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Abstract: The concentration and distribution of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn are investigated in three sediment cores representing upriver, midriver, and estuarine environments in Río Espíritu Santo (RES), Rio Grande, Puerto Rico. Grain-size distribution, organic matter and carbonate content were determined to assess their influence on metal concentration. Minimum biotoxicity levels of Ni and Cu were exceeded in the upriver and midriver sites, while only Cu was exceeded in the estuary location. Pb concentration decreased by ~ 35 % in the upper portion of Cores 2 and 3, possibly as a consequence of leaded gasoline regulation. Enrichment Factors and Geoaccumulation Indices were calculated for each metal revealing high contamination levels of Cu in all three cores, likely originating in a copper deposit in the northern Luquillo Mountains. Results show that the RES possesses low level of contamination, with the exception of Cu, which is of natural origin.

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Dear Editor,

The manuscript titled "Spatial and vertical distribution of metals in sediment cores from Río Espíritu Santo estuary, Puerto Rico, United States" is submitted here for your review. The paper investigates degree of metal contamination in a fluvial-estuarine system in northeastern Puerto Rico. This location exists at the nexus of a protected rain forest and a highly developed urban area. We characterize the grain size, organic matter and carbonate content, and concentration of a suite of trace metals indicative of the health of the system. We determine the degree of metal pollution, propose possible sources for contaminants, estimate potential ecological risk associated with contamination, and provide a baseline for future assessment of the RES fluvial-estuarine system. I believe this research is of significant interest to your readership and therefore appropriate for publication in Marine Pollution Bulletin.

This article (or closely related research) has not been published or accepted for publication. It is not under consideration at another journal. No other papers using the same data have been published.

The authors do not have commercial affiliations or financial arrangements that may pose a conflict of interest.

Sincerely, Prof. Karin A. Block Department of Earth and Atmospheric Sciences City College of New York 160 Convent Avenue, Room MR-106 New York, NY 10031

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Highlights

Highlights

- A suite of trace metals was analyzed in upriver, midriver and estuarine cores.
- Minimum biotoxicity levels of Ni were exceeded in the upriver and midriver sites.
- Biotoxicity levels of Cu exceeding ERL were found in all three sites.
- Pb decreased ~ 35% in the upper portion of the midriver and estuary cores.
- High levels of Cu contamination are likely of natural origin.

Spatial and vertical distribution of metals in sediment cores from Río Espíritu Santo estuary,

Puerto Rico, United States

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Abstract

which is of natural origin.

The concentration and distribution of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn are investigated in three sediment cores representing upriver, midriver, and estuarine environments in Río Espíritu Santo (RES), Rio Grande, Puerto Rico. Grain-size distribution, organic matter and carbonate content were determined to assess their influence on metal concentration. Minimum biotoxicity levels of Ni and Cu were exceeded in the upriver and midriver sites, while only Cu was exceeded in the estuary location. Pb concentration decreased by ~35 % in the upper portion of Cores 2 and 3, possibly as a consequence of leaded gasoline regulation. Enrichment Factors and Geoaccumulation Indices were calculated for each metal revealing high contamination levels of Cu in all three cores, likely originating in a copper deposit in the northern Luquillo Mountains. Results show that the RES possesses low level of contamination, with the exception of Cu,

Keywords: Puerto Rico; Metals; Estuary; Sediment; Pollution; Caribbean

Sediments transporting contaminants from terrestrial areas can enter coastal and marine systems, compromising ecosystem health and function (Birch and Olmos, 2008; Chapman and Wang, 2001). The island of Puerto Rico, a United States territory, is characterized by a large population density along the coast and a strong dependence on coastal resources for food and tourism. Puerto Rico has undergone significant changes in land use over the last 100 years, possesses a mountainous interior, and is subject to high rainfall, making water and sediment quality in the terrestrial and marine domains of particular importance (Gould et al., 2012).

This study examines sediments from three sites along Río Espíritu Santo (RES) in Rio Grande, a municipality on the northeast coast of Puerto Rico with one of the highest population densities in Puerto Rico (345.88 persons/km²; U.S. Census Bureau, 2013). RES is one of nine rivers draining the Caribbean National Forest (CNF). The vegetation associated with the estuary consists of tropical and subtropical plants and mangrove forest at the fringes of the river's mouth. The results of trace metal analyses are reported to provide a measure of metal accumulation in the fluvial-estuarine-coastal system and the relative influence of contrasting land use along its profile. The goal is to determine the degree of pollution, propose possible sources for contaminants, and estimate potential ecological risk associated with contamination to provide a baseline for future assessment.

Figure 1 here

Three sediment cores were collected along a longitudinal profile within RES in June and July of 2007 and August 2008 using a push-corer made of polyethylene tubing. Sampling locations were selected on the basis of accessibility to the stream channel with the goal of capturing variations in hydrology associated with freshwater, intermediate, and estuarine environments. Core lengths varied due to inherent differences in substratum. The upper 10 cm of

each core was sliced into 0.5 cm and 1 cm sections using a PVC spatula. Sediment fractions were freeze-dried prior to analysis.

Subsamples were analyzed for grain size, organic matter and calcium carbonate content. Grain-size distribution was determined by wet sieving samples through a 63 µm mesh sieve. Particles larger than 63 µm were categorized as sand and gravel. Percent silt and clay was determined on fine-grained material (< 63 µm) using a particle size analyzer (Micromeritics, Saturn DigiSizer 5200, Norcross, Georgia). Sequential weight loss on ignition (LOI) was used to determine organic matter at 550 °C and calcium carbonate content at 950 °C; (Dean Jr, 1974; Heiri et al., 2001).

Partial metal concentrations were determined using US EPA Method 200.8 (USEPA, 1999). Approximately 1.0 g aliquot of subsample was digested in 4 mL of (1:1) HNO₃ and 10 mL (1:4) HCl (Trace Metal Grade; Fisher Scientific, Waltham, MA). Trace metals were leached by reflux at approximately 95 °C for 30 min. After reflux, samples were cooled, filtered and diluted to 100 mL using high purity deionized water. Cd, Cr, Cu, Mn, Ni, Pb and Zn concentrations were determined by inductively coupled plasma-mass spectrometry (ICP-MS; Thermo Fisher Scientific X-Series 2). Quality control and assurance was established by consistently monitoring instrument performance using a five-point calibration curve and a multielement standard (SPEX CertiPrep, Inc. Metuchen, New Jersey) and analysis of reagent blanks interspersed with sediment samples for further quality control. Reported concentrations represent the average of three determinations. The average relative standard deviations for each metal were Cd (8.9%), Cr (5.4%), Cu (4.1%), Mn (5.1%), Ni (4.6%), Pb (1.7%) and Zn (3.6%). Iron concentrations were determined using a ThermoScientific Atomic Absorption Spectrometer in flame mode. Standard detection limits are in the μg/kg range.

Descriptive statistics were generated for grain-size distribution, organic matter, carbonate content and metal concentrations. Normality was evaluated using the Kolmogorov-Smirnov test. Square root transformation was applied for all elements in preparation of parametric tests. One-way ANOVA was conducted to test for significant differences in metal concentrations with respect to the location of sediment cores. The Duncan multiple range test was used for comparing means. Pearson correlation analysis was conducted between metals, silt, clay and organic matter. Statistical significance from all analyses was determined at the p < 0.05 and/or p < 0.01.

The degree the metal contamination in sediment samples was assessed using the Geoaccumulation Index (I_{geo} ; Müller, 1969; Equation 1) and Enrichment Factor (EF).

$$I_{geo} = Log_2 ([C_n]/1.5(B_n)$$
Equation (1)

where, C_n is the measured concentration of the trace element in sediments, B_n is the average background value of element n in shale (Turekian and Wedepohl, 1961), 1.5 is a correction factor applied to address lithogenic effects (Lin et al., 2008). The (Förstner et al., 1993) classification for geoaccumulation is utilized here to evaluate I_{geo} from RES.

EF is widely used to determine sediment contamination metals (Çevik et al., 2009; Chatterjee et al., 2007; Garcia et al., 2009; Magesh et al., 2011; Rubio et al., 2000) in spite of the limitations presented by Reimann and De Caritat (2005). Contamination is determined by comparing measured concentration to background values in crustal or shale matrices. The EF for a given metal is computed as follows:

$$EF = ([Me_s]/[Fe_s])/([Me_{shale}/Fe_{shale}])$$
 Equation (2)

Where Me_s and Fe_s represent concentration of total metal (Me) and iron (Fe) in sediment samples. Me_{shale} and Fe_{shale} represent the background metal and Fe concentrations in shale. In this study, Fe was used to normalize metal concentrations because of its abundance in soils for this area (Chacon et al., 2006). The Sutherland (2000) classification is used in this work to evaluate calculated enrichment factors.

Table 1 here

Sediment cores possessed admixtures of sand and gravel, silt and clay-size particles (Table 1). Average clay content was highest (~22%) in Core 1 at the upriver sampling site; midriver Core 2 contained the highest average silt content (~61%) and 19% clay content; Core 3 contained the highest average total sand and gravel content (~36%). The spatial variation in grain-size distribution reflects changes in hydrodynamic environment. The dominance of fine-fraction (clay + silt) in Cores 1 and 2 suggests that lower-energy settings are prevalent in the upper portion of the system, whereas a higher-energy environment influenced sediment distribution within the lower fluvial-estuarine system as reflected in the higher sand-gravel content in Core 3.

Figure 2 here

Mean values for organic matter (OM) and carbonate for each core are shown in Table 1; the complete dataset is available in Table A1 in the Supplementary Materials. The OM ranged from approximately 10 wt. % to 16 wt. % in Core 1, 12 wt. % to 20 wt. % in Core 2, and 13 wt. % to 25% in Core 3. Carbonate content ranged from 1.7 wt. % to 2.8 wt. % in Core 1, with the exception of a sample at 10 cm depth which contained 6 wt. %. Core 2 carbonate range was 2.25 wt. % to 5 wt. % and Core 3 range was 2.7 wt. % to 6.5 wt. %. Vertical profiles of organic matter and carbonate content within each of the three cores are shown in Fig. 2. Both Core 2 and Core 3 contained larger amounts of OM in surface samples and lower amounts at depth. Overall, the carbonate content profiles for each core fell within a narrow 2-4 % range of mean carbonate. Core 3 possessed the highest carbonate content on average.

Table 2 here

The mean and standard deviation of trace metal concentrations within each of the sediment cores are presented in Table 2, along with average shale concentrations of Turekian and Wedepohl (1961), and evaluation parameters for aquatic toxicity (Long et al., 1995), effects-range low (ERL) and effects-range median (ERM). The complete dataset is available in Table A2 in the Supplementary Materials The mean concentrations of Cd, Cr, Ni, Mn, Pb and Zn in all three cores were lower than average shale values. Cu exceeded average shale values in all three cores, while Fe values exceeded average shale values in Cores 1 and 2.

Mean Cd concentrations within core corresponded to a seaward increase with the highest level identified in Core 3 (0.23 mg/kg). Mean concentrations of Cu (156 mg/kg), Zn (83 mg/kg) and Mn (492 mg/kg) were also the highest in Core 3. Conversely, mean Fe concentrations decreased in the seaward direction with Core 1 containing the highest concentration (~7 %) on average. Core 1 also possessed the highest mean concentrations of Cr (55mg/kg) and Ni (26 mg/kg). Pb was highest in Cores 2 (13 mg/kg) and 3 (13 mg/kg). Two elements exhibited potential toxic effects: in all three cores, the average concentration of Cu was above ERL and, in Core 3, some depths approached or exceeded ERM. Ni concentration exceeded ERL values in Cores 1 and 2, with the highest average concentration in Core 1, reflecting provenance from the igneous source.

Vertical profiles of metal concentrations for each core are shown in Fig. 3. The concentration of all metals in all three cores fluctuated slightly with some exceptions. In Cores 1 and 2, concentrations of Cd, Cr, Mn, Ni, Pb, and Fe produced similar patterns downcore. In Core 2, Mn concentration occupied a broad range and reached nearly double the average concentration at 33 cm depth; at 31 cm depth in Core 2, the Mn concentration is 3241 mg/kg, which we consider an outlier due to experimental error. Additionally, Zn exhibited higher variability in

Core 2 but was on average lower than in Cores 1 and 3.. The average concentration of Pb in the lower part of Core 2 below 21 cm depth was 15.6 mg/kg, notably higher than in the upper part of the core where the average concentration was 9.5 mg/kg.

Cu concentration was highest and experienced the most fluctuation in Core 3, with peaks in concentration at 15 cm to 21 cm, 23 cm to 25 cm, and 37 cm to 39 cm depth. Mn concentration in Core 3 was relatively constant with the exception of a significant jump from 400 to 600 mg/kg between 25 cm and 45 cm depth, possibly due to a sudden increase in sediment input possibly from a storm event. Pb concentration in Core 3 is significantly higher below 27 cm depth, was 16.3 mg/kg, substantially higher than in the upper part of the core where the average concentration was 10.5 mg/kg, and similar to the pattern observed in Core 2.

One-way analysis of variance (ANOVA) and Pearson correlation analyses were performed to detect intermetallic relationships and assess influence of sediment characteristics on metal concentrations. Results from ANOVA indicated that all metal concentrations with the exception of Pb were significantly different at p < 0.01. For grain size and OM, correlations are reported for a statistical significance of p < 0.05 or better.

A matrix of Pearson correlation coefficients for Core 1 is shown in Table 3. The sediments of Core 1 exhibited positive correlations between Cd, Cr, Ni, Pb, Mn and Fe. Cd was negatively correlated with Cu and Zn. Cr possessed strong positive correlation with Fe, Mn, and Ni. Mn and Ni were strongly correlated with each other. The strong correlation for Fe and Mn is interpreted as a consequence of the natural affinity of the two metals for oxyhydroxide formation. Grain-size and OM content influenced trace metal distribution in Core 1 and that all metals, except Ni and Fe, positively correlated to silt content. Cd, Cr, Cu, Pb and Zn positively correlated to OM content. All metals, except Pb and Zn, positively correlated to clay-sized

particles. Cd, Cr, Cu, Pb were positively correlated with OM, while Zn. Fe, Ni and Mn were negatively correlated with OM.

Table 3 here

A matrix of Pearson correlation coefficients for Core 2 is shown in Table 4: Cd was positively correlated to Cr, Ni, Zn, Cu, Fe, Mn, Pb. Strong, positive and statistically significant relationships were found between Cr and Ni, Cr and Zn, and Ni and Zn. Cd, Cu, Fe, Mn, and Pb were positively correlated to silt and clay fractions, while Cr, Ni and Zn were negatively correlated. Negative correlations were found between Ni and clay, Ni and silt, Zn and clay, and between OM and all metals.

Table 4 here

A matrix of Pearson correlation coefficients for Core 3 is shown in Table 5. Cd was positively correlated with Cr, Fe, Mn and Pb. Negative correlation relations were found between Cd and Cu, Cd and Ni, and Cd and Zn. Positive correlations were found between Cr and Fe and between Cr and Pb. Ni significantly correlated with Zn, but neither metal correlated strongly with Cu. Cd, Fe, Mn and Pb all positively correlated to silt, clay and OM. Cu, Fe, and Mn correlated with silt content.

Table 5 here

 I_{geo} and EF were calculated to assess the degree of contamination in RES (Table 6). The average I_{geo} values for each core indicated that all metals (Cd, Cr, Fe, Mn, Ni, Pb, Zn) with the exception of Cu occurred below contamination levels. The I_{geo} values for Fe in all three cores were close to zero, which suggest that Fe behaved conservatively in the estuarine environment and making Fe a suitable parameter for normalization in EF analysis. I_{geo} values calculated for Cu in the sediment cores ranged from 0.59 to 1.05.

Table 6 here

EF values showed that all analyzed metals, with the exception of Cu, were either deficient or minimally enriched. However, Cu was moderately enriched in all three hydrologic environments. The incidence of high Cu EF values in all three cores, in the absence of high values for other chemical indicators of anthropogenic contamination, point toward a geologic source for this metal. Mineable copper porphyry deposits are found in several locations across the central mountain ranges of Puerto Rico, with a copper/gold porphyry and copper skarn within a few kilometers of the RES Watershed (Marsh, 1998). Based on this evidence, we propose that a Cu deposit on the northern flank of the Luquillo Mountains may be the source of anomalous Cu concentrations found in this study, and possibly presenting a natural contamination threat to coastal biota near the RES estuary.

Spatiotemporal analysis of metals in the RES, revealed that on average the fluvial-estuarine system contains low levels of contamination. The upper and midriver locations were dominated by a low energy hydrologic environment, as reflected in grain size distributions, while the estuarine core was subject to higher energy hydrologic environment resulting in a larger fraction of sand and gravel. The prevalence of fine grained sediments in the upper and midriver regime appear to have influenced the longitudinal distribution of metals, promoting aggregation and settling of Cd, Cr, Mn, Ni, Pb, and Fe, reflected in down core profiles of Cores 1 and 2.

The midriver core contained the highest fraction of fine-grained sediments. However, clay and silt in this core did not correlate with metal content or OM. This suggests a rapid drop in water velocity, which leads to abrupt settling of fines and impacting the ability for OM and metals to aggregate with sediment. Average Fe concentration decreased with distance from the

igneous source, while Mn in sediments increased downriver, possibly as a result of interaction with dissolved carbonate in the estuary.

Intermetallic relationships were distinct within each of the three cores. Combined with the strong positive and negative correlations among metals and the overall low levels of contamination in RES, this suggests that the downstream transport regime, as dictated by topography and the resulting grain size distribution, was a strong driver of metal abundance in the sediments. While the fine fraction (silt and clay) correlated with a large number of metals in Cores 1 and 3, the correlation is absent in Core 2 despite having the highest relative amount of fine-grained sediments. A notable relationship is the strong correlation of Fe with Mn for Cores 1 and 2, but absent in Core 3. This suggests that the hydrologic and geochemical conditions favored the aggregation and deposition of these two metals in tandem in the upriver and midriver settings, but not in the downriver/estuarine environment. Mn – Fe variation and distinct fields roughly correspond typical trends in each environment are shown in Fig. 4. Upriver (primarily Core 1 sediments) sediments occupy a high Fe, high Mn cluster (horizontal line pattern). Midriver sediments occur in all three fields however, a large number are characterized by low Mn concentrations (cross pattern). Some sediments from Cores 1 and 2, and the majority of sediments from Core 3 form a downriver/seaward array (diagonal line pattern) characterized by low Fe and high Mn concentrations.

A downriver increase in carbonate content may lead to precipitation of MnCO₃ in the sediment without co-precipitation with Fe. Downriver decreases in Fe, Ni, and Cr, all of which are likely to have weathered from the source igneous rocks, may be the result of fast settling in the upper regime of the stream, leading to depletion as the stream moves away from the source. Table 7 here

Table 7 shows the average concentrations of metals reported for other studies in Puerto Rico and Jamaica. The concentrations of all metals in RES are higher than in uncontaminated sites in Jobos Bay, PR (Aldarondo-Torres et al., 2010) and Joyuda, PR (Acevedo-Figueroa et al., 2006). In the uncontaminated site of La Parguera, PR (Pait et al., 2008), Ni exceeded average concentrations found in RES. In Montego Bay, Jamaica (Jaffé et al., 2003) Cd and Ni also occurred at higher levels than in RES, Despite generally low contamination levels in RES, average Cu concentration exceeded the level found at the contaminated site in San José Lagoon, PR (Acevedo-Figueroa et al., 2006). Because Cu concentration does not correlate with any other potential anthropogenic contaminants, we conclude that Cu contamination is of natural origin. In the estuarine core, spikes in Cu concentration reach ERM levels, which may be driven by higher salinity in this environment (Du Laing et al., 2009). The naturally high Cu concentrations in all the cores can be explained by the existence of copper deposits in the northern Luquillo Mountains within a few kilometers of the RES watershed (Marsh, 1998).

6. Acknowledgements

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List of Figures

Figure 1. Map of study area with inset showing location of the Río Espíritu Santo watershed and sampling locations. Modified map of Greater Antilles used by permission: Creative Commons License SA-3.0.

Figure 2. Vertical profiles for organic matter and calcium carbonate content (wt. %) in all three sediment cores. Core 1 profile is represented by solid black lines, Core 2 by solid grey lines, and Core 3 by dashed black lines.

Figure 3. Depth profiles of Cd, Cr, Cu, Mn, Ni, Pb, Zn (mg/kg) and Fe (wt. %) concentrations. Mn concentration in Core 2 at 31 cm (off-scale) is 3241 mg/kg. Symbols and grayscale colors are the same as in Fig. 2.

Figure 4. Mn – Fe variation in core sediments. Concentrations are in mg/kg. Core 1 sediments are represented by open triangles, Core 2 sediments are represented by filled triangles, and Core 3 are represented by open squares. The horizontal line pattern primarily captures sediments characteristic of upriver environment, stippled pattern represents midriver sediments and diagonal pattern indicates a downriver trend primarily occupied by midriver and estuarine sediments.

Table 1 Average values for sand and gravel, silt, clay, organic matter and calcium carbonate content (%) in samples from three sediment cores % Sand + % Fine Environment Gravel % Silt % Clay Fraction % OM Carbonate Core Up-River 73 Core 1 2.7 51 22 2.3 Intermediate Core 2 20 61 19 80 16 3.6 Mouth - Estuary 4.3 Core 3 36 49 16 64

All concentrations are expressed in units of ppm with the exception of Fe (%)

 20 ± 1.45

68

20.9

51.6

 13 ± 3.29

20

46.7

218

 83 ± 6.78

95

150

410

 492 ± 85.8

850

na

na

 6.46 ± 3.80

 4.27 ± 0.93

4.72

na

na

Sample N Cd Cr Cu Ni Pb Zn Mn Fe

Core 1 14 0.13 ± 0.03 55 ± 13.0 106 ± 31.0 26 ± 4.90 11 ± 2.29 78 ± 7.67 428 ± 72.1 6.82 ± 2.94

Core 1 14 0.13 ± 0.03 55 ± 13.0 106 ± 31.0 26 ± 4.90 11 ± 2.29 78 ± 7.67 428 ± 72.1 Core 2 20 0.18 ± 0.06 42 ± 11.4 104 ± 51.3 18 ± 4.47 13 ± 5.20 68 ± 14.1 474 ± 669

 156 ± 75.5

45

34

270

Table 22 Mean and standard deviation of trace metal concentrations in sediments.

 47 ± 3.57

90

81

370

Core 3

Average Shale^a

 ERL^b

 ERM^b

^b Long et al. (1995)

26

^a Turekian and Wedepohl (1961)

 0.23 ± 0.06

0.3

9.6

Cd Cr Cu Fe Mn Ni Pb Zn Silt Clay OM Cd 1 Cr 0.79** 1

Table 33 Pearson correlation coefficient values between metals, silt, clay and organic matter for Core 1.

0.94**

0.73**

0.34

0.16

0.25

-0.04

0.51

-0.56*

-0.39

0.31

-0.21

0.12

0.36

-0.03

0.3

0.66*

-0.53*

0.60*

-0.45

0.73**

0.75**

-0.58*

0.76**

0.77**

0.73**

0.48**

0.20**

0.36

0.25

-0.21**

Cu Fe

Mn

Ni

Pb

Zn

Silt

Clay

OM

-0.71

0.81**

0.89**

0.92**

0.47

0.63*

0.47

0.53

0.4

* significance level of p< 0.05
** significance level of p<0.01

-0.46

0.62*

0.74**

-0.15*

0.70**

0.4

0.12

0.22

0.75**

0.74**

0.44

0.35

-0.48

0.55*

-0.56*

Cd Cr

Cr

Cu

Fe

Mn

Ni

Pb

Zn

Silt

Clay

OM

0.47

0.65**

0.68**

0.57**

0.85**

0.50*

0.36

0.19

-0.44

0.24

0.22

0.36

0.19

0.91**

0.49**

0.94**

-0.38

-0.47

-0.7

* significance level of p< 0.05 ** significance level of p<0.01

Cu

0.77**

0.06

0.24

0.38

0.41

0.1

0.01

-0.21

Fe

0.14

0.33

0.44

0.45

0.23

0.15

-0.38

Table-4 Pearson correlation coefficient values between metals, silt, clay and organic matter for Core 2.

Ni

0.15

0.86**

-0.52*

-0.52*

-0.61**

Pb

0.47

0.33

0.2

-0.47

Zn

-0.46

-0.52*

-0.64**

Silt

0 91**

0.11

Clay

0.2

OM

Mn

-0.18

0.2

0.47

0.36

-0.32

0.69**

Cd Cr Cu

-0.17

0.39

0.34

0.34

0.3

0.3

* significance level of p< 0.05 ** significance level of p<0.01

0.28

0.54**

0.61**

0

-0.32

0.13

-0.21

0.33

0.44*

-0.24

-0.33

0.34

-0.19

0.49*

-0.44*

0 79**

-0.53**

0.46*

0 72**

0 54**

0.17

Cr

Cu

Fe

Mn

Ni

Pb

Zn

Silt

Clay

OM

Table 55 Pearson correlation coefficient values between metals, silt, clay and organic matter for Core 3.

Ni

0.24

0.47*

-0.25

-0.35

-0.21

Pb

-0.23

0.48*

0.69**

0.51**

Zn

-0.25

-0.28

-0.46

Silt

0.82**

0.66**

Mn

0.24

0.22

0.31

0.42*

0.35

0.60**

Fe

0.29

-0.09

0.14

0.39

0.36

0.51**

0.59**

Clay

0.58*

OM

Table 6 Average enrichment factor (EF) and geoaccumulation index (Igeo) of trace metals in the three cores. Sample ID **EF** I_{geo} Core 1 Cd 0.54 -1.39Cr 0.49 -1.37Cu 3.03 0.59 Fe N/A -0.29-1.6 Mn 0.45 Ni 0.03 -2.3Pb 0.52 -1.48 -0.87 0.91 Zn Core 2 Cd 0.53 -1.39Cr 0.42 -1.761.94 Cu 0.45 Fe N/A -0.38Mn 0.42 -1.970.24 Ni -2.55Ph 0.55 -1.43 Zn 0.66 -1.12 Core 3 -0.95 Cd 0.89 Cr 0.6 -1.5 Cu 3.99 1.05

N/A

0.65

0.33

0.75

0.74

-0.17

-1.39

-2.36

-1.19

-0.81

Fe

Mn

Ni

Pb

Zn

Reference Location Río Espíritu Santo, PR Riverine/Estuarine This study

Aldarondo-Torres et

Pait et al. 2008

et al. 2006

Acevedo-Figueroa

Jaffe et al. 2003

nm = not measured

* values are represented as a percentage

al. 2010

Table 7. Average metal concentrations found in sediments in Puerto Rico and Jamaica

Jobos Bay, PR

La Parguera, PR

San José Lagoon, PR

Joyuda Lagoon, PR

Montego Bay, Jamaica

Environment

Estuary

Nearshore, Marine

Estuary

Estuary

Bay

Cd

0.18

0.06

0.1

1.8

0.1

5.4

Cu

122

29

5.21

105

22

44.3

Cr

48

nm

31.2

nm

nm

22.4

Ni

5.2

nm

26.6

nm

nm

16.8

Mn

464

nm

109

nm

nm

nm

Pb

37

11

1.93

219

7.6

30.5

Zn

76.3

64

7.99

531

52

59.6

Fe*

5.9

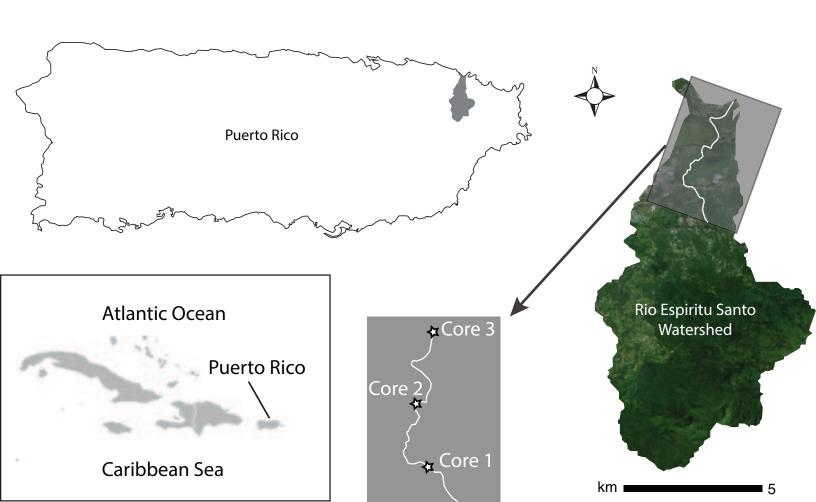
2.6

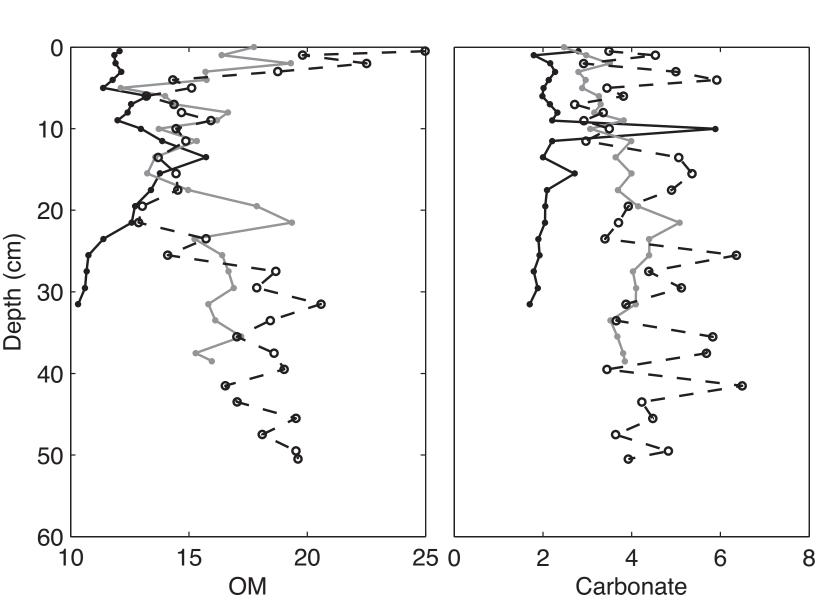
5.2

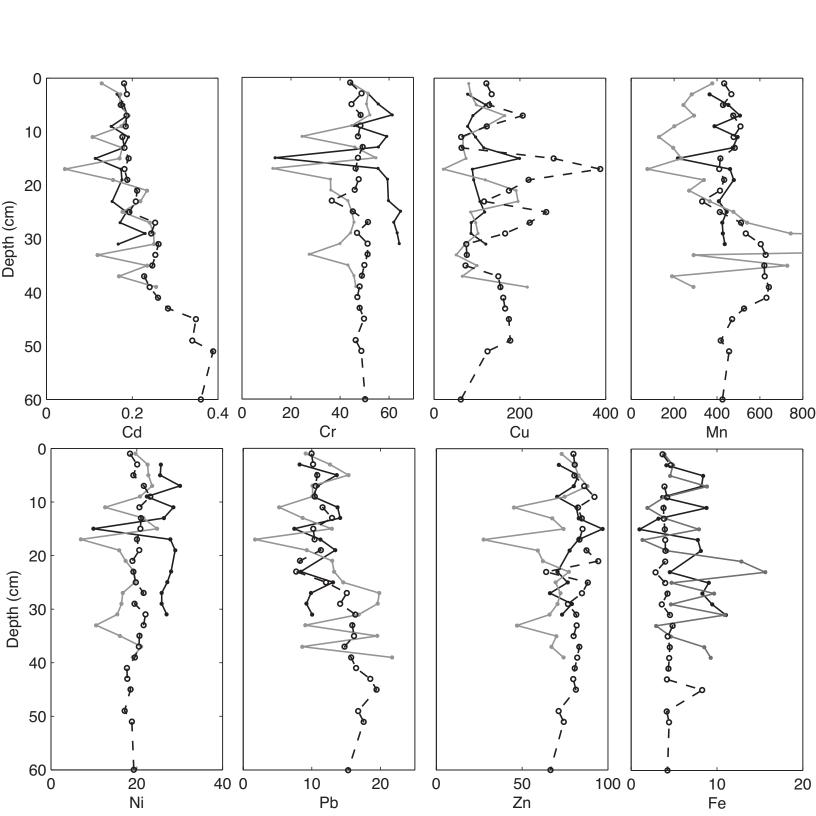
3.9

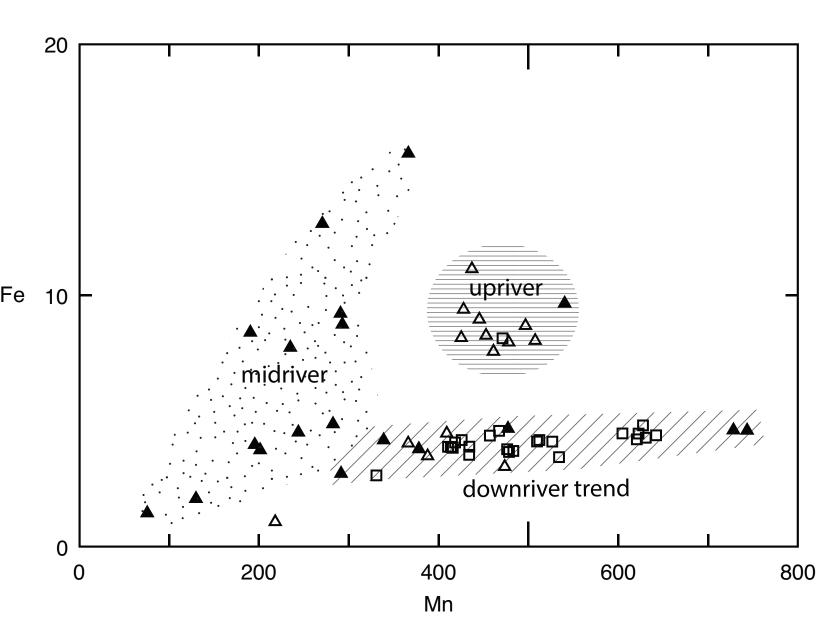
4.9

nm









Supplementary Data
Click here to download Supplementary Data: Table A1.xlsx

Supplementary Data
Click here to download Supplementary Data: Table A2.xlsx