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Investigating the Potential Impact of Louisiana Coastal Restoration on the Trace Metal Geochemistry of Constructed Marshlands

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Abstract: Coastal restoration through diversion of suspended sediments from the Lower Mississippi River (LMR) into hydrologically isolated marshlands of Mid-Barataria Bay and Mid-Breton Sounds in southern Louisiana has the potential to mobilize lead (Pb), and other trace elements. We investigate the potential impact(s) of the diversion on marsh porewater through analysis of modern riverbank and suspended sediments, compared to sediments from pre-industrial deltaic deposits of LMR. Sequential extraction methods were used to evaluate Pb, cobalt (Co), copper (Cu), nickel (Ni), and zinc (Zn) in the sediments. Our results show that metal contents are higher (e.g., 8- to 10-fold for Pb) in the modern sediments relative to pre-industrial deposits. Also, the reducible fraction, presumably iron/manganese (Fe/Mn) oxides/oxyhydroxides, is the chief reservoir of environmentally available metals. The substantially higher trace metal contents of the modern relative to pre-industrial sediments suggest that the modern sediments contain a sizeable amount of anthropogenic contributions. Furthermore, the concentration of the trace metals in the reducible fraction suggests bioavailability to marsh organisms upon reductive dissolution within the planned, constructed coastal marshes. Still, additional sediment samples from the marshlands during the diversion implementation phase will be necessary to support the preliminary findings in this contribution as it affects coastal marshes and vital local fisheries.

Keywords: Trace metals; sequential extractions; contaminated sediment; wetlands/marshlands; Lower Mississippi River; diversions; redox conditions; Fe/Mn oxides/oxyhydroxides

1. Introduction

Coastal areas like southern Louisiana are currently threatened by rising sea levels, increasing intensities of tropical cyclones and their associated storm surge, and land subsidence in sediment-starved locations (e.g., [1–7]). The combination of these processes has been met by building flood control structures as well as numerous coastal restoration projects (e.g., [8–17]). Developing innovative coastal management solutions is especially important in southern Louisiana where land loss within the coastal marshes has been severe (ca. 62 km^2 a^{-1} over the past 80 years) and is likely to continue due to a combination of factors including sea-level rise, land subsidence, and anthropogenic activities [18,19] even under the best management solutions [20]. For example, the extensive artificial levee system along the Mississippi River currently prevents deposition of river-borne sediments to the adjacent marshes, which under natural conditions maintains the marshlands and counters land subsidence. The coastal marshes of southern Louisiana are critically important for sustaining local fisheries, as the first line of defense against storm surge from tropical cyclones, and in preserving the unique cultural heritage of the region [7,21–24].

To combat land loss in the Lower Mississippi River (LMR) delta and associated coastal marshes, the Coastal Protection and Restoration Authority of Louisiana (CPRA) proposed a number of diversion projects within its comprehensive coastal master plan to restore marshlands and protect coastal areas [21,22]. Two of these diversion projects involve building gated control structures and outfall channels capable of diverting between ca. 1420 m^3/s to ca. 2124 m^3/s of Mississippi River water and suspended sediments during the maximum flow season (i.e., December to June) into the adjacent brackish marshlands of Mid-Barataria Bay and Mid-Breton Sound [25–28]. A 50-year model simulation of these proposed diversions estimated that the total cumulative suspended sand load, at different discharge configurations between 141 m^3/s to 12,742 m^3/s, to the Mid-Breton Sound and Mid-Barataria Bay marshlands will be greater than 137 and 48 million tons, respectively [29]. Furthermore, if these marshlands are not protected from inundation, an estimated 1420 km^2 of land will be lost in the next 50 years owing to the above-mentioned processes, with potentially dire consequences to the local communities, including the city of New Orleans [30].

Although it is widely accepted that the planned coastal restoration projects will be beneficial to the community and society at large in southern Louisiana, there are limited investigations into the possible impact of diverted river sediments on water quality of the local coastal marshes [31–33]. The Mississippi River drains 40 percent of the contiguous United States and delivers a sediment load of 210 × 10^6 tons per year into the Gulf of Mexico [34,35]. Previous investigations demonstrated that these river sediments carry a substantial lead (Pb) load, and other potentially toxic trace metals like cadmium (Cd), into the Gulf of Mexico that are subsequently deposited in the offshore sediments [36–38]. Although the Pb load of Mississippi River sediments has decreased since the reduction of leaded gasoline began in the USA during the late 1970s and was completely phased out by the mid-1990s [34,39], the legacy of industrial Pb in sediments and soils of numerous communities remain a substantial environmental and human health problem (e.g., [40–48]). The Mississippi River and its tributaries (e.g., the Ohio River and Missouri River) drains much of the industrial and agricultural heartland of the USA, which also includes a number of large metropolitan regions such as Minneapolis-St. Paul (Minnesota), St. Louis, and Kansas City (both in Missouri), Davenport (Iowa), Memphis (Tennessee), Cincinnati (Ohio), Pittsburg (Pennsylvania), as well as Baton Rouge and New Orleans in Louisiana. Consequently, soil/sediment Pb re-mobilized from these or other population centers along the Mississippi River, and its tributary still likely contributes Pb and other potentially toxic trace elements to the river system and the Gulf of Mexico. To the best of our knowledge, the possible fate and transport of these potentially toxic, river-transported metals once the river sediments are diverted into the coastal marshes along the LMR has not been investigated.

It is well known that estuaries and marshlands can act as traps for metals and other anthropogenic contaminants, and may provide long-term, natural storage of such compounds [49–54]. However, it is also possible for these metals to be mobilized from estuarine and marsh sediments if the environmental

conditions change (e.g., changes in salinity, pH, and/or redox conditions; [55–61]). Such changes could occur by natural processes like subsidence and associated flooding of coastal freshwater marshes by seawater, burial and accompanying anaerobic respiration, early diagenesis, or via anthropogenic modifications like dredging and disposal of dredge spoils. Indeed, studies have clearly shown that when sediments are dredged or diverted, biogeochemical reactions occur that can modify the chemical compositions, including the redox conditions of pore water at the new placement site [32,33,62,63].

The chief sources of sediments to the planned Mid-Barataria Bay and Mid-Breton Sound diversions will be suspended sediments from the LMR, and perhaps some bed-load, both of which are currently transported by well-oxygenated Mississippi River water [21,22,64]. Consequently, possible effects of changing redox conditions on these sediments after deposition within the coastal marshes as they undergo early diagenesis driven, in part, by anaerobic respiration, necessitates careful investigation of the fate and transport of potentially toxic trace elements in these coastal marsh systems. Under the anaerobic redox conditions expected to predominate in these constructed marsh sediments (e.g., [33,65–68]), trace metals associated with reducible Fe(III)/Mn(IV) oxides/oxyhydroxides and/or oxidizable organic matter and sulfide minerals that are transported with the river sediments, could be mobilized into the marsh pore waters and possibly negatively impact marsh biota.

Although several studies have investigated the impact of the planned diversion projects on the LMR coastal marshes, these chiefly focused on sediment discharge, depositional dynamics, salinity gradients, nutrient accretion, and wetland restoration [69–74]. To our knowledge, none has explored the impact of changing redox conditions on trace metal mobilization as oxic river sediments are buried in the anaerobic, constructed coastal marshes. Here, we investigate the content of a number of potentially toxic trace metals (i.e., Co, Cu, Ni, Pb, and Zn) in modern Mississippi River suspended sediments collected from the water column and modern river sediments deposited along the riverbank in New Orleans, Louisiana. We also examine the content of these trace metals from Late-Holocene-aged sedimentary deposits collected from a borehole near the proposed Mid-Barataria Bay diversion site [75] as local controls for pre-industrial metal loading to the environment. All of these sediments were also subjected to sequential extraction analysis to examine metal speciation between five, operationally defined fractions that include, weakly adsorbed and easily exchangeable metals, weak acid leachable metals associated with carbonate minerals, metals associated with reducible Fe(III)/Mn(IV) oxides/oxyhydroxides, metals associated with oxidizable organic matter and/or sulfide minerals, and the residual metals contained within the crystalline lattice of alumino-silicate minerals that make up the bulk of the sediments. The results of the geochemical analyses of these LMR sediments are then employed to infer possible anthropogenic sources (e.g., Pb), and hypothesize the fate and transport of these potentially toxic trace metals carried by the river suspended sediments after diversion and burial within the coastal marshes.

2. Study Site

The study area consists of sites across the LMR delta plain associated with the planned "land building" projects described in the Coastal Master Plan of Louisiana [21,22]. Specifically, Figure 1 shows the locations of two planned river diversions along the LMR that are located approximately 35 km southeast of New Orleans [28]. These include the Mid-Barataria Bay Diversion Site located to the west of the river and the Mid-Breton Sound Diversion Site further south and east (Figure 1). The estimated mean annual water discharge for the planned Mid-Barataria and Mid-Breton diversions are 67 km^3/year and 31 km^3/year, respectively [27]. The region of the Mississippi River where suspended river sediments and water will be diverted to these sites is also shown and labeled "Site 2" in Figure 1. The modern suspended river sediments analyzed in this contribution were collected from this location [76]; previous research has shown that silts are generally well mixed within the water column of the Mississippi River along this reach due to turbidity [77]. Mississippi River sediments were also collected from the modern riverbank deposits in New Orleans adjacent to Tulane University on an aggrading point bar of the river (Site 1; Figure 1), as well as from Late-Holocene-aged deltaic sedimentary deposits obtained from

a borehole (Site 5) located southeast of New Orleans [75]. Sampling sites were selected to characterize past and present concentrations of potentially toxic trace metals in sediments of the LMR and to help infer anthropogenic metal loading compared to the probable natural background levels.
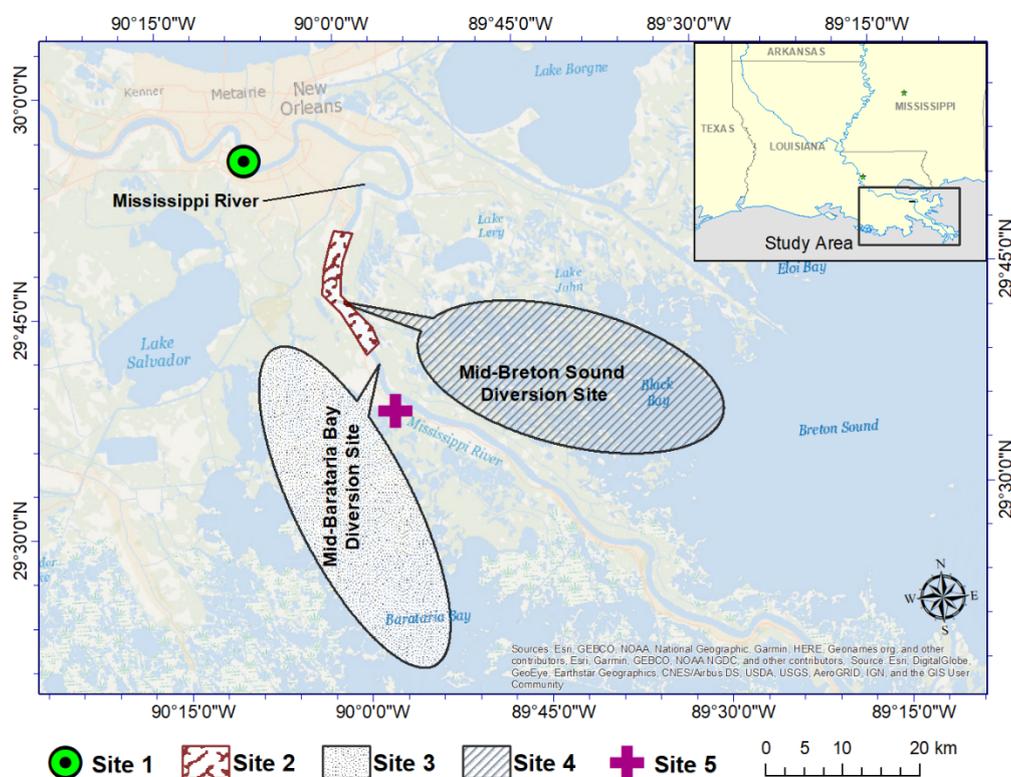
Figure 1. Map of the Lower Mississippi River delta showing the proposed diversion sites, and the sampling locations. Land is shown as yellow areas, whereas bodies of water are the blue regions. The sampling sites are located on the west and east side of the Lower Mississippi River (LMR) and deltaic plain: The green circle is Site 1 located at LMR bank near Tulane University. The light red polygon is Site 2, the proposed section of the LMR reach where suspended sediments will be diverted. The two polygons labeled "Mid-Barataria diversion" and "Mid-Breton diversion" are Site 3 and 4, respectively. The pink cross, Site 5, is the location of the pre-industrial deltaic deposits. Base map from ArcGIS. Inset shows the location of the study area within the State of Louisiana, USA.

Shallow subsurface sediments of Barataria Bay and Breton Sound consists of unconsolidated organic-rich muds and peats (i.e., >40% organic content; [78]) overlaying sand and silt beds [79,80]. The porosity of the marshland sediments is estimated to be 89 ± 3% (see [67,81]) with the bulk sediment consisting of ca. 80% mud and ca. 20% sand [25,28,74].

The proposed diversions that will feed new sediment to this region are slated for activation during periods of high suspended load, low saltwater intrusion, flooding, and high river discharge of about 28 to 7080 m^3/s [22,74,82]. The estimated average sediment load to be diverted onto the marshlands is between 1.5 to 2.3 million cubic meters per year, with a cumulative load of 76 to 115 million cubic meters in 50 years [83]. Currently, a detailed written Environmental Impact statement (EIS) is being prepared following the National Environmental Policy Act (NEPA) and Council on Environmental Quality (CEQ) regulations to analyze and disclose all possible significant impacts of the sediment diversion projects on the environment for permitting purposes [30]. The Mid-Barataria Bay and Mid-Breton Sound diversion projects are expected to commence after the completion of the environmental review and permitting process in the years 2023 and 2024, respectively [84,85]. The evaluation of both modern river sediments and Late-Holocene-aged sediments provide a means to investigate current metal loads of materials that will be diverted into the planned, brackish Mid-Barataria Bay and Mid-Breton Sound to help build

new marshland because the former provides information on present-day metal concentrations and the latter provides control to gauge pre-industrial metal concentrations in the LMR sediments.

3. Materials and Methods

3.1. Sample Collection

Sediment samples were collected from three different locations; the Mississippi riverbank near Tulane University (Figure 1, Site 1), the section of the LMR reach that is proposed as the chief sediment source for both the Mid-Barataria Bay and the Mid-Breton Sound diversions (suspended river sediments; Figure 1, Site 2), and from undisturbed sandy layers at ~5.4 and 10.8 m depth within a borehole (Figure 1, Site 5). The riverbank deposits (more than 2 kg) were obtained by grab sampling from the partly submerged riverbank into Ziplock® style polyethylene plastic bags in 2018. The suspended sediments were collected from the LMR water column on 18 April 2014, a period of high river discharge and sediment load (see [25,86]; for details of suspended sediment sampling). Briefly, suspended sediments were collected using a P-6-200 point-integrative isokinetic sampler obtained from Carnet Technology in Terry, MS. Sampling followed the standard USGS suspended sediment method at five individual water depths (0, 0.3, 0.5, 0.7, and 0.9 fractions of the total water depth). Samples were collected in duplicate at each depth using one-liter bottles (e.g., [87]). After collection, water samples were first filtered using a 63 μm sieve to separate the sand fraction, and then vacuum-filtered using 0.4 μm polycarbonate filters (i.e., the "mud fraction"; <63 μm). The filters containing the suspended sediments were then placed in airtight doubled polyethylene bags and stored at room temperature until analysis.

Late-Holocene-aged deltaic deposits were taken in 2017 from sandy units at ~5.4 m (TU 169, NCL-1217135) and ~10.8 m (TU 171, NCL-1217137) depth within a hand-drilled borehole situated in a modern marsh near the proposed Mid-Barataria diversion site. These sand units have been previously dated to ~1.3 and ~3.6 ka, respectively, and represent sediments deposited by past pathways of the Mississippi River [75]. The shallower sample is associated with the Balize (or, Plaquemines-Modern) lobe, and the deeper sample is associated with the St. Bernard lobe [75]. For a lobe chronology and synthesis of the Late Holocene evolution of the LMR delta, see Hijma et al. [88]. The sampled materials have not, to the best of our knowledge, been impacted by disturbances based on intact (not post-depositionally zeroed) luminescence signals and undisturbed stratigraphic layers within the borehole from which they were collected [75] and thus represent a pre-industrial baseline for trace metals in sediments of the LMR delta.

3.2. Leaching Procedures and Reagents

To investigate the speciation of Pb and the other potentially toxic trace elements (i.e., Co, Cu, Ni, and Zn) in the selected Mississippi River sediments, we subjected 0.5 g initial dry weight of each sample to the sequential extraction procedure (SEP) described by Tessier et al. [89], which is outlined in Table 1. The four sediment samples were dried at 80 °C in an air oven and then ground using an agate mortar and pestle to achieve homogeneity. These samples were also examined by X-ray diffraction (XRD) to determine their mineral composition.

Regarding the sequential extraction procedure, the four sediment samples were leached with progressively stronger reagents designed to attack operationally defined fractions of the sediment, and the concentrations of Co, Cu, Ni, Pb, and Zn were measured in each leachate fraction (see Table 1; [63,90]). The various reagents allow for the evaluation of potential trace element mobilization from the sediments owing to changes in pH, redox conditions, and possibly salinity by extracting the environmentally labile fractions of each trace metal [34,63]. Specifically, the fractions targeted by the SEP include: the easily exchangeable surface adsorbed fraction (Fraction 1); the acid leachable fraction associated with carbonate minerals (Fraction 2); the reducible fraction associated with Fe/Mn oxides/oxyhydroxides (Fraction 3); the oxidizable fraction associated with organic matter and possibly some sulfide minerals

(Fraction 4); and the residual fraction associated with silicate and aluminosilicate minerals (Fraction 5; see Table 1). The first four fractions essentially target trace metals that are environmentally labile, which can be mobilized as environmental conditions change (e.g., changes in redox conditions, pH, and salinity). Hence, the environmentally labile fractions of these trace metals are likely to be available to organisms (i.e., bioavailable) living in the sediments and/or associated pore waters. In contrast, trace elements associated with Fraction 5 are not environmentally mobile as they are considered to be contained within silicate mineral lattices [89].

Table 1. Details of the sequential extraction methods used to investigate trace element (TE) speciation in Mississippi River sediments. See Tessier et al. [89] for more details.

Fraction	Reagent	Target Phase
1	1 M CH_3COONa; pH 8.2, 1 h shaking (25 °C)	TE weakly adsorbed on mineral surfaces
2	1 M CH_3COONa adjusted to pH 5 with CH_3COOH: 5 h shaking (25 °C)	TE associated with carbonate minerals
3	0.04 M $NH_2OH \bullet HCl$ in 25% (*v/v*) CH_3COOH; 6 h shaking (96 °C)	TE associated with reducible Fe/Mn oxides/oxyhydroxides
4	0.02 M HNO_3 + 30% H_2O_2 adjusted to pH 2 with HNO_3; 5 h shaking (85 °C). Then 3.2 M CH_3COONH_4 in 20% HNO_3; shaking for 30 min (25 °C)	TE associated with oxidizable sedimentary organic matter and some sulfide minerals
5	Concentrated HNO_3 and HF (heated to near dryness and re-dissolved in 2% HNO_3	TE within the crystalline structure of silicate minerals

The resultant solutions from each successive extraction were separated at 3000 rpm and 1950 RCF by centrifugation (IEC Centra $Cl_2^{®}$) for 10 mins. The supernatant (or leachate) was decanted into a 25 mL bottle, acidified with ultrapure nitric acid (HNO_3) to bring the pH below 2, and then stored at a temperature of 4 °C until analysis to avoid the re-adsorption of constituents to the sediments or container walls. After each extraction, the residual sediment was rinsed with 8 mL of ultrapure deionized water (i.e., 18.2 MΩ cm) from a Millipore Element water system (hereafter Q-water) and centrifuged for 10 min. Then, the second supernatant was discarded to remove any reagent left in the residue before use in the next leaching step. Note that the residue from the previous step served as the leach solid for the next extraction.

3.3. Total Digestion of Sediment Samples

In addition to the sequential extractions, aliquots of each sediment samples were digested entirely to determine their total contents of Co, Cu, Ni, Pb, and Zn. The total sediment digestions were also used to check the recovery of the sequential extractions, which, when added together, should be equal to the total sediment content for each trace element. Here, 0.2 g initial dry weight of the four sediment samples were digested in separate 50 mL Teflon® beakers (with lid; Savillex, Eden Prairie, MN) using 10 mL of trace metal grade HF and 10 mL of trace metal grade HNO_3. The sediment-solution slurry was heated until near dryness, and the resulting residue was re-dissolved in 2% (*v/v*) ultrapure (Optima™ grade) HNO_3 and then diluted up to 25 mL with ultrapure Q-water. All labware used for experimental analysis was previously cleaned with reagent grade HNO_3, followed by trace metal grade HNO_3, and rinsed with Q-water. The reagents used were all trace metal grade or Optima™ grade to avoid possible metal contamination.

3.4. Analytical Methods

The concentrations of Co, Cu, Ni, Pb, and Zn in the sequential leachates and total sediment digestions were analyzed by sector-field inductively coupled plasma mass spectrometry (ICP-MS; Thermo Fisher Element 2) at Tulane University. The leachates for all fractions and sample types were diluted with Q-water within the ICP-MS's linear working range (i.e., factors of 10 and 100) because each metal was present at high concentrations in the leach solutions. This ensures that the concentration of each targeted trace element in the diluted sample is within this linear working range of 1 ng/L to 10 ng/L for this ICP-MS.

Before loading the diluted samples, the ICP-MS sampler was rinsed with Q-water, followed by sequence control 2% nitric acid blanks. The ICP-MS was calibrated for each trace element using a calibration curve made up of eight calibration standards (e.g., concentrations of 0.5 μg/L, 1 μg/L, 10 μg/L, 25 μg/L, 50 μg/L, 125 μg/L, 250 μg/L, and 500 μg/L) prepared from a 10 mg/L Spex CertiPrep® multi-element 2 calibration standard. In addition, each sample aliquot was spiked with 10 μg/L of a single-element scandium solution as an internal standard for monitoring instrument drift. Subsequently, every batch of the diluted sample solutions was run at low, medium, and high resolutions to measure the trace element concentrations and minimize the polyatomic, oxide/hydroxide, and other possible mass interferences. The detection limits were below 1 μg/L for Pb, Cu, Zn, Ni, and Co, and above 1 mg/L for Fe, Al, Mg, K, Ca, and Ba in extracted solutions.

4. Results

Concentrations (in mg/kg of the dry weight of sediment sample = mg/L) of Co, Cu, Ni, Pb, and Zn in the sequential extracts of the pre-industrial sedimentary deposits (i.e., samples TU 169 and TU 171), modern Mississippi River suspended sediment (MRSS), and the modern Mississippi riverbank sedimentary deposits (MRBS) are presented in Table 2 along with their concentrations from the total sediment digestion analysis. Differences between the summation of all five sequential extractions of each sediment sample and the results of the total digestion analyses are in good agreement, with recoveries of each trace metals in the sequential extractions ranging between 95% and 104% of the total digestion values (Table 2), and exhibiting a mean ± 1σ recovery of 100.4 ± 3.44% (Table 2). The concentrations of these trace metals in the five sequential extracts of the examined LMR sediments are presented graphically in Figure 2. In Table A1 (see Appendix A), we present the relative amount of Co, Cu, Ni, Pb, and Zn determined in each sequential extract as a percent of the total content of each metal in the LMR sediment samples. The relative amounts (as percentages) of total individual metal contents of the sequential extractions are also graphically depicted in Figure A1 (see Appendix A). The mineral composition of the Mississippi River sediments from the XRD analysis are also presented in Table A2 and Figure A2 (see Appendix A). Based on the pre- and post-dissolution quantitative XRD results, the MRBS sediment consists mostly of quartz (~77–83%), microcline (12–22%), albite (~4.3%. post-dissolution XRD only) with traces of mica and clay minerals (Appendix A).

The modern suspended sediment sample from the Mississippi River water column exhibits the highest contents of all five trace metals of the sediments analyzed, whereas the Late-Holocene-aged sediments collected from buried pre-industrial deltaic sands exhibit the lowest contents of these metals (Figure 2). The sequential extraction analysis indicates that the degree of environmental lability of metals in the LMR suspended sediments follows the order: Pb > Cu > Co > Zn > Ni (Tables 3 and A1; Figure A1). Moreover, the total Pb content of the modern suspended sediment sample (50.9 mg/kg) is between 7.9 and 9.7 times higher than the total Pb content measured in the pre-industrial deposits (5.26 and 6.48 mg/kg) and 4-fold higher than the Pb content of the modern riverbank deposits (MRBS; 12.7 mg/kg; Table 2). A remarkable feature of the Pb data, however, is that the amount contained within the residual fraction (i.e., aluminosilicate minerals) is similar for all four sediment samples analyzed (Figure 2). Specifically, the Pb content of the residual fraction of the modern suspended sediments (7.91 mg/kg) is within a factor of 2 of the residual Pb content of the pre-industrial deltaic sand deposits (4.1 and 5.1 mg/kg) and is nearly identical to the Pb content of the residual fraction of the modern riverbank sediment (6.39 mg/kg; Table 2; Figure 2). This finding underscores the importance of the environmentally labile Pb content of Mississippi River suspended sediments.
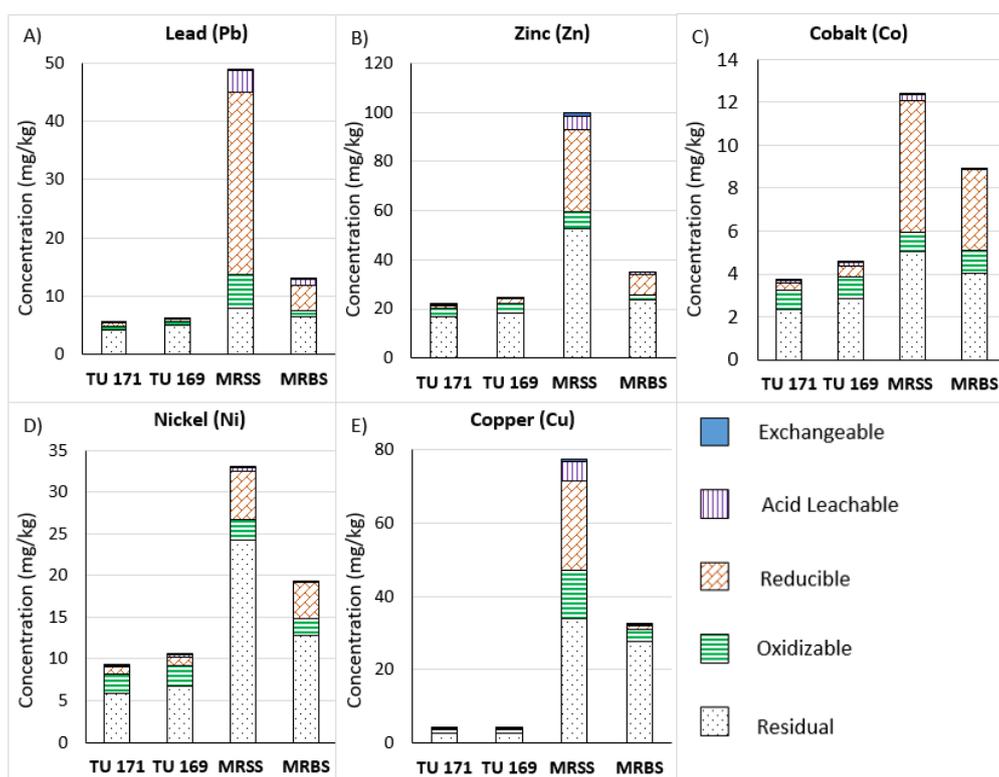
Figure 2. Concentrations of trace elements in sequential leachates of sediments from the LMR. Panels (**A–E**) present results for Pb, Zn, Co, Ni, and Cu, respectively, in mg/kg of dry weight total sediment. TU 171 is the older (~3.6 ka) and TU 169 is the younger (~1.3 ka) of the pre-industrial deltaic deposits, whereas the Mississippi River suspended sediment (MRSS) and Mississippi riverbank sedimentary deposits (MRBS) are modern sediments of the LMR. Note, that the concentration ranges on each panel differ.

The distribution of Pb in the five sequential extractions of the MRSS sample follows the order: reducible (31.3 mg/kg) > residual (7.91 mg/kg) > oxidizable (5.77 mg/kg) > acid leachable (3.71 mg/kg) > exchangeable (0.03mg/kg; Tables 2 and 3; Figure 2A), which represents 64.2%, 16.3%, 11.9%, 7.64%, and 0.06%, respectively, of the total Pb content of this sample (Table A1). This distribution also emphasizes the importance of the environmentally labile fraction of Pb in Mississippi River suspended sediments, and in particular, the reducible fraction of Pb. Specifically, our analyses indicate that the vast majority of Pb transported by suspended sediment in the Mississippi River is associated with microbially reducible Fe(III)/Mn(IV) oxides/oxyhydroxides, which is in agreement with earlier investigations of suspended sediment in the river [37,91]. In a similar fashion, about 33% of the environmentally labile Pb in the modern riverbank sediment is also associated with Fe/Mn oxides/oxyhydroxides. In contrast, the majority of the environmentally labile Pb in the pre-industrial deltaic deposits obtained from the borehole (8–14%) are associated with the oxidizable fractions of these sediments, which presumably represent sedimentary organic matter (Figure A1).

Table 2. Concentrations of metals in the 5-phase sequentially extracted solutions. Shown are the concentrations ± the analytical error of each analysis in mg/kg.

Metal	Sample No.	Fraction 1 (mg kg^{-1})	Fraction 2 (mg kg^{-1})	Fraction 3 (mg kg^{-1})	Fraction 4 (mg kg^{-1})	Fraction 5 (mg kg^{-1})	Sum of Fractions (mg kg^{-1})	Total Sediment Digestion (mg kg^{-1})	Recovery (%)
Pb	TU 171	0.01 [a]	0.12 [a]	0.48 ± 0.14	0.76 [a]	4.1 ± 0.16	5.47	5.26 ± 0.15	104
	TU 169	b	0.17 ± 0.01	0.42 ± 0.02	0.51 ± 0.05	5.1 ± 0.20	6.19	6.48 ± 0.05	96
	MRSS	0.03 [a]	3.71 ± 0.10	31.3 ± 0.53	5.77 ± 0.17	7.91 ± 0.68	48.7	50.9 ± 0.56	96
	MRBS	0.00 [a]	0.99 ± 0.09	4.26 ± 0.03	1.20 [a]	6.39 ± 0.05	13.4	12.7 ± 0.31	106
Zn	TU 171	0.05 [a]	0.60 ± 0.01	1.14 ± 0.07	3.15 ± 0.32	17.0 ± 0.77	21.9	20.8 ± 0.81	105
	TU 169	0.04 [a]	0.36 ± 0.03	1.59 ± 0.14	3.93 ± 0.3	18.5 ± 0.5	24.4	24.9 ± 0.40	98
	MRSS	1.80 ± 0.01	5.05 ± 0.18	33.4 ± 0.73	6.97 ± 0.21	52.8 ± 1.16	100.0	105 ± 2.30	95
	MRBS	b	1.28 ± 0.03	8.07 ± 0.08	2.03 ± 0.08	23.7 ± 0.17	35.3	36.4 ± 0.34	97
Co	TU 171	0.03 [a]	0.15 [a]	0.35 ± 0.02	0.89 ± 0.02	2.35 ± 0.05	3.74	3.79 ± 0.07	99
	TU 169	0.03 [a]	0.14 ± 0.02	0.52 ± 0.03	1.05 ± 0.10	2.82 ± 0.11	4.55	4.69 ± 0.05	97
	MRSS	0.02 [a]	0.28 [a]	6.11 ± 0.23	0.92 ± 0.03	5.04 ± 0.24	12.4	11.9 ± 0.27	104
	MRBS	0.01 [a]	0.03 [a]	3.78 ± 0.08	1.05 ± 0.02	4.03 ± 0.11	8.90	8.88 ± 0.20	100
Ni	TU 171	0.02 [a]	0.22 [a]	0.86 ± 0.05	2.22 ± 0.08	5.93 ± 0.21	9.25	8.97 ± 0.54	103
	TU 169	0.02 [a]	0.22 ± 0.01	1.01 ± 0.05	2.41 ± 0.18	6.79 ± 0.12	10.5	10.1 ± 0.29	104
	MRSS	0.16 [a]	0.44 ± 0.02	5.84 ± 0.14	2.46 ± 0.08	24.2 ± 0.34	33.1	32.3 ± 0.84	103
	MRBS	b	0.15 [a]	4.34 ± 0.10	2.00 ± 0.05	12.9 ± 0.44	19.4	19.4 ± 0.19	100
Cu	TU 171	0.03 [a]	0.14 [a]	0.16 [a]	0.87 ± 0.04	2.88 ± 0.13	4.07	4.01 ± 0.28	102
	TU 169	0.02 [a]	0.12 ± 0.02	0.21 ± 0.02	0.80 ± 0.03	2.81 ± 0.18	3.95	4.02 ± 0.33	98
	MRSS	0.55 ± 0.01	5.45 ± 0.01	24.3 ± 0.34	13.2 ± 0.13	33.9 ± 1.53	77.4	79.0 ± 1.03	98
	MRBS	0.06 [a]	0.32 ± 0.01	1.20 ± 0.02	3.05 ± 0.07	27.8 ± 0.61	32.5	31.7 ± 0.76	103

[a] Concentrations lacking an associated error indicate that the analytical errors for these analyses were less than ± 0.01 mg/kg. [b] Below detection limit.

Table 3. Summary of metal affinities in bioavailable fractions [b] using the percentage distribution of concentration from Table A1.

Fraction	Oldest Pre-Industrial Deposits	Youngest Pre-Industrial Deposits	MRSS	MRBS
1	Co > Cu > Ni > Zn > Pb (0.69) (0.59) (0.24) (0.2) (0.12)	Co > Cu > Ni > Zn (0.57) (0.43) (0.20) (0.15)	Zn > Cu > Ni > Co > Pb (1.7) (0.70) (0.48) (0.13) (0.06)	Cu > Co > Pb (0.18) (0.03) (0.02)
2	Co > Cu > Zn > Ni > Pb (3.9) (3.3) (2.7) (2.4) (2.23)	Co > Cu > Pb > Ni > Zn (3.3) (2.9) (2.7) (2.2) (1.5)	Cu > Pb > Zn > Co > Ni (7.6) (6.9) (5.0) (2.25) (1.33)	Pb > Co > Zn > Ni > Cu (7.7) (3.6) (0.99) (0.76) (0.33)
3	Ni > Co > Pb > Zn > Cu (9.3) (9.1) (8.8) (5.2) (3.7)	Co > Ni > Pb > Zn > Cu (11.3) (9.7) (6.7) (6.5) (5.1)	Pb > Co > Zn > Cu > Ni (64) (49) (33) (31) (18)	Co > Pb > Zn > Ni > Cu (42.0) (33.0) (22.8) (22.4) (3.69)
4	Ni > Co > Cu > Zn > Pb (24) (23.7) (20.1) (14.4) (14)	Ni > Co > Cu > Zn > Pb (23.1) (23) (19.7) (16.1) (8.2)	Cu > Pb > Ni > Co > Zn (16.8) (11.9) (7.4) (7.3) (7)	Co > Ni > Cu > Pb > Zn (11.8) (10.3) (9.4) (9.3) (5.7)

[b] Contribution not detected are not reported.

Copper and Zn exhibit broadly similar distributions between the sediments to that of Pb. For example, the total Cu content of modern LMR suspended sediments (79 mg/kg) is nearly 20-fold higher than found in the two pre-industrial sandy deposits (4 mg/kg), and a factor of 2.5 higher than measured in the modern riverbank deposits (31.7 mg/kg), whereas Zn is between 4-fold and 5-fold higher in the modern suspended sediments (105 mg/kg) than in the ancient deposits (20.8 and 24.9 mg/kg), and about three times higher than in the modern riverbank deposits (36.4 mg/kg; Table 2; Figure 2). Unlike Pb, however, the Cu and Zn contents of the residual fraction of each sediment vary considerably, with the Cu content of the residual fraction of the suspended sediment (33.9 mg/kg) being 12 times higher than in the residual fraction of the pre-industrial sandy deposits (2.81 and 2.88 mg/kg), and the Zn content of the residual fraction of the modern suspended sediment (52.8 mg/kg) being roughly 3-fold higher than in the pre-industrial sandy deposits (17 and 18.5 mg/kg; Table 2). Furthermore, the relative amount of environmentally labile Cu and Zn associated with the modern river suspended sediment (i.e., 55.1% and 47.2%, respectively) is substantially less than for that of Pb (83.8%; Table A1; Figure A1).

The residual fraction accounts for the majority of the Cu in the LMR sediments, except for the Mississippi River suspended sediment (MRSS), where slightly more than half of the total Cu (55.1%) occurs in various environmentally labile forms, with the reducible fraction accounting for the majority of the environmentally labile Cu. More specifically, the distribution of Cu in the MRSS sample decreases in the order: residual (33.9 mg/kg) > reducible (24.3 mg/kg) > oxidizable (13.2 mg/kg) > acid leachable (5.45 mg/kg) > exchangeable (0.55 mg/kg; Table 2), which represents 42.9%, 30.7%, 16.8%, 6.9%, and 0.7%, respectively, of the total Cu content of the suspended sediment sample. In contrast, about 67% of the total Cu content of the pre-industrial deposits and more than 85% of the total Cu in the MRBS is associated with the residual fraction. Most of the remaining Cu in the pre-industrial deposits (ca. 20%) occurs in the oxidizable fraction, whereas the relative amounts of Cu in exchangeable, acid leachable, reducible, and oxidizable fractions together amount to less than 15% of the total Cu in the MRBS sample. The majority of the Zn also occurs in the residual fraction of all the sediments studied, including the modern suspended sediments (see Figure A1). Apart from the residual fraction, the oxidizable fraction dominates the environmentally labile Zn portions in the pre-industrial deposits (ca. 14 to 16%), whereas the reducible fraction dominates in the MRSS (ca. 33.4%) and MRBS (ca. 22.8%) samples (Table A1; Figure A1). For all samples, the percentage distribution of Zn in the exchangeable and acid leachable is below 7%.

The modern suspended sediment also exhibits much higher contents of Co and Ni (11.9 mg/kg and 32.3 mg/kg, respectively) compared to the pre-industrial deposits (i.e., on average 2.8- and 3.4-fold higher, respectively). However, the Co and Ni contents of the modern riverbank sediments (i.e., MRBS, 8.88 mg/kg, and 19.4 mg/kg, respectively) are only 1.3 and 1.7 times lower, respectively, than in the modern suspended sediments (Table 2, Figure 2). Most of the Ni is associated with the residual fraction (64–73%), whereas between 41% and 63% of the Co is associated with the environmentally labile fractions of each sediment sample, and in particular, the reducible (Fraction 3) and oxidizable (Fraction 4) pools of these sediments (Table A1, Figure A1). Specifically, the Co content was roughly equally distributed between the residual and reducible fractions in the modern suspended sediments and the modern riverbank deposits. In terms of the environmentally labile fractions of Ni, the oxidizable fraction dominates in the pre-industrial deposits, whereas the reducible fraction dominates in both the MRSS and MRBS. The exchangeable and acid leachable Ni fractions together account for less than 3% of the non-residual Ni in all of the sediment samples.

5. Discussion

5.1. Comparison with Previous Studies

A summary of historical trace metal data from sediments of the LMR relevant to our study is presented in Table 4. These data include analyses of suspended sediments, delta plain sediments,

and pre-industrial sediments collected from offshore. The offshore pre-industrial sediment consists of the average of six samples from a long sediment core with ages greater than ca. 800 years before present [92]. The Pb and Cu content of the LMR suspended sediment sample we analyzed (i.e., MRSS) are slightly higher than those reported previously for suspended sediments collected in the mid-1970s by Trefry and co-workers, whereas the Zn, Co, and Ni contents are lower in our sample (i.e., MRSS; Tables 2 and 4). Although the Pb content is only slightly higher (ca. 1.2 times higher) than these early measurements, the Cu content is nearly 2-fold higher in the MRSS sample. These observations could be of concern because the majority of measurements indicate a decline in Pb content between the mid-1970s and the early- to mid-1980s and early 1990s (i.e., from ca. 45 mg/kg to 32 mg/kg; [34,93]). This decrease in Pb content was attributed to the elimination of leaded gasoline in the USA [34].

The Pb content we measured in the modern LMR suspended sediment sample (i.e., 50.9 mg/kg) is, however, similar to values determined for the "colloidal" fraction of suspended sediment (i.e., 38–49 mg/kg) collected from below Belle Chase, Louisiana [64]. These authors define the "colloidal" fraction as passing through a 1 μm pore-size filter and the "suspended silt" fraction of the suspended sediment as ranging in size from 1 μm to 150 μm [64]. In addition to exhibiting higher Pb contents, their "colloidal" fraction is also enriched in Zn and Cu compared to their "suspended silt" fraction (Table 4). We used 0.4 μm pore-size filters to capture suspended sediments from the Mississippi River waters in this contribution. Hence, our sample (MRSS) contains at least a portion of the "colloidal" size fraction analyzed by Piper et al. [64], as well as any particles of greater size. The combination of inclusion of the "colloids" pool and particulate matter up to 63 μm may, in part, explain the higher Pb content we determined for MRSS compared to the study by Piper et al. [64]. The Cu content of the "colloidal" fraction reported by these authors (i.e., 62–72 mg/kg) is actually quite similar to the Cu content we determined in the MRSS sample (79 mg/kg; Tables 2 and 4), suggesting that the Cu and perhaps the Pb content of LMR suspended sediments has remained relatively constant since the early- to mid-2000s. Moreover, the Cu content, along with the Pb data discussed above, is further evidence that these metals are largely transported on small, suspended particulate matter or colloids in the LMR. Nevertheless, because Trefry and co-workers employed 0.4 μm pore-size filters to collect suspended sediments from the Mississippi River, definitive conclusions regarding the possibility that Pb (and Cu) contents of LMR suspended sediments have increased since the 1980s and 1990s, or remained constant since the early 2000s, will require more sampling.

Although the MRSS sample analyzed in this contribution is insufficient to establish whether particulate Pb loads in the Mississippi River have increased since the late 20th century, it is interesting to speculate as to what processes could lead to increases in Pb contents. We suggest that the most likely cause could be increasing urbanization within the watershed along with increasing runoff of urban soils/sediments with a legacy of atmospheric Pb deposition [45,94–98]. Moreover, urban runoff is expected to increase as more land is converted to impermeable surfaces (e.g., roads and parking lot paving, etc.). Resuspension and transport of Pb contaminated urban soils and sediments could have also increased as a result of more intense precipitation events driven by changes in climate. Such processes may also increase loading of other metals commonly attributed to urban land use such as cadmium (Cd), Co, chromium (Cr), Cu, molybdenum (Mo), vanadium (V), and Zn to rivers such as the Mississippi and its tributaries [95,96], which may also explain the increases in Cu contents we observe. Another possibility that might explain higher Pb and Cu contents could be corrosion of water distribution systems (e.g., pipes, valves, waste-water treatment facility infrastructure) owing to increasing chloride concentrations from road salts, drinking water disinfection treatments, and other industrial and urban sources (e.g., [99]).

Comparison of the trace element contents we measured in the modern riverbank sediments (MRBS) to the average of 30 sediment samples from the Mississippi Delta analyzed by Trefry and Presley [38] reveals that the modern riverbank sediments exhibit 2.8-fold lower Pb, 3.4-fold lower Zn, 2-fold lower Co and Ni contents, but nearly the same Cu contents (Tables 2 and 4). As suggested by Trefry and co-workers the generally lower metal contents of the modern riverbank sedimentary

deposits compared to these delta sediments and our modern suspended sediment sample probably reflects remobilization of the metals as environmental conditions change during deposition and early diagenesis (e.g., reductive dissolution of Fe/Mn oxides/oxyhydroxides, oxidation of organic matter) compared to the conditions within the oxic river waters [36,37,64,91,100].

On average the pre-industrial deltaic deposits obtained from the borehole (i.e., TU 169, TU 171) have Pb and Co contents that are between two and three times lower than the values reported by Swarzenski et al. [92] for pre-industrial sediments collected offshore, and 6-fold lower Cu contents than these offshore sediments (Tables 2 and 4). It is noteworthy that our pre-industrial samples represent older natural deposits than those of Swarzenski et al. [92] and are obtained from a different depositional environment (see [75]). Because our pre-industrial samples were deposited by past pathways of the Mississippi River and comprised the Late-Holocene LMR delta plain, they are a better analogue for comparison with modern river sedimentary deposits and suspended sediments than the pre-industrial samples collected offshore by others. This is because the source of offshore sediments is uncertain; it may include river input or longshore transport from elsewhere, and river sediment input may have experienced mixing with marine sediments or reworking by waves, tides, and storms in the offshore environment.

5.2. Fate of LMR Sediment-Associated Metals in New Coastal Marshlands

Our results are consistent with the studies of Trefry and co-workers who also found that trace metals like Fe, Mn, Pb, Zn, Cd, Cu, and Ni were primarily associated with environmentally labile fractions of LMR suspended sediments [36–38,91]. Furthermore, Reiman et al. [101] showed that there is a significant correlation between total suspended solids and metal concentrations (i.e., Al, Ba, Fe, Mn, P, K, Si, Tl, and V) in the Mississippi River system, which also indicates that suspended sediments are an important reservoir and mechanism of metal transport in the river. These studies, along with our analyses, clearly demonstrate that substantial portions of the metal load within the Mississippi River are transported as environmentally labile fractions within the suspended sediments that are likely to be bioavailable if conditions change following deposition of these materials (see Tables 2 and 4).

Although the readily exchangeable and acid leachable fractions (i.e., Fractions 1 and 2) account for a small percentage of the total metal contents of the LMR sediments we analyzed, our results also show that the percentage of metals that could be mobilized from suspended sediment (i.e., MRSS sample) upon deposition within a coastal marsh setting where anaerobic conditions will predominate is potentially quite high (see Figure 2). Specifically, the highest contents of environmentally labile, and hence, bioavailable fractions of the trace elements we analyzed (i.e., Cu, Co, Ni, Pb, and Zn) in the LMR sediments sample occur in the reducible fraction (i.e., Fraction 3) of the MRSS sample (Tables 2 and 3). The metal contents of the reducible fraction of the MRSS sample shows that as much as 64% of the total Pb (31.3 mg/kg), 33% of the total Zn (33.4 mg/kg), 49% of the total Co (6.11 mg/kg), 18% of the total Ni (5.84 mg/kg), and 31% of the total Cu (24.3 mg/kg) carried by LMR suspended sediments is associated with reducible Fe(III)/Mn(IV) oxides/oxyhydroxides (Figures 2 and A1). We note that these Pb, Cu, and Co distributions are consistent with results from past studies that showed the Mississippi River suspended and bank sediments are enriched in Pb and other metals that are mostly adsorbed onto Fe(III)/Mn(IV) oxides/oxyhydroxides, and to a lesser extent clay minerals and organic matter [33,34,54,91]. Moreover, Shiller [102] showed that Pb (as well as Zn) is strongly adsorbed onto Mn and Fe oxides in Mississippi River sediments and Stolpe et al. [103] presented evidence of Pb transport in the water column by Fe-rich colloidal matter exceeding 40 nm in size. Consequently, an important finding of this, and these earlier studies, is that substantial amounts of Pb, Co, Zn, and Cu could be potentially mobilized from LMR suspended sediments by reductive dissolution of the Fe(III)/Mn(IV) oxide/oxyhydroxide mineral-grain coatings and/or colloids associated with these sediments upon their deposition within the planned Mid-Barataria Bay and Mid-Breton Sound diversions to build new marshlands (Figures 1 and A1; Tables 2 and 3 and Table A1).

Table 4. Summary of trace metal content (in mg/kg) data for sediments from the Lower Mississippi River (LMR). Suspended sediment samples are labeled as SS.

	SS (1973) [a]	SS (1974) [b]	SS (1982) [c]	SS (1991) [d]	SS-BCLA [e]	Colloids-BCLA [f]	SS-North America Rivers [g]	SS-Ave. World Rivers [g]	Delta Sediments [h]	Pre-Industrial Metals [i]	Upper Crust [g]
Pb	45.5	46			30.3 ± 3.1	38, 49	22	61.1	35.1	15.1	132
Zn	184	193			160 ± 27.5	183, 212	137	208	160		134
Co	21.2	21	32 ± 3	27–34			15	22.5	18.9	11.4	20
Ni	55.6	55					50	74.5	39.3		20
Cu	42.3	45			50.7 ± 5.9	62, 72	34	75.9	29.2	24.2	25

[a] Trefry and Presley (1976b); mean of three samples collected between 1973 and 1975 [36]. [b] Presley et al. (1980) and Trefry and Shokes (1981); samples collected between 1974 and 1975 [37,91]. [c] Trefry et al. (1985); mean of 29 samples collected between 1982 and 1983 [34]. [d] Garbarino et al. (1995); samples collected between 1991 and 1992 [93]. [e] Piper et al. (2006); mean of three samples of size fraction > 1 mm referred to as "suspended silt" by the authors. BCLA refers to Belle Chase, LA, located 117 km upriver from Head of Passes [64]. [f] Piper et al. (2006); two samples of size fraction > 1 mm referred to as "colloidal" by the authors [64]. [g] Viers et al. (2009); an average of 21 major rivers from North America and the major world rivers [100]. [h] Trefry and Presley (1976a); mean of 30 sediment samples collected from the Mississippi River delta [38]. [I] Swarzenski et al. (2006); an average of six samples from a long sediment core dated to greater than 800 years in age [92].

In addition to the amounts of trace metals associated with Fe(III)/Mn(IV) oxides/oxyhydroxides, approximately 12% and 17% of the total Pb and Cu contents (i.e., 5.77 mg/kg and 13.2 mg/kg, respectively) are associated with the oxidizable fraction (i.e., Fraction 4) within the MRSS sample (Figure A1, Table A1). Lower amounts of the total Zn, Co, and Ni contents of the LMR suspended sediments (i.e., around 7% of each) are associated with the oxidizable fraction (Table A1). The oxidizable fraction of the sediments likely reflects particulate organic matter or terrestrial-sourced fulvic acid colloids previously identified within the Mississippi River water [103]. Such colloids would likely collect on 0.4 μm filters as larger suspended matter begins to clog the pores. Organic colloidal materials could also be adsorbed onto the suspended mineral sediments and thus be carried along with the larger particulate matter within the flowing river waters (e.g., [104–109]). Similar to the case for trace metals associated with the reducible Fe/Mn oxide/oxyhydroxide fraction discussed above, trace metals associated with the oxidizable organic matter fraction of the LMR suspended sediments could also be mobilized by microbial degradation of the organic matter once deposited within the anaerobic coastal marsh systems, such as those planned for Mid-Barataria Bay and Mid-Breton Sound (Figure 1). It is unlikely that the oxidizable fraction of Mississippi River suspended sediments represents metal sulfide minerals as these would be oxidized during weathering at their source, and furthermore, are likely to be too dense to be transported with suspended sediments in the river waters.

Taken together, the burial of suspended sediments from the LMR within the proposed Mid-Barataria Bay and Mid-Brenton Sound diversions [21,22] could potentially mobilize as much as 76–84% of the total Pb content (i.e., 37.1–40.8 mg/kg) carried by these suspended sediments into pore waters of the newly constructed marshes. Lead (Pb) mobilization will occur as the in situ burial conditions become progressively more reducing owing to anaerobic respiration of organic carbon where microbes utilize terminal electron acceptors like nitrate ions carried by the river waters, Fe(III)/Mn(IV) oxides/oxyhydroxide coatings on the suspended sediment grains (Fraction 3), and dissolved sulfate ions from marine sources, among others. These same early diagenetic changes of in situ conditions could also mobilize as much as 40–47% of the total Zn (40.4–47.2 mg/kg), 57–59% of the total Co (7–7.33 mg/kg), 22–26% of the total Ni (8.3–8.9 mg/kg), and 48–51% of the total Cu (37.5–43.5 mg/kg) carried by the LMR suspended sediments (Tables 2 and A1). The impacts of these mobilized metals on the marshland biota could be detrimental to these organisms as well as those occupying higher trophic levels (e.g., humans) as many metals including Pb, Cu, and Ni are known to bioaccumulate within the food chain [110–115].

The generally higher metal contents in the LMR suspended sediments compared to the modern riverbank deposits (i.e., MRBS) may indicate that microbial reduction of Fe(III)/Mn(IV) oxides/oxyhydroxides has occurred within these sediments. Here, microbial respiration may have been fueled by labile dissolved organic carbon (DOC) from the Mississippi River or organic matter associated with the sediments (e.g., Fraction 4). Such a process would mobilize Pb and the other trace elements associated with the reducible and oxidizable fractions of the sediments deposited on the modern riverbank. This notion is consistent with the more than 7-fold lower Pb content of the reducible fraction of the modern riverbank sedimentary deposits (MRBS) compared to the Pb content of the same fraction of the suspended sediment sample (MRSS; Table 2). Perhaps more remarkable is that the Cu content of the reducible fraction of MRBS is 20 times lower than in the same fraction of the LMR suspended sediment sample (Table 2). Similar observations were reported by Davranche et al. [116] in their investigation of trace metal behavior in sediments from Mortagne-du-Nord, France under reducing conditions that showed no trace metal mobilization from younger sulfide-laden sediments but an increase in trace metal contents in older oxidized, organic-rich sediments. These authors attributed these trace metal distributions to their mobilization from the sediments by reductive dissolution of Fe oxides/oxyhydroxides.

The amount of each trace element associated with the reducible fraction in the pre-industrial deltaic deposits is even lower. For example, compared to the LMR suspended sediment sample, the Pb content of the reducible fractions of the pre-industrial deltaic deposits is on average 70-fold lower than in the reducible fraction of the MRSS sample, and the Cu content is 134 times lower in the same fraction of pre-industrial deposits compared to MRSS (Table 2). Although the much lower trace metal contents of the reducible fraction of the pre-industrial deltaic deposits may reflect, at least in part, post-depositional remobilization of the trace metals by reductive dissolution of Fe(III)/Mn(IV) oxides/oxyhydroxides, we contend that the very low trace metal contents of these sediments also reflect the pre-anthropogenic lack of contaminant and heavy metal input by industry, agriculture, and infrastructure to support burgeoning populations, that characterize the post-industrial river catchment and corridor in present-day southern Louisiana.

5.3. Estimating Pore Water Trace Metal Concentrations in Newly Constructed Marshlands

The cumulative Pb contents in the modern LMR suspended sediment (i.e., MRSS) gives insight into the magnitude of potential trace metal contamination to marshland pore waters following the diversion of these materials into the planned Mid-Barataria Bay and Mid-Breton Sound receiving basins (Figure 1). We assume that the natural, background Pb content for Mississippi River sediments is roughly equal to the Pb content of the pre-industrial deltaic deposits (TU 169 and TU 171; ca. 5.9 mg/kg). Again, the low metal contents in conjunction with the intact luminescence signals and overlying deltaic strata [75] strongly suggest that modern-day events or disturbances have not impacted these sediments, and thus they likely reflect the historical background Pb concentrations in the Mississippi River before industrialization in the early 1800s [91]. Therefore, a comparison of Pb contents in the reducible fraction of the pre-industrial deltaic deposits (ranging from 0.42 to 0.48 mg/kg; mean = ca. 0.45 mg/kg) with the same fraction of modern Mississippi river suspended sediments (31.3 mg/kg) and modern bank deposits (4.26 mg/kg), suggests that present-day sediments include a sizeable component of anthropogenic Pb (i.e., future Pb isotope studies are planned to verify this supposition). Furthermore, the high Pb concentrations measured in the reducible fraction of the MRSS (i.e., ca. 64% of the total Pb content; Table A1) indicates that the suspended sediments are the chief reservoir for bioavailable Pb, which implies that diagenetic processes that result in the reduction of Fe/Mn oxides/oxyhydroxides will mobilize Pb during initial-deposition or post-deposition into the associated pore waters (see Figure 2; Table 2).

Following the approach of Hering and Kneebone [117], we estimate the concentration of Pb that could be released to pore waters in the planned marshes of the Mid-Barataria Bay and Mid-Breton Sound diversions assuming that LMR suspended sediments of the same composition as the MRSS sample analyzed herein are deposited in these planned diversion sites. Using the expression from Hering and Kneebone [117] modified for Pb, we have:

$$f = \frac{[Pb]_{diss} \times \varnothing}{M \times D \times (1 - \varnothing) \times 1000} \tag{1}$$

in which, f is the fraction of sediment bounded Pb released to support a dissolved Pb concentration in the pore waters, $[Pb]_{diss}$ is the dissolved Pb concentration in μg/kg mobilized from the sediments, M is total Pb content (i.e., Pb_{total}) of the diverted sediment in mg/kg, D_{sed} is the specific gravity of the sediment grains, and $\varnothing$ is the porosity of the sediments (see also [118]). For the MRSS sediment, the total Pb content, M, of MRSS is 50.9 mg/kg (Table 2). Piper et al. [64] report that approximately 25% of the suspended clastic sediments carried by the Mississippi River consist of quartz, which has a specific gravity of 2.65 g/cm^3. If we assume that the remaining 75% consists of clay minerals, for which the specific gravity is ca. 2.78 g/cm^3 (i.e., mean value from [119]), we compute a weighted average for the specific gravity of LMR suspended sediments of 2.76 g/cm^3. We employ an average porosity for the LMR marshland sediments of 89 ± 3%, determined by Breaux [79] and Telfeyan et al. [67]. Imputing these values into Equation (1), and assuming that only the reducible fraction (i.e., Fraction 3

or 64.2% of Pb$_{total}$ or 31.3 mg/kg; Tables 2 and A1) of the MRSS is mobilized within the newly formed marshlands, we estimate a dissolved Pb concentration in the pore waters of ca. 11 mg/kg could occur. By comparison, the U.S. EPA "action level" for Pb in drinking water is 0.015 mg/L (i.e., mg/kg; [120]). This "action level" is more than 700-fold lower than our estimate of the potential pore water Pb concentrations within the planned Mid-Barataria Bay and Mid-Breton Sound diversions if only Fe(III)/Mn(IV) oxides/oxyhydroxides associated with the LMR suspended sediments are dissolved. If all of the environmentally labile Pb were mobilized (i.e., Fractions 1–4), we estimate a potential pore water Pb concentration as high as 14.5 mg/kg. Identical calculations for Cu suggest a pore water Cu concentration of 8.27 mg/kg if only the Cu associated with Fe(III)/Mn(IV) oxides/oxyhydroxides in the MRSS is mobilized in the newly constructed marshes, and as much as 14.9 mg/kg if all of the environmentally labile Cu were mobilized. The "action level" for Cu is 1.3 mg/L (i.e., mg/kg; [120]). These simple calculations indicate that substantial amounts of environmentally labile (i.e., bioavailable) Pb and Cu in the MRSS could be mobilized at potentially ecologically concerning concentrations into pore waters of the planned coastal marshlands after diversion of river sediments into these receiving basins. The impact of these mobilized trace metals on marshland flora and fauna, and perhaps more critically, on the local seafood industry and human health warrant careful study and consideration.

6. Conclusions

We investigated the potential impact of CPRA's proposed Mid-Barataria Bay and Mid-Breton Sound diversion projects on marshland pore water quality by focusing on sediments from the Lower Mississippi River (LMR), which represent the chief material envisioned for building new marshlands in these planned diversions. Suspended sediments from the modern river, modern riverbank sedimentary deposits, and two pre-industrial samples of Late-Holocene-aged deltaic sedimentary deposits were collected and analyzed for the Co, Cu, Ni, Pb, and Zn contents. We also subjected these sediments to sequential extraction analysis to evaluate the speciation of these trace elements in these LMR sediments. The sequential extraction analysis provides a means for determining the environmentally labile fraction of these trace metals that may be bioavailable to marshland organisms. Although the majority of all of these metals typically occur within the non-labile, alumino-silicate minerals that make up the bulk of these sediments, in most cases, the environmentally labile trace metals are chiefly associated with the chemically reducible fractions of these sediments. This reducible fraction likely represents Fe(III)/Mn(IV) oxides/oxyhydroxides that occur as coatings on mineral grains from oxic environments like the Mississippi River. The other important environmentally labile pool of trace metals in the sediments are those associated with oxidizable materials like organic matter. The fate and transport of these metals will depend on the biogeochemical processes occurring in the marshlands after suspended sediment diversion. Such processes may include reductive dissolution Fe-Mn oxyhydroxides, mobilization of associated metals to the water column, re-adsorption, complexation with dissolved organic ligands, microbially mediated reduction of organic matter, and/or metal uptake and intracellular reduction by native aquatic biota. Thus, trace metals associated with the reducible fraction and oxidizable fraction of these sediments are expected to be mobilized in the new marshlands planned for the Mid-Barataria Bay and Mid-Breton Sound diversions as the pore water, and sediment condition becomes progressively anaerobic as a result of early diagenetic processes and organic matter degradation.

According to the EPA's water quality criteria for suspended and bedded sediments [121], quality and quantity of aquatic sediments can impair water bodies and alter the behavior, health, or ultimate survival of biota. The LMR diversion projects may mobilize potentially toxic metals like Pb and Cu from the diverted, buried, re-suspended, or re-deposited sediments into the pore water. These mobilized metals can be transferred into the aquatic food chain and accumulate into the tissues of aquatic biota (such as fish, crustaceans, and bivalve species), which is eventually consumed by humans especially given the popularity of the seafood industry in southern Louisiana [122–124]. There is a human health risk involved with ingesting metals (especially Pb which bioaccumulates) from fish and

other aquatic species. Therefore, further research should be conducted on the dual impact that the diversion projects have on the geochemistry and aquatic species in this marshland ecosystem.

Appendix A

Table A1. Percentage distribution of metals in their "operationally defined solid-phase" fractions. Shown are the percentage concentrations ± the analytical error of each analysis.

| Metal	Sample No.	Fraction 1 (%)	Fraction 2 (%)	Fraction 3 (%)	Fraction 4 (%)	Fraction 5 (%)
Pb	TU 171	0.12 [a]	2.23 [a]	8.77 ± 2.63	14.0 [a]	74.9 ± 3.00
	TU 169	b	2.70 ± 0.08	6.73 ± 0.29	8.19 ± 0.81	82.4 ± 3.21
	MRSS	0.06 [a]	7.64 ± 0.21	64.2 ± 1.09	11.9 ± 0.34	16.3 ± 1.40
	MRBS	0.02 [a]	7.72 ± 0.65	33.2 ± 0.22	9.34 [a]	49.7 ± 0.38
Zn	TU 171	0.24 [a]	2.74 ± 0.06	5.21 ± 0.33	14.4 ± 1.44	77.5 ± 3.49
	TU 169	0.15 [a]	1.48 ± 0.13	6.53 ± 0.59	16.1 ± 1.22	75.8 ± 2.05
	MRSS	1.79 ± 0.01	5.05 ± 0.18	33.4 ± 0.73	6.97 ± 0.21	52.8 ± 1.16
	MRBS	b	3.62 ± 0.09	22.8 ± 0.23	5.75 ± 0.23	67.1 ± 0.47
Co	TU 171	0.69 [a]	3.96 [a]	9.09 ± 0.51	23.7 ± 0.52	62.7 ± 1.45
	TU 169	0.57 [a]	3.03 ± 0.34	11.3 ± 0.69	23.0 ± 2.17	62.1 ± 2.48
	MRSS	0.13 [a]	2.25 [a]	49.4 ± 1.82	7.38 ± 0.21	40.8 ± 1.95
	MRBS	0.03 [a]	0.33 [a]	42.5 ± 0.85	11.8 ± 0.21	45.3 ± 1.27
Ni	TU 171	0.24 [a]	2.36 [a]	9.27 ± 0.56	24.0 ± 0.84	64.1 ± 2.24
	TU 169	0.20 [a]	2.12 ± 0.08	9.7 ± 0.46	23.1 ± 1.70	64.9 ± 1.16
	MRSS	0.48 [a]	1.33 ± 0.07	17.7 ± 0.42	7.43 ± 0.25	73.1 ± 1.02
	MRBS	b	0.76 [a]	22.4 ± 0.54	10.3 ± 0.27	66.5 ± 2.26
Cu	TU 171	0.59 [a]	3.27 [a]	3.68 [a]	20.1 ± 1.09	66.3 ± 3.11
	TU 169	0.43 [a]	2.88 ± 0.39	5.07 ± 0.39	19.7 ± 0.81	69.0 ± 4.62
	MRSS	0.70 ± 0.02	6.90 ± 0.13	30.7 ± 0.44	16.8 ± 0.17	42.9 ± 1.97
	MRBS	0.18 [a]	0.99 ± 0.03	3.69 ± 0.05	9.40 ± 0.23	85.7 ± 1.88

[a] Percentage concentrations lacking an associated error indicate that the analytical errors for these analyses were less than ± 0.01%. [b] Below detection limit.
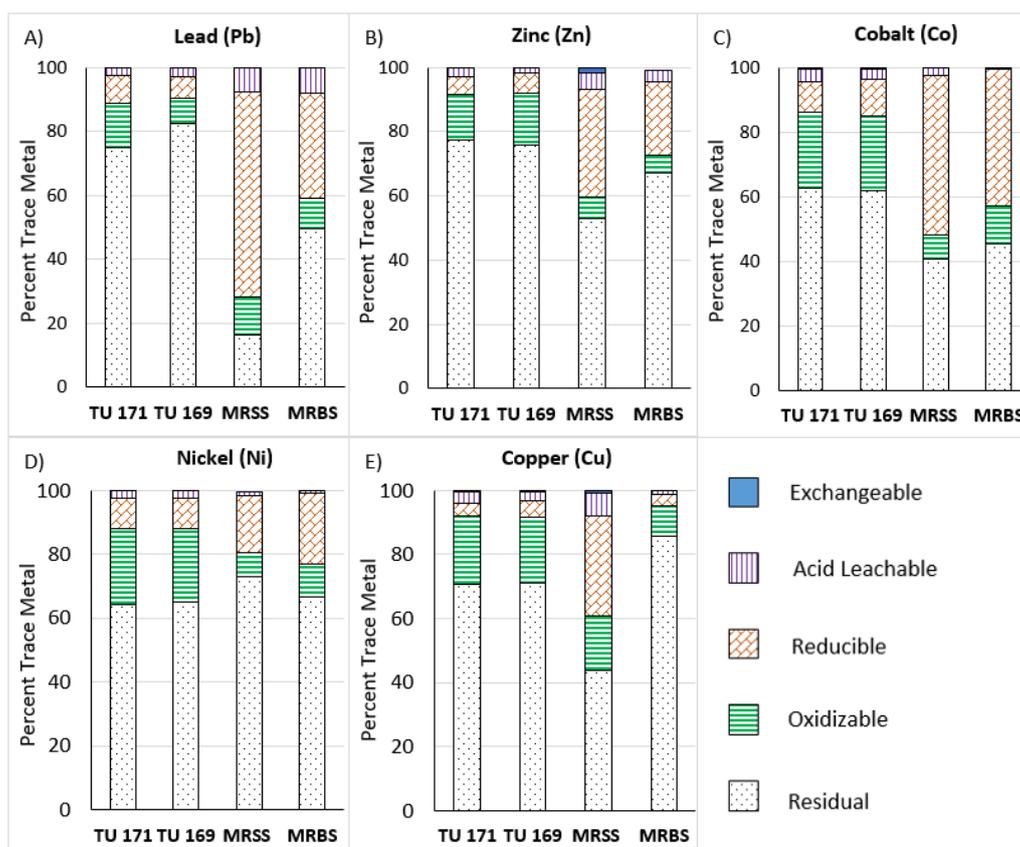
Figure A1. Percentage distribution of metals in their "operationally defined solid-phase" fractions for pre-industrial deltaic deposits (TU 171 and TU 172), modern suspended sediments, and modern riverbank deposits of the Mississippi River. The percentages are calculated based on the absolute concentrations determined by the inductively coupled plasma mass spectrometry (ICP-MS) with detection limits of the extracted solution between 1 ng/L and 1 mg/L over the sum of all five fractions. Partitioning metals: (**A**) Pb, (**B**) Zn (**C**) Co, (**D**) Ni, and (**E**) Cu in sediment into five phases. The exchangeable, acid leachable, reducible, oxidizable, and residual phases are based on the fractions that are affected by environmental conditions.

Table A2. The pre- and post-dissolution quantitative XRD result for the Mississippi River sediments.

(A) Pre-dissolution		
Mineral	001 Peak Area	Relative Percent
Quartz	49,440	82.95441199
Microcline	7571	12.70323328
Albite	2588	4.342354737
Mica/Clay		Trace
	59,599	
(B) Post-dissolution		
Mineral	001 Peak Area	Relative Percent
Quartz	39,595	77.12760777
Microcline	11,742	22.87239223
Mica/clay		Trace
	51,337	
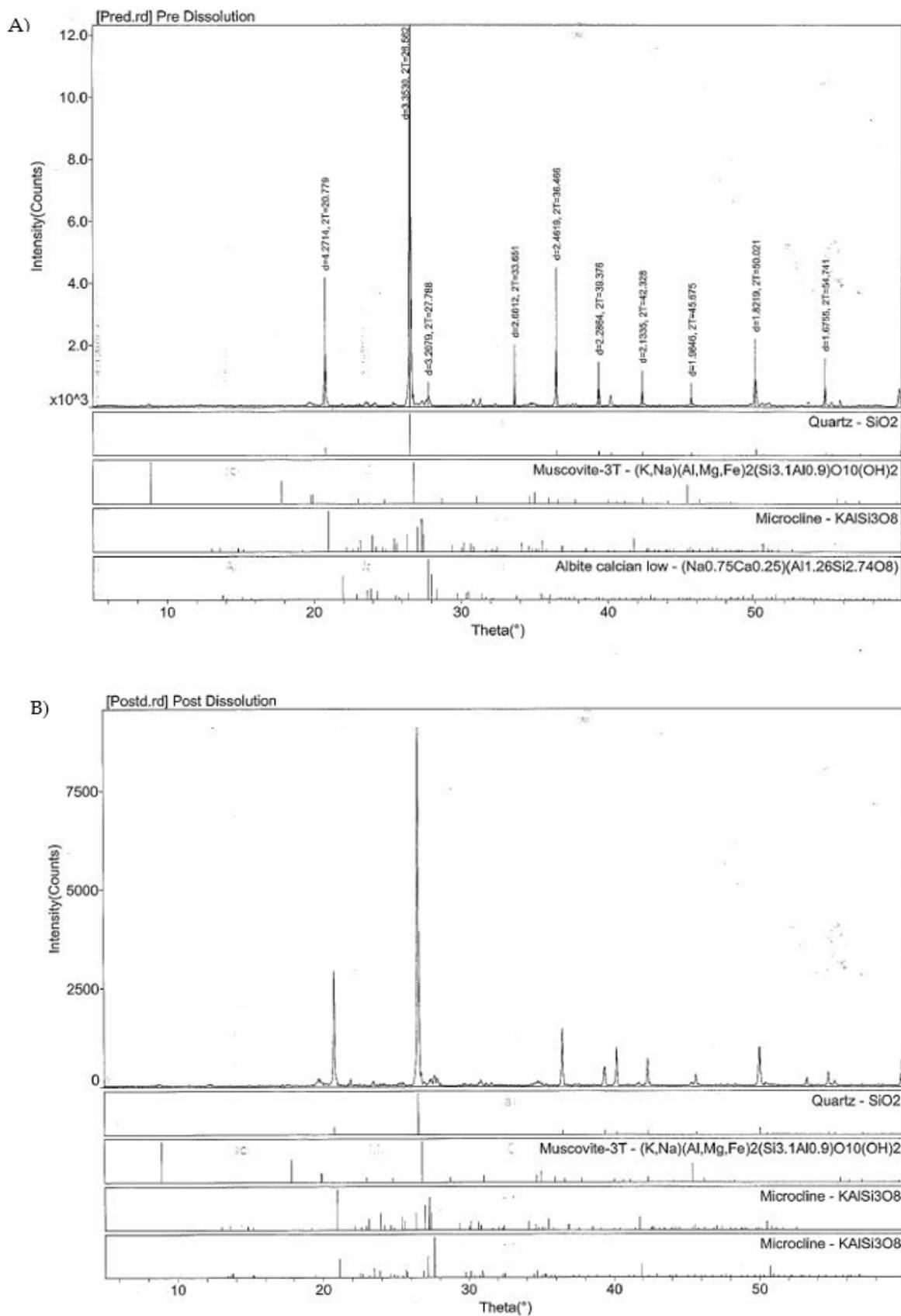
Figure A2. XRD results showing intensity and mineral relative percent for (**A**) pre-dissolution; and (**B**) post-dissolution of the Mississippi sediments.

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