TRACE METALS: INPUTS, SEDIMENTATION AND ACCUMULATION IN SAN VICENTE BAY, CHILE

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Abstract. The present study deals with sediment dynamics affecting sediment-associated metal distributions in an embayment system experiencing pollution from coastal industries. Sedimentary metal content may originate from diagenetic processes of foundation rock on the bottom, allochthonous minerals from natural sources, and metals from industrial effluents along the coast. The study presents experimental estimations of quantities of metals entering the bay in industrial wastewater, measurements of metal content in particulate material captured in sediment traps, and metals distribution in surface sediments. Quantitative estimations of metals entering the system in industrial effluent showed the relation $Pb \geq Zn > Cu > Cr \geq Ni > Cd$. That of metals associated with particulate material from traps was $Zn > Cr \approx Cu \geq Pb > Ni > Cd$ and the abundance of metals in sediments was $Zn > Cr > Cu > Pb > Ni > Cd$. Finally, rates of bottom sediment accumulation are estimated in relation to the time of residence of water in the bay. The experimental data on sedimentation and sediment abundance were consistent with field observations on distribution and accumulation at sites of major sedimentation in this bay.

Keywords: coastal zone, embayments, pollution, sediment traps, trace metals

1. Introduction

Metal distribution patterns in sediments are often related to the sedimentation of particulate matter in coastal embayments. Dissolved metals may arrive in rivers or in industrial effluents, and may adsorb on particulate organic materials or form inorganic complexes at the fresh/salt water interface (Förstner *et al.*, 1978). The coastal zone receives large quantities of metals produced by natural leaching processes on continents, as well as metals from industrial residues produced by human activity. The concentration of this fraction depends on the reactivities of the metals, chemical characteristics of the matrix, and presence of reactive substrates in receiving waters. A complex set of chemical equilibria govern the presence of metals in the water column, as well as physical-chemical processes of adsorption of metals to inorganic and organic materials, which may become sedimented in certain regions of a bay. The dynamics and behavior of metals in water and their transfer to other matrixes need to be studied in order to understand the fate of these elements in
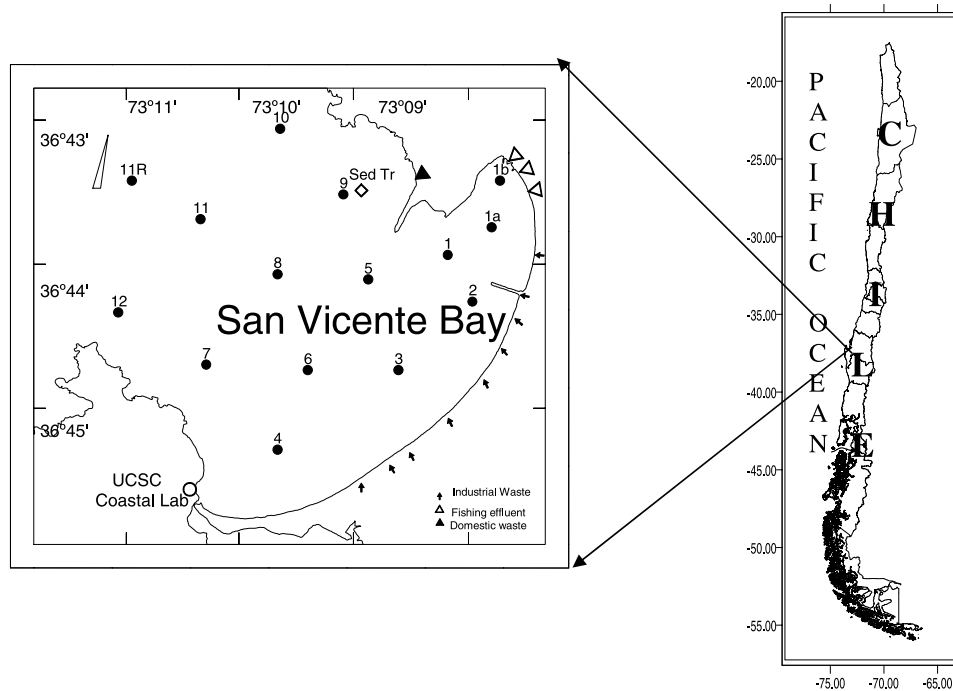
Figure 1. Map of San Vicente Bay, showing approximate locations of waste outfalls (arrows) hydrographic stations and placement location of the sediment trap.

the ocean, and produce some understanding of local metal-enrichment of bottom sediments. Movement of metals from a dissolved state to a particulate state occurs when the metals interact with organic and inorganic particulates (Salomon and Förstner, 1984; Emerson *et al.*, 1983; Krumgalz, 1989). This transformation is important in the distribution and routes of metals in the coastal zone. Metals normally enter seawater as cations, and may react with elements or compounds present to form inorganic complexes. The chlorides, carbonates and sulfates are the more important anions in this respect, and depending on the metal, may produce insoluble compounds or complexes (Buffle, 1988).

These reactions require a combination of the metal having a coordination number greater than unity, and a multidentate ligand, which may be an organic compound with numerous functional reactive groups. In order for the reaction to occur, the concentration of free ligands (chelating agents) must be much higher than that of the trace metals (Stumm and Morgan, 1981; Morel, 1983).

This paper presents experimental data on rates of sedimentation of metals in San Vicente Bay, Chile, in order to determine the relation between amounts and types of metals entering the system from industrial sources and the rate and distribution of their deposition into the bottom sediments.
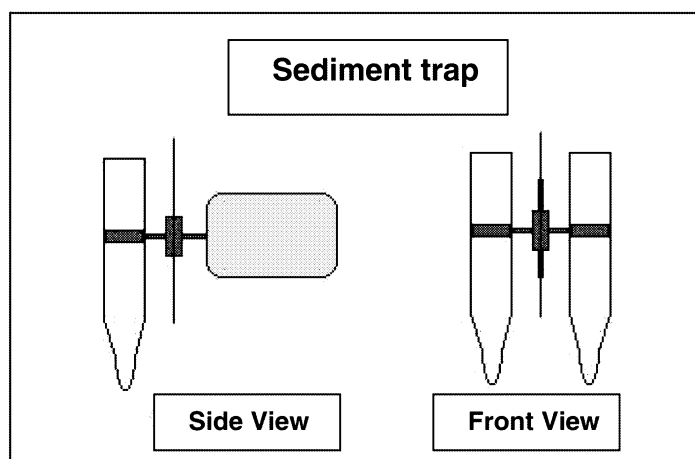
Figure 2. Twin-tube sediment trap placed in San Vicente Bay for collection of sedimenting particulate materials.

2. Methods

The mouth of San Vicente Bay ($36°44'S$) opens to the NW (Figure 1). It has a surface area of about 13.2 km^2, volume of about 260.5×106 m^3, average depth of about 20 m and residence time of the water estimated to be about 20 hr (Ahumada, 1995). Several industrial outfalls along the bay (Figure 1) release dissolved and particulate metals as industrial waste. Direct measurements of industrial outfall were made using an OTT brand, Model A, type C1 current meter. Composite 2 hr effluent samples (i.e., 15 min sampling) were collected in chemically clean, high density polypropylene 2 L bottles. Daily samples were taken for a week in the fifth sampling period. Sampling dates were between January to March of 1992. Chemical analyses of metals were carried out from an aliquot of 100 mL samples from each composite sample of the outfalls. The samples were acidified to pH 2 with Suprapur$^®$ HCl. The sample was then attacked with HClO$_4$/HNO$_3$ at 70 °C, and the residue diluted to 10 mL with Suprapur$^®$ HCl and determined for metal content using atomic absorption spectrometry (AAS). Total emissions for each outfall were then estimated by multiplying the metals content in the effluent by the effluent flow rate.

An integrated total value for each metal was calculated for a 20 hr period (approximate water residence time in the bay) to estimate the total RIL (residual industrial liquid) trace metals entering the bay during this period.

2.1. SEDIMENT COLLECTORS

Sediment traps were designed and constructed to determine sedimentation rates of particle-associated metals. Figure 2 presents a schematic view of the device used to collect particles in the process of sedimentation at the Punta Liles sector of the

TABLE I

Chemical Analysis results for the certified reference material SD-N $^1/_2$ TM

	Cd	Cr	Cu	Ni	Pb	Zn
Reactive blank	0.005	0.01	0.005	0.02	0.008	0.025
SD-N-1/2 TM	12.1±1	87.2±8.6	66.8±8.2	26.6±4.6	126.1±12	379.8±126
Analytical results	12.8±0.8	95.0±4	59.2±5	23.7±2	116.5±6	400.0±18
Analytical error%	5.8	8.9	11.4	10.9	7.6	5.3

Analysis $n = 10$.

bay (Figure 1). The location of the sediment traps was determined using a global positioning device (Apelco, GPS 15 Model). This sampling point was chosen as an example of an area undergoing active sedimentation similar to the port sector (Ahumada, 1992), but being less exposed to marine traffic. Each trap included two PVC tubes each 105 cm in length and 25.6 cm in diameter, mounted on a pivot having a directional vane designed to maintain the trap in a vertical position, and a mooring system for anchoring the trap to the bottom. This design followed the recommendations of Reynols *et al.* (1980) and Starecinic *et al.* (1982) governing the dimensions necessary for this type of trap. The bottom of the tubes were conical, and terminated in a detachable glass collector tube. Placement of the traps was done in spring and summer. The first placement of traps was carried out on 15 December at 10:10 hr at 18 m depth, where the bottom was at 25 m. Recovery of the trap was effected on 17 December at 14:30 hr. The second installation was carried out on 17 March at 12:30 hr and terminated on 19 March at 16:40 hr. Installations were done from aboard small vessels belonging to our university. Traps were installed open, and glass collector tubes inserted by divers at the initiation of the measurements; collector tubes containing sediment were recovered by divers at the end of the test period.

In the field, water overlying sediments in collectors were analyzed for pH and Eh, and sediments were saved for weighing and trace metals analysis. In the laboratory, samples were filtered onto tared (GFC) glass fiber filters of 1.2 μm porosity, and the wet weight of the entire sample was determined gravimetrically. Parallel sediment samples were centrifuged at $3000 \times g$ and supernatant water was discarded. The samples were then dried to a constant weight at 60 °C; 0.5 g; subsamples were treated with nitric and perchloric acids in Teflon vials at 60 °C until dry. Each sample was then made to 15 mL using concentrated Suprapur©HCl and analyzed by AAS equipped with a graphite oven, to determine Cd, Cu, Cr, Ni, Pb and Zn. Range of error in the AAS analyses was estimated by making parallel analyses of a standard metals mixture (SD-N 1/2 TM) distributed by the International Atomic Energy Agency (IAEA, 1986); this gave a range of errors in the determination of various metals of less than 12% (Table I).

TABLE II

Trace metals loads (kg 20 hr^{-1}) of ten industrial outfalls at San Vicente Bay

	Trace elements					
	Cd	Cr	Cu	Ni	Pb	Zn
Total metals	1.06	3.12	8.20	2.38	33.57	30.13

TABLE III

Filtered wet weight of particulates settled into twin-tube sediment traps (Figure 2) suspended at 18 m depth in San Vicente Bay, Chile

Date	Time in place	Sediment trapped in sampler (g)	
		Tube A	Tube B
15/12/1991	52 hr 40 min	4.85	4.79
17/03/1992	52 hr 20 min	4.66	4.66

Samples of bottom sediment were taken with a box corer of 30 cm^3 and sub sampled through the first 5 cm from the top layer down. Sections of 2 cm thickness were sliced and dried to 60 °C for 24 hr, then the sediment was pulverized. One gram of powdered sediments were weighed and attacked with $HClO_4/HNO_3/HF$ at 60 °C in a Teflon vessel. The residue was diluted to 10 mL with HCl Suprapur© for metal determinations by atomic absorption spectrometry analysis (AAS).

3. Results

3.1. RELEASE OF METALS TO THE BAY

Estimations of flow rate, plus values for metal content in the 10 flows studied allowed calculation of total metal emissions to San Vicente Bay over a 20 hr water exchange cycle as listed in Table II. The total additions of chemical and steel industrial wastewater input in effluents to San Vicente Bay was 126 720 m^3 20 hr^{-1}.

Sampling error in the flux measurements were near 8%. These, plus the analytical error, gave an estimate of uncertainty of about 18% for the metals input to San Vicente Bay.

TABLE IV

Concentrations of metals in particulates collected in sediment traps expressed as μg m^2/time in Place (Table III)

Elements	15 December; Spring		17 March; Summer		Means
	Tube A	Tube B	Tube A	Tube B	
Cd	1.84	1.97	1.38	1.43	1.7
Cr	56.0	52.9	60.3	55.4	56.16
Cu	45.0	44.6	50.2	55.7	48.89
Ni	32.52	36.81	36.05	38.13	35.88
Pb	49.50	46.90	40.20	37.10	43.44
Zn	193.0	208.0	179.0	181.00	190.26

TABLE V

Estimation of the rate of incorporation of metals into bottom sediments by means of particulate deposition (mg m^{-2} hr^{-1})

	Trace elements					
	Cd	Cr	Cu	Ni	Pb	Zn
Sedimentation rate:	0.06	1.97	1.72	1.26	1.53	6.69

3.2. SEDIMENTATION RATE

Table III presents results of sediment capture from the two sampling dates and Table IV presents the results of the metal analysis. The sedimentation rate was calculated from the estimation of material collected per unit area, time, and metal content analysis. The time value was approximately 52 hr, which was the Time in Place of the collector (Table III) at the moment it was sampled. Results of this calculation are given in Table V. Concentrations of metals in surface sediments represent seven replicates and the means are shown in Table VI.

The means of concentrations have a high coefficients of variation, and showed heterogeneous values of concentrations for all metals. Using a Box and Whisker plot as a discriminating tool, the values were segregated into two categories: (a) high values and (b) low values. The coefficient of variation was low for each individual group of metals. Coincidentally the separation between high and low values performed, showed a correspondent spatial segregation. Both groups represent different areas of the bay, one of them with sediments having high organic matter content, low oxygen, grain diameter <62.5 μ and highly reduced condition (Eh =

TABLE VI

Mean metals concentration (Cd, Cr, Cu, Ni, Pb and Zn) in the surface sediment for each station sampled in San Vicente Bay (μg g^{-1})

Stations	Cd	Cr	Cu	Ni	Pb	Zn
1b	5.90±0.5	87.18±1.6	77.00±1.4	42.28±2.5	55.13±0.5	272.10±12.5
1a	5.77±0.5	90.48±0.5	81.73±1.8	40.15±1.8	54.00±1.5	178.20±8.3
1	5.75±0.2	64.24±0.8	57.08±1.4	44.66±2.1	54.50±3.3	242.90±15.3
2	1.75±0.2	93.82±0.7	32.62±2.4	54.27±3.8	12.42±0.8	73.25±8.0
3	1.91±0.1	128.80±1.1	31.46±1.1	88.73±8.2	14.00±0.9	77.00±6.3
4	1.58±0.3	101.33±2.0	26.60±1.5	83.03±7.1	10.92±1.0	80.75±7.3
5	3.08±0.2	92.87±1.1	27.29±1.1	73.71±5.4	13.25±0.5	83.00±9.5
6c	2.41±0.3	98.22±2.6	30.30±0.9	79.78±5.1	14.01±0.9	83.25±5.3
7	1.50±0.3	112.85±1.7	30.30±0.9	84.11±7.5	13.17±0.6	83.00±6.2
8	2.75±0.3	62.79±1.3	26.49±1.4	48.22±3.2	9.00±1.15	78.00±4.0
9	1.33±0.3	99.16±2.0	43.12±1.9	51.15±3.6	32.75±2.1	147.15±11.3
10	1.50±0.2	70.24±1.7	17.19±0.9	29.53±1.4	11.50±0.8	49.00±3.5
11	2.88±0.2	100.40±1.2	29.43±1.5	104.49±8.2	10.79±0.6	88.10±4.8
11-R	2.88±0.2	88.10±0.8	34.44±2.1	55.08±4.2	10.75±0.2	78.00±5.2
12	2.45±0.3	79.53±1.0	28.37±1.4	66.42±5.9	10.71±0.5	83.50±8.5

–230 mV). This area showed accumulations of Cd, Cu, Pb and Zn. The second area was sandy, with low organic matter content and good oxygenation (Eh = +210 mV). This area showed higher concentration values for Cr and Ni.

4. Discussion

Results of chemical analyses of residual industrial liquids (*RIL*) released into San Vicente Bay allowed calculation of metal concentrations of human origin. The quantitative values obtained for each metal allowed establishment of a comparative sequence in order of importance as follows : Pb ≥ Zn > Cu > Cr ≥ Ni > Cd.

The characteristics of pH at the outfalls (pH < 6.0) suggested that the metals would be in dissolved form. The change in pH upon reaching the ocean, with the basic pH of seawater (pH > 8) in a matrix of high dissolved salt content increases reactivity of the metals. The change from the dissolved phase of the metals to a particulate phase occurs upon interaction of the metals with organic and inorganic particles (Förstner *et al*., 1978). This transformation is important in the distribution of metals in the coastal zone.

The metals observed have a cationic behavior in basic oxygenated water solutions, and react with chlorides and carbonates, forming insoluble complexes. Chro-

mium is an exception to the general rule, followed by the other cations of this study. This element may form compounds of an anionic nature at seawater pH (Mantoura, 1981) or even as Cr(III) may form hydroxides, which would not promote it's interaction with organic compounds.

In San Vicente Bay chelating agents arise from organic materials originating in industrial and domestic wastes, which have high organic matter content. Entry of cations to the Bay from industrial origin may result in their chemical reaction, production of flocculent material, adsorption of metals to particles, and formation of organometallic complexes due to due to the change in pH upon entering seawater. Particulate material thus formed, may be transported by advection where it may disperse, sediment, and undergo chelating reactions in bottom sediments.

Based on the location of the outfalls (near the head of the bay) and the dynamics of the bay, where surface currents have a cyclonic gyre, a preliminary estimate was, that the initial concentrations observed in the outfalls were probably diluted in half by the total bay volume. If the total volume is 260.3×10^6 m^3, then the concentration should increase by 0.25 mg L^{-1} Zn during the residence time. Probably, half of this concentration (i.e., 0.125 mg L^{-1}) may exit the bay to adjacent waters in a lapse of 10 hr. This approximation allows having a reference point in relation to the evaluation of the concentration of metals in the water column and concentrations measured in other matrices. This is without considering any reservoir (i.e., particulate organic matter, organisms; whose dynamic aspects change) or other fates (i.e., fixation in sediments as sulfides). The entry of metals to the sea and persistence of their concentrations would be defined by their dilution (molecular diffusion and turbulence), reactivity of the elements (change in ionic strength), dispersion (mixing and advection) of particles and flocculent, and sedimentation in accord with local dynamics. In this way, areas with local gyres and zones of retention of particulate matter may act as sedimentation and accumulation zones or areas of metal enrichment (Ahumada, 1992). In these areas greater enrichment would occur under conditions, which favor chemical reactions of the metals. The connection between metal content in the water column and within the sediments, is related to the sedimentation rate. This is the most important route followed by particulate organic materials of industrial (waste) origin. The rate of sedimentation is high, as is the content of trapped metals. The sequence of abundance of metals as related to the sedimentation rate was: Zn > Cr > Cu > Pb > Ni > Cd. Thus Zn was the metal with the highest rate of sedimentation, followed by Cr whose comparatively high rate of sedimentation is difficult to explain. One explanation may be that reducing conditions are produced within the interiors of the sediment traps which produced the behavior of Cr as a reduced cation with a valence of 2+ thus well adapted to form coordination compounds. The sequence from Cu on may be explained as mentioned above concerning the chemical behavior of cations in seawater.

Primary areas of sedimentation in San Vicente Bay occupy about 15% of it's area (i.e. $\cong$2 km^2), including the port sector, and the Punta Liles sector (Carro and

TABLE VII

Estimated inventory of trace metals in the sediments of San Vicente Bay and percentage of the calculated total entry to the bay of each metal as given in Table II

	Elements					
	Cd	Cr	Cu	Ni	Pb	Zn
Sedimentation rate[a]	118.8	3900.6	3405.6	2494.8	3088.8	13246.2
% of entry load	11.2	125.2	41.50	104.91	9.2	44.0
Inventory in sediment[b]	107.4	1686.2	1281.7	882.3	972.1	4159.0

Units: [a] g/20 hr; [b] Kg).

Mennickent, 1992). It is possible to make estimations of the metals which reach bottom sediments by considering the sedimentation rates estimated for the metals in Table IV. Table VII presents these values, estimated for a 20 hr period.

The sedimentation rate was calculated on basis of the quantity of metals which are transferred into the sediments via the particulate matter deposited in the bottom of the bay, over one water residence cycle (20 hr). In the same context, the value for sedimentation rate of each metal was contrasted with the entering metals load as a percentage. The percentage of Cr (125% of load charge was sedimented) showed that there are probably other sources for this metal. The same occurred with the case of Ni. Finally, the inventory of metals for the sedimentary areas of the bay was estimated as a reference point for the process being described below. For this the average concentration in the distribution of metals in the bay (Ahumada, 1992) was utilized, multiplied by the area of sedimentation. This value expressed in kg for each metal suggests that the total amount of cadmium was deposited in the first 0.5 cm of sediment (for the calculation, the value for density of the sediment was 2.0 g cm^{-3}).

The pattern of distribution of the metals in the sediment was consistent with the zones of highest sedimentation in San Vicente Bay, where enrichment of Cd, Cu, Pb and Zn was observed on the sedimentation areas (Figure 3). In contrast, Cr and Ni had highest concentrations in areas of fine, medium and coarse sands. The sediment of enrichment on reduced areas (Figure 4) exhibited the following sequence on abundance Zn > Cr >Cu > Pb> Ni > Cd. In the sediments localized at the central part of the bay, where sands were dominant, the abundance of metals showed the followed sequence: Cr > Zn > Ni > Cu > Pb > Cd.

Thus the spatial distribution of trace metals in the sediments of the bay appears to be well explained on basis of physical conditions for sedimentation in it's basins and the organic particulate material. The reducing features created by the organic sedimentation could promote the formation of metal sulfides.

Differences in concentration between Cd concentrations in particulate material and sediments, may be produced by the accumulation on sediment with time as Cd
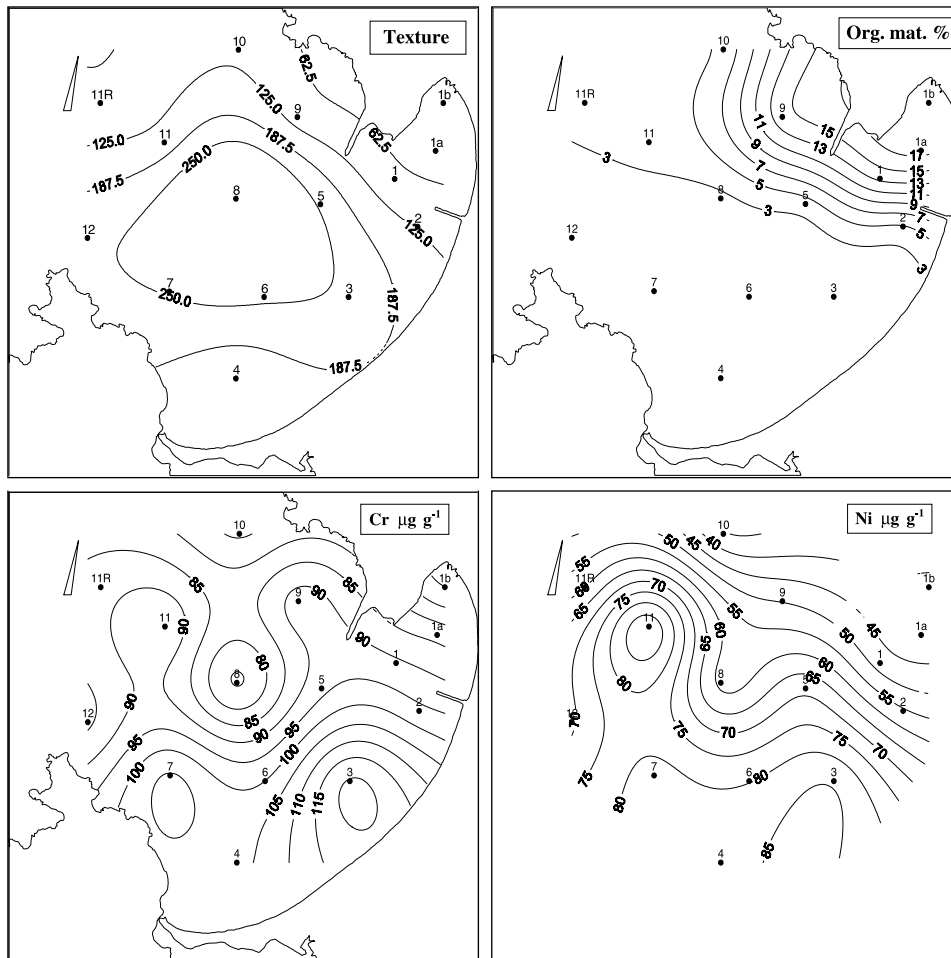
Figure 3. Distribution of texture (grain size), organic matter (organic carbon) and metals (Cr and Ni) in surface sediments at San Vicente Bay.

sulfide by the lower Kps. On the other hand, the lower concentration of Zn in the sediments compared with particulate material shows the better remobilization of Zn from the sediments.

5. Conclusions

From the present results it may be concluded that:

(a) Relative abundance of trace metals in the sediments is not directly related to the inflow of industrial effluents. Metal enrichment areas were related to the sedimentation zones.
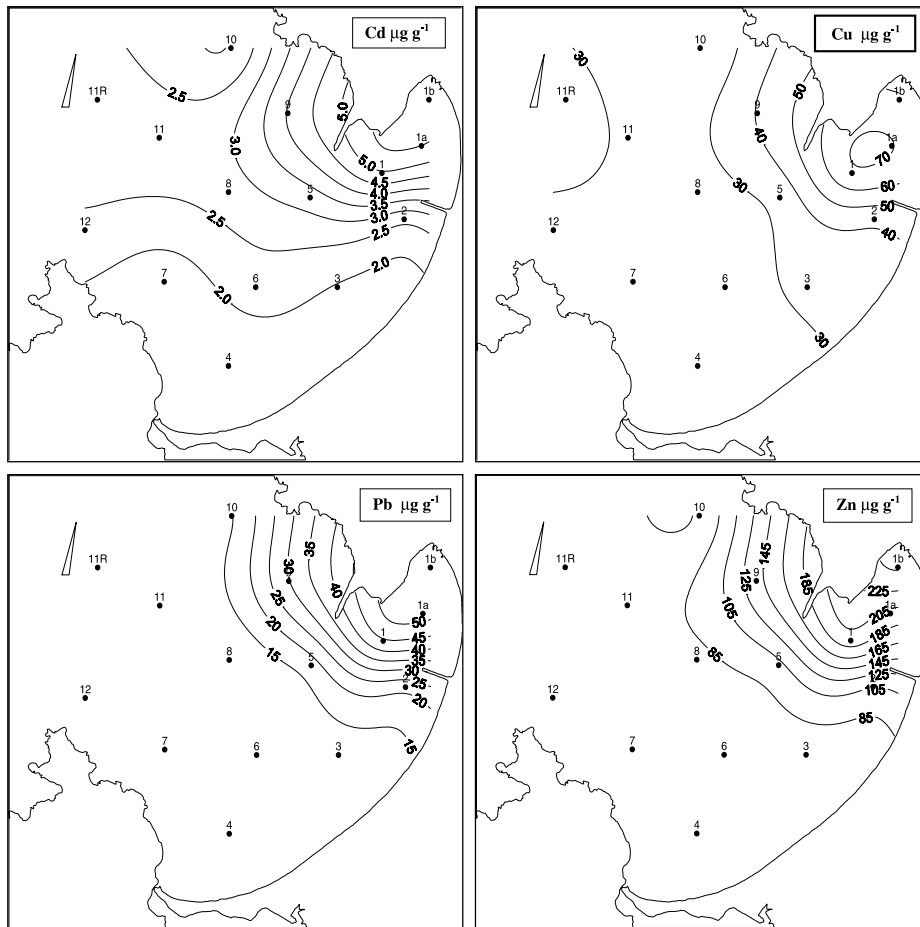
Figure 4. Distribution of metals (Cd, Cu, Pb and Zn) in surface sediments at San Vicente Bay.

(b) The relative abundance of metals measured in total industrial inputs to the bay, were not the same as metals in the enrichment areas. The differences were probably related to the chemical behavior of the cations in the marine environment. The chemical characteristics of the metals and their reactivity are important factors regulating the abundance of each element contained in the settled particulate matter.

(c) The chemical characteristics of the metals and their reactivity are important factors regulating the abundance of each element contained in the sediment.

(d) Although Zn and Cr were second and fourth, respectively, in the load ranking of metals in outfalls industrial waste waters, and showed the largest sedimentation rate, they were present in the highest concentrations, both in the water column and in the sediment in San Vicente Bay. There are two possible explanations for the above: the presence of another input source and/or a reactivity

with the particulate material affecting the relative rate of sedimentation and dissolved form or the redissolutions from sediments of different metals.

Acknowledgements

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