOM). Sr behaves biogeochemically and biologically like Ca, and Cd like Zn to some extent (Su et al., 2007). Du Laing et al. (2009) suggested that decaying plant material caused litter to accumulate and contribute to the binding of metals by adsorption, complexation and chelation. Soils with high organic matter usually bind heavy metals more efficiently (Han, 2007; Chen et al., 2010). However, the overall effect of the presence of soil organic matter on metal mobility and bioavailability depends on their nature of SOM and relative abundance of other minerals in marsh soils. On the other hand, no correlations were found between Pb, As and Hg concentrations and organic matter contents (data not shown). This may imply that these three elements are not bioaccumulated elements in the Grand Bay reserve.

3.4. Effects of anthropogenic phosphorus spilling accident

The phosphorus spilling accident in 2005 caused a significant increase in P concentrations in the Bangs Lake site compared to the other three sites (Fig. 7). The total P in samples from Bangs Lake (BL) contained 234–657 mg/kg P with an average of 369 ± 234 mg/kg in 7 years after the spilling accident. BH sites had 73–249 mg/kg P with an average of 137 ± 42

mg/kg, followed by BC and CB sites (with an average of P 110–106 mg/kg). All four sites had similar CV% at 30–31% in the CB, BC and BH and 35% in BL. This indicated that similar processes controlled the P spatial distribution in the Grand Bay Reserve: the 2005 P spilling accident.

The BL's P concentrations in the current samples after 7 years of the accident were still 3 times higher than the other three adjacent sites. In 2005, approximately 17.5 million gallons of waste water containing phosphorus (P) were accidentally released from retaining ponds into Bangs Lake. This directly resulted in approximately 8 hectares of tidal marsh and 77 hectares of upland devastation (Peterson et al., 2007). The pH of the lake was drastically decreased due to the spill and the PO_4 levels in the lake were found to be 144 μM (4.7 ppm) (Peterson et al., 2007).

Since P retaining waters contained many other trace elements and heavy metals, this accident significantly increased the concentrations of many trace elements in the Grand Bay reserve. We found strong correlations between the total P concentrations and concentrations of Ni, Co, Cr, Sr, Zn, Cu, and Cd (Fig. 8). Among these elements Ni showed the strongest correlation ($r = 0.87$) with P, followed by Co (0.85), Cr and Sr (0.83), Zn (0.81), Cu (0.71) and Cd (0.69). This indicates that the P spill clearly contributed to the accumulation of these elements in these areas. On the other hand, As, Hg, Cs and Pb were not found to have such correlation (data not shown).

Surface soil from agricultural lands and residential areas may act as an internal source for P contributing to the P in the water body (Conley et al., 2002). Anderson et al. (2008) reported that over the past decades, inputs of P and other nutrients have altered coastal nutrient cycling worldwide. This is the result of nutrient supply increasing from human activities, which lead to harmful algal blooms. Often, the mobilization of P is dependent upon organic matter degradation, desorption, and mineral dissolution reactions (Ingall et al., 1993). Conversely, coastal hypoxia has been seen to intensify the availability of P by reducing the burial of P bound to Fe oxides and to organic matter. Lin (2013) clarifies that P in aquatic environments can exist in organic and inorganic forms and particulate species may play a key role in the biogeochemical cycling of P and other trace elements, as well as the transformation of these forms in estuarine environments.

3.5. Effects of atmospheric fallouts, contribution from local coal burning power plants

Lead isotopes ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$) in the samples from the Grand Bay are presented in Fig. 9. The ratios of $^{206}\text{Pb}/^{208}\text{Pb}$ were 1.15–1.28 with an average 1.21 ± 0.03 and the ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ were in the range of 0.43–0.53 with an average of 0.48 ± 0.02 (n : 120). The Pb isotope distribution in the samples from the Grand Bay matched well with Pb isotopes of the North American coals (Díaz-Somoano et al., 2009). This indicates that the coal burning power plants may have been a significant source of current Pb concentrations in the region. The nearest coal burning power plant located in the northwest portion of the reserve has annual 1100MW capacity with coal and subbituminous coal. The tropical Atlantic gulf cyclonic wind from the North and North West can bring all gas and suspended particles into the Bay areas.

The current Pb isotopes were in a similar range of Pb isotopes reported in the sediments from Chesapeake Bay and from South Florida lakes (Marcantonio et al., 2002; Escobar et al., 2012). In the sediments from Little Lake Jackson and Little Lake Bonnet in Highlands County, Florida, the sediment records showed that changes in Pb concentration and isotope ratios correspond temporally with gasoline consumption in the USA, as well as with changes in lead ores used to produce leaded gasoline (Escobar et al., 2012). They found that Pb isotope trends were similar to the mean USA atmospheric Pb deposition records, and to Pb isotope records from Bermuda and Atlantic corals. Marcantonio et al. (2002) reported the relationship between anthropogenic $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios and the age of sediment cores in Chesapeake Bay cores. They found that the interval of sediment between top 33 and 0 cm appears to represent deposition between 1880 and 1920. The ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ were around 1.20–1.21, in agreement with the ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ in the Grand Bay reserve in the Gulf of Mexico as observed in the present study. They concluded that from about 1800 to 1930, the Pb signal in the Chesapeake Bay sediments was probably derived from the burning of coal.

However, the current Pb isotopes from the Grand Bay Reserve in the Gulf of Mexico were far from those of petroleum derived Pb (Fig. 9) (The Pb isotopes in petroleum source were from Atkinson et al., 2011). This clearly shows that the current car emission is not the major source of the Pb deposited in the soil of the Grand Bay in the Gulf of Mexico. The petroleum derived Pb may be one of the major sources for Pb in the deep deposits of soils of the area due to Pb being used as an additive to gasoline before the 1970s. Tetraethyl lead $((\text{CH}_3\text{CH}_2)_4\text{Pb})$ is an organolead compound from the 1920s through the mid-1970s. The current study suggests that Pb in the wetland and salt marsh soils of the Grand Bay Reserve in the Gulf of Mexico may be from atmospheric fallouts primarily contributed from the power plants.

4. Conclusion and ecosystem implications

Soils from wetlands and salt marshes of the Grand Bay National Reserve in the northern Gulf of Mexico were characterized by a majority of silt, and total organic matter contents varied from 0.52% to 10.2%. The wetland and salt marsh soils have low iron oxides and Mn oxides compared to most upland soils. This may be due to the frequent reduction/oxidation processes, leaching out of the most of Fe/Mn oxides. Concentrations of trace elements in the soils of the region followed the decreasing order: $\text{Pb} > \text{Sr} > \text{Cr} > \text{As} > \text{Zn} > \text{Cu}, \text{Ni} > \text{Cd}, \text{Se} > \text{Hg} > \text{Cs} > \text{Co}$. Large spatial variations were found for As, Zn, Hg and Co ($\text{CV}\% > 100\%$), where the rest of elements varied around 50%. This indicated that trace elements in the Grand Bay Reserve may be contributed from a variety of sources and controlled by different biogeochemical and anthropogenic processes.

Compared to the global concentrations of these elements in worldwide soil (unpolluted soils) and in the global lithosphere, Hg and Cd seemed to be strongly polluted by anthropogenic processes and As and Pb were also fingerprinted by anthropogenic pollution. Strong correlations were found between total organic matter contents and concentrations of elements in the following order: $\text{Ni} > \text{Cr} > \text{Sr} > \text{Co} > \text{Zn}, \text{Cd} > \text{Cu} > \text{Cs}$. This may be related to the fact that either they are essential micronutrients to plant and microbes or behave

biologically and biogeochemically like essential elements. The P spilling accident in 2005 caused a significant increase in P concentrations in the Bang Lake site collected in 2012 compared to the other three sites 7 years after the accident. We found that strong correlations exist between the total P concentrations and concentrations of Ni, Co, Cr, Sr, Zn, Cu, and Cd. Finally Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$) showed strong agreements with Pb isotopes from North American coals, implying that the Pb of current wetland soils of the Grand Bay area is mainly contributed from the coal burning power plants. The Pb isotopes were in agreement with those reported in sediments of Chesapeake Bay and South Florida Lakes. The present study implies the current occurrence of trace elements and heavy metals in the Grand Bay area are strongly affected by other biogeochemical processes such as bioaccumulation processes, anthropogenic phosphorus spilling, and atmospheric fallouts from coal power plants.

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Fig. 1. Location of the Grand Bay National Estuarine Reserve in the Gulf of Mexico and sampling sites (indicated by solid dots) (modified from Peterson et al. (2007)).

Fig. 2.
Concentrations of trace elements and heavy metals in the Grand Bay Reserve, the Gulf of Mexico, USA.

Fig. 3.
Variance in concentrations of trace elements and heavy metals in soils from the Grand Bay Reserve, the Gulf of Mexico, USA.

Fig. 4.

Ratios of concentrations of trace elements and heavy metals in the Grand Bay Reserve, The Gulf of Mexico, USA over concentrations in the lithosphere and world soil (concentrations of trace elements and heavy metals in the world soil and global lithosphere are from Han et al. (2002a,b, 2003), Taylor and McLennan (1985), Ure and Berrow (1982), Aubert and Pinta (1977), Bowen (1982), Baur and Onishi (1969), Lide (1996), Bockris (1977)).

Fig. 5. Comparisons of trace elements and heavy metals in various sites from the Grand Bay Reserve, the Gulf of Mexico, USA (CB: Crooked Bayou site; BC: Bayou Cumbest site; BH: Bayou Heron site; and BL: Bangs Lake site).

Fig. 6. Strong correlations between concentrations of trace elements and organic matter content in soils from the Grand Bay Reserve in the Gulf of Mexico, USA.

Fig. 7. Phosphorous accumulation in sites of the Grand Bay Reserve (above) and strong correlations between concentrations of P and OM% in soils (CB: Crooked Bayou site; BC: Bayou Cumbest site; BH: Bayou Heron site; and BL: Bangs Lake site).

Fig. 8. Strong correlations between concentrations of trace elements/heavy metals and total phosphorus content in soils of Grand Bay Reserve, the Gulf of Mexico, USA.

Fig. 9.

Distribution of Pb isotopes in the soil samples from the Grand Bay Reserve of the Gulf of Mexico (above) (BH: Bayou Heron site; CB: Crooked Bayou site; BL: Bangs Lake site and BC: Bayou Cumbest site) and their comparisons with reference samples (below). Pb isotopes in North American Coal, petroleum derived Pb, Chesapeake Bay sediments and South Florida lake sediments were from Díaz-Somoano et al. (2009), Landmeyer et al. (2003), Atkinson et al. (2011), Marcantonio et al. (2002) and Escobar et al. (2012), respectively.

Table 1

Selected relevant soil physicochemical properties.

	Organic matter%	Total organic N%	Clay%	Silt%	Sand%	Fe ₂ O ₃ %	MnO ₂ %
Average	3.82	0.11	2.48	53.92	43.61	0.161	0.0006
Standard deviation	2.07	0.10	2.87	10.34	10.84	0.109	0.001
CV%	54	87	116	19	25	68	234
Maximum	10.15	0.46	11.99	96.39	72.06	0.707	0.012
Minimum	0.52	0.02	0.00	27.94	3.61	0.004	0