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Characterization of land-based sources of pollution in Jobos Bay, Puerto Rico: status of heavy metal concentration in bed sediment

Dennis A. Apeti · David R. Whitall · Anthony S. Pait · Angel Dieppa · Adam G. Zitello · Gunnar G. Lauenstein

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Abstract As part of an assessment of land-based sources of pollution in Jobos Bay, Puerto Rico, sediment samples were collected at 43 sites to characterize concentrations of a suite of pollutants, including metals. Fifteen major and trace metals (Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Mn Ni, Pb, Sb, Se, Sn, and Zn) were measured along with total organic carbon and grain size in surficial sediments. For most metals, maximum concentrations were seen in the eastern bay; however, values were still within concentration ranges found in other estuarine systems. In contrast, silver was higher in the western region. In general, metal distribution in the bay was positively correlated with grain size. Additionally, correlations between Al and other metals suggest natural sources for metals. The data presented here suggest that, although the Jobos Bay watershed contains both urban centers along with industrial and agricultural developments, anthropogenic inputs of metals may be negligible.

Keywords Surficial sediment · Heavy metals · Grain size · Total organic carbon · Land-based sources

D. A. Apeti (✉) · D. R. Whitall · A. S. Pait · A. G. Zitello · G. G. Lauenstein
National Oceanic and Atmospheric Administration, National Centers for Coastal and Ocean Science, Center for Coastal Monitoring and Assessment, 1305 East-West Highway, Silver Spring, MD 20910, USA
e-mail: Dennis.Apeti@noaa.gov

A. Dieppa
Jobos Bay National Estuarine Research Reserve, PO Box 159, Aguirre, PR 00704, USA

Introduction

Jobos Bay, located on the south-central coast of Puerto Rico between the municipalities of Salinas and Guayama (Fig. 1), is the second largest estuary in Puerto Rico, with a total surface area of about 25 km^2. With a watershed that covers a total catchment area of 137 km^2, and diverse habitats, including coral reefs, mangroves, mud flats, lagoons, and freshwater wetlands, the bay is an important ecosystem both ecologically and economically. The bay serves as an important feeding and nursery ground for native and migratory birds and other wildlife (Dieppa et al. 2008). The bay is also home to many endangered and threatened species, like the West Indian manatee, the hawksbill sea turtle, and the yellow-shouldered blackbird among others. In addition to its ecological importance, Jobos Bay and its watershed are also economically vital with industrial, agricultural, recreational fishing, and ecotourism activities (Dieppa et al. 2008).

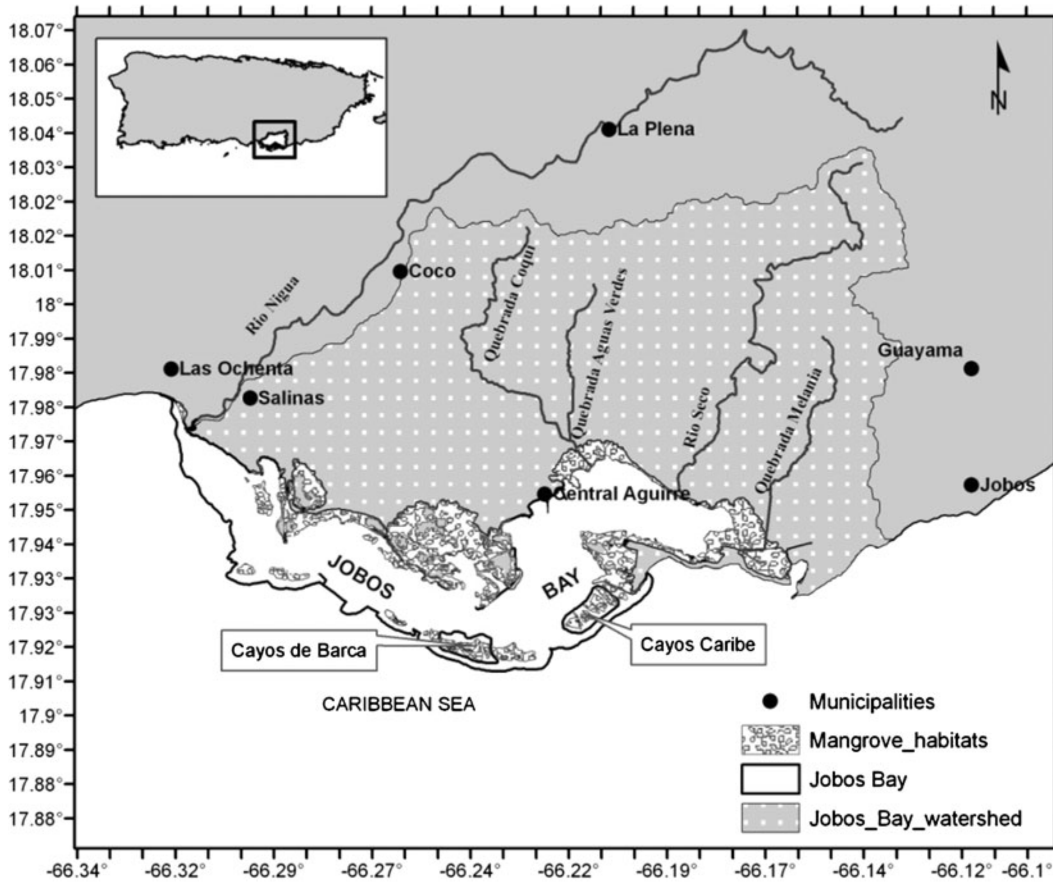

Fig. 1 Map of Jobos Bay showing its watershed, some municipalities, the barrier islands of Cayos de Barca and Cayos Caribe, and location of mangrove habitats

Jobos Bay watershed contains several centers of low-density urban municipalities as well as some industrial developments. Among the relatively new industrial developments established in the vicinity of the Jobos estuary is a 454-Mv/h coal power plant which is estimated to generate approximately 433,000 tons of ash yearly (Dieppa et al. 2008). Other industrial activities of concern in the Jobos Bay watershed include an old petroleum refinery, which is now used as a large gasoline storage facility, and several major chemical and pharmaceutical facilities. However, the predominant land use in the watershed is high-density agricultural activities that includes cultivation of plantain, bananas, papayas, sorghum, corn and hay production, and poultry and some beef cattle production.

Industrial and commercial growth in the watershed has been recognized as a concern to Jobos Bay's ecosystem health. Field et al. (2002) reported that residues of pesticides and fertilizers applied in agricultural fields in the watershed are being transported to the bay and suggested that runoff of land-based pollutants, such as metals, posed the most significant threats to water quality in the bay. Trace metals are of particular concern in the Caribbean islands (Ross and DeLorenzo 1997) because they can bioconcentrate and biomagnify along the food chain and they can be potentially toxic to aquatic wildlife and apex predators, including humans (Sauve et al. 2002; Reinfelder et al. 1998).

Currently, efforts to abate impacts of land-based pollutants in the bay are being addressed through agricultural best management practices, however, crucial monitoring efforts to assess the status and trends of pollutants in the bay are lacking. Although on a continuous basis the National

Status and Trends (NS&T) program monitors biennially a suite of pollutants, including metals in coastal Puerto Rico (Kimbrough et al. 2008), only one long-term site is established in Jobos Bay. Few other studies investigated metal concentration and distribution in Jobos Bay, these include the most recent work by Aldarondo-Torres et al. (2010), which provided a background information on sediment concentration of seven metals (As, Cd, Cu, Fe, Pb, Hg, and Zn), and a study by Jimenez-Velez et al. (2003), which assessed the atmospheric deposition of a suite of trace metals in the airborne PM_{10} particulate matters.

Jobos Bay and portions of the watershed are the site of a Conservation Effects Assessment Project, a collaborative effort involving the US Department of Agriculture, the Jobos Bay National Estuarine Research Reserve (NERR), NOAA, and local partners, to assess the benefits of implementing agricultural best management practices by farmers on the terrestrial and nearshore marine ecosystems (NOAA 2007). As part of this effort, sediment samples were collected and analyzed to assess contamination levels and spatial distribution of a suite of environmental pollutants. This study is currently the most comprehensive pollution assessment in Jobos Bay.

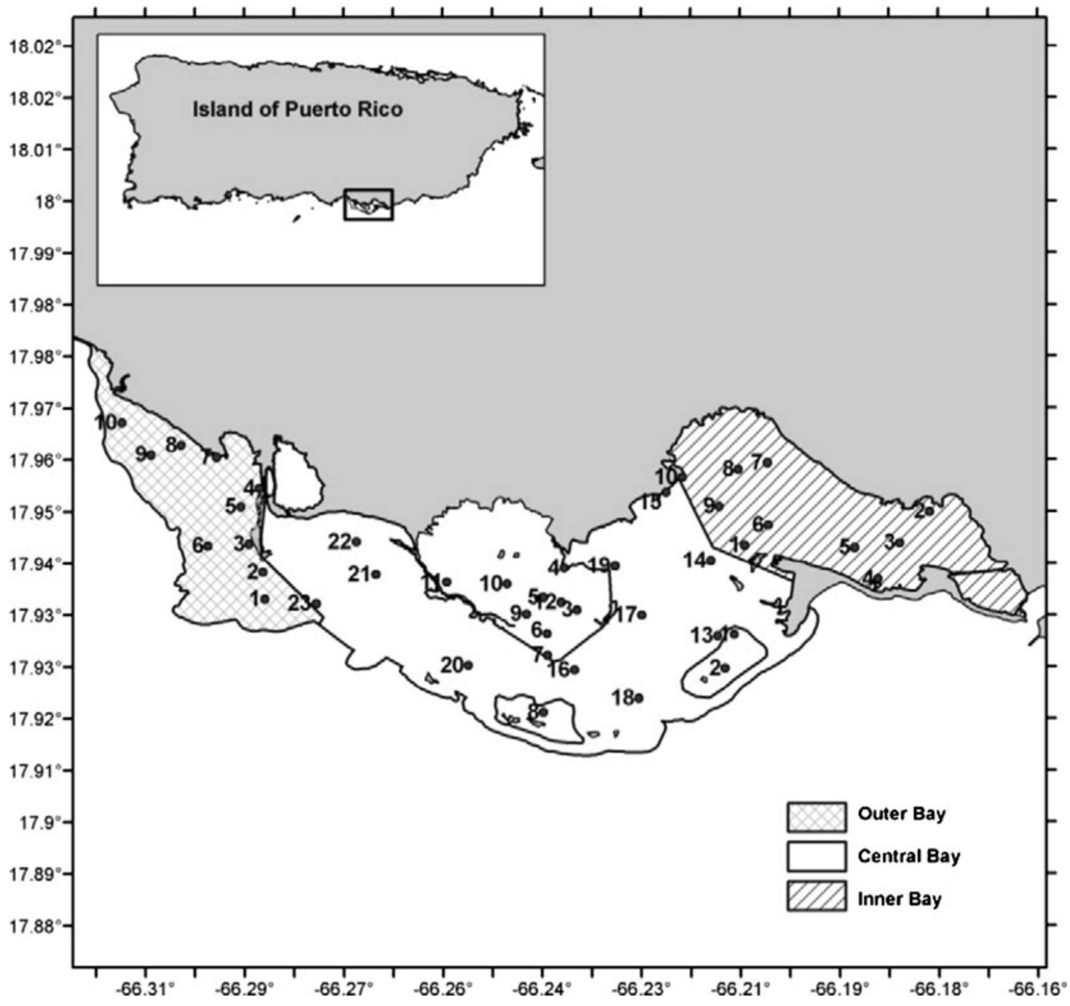

Fig. 2 Map of Jobos Bay study area showing the location of sampling sites within the Outer, Central, and Inner Bay strata

While results of organic contaminant assessment are presented elsewhere, this paper discusses major and trace metals data in the context of assessing: (1) the potential of anthropogenic enrichment, (2) the magnitude of metal concentrations relative to other coastal areas, including a comparison to NOAA's National Status and Trends (NS&T) program data, and (3) sediment quality by comparing measurements to published sediment quality guidelines.

Table 1 Sampling locations with percent TOC, silt, and clay content at each site

	Strata	Site	Latitude	Longitude	%TOC	%Silt	%Clay	%Fine
Central Bay	NERR	1	17.9302	−66.2094	0.98	42.33	13.60	55.93
	NERR	2	17.9248	−66.2110	0.96	22.41	7.64	30.05
	NERR	3	17.9341	−66.2358	2.68	60.78	22.75	83.53
	NERR	4	17.9409	−66.2380	10.91	39.15	21.69	60.84
	NERR	5	17.9361	−66.2414	3.99	55.65	22.42	78.07
	NERR	6	17.9303	−66.2408	2.32	26.16	22.48	48.64
	NERR	7	17.9268	−66.2408	1.63	60.77	25.49	86.26
	NERR	8	17.9176	−66.2415	1.79	58.11	19.65	77.76
	NERR	9	17.9335	−66.2444	2.85	49.03	25.24	74.27
	NERR	10	17.9383	−66.2475	3.87	8.44	14.35	22.79
	SWMP	11	17.9386	−66.2577	8.93	9.82	8.64	18.45
	SWMP	12	17.9353	−66.2385	10.89	24.41	51.88	76.29
	SWMP	13	17.9299	−66.2121	0.71	30.06	16.33	46.39
	Central	14	17.9421	−66.2134	2.06	13.85	15.61	29.45
	Central	15	17.9530	−66.2208	0.72	5.46	8.67	14.13
	Central	16	17.9245	−66.2362	1.09	69.18	21.36	90.54
	Central	17	17.9332	−66.2249	0.42	31.94	10.34	42.28
	Central	18	17.9199	−66.2254	0.57	44.75	12.39	57.14
	Central	19	17.9412	−66.2295	3.11	45.09	36.42	81.51
	Central	20	17.9252	−66.2540	1.02	58.65	22.60	81.25
	Central	21	17.9398	−66.2696	0.88	2.06	7.36	9.42
	Central	22	17.9451	−66.2729	0.76	0.48	4.78	5.25
	Central	23	17.9352	−66.2797	1.00	33.11	14.79	47.90
Inner Bay	Inner	1	17.9445	−66.2076	1.82	28.48	35.26	63.74
	Inner	2	17.9500	−66.1766	1.74	60.62	31.76	92.38
	Inner	3	17.9449	−66.1816	1.92	50.40	46.11	96.51
	Inner	4	17.9391	−66.1852	2.25	44.53	42.28	86.81
	Inner	5	17.9442	−66.1892	1.60	43.78	42.58	86.36
	Inner	6	17.9478	−66.2037	1.92	46.86	40.96	87.82
	Inner	7	17.9578	−66.2038	2.88	43.65	51.58	95.23
	Inner	8	17.9568	−66.2087	3.33	41.79	49.23	91.02
	Inner	9	17.9508	−66.2119	3.82	34.79	51.87	86.66
	Inner	10	17.9555	−66.2181	2.66	19.97	16.79	36.76
Outer Bay	Outer	1	17.9359	−66.2883	1.11	9.85	6.08	15.93
	Outer	2	17.9402	−66.2886	1.49	11.52	12.22	23.74
	Outer	3	17.9448	−66.2909	1.63	16.64	13.82	30.47
	Outer	4	17.9537	−66.2892	4.45	40.07	15.03	55.10
	Outer	5	17.9508	−66.2923	1.53	28.32	17.10	45.43
	Outer	6	17.9445	−66.2978	1.14	54.87	11.71	66.58
	Outer	7	17.9587	−66.2964	1.57	20.13	17.37	37.50
	Outer	8	17.9607	−66.3023	1.15	23.08	15.75	38.82
	Outer	9	17.9592	−66.3074	0.61	0.39	4.28	4.67
	Outer	10	17.9643	−66.3123	0.74	2.97	4.24	7.22

NERR National Estuarine Research Reserve, *SWMP* System Wide Monitoring Program location

Table 2 Concentration (micrograms per gram of dry wt.) of major and trace metals measured in Jobos Bay sediments

Strata	Sub-strata	Site	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Sn	Zn
Central Bay	NERR	1	0.10	41,500	10.90	0.00	14.00	24.30	25,100	0.01	590	6.81	4.20	0.25	0.18	1.19	41.00
	NERR	2	0.09	28,600	9.95	0.00	9.43	13.10	16,600	0.01	440	4.39	2.78	0.00	0.11	0.64	25.70
	NERR	3	0.10	48,000	14.90	0.00	20.60	33.00	29,500	0.04	615	9.80	7.23	0.31	0.39	1.35	54.70
	NERR	4	0.11	42,100	28.10	0.17	29.40	58.00	30,500	0.10	329	26.60	14.00	0.56	1.56	2.10	77.50
	NERR	5	0.10	44,700	20.00	0.00	27.20	36.90	38,500	0.06	514	15.00	8.25	0.34	0.68	1.23	67.70
	NERR	6	0.13	31,700	10.20	0.00	16.00	24.30	22,200	0.03	383	8.53	5.66	0.23	0.35	0.98	44.40
	NERR	7	0.09	56,400	15.70	0.00	24.80	39.00	36,500	0.04	733	14.00	8.43	0.38	0.32	1.68	70.60
	NERR	8	0.08	42,700	14.60	0.00	17.50	25.50	26,000	0.02	530	7.76	5.07	0.35	0.29	1.23	45.90
	NERR	9	0.10	45,300	17.70	0.00	23.50	35.30	33,800	0.05	527	12.20	7.06	0.23	0.55	1.16	59.30
	NERR	10	0.08	13,900	7.07	0.00	9.07	16.30	9,700	0.01	117	14.10	4.41	0.00	0.48	0.00	22.20
	SWMP	11	0.08	19,400	23.30	0.00	15.50	27.60	15,500	0.06	132	31.00	7.53	0.59	1.28	0.70	40.00
	SWMP	12	0.07	24,400	6.54	0.00	17.70	42.00	16,000	0.11	164	24.40	15.90	0.00	0.63	2.74	60.00
	SWMP	13	0.06	48,100	12.60	0.00	15.10	20.30	26,700	0.01	701	7.51	3.70	0.27	0.16	0.92	42.50
	Central	14	0.09	28,300	6.92	0.00	11.70	21.60	18,700	0.03	440	6.11	5.06	0.00	0.16	0.79	38.50
	Central	15	0.14	38,400	9.34	0.00	23.80	32.10	20,900	0.03	368	22.00	4.63	0.35	0.17	0.57	40.10
	Central	16	0.07	55,400	17.00	0.00	21.40	37.20	36,400	0.03	816	9.88	7.38	0.31	0.24	1.82	67.60
	Central	17	0.09	48,600	12.30	0.00	15.60	18.90	26,600	0.01	718	6.04	3.78	0.25	0.12	1.01	42.60
	Central	18	0.05	49,100	18.00	0.00	17.10	22.30	29,700	0.01	765	7.00	4.45	0.30	0.13	1.02	45.20
	Central	19	0.10	50,100	17.50	0.00	23.60	44.20	37,100	0.07	645	13.40	10.90	0.32	0.40	1.89	82.50
	Central	20	0.06	52,900	15.40	0.00	21.00	33.50	33,500	0.03	756	9.59	7.09	0.32	0.24	1.63	61.10
	Central	21	0.22	2,690	2.22	0.00	1.33	3.09	2,780	0.00	46	0.00	0.79	0.00	0.11	0.00	5.43
	Central	22	0.22	629	1.79	0.00	0.00	1.37	1,060	0.00	33	0.00	0.23	0.00	0.11	0.00	1.57
	Central	23	0.10	40,400	17.00	0.00	16.70	20.20	26,300	0.02	602	10.10	4.72	0.27	0.16	0.91	42.10
Inner Bay	Inner	1	0.10	51,600	11.30	0.00	21.70	50.40	36,900	0.08	709	13.00	11.40	0.27	0.29	1.65	86.20
	Inner	2	0.10	70,200	23.10	0.00	24.10	66.50	49,200	0.08	982	13.10	11.40	0.28	0.28	1.24	87.50
	Inner	3	0.11	70,200	22.40	0.00	27.60	73.70	49,300	0.10	1,130	15.40	14.30	0.32	0.28	1.64	102.00
	Inner	4	0.14	63,800	18.50	0.00	25.90	65.40	43,100	0.11	925	13.80	14.50	0.34	0.32	1.78	94.20
	Inner	5	0.12	65,400	18.00	0.00	25.80	63.60	44,100	0.12	943	14.50	15.30	0.34	0.27	1.73	92.60
	Inner	6	0.13	66,100	18.70	0.00	27.70	68.10	45,500	0.14	963	16.00	16.70	0.35	0.31	1.91	97.70
	Inner	7	0.11	73,700	15.50	0.00	28.30	72.80	50,500	0.08	799	16.70	12.10	0.25	0.39	1.91	115.00
	Inner	8	0.12	68,300	13.20	0.00	26.20	68.50	47,200	0.07	717	16.10	11.30	0.27	0.48	1.73	109.00
	Inner	9	0.12	68,200	12.90	0.00	28.90	69.00	48,100	0.07	678	18.60	12.30	0.40	0.47	2.02	117.00
	Inner	10	0.11	41,600	11.40	0.17	22.70	44.40	29,000	0.06	589	12.70	12.80	0.30	0.28	1.12	60.10

Table 2 (continued)

Strata	Sub-strata	Site	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Sn	Zn
Outer Bay	Outer	1	0.14	6,570	3.06	0.00	4.40	7.12	4,930	0.01	139	0.00	1.40	0.00	0.00	0.00	10.20
	Outer	2	0.17	7,790	3.15	0.00	4.51	7.14	5,810	0.01	10	2.07	1.27	0.00	0.18	0.00	10.60
	Outer	3	0.18	13,500	3.69	0.00	8.85	12.40	9,980	0.01	173	4.86	2.49	0.00	0.26	0.43	20.20
	Outer	4	0.14	39,700	16.00	0.00	29.80	52.30	30,700	0.07	397	14.60	8.27	0.35	0.69	2.35	74.60
	Outer	5	0.19	19,900	9.60	0.00	12.80	20.80	16,700	0.03	260	6.68	4.72	0.00	0.27	0.73	33.60
	Outer	6	0.09	44,100	14.00	0.00	19.30	26.20	27,900	0.03	641	10.10	6.15	0.27	0.22	1.18	51.10
	Outer	7	0.17	23,700	7.47	0.00	16.70	40.40	17,800	0.04	278	7.46	5.89	0.00	0.31	1.26	54.90
	Outer	8	0.15	31,300	7.83	0.00	29.10	26.30	21,800	0.02	378	10.90	3.91	0.20	0.27	1.10	43.40
	Outer	9	0.21	1,400	2.84	0.00	1.82	1.84	2,020	0.00	61	0.00	1.50	0.00	0.00	0.00	2.42
	Outer	10	0.17	17,300	4.63	0.00	13.70	12.30	13,200	0.01	216	5.62	1.65	0.00	0.13	0.00	22.40

For simplicity, the term metal is used without distinction between true metals and metalloids

NERR National Estuarine Research Reserve, *SWMP* System Wide Monitoring Program location, *wt.* weight

Study area and methods

Study area

Jobos Bay is a natural harbor protected from offshore wind and waves by a series of mangrove islands to the southwest and Punta Pozuelo to the southeast (Fig. 1). Apart from discharge from rivers such as Quebrada Coqui-Aguas Verdes and Rio Seco, Jobos Bay receives most of its water from the open ocean. Under prevailing southeasterly wind conditions, surface water is flushed from the Inner and Central Bays in a southwesterly direction, promoting extensive mixing along the eastern shore of the Inner Bay (PRNC 1975). For this study, the bay has been subdivided into three geographic zones, the Inner Bay, Central Bay, and Outer Bay (Fig. 2) based on habitat characteristic and water circulation patterns.

The Inner Bay is the eastern-most zone of the estuary and is enclosed by the Puerto Rican mainland and Punta Pozuelo on three sides. It experiences the least water exchange with the open ocean as it connects only to the Central Bay on its western side. The Inner Bay is also the shallowest of the zones with an average depth of about 3 m; however, depths range from less than 1 m on the shelf near the mouth of the Inner Bay to 8 m in the dredged channel near the south shore (NGDC 2007). The confluent Quebrada Coqui-Aguas Verdes, which runs through urban and cultivated lands and discharges into the northern coast of the Inner Bay, may represent the primary surface water input to Jobos Bay. Rio Seco, which stays dry a significant part of the year, also discharges into the Inner Bay during wet seasons. The Inner Bay has a silty bottom that is regularly stirred up by wind, creating persistently turbid water (PRNC 1972).

The Central Bay is the largest and most complex estuarine stratum of Jobos Bay. Unlike the Inner Bay, the Central Bay has regular water exchange with the Caribbean Sea. The mangrove islands Cayos Caribe and Cayos de Barca, which form the southern boundary, allow Caribbean waters to pass through their shallow channels during incoming tides and surface wind driven currents. Furthermore, Boca Del Infierno, a natural channel of 4 m depth, provides an unobstructed exchange of water with the Caribbean Sea. The Central Bay has an average depth of approximately 5 m, but varies widely between the mangrove forests at the bay edges to the Aguirre Navigational Channel through the middle of the bay.

The Outer Bay is characterized by its exposure to the Caribbean Sea to the west and restricted flow with the Central Bay. The Outer Bay is distinguished from the Central Bay by extension of the mainland at Punta Arenas. A 10- to 14-m deep channel allows water exchange between the adjacent estuarine zones. The Outer Bay has an average depth of just over 4 m. Given its open exposure to the Caribbean Sea, the Outer Bay is mostly influenced by ocean currents.

Methods

Sediment sample collection

In order to make inferences about the entire study area and improve sampling efficiency, a stratified random sampling design was implemented. Jobos Bay was operationally divided into three main strata corresponding to the different zones. Between the eastern (Inner Bay) and western (Outer Bay) strata, is the central stratum (Central Bay), which contains a sub-stratum representing the NERR monitoring zones in Jobos Bay. Within each stratum and sub-strata, ten sites were randomly selected in addition to three existing system-wide monitoring program (SWMP)

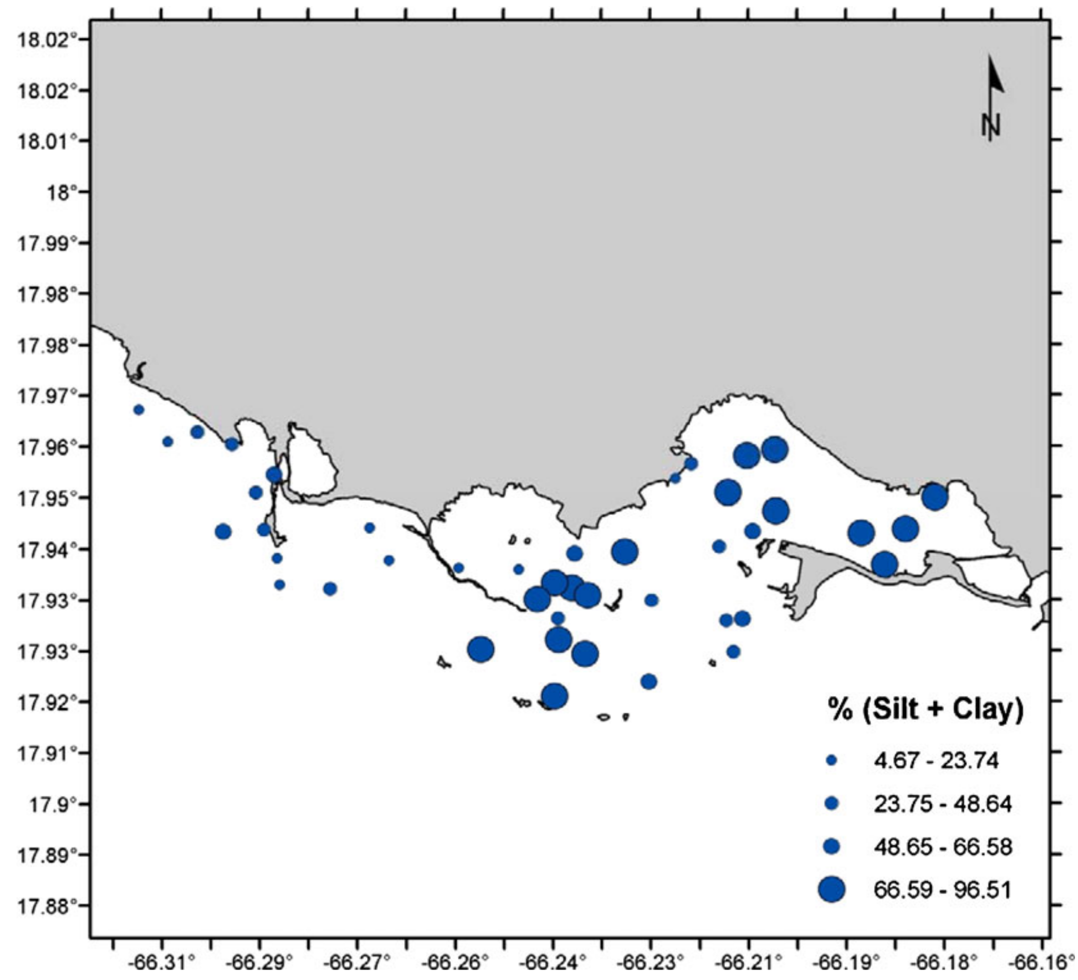

Fig. 3 Percent sediment fine fraction in Jobos Bay

(NERRS 2008) sites for sediment sampling (Table 1). Surficial sediments were collected at each station using Young-modified van Veen grab sampler following the NS&T protocols (Lauenstein and Cantillo 1998). Because the sediments collected were to be analyzed for chemical contaminants, protocols were used to avoid contamination of samples by equipment and cross-contamination between samples. All equipment were rinsed with acetone and then distilled water just prior to use to reduce the possibility of contaminating the sediment sample. Personnel handling the samples also wore disposable nitrile gloves. From each grab, the top 3 cm fraction of the sediment were sub-sampled with a Kynar-coated scoop and placed in certified clean IChem® 250 ml glass containers. Rocks or bits of seagrass were removed. If a particular grab did not result in 200–300 g of sediment being attained, a second grab was made and composited with material from the first grab. If enough sediment had not been collected after three deployments of the grab, the site was abandoned and the boat moved on to an alternative location. Sediment samples for metals analysis were stored on ice in the field and shipped frozen to the laboratory and stored at −20°C until analyzed. Samples for grain size analysis were stored refrigerated to avoid altering the grain size structure of the sediment via freezing.

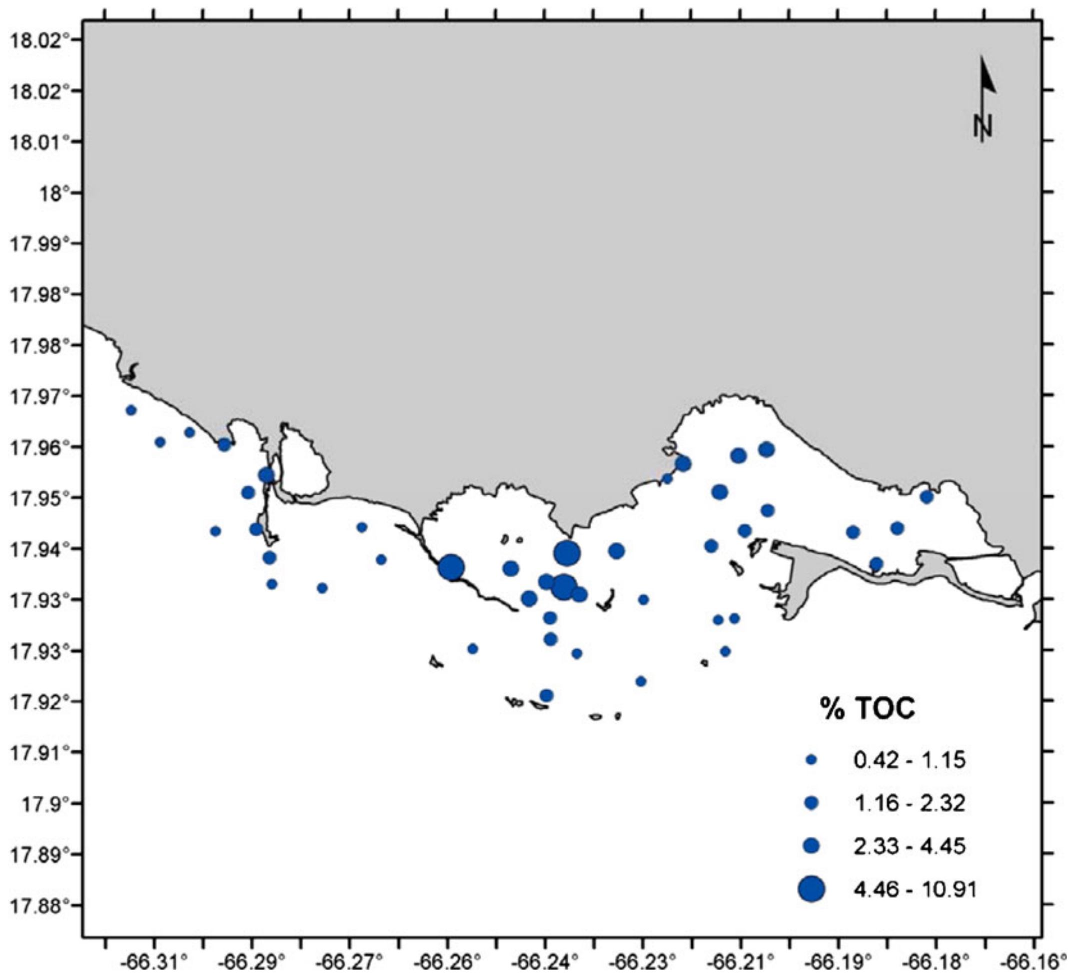

Fig. 4 Percent sediment TOC distribution in Jobos Bay

Analytical methods

Chemical analyses were performed by TDI-Brooks Inc., a government contracted laboratory. A list of trace metals discussed in this study is provided in Table 2. Chemical analyses of these metals followed procedures routinely used in the NOAA NS&T program (Kimbrough and Lauenstein 2006). For most trace and major elements, samples were analyzed using inductively coupled plasma/mass spectrometry analysis. Atomic fluorescence spectrometry was utilized to measure arsenic and selenium, while cold vapor atomic absorption spectrometry was used for mercury analysis. In general, samples were homogenized and freeze dried. Aliquots of 0.10–0.45 g dried sediment were digested in a sequence of heating steps with metal grade HNO_3, HF, and boric acid. For analysis of Hg, sediment samples were digested based on a modified version of EPA method 245.5 using a concentrated H_2SO_4 and HNO_3, followed by addition of $KMnO_4$, and $K_2S_2O_8$, and a second digestion. Before analysis, 5 mL of 10% (*w*/*w*) $NH_2OH{\cdot}HCl$ were added to reduce excess permanganate and the volume was brought to 40 mL with distilled water.

Quality control samples, including the marine sediment reference materials HISS-1, MESS-3, and PACS-2 from the National Research Council Canada, were processed in a manner identical to field samples. A method blank was run with every 20 samples, or with every sample set, whichever was more frequent. Matrix spike/matrix spike duplicate samples were run with every 20 samples, or with every sample set. Calibration standards (representative of sample concentration) are prepared from dilutions of NIST-traceable multi-element standards. The low concentration standard is based on instrument sensitivity (e.g., 0.05 ppb for Pb, 0.5 ppb for Al). Mid and high standards are at 20 and 200 ppb, respectively. Other reference materials (NIST 1640 Trace Elements in Water) are used as check standards. Calibration verification was performed periodically with a blank and mid-range standard (20 ppb). Quality control criteria for target analytes specify recoveries between 8% and 120% for spiked samples and ±20% for SRM. The results are reported on a dry weight (wt.) basis.

Other ancillary parameters included grain size and total organic and inorganic carbon (TOC, TIC). TOC and TIC were determined using methods involving incineration, and grain size determination was based on the Wentworth scale method which utilizes a combination of sifting and pipetting techniques (McDonald et al. 2006). Grain size, TOC, and TIC measurements are reported as percentages of the total sample weight.

Statistical analysis

Primary statistical analyses were conducted using JMP-5.1™ system statistical package. The data was tested for normality using Shapiro Wilks “goodness of fit.” Multivariate cluster analyses were conducted to determine natural breaks within the concentration range of each metal. Cluster analysis was used in order to adequately assess the spatial distribution of metal concentrations. Wilcoxon rank-sum or Kruskal–Wallis rank tests were used to assess differences between cluster groups and inter-strata comparison. Relationships between variables (e.g., inter-metal correlations) were assessed using Spearman rank correlation. Significance of statistical tests were reported at $p = 0.05$.

Table 3 Metals range of concentrations (micrograms per gram of dry wt.) in surficial sediment from Jobos Bay

Analyte	Minimum	Maximum	Median
Ag	0.051	0.219	0.105
Al	629	73,700	41,850
As	1.79	28.1	12.8
Cd	0	0.174	0
Cr	0	29.8	18.5
Cu	1.37	73.7	29.9
Fe	1,060	50,500	26,650
Hg	0.0014	0.144	0.0309
Mn	33.1	1,130	529
Ni	0	31	10.1
Pb	0.227	16.7	6.02
Sb	0	0.589	0.269
Se	0	1.56	0.276
Sn	0	2.74	1.17
Zn	1.57	117	48.5

Zero values represent concentrations below detection limits
wt. weight

Results

Sediment grain size and TOC

The distributions of the fine-grained sediment (clay + silt) and TOC in Jobos Bay surficial sediment are illustrated in Figs. 3 and 4. Pockets of fine-grained sediment were observed throughout the study area. However, the prevalence of fine sediments (clay + silt > 80%) was observed only in the eastern part of the bay (Inner Bay). The proportions of fine-grained sediment decreased westward with the lowest (4.7%) found around the western area (Outer Bay). Sediment organic and inorganic components are presented in Table 1. Major sediment components that influence metal concentration, fine fraction (clay + silt), and TOC are discussed below. Maximum percent TOC values of 10.9, 10.8, and 8.9 were observed respectively at sites 4, 12, and 11 within the Central Bay (Table 1). With the exception of these three sites, TOC content in the sediment varied between 0.4% and 4.5% across the bay (Fig. 4). The overall distribution of TOC in the study did not show any marked pattern like that observed in the distribution of grain size (Fig. 4).

Concentration and distribution of metals

Table 2 illustrates the overall metal concentrations in sediment at each site. To explore the general distribution pattern of metals in the study area, a summary of concentration ranges and median values were calculated (Table 3). The results showed a broad variation within the concentration values of each metal. In general, concentration differences between the minimum and maximum values of individual metal reached two orders of magnitude (Table 3). Results indicated cadmium was below the detection limit at all but two sites. For the majority of the metals, elevated concentrations were observed mostly in sediment collected from the Inner Bay in the eastern stratum. In contrast, the minimum concentration values of these aforementioned metals were predominantly observed at sites located in the western area of the bay. However, spikes of

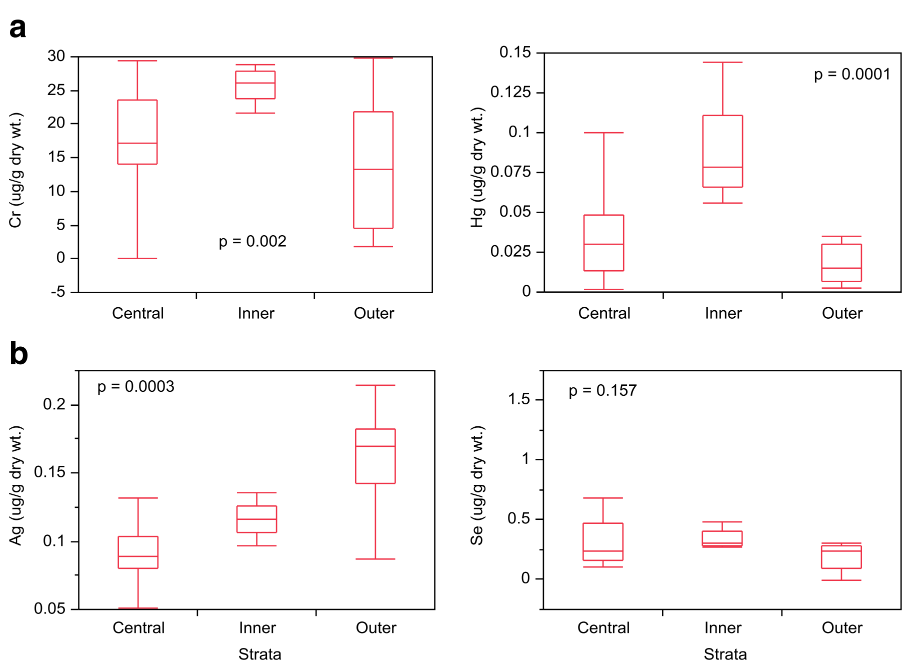

Fig. 5 Typical pattern of metal distribution in Jobos Bay. Cr and Hg exemplify the distribution of the majority of the metals with higher concentrations in the Inner Bay. Ag was higher in the Outer Bay and Se was not significantly different in either zone

relatively elevated concentrations were observed for some metals throughout the study area. For instance, maximum concentrations were observed at sites 4 and 11 in Central Bay for As; Cr were elevated at sites 4 and 8 of the Central and Outer Bays, respectively; and maximum concentration for Ni was found at sites 4, 11, and 12 in Central Bay.

Further assessments to compare metal concentrations in the three strata were conducted using nonparametric Wilcoxon tests. The results showed that the proportion of the measured metals varied widely within strata (Fig. 5a and b) confirming earlier observations illustrated in Table 3. Metals concentrations were significantly higher ($p < 0.05$) in the Inner Bay relative to the Central and Outer Bays (Fig. 5a), with the exception of Ag and Se (Fig. 5b). In contrast to the general observation, Ag was measured at significantly higher concentrations in the Outer Bay ($p < 0.05$) relative to the other zones of the study area. Concentrations of Se, on the other hand, showed no statistical difference between the three strata ($p > 0.05$).

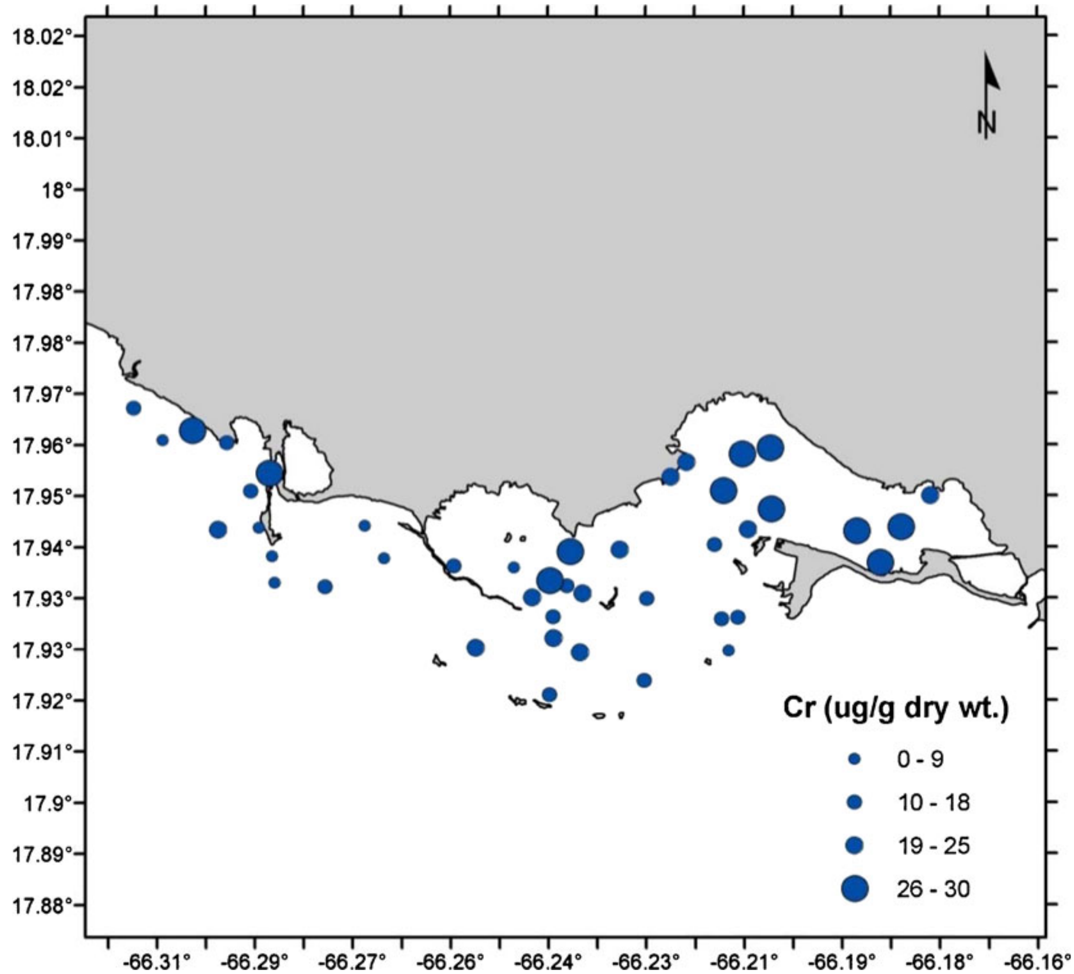

Fig. 6 Distribution of Cr in the sediment of Jobos Bay

Cluster analysis, applied to the concentration range of individual metal, followed by Wilcoxon tests were used to assess the spatial distribution of metals in Jobos Bay sediment. Metals such as Al, As, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sn, and Zn were shown to have similar distribution patterns. These distributions were illustrated by the Cr and Fe results in Figs. 6 and 7. In general, these metals showed a characteristic distribution pattern with decreasing concentration from east to west (Figs. 6 and 7). The distribution of Ag, however, contrasted with that of the general pattern (Fig. 8) with elevated concentrations of Ag mainly observed in the western stratum.

Inter-metal and grain size correlation

Spearman rank correlations among all metals, grain size, and TOC are shown in Table 4. Spearman coefficient Rho values of 0.707 or higher were discussed as indicative of strong correlation, while values below 0.707 indicate weak correlation. Strong associations were found among several groups of metals. Among the major elements,

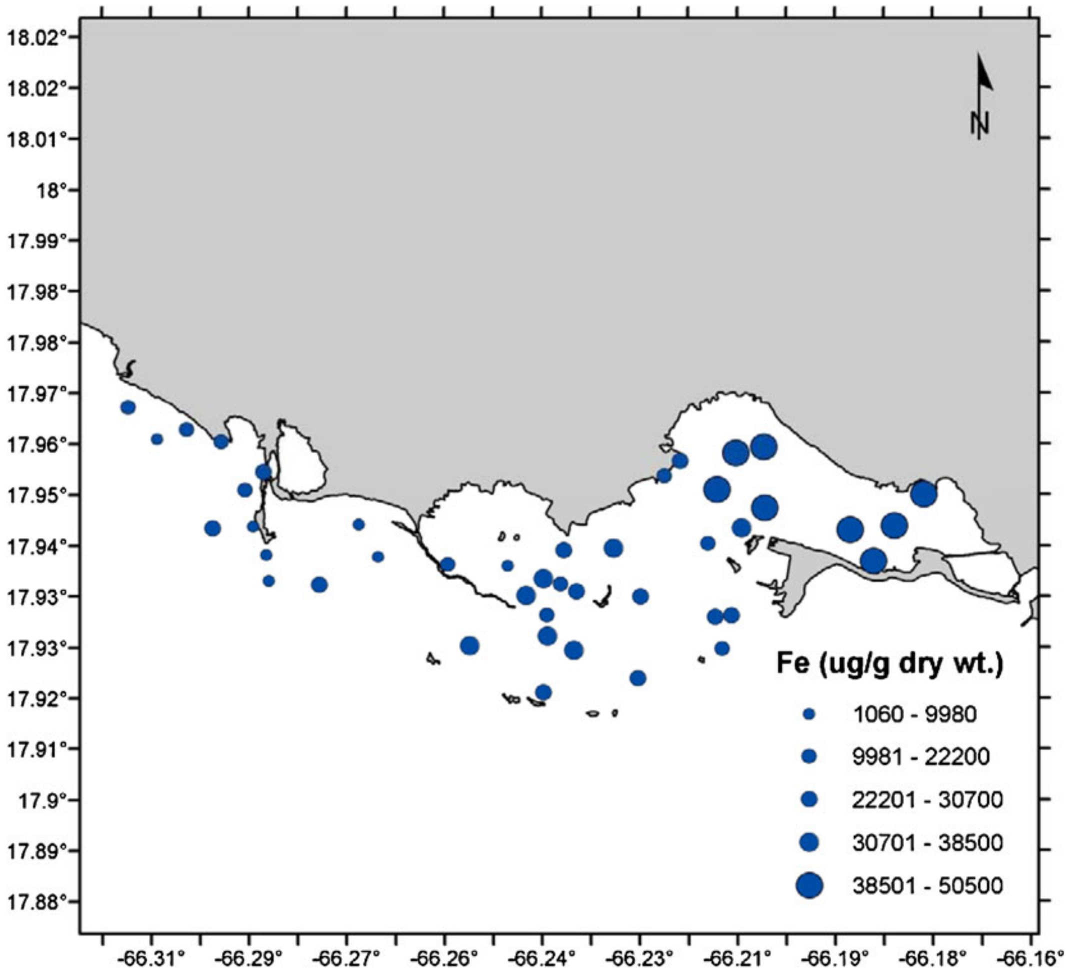

Fig. 7 Distribution of Fe in the sediment of Jobos Bay

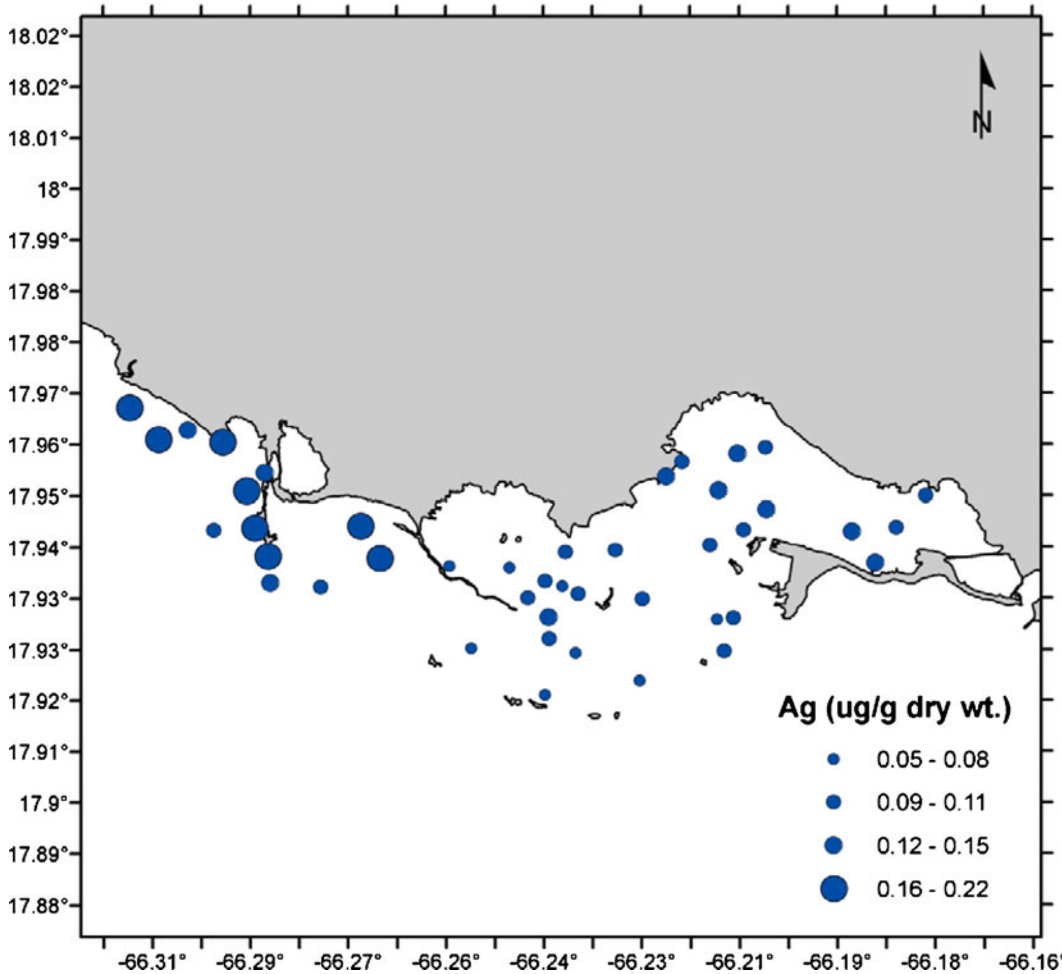

Fig. 8 Distribution of Ag in the sediment of Jobos Bay

Al and Fe showed strong and direct correlations with each other and with virtually all trace metals except Ag. Also, Mn was positively correlated with Al, Fe, and all other trace elements except Se ($p > 0.05$). Apart from Ag, which had a poor and inverse correlation; the results indicated that, in general, inter-metal correlations were positive. Other studies have reported significant correlations between major elements, such as Al, Fe, and Mn, and trace metals in similar habitats off the southeastern coast of the USA (Windom et al. 1989; Schropp et al. 1990; Caccia et al. 2003). These studies suggest that Al and Fe can be used as normalizing factors for metals in natural estuaries and coastal environments to assess anthropogenic enrichment.

Grain size and sediment TOC were found to be positively correlated with all major and trace elements, excluding Ag. Relative to TOC, grain size showed stronger correlations (Rho > 0.707) with the major and trace metals. These results confirm that elemental concentrations are elevated in finer sediments because of higher surface to volume ratio (Forstner and Wittmann 1981). The depositional zone in the Inner Bay stratum had metal concentrations greater than the other strata (Figs. 6 and 7), likely due to grain size and proximity to metal sources. Total organic carbon

Table 4 Spearman rank correlations between metals, grain size (clay + silt), and TOC in sediment from Jobos Bay

Label	%TOC	%Fine	Ag	Al	As	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Sn
%Fine	**0.424**														
	0.005														
Ag	**−0.111**	**−0.316**													
	0.479	0.039													
Al	**0.239**	**0.911**	**−0.366**												
	0.122	0.000	0.016												
As	**0.405**	**0.720**	**−0.398**	**0.740**											
	0.007	0.000	0.008	0.000											
Cr	**0.520**	**0.739**	**−0.075**	**0.752**	**0.700**										
	0.000	0.000	0.632	0.000	0.000										
Cu	**0.619**	**0.822**	**−0.133**	**0.801**	**0.683**	**0.892**									
	0.000	0.000	0.394	0.000	0.000	0.000									
Fe	**0.390**	**0.911**	**−0.252**	**0.965**	**0.787**	**0.845**	**0.873**								
	0.010	0.000	0.102	0.000	0.000	0.000	0.000								
Hg	**0.693**	**0.747**	**−0.169**	**0.696**	**0.700**	**0.815**	**0.941**	**0.781**							
	0.000	0.000	0.279	0.000	0.000	0.000	0.000	0.000							
Mn	**0.039**	**0.839**	**−0.402**	**0.952**	**0.696**	**0.615**	**0.670**	**0.887**	**0.582**						
	0.801	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000						
Ni	**0.708**	**0.573**	**−0.239**	**0.555**	**0.639**	**0.800**	**0.814**	**0.631**	**0.831**	**0.373**					
	0.000	0.000	0.122	0.000	0.000	0.000	0.000	0.000	0.000	0.014					
Pb	**0.689**	**0.784**	**−0.233**	**0.722**	**0.700**	**0.798**	**0.938**	**0.793**	**0.975**	**0.612**	**0.824**				
	0.000	0.000	0.132	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000				
Sb	**0.368**	**0.559**	**−0.286**	**0.633**	**0.790**	**0.725**	**0.648**	**0.665**	**0.622**	**0.539**	**0.697**	**0.642**			
	0.015	0.000	0.063	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000			
Se	**0.918**	**0.510**	**−0.156**	**0.353**	**0.521**	**0.639**	**0.687**	**0.482**	**0.721**	**0.137**	**0.789**	**0.709**	**0.497**		
	0.000	0.000	0.318	0.020	0.000	0.000	0.000	0.001	0.000	0.380	0.000	0.000	0.001		
Sn	**0.560**	**0.842**	**−0.253**	**0.747**	**0.626**	**0.823**	**0.887**	**0.798**	**0.852**	**0.635**	**0.686**	**0.868**	**0.607**	**0.650**	
	0.000	0.000	0.102	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Zn	**0.541**	**0.900**	**−0.200**	**0.893**	**0.720**	**0.891**	**0.964**	**0.945**	**0.891**	**0.777**	**0.735**	**0.906**	**0.654**	**0.627**	**0.914**
	0.000	0.000	0.199	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Bolded lettering represents the Rho value (ρ) and standard script represents p values ranged from 0.3% to 4.3% and was only weakly correlated with metals.

Discussion

The highest percentages of TOC were observed in sediment from the central stratum, while sediments from the eastern and western strata were relatively low in TOC content. Except for Ni and Se, TOC content was not strongly correlated with metals suggesting that the influence of organic matter on metal distribution may be far less important than that of grain size. This observation corroborates the assertions by Forstner and Wittmann (1981) and Windom et al. (1989), which indicated that in natural estuarine and coastal sediments, concentrations of metal are predominantly determined by detrital inorganic material rather than organic and nondetrital materials.

In Jobos Bay, the distribution of inorganic material (grain size) demonstrated a distinctive general pattern. Fine-grained material showed a decreasing gradient from the eastern to the western zone of the study area (Fig. 3). These findings are in agreement with previous results reported by the PRNC (1972), which characterized the eastern area (Inner Bay) stratum as having silty bottom sediment relative to areas of the bay where sediments are more or less sandy.

The predominantly elevated proportion of fine sediment materials in the Inner Bay indicated that the area is a low-energy depositional zone. Physical conditions and the water circulation in the Inner Bay are suitable for sedimentation of terrigenous fine particles suspended in runoff waters. Sedimentation of these fine particles in the Inner Bay may be favored as a result of surface water input from Quebrada Coqui-Aguas Verdes and Rio Seco, the shallowness of the bay and the fact that the Inner Bay is semi-enclosed (PRNC 1972).

The concentrations of the majority of metals showed similar distributions as that of grain size. Relative to the Outer and Central Bays, significantly high ($p < 0.05$) metal concentrations are found in the Inner Bay stratum located in the eastern area of the bay (Tables 2 and 3, Figs. 6 and 7). The physiographic characteristics of the stratum and the sediment texture may be the cause of the relatively high metal concentrations in the Inner Bay stratum. The Inner Bay is the receiving basin for Quebrada Coqui-Aguas Verdes and Rio Seco, which transport terrigenous detrital materials from the upland. Being physically protected from the scouring of offshore water, the Inner Bay acts like a depositional area characterized by calm waters. As a result, sediment materials transported by Quebrada Coqui-Aguas Verdes and Rio Seco are deposited along with metals. Furthermore, the presence of metals in elevated concentrations in the Inner Bay may be linked to its characteristically fine-grained sediment. It has been shown that because of their high surface to volume ratio, fine sediments like those found in the Inner Bay tend to sequester higher concentrations of metals (Forstner and Wittmann 1981; Ujevic et al. 2000; Orescanin et al. 2004). Conversely, the relatively low concentration of metals found in the Outer and Central Bays may be due to the presence of a sandier type of sediment, and particularly to the fact that these systems are well flushed by offshore water.

Cadmium was measured at very low concentrations at virtually all the sites in the study area. Chemically, Cd is strongly affected by diagenic processes that impact its equilibrium between pore water and the overlying water column (Rosenthal et al. 1995). During this process, Cd migrates into porewater in the top oxidized sediment layer while the inverse occurs in the reduced deeper layers. The diagenetic behavior of Cd is usually linked to its depletion in the upper oxidized layer of sediments (Rosenthal et al. 1995; Apeti et al. 2009). Because of its low concentrations in this study, Cd is not included in any subsequent discussion.

Metal concentrations in Jobos Bay were compared to other studies from similar habitat environments (Table 5). In general, concentration values were within the ranges found in Jobos Bay (Aldarondo-Torres et al. 2010; NS&T 2011), southwest Puerto Rico (Pait et al. 2008), and southwest Florida (Cantillo et al. 1999a). However, maximum concentrations for As, Cu, Mn, Sn, and Zn in Jobos were elevated relative to those in Tampa Bay, which was once considered polluted (Lewis et al. 1998). NOAA's NS&T

Table 5 Range of metal concentration in surficial sediment from Jobos Bay compared to published data from similar habitat environments

Area	Ag	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Se	Sn	Zn	Reference
This study	0.1–0.2	1.8–28	0.0–0.2	0.0–30	1.4–74	0.0–0.1	33–1,130	0.0–31	0.2–17	0.0–0.6	0.0–1.6	0–2.74	1.8–117	This study (median)
Jobos Bay	–	9.6–27	0.02–0.2	–	1.6–53	–	–	–	1.5–22	–	–	–	11–130	Aldarondo-Torres et al. (2010)
Jobos Bay	0.0–0.1	11–12	0.0–0.2	37–273	11–155	0.03–0.1	508–990	9.2–258	6.7–12	–	0.2–0.3	2.4–1.4	75–139	NS&T (2011)
South Florida	0.1–0.3	2.5–10	0.1–0.3	20–80	10–40	0.1–0.2	20–100	10–20	5–20	0.2–0.6	0.2 –0.8	1–3	20–100	Cantillo et al. (1999a)
Tampa Bay	0.1–0.2	1–5	0.3–0.8	20–60	10–20	0.1–0.2	20–60	5–10	20–60		0.3–0.8	0.5–1.5	20–80	Cantillo et al. (1999b)
Southwest PR	<001	0.01	0.01	31.2	5.21	<0.01	109	26.6	1.93	0.1	0.2	0.21	8	Pait et al. (2008)
ERL[a]	1.0	8.2	1.2	81	34	0.15	–	20.9	46.7	–	–	–	150	Long et al. (1996)
ERM[a]	3.7	70	9.6	370	270	0.71	–	51.6	–	–	–	–	410	Long et al. (1996)

Concentration values are in micrograms per gram of dry weight. Values are rounded up. Fe was not included due to lack of published values. Values for southwest Puerto Rico (Pait et al. 2008) are averages

[a]Sediment quality guidelines were not developed for all metals monitored by the NOAA's National Status and Trends Program

program has maintained monitoring sites along the Puerto Rican coastline, including Jobos Bay, since 1992 (NS&T 2011). Although, concentration ranges of metals were similar (Table 5), the NS&T data indicated extremely high concentration for Ni (258 μg/g dry wt.) and Cr (27 μg/g dry wt.) in Bahia de Boquerón. Runoff from a landfill in the vicinity of the NST monitoring site in the region was assumed to be the possible source of contamination.

Further evaluation of the degree of metal contamination in Jobos Bay was assessed using the previously published numerical sediment quality guidelines (SQG) known as effects range-low (ERL) and effects range-median (ERM) developed by Long and Morgan (1990) and Long et al. (1996). The SQG value was not defined for all metals; existing guideline values are presented in Table 5. These guidelines are statistically derived levels of contamination above which toxic effects would be expected to be observed with at least a 50% frequency (ERM), and below which effects were rarely (<10%) expected (ERL). In Jobos Bay, metals concentrations were all below the ERM values, but maximum values for As, Cu, and Ni were above their respective ERL values at sites located in the Inner and Central strata. Mercury was found at the ERL level at site 6 of the Inner Bay stratum. Overall, the degree of metal concentrations does not suggest a high level of sediment metal-related toxicity in the bay.

The presence of metals at relatively elevated concentrations in the eastern area of Jobos Bay may be linked to diffuse nonpoint sources of natural and anthropogenic origins. Jobos Bay watershed is host to a variety of residential, commercial, and industrial activities, most notably a coal power plant, a petroleum refinery, and pharmaceutical facilities (Dieppa et al. 2008), that likely contribute pollutants to the bay. Coal burning is associated with atmospheric pollution by metals, such as As, Cd, Cu, Hg, Pb, Ni, and Zn found in fly ash (Theis et al. 1978; McBride et al. 1978). Atmospheric deposition for metals from industrial emissions in the vicinity of Jobos Bay were assessed (Jimenez-Velez et al. 2003, 2009; Gioda et al. 2005). Relative to other regions in Puerto Rico, concentrations of metals in airborne particles were higher in the Salinas watershed, which incorporates Jobos Bay (Jimenez-Velez et al. 2003). Gioda et al. (2005) also concluded that the presence of Cd, Cu, Fe, Ni, Hg, and Pb in airborne particles in the Jobos Bay may be linked to both long-range atmospheric transport and anthropogenic activities in the bay's watershed. Rather than local industrial activities, previous studies indicated that concerns of water quality in Jobos Bay may be linked to land-based sources from agricultural runoff and soil erosion (Field et al. 2002).

Preliminary studies (Altieri-Rijos 2004) revealed that pesticides and fertilizers applied in agricultural fields were also being transported to the Reserve bay (Field et al. 2002). Although metals such as Cd, Cr, Cu, Fe, Hg, Mn, Pb, Ni, and Zn are constituents of phosphorus fertilizers (Forstner and Wittmann 1981), they also occur naturally. Copper is also used as an agricultural fungicide, and in anti-fouling boat paint. As a result, it is difficult to distinguish between natural and anthropogenic sources. Metallic contaminants, whether from natural or anthropogenic sources, are supplied in solution or in association with fine-grained suspended solids and colloidal inorganic particles. These particles are usually deposited in areas of low hydrodynamic energy along streams or are transported to estuaries or the ocean during times of increased river flow (Simpson et al. 2000).

A number of methods, based on geochemical processes that control behavior and fate of metals in coastal waters, have been proposed (Forstner and Wittmann 1981; Schropp and Windom 1987). In natural coastal waters, trace metals co-precipitate with the oxide/hydroxides of Al, Fe, and Mn usually into the fine-grained fraction (clay or aluminosilicate) of sediments (Schropp and Windom 1987). Since aluminosilicates are the metal-rich phase of bottom sediment, many approaches to delineate anthropogenic versus natural sources are based on grain size, using Al and Fe for normalization (Windom et al. 1989; Forstner and Wittmann 1981; MacDonald 1994). That is, without anthropogenic inputs, metal concentrations are expected to co-vary among each other and with Al, Fe, and Mn, given that factors such as precipitation or diagenesis are very small. Deviations from direct metal-Al/Fe or metal-grain size correlations are interpreted as anthropogenic enrichment (Windom et al. 1989; MacDonald 1994; Carvalho et al. 2002).

In Jobos Bay, most of the metals, except Ag, were found to be positively correlated with grain size (Table 4). Correlations of metals versus grain size and Al are exemplified using results for Ag, Fe, Mn, and Zn (Figs. 9 and 10). The positive correlations suggest that sediment texture greatly influences the distribution of metals. Additionally, the positive inter-metal correlations, including those between Al, indicate that metal concentrations in Jobos Bay may be of natural origins.

Considering the arid conditions in the watershed and lack of surface flow, other contributions of metals to Jobos Bay may include stormwater runoff, inputs from Quebrada Coqui-Aguas Verdes and Rio Seco, and atmospheric deposition. Weathering of bedrock and soil erosion

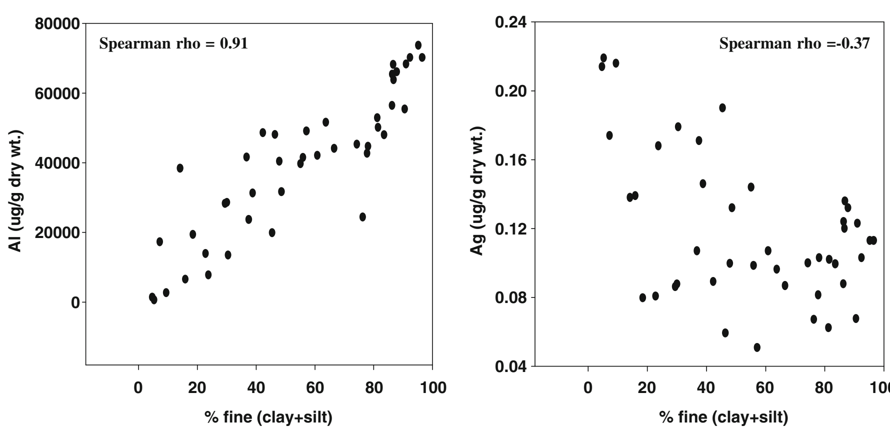

Fig. 9 Correlation of Al and Ag vs. the percentage of fine grained (clay + silt) sediment in Jobos Bay

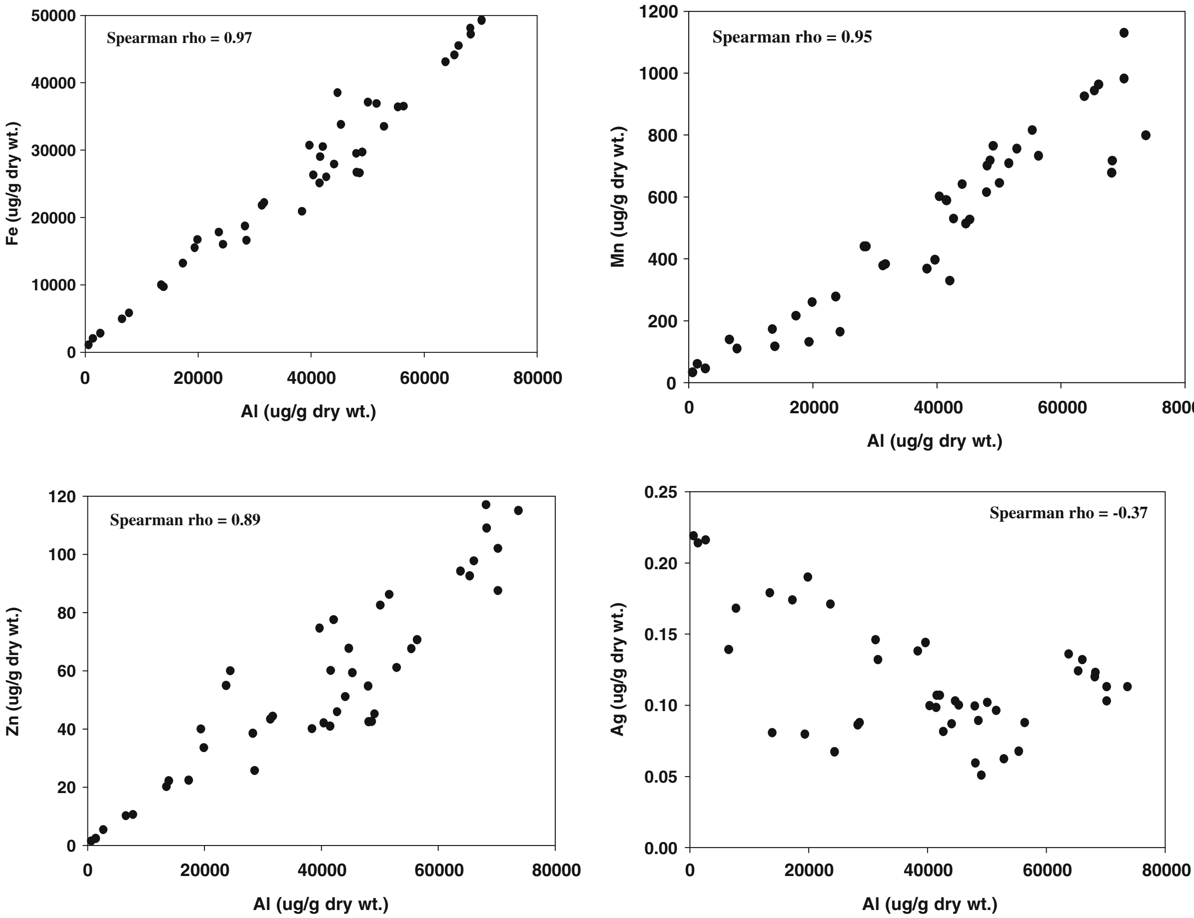

Fig. 10 Inter-metal correlation of Fe, Mn, Zn, and Ag versus Al

produce mineral debris that are natural sources of metal in sediment transported into coastal waters (Forstner and Wittmann 1981). Transport of detrital materials within the watershed by stormwater and runoff from Quebrada Coqui-Aguas Verdes may constitute the largest source of metals in Jobos Bay. Although Rio Seco is a seasonal intermittent river, it may also contribute to metal-bound sediment transport into the bay, especially during wet seasons. However, the characteristic deviations of Ag from direct positive correlation with both Al and grain size may be interpreted as having anthropogenic inputs.

Of the 15 metals, only Ag was found to have a spatial distribution that contrasted with that of the general east–west decreasing pattern (Fig. 8). Additionally, Ag did not show a direct correlation with Al and grain size. Current levels of Ag concentration in Jobos Bay are lower than the ERL and ERM values, but the fact that it has relatively elevated concentrations in the more sandy western area of the bay (Fig. 8), suggests enrichment. Possible sources of Ag in the western stratum may include industrial discharges or runoff.

Conclusion

Sediment characteristics, such as grain size and TOC, and baseline metal concentrations have been assessed in Jobos Bay. Overall, the distributions of sediment grain size and TOC content suggested heterogeneous bottom substrates in Jobos Bay. Grain size appears to heavily influence the distribution of all metals except that of Ag. Most metals were found to be significantly higher in the eastern area of the bay relative to the central and western areas. However, maximum concentration values were within concentration ranges found in other similar estuarine systems. Sediment normalizing factors, such Al and grain size, were positively correlated with virtually all metals. This suggests that although the watershed contains several low-density population centers and some industrial plants, anthropogenic inputs may be negligible. Likely sources of metals in Jobos Bay may include natural bedrock weathering and transportation of detrital materials by Quebrada Coqui-Aguas Verdes and Rio Seco. The more diffuse nonpoint source of atmospheric deposition resulting from local and long-range transboundary airborne particles are also possible sources, which may be contributing to the overall metal concentration in Jobos Bay. The lack of correlation of Ag with normalizing factors suggested enrichment from industrial effluents for this metal. However, the concentrations of Ag as well as those of other metals were well below sediment quality guidelines suggesting that metal toxicity to biota is limited in Jobos Bay. This study is the first comprehensive assessment of metals in Jobos Bay and the associated data serve as baseline information for further assessments and monitoring.

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