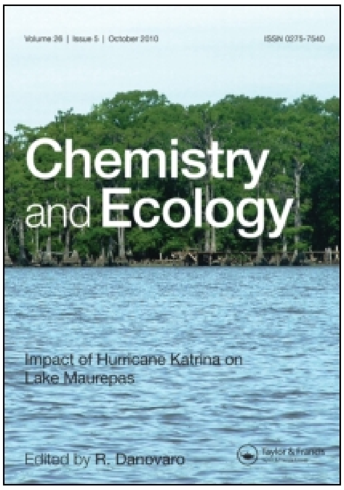

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HEAVY METALS IN LITTORAL DEPOSITS OFF HAVANA CITY, CUBA

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The content of Al, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Zn, C org and organic matter was investigated in sediment samples taken in the littoral zone off Havana City. The results revealed three areas affected by contamination: (a) Chivo Beach with a submarine sewage outfall, (b) the mouth of the Havana Bay and (c) the estuarine area of the Almendares River. The normalization of the heavy metals contents with respect to aluminium and organic matter combined with multivariate statistical methods was found valuable for a proper interpretation of the analytical results.

1. INTRODUCTION

Havana City is the most populated area of Cuba and its major industrial and harbour centre. This results in a high degree of heavy metal contamination of Havana Bay (González *et al.*, 1985a; González and Torres, 1988) and in negative influences on the western part of the littoral zone (González *et al.*, 1985b).

The city province has a shore-line of about 60 km, with features which favour an intensive exchange of water with the open sea (Martínez, 1987). Thereby, the dilution of the contaminant input through small rivers and sewage outfalls is facilitated. The most important sources for contamination of the littoral zone should be waters originating from Havana Bay, from the Almendares River (180,000 m^3/day) and from a submarine sewage outfall located at Chivo Beach (233,000 m^3/day). Studies carried out in other countries like Ivory Coast (Kouadio and Trefry, 1987), France (Augier *et al.*, 1984), Argentine (Marcovecchio *et al.*, 1986), Spain (Modamio, 1986), Turkey (Salihoğlu *et al.*, 1987), Greece (Voutsinou-Taliadouri *et al.*, 1989) and Hong Kong (Yim and Fung, 1981) have already shown that municipal and/or industrial waste waters discharged into coastal zones are the most important sources for a contamination of waters and sediments with heavy metals. Depending on the features of the different littoral zones, the level of contamination decreases with the distance from the point of discharge. This work describes the level of contamination in sediments of the littoral zone off Havana City and reveals the main sources of contamination by heavy metals. In order to distinguish between the natural and anthropogenic origin of the heavy metal contents in sediments and to facilitate the interpretation of the analytical results, the data were normalized in relation to background factors (Araujo *et al.*, 1988; González and Torres, 1988; Kouadio

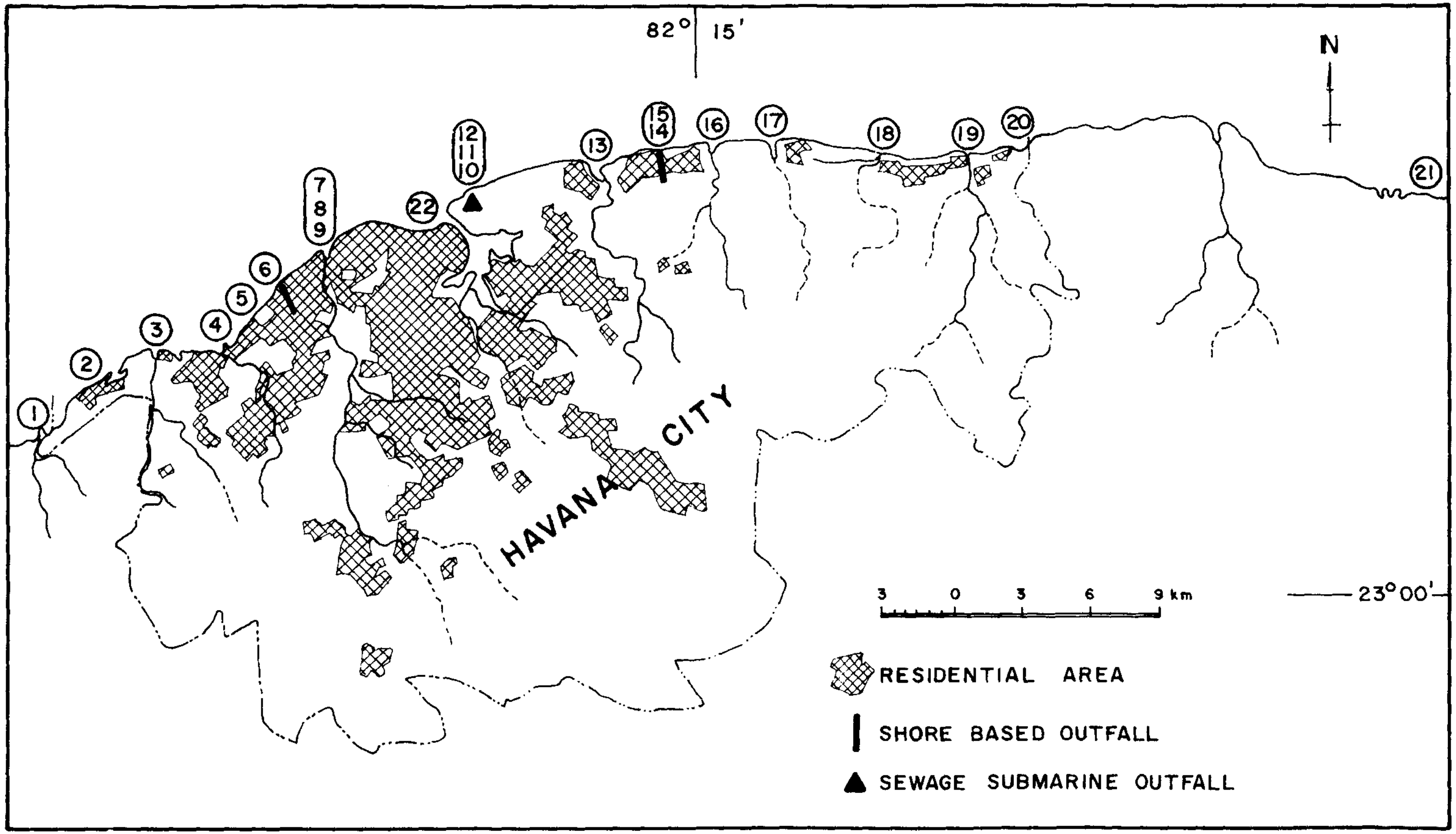

Figure 1 Sediment sampling stations in the littoral zone off Havana City (1—Santa Ana River; 2—Santa Fe Beach; 3—Jaimanitas River; 4—Quibú River; 5—Náutico Beach; 6—shore-based outfall in Tritón area; 7–9—Almendares River; 10–12—submarine sewage outfall in Chivo Beach; 13—Cojímar River; 14/15—shore-based outfall in Almar; 16—Bacuranao River; 17—Tarará River; 18—Boca Ciega River; 19—Guanabo River; 20—Rincón de Guanabo; 21—reference station; 22—mouth of Havana Bay).

and Trefry, 1987; Lyngby and Brix, 1987). In addition, different multivariate methods, increasingly applied by other authors in recent years (Araujo *et al.*, 1988; Doyle and Feldhausen, 1981; González *et al.*, 1985a; Loring, 1984; Pavoni *et al.*, 1987), were used.

2. MATERIALS AND METHODS

In September 1986, twenty two sediment samples were collected by SCUBA divers in 17 areas of the littoral zone off Havana City (Figure 1) at depths between 4 and 15 m, at a distance from the shore between 150 and 200 m. The sampling network included the mouths of all small rivers draining into that zone, the discharge area of shore-based outfalls, the submarine sewage outfall of the city and a reference station located about 20 km from the eastern border of the city.

The samples were oven-dried at 105°C for 48 h (a drying temperature of 45°C was applied for a subsample destined for the determination of mercury). In each case, the fraction $<150\,\mu m$ was separated by dry-sieving for the subsequent analysis.

For the determination of mercury (Randlesome and Aston, 1980) and of the other metals (Al, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) (McKown *et al.*, 1978) different HNO_3/HCl mixtures were used for the digestion of the samples. Mercury was analysed by the cold vapour technique and the accuracy of the analyses was verified by using the NBS river sediment reference sample SRM 1645 (certified value $1.1 \pm 0.5\,\mu g/g$ Hg, obtained value 0.88 ± 0.10, $n = 6$). The other metals were analysed by flame atomic absorption spectroscopy with deuterium background correction; the precision ($n = 5$) was between 3.4% (Mn) and 8.9% (Ni).

The organic matter content (o.m.) was derived from the ignition loss at 550°C/3 h, the organic carbon (C org) was determined by wet oxidation with $K_2Cr_2O_7/H_2SO_4$ and the organic nitrogen content by a Kjeldhal analysis.

The metal content of the sediment samples was normalized in relation to the content of aluminium, organic matter and organic content, respectively. The "Statistical Program for Social Sciences" (SPSS) was used for the statistical analysis of the data. This was performed on auto-normalized data (Doyle and Feldhausen, 1981; Pavoni *et al.*, 1987) in order to harmonize the broad range of contents for the different metals, e.g., from only 0.01 $\mu g/g$ for mercury up to 50,700 $\mu g/g$ for iron (see Table 1).

3. RESULTS AND DISCUSSION

The analytical results are presented in Table 1. The 22 stations were separated into four groups:

A) The stations 10, 11 and 12 are located in the discharge area of the submarine sewage outfall of the city. These sediments are characterized by relatively high contents of more or less all the metals, particularly, however, of copper, lead and zinc which are considered typical indicators of contamination

Table 1 Content of metals, organic matter and organic carbon in sediments of four different coastal areas off Havana City.

Area *Stations*	"*A*" (*submarine sewage outfall*) 10–12	"*B*" (*mouth of Havana Bay*) 22	"*C*" (*Almendares River*) 7–9	"*D*" (*other stations*) 1–6, 13–21
Al	0.75–1.24	0.28	0.71–2.57	0.13–1.32
Cd	3.9–11.2	1.2	1.5–3.5	0.86–1.9
Co	4.3–12.4	4.1	1.8–6.7	2.2–10.8
Cu	569–978	297	97–199	4–29
Fe	2.03–5.07	0.83	0.99–2.18	0.09–1.30
Hg	54–77	7.2	0.47–1.4	0.01–0.17
Mn	175–229	86	213–280	40–241
Ni	56–109	15	13–38	3–150
Pb	905–1643	340	102–143	8–24
Zn	1430–3865	234	126–646	8–75
o.m.	12.8–19.0	n.d.	6.7–29.5	2.2–8.4
C org	4.4–7.1	n.d.	1.7–9.4	0.2–2.2

Metal contents in μg/g dry weight; Al, Fe, o.m. and C org in %. (n.d. = not determined).

from mixed industrial and domestic sources (Voutsinou-Taliadouri *et al.*, 1989; Salomons and Förstner, 1984; Yim and Fung, 1981). In addition, very high contents were observed for mercury which has demonstrated by other authors to indicate waste waters discharged into coastal areas (Augier *et al.*, 1984); Kouadio and Trefry, 1987; Marcovecchio *et al.*, 1986; Modamio, 1986; Salihoğlu *et al.*, 1987). In the Cuban bays of Havana, Santiago de Cuba and Matanzas, it could be shown earlier (González and Torres, 1988) that this element reflects satisfactorily the general level of contamination by heavy metals in spite of the absence of distinct sources.

B) The station 22 is located at the mouth of Havana Bay. In relation to background values significantly higher contents for copper, lead, zinc and mercury reflect the impact provoked by the bay. However, the level of most metals is already lower than at stations 10, 11 and 12 described above.

C) Stations 7, 8 and 9 are located in the estuarine zone of the Almendares River. The metal content of the sediments is again lower than from A or B stations. Nevertheless, they are still significantly contaminated. This is caused by different industrial and urban point sources and diffuse inputs drained by this river when flowing through the city.

D) At the remaining 15 stations (by up to three orders of magnitude) lower contents of copper, lead, zinc and mercury were found in comparison with the former groups (A–C), which are considered as "significantly contaminated" and/or "contaminated hot spots" in this zone. Inside the area of group D stations it was not possible to find further distinct differences of the elemental distribution patterns. Therefore, all these stations have been considered as "not contaminated".

When normalizing the metal contents in relation to the content of aluminium, organic matter or C org, the different level of contamination for the four groups of stations was confirmed.

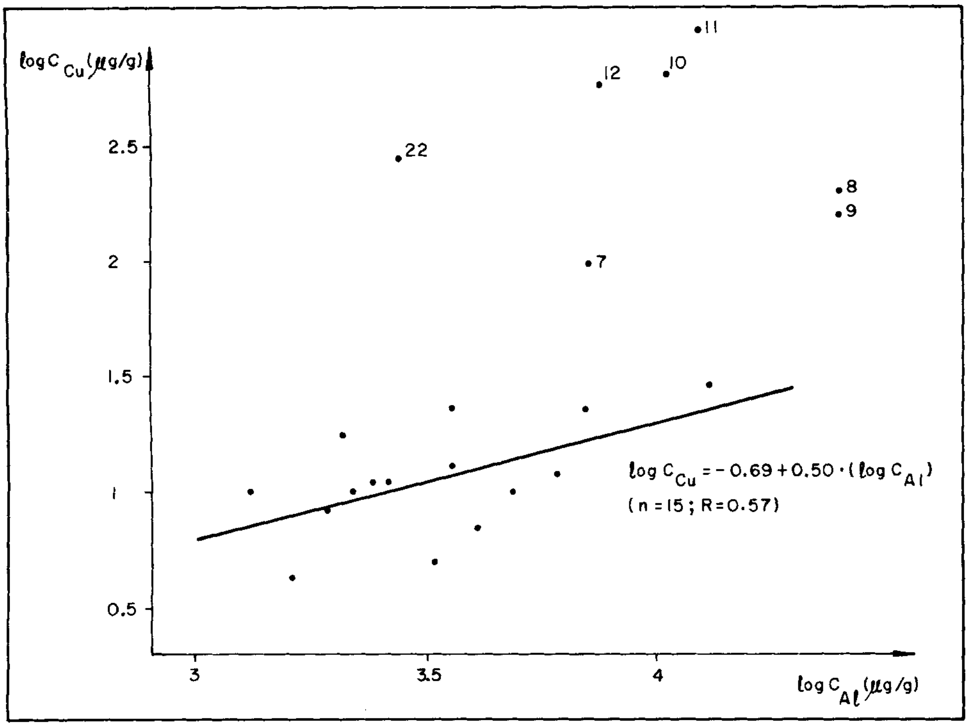

Figure 2 Plot of copper vs. aluminium content (original values in logarithmic form; regression line for 15 stations, nos. 1–6, 13–21).

In Figure 2, the relationship between the copper and aluminium contents is shown. Stations 7–9, 10–12 and 22 are clearly separated from the bulk of the data. Plots of zinc vs. lead values both normalized to organic matter are given in Figure 3. This illustrates again the clear separation of different groups of stations.

In Table 2, "enrichment factors" with respect to the aluminium content, calculated according to Robbe (1984), are presented. Obviously, the major part of elements like copper, mercury, lead and zinc in sediments of areas A, B and C cannot be explained by the natural composition of the sediments reflected by aluminium, but must be derived from the anthropogenic load. The enrichment of mercury in the sediments from Chivo Beach is extremely high. Figure 4 shows the result of a hierarchical cluster analysis of aluminium normalized metal contents. The stations are separated into those four groups already identified above. Station 5, owing to its very low aluminium content, is matched to the more "problematic" stations. However, at this station only sediments with very low heavy metal contents were found. The results from principal component analysis (Figure 5) give the same pattern of stations as from cluster analysis. The anthropogenically most influenced metals (Cd, Cu, Hg, Pb and Zn) are clearly separated from those representing more the lithogenic fraction of the sediment.

Summarizing, all results demonstrate the level of contamination for the littoral zone off Havana City as follows: submarine sewage outfall > mouth of Havana Bay > Almendares River estuary > other stations.

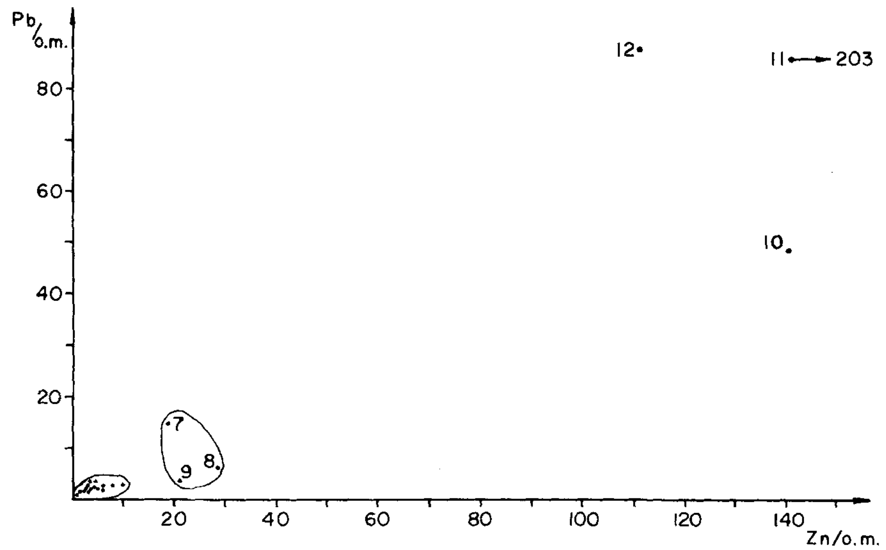

Figure 3 Plot of lead vs. zinc content (values normalized in relation to the content of organic matter).

This pattern is in good agreement with the present known contaminant load discharged into the littoral zone.

The content of organic carbon and nitrogen in the samples was used to characterize the sediments according to the two methods proposed by Ballinger and McKee (1971):

a) "organic index of sediments"; only the stations 8 to 11 were found in a "decomposition state".

b) contents of organic carbon and nitrogen; the majority of the samples are considered "stable". At stations 1, 3 and 13 the sediments are nitrogenated, that is "unstable". At Chivo Beach the samples were partially stable with high

Table 2 Enrichment factors with respect to aluminium content, calculated according to Robbe (1984).

Zone	*Station*	*Cu*	*Hg*	*Pb*	*Zn*
Almendares River	7	5.4	5.3	6.3	3.3
	8	4.1	5.5	4.3	5.7
	9	3.2	3.4	3.1	5.5
Mouth of Havana Bay	22	27	144	27	11
Chivo Beach	10	26	446	46	49
	11	36	569	78	65
	12	30	615	67	36

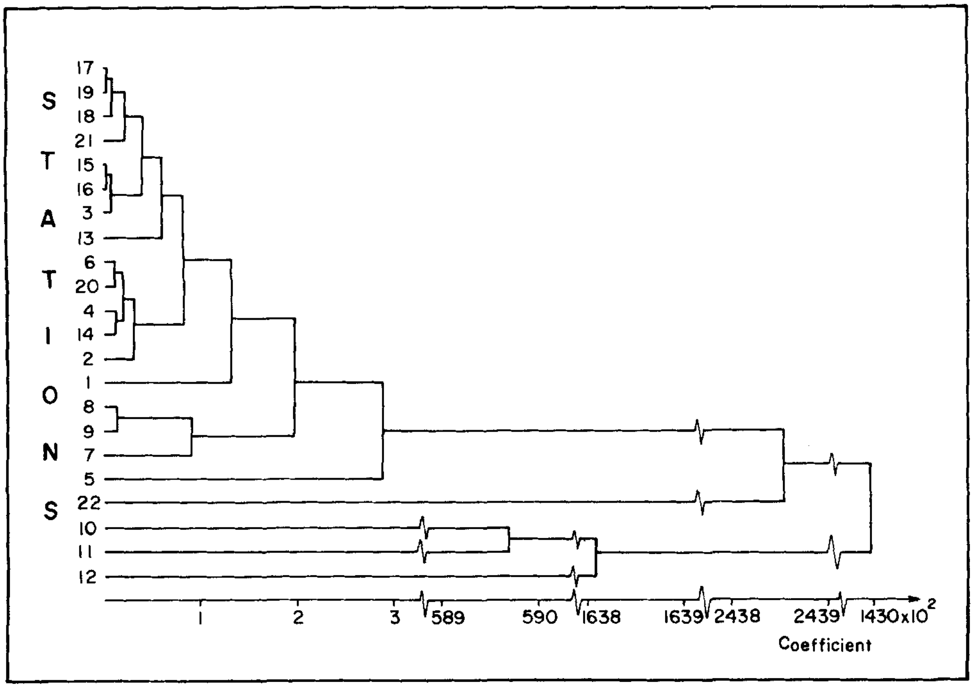

Figure 4 Dendrogram for the sampling stations (variables used for the cluster analysis are the metal contents normalized in relation to aluminium).

organic carbon contents. Only at the outflow of the Almendares River were the sediments in an active decomposition state.

The C/N ratio was used to indicate the origin of the organic matter in the sediments (Guerzoni and Rovatti, 1987). A ratio $C/N < 20$ is suggested to indicate marine origin (Cenciarini *et al.*, 1980). However, the choice of this threshold seems somewhat arbitrary. Therefore, we preferred to compare the C/N ratios only inside the study area; these values exceeded 20 at Chivo Beach (44) and at the Almendares River outflow (27). At the other stations, the C/N ratio was below 16. Thus, it is once again corroborated that the contamination observed at stations 7 to 12 is provoked by the industrial/urban waste waters discharged into these areas of the littoral zone.

4. CONCLUSIONS

Most sediments taken from the littoral zone off Havana City are relatively uncontaminated with respect to those heavy metals investigated. However, there are at least three areas which are strongly affected by anthropogenic sources. This is reflected by higher contents for mercury, copper, lead and zinc. These contaminated areas include the submarine sewage outfall of the city at Chivo Beach, the mouth of the Havana Bay and to a lower degree the estuarine zone of the Almendares River which drains a major part of the city.

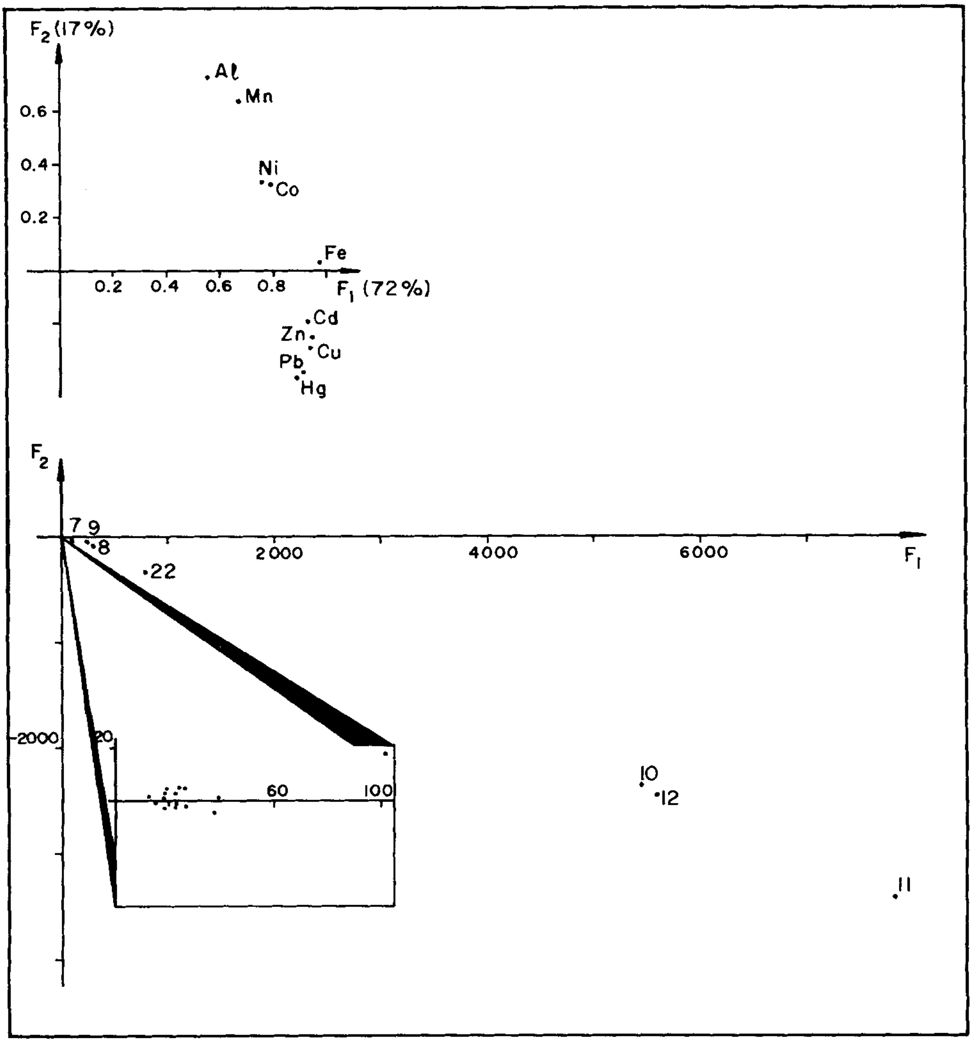

Figure 5 Results of a principal component analysis for the sampling stations (variables are the metal contents, original values auto-normalized).

Normalization of the metal contents in relation to aluminium or organic matter (carbon) and the application of multivariate statistical techniques such as hierarchical cluster and principal component analysis have proved to be useful tools for characterizing the contamination load for different sampling areas.

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