



Pollution assessment and land use land cover influence on trace metal distribution in sediments from five aquatic systems in southern USA



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HIGHLIGHTS

- Pollution levels in sediments were high for Pb, Cd and U in Southern USA.
- Agricultural and coastal regions exhibit high degree of anthropogenic modification.
- Agricultural ponds, previously unexplored, are identified as key metal concentration zones.
- Multiple land activities complicate metal accumulation, making source identification difficult.

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ABSTRACT

Trace elements and heavy metals concentrate in aquatic sediments, potentially endangering benthic organisms. Comparing the concentration of metals in different aquatic bodies will help evaluate their accumulation and distribution characteristics within these systems. Metal pollution and enrichment indices in sediments from diverse aquatic systems in Southern USA, including agricultural ponds, man-made reservoir, river, swamp, and coastal environment were investigated. Following total digestion of the sediments, the concentrations of chromium (Cr), cobalt (Co), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), antimony (Sb), lead (Pb), and uranium (U) were measured using inductively coupled plasma-mass spectrometry (ICP-MS). Pb was found to be highly enriched in the sediment samples from all five environments. The samples from coastal and agricultural ponds showed highest degree of anthropogenic modification (enrichment factor >10), especially with Se, U, and Pb. Agricultural ponds, previously unknown as a metal hotspot, had the most deteriorated sediment quality as determined by high pollution load index (>1) and contamination factor (>6) for Cd and U. Principal component analysis comparing land use land cover distribution surrounding the aquatic systems to metal concentrations confirmed that agriculture-related land activities correlated well with majority of the metals. Overall, compared to agricultural ponds and coastal regions, sediments in river, swamp and man-made reservoir systems contained relatively fewer metal pollutants, the former two serving as collection points for metal-laden fertilizers and chemicals. The research provides key insights into simultaneously comparing metal accumulation in multiple water bodies and is useful to test and develop effective sediment quality guidelines.

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1. Introduction

Heavy metals have been documented to be present in a wide range of environmental settings from deep sea (Mart et al., 1982) to glaciers (Do Hur et al., 2007). Metal pollution has resulted in health

issues in aquatic and terrestrial living organisms, including humans (Castro-González and Méndez-Armenta, 2008; Jaishankar et al., 2014). Their prolonged persistence in the environment is one of the reasons for the potential negative effects on biota and difficulty in remediation. The complex and varied natural and anthropogenic origins for these metals, along with their diverse mobility, bioavailability and toxicity complicate investigations on metal transportation and fate.

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While strict contamination limits are set for water, such guidelines exist for sediments only in terms of toxicity to benthic organisms, making it difficult to determine their overall toxicity (MacDonald et al., 2000), and other harmful effects to animals, such as poisoning, diseases or even death in fish (Zeitoun et al., 2014), or the potential risk of causing cancer in humans (Alves et al., 2014). Metals released through natural weathering processes or anthropogenic activities accumulate in terrestrial and aquatic sediments. In some river systems, for example, the metals can be 100–10,000 times more concentrated in the sediments through years of accumulation than the overlying water column (Yujun et al., 2008), and could lead to secondary pollution of the aquatic systems (Linnik and Zubenko, 2000). An understanding of trace elements and heavy metal accumulation in sediments is very important because many benthic organisms thrive and establish their habitat in this environment. Elevated concentrations of trace elements and heavy metals is detrimental to these populations as these elements tend to bioaccumulate and negatively affect the food chain (Yujun et al., 2008; Mason, 2001; Post et al., 1996).

Many studies have focused on metal concentration in sediments in a variety of aquatic systems including wetlands (Sheoran and Sheoran, 2006; Kalbitz and Wennrich, 1998), rivers (Gaur et al., 2005; Garbarino et al., 1996), lakes (Suresh et al., 2012; Shen et al., 2007), estuaries (Summers et al., 1996; Tomlinson et al., 1980) and deep oceans (Armstrong-Altrin and Machain-Castillo, 2016; Erlenkeuser et al., 1974). Estuaries and bay regions are of particular interest as they tend to be the culmination points for metals that would be transported terrestrially through rivers and streams. Identifying the concentration and distribution of metals in sediments provides a better understanding of their source, transport and fate, while allowing for targeted remediation and developing better sediment quality guidelines (Benson et al., 2018; Lintern et al., 2016; MacDonald et al., 2000; Gonçalves et al., 1992; Allen et al., 1980). Furthermore, land use land cover (LULC) analysis has been shown to be an essential tool to improve point and non-point source tracking and identify potential contamination regions (Liu et al., 2017; Xiao and Ji, 2007).

The Southern states of Mississippi and Alabama in USA are dominated by forests, wetlands, and agricultural lands. The Mississippi River and other smaller rivers deposit their sediment load to the Gulf of Mexico Coast and coastal estuaries along with metals (Sankar et al., 2019; Summers et al., 1996). These metals are typically transported either as an adsorbed component to the solid minerals in the sediments or organic materials, in the dissolved phase through the water column, deposited directly as aerosols, or a combination of these three processes (Sankar et al., 2019; Wang et al., 2013). Industrial discharges, military bases, and other non-point sources such as agricultural activities have been shown to be responsible for metal accumulation in the Gulf of Mexico estuaries (Summers et al., 1996). Some of the inland lakes and reservoir in these states have also been studied for their metal content in the water, sediments and aquatic species, with mercury being an important contaminant (Dash et al., 2015; Huggett et al., 2001). In general, investigations focused on inland water bodies and the contamination potential of the sediments in this region are very limited (Grabowski et al., 2001; Price and Knight, 1978). In particular, irrigation and agricultural ponds have not received attention with respect to the metal content in their sediments, except when such ponds are exclusively used for aquaculture (Adeyeye, 1994).

Several methods exist to assess the contamination of metals in sediments (Shen et al., 2019; Islam et al., 2015; Loska and Wiechuta, 2003). Assessing the metal content in the sediments is advantageous because unlike water analysis, where metal content could fluctuate depending on precipitation and rate of contaminant release, the sediments provide a more stable, long-term record of

the metal loads in the environment (Loska et al., 1997). Various indices are available to estimate the degree of pollution in the sediments, including contamination factor (CF), pollution load index (PLI), geoaccumulation index (Igeo), and enrichment factors (EF) (Islam et al., 2015; Loska et al., 1997). These factors are calculated by a series of mathematical equations and are evaluated based on set threshold values that provide an accurate representation of the degree of contamination in the sediments.

The primary purpose of this study was to evaluate the concentration of ten trace transition elements and heavy metals in five different aquatic settings in the Southern states of Mississippi and Alabama, USA. The degree of contamination as evaluated through four pollution assessment indices and influence of land use land cover within these systems were then compared and contrasted. This research provides some of the first comparative observations into the enrichment of trace elements and heavy metals in the sediments of the aquatic settings considered.

2. Methodology

2.1. Sediment sample collection

Sediment samples were collected from the bottom of the five spatially separate and diverse types of water bodies including bay/estuary/coastal (hereafter referred to as coastal), river, agricultural ponds, man-made reservoir, and forested swamp (Table 1, Fig. 1 and S1-S3). The samples from the coastal locations ($n = 6$) were collected from Weeks Bay (Alabama), West Mississippi Sound (Mississippi), and a larger bay called Bay St. Louis, Mississippi. The river system samples ($n = 3$) were from Lower Pearl River, Mississippi. The agricultural ponds ($n = 6$) included three different locations: a small pond in the middle of an agricultural field (Brooksville Pond, Mississippi), a small pond located in proximity to a fertilizer plant, forest, and agricultural field (Pontotoc Pond, Mississippi), and a small lake near a small household in a rangeland (Kemper Lake, Mississippi). The man-made reservoir samples ($n = 3$) were from the Ross Barnett Reservoir, which is the primary drinking water to the city of Jackson, capital of Mississippi. Finally, the forested swamp system ($n = 3$) samples were collected from Bluff Lake, located within Sam D. Hamilton Noxubee National Wildlife Refuge, Mississippi. All samples were collected between 2016 and 2018. At each location, undisturbed surficial sediment samples were collected either using an extendable grab sampler from a boat or by scooping soft, surface sediments away from the shore. Each sediment sample collected weighed approximately one (1.0) kg. After collection, the sediments were immediately stored in an O₂-impermeable Remel® bag and transported to the laboratory at Mississippi State University (MSU) in an ice-filled, airtight cooler. The sediment samples were stored in a freezer at -80 °C until further processing and analysis.

2.2. Sediment characterization and geochemical analysis

Prior to analysis, approximately 200 g of the sediments were transferred into dry, acid washed, pre-cleaned porcelain crucibles with caps for drying. The crucibles containing sediments were air-dried in a clean chemical hood in the laboratory at room temperature (25 °C). The dried samples were ground for homogenization by using a clean agate mortar and pestle. Visible remains of organic matter such as leaf, root, and shells of organisms were removed prior to grinding using sterilized forceps. To avoid cross-contamination after successive sample grinding, the agate mortar, pestle, and forceps were cleaned by washing three times with de-ionized water, once with acetone, followed by drying in an oven at 100 °C.

Table 1

Information about the location, ID, date of collection and number of samples from the five aquatic systems.

| Type of Waterbody | Location | Sample ID | Coordinates | Date of collection | Number of samples | |
|---------------------------------|------------------------|---------------------|--------------------------------------|--------------------|-------------------|-----------------|
| River | Lower Pearl River | LPR | 30.24, -89.62 | 06/27/2016 | 3 | |
| | | LPR-1 | 30.28, -89.63 | December 06, 2018 | | |
| | | LPR2 | 30.46, -89.69 | December 06, 2018 | | |
| Bay/Estuary /Coastal | Weeks Bay | WB | 30.41, -87.83 | 06/19/2016 | 1 | |
| | | Bay St. Louis | BSL-1 | 30.34, -89.29 | | August 03, 2018 |
| | | | BSL-6B | 30.34, -89.38 | | August 03, 2018 |
| | West Mississippi Sound | WMS-2 | WMS-2 | 30.30, -89.25 | June 03, 2018 | 2 |
| | | | WMS-5 | 30.29, -89.26 | July 03, 2018 | |
| | | Swamp/Forest | Bluff Lake (lake in a forested area) | NB | 33.29, -88.79 | |
| NX LOC-1 | 33.27, -88.78 | | | 05/24/2018 | | |
| NX LOC-2 | 33.27, -88.78 | | | 05/24/2018 | | |
| Agricultural ponds | Brooksville Pond | BP | 33.26, -88.54 | 07/13/2016 | 2 | |
| | | BP-1 | 33.26, -88.54 | 06/24/2018 | | |
| | Kemper Lake | KC-1 | 32.89, -88.78 | 05/24/2018 | 1 | |
| | | Pontotoc Pond | Site-2 | 34.32, -89.02 | | 07/29/2018 |
| | Pontotoc Pond | | Site-3 | 34.32, -89.03 | 07/29/2018 | 3 |
| | | Site-4 | 34.32, -89.04 | 07/29/2018 | | |
| Man-made reservoir/Lake | Ross Barnett Reservoir | RB-1A | 32.41, -90.07 | August 08, 2016 | 3 | |
| | | RB-6 | 32.46, -89.95 | August 08, 2016 | | |
| | | RB-12 | 32.51, -89.94 | August 08, 2016 | | |

The pulverized samples were then passed through a number 10 (2 mm) mesh sieve (ASTM, 1999), and the finer particles were used for subsequent characterization (Barbieri, 2016). Total digestion of each sediment sample was performed in triplicate in Teflon vessels of a block digestion system (Digi PREP MS, SCP SCIENCE®) according to Denmark et al. (2018). Approximately 0.1 g of the homogenized sample was transferred into acid-washed Teflon® digestion tube (Saville, 70-mL inner volume). Then, 5 mL of trace metal grade nitric acid (HNO₃) (AriStar Plus, VWR) and 1 mL of trace metal grade hydrofluoric acid (HF) (AriStar Plus, VWR) were added. After adding the acids to each sample separately, the digestion tubes were placed into the block digestion system and digested at 140 °C for 2 h in a fume hood. The temperature was increased to 160 °C and the digestion was continued for another 4 h. After digestion, the contents were cooled to room temperature first and then transferred to acid-washed 15 mL centrifuge tubes. The digestion tubes were rinsed with deionized water, following which the washings were added to new 15 mL tubes and the volume was completed to 10 mL with deionized water. A volume of 0.5 mL of each digest was pipetted into another acid-washed 15-mL centrifuge tubes and diluted to 10 mL with 2% HNO₃ (i.e., digests were diluted 10-fold for analysis). To evaluate the effectiveness of the total digestion process, NIST SRM 2711 (Montana soil standard reference material) was used as a quality control. The standard was similarly digested in triplicate, and was analyzed along with digests from the processed sediment samples.

Samples were analyzed for a suite of trace transition elements and heavy metals, including lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cobalt (Co), antimony (Sb), and uranium (U) by using a Varian 820-MS inductively coupled plasma mass spectrometry (ICP-MS) instrument (Varian, Inc., Palo Alto, CA, USA). Manganese (Mn) was also measured in samples but the values obtained for Mn were solely used for assessing contamination, as explained later. The lower limits of detection for Pb, Cr, Cd, Cu, Zn, As, Se, Sb, U, Mn and Co using ICP-MS were 0.031, 0.017, 0.028, 0.095, 0.011, 0.026, 0.018, 0.015, 0.004, 0.012, and 0.016 µg/L, respectively. Calibration was made with aqueous standard solutions in 2% (v/v) nitric acid extending from 0.5 to 200 µg/L for ICP-MS analysis. At least five standard solutions that bracket the concentration of analytes of interest were used in calibration.

2.3. Pollution assessment

To assess the potential contamination in the different sites, four factors were determined in this study: contamination factor (CF), pollution load index (PLI), geoaccumulation index (I_{geo}) and enrichment factor (EF). The formula, variables, and the classification scheme for designating pollution levels in the sediments are provided in Table 2. The thresholds for each index were standardized and the classification schemes were adopted from previous studies that used these indices to evaluate sediments across a wide range of environments (Islam et al., 2015; Birch and Olmos, 2008; Zhang and Liu, 2002). These indices used global background values, and therefore allowed for simultaneous evaluation of different environments without needing modifications (Wang et al., 2017), and were calculated by comparing the obtained concentrations of the elements of interest to a reference baseline (background or pre-industrial values). One of the common baselines used here, as well as in other studies, was the average shale values (Shen et al., 2019; Islam et al., 2015; Loska and Wiechula, 2003). These values were obtained from a comprehensive database of metal concentration in various rock types as reported in Turekian and Wedepohl (1961), and has been used extensively as a global standard, including USA (Swarzenski et al., 2008). It is important to note that in the indices calculated here and in previous studies, the terms contamination and pollution would sometimes be used interchangeably; however, contamination referred to metal or other elements that are present in a higher concentration than what would be naturally present in a particular system, whereas pollution referred to a scenario where the contaminants are large enough to cause harm to humans or other biota in that system. CF was useful to assess contamination in an environment due to a single metal overtime in the individual samples by calculating the ratio of measured metal concentration to the natural background value of the metal (Turekian and Wedepohl, 1961). Depending on the calculated value of CF, the degree of contamination was divided into four categories: low, moderate, considerable, very high (Loska et al., 1997). The overall combined toxicity of the sample for each environment was determined by PLI, which standardizes the contribution from all the ten metals and could be used to indicate bioavailability (Angulo, 1996). Sediments with PLI value of zero would indicate a truly unpolluted sample, whereas a value above one showed progressive

Table 2
Formula and classification scheme for assessing metals.

| Factor | Formula ^a | Classification Scheme ^a |
|--|---|--|
| Contamination factor (CF) | $\frac{C_m}{B_m}$ | <1, low degree of contamination 1-3, moderate degree of contamination 3-6, considerable degree of contamination >6, very high degree of contamination |
| Pollution load index (PLI) | $\frac{1}{(CF_1 * CF_2 * CF_3 * \dots * CF_n)^n}$ | 0, no pollution 0-1, only baseline pollutants >1, progressive deterioration |
| Geoaccumulation index (I_{geo}) [*] | $\log_2 \left(\frac{C_m}{1.5 * B_m} \right)$ | ≤0, no contamination 0-1, none to moderate contamination 1-2, moderate contamination 2-3, moderate to heavy contamination 3-4, heavy contamination 4-5, heavy to extreme contamination >5, extreme contamination |
| Enrichment factor (EF) | $\frac{\left(\frac{C_m}{C_{Mn}} \right)}{\left(\frac{B_m}{B_{Mn}} \right)}$ | 0–1.5, natural processes 1.5–3, minor anthropogenic modification 3–5, moderate anthropogenic modification 5–10, severe anthropogenic modification >10, very severe anthropogenic modification |

C_m , concentration of the individual metal; B_m , concentration of background metal; CF, contamination factor of metals 1, 2, 3 ... n; n, number of metals; C_{Mn} and B_{Mn} , concentration of Mn in the respective sample and background, respectively. C_{Mn} values are provided in Table S1. B_{Mn} value from Turekian and Wedepohl (1961) is 850 µg/g.

^aFormula and classification schemes for the indices were based on the methods used by Islam et al. (2015); Birch and Olmos (2008); and Zhang and Liu (2002).

^{*}The background metal value is multiplied by 1.5 to minimize possible variations attributed to lithological differences.

deterioration of the sediment with respect to all or most of the metals (Tomlinson et al., 1980). The intensity of contamination from these metals in the sediments was assessed by I_{geo} , calculated in a similar manner to CF and PLI by incorporating background metal concentration. The threshold values used to describe I_{geo} were usually applied in seven different classification schemes, beginning from no contamination to extreme contamination (Barbieri et al., 2016). The final pollution assessment index calculated in this study was EF, which allowed to determine the magnitude of the metal contaminants to be evaluated in toxicological studies (Buat-Menard and Chesselet, 1979; Barbieri et al., 2016). The purpose of this factor was to analyze natural fluctuations in the content of a given metal and to detect even very small anthropogenic influence. An EF value less than 1.5 would indicate that the metal accumulation in the environment was due to natural processes, but any value above 1.5 would indicate progressive addition of metals from anthropogenic point or non-point sources, or even by concentration through biota (Barbieri et al., 2016). The concentration of Mn in the individual samples was chosen as the reference element (Loska et al., 1997). Use of Mn as a reference element has been successfully advocated before because it is a geochemically characteristic element that is present in large quantities, but has no synergistic or antagonistic effect on the investigated elements (Loska et al., 1997).

2.4. Land use land cover analysis

The land-use/land-cover (LULC) analysis was performed to understand if the measured concentrations of the metals in the sediments from these various aquatic systems have any correlation with the type of LULC. The LULC for the selected regions was performed beginning with the delineation of the sub-watersheds. First, the respective boundaries were generated by combining United State Geological Survey (USGS) hydrological unit code (HUC) 8 and 10 watershed boundaries downloaded from United States Department of Agriculture (USDA) data gateway, while simultaneously comparing those with the statewide digital elevation model (DEM) downloaded from the Mississippi Automated Resource Information System (MARIS). The river and the coastal sample locations were delineated based on HUC 8 level and the

others on HUC 10. The HUC partitions, the slope and elevation from the DEM were downloaded from USDA data gateway and helped in determining the respective boundaries for the different aquatic systems. Subsequently, the land use land cover dataset of year 2017 for the state of Mississippi and Alabama downloaded from the USDA data gateway was cropped using the delineated watershed boundary dataset, generating a LULC map with the 15 classes present in the region. The 15 classes were then sub-grouped into six final classes: open water, developed, forest, shrub/herbaceous, agriculture, and wetlands.

2.5. Principal Component Analysis

Principal Component Analysis (PCA) was used to determine the association of the different variables by reducing the dimensionality in the dataset. The concentrations of the elements from the five aquatic systems along with the six, final LULC classes were used as variables for PCA. The variables were combined as principal components, where the eigen values indicate the measure of covariance. The level of contribution of the different variables to that particular component were represented by 'loadings', and the original value for the variables were transformed into a new value referred to as 'scores'. SPSS statistical software (version 25) was used for performing the statistical analyses.

3. Results and discussion

3.1. Metal concentration in sediments from various aquatic systems and their potential sources

The results for elemental concentrations measured in sediment samples collected from five different aquatic systems were averaged and summarized in Table 3. Since each sample was digested and analyzed in triplicate, the values shown in Table 3 are the average of the three measurements. The average values along with the standard deviation (SD) are given separately in Table S1. While in most elements and samples, variability within measurements were minimal, some elements like Cd, Se and Sb showed large SD values within the triplicate readings, which would be common

Table 3Metal concentration ($\mu\text{g/g}$) found in sediments from the five systems along with their average and standard deviation (SD).

| Systems | Sample ID | Cr | Co | Cu | Zn | As | Se | Cd | Sb | Pb | U |
|------------------------------------|-------------|------|------|------|------|------|------|------|-----|------|------|
| River | LPR | 23.9 | 5.4 | 15.0 | 75.1 | 3.1 | 0.6 | 0.1 | 0.4 | 47.2 | 1.8 |
| | LPR-1 | 20.4 | 4.1 | 22.6 | 52.0 | 2.0 | 0.0 | 0.1 | 3.0 | 33.1 | 1.9 |
| | LPR-2 | 12.9 | 2.4 | 4.5 | 19.8 | 1.8 | 0.0 | 0.0 | 0.3 | 8.6 | 1.1 |
| Average | | 19.1 | 4.0 | 14.0 | 49.0 | 2.3 | 0.2 | 0.0 | 1.2 | 29.6 | 1.6 |
| SD | | 5.7 | 1.5 | 9.1 | 27.8 | 0.7 | 0.3 | 0.0 | 1.5 | 19.6 | 0.4 |
| Bay/Estuary/Coastal | BSL-1 | 8.0 | 1.1 | 4.3 | 16.6 | 1.2 | 0.0 | 0.0 | 0.1 | 4.2 | 0.7 |
| | BSL-6B | 35.9 | 6.3 | 10.5 | 48.7 | 6.3 | 0.6 | 0.1 | 0.4 | 12.6 | 2.6 |
| | BSL-3 | 27.7 | 5.0 | 7.9 | 36.8 | 4.6 | 0.0 | 0.0 | 0.3 | 9.7 | 2.0 |
| | WB | 47.8 | 6.0 | 10.5 | 56.5 | 10.0 | 1.6 | 0.0 | 0.2 | 11.8 | 2.5 |
| | WMS-1 | 50.1 | 10.9 | 14.9 | 76.1 | 8.6 | 2.5 | 0.0 | 0.4 | 16.6 | 1.3 |
| | WMS-05 | 22.6 | 6.5 | 6.1 | 37.0 | 4.1 | 0.3 | 0.0 | 0.2 | 8.1 | 1.2 |
| Average | | 32.0 | 6.0 | 9.0 | 45.3 | 5.8 | 0.8 | 0.0 | 0.3 | 10.5 | 1.7 |
| SD | | 16.0 | 3.2 | 3.8 | 20.3 | 3.2 | 1.0 | 0.1 | 0.1 | 4.2 | 0.8 |
| Swamp/Forest | NB | 53.1 | 11.1 | 22.6 | 100 | 5.3 | 1.2 | 0.2 | 0.8 | 20.1 | 2.7 |
| | NXLOC-1 | 39.0 | 10.3 | 7.4 | 45.0 | 3.3 | 0.0 | 0.0 | 0.3 | 12.6 | 1.9 |
| | NXLOC-3 | 23.6 | 2.6 | 7.2 | 25.5 | 2.9 | 0.7 | 0.0 | 0.3 | 10.5 | 1.4 |
| Average | | 38.6 | 8.0 | 12.4 | 56.9 | 3.8 | 0.7 | 0.1 | 0.5 | 14.4 | 2.0 |
| SD | | 14.7 | 4.7 | 8.8 | 38.8 | 1.3 | 0.6 | 0.1 | 0.3 | 5.0 | 0.7 |
| Agricultural Ponds | KC-1 | 21.2 | 1.7 | 6.1 | 23.8 | 1.2 | 0.4 | 0.0 | 0.3 | 8.1 | 1.3 |
| | Site-3 Pond | 122 | 5.7 | 23.7 | 65.8 | 15.9 | 0.0 | 0.0 | 0.9 | 17.3 | 2.8 |
| | Site-4 Pond | 106 | 18.9 | 40.7 | 469 | 15.7 | 1.7 | 4.4 | 1.6 | 16.7 | 30.7 |
| | Site-2 Pond | 179 | 7.0 | 11.0 | 39.6 | 27.1 | 0.0 | 0.0 | 1.0 | 14.3 | 2.1 |
| | BP-1 | 135 | 20.8 | 29.2 | 141 | 17.3 | 1.4 | 0.5 | 1.2 | 20.5 | 3.2 |
| | BP | 62.6 | 20.9 | 23.7 | 105 | 13.4 | 3.1 | 0.3 | 0.8 | 10.1 | 4.4 |
| Average | | 104 | 12.5 | 22.4 | 141 | 15.1 | 1.1 | 0.9 | 0.9 | 14.5 | 7.4 |
| SD | | 55.6 | 8.6 | 12.5 | 167 | 8.3 | 1.2 | 1.7 | 0.4 | 4.7 | 11.4 |
| Reservoir/Lake | RB-1A | 65.1 | 12.9 | 18.0 | 90.0 | 9.1 | 0.5 | 0.1 | 0.6 | 19.2 | 2.0 |
| | RB-6 | 43.4 | 6.9 | 12.7 | 53.2 | 5.2 | 0.5 | 0.0 | 0.5 | 15.3 | 1.9 |
| | RB-12 | 12.2 | 1.6 | 3.2 | 18.0 | 1.4 | -0.2 | 0.0 | 0.1 | 6.0 | 0.8 |
| Average | | 40.2 | 7.2 | 11.3 | 53.7 | 5.2 | 0.3 | 0.0 | 0.4 | 13.5 | 1.6 |
| SD | | 26.6 | 5.7 | 7.5 | 36.0 | 3.8 | 0.4 | 0.0 | 0.3 | 6.8 | 0.6 |
| Background value (B _m) | | 90 | 19 | 45 | 95 | 13 | 0.6 | 0.3 | 1.5 | 20 | 3.7 |
| Consensus-based TEC | | 43.4 | N/A | 31.6 | 121 | 9.79 | N/A | 0.99 | N/A | 35.8 | N/A |
| Consensus-bases PEC | | 111 | N/A | 149 | 459 | 33 | N/A | 4.98 | N/A | 128 | N/A |

Background metal values (B_m) from Turekian and Wedepohl (1961); TEC and PEC, threshold effect concentration and probable effect concentration, respectively.

when even small variations occur at low concentrations. To evaluate accuracy of the digestion procedure, recovery of the individual elements was calculated for Montana soil standard reference material (SRM 2711) using the procedure described by Yuan et al. (2004). The total digestion procedure for all elements in the reference material showed highly satisfactory recovery percentages, ranging between 95.9% and 107.7% (Table S2), and indicating a successful digestion procedure.

Shapiro-Wilk normality test indicated that the metal concentrations were not normally distributed ($p < 0.05$), which was expected because of the low sample numbers. The elements Se, Cd, Sb and U levels, for the most part, were the lowest in the sediment samples of all aquatic systems. The concentration of Pb was above $10 \mu\text{g/g}$ in all samples, with the highest value recorded in one of the river samples (LPR at $47 \mu\text{g/g}$). Pb, As and Co were high in the man-made reservoir samples with an average of $14 \pm 7 \mu\text{g/g}$, $5 \pm 4 \mu\text{g/g}$, and $7 \pm 6 \mu\text{g/g}$, respectively. Se was highest in the coastal and agricultural pond samples ($\sim 3 \mu\text{g/g}$ each). Apart from agricultural ponds, river samples also contained high Cd levels ($3 \mu\text{g/g}$). The river samples LPR, LPR-1 and LPR-2 showed a wide degree of variation especially for Zn ($49 \pm 28 \mu\text{g/g}$), Pb ($30 \pm 20 \mu\text{g/g}$), and Cu ($14 \pm 9 \mu\text{g/g}$). Cr was also relatively high in the river samples with an average concentration of $19 \pm 6 \mu\text{g/g}$ compared to other elements. Among all the elements, Zn showed very high levels in all sites, with the highest concentration of $469 \mu\text{g/g}$ in an agricultural pond sample. In the coastal system, Cr was present in large quantities ($32 \pm 16 \mu\text{g/g}$), followed by Pb ($10 \pm 4 \mu\text{g/g}$), Cu ($9 \pm 4 \mu\text{g/g}$), Co ($6 \pm 3 \mu\text{g/g}$), and As ($6 \pm 3 \mu\text{g/g}$).

Tanneries are one of the most prominent sources for Cr, where salts formulated with this element are used for finishing leather,

increasing its stability and resistance to shrinkage. Many river and estuarine systems are contaminated with Cr globally (Pawlikowski et al., 2006; Khwaja et al., 2001). Oil refineries, leaky underground storage tanks (LUSTs), and accidental oil spills are also considered to be contributors of heavy metals, particularly Pb, Cd, Cr, Zn and As, to rivers, lakes, and coastal sediments (Fiedler et al., 2009). LUSTs were found in sites in and around Bay St. Louis region releasing metals, such as Cu, Pb and Hg, whereas Cr and Pb were found in locations closer to the Lower Pearl River (MDEQ, 2020). The Gulf of Mexico Coast and inland region of SE United States has a number of oil refineries that could be contributing to the metal load. The presence of a titanium dioxide refinery next to the BSL region could likely be a source of Cr and Pb; the two metals were previously detected in oyster tissues obtained from that area (Elston et al., 2005). Similarly, Se, a metalloid, was also found in the sediments of BSL in a previous study (Lytle and Lytle, 1982). In our investigation, Se levels were 1.6 and $2.5 \mu\text{g/g}$ in Week's Bay (WB) and West Mississippi Sound (WMS), respectively, which were comparatively higher than other aquatic systems. Previous investigations in the coastal region near our study sites revealed contamination of sediments and plants with heavy metals, such as Cd, As, Cu, U, Zn, Ni and Hg, with some of the metals exhibiting a flux dependency on precipitation events and salinity (Lafabrie et al., 2013; Sankar et al., 2019).

The swamp/forest systems along with the coastal and lake samples had somewhat similar overall distribution of metal concentrations, with less than 20% variation in all these systems. The forest sediments were obtained from Noxubee National Wildlife Refuge, half of which were mature bottomland hardwood forest consisting of oaks, other hardwood trees, and bald cypress. One of

the small creeks that fed into the Noxubee River, which was part of the refuge, was the Hollis Creek. A previous report indicated that sewage released from a wastewater treatment plant impaired the water quality in the creek by releasing metals and polycyclic aromatic hydrocarbons (Winger et al., 2000). Heavy metals could accumulate in the forested swampy region where the low gradient and corresponding slow water movement allowed for a longer settling time in the sediments. In the forest samples, Zn, Cr, and Pb all had high concentration (60 ± 39 , 37 ± 15 , 14 ± 5 $\mu\text{g/g}$, respectively) comparable to coastal or lake samples, but less than agricultural ponds. Wetland systems in the coastal region of SE USA and other locations in the world have been shown to be important storage points for metals (Pardue et al., 1992; Bai et al., 2012). While wetlands would be effective in controlling the release of metal contaminants to the ocean, the accumulated metals could in turn be harmful to the aquatic organisms inhabiting the swampy regions (Tchounwou et al., 1996; Jafari and SobhanarDakanl, 2014).

The six samples collected from various agricultural pond sediments collectively had the highest concentrations for all metals. The order of elements from highest to lowest concentration in the agricultural system was $\text{Zn} > \text{Cr} > \text{Cu} > \text{As} > \text{Pb} > \text{Co} > \text{U} > \text{Se} > \text{Cd} > \text{Sb}$. Particularly site-4 pond had the highest U levels (31 $\mu\text{g/g}$) among all samples in any system. Other examples of metal concentrations in the agricultural ponds included Cr, Cu and As with average values of 104 ± 56 $\mu\text{g/g}$, 22 ± 13 $\mu\text{g/g}$, and 15 ± 8 $\mu\text{g/g}$, respectively. The agricultural ponds were situated at or near large plots of crop land. These ponds were used primarily to capture, store and distribute water to be used for irrigation and groundwater recharge, while some were used as tailwater ponds to collect water from crop lands and recycle the water. During periods of flooding or heavy rainfall, water would spill from the crop land into these ponds, thereby bringing in soil along with the fertilizers, pesticides, and other farm additives (Cooper and Gillespie, 2001). Both current and historical use of metal-based amendments in agriculture were likely responsible for contamination in these systems. Pb–As insecticides for cotton boll weevil, As herbicides (e.g., monosodium methane arsenate) for weed control, and Cu as an algicide in catfish farmers, were all examples of agricultural contribution of metals to water bodies in this region (Cooper and Gillespie, 2001; Schrader and Harries, 2001; Knight et al., 2009). Similar ponds in SE USA were used for aquaculture and some have been shown to contain toxic metals (Santerre et al., 2001). In addition to irrigation, there have been important incentives to develop and use these ponds, for example, as a habitat for waterfowls (Sebastián-González et al., 2010), and therefore requires routine water and sediment quality monitoring. With such a high potential for contaminating groundwater and plants, it was surprising that agricultural ponds have not been previously investigated for their metal content. We present one of the first reports into identifying these ponds as a major hotspot for metal accumulation and contamination.

Interestingly, U concentration was high (1.3 – 30.7 $\mu\text{g/g}$) in some of the agricultural ponds compared to all other systems because U is not typically expected to be an agricultural contaminant. However, the application of inorganic P fertilizers has been shown to be responsible for contaminating agricultural soil and water with U (Jacques et al., 2008; Schipper et al., 2011). Similarly, Cd (up to 4.4 $\mu\text{g/g}$) was detected in the pond sediment, and reported in other aquaculture-based agricultural ponds globally (e.g., Zhang and Shan, 2008). In addition to the crop lands, the Pontotoc pond was located next to several furniture, automotive, and fertilizer stores, two of which have or had contamination issues (MDEQ, 2020). Such industries and land activities nearby could have potentially contributed to the high metal concentration observed in these

selected ponds. Such a complex industrial-agricultural setting underscored the need to carefully investigate and identify if the sources for these contaminants were point or non-point, because many locations have multiple land uses in proximal distances.

In the man-made reservoir/lake system, the metals were concentrated more towards the inlet of the lake and progressively decreased away from the inlet. For example, concentrations at the inlet, mid-point and downstream region of the reservoir were 65 , 43 , and 12 $\mu\text{g/g}$, respectively for Cr, and 19 , 15 and 6 $\mu\text{g/g}$ for Pb, respectively. Other elements also followed a similar trend, which indicated that the Upper Pearl River, bringing in water and sediments to the Ross Barnett Reservoir (RBR), was the primary source for these contaminants. This identification was important because metal remediation efforts can then be focused on areas experiencing the most contamination. In addition to RBR, elevated Pb, Cr, As and Cd were found in the waters of three other man-made lakes in Mississippi (Dash et al., 2015). Analysis of fish, clams, soil and sediments in Sardis Reservoir and Enid Lake, both in Mississippi, indicated that metal(loid)s, such as Hg, Cd, Pb and As were found in both living organisms and the sediments (Knight and Cooper, 1996; Price and Knight, 1978). The high concentrations of metals in the sediments can easily move up the food chain, leading to biomagnification. Ross Barnett Reservoir water has been used as the primary drinking water source for the city of Jackson, capital of Mississippi, and also for recreation and fishing by the local community. Therefore, the quality of water and sediments is of vital importance because consumption of bottom-feeding fish such as catfish, which are common in the reservoir, Fig. 1 could provide a direct pathway by which humans can potentially ingest toxic metals.

3.2. Contamination factor and pollution load index

Various methods were used to assess the degree of elemental pollution in the sediments. Contamination factor (CF), which helped to assess the degree of contamination through a single contaminant overtime, was generally low ($\text{CF} < 1$) for most samples and systems (Table S3). In general, though the average Se concentration was low in all samples, one each of coastal and agricultural ponds showed considerable contamination (CF 3–6), whereas

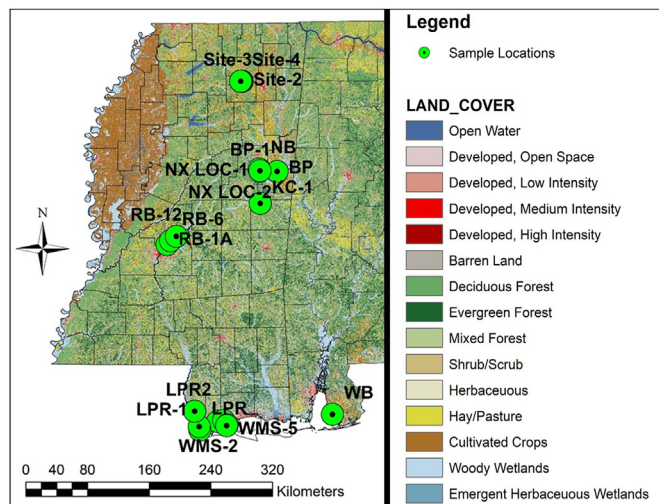


Fig. 1. A Land Use/Cover map showing the states of Mississippi and Western half of Alabama in southern USA with the sediment sample locations. Legend shows the color coding for the different land cover classifications. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

forest, coastal and agricultural ponds each had moderate contamination (CF 1–3) for this metalloid. Site-4 pond of the agricultural system showed extreme contamination (CF > 6) for both U and Cd, and moderate contamination with respect to Zn. Phosphate fertilizers, sewage sludge, and natural weathering of minerals, such as sphalerite are all likely sources for U, Cd and Zn (Robson et al., 2014). All of the lake samples showed low degree of metal pollution, with the exception of Pb, which was on the border between low and moderate. Pb was also shown to be moderately contaminating the river samples. At least 67% of the agricultural pond samples showed moderate levels of As and Cr contamination. Cu was the only element that showed low contamination across all locations.

Pollution Load Index (PLI) was a comprehensive term to indicate the contribution of all metals in the sediments and compares summative CF of the metal(loid)s discussed above to its background (baseline) values. A PLI value of zero indicated an unpolluted setting. As expected, all samples had values higher than zero indicating that the sediments had metal concentrations higher than, if not equal to, their baseline levels (Fig. 2). Three of the agricultural pond samples showed a PLI value of more than one, indicating a progressive deterioration of these environments. U, Zn, As, Se and Cd were principal contributors to the high PLI values. PLI levels can also be used as a useful communication tool to

meaningfully convey the scientific information to the farmers and decision makers on the standing of the region with respect to pollution (Suresh et al., 2012). In this study, agricultural ponds were shown to have some of the highest PLI values, highlighting the need to have effective management techniques, such as setting up limits on the type and amount of fertilizer used, and ensuring proper guidelines especially when agricultural farms could be located in proximity to industries.

3.3. Geoaccumulation index, enrichment factor and sediment quality guidelines

Geoaccumulation index (I_{geo}) was a measure of assessing metal contamination that showed degree of accumulation of individual metals from pre-industrial background values (Table S4). None of the metals showed a heavy or extreme contamination index ($I_{geo} > 3$). About 86% of all samples showed no contamination ($I_{geo} \leq 0$). Co and Cu in all systems were shown to be uncontaminated. A low to moderate contamination ($I_{geo} 0-1$) was seen in the case of Se, Sb and Pb in the river samples. Se and Zn were shown to be of moderate contamination ($I_{geo} 1-2$), one in each sample of agricultural pond and coastal. Only the site 4 agricultural pond sample showed moderate to heavy contamination for Cd and U, with I_{geo} values of 3.3 and 2.5, respectively.

The metal fractions that were associated with sediments can be normalized and categorized using enrichment factor (EF), which indicated the degree of anthropogenic modifications to the sediments in different environments. The average EF values are shown in Fig. 3 along with their standard deviation (SD). The SD values were large for all samples in all systems indicating that even within a similar system, the sources and their contributions could vary notably. Similar to the results obtained from previous indicators, agricultural pond samples showed some of the highest anthropogenic modification (EF more than 1.0). Except for the river samples, the remaining systems showed very severe anthropogenic modification in the case of Pb (EF > 10). The EF for Pb in the reservoir samples followed a similar trend to the metal concentration; higher (20.2) at the inlet of the Upper Pearl River into the reservoir, and progressively decreasing moving away (14.5 at midpoint, and 10.0 near the downstream end). Only Se in two of the coastal samples, and Cd and U in site 4 agricultural pond showed similarly high values. Se, which showed severe modification values (EF 5–10) in some of the forest, and river samples, has been known to cause toxicity to waterfowls, which commonly aggregate in coastal

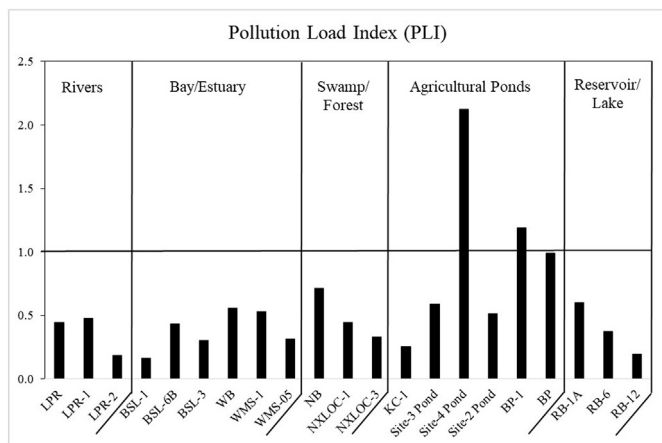


Fig. 2. Pollution Load Index (PLI) calculated for the sediments. A PLI value of more than one indicates that the metal concentration in that sample was heavily contaminated.

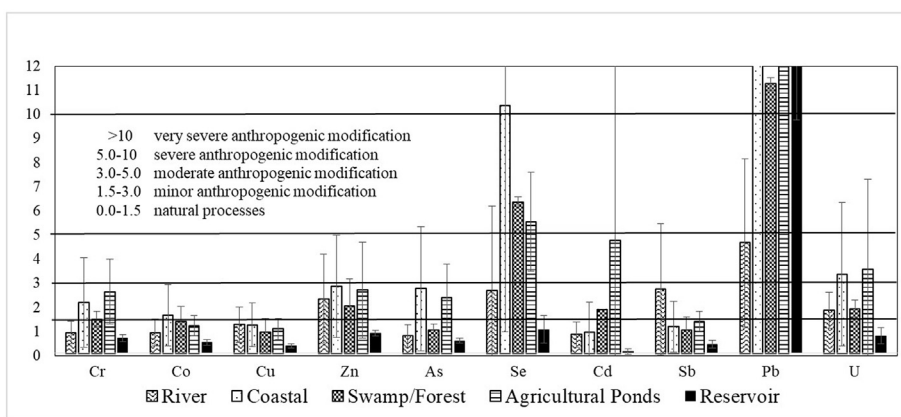


Fig. 3. Average enrichment factor (EF) values calculated for the sediments from the five aquatic systems. The classification criteria for indicating degree of anthropogenic modification is also shown (0.0–1.5, natural processes; 1.5–3.0, minor anthropogenic modification; 3.0–5.0, moderate anthropogenic modification; 5.0–10, severe anthropogenic modification, and >10 very severe anthropogenic modification). Error bars show the standard deviation of the average values.

regions and wetlands for breeding (Wu, 2004). The source of Se varies and could range from coal combustion and mining to agricultural and municipal waste, all of which were possible sources in the samples tested here (Lemly, 2004). High EF for Se have been shown to be dangerous for aquatic organisms (Sprovieri et al., 2007). The coastal samples showed some severe modification with U, Zn and As, as well as moderate modification (EF 3–5) with respect to Cr. The forest samples had minor modification (EF 1.5–3.0) reported for the metals Co and U. Among the agricultural samples, more than 60% of Pb, Cr, U, Zn, and As showed minor or higher anthropogenic modification, compared to other systems. About 45% of samples showed metal concentrations to be within the natural limit and were attributed to natural processes (EF < 1.5). EF and I_{geo} in a previous study at locations in the Gulf of Mexico sediments revealed that the influence of anthropogenic sources was minimal (EF < 2, I_{geo} < 1; Armstrong-Altrin et al., 2019). Most of the background metal concentration in the Gulf of Mexico coast has been attributed to the sediment load brought in by the Mississippi and other river systems (Santschi et al., 2001). However, pollution due to oil refineries, agricultural activities, and other industries were often cited as contributors to elevated metal and other contaminants. For example, sediments collected from Louisiana Gulf Coast near a petroleum refinery had EF values higher than 10 for the metals Cd, Sb, V, As, and Se (Zhang et al., 2015).

The concentrations of Cr, Cu, Zn, As, Cd and Pb were compared with numerical sediment quality guidelines (SQG) to determine the potential of the contaminant to cause adverse effects on sediment-dwelling organisms (Long and MacDonald, 1998). A consensus-based SQG, namely threshold effect concentration (TEC) and probable effect concentration (PEC) for these elements were employed in this study (MacDonald et al., 2000). TEC indicated the concentration below which adverse effects of the particular metal or contaminant to sediment dwellers were not expected to occur, whereas PEC referred to concentration above which effects would be more frequently expected (Zahra et al., 2014). Values intermediate to TEC and PEC may or may not cause potential toxic effects. The consensus-based TEC and PEC values for Cr, Cu, Zn, As, Cd and Pb are provided in Table 3. On an average, about 84% of all samples in all categories had metal values below TEC, indicating that most samples will most likely not pose a threat to the organisms that dwell in the bottom profile of the aquatic system under consideration. Among these elements, Cu, As, Cd and Pb did not exceed the PEC values for any of the samples. 50% of the agricultural pond samples exceeded Fig. 4 PEC values for Cr, whereas one of the six samples in this category exceeded PEC value for Zn. None of the other four systems had metal(loid) values exceeding PEC. Cr was the most important metal that could lead to toxicity, and was reported in other regions as well (Li et al., 2014). Very few benthic

organisms would be expected to exist in agricultural ponds and therefore the high TEC values may not be detrimental. However, since these ponds are used for irrigation, if the sediment metal concentration continue to increase overtime, it could lead to secondary pollution. In such a scenario, the sediments themselves can act as a source (legacy effect) to pollute overlying water, and can increase metal concentration in the soil and crops (Lutgen et al., 2020; Santiago-Martin et al., 2020).

While SQG would be useful in predicting the health of a benthic environment, it should by no means considered to be a universal approach. Other factors, such as physico-chemical conditions, biological target, and metal speciation would also affect the toxicity of metals (Simpson and Batley, 2007). Additionally, it should be noted that the values used from MacDonald et al. (2000) were originally intended for freshwater sediments, so these guidelines may not be strictly applicable for coastal sediments. Nevertheless, these values are still helpful to interpret historical data and assess ecological risk (Long and MacDonald, 1998). Our comparative study was especially beneficial for testing these guidelines against different aquatic systems in a single effort. While a global solution may not be applicable when proposing guidelines for complex environments, it is clear that more of such comparative studies would be essential to develop a more standardized set of guidelines for sediment quality.

3.4. Land use land cover and Principal Component Analysis

The 15 LULC classes obtained were based on HUC 8 and HUC 10 watershed levels, which were then manually grouped into six classes. For example, deciduous, evergreen and mixed forests were collectively grouped under a single group, 'forest'. The class groupings for this study and the respective percentage distributions are given in Tables S5 and S6, respectively. All five aquatic systems had varied distributions of LULC classes, which was important to understand the source of the metals (Fig. 4 and S1–S3). In the river system, forest and shrubs occupied ~30% of the watershed area, followed by wetlands (25%). Open waters, agricultural and developed land were less than 6% each in this system. Coastal estuary systems had roughly the same LULC as rivers, except that the developed portion was highest among all systems (16%). Such urban and developed regions in the coastal setting were commonly associated with heavy metal pollution and served as collection points (Feng et al., 1998). The aquatic systems classified as swamp/forest were dominated by forest land (40%) followed by wetlands and shrubs at ~25% each. As expected, the agricultural ponds and lakes had the highest percentages of crops (18%) and open waters (20%), respectively in their watersheds. It is also important to note that land cover 'hay/pasture' was classified under 'shrubs', because these land types could also be amended with fertilizers and additives, which in turn could serve as non-point sources for pollution.

To understand the relationship between the metals and LULC, identify association patterns in the data, and predict sources, LULC percentages was compared with sediment metal concentration using PCA. Similar approaches using LULC analysis to identify contamination hotspots in specific study areas have been undertaken recently, where proximity to urban and semi-urban areas and mining areas resulted in some of the highest metal toxicities (Ma et al., 2020; El-Alfy et al., 2020). The analysis presented here took a slightly different approach from these previous studies in that the actual percentages of LULC from a sub-watershed level were compared with the metal concentration considered to be representative of that region (Liu et al., 2017). PCA is a multi-variate statistical method to handle large datasets with a primary goal of reducing the number of data points to more meaningful components and understand the relationship between the variables. Six

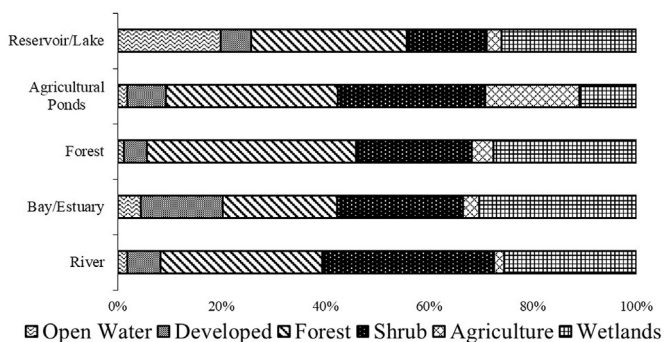


Fig. 4. Land use Land cover classification for the five aquatic systems.

principal components with eigen values more than one were extracted, indicating that each component contained more information than one original variable. These six components explained 92% of the total variance (information) seen in the samples. The first two components, which together explained ~55% of the total variance were described here to understand the relation between the variables. The contributions of the original values to the components (called as loadings), indicated that the first component, PC1, explained 40.1% of the variance in the samples with a large eigen value of 6.4 (Table S7). The variables that contributed to PC1 included the metal(loid)s Cu, Zn, U, Cd, As, Cr and Co, and two land covers, namely agriculture and wetlands (Table S7). The second major component, PC2, explained 14.6% of the variance and received contribution from the land covers shrub, forest, open water, and developed, the metal Pb, and metalloid Se. While both of these elements had a wide range of natural and anthropogenic sources, Pb had more of an urban influence due to its use in paints, pipes, and fossil fuel industries (Patterson, 1965). PC3, the third component, explained 12.4% of the variance in the data, and received contribution from Cr and As, and the land covers developed, agriculture and wetlands. This pattern agreed with our earlier-mentioned evaluation of these metal(loid)s and their likely sources, such as fertilizers, urban runoff, industries and tanneries. The other components (PC4-PC6) have 10% or less variance and are not discussed here.

The PCA biplot shown in Fig. 5 correspond to PC1 and PC2. The longer the length of the variable, the greater that particular variable's influence on that component. Similarly, the angle between any two variables approximately reflected the correlation between them. The relatively smaller angles between the PC1 variables indicated that they are well-correlated to each other. It was clear that agricultural land was most correlated with most of the toxic metals, showing that agricultural practices had an important influence on the metal pollution. Wetland was negatively correlated with agriculture and most metals, indicating that the concentration of metals decreases with larger wetland area and vice versa. The soil and vegetation in wetlands served as excellent buffers for sequestering a variety of contaminants including metals (Peltier et al., 2003).

The contribution of all other LULC classes, including open waters, served to elucidate the point that these LULC classes had varying influence on the metals. If our study had included sediments from ponds and lakes from urban and sub-urban-dominated land uses, it would likely result in high metal concentrations in those regions (Allinson et al., 2015). The main message from the PCA and LULC analysis was that agriculture plays a very important

role in influencing heavy metal accumulation in sediments. Such agricultural settings, when placed in proximity to industries and urban systems, may likely compound the type and concentration of contaminants entering into ponds, lakes, and rivers.

4. Conclusions

The study comparing and assessing the trace transition elements and heavy metal concentration and distribution in five different aquatic systems indicated that the sediments in agricultural ponds were the most polluted, followed by coastal bays and estuaries. Fertilizer use was considered to be one of the most important contributing factors for the metals in these different systems belonging to the agriculture-intensive Southern USA. Majority of the samples had metal concentrations similar to their background levels, though some systems positively indicated anthropogenic metal contamination. Among the various metals, U and Cd in the agricultural ponds showed very high contamination factor and geoaccumulation index values, with this system also having the highest pollution load index. In some of the forest, coastal and river samples, Se and Pb showed moderate to severe modification with respect to their background levels as determined by enrichment factor. Evaluation of sediment quality guidelines indicated that Cr and Zn had toxicity levels that could potentially affect benthic organisms, especially in agricultural ponds. Principal component analysis using land use land cover data further confirmed the influence of the various land activities on the metal concentration, with larger agricultural areas correlating well with most metals. As agricultural ponds were identified as some of the most polluted systems among the water bodies tested, we urgently propose that more investigations be conducted in such ponds, since these could serve as easy transportation routes of metals and farm additives to plants and subsurface aquifers.

Though the acid digestion procedure performed here allowed for estimating the total amount of metals bound to sediments, it is important to note that bioavailability and toxicity of the contaminants depends on speciation and the fraction of the sediment where the metals are present. Sequential extraction of the metals in the sediments will be performed in the future to help in understanding the various sediment fractions (organic, iron hydroxides, carbonate, and silicate). While there are studies being conducted to establish guidelines for sediment quality in terms of numerical metal concentration, the variations in land use land cover, climatic conditions along with other factors, such as population density, compound the negative impacts. Furthermore, the guidelines developed in one location may not be suitable for another location, because toxicity levels could be biota or environment-specific (Bai et al., 2019; Chen et al., 2017). Our study provides an enhanced approach to compare metals in sediments from multiple aquatic systems in a single, concerted effort, thereby serving as a model to help test and generate robust guidelines. Such information will help address the knowledge gap in developing pollution limits for sediments in various environmental settings. We propose that environment-specific guidelines be developed in parallel to toxicity tests, which can in turn be expanded to a larger state- or nationwide level.

Author contribution

Varun Paul, Supervision, Conceptualization, Investigation, Writing-original draft preparation. M.S. Sankar, Methodology, Formal analysis, Writing - review & editing. Shannon Vattikuti, Methodology, Formal analysis, Writing - review & editing. Padmanava Dash, Resources, Investigation, Writing - review & editing. Zikri Arslan, Methodology, Writing - review & editing.

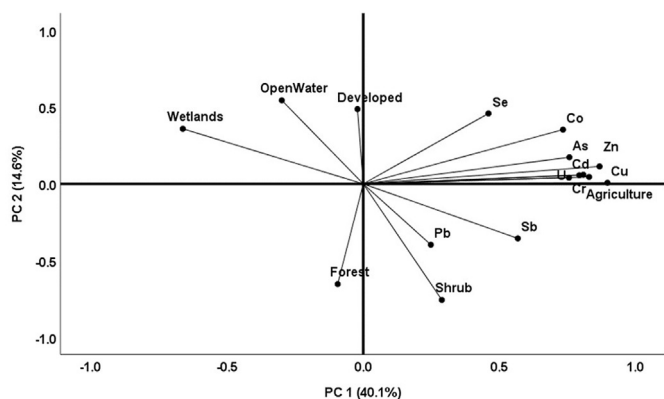


Fig. 5. Principal Component Analysis results showing the loadings plots for the first two extracted components.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.128243>.

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