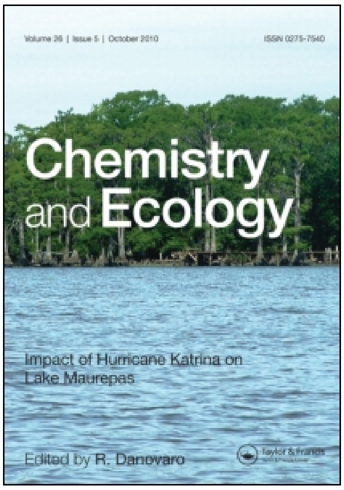

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Heavy Metals in Sediments of Matanzas Bay, Cuba

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HEAVY METALS IN SEDIMENTS OF MATANZAS BAY, CUBA

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Different granulometric fractions of surface sediment samples and dissected sediment cores taken from Matanzas Bay and from three inflowing rivers were investigated for the content of metals (Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn) and organic matter. The data on 'total' and easily extractable metal fractions were normalized and statistically treated with the aim of finding procedures applicable for assessment of the sources and levels of contamination. The results show clearly that the investigated area is not much contaminated with respect to those determinands. However, sewage effluents, urban runoff and industrial discharges from Matanzas City draining to the bay via two rivers cause elevated heavy metal levels in sediments of the rivers and of the adjacent coastal areas. In addition, a tannery discharge was revealed as a contamination 'hot spot' for chromium.

KEY WORDS Sediments, heavy metals, contamination patterns

1. INTRODUCTION

Matanzas Bay is located at 23°03'N and 81°34'W in the northern coastal zone of Cuba. The bay has a width of about 5 km at the mouth, a surface area of 35.8 km^2, a volume of 7.62 km^3 and a median depth of 200 m. The length of the bay is 9 km with a coast line of about 19 km. These features favour an extensive exchange of water with the open sea. The city of Matanzas, accommodating important industries and a harbour, is located at the innermost part of the bay. Three rivers drain into the bay and two of them, Yumuri and San Juan, receive waste waters of industrial and domestic origin from Matanzas City. Therefore, *a priori,* they could be considered potential sources of contaminants for the bay, especially in the relatively shallow zone in the mouths of these rivers.

Commonly, sediments are considered effective sinks for heavy metals supplied to the aquatic system. From study of the surface sediments we can obtain a good picture of the present situation and from core samples, we can understand the historical development of contamination in the investigated area. The present work aims to uncover the contaminant level in Matanzas Bay and to show the principal sources of heavy metals which could affect this ecosystem. Different methods of treatment of the analytical data will be applied to support their interpretation. In recent years, the use of normalization procedures has become a useful tool to distinguish between the natural and/or anthropogenic origin of heavy metal contents in sediments (Aranjo *et al.*, 1988; Kouadio and Trefry, 1987; Larsen *et al.*, 1983; White and Tittlebaum, 1984; Wilson *et al.*, 1986; Windom *et al.*, 1986). In addition, different multivariate statistical methods including principal component analysis and cluster analysis are employed increasingly to support the interpretation of the results obtained (Aranjo *et al.*, 1988; Guerzoni *et al.*, 1984; Liu, 1983; Loring, 1984; Pavoni *et al.*, 1987; Takematsu *et al.*, 1981).

2. MATERIALS AND METHODS

Figure 1 shows the study area with the major contaminant sources and the sampling stations. Due to limitations in available sampling techniques, only the coastal area of the bay could be investigated. The water depth at the stations where sediment samples were taken was in the range between 5 and 20 m. In November 1985, sampling was performed with a Van Veen grab at eight locations close to expected contaminant inlets. In March 1987, four sediment cores were collected with a gravity corer from the estuarine zone of the rivers and from another part of the bay. In addition, different grab samples were taken in the rivers; from Yumuri and San Juan Rivers upstream and inside the city, and from the Canimar River at locations considered as background reference stations. A

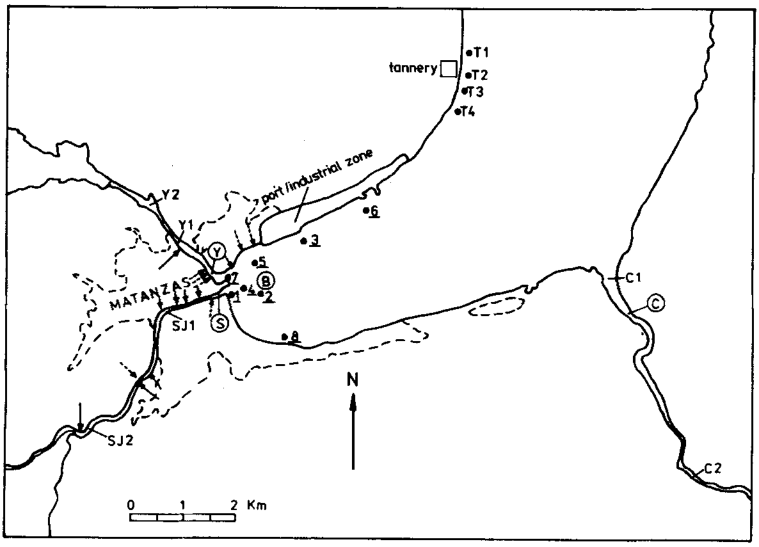

Figure 1 Sampling area (underlined numbers: surface samples taken 11/85; "T": surface samples taken 3/87; "O": cores taken 3/87; "C": Canimar River; "Y": Yumuri River; "SJ": San Juan River; "B": Matanzas Bay; arrows: input of untreated industrial wastes; arrows with broken lines: inputs of untreated urban wastes)

special study area was the zone of the bay where a tannery discharges waste waters enriched in chromium and other metals (Tur and Gonzalez, 1988).

The uppermost 5 cm layer was taken from corers and grabs to represent "surface samples." The remaining part of the cores was dissected into 3 cm slices. The samples were dried 24 h at 105°C. For the determination of mercury, subsamples were dried at 45°C. Different grain size fractions were separated. A fraction $<150\ \mu m$ was obtained by dry-sieving from the core slices and from those samples taken in the tannery area. Fractions $<63\ \mu m$ and 63–150 μm were separated by wet and dry-sieving from samples taken in the rivers and other parts of the bay.

Digestion, using mixtures of HNO_3 and HCl, was used for the determination of mercury (Randlesome and Aston, 1980) and other metals (McKown *et al.*, 1978). The resulting digests were analyzed by flame atomic absorption spectroscopy with deuterium background correction. The "cold-vapour" reduction/aeration method was used for Hg. The precision of these measurements for five parallel samples was better than 10%. The organic matter content was derived from the ignition loss at 550°C after 3 h. The NBS reference sample "SRM 1645/river sediment" was used to check the accuracy of our analyses. For the investigated elements, our data were within the standard deviation range of the certified values.

In addition, for the bay samples, weak digestion with 0.5 N HCl (Chester and Voutsinou, 1981) was performed to characterize those fractions which are easily available, especially, when the environmental background conditions were changing. The data were normalized to the contents of aluminium and organic matter. For the statistical analysis the "Statistical Program for Social Sciences" (SPSS) was used. Following Pavoni *et al.* (1987), all data were auto-normalized prior to the statistical processing in order to harmonize the relatively broad range of contents found for the different metals in the sediments, e.g. from 0.02 $\mu g/g$ for Hg to 47,700 $\mu g/g$ for Al (see Table 1).

3. RESULTS AND DISCUSSION

3.1. *Bay/Surface samples*

The results are given in Table 1.1. The samples taken in 1985 showed a range in their content of organic matter and metals up to two orders of magnitude (zinc). These variations cause problems when stations with unusual behaviour are selected and distinguished from each other. Therefore, taking into account that the heavy metal content in sediments originates partly from the organic material and/or the lithogenic fraction, the data were normalized according to the contents of *organic matter* and aluminium. Figure 2 shows the results of hierarchical cluster analysis to separate station *1*, and also stations *6* and *7*, from the others. It seems a logical step, because stations *1* and *7* are located in the mouths of the San Juan and Yumuri Rivers that receive, without much dilution, the mixed domestic and industrial waste waters of Matanzas City. Station *6*, located in the vicinity of the harbour and industrial zone, seems to reflect local anthropogenic inputs. Principal component analysis of normalized values resulted in similar patterns with a clear distinction between stations *1*/*7* and the others (Figure 3). However,

Table 1 Heavy metal contents in Matanzas Bay sediments (*Mean values* ± s.d. (ranges))

1.1 *Matanzas Bay/Surface samples*

Fraction	63–150 μm ($n = 8$) *wet sieved*	<63 μm ($n = 8$) *wet sieved*	<63 μm ($n = 8$) *dry sieved*	<63 μm ($n = 8$) 0.5 N HCl-*extr.*	<150 μm ($n = 4$) *tannery zone*
Al	*1.07* ± 0.62 (0.13–1.88)	*2.05* ± 0.73 (1.11–3.32)	*1.38* ± 0.59 (0.53–2.10)	*0.07* ± 0.04 (0.03–0.13)	*0.12* ± 0.06 (0.06–0.19)
Cd	*0.87* ± 0.13 (0.73–1.10)	*1.05* ± 0.45 (0.73–1.90)	*0.87* ± 0.13 (0.73–1.10)	n.d.	n.d.
Co	*15.6* ± 4.9 (6.0–22.0)	*19.9* ± 5.4 (11.8–28.1)	*16.8* ± 5.2 (8.0–24.3)	n.d.	4.5 ± 1.3 (3.2–6.2)
Cr	n.d.	n.d.	n.d.	n.d.	*3215* ± 3263 (365–7915)
Cu	*28.0* ± 14.8 (7.0–50.2)	*43.6* ± 13.7 (26.9–59.7)	*32.5* ± 13.4 (14.8–52.2)	10.8 ± 5.6 (4.0–18.7)	*157* ± 156 (13–357)
Fe	*1.57* ± 0.90 (0.18–2.98)	*2.71* ± 0.86 (1.42–4.10)	*1.93* ± 0.90 (0.53–3.43)	*0.09* ± 0.05 (0.04–0.19)	*0.46* ± 0.20 (0.20–0.64)
Hg	*0.14* ± 0.08 (0.02–0.25)	*0.22* ± 0.11 (0.09–0.40)	n.d.	n.d.	n.d.
Mn	*188* ± 74 (25–254)	*259* ± 75 (100–325)	*211* ± 71 (54–274)	*140* ± 42 (51–195)	*42* ± 16 (18–54)
Ni	*119* ± 52 (13–173)	*165* ± 55 (76–229)	*130* ± 49 (42–197)	n.d.	*10* ± 4 (5–13)
Pb	*30* ± 11 (20–52)	*39* ± 10 (27–56)	*33* ± 13 (20–55)	*20* ± 7 (12–29)	*174* ± 90 (45–251)
Zn	*59* ± 38 (4–115)	*103* ± 40 (59–152)	*74* ± 41 (20–130)	*33* ± 19 (9–53)	*54* ± 30 (15–81)
organic matter	n.d.	n.d.	*13.6* ± 4.9 (6.5–20.2)	n.d.	*5.7* ± 1.9 (3.8–7.7)

Metal contents given as μg/g dry weight; Al, Fe and organic matter as %.
(n.d. = not determined).

Table 1 (continued)

1.2 *Core samples* (*fraction* <*150* μm)

Metal	*Canimar river* *Core "C"* ($n = 9$)	*Matanzas Bay* *Core "B"* ($n = 9$)	*Yumuri river* *Core "Y"* ($n = 11$)	*San Juan river* *Core "S"* ($n = 6$)
Al	*4.45* ± 0.30 (3.94–4.77)	*2.54* ± 0.25 (2.28–3.12)	*3.24* ± 0.22 (2.70–3.52)	*2.64* ± 0.28 (2.35–3.04)
Co	*17.2* ± 0.5 (16.2–17.9)	*11.8* ± 1.2 (10.3–14.1)	*15.6* ± 0.8 (13.8–16.2)	*13.3* ± 0.7 (12.4–14.1)
Cr	*127* ± 5 (121–138)	*144* ± 11 (131–169)	*214* ± 21 (177–246)	*180* ± 5 (172–186)
Cu	*40.8* ± 2.4 (37.9–45.1)	*39.8* ± 5.2 (32.2–48.0)	*86.5* ± 9.7 (70.9–104)	*161* ± 61 (114–264)
Fe	*3.53* ± 0.13 (3.35–3.71)	*2.48* ± 0.24 (2.08–2.91)	*3.35* ± 0.19 (2.99–3.59)	*3.46* ± 0.62 (2.70–4.50)
Mn	*448* ± 47 (393–512)	*288* ± 16 (270–306)	*409* ± 32 (332–447)	*352* ± 52 (283–409)
Ni	*152* ± 15 (127–174)	*177* ± 10 (106–139)	*227* ± 20 (201–266)	*168* ± 9 (157–182)
Pb	*12* ± 2 (10–17)	*28* ± 5 (20–33)	*70* ± 11 (57–88)	*171* ± 23 (138–203)
Zn	*82* ± 3 (81–90)	*73* ± 7 (65–87)	*240* ± 31 (203–291)	*326* ± 22 (305–365)
organic matter	*20.5* ± 1.3 (18.0–21.9)	*18.4* ± 3.1 (15.1–23.2)	*30.7* ± 1.9 (29.0–35.3)	*24.7* ± 1.7 (21.9–26.9)

Table 1 (continued)

1.3 *Rivers/Surface samples (fraction* $<63\,\mu$m)

Metal	*San Juan river*	*Yumuri river*		*Canimar river*	
	I/II^a	I/II^a	*Mouth*	IIa^b	IIb^b
Al	3.40/3.59	2.46/4.11	0.96	4.65	4.60
Co	14.5/18.8	19.6/23.1	6.0	20.9	17.9
Cr	179/176	211/232	69	156	108
Cu	102/52.9	137/64.4	18.5	48.6	42.9
Fe	2.42/2.65	2.27/3.86	0.08	2.78	3.22
Hg	0.47/0.39	1.04/0.47	0.22	0.36	0.32
Mn	359/323	395/503	242	661	1190
Ni	146/183	282/291	45	160	115
Pb	73/8	137/11	5	6	5
Zn	300/88	377/160	24	87	86
organic matter	30.9/30.5	30.7/24.8	17.7	29.7	28.0

[a] "I"—inside Matanzas City; "II"—up-stream the town.
[b] Up-stream Canimar river.

using the original data, this difference was not evident because stations *2* and *4* also showed relatively high contents of copper and zinc, which are both considered good indicators of contamination from mixed industrial and domestic sources (Salomon and Förstner, 1984). In addition, the original contents of Al, Co, Fe, Mn and Ni at *2/4* were of the same order of magnitude as at stations *1/7*. This demonstrates the usefulness of applying normalization procedures.

The difference of the absolute metal contents including Cu, Pb and Zn between stations considered to be affected by anthropogenic sources (stations *1*, *6* and *7*) and those considered "clean" is not very pronounced. Therefore, even the more anthropogenically influenced parts of Matanzas Bay cannot be classed "strongly contaminated." Unfortunately, it was not possible to take sediment samples from the deeper parts of the bay where finer particulate fractions of the suspended matter, probably more enriched in heavy metals, could be expected as deposits. However, there is a chance that such fine matter would mainly be swept out into

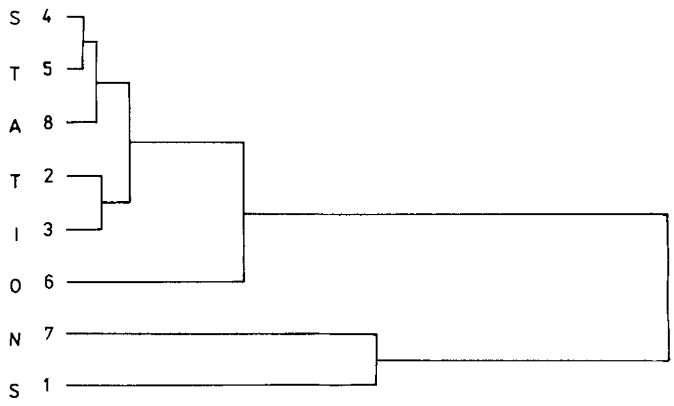

Figure 2 Dendogram for the surface sampling stations (variables used for the cluster analysis are the metal contents in the dry-sieved fraction $<63\,\mu$m, normalized to the organic matter content).

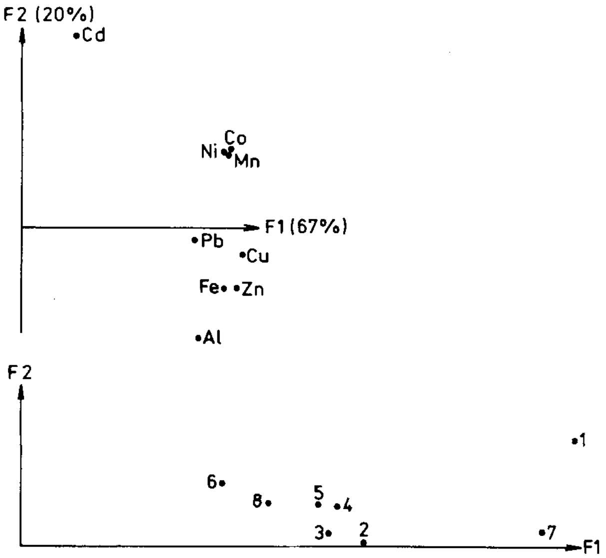

Figure 3 Results of a principal component analysis for the surface sampling stations (variables are the metal contents in dry sieved fraction <63 μm, normalized to the organic matter content).

the adjacent open sea due to strong surface currents flowing in the offshore direction, as well as to other components of the extensive water exchange of the bay with the ocean.

If the metal contents found after a weak extraction of the sediments with 0.5 N HCl are compared with those from a strong HNO_3/HCl digestion, an element dependent behaviour with respect to the portions of the easily available fraction is found. These fractions cover a range from only 2% (Al) to 73% (Pb) of the "total" content. Elements like Fe (5%), Cu (15%), Zn (33%) and Mn (35%) fall into the range between these very low and high values.

Maximum metal contents were found in the central part of the study area (stations *1*, *2*, *4* and *7*). Compared with natural background levels, however, these values are only slightly elevated and in no case do they exceed the doubled means. Following Al normalization, only at station *1* did the copper and zinc values exceed the normalized means more than twofold.

The case study close to the outlet of the tannery revealed extremely high contents of chromium and increased levels of lead and zinc. Obviously, this factory is an important contaminating source with respect to at least these three metals. A typical "hot spot" has developed around the discharge point (T2) of the waste waters, which are released without further treatment directly into the sea. The most contaminated sediments were found south from the waste outlet. Currents which could disperse the waste plume and/or contaminated sediments are induced by prevailing wind directions and anti-clockwise eddies during the neap-tide (Galocha, pers. comm.). Based on the outcome of the present investigation, studies now have been set up to treat these waste waters with the aims of protecting the environment and recovering the chromium.

3.2. *Core samples*

Table 1.2 and Figure 4 show the results of heavy metal determinations of dissected core samples. For Al, Co, Fe and Mn, which are more or less characteristic of the lithogenic sediments, no significant differences between the four cores could be detected. For Cr and Ni, contents in cores taken in the Yumuri (Y) and San Juan Rivers (SJ) are only about two times higher than in those taken from the Canimar River (C) and from the Bay (B). However, for Cu, Pb and Zn, greater differences of their contents in the 4 cores were observed (see Figures 4 and 5). The contents differ up to an order of magnitude. These three metals behaved similarly with respect to their relative abundance between cores:

$$\text{San Juan} > \text{Yumuri} > \text{Bay} = \text{Canimar}$$

The cores from the Canimar River and from the Bay show a mostly uniform distribution of Cu, Pb and Zn with depth. There was no clear tendency apparent in the slight variations observed. On the other hand, the core from the Yumuri River showed higher metal contents in the upper segments. The limited length of the San Juan River core (20 cm) did not permit any conclusion in this respect.

The sedimentation rates in the different parts of Matanzas Bay are unknown. For this reason, it was not possible to identify a core depth at which natural background levels of the metal contents are present. Nevertheless, the practically uniform and low metal contents in the Canimar River core support our assumption that in the drainage area of this river no significant contaminant sources are located. This allows us to take these low contents as representing nearly natural background levels.

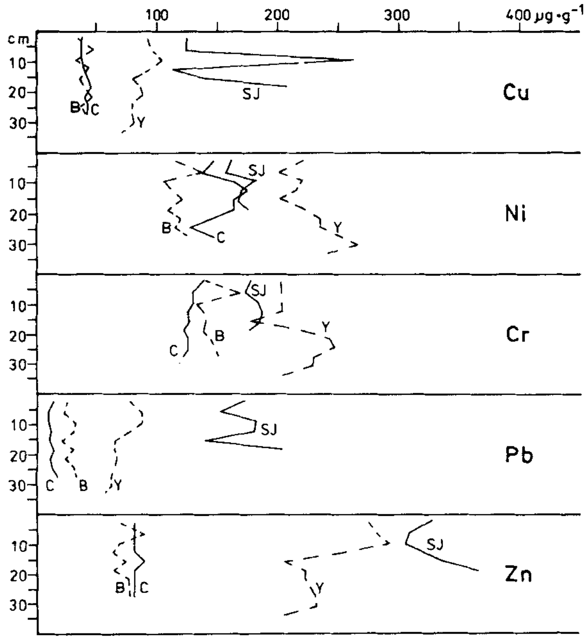

Figure 4 Profiles of the heavy metal contents in 4 cores ("B": Matanzas Bay; "C": Canimar River; "SJ": San Juan River; "Y": Yumuri River).

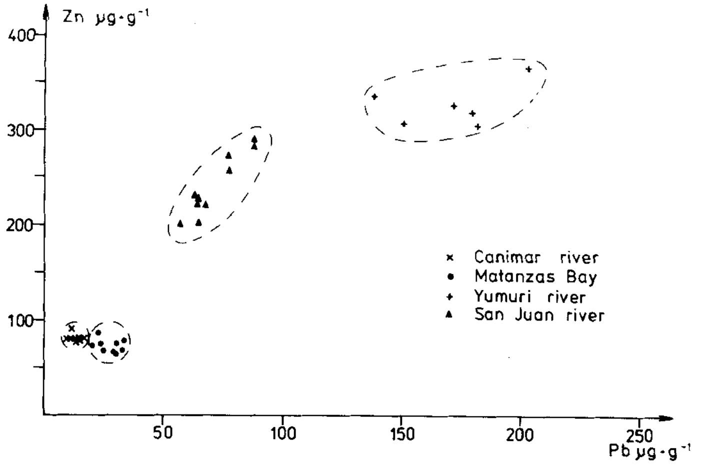

Figure 5 Two dimensional plot of Pb vs. Zn contents of sub-samples from 4 cores.

The plots of values normalized to aluminium (Figure 6) or to organic matter show the same patterns. The normalized metal contents seem to reflect the degree of contamination adequately: high values for the cores from Yumuri and especially from the San Juan River are due to anthropogenic influences and are in contrast to the low levels for the Bay and the Canimar River.

3.3. *River/Surface samples*

The results (Table 1.3) corroborate the distribution patterns already discussed in para 3.2 with respect to the core samples. Again, no anthropogenic impact was

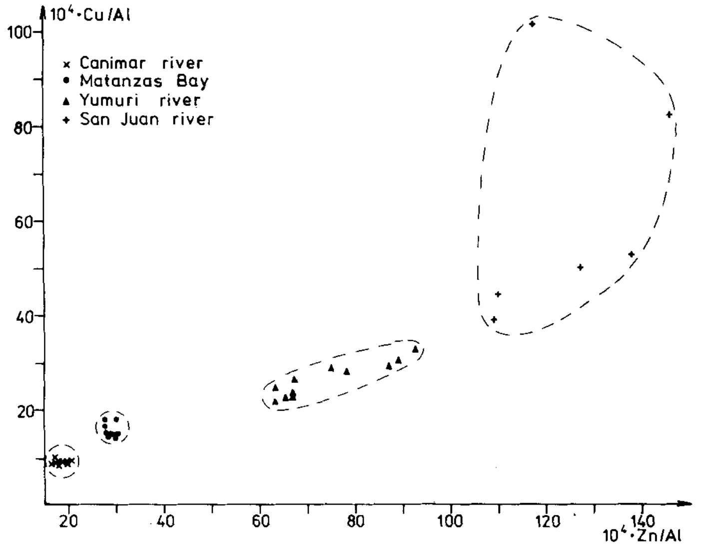

Figure 6 Two dimensional plot of Cu vs. Zn contents of sub-samples from 4 cores, both elements normalized to the Al content.

evident for the Canimar River samples. Recognized inputs from Matanzas City into the Yumuri and San Juan Rivers are reflected by the contents of Cu, Hg, Zn and particularly Pb. Exhaust gases from cars reach the rivers via atmospheric deposition and run-off from the streets. They are considered the main source for this lead contamination.

The metal content of the coarse fraction (63–150 um) was lower than that of the silt/clay fraction (<63 um). This finding is in agreement with the literature (e.g. Salomon and Förstner, 1984). However, in both granulometric fractions, the general spatial distribution patterns of the metal contents and the interelemental relationship are nearly identical.

4. CONCLUSIONS

The coastal zone of Matanzas Bay seems to be only slightly contaminated with respect to heavy metals. However, some restricted sub-areas are clearly affected by anthropogenic sources. These include the port, the discharge zone of a tannery, and the mouths of two rivers receiving waste waters enriched in Cu, Pb and Zn from the city. Investigations on sediment cores and surface sediment samples from the rivers support this conclusion. The application of normalization procedures combined with multivariate statistical methods facilitates the interpretation of the analytical results.

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