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Heavy metal surveys in sediments of five important Cuban Bays

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Abstract. This paper presents data obtained between 1983 and 1989 on concentration of heavy metals in sediments of five Cuban bays having different physical and geographical characteristics and differing degrees of anthropogenic activities. Data are normalized with respect to Al, Fe, and organic content and processed through statistical techniques of multivariate analysis. The degree of heavy metal pollution among the harbors decreases in the following order: Havana, Santiago de Cuba, Cienfuegos ≈ Matanzas, Cárdenas.

Introduction

Many of the main cities of Cuba have been developed near the sea and are important industrial centers as well as ports. Havana, Matanzas, Cárdenas, Santiago de Cuba, and Cienfuegos are among the largest cities whose bays have been studied since 1983 in order to determine the levels and origins of heavy metals and, consequently, to recommend measures for solving the problems of pollution. Some of the results have been previously reported, but only in an isolated way (González, Torres & Lera 1985; González, Lera & Torres 1985; González & Torres 1988; González & Brugmann 1989). The present article has two objectives: first, to ascertain the state of these bays through the presentation of the most recent data and second, to make, for the first time in the country, a comparison of the heavy metal pollution levels in these five important bays. This is valuable since the methodology used was similar for all the different cases (González 1989).

Materials and methods

Figure 1 shows each of the five bays, the sampling stations, and the main

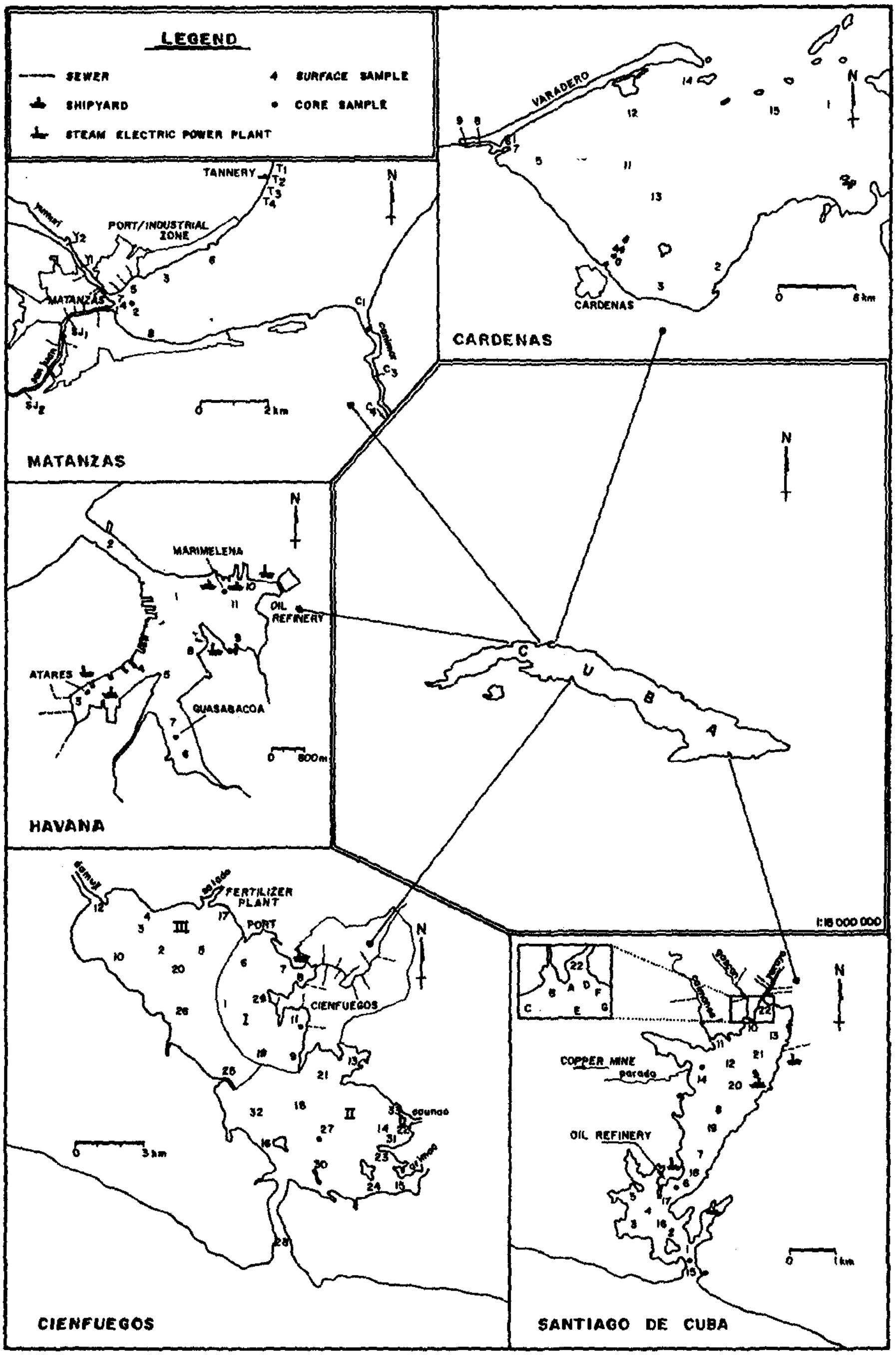

Fig. 1. The island of Cuba showing the five bays studied, along with the sampling stations and the main activities.

industrial activities. Three of these bays, Havana, Matanzas, and Cárdenas, are situated on the northern coast, while the other two, Cienfuegos and Santiago de Cuba are in the south. Havana, a port city and the capital of Cuba, with a population of over two million inhabitants, is the main population and industrial center. Havana Bay is a typical semiclosed bay with an area of only 5.2 km^2, 18 km of inner coasts, and a median depth of 9 m. Several small rivers and sewers flow into the bay, discharging an average of 330,000 m^3 day^{-1} of urban and industrial wastewater. Several different industries such as a refinery, three steam electric power plants, and three shipyards are situated along their borders and discharge directly into the bay.

Matanzas Bay has a coast line of 19 km, a surface area of 35.8 km^2, and a median depth of 200 m. Its open shape favours an extensive exchange of water with the open sea and therefore the dilution of pollutants from rivers and urban sewers.

Cárdenas Bay also has an open shape, but it is not as deep, has little fresh water input, and is surrounded by keys. The exchange of water with the open sea is limited. This bay is the least important of the bays studied here as a port or industrial center, although it has become a zone of prospecting and extraction of petroleum on an increasing scale.

After Havana Bay, Santiago de Cuba has the greatest number of urban and harbour activities, together with some important industries. It has a typical semiclosed bay of 11.9 km^2 with a median depth of 11 m into which 40,000 m^3 of water enriched with urban and industrial wastes are discharged daily.

Cienfuegos Bay with 89.9 km^2, 100 km of coast, and a median depth of 9.7 m, is the largest of the semiclosed bays studied. Four rivers flow into it, discharging 2×10^6 m^3 of fresh water daily to which can be added a quantity of wastewater (30 times lower) mainly of urban origin. A steam electric power plant, a fertilizer plant, a fishing industry, and a factory for constructing irrigation equipment are among the main industries.

The descriptions above show the diversity of the bays studied, both with regard to their physical and geographical characteristics and the anthropogenic activities that influence them.

The methodology used throughout all the research, from the collection of samples through to the interpretation of results, has been described elsewhere (González 1989). In brief, the surface sediment samples were obtained through diving or by a Van Veen dredge. Core samples were taken with a gravity corer. The samples were dried at 105 °C (45 °C for Hg) or freeze-dried. Fractions of fine sand and/or silt and clay were obtained. Different combinations of HNO_3/HCl were used for the digestion, and determinations were made by flame atomic absorption spectrometry with deuterium background correction and the cold vapour technique for Hg. Accuracy and precision were periodically checked; the latter was better than 10%. The metal concentrations were normalized with respect to Al, Fe, and organic matter. In order to harmonize the broad range of contents for the different metals in the sediments, all data were autonormalized prior to statistical processing by means of multivariate statistical methods (cluster and principal component analysis) which were found to be valuable tools for interpretation.

Table 1 summarizes the data. In each case, the metals analyzed, were chosen by taking into account the characteristics of each bay, the possible pollutant sources, and the objectives of the study. Nevertheless, Cu, Pb, and Zn were always measured because they are ubiquitous indicators of human pollution, both urban and industrial (Forstner & Wittmann 1979; Salomons & Forstner 1984).

Results and discussion

Havana Bay

During 1983—1984, the amounts of Cu, Pb, and Zn, together with Cd, Cr, and Hg, characterized the pollution of mixed urban and industrial origin that is received by the bay, mainly through the sewers that flow into the Atarés inlet (station 3, see Fig. 1). On the other hand, the metals Ni and V, which are typical indicators of industrial pollution (Forstner & Wittmann 1979), clearly showed that they are derived from the steam electric power plants (Becerra et al. 1985), with higher amounts in the Marimelena inlet where two plants discharge their waste (stations 9, 10, and 11). Table 2 summarizes the results obtained and shows that the high level of pollution in this bay has been kept stable. That organic matter forms associations with different metals has been widely recognized (Badri & Aston 1983; Dissanayake et al. 1983; Pelletier & Canuel 1988; Reboredo & Pais 1984), so we used organic matter as a variable to normalize the different metals (Cato 1989; Larsen et al. 1983; Robbe 1984; Thomson et al. 1984). Havana Bay receives much organic matter (Espinosa et al. 1985; Becerra & Diaz 1985) and this correlates ($P < 0.01$) with Cu, Pb, and Zn in sediments. Figure 2 presents the normalization of these elements with respect to the organic matter content and permits us to distinguish, despite the limited extension of the bay, the variation in pollution in each of the areas, which is also related to the different depositional environments (Villasol et al. 1985). The Atarés inlet presents the worst state. Similar behaviour of metals can be found in the

Table 1. Relation of studies realized.

Bay	Year	Type and number of samples	Fraction (μm)	Al	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	V	Zn
Havana	1983	S-11	< 117	x	x	x	x	x	x	x	x	x	x	x	x
	1984	C-3	< 55		x	x		x			x	x	x		x
	1989	S-5	< 63	x		x		x	x		x	x	x		x
Matanzas	1985	S-8	< 63, 63—150	x	x	x		x	x	x	x	x	x		x
	1987	S/C-11/4	< 63, 63—150	x		x	x	x	x	x	x	x	x		x
Cárdenas	1989	S-15	< 63	x		x		x	x		x	x	x		x
Santiago de Cuba	1983	S-15	< 117	x	x	x		x	x	x	x	x	x		x
	1984	C-3	< 55		x	x		x			x	x	x		x
	1987	S-9	< 63	x		x		x	x	x	x	x	x		x
	1988	S-16	< 63	x		x		x	x		x	x	x		x
	1989	S-16	< 63	x		x		x	x		x	x	x		x
Cienfuegos	1988	S-57	< 63	x		x		x	x		x	x	x		x
	1987	S/C-28/2	< 63	x		x		x	x		x	x	x		x

S-surface
C-core

Table 2. Range of the content of heavy metal in Havana Bay sediments.

	1983	1984	1989
Al	0.18—0.52	—	1.63—3.58
Cd	1.7—6.5	1.0—3.5	—
Co	18—34	14—35	4.5—12
Cr	50—343	—	—
Cu	77—355	43—351	97—276
Fe	1.74—3.51	—	1.90—3.35
Hg	0.27—3.24	—	—
Mn	253—564	271—751	274—425
Ni	51—248	42—332	32—102
Pb	86—397	16—395	42—301
V	51—88	—	—
Zn	148—987	66—1167	142—995
Organic matter	7.8—20.0	6.8—32.2	22.8—26.8

Metal contents in $\mu g.g^{-1}$
Al, Fe and organic matter in %

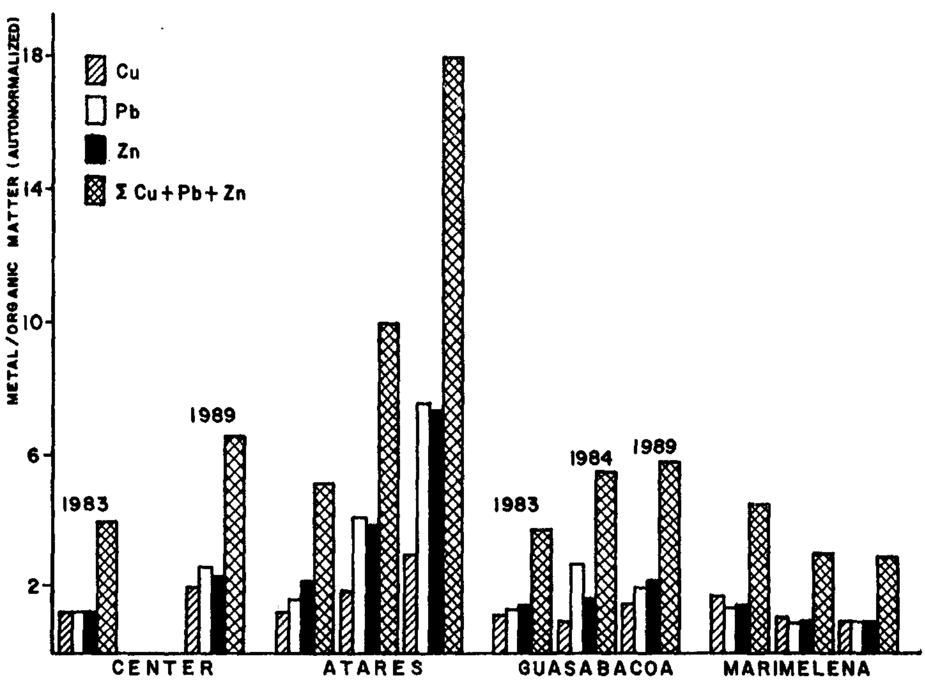

Fig. 2. Havana Bay: normalization of Cu, Pb, and Zn contents in relation to the organic matter content.

Guasabacoa inlet, the receiver of two small rivers, and in the central zone of the bay, which is caused by the different pollutant loads that are discharged into some areas of the bay.

Mantanzas Bay

The results for Matanzas Bay (Table 3) show the possibility of using

Table 3. Range of the content of heavy metal in Matanzas Bay sediments.

(3a) Core samples

	Canimar River ($n = 9$)	Bay ($n = 9$)	Yumuri River ($n = 11$)	San Juan River ($n = 6$)
Al	3.94—4.77	2.28—3.12	2.70—3.52	2.35—3.04
Co	16—18	10—14	14—16	12—14
Cr	121—138	131—169	177—246	172—186
Cu	38—45	32—48	71—104	114—264
Fe	3.35—3.71	2.08—2.91	2.99—3.59	2.70—4.50
Mn	393—512	270—306	332—447	283—409
Ni	127—174	106—139	201—266	157—182
Pb	10—17	20—33	57—88	138—203
Zn	81—90	65—87	203—291	305—365
Organic matter	18.0—21.9	15.1—23.2	29.0—35.8	21.9—36.9

(3b) Surface samples

	Bay	San Juan I/II	Yumuri I/II	Canimar
Al	0.13—3.32	3.40/3.59	2.46/4.11	4.60—4.65
Co	6.0—28	15/19	20/23	18—21
Cr	—	179/176	211/232	108—156
Cu	7.0—60	102/53	137/64	43—49
Fe	0.18—4.10	2.42/2.65	2.27/3.86	2.78—3.22
Hg	0.02—0.40	0.47/0.39	1.04/0.47	0.32—0.36
Mn	25—325	359/323	395/503	661—1190
Ni	13—229	146/183	282/291	115—160
Pb	20—56	73/8.0	137/11	5.0—6.0
Zn	4.0—152	300/88	377/160	86—87
Organic matter	6.5—20.2	30.9/30.5	30.7/24.8	28.0—29.7

I — inside Matanzas City
II — upstream of the town, metal contents in $\mu g.g^{-1}$
Al, Fe and organic matter in %

different granulometric fractions to assess pollution levels. As an example, Fig. 3 shows the results of a cluster analysis that separates stations 1 and 7 from the others. This seems logical, since these stations are placed at the mouths of the San Juan and Yumuri rivers, which flow through the city, receiving the discharges of urban and industrial wastewater. One particular case is the discharge zone of wastewater from a tannery (stations T1 to T4), with high amounts of Cr (365-7915 $\mu g.g^{-1}$), i.e. they are even higher by an order of magnitude than the rest of the area. These results have motivated us to study the treatment of these wastewaters with the double aim of protecting the marine environment and recovering the chromium. For the core samples (Table 3a), the most remarkable differences, in absolute metal contents as well as in normalized values with respect to Al and organic matter contents, were for Cu, Pb, and Zn, with similar relative abundances among the cores: San Juan > Yumuri > Bay ≈ Canimar. In the core of the bay, a decrease in concentrations of these elements is observed. As stated before, the characteristics of the bay favor an extensive exchange of water with the open sea and the dilution of the pollutants which are transported by the rivers. To confirm the anthropogenic origin of the high levels of these elements is due to the influence of the city, Table 3b shows the results of the surface samples of the rivers. There is no evidence of anthropogenic impact in the Canimar River. This, together with the practically uniform and low metal concentrations in the core sample of this river and the absence of important pollutant sources in its drainage area, allow us to consider the reported values as representa-

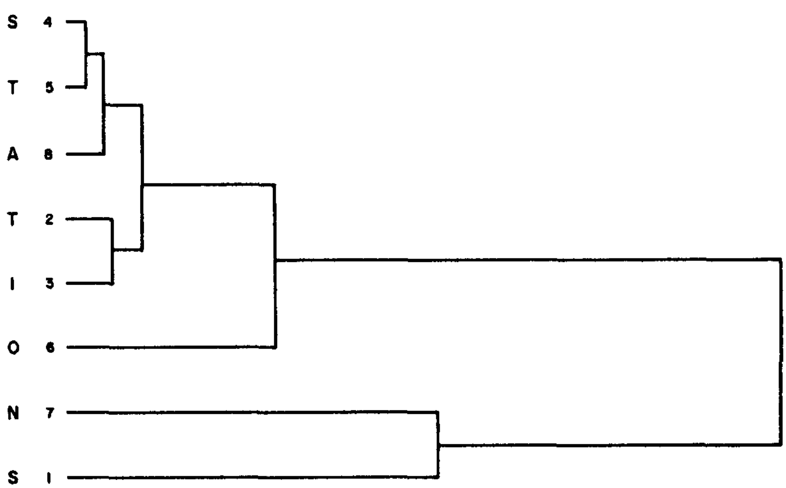

Fig. 3. Matanzas Bay: dendrogram for the surface sampling stations in 1985. The variables used for the cluster analysis are the metal contents in the fraction < 63 μm, normalized to the organic matter content.

tive of the natural background levels in the area despite the unknown sedimentation rates. Then, this bay can be considered to be slightly polluted, with some restricted sub-areas clearly affected by anthropogenic sources.

Cárdenas Bay

The levels of heavy metals in sediments are generally low (Table 6), in accord with the industrial activities in the area. The highest values of the indicators of mixed urban and industrial pollution (Cu, Pb, and Zn) and of purely industrial pollution (Ni) are found at stations 6, 8, and 9 placed at the Paso Malo channel, where there is a marine and fishing port, and at station 4, which is in front of Cárdenas City. Figure 4 is an example for Pb and Zn and shows the anthropogenic impact of the existing pollutant sources. It is important to point out that the activities of drilling and extraction of petroleum have not produced an increase in the levels of heavy metals, although studies relating to these are continuing since such activities have shown adverse environmental effects elsewhere (Wheeler et al. 1978; Boothe & Presley 1987; Trocine & Trefry 1983).

Santiago de Cuba Bay

Table 4 summarizes the comparative results between 1983 and 1989. The

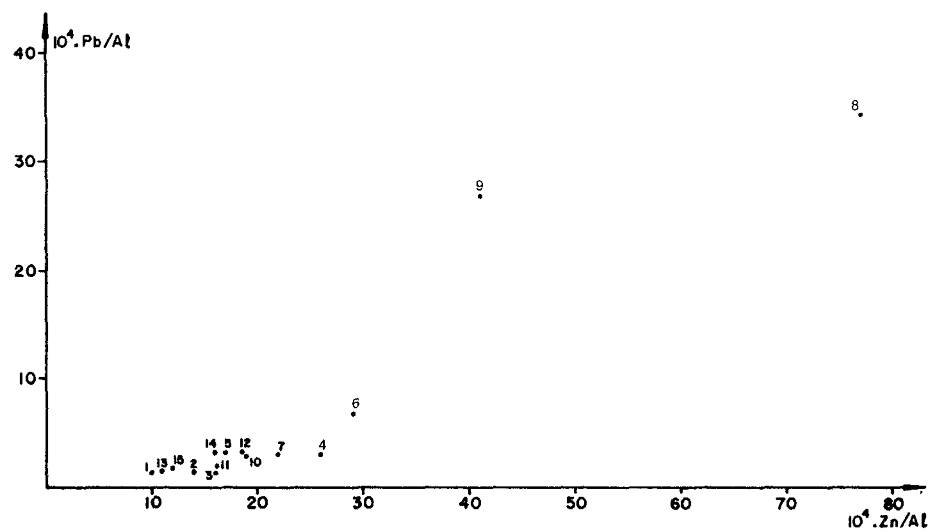

Fig. 4. Cárdenas Bay: two-dimensional plot of Pb vs. Zn. both elements normalized to the Al content.

Table 4. Range of the content of heavy metal in Santiago de Cuba Bay sediments.

	1983	1984	1987	1988	1989
Al	0.09—0.73	—	1.30—4.18	0.77—4.67	0.50—4.18
Cd	1.3—4.0	1.4—2.0	—	—	—
Co	16—22	15—18	2.0—8.6	3.1—6.6	2.3—9.5
Cu	25—675	227—497	161—424	31—463	43—375
Fe	0.69—4.37	—	1.88—7.70	1.04—5.48	0.74—4.28
Hg	0.21—0.56	—	0.12—5.6	—	—
Mn	336—1405	829—1242	509—1915	311—1211	259—1223
Ni	13—28	8.0—27	9.0—19	9.0—26	3.0—12
Pb	16—68	26—37	11—107	14—123	9.0—146
Zn	33—154	124—182	92—699	41—450	36—498
Organic matter	1.6—14.1	17.0—22.9	7.3—23.0	6.4—21.2	12.1—27.2

Metal contents in $\mu g.g^{-1}$
Al, Fe and organic matter in %

first study, made in 1983 on surface sediments (stations 1 to 15, Fig. 1), showed a relatively uniform distribution for most of the metals, with the exception of Cu. Cu has a zone of high concentrations (stations 8, 9, 12, and 14) due to natural drainage and the discharge of wastewaters enriched by Cu coming from a zone of exploitation of copper deposits that is crossed by the Parada River, which previously flowed into the bay before it was dammed. The core samples obtained a year later corroborated this pattern and, especially for Cu (Fig. 5), showed a gradual recovery of the

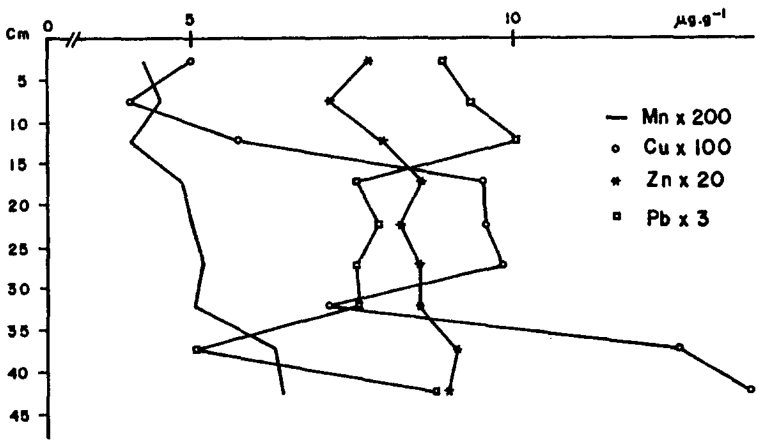

Fig. 5. Santiago de Cuba Bay: profiles of the heavy meal contents in the core of station 14.

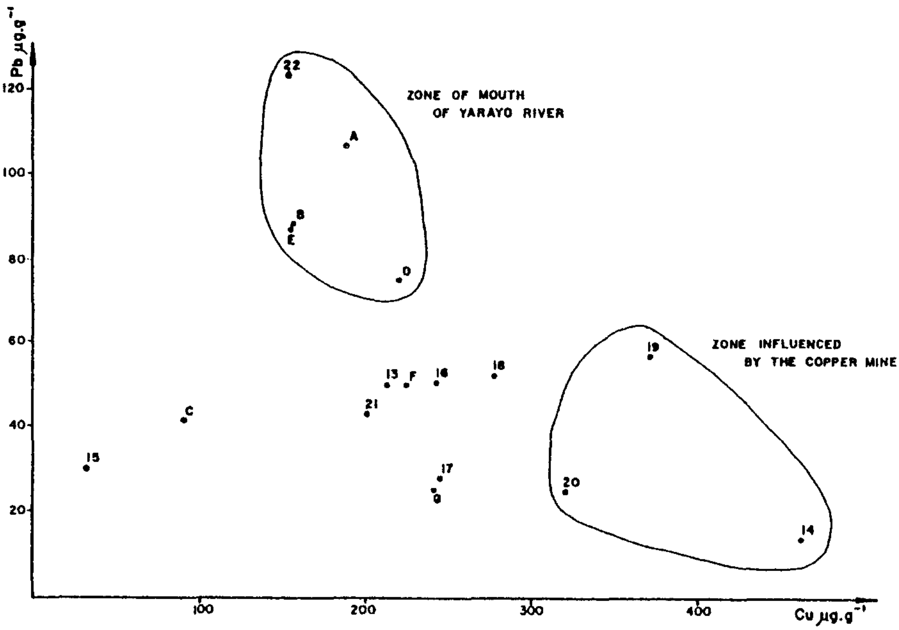

Fig. 6. Santiago de Cuba Bay: two-dimensional plot vs. Cu of surface sampling stations in 1988.

system. The increasing amounts of Pb, Zn, and Hg found in 1987—1989 (stations 13 to 22 and A to G), were due to the location of sampling sites at the mouth of the Yarayó River, which, while flowing throughout the city, acts as a receptor of mixed wastewater. This is not the case for Cu, with highest amounts in stations 14, 19 and 20 (Fig. 6), still showing the influence of the mining zone. For Pb and Zn, correlations are high ($P < 0.05$), for both absolute and normalized values with respect to Al, Fe, and organic matter. Normally the relationship of Cu, Pb and Zn indicates mixed wastewater, however, the influence of mining leads to a poor Cu correlation with Pb and Zn. This is in contrast to areas such as Havana Bay and its adjacent littoral zone which have higher amounts of both urban and industrial waste (Gonzálezz & Brugmann 1991). This confirms the mining source of Cu to Santiago de Cuba Bay via the Parada River.

Cienfuegos Bay

Table 5 shows the results of the four sampling cruises of surface sediments in Cienfuegos Bay. The analysis of the first cruise enabled us to distinguish the most polluted stations (8 and 11) and those metals with the greatest differences in concentrations, Pb and, to a lesser extent, Zn. In June 1988, torrential rains affected the area, so the second sampling was aimed at

Table 5. Heavy metal contents in surface sediments of Cienfuegos Bay.

	1988		1989	
	April	September	March	September
n	31	26	13	15
Al	4.56/29 (1.78–6.97)	4.07/29 (1.84–6.50)	3.97/28 (2.52–6.36)	3.26/18 (2.37–4.11)
Co	8.0/27 (3.2–5)	8.0/32 (3.6–14)	8.4/26 (5.4–12)	7.5/30 (5.1–13)
Cu	56/29 (30–113)	64/40 (25–145)	50/25 (34–89)	47/34 (27–92)
Fe	4.13/23 (1.69–5.59)	4.58/26 (2.45–7.01)	4.45/15 (3.10–5.41)	3.22/21 (2.35–4.65)
Mn	764/72 (282–2134)	599/48 (303–1477)	469/35 (347–956)	543/89 (287–2302)
Ni	37/24 (20–56)	32/27 (16–46)	32/23 (20–43)	34/29 (20–54)
Pb	16/194 (2.0–156)	8.2/109 (2.0–48)	9.9/85 (2.5–28)	23/40 (13–45)
Zn	79/23 (46–114)	92/28 (40–157)	107/22 (75–166)	80/27 (52–119)
Organic matter	19.8/18 (10.1–24.7)	19.0/22 (8.6–24.1)	18.1/16 (13.0–22.3)	18.1/28 (11.7–22.4)

n: number of sampling stations
metal contents in $\mu g.g^{-1}$

Al, Fe and organic matter in %
mean/coefficient of variation (in %) (range)

finding possible changes in this bay. These changes were mainly a decrease in Pb (49% and 69% of the mean and maximum values, respectively). It is perhaps logical to think of a “cleaning” or diluting effect due to the lower amount of this metal in the terrigenous material provided by the rivers. However, the most affected stations and the metals which are the best indicators of pollution coincide, as is clearly shown by the results of a principal component analysis (Fig. 7). In 1989, the number of stations were reduced because the study was mainly directed at the zone of greatest pollution. The most relevant aspects were, again, the outstanding contrasts for Pb and Zn with the greatest amounts in the zone that is nearby the city where the most remarkable stations were 8 and 11.

It was possible to divide the bay into three zones which are shown in Fig. 1.

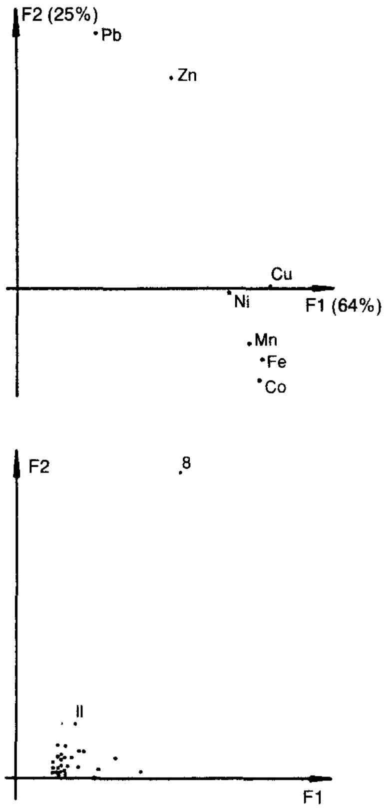

Fig. 7. Cienfuegos Bay: results of a principal component analysis for the surface sampling stations in September 1988. The variables are the metal contents normalized to the organic matter content.

- Zone I is situated near the city and the industrial area and is considered to be polluted, mainly at stations 8 and 11 which are located at inlets receiving discharge from different sewers. The extent of contamination by metals in decreasing order, is Pb, Zn, and Cu, which shows the urban and industrial character of the wastes discharged. The Pb, derived mainly from automotive transportation, can arrive at the bay via the atmosphere or through run-off from the streets.
- Zone II is formed by the outer part of the bay and can be considered as relatively clean. It has high values for Mn, Al, Fe, Co, and Cu. The fact that the first four elements are more or less characteristic of the lithogenic sediments and that there are no pollutant sources for Cu, evidences it natural origins.
- Zone III is formed by the inner part (except zone I) and is the same as zone II, so can be considered to be relatively clean.

The core samples (September 1989) obtained in zones I and II confirm the results of surface sediments: for Co, Fe, Mn, and Al, station 27 > station 11; for Ni and Cu, similar values, and for Pb and Zn, higher values near the city.

Conclusions

Table 6 is a summary of the most recent results found in each of the bays studied which permits us to make a comparison between them. The geochemical and natural characteristics of the bays and of the drainage basins of the tributary rivers may imply variations in the amounts of the metals. Nevertheless, the most remarkable differences were observed for Cu, Pb, and Zn, which are good indicators of pollution; within each bay, they distinguish the most affected zones. This also is true among the bays and permits us to establish the following degree of pollution:

Havana > Santiago de Cuba > Cienfuegos ≈ Matanzas > Cárdenas.

These trends result both from the anthropogenic sources of heavy metals present in each bay as well as the physical and geographical characteristics that, in some bays, contribute toward diminishing the degree of pollution. These data and those of others (Ramírez et al. 1990; Ablanedo et al. 1990; Ramírez et al. 1988) have been used to suggest control measures to the authorities with the aim of eliminating or reducing the pollutant load in order to preserve or restore the quality of each ecosystem.

Table 6. Comparison between the studied bays

	Cárdenas	Matanzas	Cienfuegos	S. de Cuba	Havana
Al	0.16—2.75	0.53—3.32	1.78—6.97	0.50—4.67	1.63—3.58
Co	<5.0—7.5	8.0—28	3.2—15	2.0—9.5	4.5—12
Cu	4.3—42	15—60	25—145	31—463	97—276
Fe	0.44—2.80	0.53—4.10	1.69—7.01	0.74—7.70	1.9—3.35
Mn	65—577	54—325	282—2302	259—1915	274—425
Ni	5.0—104	42—229	16—56	3.0—26	32—102
Pb	<2.5—30	20—56	2.0—156	9.0—146	42—301
Zn	1.1—67	20—152	40—166	36—699	142—995
Organic matter	11.4—40.1	6.5—20.2	8.6—24.7	6.4—27.2	22.8—26.8

Range: fraction <63 μm, metal contents in $\mu g.g^{-1}$
Al, Fe and organic matter in %

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