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Vertical profiles of cobalt and zinc in marine sediments of the Santa Rosalía mining region, Gulf of California, Mexico

Perfiles verticales del cobalto y zinc en los sedimentos marinos de la región minera de Santa Rosalía, Golfo de California, México

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Abstract

Core sediments that were sampled from the coastal zone of the Santa Rosalía mining region and the adjacent deeper area of the Gulf of California were analysed by an instrumental neutron activation analysis (INAA). The levels of Co, Sc and Zn were used to assess the effect of pollution from the solid wastes of a copper smelter on the sediment composition in the study area. The Co/Sc and Zn/Sc ratio vertical distributions were compared to Co/Sc and Zn/Sc ratios of the earth's crust and to a lower layer of the sediment cores and therefore less affected by pollution. The ratios of Co/Sc and Zn/Sc in cores from a predominant pollution "hot spot" near Santa Rosalía port are very high (40-150 and 150-350, respectively), suggesting that the thickness of the polluted layer exceeded the length of the cores (75-93 cm). The values of Co/Sc and Zn/Sc ratios decrease drastically in the cores collected outside the main "hot spot". In this case, the values obtained from core depths of 20-34 cm approached the regional coastal surface sediment background (approximately 2 and 5-10 for Co/Sc and Zn/Sc, respectivelly). The Co/Sc ratios for the sediments of the deeper and further from the coast cores are slightly variable, but at sediment depths below 15 cm they are nearly constant and approximately equal to the Co/Sc ratio of the earth´s crust. In the upper part of these cores (0-15 cm), the Zn/Sc ratios are higher (10-20) than the Zn/Sc ratio of the earth´s crust, which was probably due to the additional input of incompletely mineralised biogenic particulate Zn from the photic layer of the water column. The shape of the vertical profile the Zn/Sc ratio of SR22 sediment core (depth 360 m) in front of the main pollution "hot spot" shows that the maximum levels of pollution occurred in the past, and self-purification/restoration of the natural pollutant levels in the fine deep-water sediments can be observed during recent years.

Keywords: cobalt, zinc, pollution, marine sediments, Santa Rosalía mining region, Baja California peninsula, Mexico

Resumen

Los sedimentos de los testigos muestreados en la zona costera de la región minera de Santa Rosalía y en el área adyacente más profunda del Golfo de California se analizaron con el análisis instrumental de la activación neutrónica (AIAN). Los niveles de Co, Sc y Zn se usaron para evaluar el efecto de la polución producida por los desechos sólidos de la fundidora de cobre sobre los sedimentos del área de estudio. Las distribuciones verticales de las relaciones Co/Sc y Zn/Sc se compararon con las relaciones Co/Sc y

Zn/Sc de la corteza terrestre y con las obtenidas en la capa inferior de los testigos de sedimentos menos afectados por la polución. Las relaciones de Co/Sc and Zn/Sc en los testigos de sedimentos del área con mayor polución cerca del puerto de Santa Rosalía son muy altas, oscilando desde 40 hasta 150 y de 150 hasta 350 respectivamente, sugiriendo que el espesor de la capa altamente contaminada excede la longitud de los testigos (75-93 cm). Los valores de las relaciones Co/Sc y Zn/Sc disminuyen drásticamente en los testigos muestreados fuera de la principal área de polución. En este caso, los valores obtenidos en la profundidad de 20-34 cm del testigo se aproximan a los valores regionales de fondo de las relaciones para los sedimentos superficiales costeros (cerca a 2 para Co/Sc y a 5-10 para Zn/Sc). Las relaciones Co/Sc para los sedimentos de los testigos, muestreados a mayor profundidad y distancia de la costa son ligeramente variables, pero por debajo de 15 cm son casi constantes y aproximadamente iguales a la relación de Co/Sc para la corteza terrestre. En la parte superior (0-15 cm) de estos testigos de sedimentos, las relaciones Zn/Sc son más altas (10-20) que las relaciones Zn/Sc para la corteza terrestre, debido, probablemente, al aporte adicional del Zn biogénico particulado desde la capa fótica de la columna del agua. La forma del perfil vertical de las relaciones Zn/Sc del testigo de sedimentos SR22 (360 m de profundidad) frente al área de mayor polución muestra que los niveles máximos de polución ocurrieron en el pasado, y una autopurificación/restauración de los niveles naturales de los contaminantes en los sedimentos finos profundos se puede observar durante los últimos años.

Palabras clave: cobalto, zinc, contaminación, sedimentos marinos, región minera de Santa Rosalía, península de Baja California, México

1. Introduction

The metal mining and smelting on the sea shore is quite common because of the close proximity of mineral deposits to the tectonically active areas of land-sea interfaces where ancient hydrothermal vents have been uplifted and exposed on the continental margins. The most well-known cases include copper deposits and mines along the Pacific coast of Canada (e.g., the "Brittania" mine in British Columbia), along the coast of northern Chile (near Antofagasta) and in West Greenland (Elberling *et al.,* 2002), in addition to a Pb smelter in the East of Russia on the shore of the Sea of Japan (i.e., near Dalnegorsk in the Primorye region) (Shulkin, 1998). The dumping of mining tailings and solid smelting wastes into the adjacent sea used to be a widespread practice in the past.

One of these sites where sediments are strongly contaminated is a coastal zone along the Santa Rosalía mining region on the eastern shore in the centre of the Baja California peninsula in Mexico (Fig. 1). This area displays high levels of metals that are associated with former copper mining and smelting activities that were performed for nearly a century (Wilson and Rocha, 1955; Rodríguez Figueroa, 2004). There is clear evidence of the pollution of surface sediments by such solid waste dumping (Shumilin *et al.,* 2000; Rodríguez Figueroa, 2004, 2010); however, recent data were somewhat encouraging, as the heavy metals from highly polluted sites were shown to be mainly concentrated in the residual fraction of the surface sediments (Shumilin *et al.,* 2011). Additionally, an analysis of the metal levels in brown seaweeds showed that most toxic metals were retained in the sediments and were not released to the water column (Choumiline *et al.,* 2006; Rodríguez Figueroa, 2010; Rodríguez-Figueroa *et al.,* 2010). However, various severe environmental problems are still very real. For example, while the mining and smelting activities in Santa Rosalía closed more than twenty years ago, the self-cleaning/restoration dynamics of the pollution "hot spot" have not

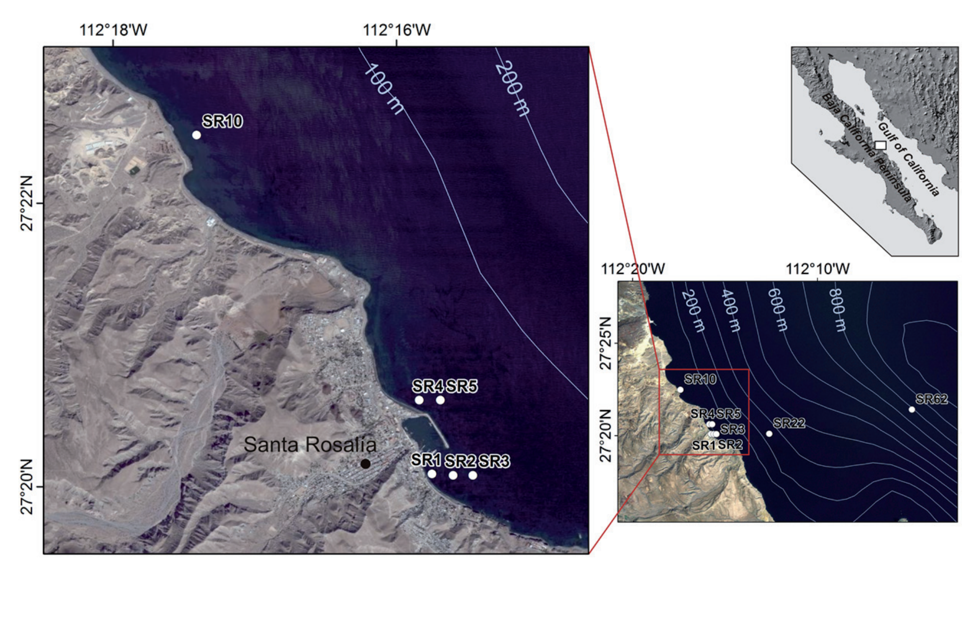

Fig. 1.- Study area and locations of the sampling sites for sediment cores in the coastal zone of the Santa Rosalía copper mining region in the Gulf of California.

Fig. 1.- Área de estudio y localización de los sitios de muestreo de los testigos de sedimentos en la zona costera de la región minera cuprífera de Santa Rosalía en el Golfo de California.

yet been characterised.

Cobalt and zinc are environmentally important trace metals (Smith and Carson, 1981). The concept of geochemical provinces has been considered in relation to their regional availability and their transfer through the food chain to humans (Hamilton, 1994). Both cobalt and zinc are essential micronutrients for marine phytoplankton growth. They are supplied to the ocean mainly through estuarine systems from land (Tovar-Sánchez *et al.,* 2004). Interestingly, these two elements can replace one another metabolically in marine phytoplankton that has been cultivated under laboratory conditions (Sunda and Huntsman, 1995). Co and, to a lesser extent, Zn are significantly enriched in the marine sediments of the Gulf of Iskenderen (Turkey) relative to their average crustal abundance. This enrichment is mainly due to the input of the weathered products of basic and ultrabasic source rocks that are present on the adjacent coast and hinterland (Ergin *et al.,* 1996). Sometimes, Co and Zn are greatly enriched in the environment, for example, in fjord sediments near a former mine in West Greenland (Elberling *et al.,* 2002) or in the "Boleo" copper mining district on the eastern coast of the Baja California peninsula, near the town of Santa Rosalía (Wilson and Rocha, 1955; Shumilin *et al.,* 2000; Rodríguez Figueroa, 2004).

Because of natural Cu-Co-Zn mineralization, the Santa Rosalía mining region was extensively used for copper mining and smelting throughout the past century. As a result, local beach sands and coastal marine sediments are strongly contaminated by Cu, Co, Zn and other heavy metals (Shumilin *et al.,* 2000; 2005). However, the impacted zones and the penetration depth into the sedimentary column are ostensibly limited in size (Rodríguez Figueroa, 2010; Rodríguez *et al.,* 1998; Shumilin *et al.,* 2000a, 2000b).

The objective of this study was to determine the vertical distribution of the anthropogenic contaminants at certain sites that were selected within the impacted area and a supposedly unaffected zone of the adjacent part of the Gulf of California to determine the depth at which the sedimentary column is affected by the pollution and to discover any evidence of self-cleaning processes. Our previous studies of smelting wastes, arroyo sediments, beach sands and surface marine sediments showed that there is a significant presence of Cu, Co, Mn and Zn in contaminated sedimentary materials. However, Co and Zn are especially convenient elements for accomplishing this type of environmental assessment because instrumental neutron activation analysis (INAA) for these elements is a very effective tool to analyse a considerable quantity of subsamples rapidly and inexpensively. Other contaminants, such as Cu and Mn, cannot be measured by the traditional INAA technique and require a laborious strong acid digestion to obtain solutions that can finally be measured by flame atomic absorption spectrophotometry or ICP-AES. Moreover, there have been some indications that the complete digestion of materials originating from a smelter in Santa Rosalía is difficult to achieve (Rodríguez Figueroa, 2010). To minimise any possible effects of grain size and dilution by biogenic calcium carbonate or biogenic silica on the levels of Co and Zn in the sediments, the normalisation of their absolute values with scandium was applied (Dias and Prudêncio, 1998; Grousset *et al*., 1995; Monna *et al*., 2004). Scandium belongs to a group of terrigenous indicators (i.e., Al, Cs, Ti, Li, Sc and Th) that are strongly associated with aluminosilicates in soils and sediments, and it was selected for our study because it is the only element of this group that can easily be measured by INAA in a solid matrix with high precision. Moreover, the linear regressions of the levels of many elements versus the levels of Sc in the sedimentary materials from the coastal environments of southern Baja California have displayed the best correlation coefficients when compared with Al, Ti or Fe (Rodríguez Castañeda, 2008). The Co/Sc and Zn/Sc ratio vertical profiles were prepared and taken into consideration to assess the depth of penetration of the contaminants into the marine sediments.

Element	Median certified value (mg kg^{-1})	Certified range (mg kg^{-1})	Measured concentration (mg kg^{-1})	Accuracy (%)
Cobalt	15.0	14.1-16.4	14.7±0.7	2.0
Scandium	6.90	6.75-9.99	7.10±0.15	2.9
Zinc	977	936-1019	1170±79	19.8

Table 1.- Accuracy information (%) of Co, Sc and Zn determinations in the certified reference material "IAEA-356" (polluted marine sediment).

Tabla 1.- Información sobre la exactitud de las determinaciones de Co, Sc y Zn en el material de referencia estándar certificado "IAEA-356" (sedimento marino contaminado).

2. Materials and methods

2.1. Sampling

The study area and the locations of the sampling stations are shown in Figure 1. The SR1-SR-5 and SR-10 sediment core samples were collected in April 2006 using a manual corer (length 100 cm) by scuba divers from a small plastic motorboat that was used as a platform for separating the core sediment samples.

The coastal core samples were thoroughly extracted from the core and, depending on the results of visual ob-

Sediment depth, cm	Cobalt (Co)	Scandium (Sc)	Zinc (Zn)
Core SR1			
0-2	1037	7.26	2475
2-4	1218	11.1	3780
4-6	1079	10.8	2180
6-10	930	9.46	2360
10-15	995	9.40	2820
15-20	1103	9.69	2650
20-25	1097	9.48	2440
25-30	1232	9.32	2720
30-40	1193	9.09	3100
40-50	1084	10.3	2800
50-60	1060	10.5	2850
60-70	1131	7.48	2470
70-80	968	9.41	2340
80-86	1103	11.4	2880
86-91	790	10.2	1720
Core SR2			
0-5	764	9.9	2385
5-10	806	11.2	1820
10-15	951	12.5	2350
15-20	945	11.1	2650
20-25	885	10.8	2110
25-30	1006	11.4	3110
30-35	738	8.46	2440
35-40	1028	10.0	3150
40-50	743	8.68	2520
50-60	921	10.1	3230
60-70	901	10.4	3140
70-78	1242	10.9	3040
Core SR 3			
0-5	45.5	13.0	210
5-10	45.8	15.0	180
10-15	45.7	16.6	140
15-20	45.7	14.2	190
20-30	65.9	14.5	430
30-40	28.8	14.6	40
40-50	21.9	13.9	30
50-60	22.9	13.2	10
60-70	20.6	14.6	90
70-77	32.3	16.0	150

Sediment depth, cm	Cobalt (Co)	Scandium (Sc)	Zinc (Zn)
Core SR4			
0-5	771	11.9	2990
5-10	674	11.8	2860
10-15	741	11.7	3040
15-20	583	12.7	2250
20-30	548	11.5	2440
30-40	566	13.2	2060
40-50	644	12.4	2920
50-60	609	11.5	2880
60-70	688	11.8	2580
70-80	555	11.6	2460
80-90	547	13.0	2110
90-96	570	11.6	2220
Core SR 5			
0-2.5	63	13.8	300
2.5-5	49.4	13.5	80
5-10	56.8	12.1	180
10-15	46.8	11.3	260
15-20	40.4	15.1	40
20-25	23.2	15.2	130
25-30	18.6	13.2	70
30-35	18.9	13.7	10
35-40	20.8	13.1	110
40-45	21.8	16.2	40
45-50	19.1	13.8	80
50-56	33.7	16.3	120
Core SR 10			
0-2.5	28.5	13.2	115
2.5-5	27.8	13.6	120
5-7.5	26.6	14.3	70
7.5-10	25.2	15.2	150
10-12.5	24.8	14.2	90
12.5-15	36.0	11.0	340
15-17.5	27.9	13.4	140
17.5-20	28.0	13.0	150
20-22.5	27.5	13.7	40
22.5-25	37.2	12.1	250
25-27.5	30.0	13.0	120
27.5-30	18.8	13.9	80
30-32.5	23.9	14.1	90
32.5-35	16.7	12.1	120
35-37.5	17.5	13.8	50
39-41	13.8	15.5	10

Table 2.- Concentrations of Co, Sc and Zn (mg kg^{-1}) in the sediments of cores SR1 to SR5 and SR10 from the coastal zone of the Santa Rosalía mining region.

Tabla 2.- Concentraciones de Co, Sc y Zn (mg kg^{-1}) en los sedimentos de los testigos SR1 a SR5 y SR10 de la zona costera de la región minera de Santa Rosalía.

servation of the opened core directly after sampling, were separated into layers (1 cm, 2.5 cm and 5 cm thick) using a plastic knife and a ruler. Then, they were transferred with a plastic spoon into pre-cleaned polyethylene packets and stored in a freezer until processing. In the laboratory, the samples were thawed and split into subsamples before treatment.

Two deep-water cores, SR22 and SR62, were sampled in 1994 by a box corer in the Gulf of California in front of the Santa Rosalía port during the "El Puma" cruise (Fig. 1) and were sliced into 2 cm thick sediment subsamples. Related data on the composition of the sediments of SR22 and SR62 cores have been described previously (Shumilin *et al.*, 2000a; Choumiline *et al.*, 2006).

2.2. Analysis

The levels of Co, Sc and Zn in the samples of finely ground and dried sediments were determined using INAA (Shumilin *et al.*, 2000a). The samples were dried in an electrical oven at 60°C for 24 h, and homogenised in an agate mortar. Then, 20 mg subsamples, in addition to certified standard reference material IAEA-356 (polluted marine sediment), homemade Russian standard reference materials (RCC-1, SARM-7, ST, SGD, KH, RUS, TB) and the stone meteorite "Allende" were irradiated simultaneously in an experimental nuclear reactor with a flux of thermal neutrons of 2.8×10^{13} n s^{-1} cm^{-2} at 150°C. After "cooling", the gamma-spectrometric measurements of the irradiated samples were conducted with a semiconductor Ge (Li) detector that was coupled to a 4096-channel high resolution pulse analyser LP-4900 ("Nokia", Finland). The elemental composition calculations of the irradiated samples were performed using statistical software that was developed *ad hoc*. This procedure confirmed that the precision (less than 4.6 % for Co, less than 4 % for Sc and less than 13 % for Zn) and accuracy of the determination of the concentration of the elements in the sediments were generally acceptable (Table 1). The detection limits were 0.05 mg kg^{-1} for Co and Sc and 10 mg kg^{-1} for Zn.

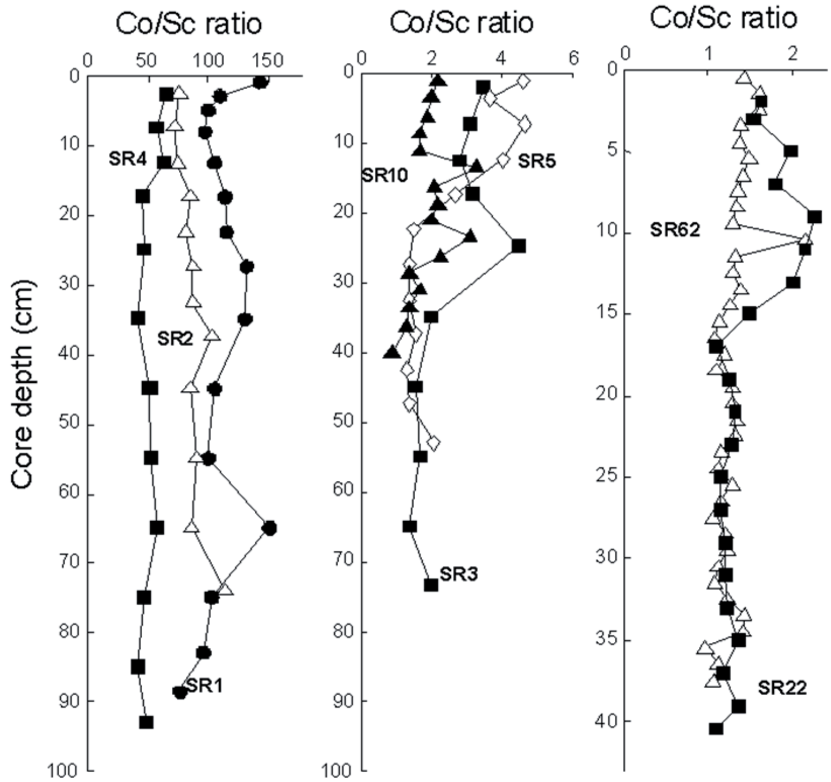

Fig. 2.- Vertical profiles of Co/Sc ratios in cores SR1-SR5, SR10, SR22 and SR62 from the coastal zone of the Santa Rosalía mining region.

Fig. 2.- Perfiles verticales de las relaciones Co/Sc en los testigos SR1-SR5, SR10 y SR 62 de la zona costera de la región minera de Santa Rosalía.

Sedimentary material	Co/Sc (n)$	Zn/Sc (n)$
Core SR1	112±20 (15) 77-151	276±51 (15) 169-341
Core SR2	87±12 (12) 72-114	258±52 (12) 162-320
Core SR3	2.6±1.0 (10) 1.4-4.5	10.1±8.5 (10) 0.8-29.7
Core SR4	52±8 (12) 42-65	214±36 (12) 156-260
Core SR5	2.5±1.4 (12) 1.3-4.7	8.9±7.3 (12) 0.7-23.0
Core SR10	1.9±0.6 (16) 0.9-3.3	9.4±7.3 (16) (8.0±4.7) (15)$ 0.6-30.9 (0.6-20.7)$
Core SR22*	1.4±0.4 (21) 0.4-2.3	15.2±5.4 (21) 5.5-25.0
Core SR62**	1.3±0.2 (38) 1.0-2.1	16.6±3.4 (38) 6.8-23.9
Surficial sediments, northern margin**	1.0± 0.4 (18) 0.4-2.5	8.2±4.9 (18) 3.5-24.7
Surficial sediments, southern margin**	1.7±0.7 (20) 0.9-3.8	11.5±7.4 (20) 2.1-22.7

$ Co/Sc and Zn/Sc ratios were tested for discordant outliers using the computer program DODESSYS (Verma and Díaz-González, 2012) under the option of all single-outlier tests and new precise critical values by Verma *et al.* (2008) before computing the mean and standard deviation values. Only for one core (SR10) one discordant outlier was detected. Average ± S.D (number of observations = n); range is reported in the second row.
* Shumilin *et al.* (2000a); ** Choumiline *et al.* (2006)

Table 3.- Co/Sc and Zn/Sc ratios for the sediment cores and surface sediments of northern and southern margins off the Santa Rosalía mining region

Tabla 3.- Relaciones Co/Sc y Zn/Sc para los sedimentos de los testigos y los sedimentos superficiales de los márgenes norte y sur al frente de la región minera de Santa Rosalía

3. Results

The concentrations of Co, Sc and Zn that were measured in the sediments of the coastal cores SR1- SR4 and SR10 are given in Table 2.

The concentrations of Co and Zn that were heavily influenced by the Santa Rosalía copper smelter were very high in cores SR1, SR2 and SR3. The levels of Co and Zn were lower in cores SR4 and SR5 in core SR10, which was collected north of the principal pollution "hot spot" of Santa Rosalía (Shumilin *et al.*, 2000 b; Choumiline *et al.*, 2006; Rodríguez Figueroa, 2010).

If we apply the sediment quality guidelines that were proposed by Long *et al.* (1995) for Zn (Effect Range Low (ERL) = 150 mg kg^{-1} and Effect Range Medium (ERM) = 410 mg kg^{-1}), the concentrations of Zn in all of the sediment depths in cores SR1, SR2 and SR4 were much higher than its ERM sediment quality guideline values, indicating potential risks for the marine biota. The Zn concentrations in the upper 20 cm of the SR3 core and in the upper 13 cm of the SR5 core were lower than its ERM sediment quality guidelines values but were still higher than the ERL guidelines values. However, below these sediment depths, the concentrations of Zn ostensibly would not represent any ecological risk. The sediment core SR10 from the northern margin that was collected in front of the El Boleo arroyo displayed Zn concentrations that were equal or slightly higher than the ERL guide-

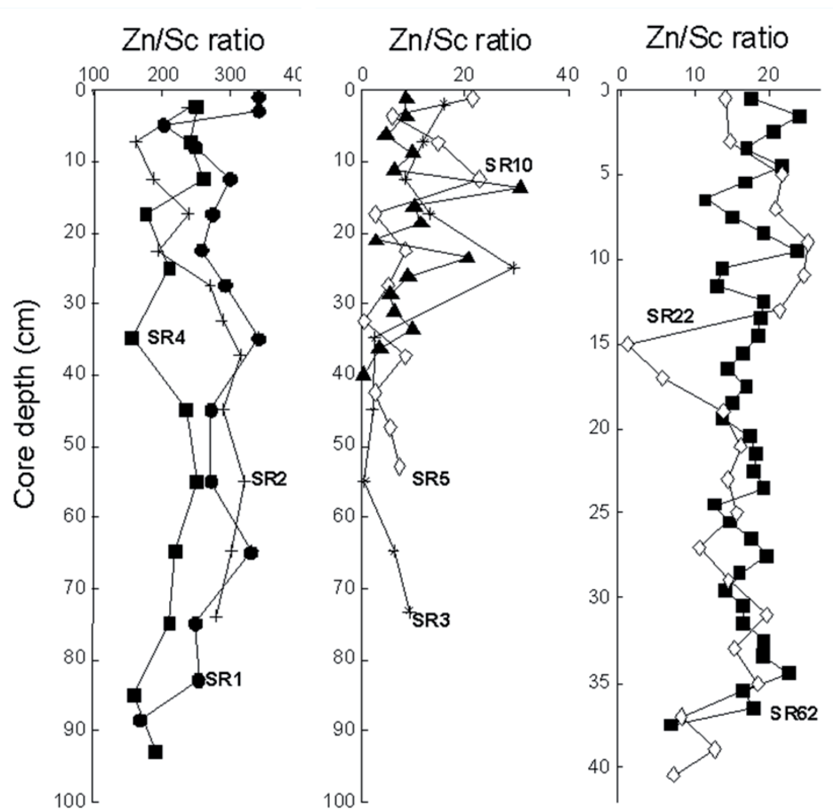

Fig. 3.- Vertical profiles of Zn/Sc ratios in cores SR1-SR5, SR10, SR22 and SR62 from the coastal zone of the Santa Rosalía mining region.

Fig. 3.- Perfiles verticales de las relaciones Zn/Sc en los testigos SR1-SR5, SR10, SR22 y SR 62 de la zona costera de la región minera de Santa Rosalía.

line sediment quality value at certain layers of the core (7.5-10 cm, 12.5-15 cm, 17.5-20 cm and 22.5-25 cm), but the Zn concentrations were generally lower than the ERL guideline values.

4. Discussion

The grain size of the coastal sediments from Santa Rosalía mining region is very heterogeneous due to its specific lithology and the occurrence of anthropogenic solid waste dumping (Rodríguez Figueroa, 2010). Generally, mixtures of particles of different sizes and origins are observed on spatial and temporal scales (Rodríguez Figueroa, 2010). To minimise possible effects of grain size variability and dilution of the contaminants in the sediments by inert quartz, by biogenic calcium carbonate or silica, the concentrations of Co and Zn were normalised with Sc. The regional background levels of the Co/Sc and Zn/Sc ratios in the study area and the shapes of the Co/Sc and Zn/Sc ratios vertical profiles were useful to evaluate the depth of penetration of tailing and smelting solid waste particles into the coastal marine sediments.

General information about the values of the Co/Sc and Zn/Sc ratios in the coastal and deep marine sediments in front of the Santa Rosalía mining region is presented in Table 3. The vertical profiles of Co/Sc and Zn/Sc ratios in the sediment cores of this study (cores SR1-5, SR10) as well as SR22 (from Shumilin *et al.,* 2000a) and SR62 (from Choumiline *et al.*, 2006) are shown in Figures 2 and 3.

As shown in Table 3, high mean values of Co/Sc ratio that ranged from 52 to 106 were detected for cores SR1, SR2 and SR4, and they were much lower for cores SR3, SR5 and SR10 (a range of 1.9-2.9). The lowest, most likely background, values were found in cores SR22 and SR62, where they ranged from 1.11 to 1.26. The highest Zn/Sc ratios were also found in SR1, SR2 and SR4 cores (a range of 214-262), followed by the open-sea core SR62 (a range of 11.7-24.1) and then cores SR3, SR5 and SR10 (a range of 8.9-10.1).

The observed Co/Sc ratios in the lower depths of cores SR3, SR5, SR10 and SR22 most likely corresponded to the local background conditions. Surface coastal sediments outside the study area showed slightly higher values of Co/Sc ratio that ranged from 1.6 to 6.0 (mean 3.4±1.2) along the northern margin and from 0.9 to 8.7 (mean 3.8±1.8) along the southern margin, supposedly reflecting the shore littoral transport of the contaminants from the highly polluted areas located near the town of Santa Rosalía.

The shape of the vertical profile Co/Sc ratio of SR22 sediment core (depth 360 m) in front of the main pollution "hot spot" showed that the maximum levels of pollution occurred in the past (see increased Co/Sc ratio values for samples collected from about 5-15 cm subsurface depth interval in Fig. 2), and self-purification/restoration of the natural pollutant levels in the fine grained deep-water sediments has occurred during recent years (see decreasing Co/Sc values for samples collected from about <5 cm depth in Figure 2).

The Zn/Sc ratios of the surficial sediments from the northern and southern margin did not exhibit the same tendency for the Co/Sc ratios as for the Zn/Sc ratios as was the case for the deeper cores SR22 and SR62. This situation could be due to the lower influence of contamination of the deep sediments in the central portion and slightly elevated contributions of accumulated biogenic particulate Zn from the water column in cores SR22 and SR62.

Cobalt is not a typical contaminant found in the coastal marine sedimentary environment, as it predominantly appears at background levels (Cobelo-García and Prego, 2003). Being mainly of terrigenous origin in coastal sediments, it is usually incorporated into natural resistant aluminosilicate matrices of marine sediments, and for that reason, cobalt was proposed as an additional terrigenous indicator or normaliser to identify the anthropogenic impacts of Cu, Pb and Zn on coastal marine sediments from the continental margin adjacent to Sydney, Australia (Matthai and Birch, 2001). However, certain levels of non-detrital Co in surface sediments from the Bay of Bengal have previously been attributed to anthropogenic contamination (Selvaraj *et al.*, 2004). In contrast, marine sediments formed in the areas of high biological productivity and driven by coastal upwellings are often depleted in Co due to the remobilisation of this element from particles in oxygen-depleted water and sedimentary environments (Brumsack, 2006).

Somewhat higher Zn/Sc ratio values in open-sea sediment cores (Shumilin *et al.*, 2000a; Choumiline *et al.*, 2006) relative to coastal “background” cores are most likely a result of the bioaccumulation of Zn in plankton organisms with the subsequent inclusion of their debris into the sea floor sediments. Additionally, it is hard to say to what extent the nearby Guaymas Basin with its hydrothermal sources influences the Zn concentrations, as direct observations over a hydrothermal area have previously indicated elevated levels of dissolved and particulate Zn no higher than 600 m above a 2000 m deep sea floor (Tambiev and Demina, 1992).

5. Conclusions

The ratios of Co/Sc and Zn/Sc in cores from the predominant pollution “hot spot” near Santa Rosalía port were very high (40-150 and 150-350, respectively). The values of Co/Sc and Zn/Sc ratios decreased drastically in the cores that were collected outside the main “hot spot” below a core depth of 20-34 cm and approached the regional coastal surface sediment background ratios (approximately 2 and 5-10 for Co/Sc and Zn/Sc, respectively).

The Co/Sc ratios for the sediments of the deeper cores were slightly variable, but they were nearly constant and were approximately equal to the Co/Sc ratio of the earth´s crust at sediment depths below 15 cm. The Zn/Sc ratios in the same cores were higher (10-20) than the Zn/Sc ratio of the earth´s crust, which was probably due to the additional input of incompletely mineralised biogenic particulate Zn from the photic zone of the water column. Co/Sc ratios along core SR22 showed that the maximum levels of pollution occurred in the past, and self-purification/restoration of the natural pollutant levels in the fine deep-water sediments has occurred during recent years.

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