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ORIGINAL PAPER

Spatial controls on riverbed sediment chemistry in three anthropogenically modified tropical mountainous watersheds

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Abstract

Tropical mountainous rivers transport a disproportionate amount of sediment to the global ocean. While these systems also deliver sediment-related pollutants (i.e., metals) to the coast, the potential accumulation of metal contaminants within these systems has been largely unexplored. This study analyzed the trace metal concentrations of fine riverbed sediment (<0.63 µm) collected from Rio Loco, Rio Yauco and Rio Guamaní in Puerto Rico. A total of 17 samples were collected in June 2019 (~21 months following Hurricane Maria) from these watersheds. Metal concentrations (Al, Ba, Cd, Cu, Cr, Fe, Mn, Ni, Sb, Sn, U and Zn) were quantified with acid digestion and inductively coupled plasma mass spectrometry. Strong positive correlations were found between Cd, Pb, Sb and Sn ($r_{avg} > 0.60$, $p < 0.05$) as well as between Ba, Cr and Ni ($r_{avg} > 0.81$, $p < 0.05$). A comparison of land cover with metal concentrations revealed positive statistical relationships between Cu, Sb, Sn and Zn with developed land and Cr, Ni and U with agricultural land. Between 7 and 50% of the samples exhibited enrichment factor values indicative of moderate to significant levels of contamination (EF > 2) for each metal. Additionally, several metal concentrations exceeded the consensus-based threshold effect and probable effect values. Altogether, these data confirm that metals do accumulate in tropical mountainous watersheds and can be found at concentrations that impact freshwater ecosystems. These elevated metal concentrations coupled with periodic flushing events, regularly supported by hurricanes, suggest a threat to nearshore ecosystems such as coral reefs.

Keywords Bed sediment chemistry · Metals · Ecotoxicity

Introduction

Tropical small mountainous rivers deliver a disproportionate amount of sediment to the global ocean (Milliman and Syvitski, 1992). Their characteristic steep slopes often result in "flashy" hydrographs, with large amounts of water and sediment delivered during intense aperiodic precipitation events, such as monsoonal activity or tropical cyclones (Milliman and Syvitski, 1992; Goldsmith et al., 2008; Smith et al. 2020). More recently, anthropogenic activities such as deforestation (Vanacker et al., 2003; Syvitski et al. 2005; Warne et al., 2005), agriculture (Kao and Milliman, 2008; Ramos-Scharrón and Thomaz, 2017) and unpaved roads (Kao and Liu, 2002; Scharrón, 2010; Ramos-Scharrón, 2018) have been shown to increase both erosion and sediment delivery in these systems. For example, coffee farms in the mountainous areas of Puerto Rico produced sediment yields approximately two orders of magnitude higher than the forested catchments (Ramos-Scharrón and Thomaz, 2017). The subsequent transport of these excess sediments, along with associated contaminants (e.g., metals), to the ocean can have a profound impact on coastal ecosystems, such as nearshore coral reefs (Warne et al., 2005).

Recent studies have begun to assess sediment quality within mostly non-mountainous subtropical and tropical watersheds. These studies have identified data patterns similar to their temperate counterparts, with elevated metal concentrations linked to increased impervious surfaces and/or historical industrial activity within the watershed (Sutherland et al. 2000; Qu et al. 2017; Strady et al. 2017; Li et al. 2019). For example, Strady et al (2017) found a severalfold increase in chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) metal concentrations in the sediments

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transported through the Ho Chi Minh City area of the Saigon River basin. Similarly, Sutherland et al. (2000) found elevated concentrations of Cu, Pb and Zn in sediments deposited from stormwater runoff in the Manoa Stream of Hawaii. More specifically, metals in stormwater runoff sediments have been linked to the frictional wear of brake linings (e.g., Cr, Cu, Ni and Pb) and tires (e.g., Zn) (Callender and Rice, 2000; Davis et al. 2001; Sebastiao et al. 2017). Additionally, road runoff also contained metals found in lubrication and motor oils, such as arsenic (As), cadmium (Cd), Cu and Zn that can readily sorb to sediment surfaces (Chambers et al. 2016; Sebastiao et al. 2017). Likewise, increased Pb concentrations in urban-derived sediments have been linked to atmospheric inputs from the legacy use of leaded gasoline (Callender and Rice 2000; Polidoro et al. 2017).

Agricultural land use/land cover (LULC) characteristics have also been linked to elevated metal concentrations in tropical soils and bed sediments. From a source perspective, Cu, Ni and Zn have been historically used in fungicides (Rowell 1968; Van-Zwieten et al. 2004; and Henriques et al. 1997), while As and Cu have been associated with pesticides (Thrupp 1990; Das et al. 2013). As, Cd and U have also been found as microcontaminants in phosphate-based fertilizers (Rutherford et al. 1995; Schnug et al. 2013). From a sink perspective, Buttermore et al. (2018) attributed elevated Ni concentrations in bed sediments within agricultural watersheds in Puerto Rico to the use of nickel-based fungicides associated with banana plantations. Likewise, elevated concentrations of Cd, Cu and Zn were identified in bed sediments in agricultural portions of the Yangtze watershed (Ye et al. 2019). Additionally, the absence of riparian buffers has also been shown to play a role in sediment metal concentrations. For example, Akindale et al. (2020) identified elevated concentrations of Cd, Cu and Zn in areas where cocoa and plantain fields directly abutted the stream channel compared to stream reaches that were forested.

Compared to non-mountainous watersheds, prior studies of sediment quality of tropical mountainous watersheds have been more limited in geographic extent with the majority focused on contaminant accumulation in nearshore environments (i.e., bays, estuaries or nearshore ocean). In Puerto Rico, previous studies found a link between sediment metal concentrations with relative human population density and types of development. For example, metal concentrations (e.g., Cd, Cu, Pb and Zn) in estuarine sediments near the urban areas of San Juan were ~ 5 to 27 × higher than those surrounded by a forested catchment (Acevedo-Figueroa, et al. 2006). Others have found relatively higher concentrations of Cu, Pb, Ni and Zn in nearshore sediment in areas receiving stormwater runoff compared to their non-developed counterparts (Hertler et al. 2009). In addition, elevated sediment metal concentrations in Guánica Bay in southwest Puerto Rico have been attributed to a combination of localized inputs from historical sugar processing activities, agriculture fields and stormwater runoff (Whitall et al. 2014).

Although informative, the aforementioned studies do not address the extent to which metals accumulate in tropical mountainous river sediments or whether they are routinely "flushed" from the system (Wohl et al. 2015). Understanding metal retention levels in these systems can elucidate the risks to instream aquatic communities, such as macroinvertebrates. Few studies in tropical watersheds have attempted to statistically link metal concentration with relative LULC practices of the upstream areas. This study addresses these existing knowledge gaps by evaluating whether sediment-based pollutants can accumulate in tropical mountainous watersheds and if so, does contamination correlate with relative LULC characteristics of the upstream areas. Subwatershed scale sampling was performed at a total of 17 locations in three Puerto Rico watersheds (Rio Loco, Rio Yauco and Rio Guamaní) approximately 21 months following direct landfall of Hurricane Maria, a Category 5 Hurricane. A GIS analysis was also performed to determine the relative LULC characteristics upstream of each sampling locations. Finally, sediment chemistry data were compared to regulatory thresholds to evaluate the associated impact on aquatic ecosystems.

Materials and methods

Study location

The Rio Loco, Rio Yauco and Rio Guamaní watersheds are all located in southern Puerto Rico (Fig. 1). All three watersheds contain constructed reservoirs in the headwaters and receive lesser inputs from downstream tributaries. Each of the three watersheds is underlain by a mix of Tertiary and Cretaceous age volcaniclastic rock in the mountainous interior with Quaternary age alluvium in the associated floodplains (Bawiec 1998). Localized outcrops of limestone are located in the extreme lower portions of the Rio Loco and Yauco watersheds.

The island of Puerto Rico experiences a dry season from January to April and a rainy season from May to December (Gellis, 2013), during which the island is subject to heavy rainfall (Fig. 2; Williams & Block, 2015). In addition, the island has a major hurricane recurrence frequency of 10 to 20 years (Warne et al. 2005). Average annual rainfall for each of the three watersheds substantially varies with elevation: 75–90 cm at sea level to greater than 220 cm in the mountainous interior (NOAA 2020). Average annual temperatures for Puerto Rico range from 24 °C to 29 °C (Murphy et al. 2012).

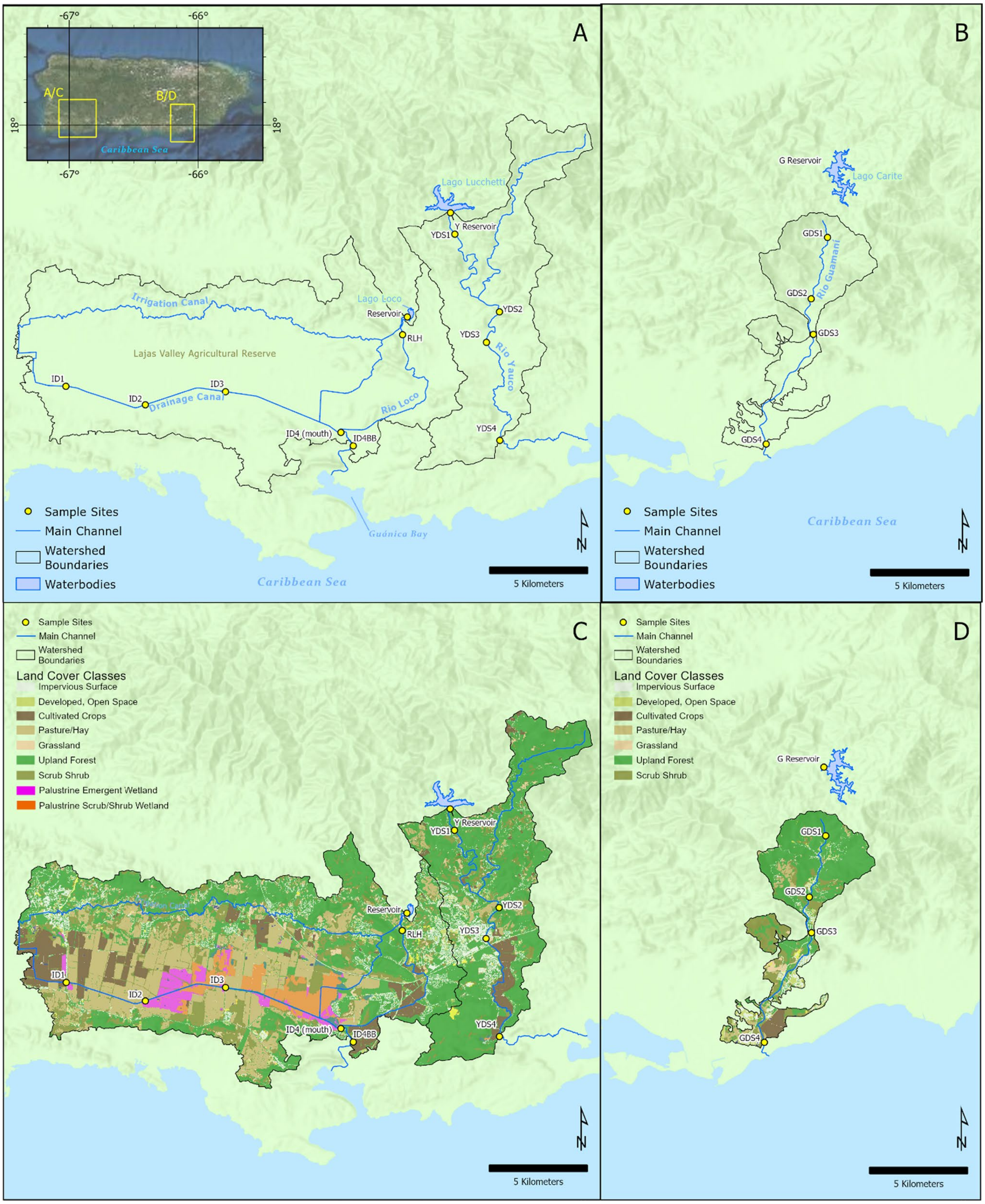

Fig. 1 Sampling locations (yellow circles) in the (**a**) Rio Loco, Rio Yauco and (**b**) Rio Guamaní watersheds. National Oceanic and Atmospheric Administration (NOAA) Coastal Change Analysis Program (C-CAP) land use/land cover (LULC) characteristics of the (**c**) Rio Loco, Rio Yauco and (**d**) Rio Guamaní watersheds. Inset shows the locations of watersheds within island of Puerto Rico

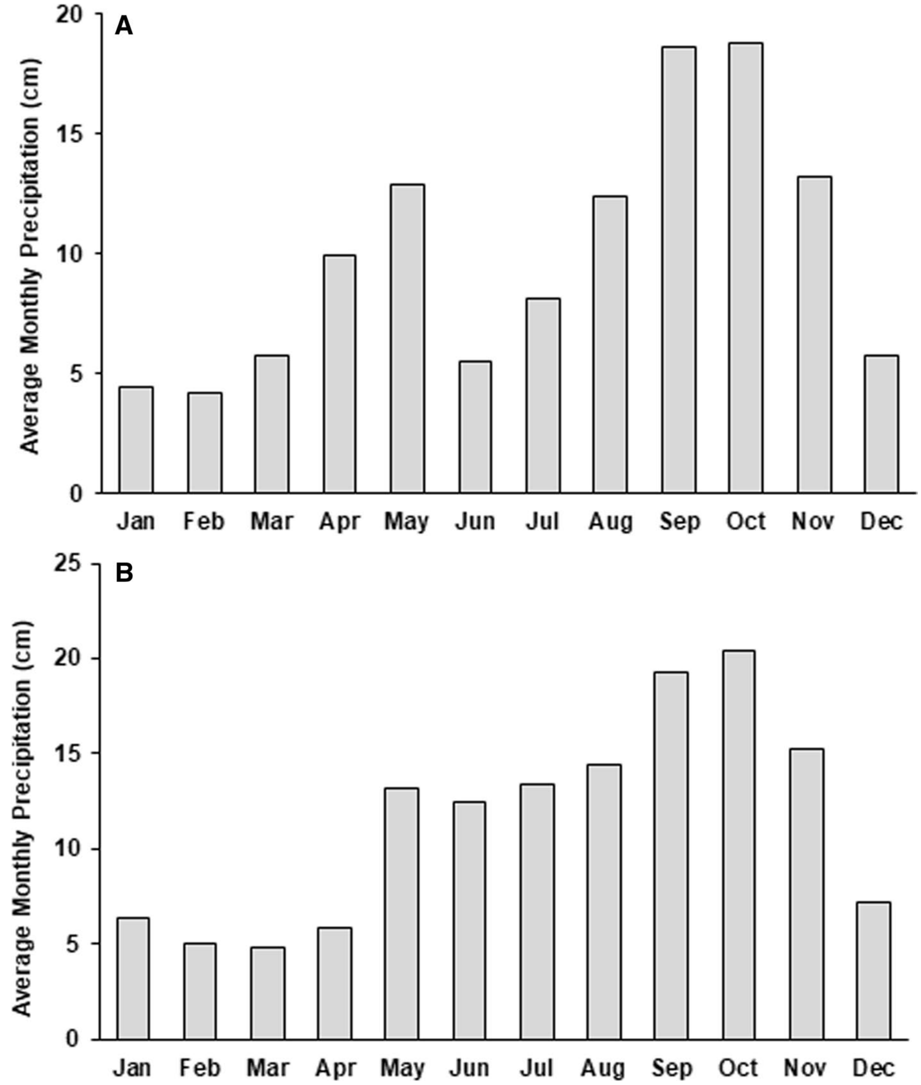

Fig. 2 NOAA average monthly rainfall 30-year averages (1981–2010) for (**a**) Sabana Grande (Station ID#2,391,501) and (**b**) Guayama (Station ID#2,391,532), Puerto Rico. The Sabana Grande station is representative of climate conditions for the Rio Loco and Rio Yauco watersheds

The Rio Loco watershed (~175 km^2), located in southwest Puerto Rico, has undergone extensive hydrological modification. In the 1950s, a system of five reservoirs, inter-basin transfers, water intakes, two hydroelectric power plants and irrigation canals were constructed to divert water from the Central Cordillera to the Lajas Valley Agricultural Reserve (LVAR) and to provide electricity and potable water for downstream municipalities (CWP 2008). The lower Rio Loco watershed begins at Lago Loco, the lowest most reservoir in the system, where concrete-lined irrigation channels divert water from the Rio Loco westward to the LVAR, where hay, sugarcane, fruits and vegetables are grown. Wastewater from the LVAR returns eastward via a drainage canal that reenters the natural Rio Loco channel further downstream, before its discharge into Guánica Bay. The aforementioned irrigation canals act as a constant, year-long source of diversion from the Rio Loco channel, causing large parts of the main channel to go dry except during the wet season (CWP 2008). The main channel of the Rio Loco abuts the western portion of the City of Yauco (pop: 17,186; US Census Bureau, 2010) before its confluence with the LVAR drainage network.

The Rio Yauco watershed (72.9 km^2) is adjacent to the eastern border of the Rio Loco watershed. The watershed begins at Lago Lucchetti, and the headwater regions predominately consist of forest interspersed with individual dwellings. The Rio Yauco flows directly through the City of Yauco before reaching an agricultural valley largely characterized by pineapple and banana plantations (CWP 2008).

The Rio Guamaní watershed (33.8 km^2) is located approximately 75 km to the east of the Rio Loco and Yauco watersheds. Similar to the Loco, the Guamaní has undergone extensive hydrological alteration. The watershed begins at Lago Carite, and the headwater regions predominantly consist of forest interspersed with individual dwellings. The river flows directly through the City of Guayama (pop: 22,691; US Census Bureau, 2010), before entering a broad flood plain used for agriculture.

Sediment collection and preparation

Bed sediments were collected from a total of 17 sites in the three watersheds in June 2019: Rio Loco ($n = 7$), Rio Yauco ($n = 5$) and Rio Guamaní ($n = 5$) (Fig. 1, Table S1). One surficial grab sample was collected from each site approximately 21 months following Hurricane Maria. Bed sediments were collected using a modified method of Förstner (1980), whereas sediments were collected from the most recent high-water line in each streambed using a stainless-steel spatula. Sediments were placed in whirl packs, stored in a dark cooler on ice and shipped to Villanova University for analysis. Upon arrival, samples were defrosted and dried at 60 °C for ~ 72 h. The samples were then sieved to < 63 µm to isolate the silt and clay fraction. Sieved material was then stored until further analysis.

Sample preparation and analysis

Total digestions

Approximately, 0.25 g of the sieved (< 63 µm) sediment samples were sent to ALS Chemix (Reno, NV) for four-acid digestion (HNO_3–$HClO_4$–HF acid digestion and HCl leach). Digestions were then analyzed for 14 metals (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Sn, Sb, Pb and U) and phosphorus (P) using an inductively coupled plasma mass spectrometer (ICP-MS). Standards, blanks and duplicates were all evaluated as part of the analytical procedures. External standard OREAS 4F, a blend of mineralized lateritic soil, barren lateritic soil and minor additions of gold and nickel ores, was analyzed as an independent check standard and revealed sample recoveries generally greater than 92% of the reference value. Sb was the exception with a recovery of 88%. Shortfalls are attributed to incomplete digestion of silicate minerals in the residual phase.

Loss on ignition

Loss on ignition was performed on the sieved samples to determine their particulate organic carbon (POC) concentrations. We modified the method of Lyons et al. (2002); specifically, dried samples were combusted at 550 °C for 4 h and the POC concentration was calculated as 33% of the weight loss for each sample. The relative standard deviations of multiple analyses were < 7%, with the majority < 3%.

GIS analyses

Using Environmental Systems Research Institute's (ESRI's) ArcGIS™ Desktop 10.7.1, a digital elevation model (DEM) from the USGS was modified to reflect anthropogenic changes made to the landscape. Rivers and manmade canals were manually digitized from aerial imagery and "burned" into the DEM, providing a more accurate representation of the flow of water across the study area. This modified DEM was used to delineate all sub-watersheds using the Spatial Analyst™ extension's Hydrology Toolset. The modified DEM was used to delineate the three watersheds and associated 13 sub-watersheds. Land cover data for the study region were obtained from the 2010 Coastal Change Analysis Program (C-CAP) 2 m resolution land cover dataset, while geology data were sourced from the 1963 United States Geological Survey (USGS) vector geology dataset. The relative percentages of LULC above each sampling site were calculated for the total sub-watershed area.

Statistical analyses

Data were initially tested for normality using Wilcoxon/Kruskal–Wallis; however, those not normally distributed were either log-transformed or evaluated using a nonparametric alternative. Statistical analyses were then performed, including one-way analyses of variance (ANOVA), post hoc Tukey tests, two-tailed t tests, a Pearson correlation matrix and stepwise linear regressions using JMP™ Pro 15 software.

A pooled dataset comparison between sub-watershed metal concentrations and select LULC categories was carried out using stepwise multiple regressions after Li et al. (2009). This approach was appropriate because the three watersheds exhibit similar LULC patterns in terms of land cover (forests in the mountainous areas and agriculture in the downstream areas) and geology (volcaniclastic material in the mountains and alluvium in the downstream areas). Therefore, relative differences in sediment chemistry in these downstream areas should largely be a function of relative LULC characteristics in the upstream areas, though geogenic factors could also play a role. Prior to running the regressions, a series of LULC categories were combined into one variable due to their high correlation: 1. "Impervious Surface" and "Developed, Open Space" ($r = 0.81$, $p = 0.002$), hereafter referred to as "Impervious/Developed"; 2. "Cultivated Crops" and "Pasture/Hay" ($r = 0.76$, $p = 0.0007$), hereafter referred to as "Agriculture."

Enrichment factor calculations

Enrichment factors (EFs) are commonly utilized in geochemical studies to determine the relative level of enrichment or depletion of a sediment sample with respect to its parent material. EFs are typically calculated by normalizing to a reference element that is largely resilient to weathering processes. Aluminum (Al) was used as a reference material due to its common use as a normalizing element for tropical geochemical studies as well as its uniform concentration in our background samples. EFs were calculated using the following equation from Lee et al. (1997) and Sutherland (2000a, b):

$$\mathrm{EF} = \left(\left[Me_s\right]/\left[Al_s\right]\right)/\left(\left[Me_{background}\right]/\left[Al_{background}\right]\right)$$

where Me_s and Al_s are the concentration of total metal (Me) and Al in a given sediment sample and $Me_{background}$ and $Al_{background}$ are the total Me and Al concentrations for reference material, respectively. For this study, metal concentrations from each of the three upstream reservoirs were used for watershed-specific background values. Consequently, relative increases in downstream EV values should largely be attributed to local LULC-related inputs. Calculated EF values were then compared to the following five-tier ranking system established by Sutherland (2000a, b):

1. EF < 2 Depletion to minimal enrichment suggestive of no or minimal pollution
2. EF 2–5 Moderate enrichment, suggestive of moderate pollution
3. EF 5–20 Significant enrichment, suggestive of significant pollution signal
4. EF 20–40 Very highly enriched, indicating a very strong pollution signal
5. EF > 40 Extremely enriched, indicating an extreme pollution signal

Sediment quality guidelines

Concentrations of As, Cu, Cr, Zn and Pb for all sediment samples were compared to the numerical sediment quality guidelines (SQGs) for freshwater ecosystems established by MacDonald et al. (2000). This study utilized threshold effect concentrations (TECs) and probable effect concentrations (PECs). TEC values indicate the highest pollutant level that adverse effects are not expected to occur, while PEC values indicate the minimum pollutant level that adverse effects are expected to occur.

Results and discussion

Results

GIS analyses

Relative variations in total LULC characteristics were identified for the three watersheds (Table S1). For the Loco watershed, the dominant LULC type was upland forest (35%), followed by agriculture (32%), scrub/shrub (15%), developed (6%) and grassland (2%). For the Guamaní watershed, upland forest (58%) was the dominant LULC type followed by scrub/shrub (18%), developed (12%), agriculture (8%) and grassland (2%). For the Yauco watershed, the dominant LULC type was upland forest (74%), followed by agriculture (7%), scrub/shrub (8%), developed (7%) and grassland (2%). Remaining land cover types in each watershed consisted of some combination of wetlands and open water. Noticeable variations in % LULC were observed between the sub-watershed sampling sites both within and between watersheds. For example, % agriculture ranged from 0% (GDS1) to 35% (ID3), while % developed ranged from 1.64% (GDS1) to 12.2% (GDS4).

Table 1 Descriptive statistics for select metal concentrations and particulate organic carbon (POC) in samples collected from the Rio Loco, Rio Yauco and Rio Guamaní compared to their respective consensus-based threshold effect concentrations (TECs) and probable effect concentrations (PECs). All concentrations are in mg kg^{-1} unless otherwise noted

Metal	Mean ± std dev	Min	Max	TEC	PEC
Al %	7.27 ± 1.26	4.16	8.77		
As	4.25 ± 2.28	1.24	10.6	9.79	33
Ba	472 ± 177	161	720		
Cd	0.15 ± 0.07	0.05	0.27	0.99	4.98
Cr	234 ± 262	20.8	852	43.4	111
Cu	97.6 ± 29.3	50	149	31.6	149
Fe %	6.30 ± 1.12	3.31	8.52		
Mn	2047 ± 1685	1035	8030		
Ni	176 ± 243	10.9	887	22.7	48.6
P %	0.09 ± 0.03	0.04	0.15		
Pb	14.6 ± 16.2	4.27	68.8	35.8	128
Sb	0.53 ± 0.27	0.24	1.21		
Sn	3.56 ± 4.39	0.83	19		
U	0.71 ± 0.30	0.26	1.34		
V	206 ± 48.5	122	299		
Zn	117 ± 43.7	57.3	243	121	459
%POC	3.15 ± 0.52	2.54	4.39		

Table 2 Average metal concentrations (mg kg^{-1}) for this study and select subtropical/tropical watersheds worldwide

Study	Location	Environment	As	Cd	Cr	Cu	Ni	Pb	Sb	Zn
Puerto Rico										
Acevedo et al. (2006)	Joyuda Lagoon	Lagoon	18.4	1.8	n/a	22.0		7.60		52
	San Jose Lagoon	Lagoon	13.3	0.1	n/a	105		219		531
Pait et al. (2007)	Southwest Puerto Rico	Coastal	1.73	0.01	31.2	5.21		1.93		7.99
Hertler et al. (2009)	La Parguera–Old Development	Coastal			38	39.9	25.4	9.15		68.4
	La Parguera–New Development				48.7	63.9	39.1	13.6		96.9
Apeti et al. (2012)	Jobos Bay	Coastal	12.8		18.5	29.9		6.02	0.27	48.5
Whithall et al. (2014)	Guanica Bay	Bay	4.77	0.02	286	29.2	229	6.08	0.14	46.7
Williams and Block (2015)	Rio Espiritu—Core 1	River		0.13	55.0	106	26.0	11.0		78
	Rio Espiritu—Core 2	River		0.18	42.0	104	18.0	13.0		68
	Rio Espiritu—Core 3	River		0.23	47.0	156	20.0	13.0		83
This study	Rio Loco	River	3.76	0.13	410	75.9	338	8.84	0.41	101
	Rio Yauco	River	2.33	0.15	194	112	112	21.6	0.52	119
	Rio Guamani	River	6.85	0.20	27.5	114	13.0	15.6	0.71	139
Other Subtropical/Tropical Watersheds										
Ma et al. (2016)	Yellow River, China	River				17.3	22.4	17.2		22.4
Liu et al. (2018)	Jinjiang River, China	River	6.20	0.51	58.7	26.0	24.5	23.8	0.55	104
Wong et al. (2017)	Langat River, Malaysia	River	63.8	0.34	39.2	17.4	13.7	64.3		66.3

[a]downstream location, only

Metal concentrations

Mean and maximum metal concentrations were at the mid- to the upper end of what has been reported for Puerto Rico streams and estuaries (Tables 1 and 2). High standard deviation valuations for each of the metals (usually greater than 33% of the mean value, except for Al and Fe) reflect the high spatial heterogeneity in the dataset and suggest anthropogenic inputs (e.g., urban and/or agricultural runoff) are influencing sediment concentrations. Average metal concentrations for the combined dataset showed the following relative order of abundance: Mn > Ba > Cr > V > Ni > Zn > Cu > Pb > Fe > Zn > As > Sn > U > Cd.

A series of one-way analysis of variance (ANOVA) tests followed by Tukey post hoc tests ($p < 0.05$) confirmed statistical differences in average metal concentrations between the three study watersheds. The following watersheds exhibited statistically higher metal concentrations ($p < 0.05$) than their two counterparts: Guamaní (As and Sn), Loco (Ba and Cr) and Yauco (Pb). Additionally, the Yauco and Guamaní had statistically higher concentrations of Cu than the Loco, while the Loco and Yauco had statistically higher concentrations of U and V than the Guamaní. Al, Cd, Fe, Mn, Sb and V were statistically similar between all three watersheds.

Overall, Cd, Pb, Sn, Sb and Zn concentrations increased downstream in both the Yauco and Guamaní watersheds (Table S1; Figs. 3 and 4). Similarly, As, Cr, Ni and U increased downstream in the Yauco watershed. Overall, Mn, Ni and Cr decreased downstream in both the Guamaní and Loco watersheds. Additionally, As, Ba, Cr and Fe decreased downstream in the Guamaní watershed. More variable downstream trends in concentration were observed for the remaining metals in the study watersheds.

All metals increased in concentration between the site immediately above and within the City of Yauco (YDS-2 and YDS-3, respectively) (Figs. 3 and 4). Several metals increased in concentration by > 50%: As (74%), Ba (70%), Cd (86%), Cr (249%), Fe (105%), Ni (328%), Pb (571%), Sb (227%), V (95%) and Zn (324%), Cd (22%), Pb (52%), Sb (130%), Sn (805%) and Zn (22%) also increased in concentration above and below the City of Guayama in the Guamaní watershed (Sites GDS3 and GDS4).

A Pearson correlation matrix was calculated to determine the interrelatedness of metal concentrations (Table 3). The strongest overall correlation was observed between Cr and Ni ($r = 0.98$, $p < 0.001$). There were a series of positive statistical relationships ($r_{avg} > 0.60$, $p < 0.05$) among Cd, Pb, Sb and Zn, indicating a strong interrelationship among these metals. Positive statistical relationships were also observed among Ba, Cr and Ni ($r_{avg} > 0.81$, $p < 0.05$) and among Al, Fe and Mn ($r_{avg} = 0.53$, $p < 0.05$). The majority of the metals showed a negative relationship with POC.

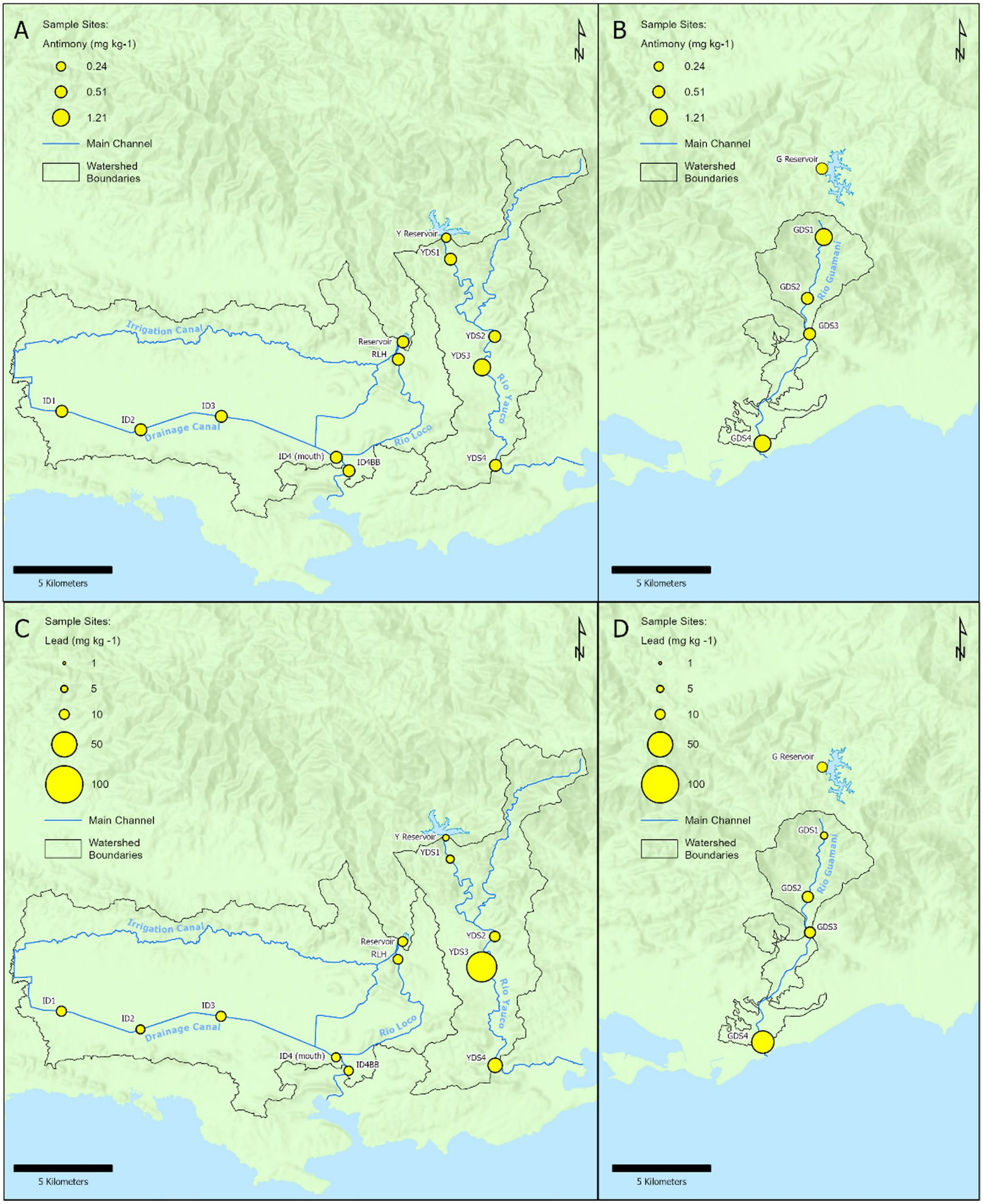

Fig. 3 Concentrations (mg kg^{-1}) of antimony (**a**, **b**) and lead (**c**, **d**) at each sampling site in the three study watersheds

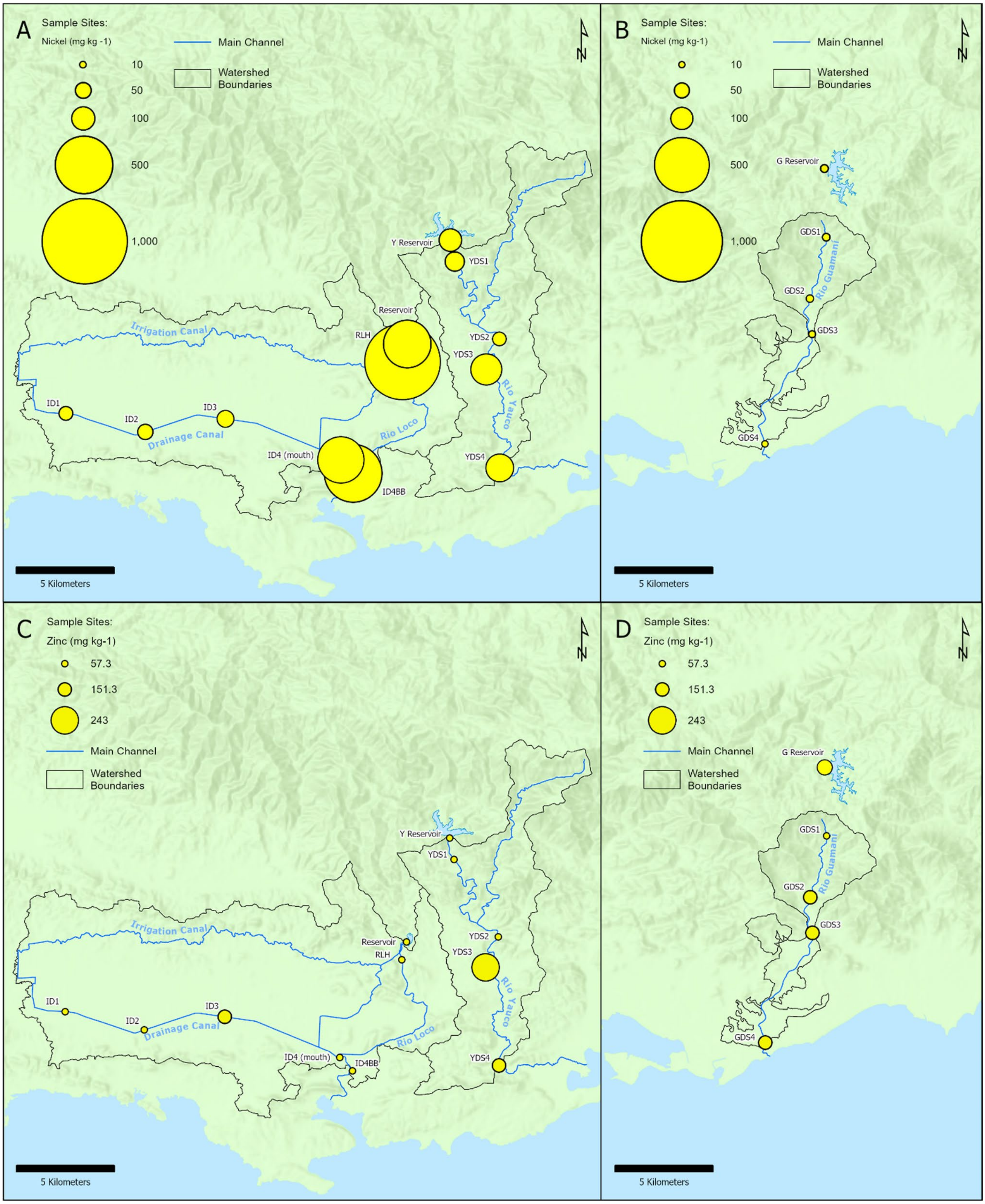

Fig. 4 Concentrations (mg kg^{-1}) of nickel (**a**, **b**) and zinc (**c**, **d**) at each sampling site in the three study watersheds

Table 3 Pearson correlation coefficient matrix for all metals and %POC OGRF

	Al	As	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Sn	U	V	Zn	%POC[c]
Al	1															
As	0.39	1														
Ba	−0.34	−0.04	1													
Cd	−0.06	0.42	−0.04	1												
Cr	−0.47	−0.50[a]	0.70[b]	−0.37	1											
Cu	0.38	−0.01	−0.47	0.11	−0.43	1										
Fe	0.63	0.25	−0.07	−0.27	0.03	0.43	1									
Mn	0.39	0.60	−0.06	−0.18	−0.27	0.40	0.56	1								
Ni	−0.48	−0.42	0.73	−0.30	0.99	−0.51	−0.01	−0.29	1							
Pb	−0.11	0.14	−0.02	0.75	−0.12	−0.01	−0.07	−0.28	−0.07	1						
Sb	0.13	0.70	−0.12	0.55	−0.30	0.09	0.27	0.40	−0.25	0.64	1					
Sn	−0.16	0.06	0.00	0.54	−0.17	−0.20	−0.19	−0.31	−0.12	0.76	0.34	1				
U	−0.39	−0.54	0.77	−0.20	0.78	−0.34	−0.22	−0.42	0.77	−0.05	−0.40	−0.04	1			
V	0.63	−0.01	−0.37	−0.11	−0.27	0.75	0.79	0.35	−0.36	0.05	0.16	−0.06	−0.25	1		
Zn	0.40	0.48	−0.06	0.63	−0.29	−0.02	0.22	−0.07	−0.23	0.77	0.67	0.47	−0.26	0.20	1	
%POC	−0.04	−0.10	−0.46	0.31	−0.51	0.25	−0.61	−0.24	−0.49	0.06	−0.16	0.03	−0.25	−0.24	−0.03	1

[a]Samples where $-0.61 < r \leq -0.50$ or $0.50 \leq r < 0.61$ are statistically significant at $p = 0.05$

[b]Samples where $r \leq -0.61$ or $r \geq 0.61$ are statistically significant at $p = 0.01$

[c]Particulate organic carbon

Table 4 Stepwise multiple regression models for metal and land use land cover (LULC; agriculture and developed, only)

Metal	Equation	R^2	Adjusted R^2	P value
Al	7.55–0.65(log agriculture)	0.12	0.04	0.23
log As	0.71–0.16(log agriculture)	0.28	0.22	0.05
log Cd	0.61–0.11(developed)	0.60	0.53	0.01
log Cr	2.44–1.14(log developed) + 0.62(log agriculture)	0.50	0.40	0.03
Cu	110 + 36.5(log developed)–39.2(log agriculture)	0.75	0.70	< 0.01
Fe	6.91–0.89(log agriculture)	0.27	0.21	0.06
Mn	3686–2128(log agriculture)	0.60	0.57	< 0.01
log Ni	2.24–1.58(log developed) + 0.73(log agriculture)	0.49	0.38	0.04
log Pb	0.66 + 0.65(log developed)	0.24	0.17	0.08
Sb	− 0.38 + 0.30(log developed)	0.39	0.26	0.09
Sn	− 0.27 + 1.07(log developed)	0.53	0.48	0.01
log U	− 1.11–0.56(log developed)	0.75	0.70	0.00
V	232–32.9(log agriculture)	0.24	0.18	0.08
Zn	58.87 + 107(log developed)	0.63	0.56	0.01

Stepwise regressions with LULC characteristics

The stepwise multiple regressions identified several statistically significant relationships between metal concentrations and one or more of the relative LULC types in the upstream area, with the majority showing a positive relationship with percent developed land (Table 4). For example, Sn had a positive statistical relationship (adjusted $r^2 = 0.48$; $p = 0.01$) with percent developed land in the upstream areas across all watersheds. Two additional metals were marginally statistically significant with developed land: Sb (adjusted $r^2 = 0.26$; $p = 0.09$) and Pb (adjusted $r^2 = 0.17$; $p = 0.08$). Additionally, Cd, Cu and Zn were positively correlated with percent developed land that coupled with a negative statistical relationship with percent agricultural land (adjusted $r^2_{avg} = 0.60$; $p \leq 0.01$).

Other statistical relationships between metal concentrations and LULC characteristics were identified. Cr, Ni and U were positively correlated with percent cropland coupled with a negative correlation with percent developed land (adjusted $r^2_{avg} = 0.49$; $p \leq 0.02$). Finally, As and Mn were negatively correlated (adjusted $r^2_{avg} = 0.40$; $p \leq 0.05$) and Fe was marginally statistically significant (adjusted $r^2 = 0.21$; $p = 0.06$) with percent agricultural land.

Table 5 Enrichment factor (EF) values in each pollution category and median, minimum and maximum EF values for metals in the study watersheds

	< 2[a]	2–5	5–20	20–40	> 40	Median[d]	Minimum	Maximum
As	0.71[b] (10)[c]	0.29 (4)				0.99	0.63	1.18
Ba	0.71 (10)	0.29 (4)				1.31	0.76	4.15
Cd	0.50 (7)	0.36 (5)	0.14 (2)			1.95	94	7.15
Cr	0.71 (10)	0.29 (4)				1.28	0.22	3.03
Cu	0.71 (10)	0.29 (4)				1.43	0.88	3.08
Ni	0.86 (12)	0.14 (2)				1.13	0.12	3.1
Pb	0.71 (10)	0.07 (1)	0.21 (3)			1.29	0.57	19.9
Sb	0.79 (11)	0.14 (2)	0.07 (1)			1.46	0.59	6.24
Sn	0.64 (9)	0.07 (1)	0.29 (4)			0.92	0.39	12.2
U	0.93 (13)	0.07 (1)				1.4	1.01	2.03
V	1 (14)					1.28	0.85	1.93
Zn	0.93 (13)	0.07 (1)				1.18	0.58	4.32

[a]EF values adhere to the ranking systems of Sutherland et al. (2000)

[b]Percentage of samples falling within each pollution category

[c]Number of samples falling within each pollution category

[d]Median, minimum and maximum represent values and not percentages

Enrichment factors

A minimum of 14% of the sites had values indicative of "moderate" enrichment for nine metals, As, Ba, Cd, Cr, Cu, Ni, Pb, Sb and Sn, and a minimum of 7% of the sites exceeded the "significant" enrichment threshold for Cd, Pb, Sb, Se and Sn (Table 5). The order of average EF values by metal for the combined dataset is as follows: Pb (3.31) > Sn (3.18) > Cd (2.72) > Ba (2.05) > Sb (1.77) > Cu (1.72) > As (1.47) > Zn (1.43) > U (1.41) > Cr (1.29) > V (1.29) > Ni (1.20) > Fe (1.09) > Mn (0.99). Site YDS3, located within the City of Yauco, exhibited the highest EF values for Pb (19.9), Sb (6.24), Cd (7.15), Zn (4.32), Ba (4.15) and As (3.37). There were greater site and watershed variability in the highest overall EF values for the remaining metals. For example, the highest EF value for Sn (12.2) was identified at site YDS4 in the Yauco, while the highest EF values for Cr (3.03) and Ni (3.10) were identified at site RLH in the Loco watersheds.

A series of one-way analysis of variance (ANOVA) tests followed by Tukey post hoc tests ($p < 0.05$) confirmed statistical differences in EF values among the three watersheds. The following watersheds had statistically higher metal concentrations than their two counterparts: Yauco (As and Cd) and Guamaní (Cu and V). In addition, the Yauco and Loco watersheds both had statistically higher EF values for U than the Guamaní.

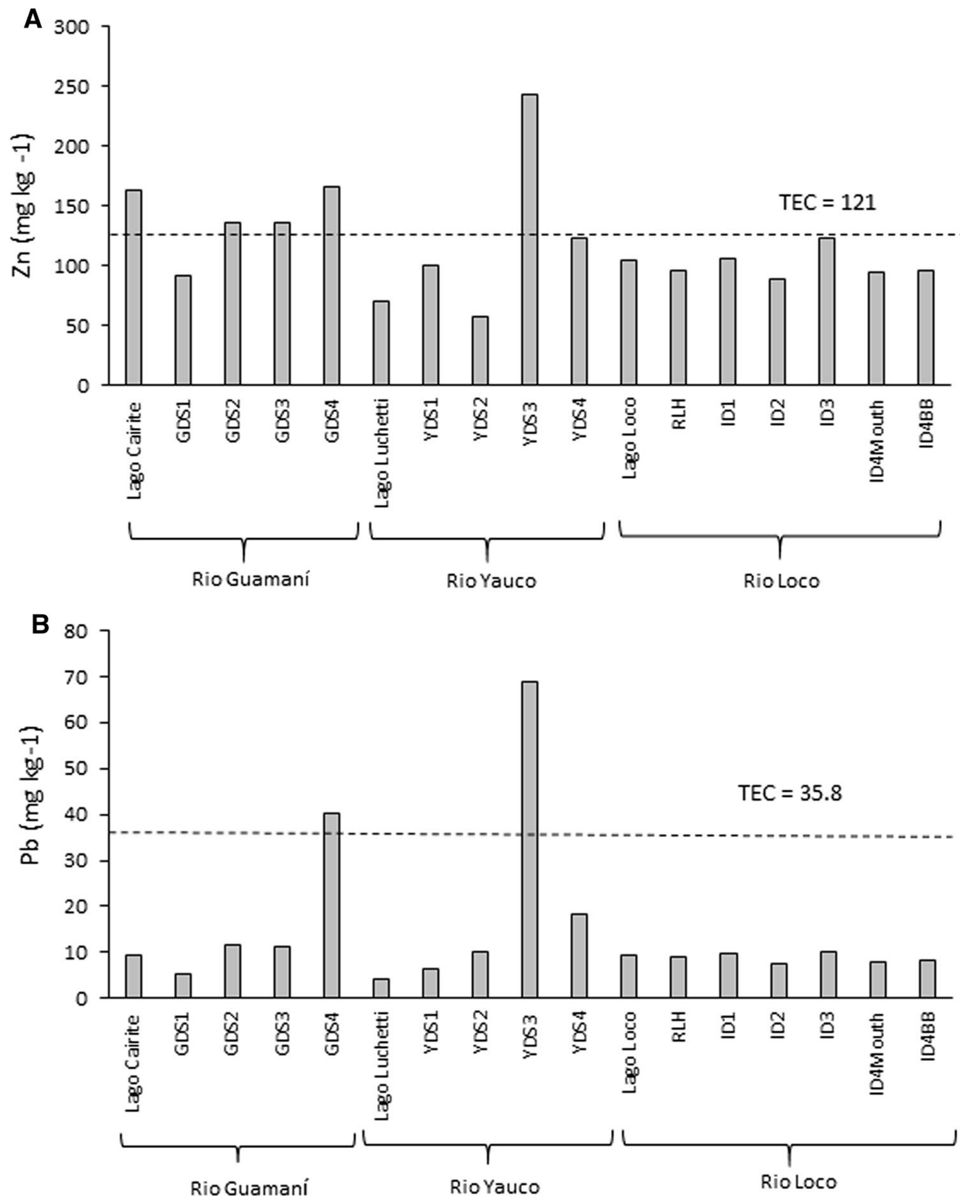

Fig. 5 Concentrations of (**a**) zinc and (**b**) lead (mg kg^{-1}) in each of the three study watersheds; within each watershed, sample sites are listed from upstream to downstream. Metal-specific consensus-based threshold effect concentrations (TECs) of MacDonald et al. (2000) are also provided

TEC/PEC exceedances

Exceedances of respective TEC and/or PEC values established by McDonald et al. (2000) were identified for As, Cr, Cu, Ni, Pb and Zn. Average number of exceedances of PEC values ranged as follows: Ni ($n=12$) > Cr ($n=10$) > Cu ($n=2$) (Fig. 5). However, both Ni and Cr concentrations were far more than their respective PEC value (1.6–18.2 × and 1.3–7.7x, respectively). An additional number of samples in excess of their TEC values were as follows: Zn ($n=5$), Cu ($n=2$) and Pb ($n=2$).

Discussion

Data in context

Average metal concentrations in bed sediments were generally greater than those for all previous studies in Puerto Rico with the exception of samples collected from San Jose Lagoon within the municipality of San Juan (Acevedo-Figueroa et al., 2006) (Table 2). Average As, Cd, Pb and Zn concentrations from the study watersheds ranged from 4 to 20% of those reported for San Jose Lagoon, likely reflecting historical differences in anthropogenic activities and population density between the two regions. However, similar average Cu concentrations between the two locations (101 and 105 mg kg^{-1}, respectively) suggest that geogenic factors may play a larger role for this element. Both the mean and range of concentrations of Ni for this study was higher than those quantified in an island-wide synoptic sampling (i.e., one downstream location, only) by Buttermore et al. (2018). While the previous study found the highest concentrations in watersheds designated as "agricultural," a more variable response was found for this present study both within and between watersheds. Additionally, the range of Cd, Pb and Zn concentrations for this present study were higher than those previously identified in nearshore sediments collected from developed areas of La Parguera (Hertler et al., 2009), a popular tourist town located adjacent to the west of the Loco watershed.

Average Cu, Pb and Zn concentrations for the study watersheds were also in the range for those of other tropical and subtropical watersheds with relative population densities similar to the study area (Table 2). For example, mean Cu (101 mg kg^{-1}), Pb (9.39 mg kg^{-1}) and Zn (105 mg kg^{-1}) concentrations were similar to those reported for the Langat River in Malaysia (17.4, 64.3 and 66.3 mg kg^{-1}, respectively; Wong et al. 2017) as well as the upstream portion of the Yellow River basin (17.3, 17.2 and 22.4 mg kg^{-1}, respectively; Ma et al. 2016). Mean Cu and Zn concentrations are at the lower end of those reported for road-derived sediments in southeast Pennsylvania (623 and 555 mg kg^{-1}, respectively; Sebastiao et al. 2017) and stormwater-derived suspended sediments (129 and 528 mg kg^{-1}, respectively) from an urban catchment in New Zealand (Brown and Peak 2006). These lower concentrations likely result from multiple factors, including relatively low traffic density for the region as well as shorter retention time within the system. Although there were fewer data available in the literature for Sb, average values for this study (0.46 mg kg^{-1}) were similar to those reported for the Jinjiang River in western China (0.58 mg kg^{-1}; Liu et al. 2018), though well below those reported for roadside dust in Shanghai, China (2.3 mg kg^{-1}; Yan et al. 2018).

Spatial controls on metal concentrations

Several metals were positively correlated with either percent developed or agricultural land in the upstream areas of all watersheds (Table 4). The influence of urban runoff on Cu, Pb, Sb, Sn and Zn concentration has been well documented in the literature. For example, Cu has been linked to frictional wear of brake pad linings, while Zn has been associated with automotive exhaust and tire wear (Ward 1990; Davis et al. 2001; Sebastiao et al. 2017). However, a comparison of median downstream Zn/Cu (0.70), Pb/Cu (0.11) and Cd/Cu (0.002) ratios for this study with those calculated for brake linings (1.18, 0.04 and 0.0066, respectively; Davis et al. 2001) suggests additional sources for Cu and Pb in southern Puerto Rico. Previous studies of urban streams in northern Puerto Rico have suggested that illicit sewer discharges could be partially responsible for increased export of nutrients (Potter et al., 2013). These discharge events might also introduce metals, such as Cu, into streams via weathering of water supply pipes within older homes.

Other urban sources could also contribute to the elevated concentrations of these metals. For examples, used motor oil was a substantial source of Zn (9×10^4 ug l^{-1}), Cu (770 ug/L) and Pb (270 ug l^{-1}) (Davis et al., 2001) and much lesser amounts of Sn (31 ug l^{-1}) (Gourgouillon et al., 2000). Lubricating oils contained elevated amounts of Cd, Cu, V and Zn (Ward, 1990). Atmospheric deposition from historical combustion of leaded gasoline has been associated with elevated Pb concentrations in bed sediments (Dunlap et al., 2000; Jiao et al., 2015). More recently, elevated concentrations of Sb have been found in roadside dust and soils and were positively related to traffic density (Yan et al., 2018), suggesting that wear and tear of brake pads is a potential source (Hjortenkrans et al. 2007).

Elevated Sn concentrations in urban sediments have been linked to runoff from tin roofs (Chen et al. 2014). The increased Sn concentrations that progressed downstream in both the Yauco and Guánica watersheds support this prior finding. Residential homes with tin roofs are located along roads that are adjacent to these streams, likely contributing Sn to streams. Additionally, both streams showed a substantial increase in Sn concentrations downstream of their respective urban areas.

The positive statistical correlation between Ni and U with percent agriculture coupled with a negative statistical correlation with developed land can also support previous research findings (Schnug and Haneklaus, 2008; Schnug et al. 2013; Lyons et al., 2020). For example, long-term application of P-based fertilizer was linked to the accumulation of U in agricultural soils (Schnug et al. 2013) and increased export to streams (Schnug and Haneklaus 2008; Lyons et al. 2020). This mode of causation is supported by a statistical relationship between U and P in our sediment samples ($r = 0.53$, $p = 0.05$). The positive association with Ni and agricultural land could, in part, be explained by the historical application of Ni-based fungicides. There was a substantial increase in Ni concentration within downstream agricultural areas of the Yauco watershed characterized by historical and modern-day banana and pineapple plantations. Furthermore, Buttermore et al. (2018) found similarly elevated Ni concentrations in Puerto Rico watersheds characterized by high amounts of agricultural land. Despite a positive statistical relationship with agricultural land, the highest overall Cr concentrations were identified in the reservoirs for both the Loco and Yauco watersheds. Either local geology (Whitall et al. 2014) and/or metal fragments from welded metal plating associated with hydroelectric infrastructure (Ward et al. 1990) may be additional sources for this element.

The negative association among Al, Fe and Mn with % agriculture and coupled with a lack of correlation with % developed land suggests a natural source for these metals. The strong correlation among the three metals has been attributed to their affinity for oxyhydroxide formation (Williams and Block 2015). Highly weathered oxyhydroxide soils are common in the wet mountainous interior of Puerto Rico (Siebert et al. 2015), and the highest concentration of all three metals was generally found at the upstream reservoirs. The only exception to this trend was Mn, where the highest concentration (GDS1, 8,030 mg kg^{-1}) coincided with the location of an electrical substation for the power grid.

Impacts on aquatic ecosystems

EF values confirmed varying degrees of anthropogenic contamination for at least two or more metals in the majority of our riverbed samples. Several metals (Cd, Pb, Sb and Sn) exhibited concentrations of significant enrichment. The high interrelatedness of these metals ($r_{avg} > 0.60$, $p < 0.05$) coupled with their positive statistical relationship with urban land confirms a strong anthropogenic influence on metal concentrations in the bed sediments. Yan et al. (2018) also reported a strong enrichment and interrelationship among Cd, Pb and Sb in roadside soils in Shanghai with higher values attributed to increased traffic density. Similarly, the highest EF values for Cd, Pb and Sb in this study were located at the sampling site within the City of Yauco.

The range of EF values for this study was generally greater than those reported for river sediment cores in the mostly forested Rio Espíritu Santo watershed in northeastern Puerto Rico, except for Cu (this study: 1.43–3.06; Rio Espíritu Santo: 1.94–3.99, Williams and Block, 2015). While elevated EF values for Cu in the Rio Espiritu were attributed to localized outcrops of copper/gold porphyry and copper skarn, this result could partially be attributed to the authors' use of world average shale for normalization; use of similar normalization values would increase the difference between the two datasets. While we cannot rule out the presence of copper-bearing units within the upper portions of our study watersheds, existing studies limit the presence of porphyry outcrops to northcentral Puerto Rico (Marsh 1998) and in bed sediments of rivers that drain to the north side of the island (Learned et al. 1985; Miller et al. 1982). Regardless, downstream increases in EF values for several metals (Cd, Cu, Pb and Zn) in surficial sediments were also attributed to a corresponding change in development (Williams and Block 2015).

Whitall et al. (2014) previously attributed elevated Cr and Ni concentrations in bed sediments from both the Loco watershed and Guánica Bay to the local bedrock. This idea is supported by Cr and Ni concentrations at Lago Loco and Lago Lucchetti, the headwaters of the Loco and Yauco watersheds, that are in excess of their respective PEC values. Additionally, these two elements were strongly correlated

($r = 0.98$, $p < 0.001$) suggesting a common source. However, both elements progressively increased downstream in both watersheds, suggesting additional localized inputs or cumulative enrichment. All but one sediment sample in the three study watersheds exceeded the PEC value for Cu, also suggesting influence from a geogenic source. Exceedances of the TEC value for lead were limited to the locations immediately within and/or downstream of the cities of Yauco and Guayama.

Collectively, the EF values and TEC/PEC exceedances confirm that metals can accumulate in tropical small mountainous bed sediments at levels harmful to aquatic organisms, despite repeated sediment "flushing" events, in this case, Hurricane Maria. Interestingly, our metal concentrations in the lower Yauco watershed were higher than those observed in a pre-Hurricane Maria study for a similar sampling location (Buttermore et al. 2018). The municipality of Yauco received a storm rainfall total of > 40 cm (NOAA 2020), and technical studies confirmed that Hurricane Maria-induced elevated river flows and led to structural damage of a highway bridge in the middle of the Yauco watershed (Silva-Tulla, et al. 2020). This "flushing" event could have resulted in the downstream deposition of sediments of urban origin that were sourced from the City of Yauco. Therefore, typical wet season precipitation events should have pulsed at least some of this contamination from the system. This idea is supported by increased Al concentrations in sediment between the two downstream samples sites (YDS3 and YDS4), suggesting a local contribution from a more weathered, flood plain-derived, agricultural soil.

Metal concentrations in bed sediments reaching harmful levels, coupled with periodic "flushing" events, suggest that ecological threats are not solely limited to freshwater systems. Both modeling and empirical studies have shown that agricultural practices in Puerto Rico supply significant amounts of sediment to the coast (Warne et al. 2005; Korman et al. 2020). In turn, this sediment flux to nearshore reefs has been linked to decreased total coral cover and species diversity (Acevedo et al., 1989; Hughes, 1994). Salinity-driven desorption of metals from sediment surfaces can result in incorporation of metals in coral skeletons via direct substitution with calcium (McCulloch et al. 2003; Prouty et al. 2008). Additionally, resuspension of sediments deposited near reefs could lead to their entrainment in coral tissue (Pait et al. 2009; Whitall et al. 2014) and ultimately its skeletal matrix (Howard and Brown, 1984; Acevedo et al. 1989). Regardless of the delivery mechanism, land-based sources of pollutants (LBSP) associated with sediments have been suggested as the primary cause of elevated Ni, Cu and Zn concentrations in Guánica Bay and uptake by coral tissues (Whitall et al., 2014). Our findings for the Loco watershed that drains into Guánica Bay provide direct evidence of this assertion; LBSP in the form of metals in sediments are transported downstream to the coast. These findings, in combination with those for the Yauco and Guamaní watersheds, further suggest that metals in bed sediments will similarly threaten nearshore coral reef systems adjacent to anthropogenically modified tropical SMRs elsewhere.

Conclusion

Metal concentrations were well above background levels in sediments extracted from the three study watersheds in southern Puerto Rico. Additionally, the following selected metals were positively correlated with either percent developed (Cu, Sb, Sn and Zn) or agricultural land (Cr, Ni and U) in the upstream area. EF values indicative of moderate to significant contamination and absolute concentrations in excess of respective TEC and PEC values indicated a direct threat to freshwater aquatic ecosystems. Metal contamination was observed approximately 21 months following a significant flushing event (i.e., Hurricane Maria), thus not only confirming the potential for metal accumulation in tropical mountainous watersheds but also elucidating the threat to downstream nearshore coastal ecosystems, such as coral reefs.

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Compliance with ethical standards

Conflict of interest The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest in the subject matter or materials discussed in this manuscript.

Availability of data and material Full dataset is provided as supplementary materials.

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