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Grain Size Effect on Trace Metals Distribution in Sediments from Two Coastal Areas of Chile

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Marine environment contamination by trace metals has received increased global attention during recent years. Presently it is widely recognised that marine ecosystem can become contamined by trace metals from numerous and diverse sources. However, anthropogenic activities, such as mining and industrial processing of ores and metals, still remain the principal cause of the increased amount of heavy metals which have been dumped into oceans. After entering the aquatic environment, trace metals are distributed among water, biotic and sediment compartments, this latter serving as a final sink for metal pollutants. The magnitude of this scavenging action of sediments depends on the physical, chemical and biological properties of the sediments. Concentrations of trace metals in sediments are usually of a greater magnitude order than concentrations in water (Förstner and Wittman 1981; Kevin and Worsfold 1990). Sediments were considered as an important indicator for environmental pollution, they act as permanent or temporary traps for material spread into the environment (Combest 1991; Schintu et al. 1991; Scordano et al. 1992; Long 1989 and 1992; Pardo et al. 1990).

One of the most significant parameters influencing trace metal levels in sediment is particle dimension. Bioavailable sediment-bound metals depends to a significant extent on the particle size fraction with which a metal is associated. Some studies have shown that the highest concentrations of metals are associated with fine grained sediment particles, the trace elements being mainly present in the clay-silt particles with grain size less than 63 µm, due to the increase in specific surface properties of this fraction. (Thorne and Nickless 1981; Förstner et al. 1982; Arujo et al. 1988; Cauwet 1987). However, anomalous fraction distribution of trace metals were found, where the metal concentrations did not increase with decreasing particle size and the highest metal

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concentrations were in the silt coarse and larger size fractions (Moore et al. 1989; Ramesh et al. 1990; Kreemgalz 1989; Combest 1991). These exceptions demonstrate that metal concentrations were not controlled exclusively by particle size; there are other sediment parameters, such as chemical and mineralogical composition, degree of surface oxidation and organic matter level influencing trace metal content in a sediment fraction. (Martinic et al. 1990; Kreemgalz, 1989).

The purpose of this study was to determine the grain size effect on the Cu, Cd and Zn levels distribution in surface marine sediments, collected in two geographical areas from the Chilean coast, with similar abundances of the sediment fractions. One of these zones is located near a copper smelting and electrorefinery plant. The choice of this area was made in order to study to what extent the proximity of one anthropogenic metal source can influence the metal distribution on the basis of the sediment grain size and demonstrate in which sediment fraction metals were concentrated in this area. The other station was selected for two reasons: first, it is distant from a recognized metal source and; secondly, because the granulometric composition of sediments was most similar to the other. (De Gregori et al. 1994).

MATERIALS AND METHODS

The location of the sampling areas is presented in Fig. 1. Station 1 is situated at the north of La Serena city and station 2 at the north of Valparaiso city (Quintero Bay) in proximity to Las Ventanas, one of the largest copper smelter and electrorefinery plant in Chile. For metal trends, three sub-stations (2-1, 2-2 and 2-3) were located in this zone.

Samples of sediment were collected by divers in September 1992 and January 1993 simultaneously in both sampling stations. Superficial sediments were taken with a hand held plastic scoop, and were placed in plastic flasks. Overlying water was carefully drained from the sediment samples, then they were frozen and transported to the laboratory in plastic containers. They were stored at -20°C until treatment. All material from each station (aproximately 5 kg wet weight) was composited to yield one sediment sample per station, in each sampling. Sediment samples were thawed in a microwave oven, transfered to plastic plates and dried for 3 days at 50°C in a conventional oven. For granulometric composition determination the dry sample was homogenized and separated into particle size fractions, using a series of nylon and nytal mesh sieves (Seidengaze fabric AG Thal, Switzerland). The sieves were supported in a home made demountable plastic plate and shaked with a Tyler Rotap. In all cases the

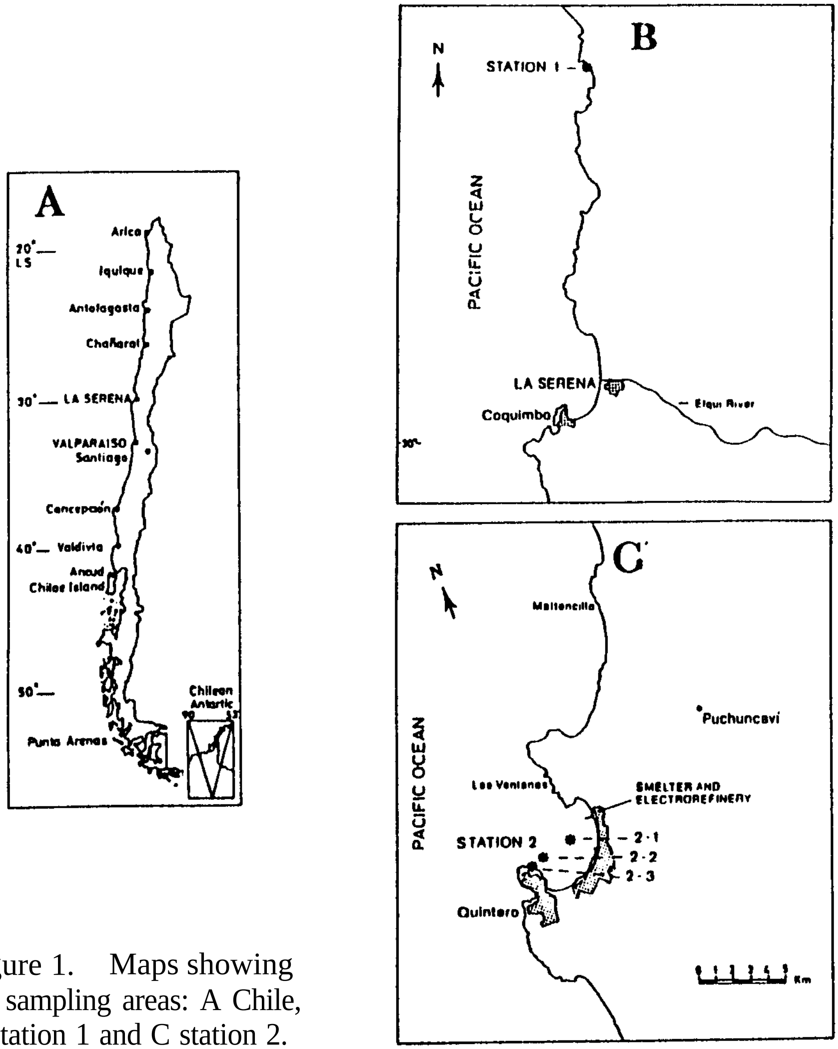

Figure 1. Maps showing the sampling areas: A Chile, B station 1 and C station 2.

sieves were thoroughly cleaned before use by several acid treatments (diluted HNO_3, 10%) and finally soaked in demineralized water to allow the mesh to assume the correct pore size. The sediment fractions were thoroughly mixed and weighed. The nominal size range of sediments were: fraction A > 400 µm; fraction B < 400 and > 200 µm; fraction C < 200 and > 63 µm and fraction D < 63 µm .

About 1.0 g of sediment from each of the size fractions was digested in closed Teflon vessels. The sample was allowed to rest overnight in a mixture of 4.5 mL, cont. HNO_3 of and 1.5 mL, of conc. HCl at room temperature. The digestion was carried under pressure at 150°C, 3 hr. Finally the cooled sample was quantitatively filtered with precleaned filter paper (HCl 1 M) and the volume was made up to 25 mL with deionized water. Samples were analysed in duplicate or triplicate and the measurements were made in duplicate. Blank samples were run simultaneously with samples. All reagents were of the suprapure (Merck, Germany) or trace metal grade (Fisher Scientific, Canada). Cu and Zn were determined by flame atomic absorption spectrometry (FAAS) using a GBC 950 PB Atomic Absorption spectrophotometer. Cd determinations were made by graphite furnace AAS using a PAL 3000 autosampler. Pyrolitic graphite coated tubes with graphite platforms (L'vov platform, GBC) were used for all Cd measurements. A mixture of $Mg(NO_3)_2$ and $NH_4H_2PO_4$ was used as a matrix modifier. For the metal determinations the standard addition method was employed.

Dry weight determination (105°C) was made on further aliquots of sample, which were further discarded. Results for trace metal are reported as mean ± confidence limit (95% P) on dry weight basis (d.w.). The quality assurance is an important and necessary part to realise for monitoring trace elements in environmental samples. Sediments reference material from NRCC (BCSS-1, marine sediment) and NIST (SRM-1646, Estuarine sediment) certified for Cd, Cu and Zn, were used to check accuracy and precision of analytical methodology applied in the analysis of these elements in sediments. Solutions of reference materials were analyzed at the beginning and the end of each set of sediment samples.

RESULTS AND DISCUSSION

The percentage distribution of different size fractions and their associated metal concentration, in sediments from stations 1 and 2 (2-l; 2-2 and 2-3) are shown in Table 1 (sampling 1 September 1992 and sampling 2 January 1993). Sediments from station 2-3 were not taken in the first sampling campaign. As can be seen the % contribution of each grain size fraction of sediments from the same station was similar in both samplings. There are no changes in the granulometric composition of sediments in spite of time elapsed between both samplings, Most noticeable, the amount of the finest size fraction D (< 63 pm) was in any case the smallest with values under 1%. However, in spite of their proximity, the % contributions of the other size fractions of sediments collected in the same campaign at the three sub-stations from site 2 were different. Sub-station 2-l was situated in the middle of Quintero bay at a distance of 4 km aproximately from sub-station 2-3, located at the shore. Sediments from station 2-1 were taken at a depth of 6-7 m and contained a large proportion (> 90%) of particles of size C (63-200 µm). The station 2-2 was located at a distance of 0.5 km from the station 2-3 and the sediments collected at a depth of 2-3 m

Table 1. Percentage contributions and trace metals levels associated with different particle size fractions of sediments of Chile collected in September 1992 (Sampling 1) and January 1993 (Sampling 2).

SITE		SIZE FRACTION	% p/p	METAL CONCENTRATION (ug g^{-1} d.w.)		
				Cu	Zn	Cd
SAMPLING 1						
STATION 1		A	34.7	11 ± 1	9.0 ± 0.5	0.3 ± 0.1
		B	40.1	9.8 ± 0.6	5.7 ± 0.6	0.16 ± 0.02
		C	25.1	8.6 ± 0.7	7.0 ± 0.4	0.22 ± 0.04
		D	0.1	30 ± 1	21 ± 1	1.0 ± 0.2
STATION 2	2-1	A	3.6	42 ± 3	25 ± 1	0.19 ± 0.02
		B	3.0	43 ± 2	73 ± 2	0.08 ± 0.01
		C	92.6	46 ± 2	41 ± 2	0.22 ± 0.04
		D	0.8	620 ± 38	160 ± 13	1.0 ± 0.2
	2-2	A	46.0	23 ± 1	8 ± 1	0.14 ± 0.02
		B	31.2	37 ± 2	31 ± 2	0.18 ± 0.05
		C	22.5	47 ± 1	48 ± 1	0.15 ± 0.05
		D	0.3	480 ± 12	76 ± 4	0.5 ± 0.1
SAMPLING 2						
STATION 1		A	36.6	9 ± 1	11 ± 2	0.15 ± 0.01
		B	36.8	9 ± 2	6.9 ± 0.6	0.15 ± 0.02
		C	26.5	9 ± 1	6.1 ± 0.3	0.23 ± 0.02
		D	0.1	32 ± 1	17 ± 2	0.24 ± 0.02
STATION 2	2-1	A	2.9	39 ± 8	28 ± 1	0.14 ± 0.02
		B	2.8	43 ± 1	63 ± 5	0.17 ± 0.02
		C	93.7	40 ± 2	37 ± 1	0.12 ± 0.02
		D	0.6	648 ± 40	161 ± 5	0.58 ± 0.07
	2-2	A	46.5	25 ± 3	9 ± 1	0.33 ± 0.03
		B	30.4	40 ± 1	27 ± 3	0.4 ± 0.1
		C	22.9	50 ± 1	47 ± 2	0.34 ± 0.03
		D	0.2	548 ± 21	108 ± 4	0.60 ± 0.09
	2-3	A	38.8	30 ± 2	12 ± 1	0.12 ± 0.01
		B	35.5	45 ± 2	44 ± 2	0.07 ± 0.02
		C	25.4	54 ± 1	79 ± 5	0.09 ± 0.02
		D	0.3	463 ± 6	92 ± 2	0.33 ± 0.04

aproximately have a size fraction distribution similar to that of sediments from station 2-3.

The metal concentrations within the different particle size fractions at these two survey stations appear to show some similar behaviour. Within all sediments studied, Cd is the metal found in lowest concentration followed by Zn and Cu. This last behaviour correlate inversely with their toxicity and their relative abundance in sediments. Within all G-actions analysed the maxima in the metal concentrations were observed in the finest fractions (< 63 µm). This is in agreement with the fine-grained particles, which have large adsorption surface areas. On the other hand, no statistical temporal variations were observed in the concentrations of the three metals in sediments collected in September 1992 and January 1993 in both sampling stations (statistically tested by the one way analysis of variance, ANOVA program 95% P).

Cd levels in samples from both sites presented the same order of magnitude. No clear trends were observed in regard to particles size tractions. However, significant differences were observed in the Cu and Zn levels in sediments from stations 1 and 2, the highest metal concentrations being found at station 2 especially in the smallest particle size fractions. The same fraction from station 1 contained eight to ten fold lower concentrations of Zn and five to twenty fold lower concentrations of Cu as compared with the sediments from sub-stations of site 2 (with the exception of the Zn levels in fraction A > 400 µm). The different behaviour between both stations was best observed when the metal concentration ratios were evaluated. For sediments from station 1 the Zn/Cd ratios ranged between 20 and 70 and the Cu/Cd ratios between 30 and 61 while in station 2 the same ratios ranged between 68-912 and 100-1403 respectively (with the exception of values for sediments from station 2-2 fraction A). The Zn/Cd ratios for site 2 indicate the presence of solid ore or technical debris. It is necessary to take into account that station 2 was located near the smelter and electrorefinery plant of Cu ores (Fig. 1) and received the impacts of these activities. Huge quantities of dust, sulfur fumes and particles containing high metal levels are emitted during the roasting and processing of Cu ores. The pollution effect can be confirmed through the results obtained for the spatial distribution of Cu levels in the smallest fraction of sediments from the three sub-stations of site 2. The Cu levels decreased while the distance of the sampling station from the metal source increased (the Cu concentrations were 648; 548 and 463 µg g^{-1} for sub-stations 1, 2 and 3 respectively). It is clear from these results that smelting and electrorefinery works at Las Ventanas were a source of metals, especially Cu. The contamination from this source is a serious problem for the surrounding marine ecosystem and also for all the nearly region, where damage in agriculture were also noted (Chiang et al. 1985). Even if the metals were present in ores in small quantities they were carried by air and water, attaining high concentrations, especially in the smallest sediment size fractions, with the aggravation that bioavailability of sediments-bound metals depends to a significant extent on the particle size fraction with which a metal is associated.

Other differences can be observed in the metal concentration levels of different particle size fractions of sediments from station 1 as compared with the sub-stations of site 2. The sediment fractions A, B and C from station 1 exhibit a very similar tendency to concentrate Cu and Zn. On the contrary at sub-stations 2-2 and 2-3 the Zn and Cu levels increase while the particle size decreases, with a noticeable increase in the metals content in the finest fraction. At sub-station 2-l an abnormal distribution was observed for the Zn levels based on the sediments grain size. The concentration of Zn associated with fraction B(200-400 µm) was higher than that obtained in fraction C. although it is of a smaller particle size (63-200 pm). This behaviour was observed in sediments of both campaigns and it can not be explained only on the basis of the granulometric characteristics of these sediments.

Today pollution from smelter and mining operation can be reduced and actions and corrections can be made. In our country, there are encouraging signs and actions that these are being achieved. In the last years, great efforts were made to control the emission from smelting and mining activities. The first step has been carried out, a sulphuric acid plant has been installed at Las Ventanas smelter.

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