Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23°S), Northern Chile: Geochemical and statistical approach

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Abstract

A suite of 36 surface sediment samples, taken between 10 and 100 m water depth in Mejillones Bay (Northern Chile), were analyzed for mineralogy, grain size, total organic carbon, Al, and heavy metal content (Cd, Zn, Ni, Mn, V, Mo). Quartz and feldspars were the main lithogenic minerals and carbonate the predominant biogenic mineral. Sediments were fine sands in the shallow zone and organic silt in the deeper zone.

Enrichment Factor and Factor Analysis approach showed that the presence of Mn in the marine sediment of Mejillones is due to a partial influence of continental input, while all other metals are not supported by lithogenic debris. Although all metals showed high concentrations in the marine sediment of Mejillones Bay, comparison between metal concentration in surface sediments and preindustrial levels in this bay, show that present values agree with natural levels.

Keywords: Sediments; Geochemistry; Metals; Mineralogy; Mejillones; Chile

1. Introduction

Marine sediments result from accumulated autochthonous organic compounds derived from biological productivity and continental materials supplied through aeolian and alluvial processes (Libes, 1992; Emelyanov, 2001). In oxygenated environments physical, chemical, and biological processes in the water column, and even at the sediment—water interface, can destroy a large fraction of these particles before their final remineralization (Calvert and Pedersen, 1993).

Sediments in the coastal zone are normally dominated by terrigenous particles due to the important supply of continental material. However, sediments in areas of frequent upwelling are mainly composed of organic matter and phytoplankton debris. Such areas are characterized by high accumulation rates. These rates together with hypoxic bottom environment favor the preservation of biogenic debris within the sediments. This situation combines with the bottom environment's hydrodynamic conditions, the sedimentary composition (mineral and organic matter content) and grain size, to control the behavior of many chemical substances, including heavy metals (Lallier-Verges and Albéric, 1990; Murray and Kuivila, 1990; Dean et al., 1997; Keil and Cowie, 1999).

Heavy metals are present in marine waters in both dissolved and solid forms and play a role in many biogeochemical cycles. These metals are rapidly and efficiently removed to the sediment via adsorption onto

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surfaces particles, precipitation, and incorporation into biogenic material (Cauwet, 1987; Szefer and Skwarzec, 1988; Alongi et al., 1996; Morford and Emerson, 1999; Cho et al., 1999). Many metals can also be incorporated into marine ecosystems as the result of human activities, creating anomalously high concentrations in coastal sediments where industrial development is intense (i.e. harbors). Metals such as V, Al, Ni, Cd, Mn, Zn and others are usually used in base line and contamination studies in marine systems, due to their relationships with anthropogenic activities (Caccia et al., 2003; Zwolsman et al., 1996; Srinivasa et al., 2004; Burton et al., 2004; Muñuz-Barbosa et al., 2004).

In recent years, much attention has been paid to the chemical composition of marine sediments in coastal regions near large industrial and urban areas because it is linked to the deterioration of oceanic ecosystems (Mudroch et al., 1988). Pollution problems in such areas can increase heavy metal concentrations (e.g. Zn, Pb, Cd, and Cu) to values 5 or 10 times higher than those characteristic of 50 or 100 years ago (Ridway and Price, 1987; Owens and Cornwell, 1995; Cardoso et al., 2001).

According to Zwolsman et al. (1996), there are three main reasons for studying the distribution of trace metals in sediments.

- An important fraction of trace metals accumulated in sediment exist in unstable forms, making them available for incorporation into the life cycle of the benthic fauna.
- 2. Sediments can become a source of metals to the water column if the equilibrium between the surface sediments and the overlying water column is broken.
- 3. Sediment trace metal data can be used to uncover the pollution history of an aquatic system, because they are more widely available, and more reliable than dissolved metal concentrations in a water system.

This study will focus on the third objective, to provide baseline measurements for monitoring purposes in this bay.

1.1. Geographic and oceanographic setting of Mejillones Bay (23°S)

The coast of Northern Chile is particularly interesting for the study of marine sediment geochemistry because (1) it is an arid environment where the supply of continental material is strongly limited to aeolian particle inputs, (2) coastal upwelling centers induce high biogenic accumulation rates in some areas, and (3) the subsuperficial oxygen minimum zone (OMZ) in the water column (Morales et al., 1996) strongly limits degradation processes and favors the preservation of the sediment's organic compounds.

Mejillones Bay is a small basin (15 km wide) on the coast of the Atacama Desert, the planet's most arid environment (Fig. 1). The mean total annual rainfall in this area is 4 mm year⁻¹ (period 1904–1998), although heavy rainfall (20–40 mm in 3 h) during some ENSO events can produce local flooding but debris flows are limited to zones near the alluvial fans (Vargas et al., 2000).

The bay is near an important upwelling system at Punta Angamos, one of the most productive cells along Chile's northern coast (Escribano, 1998; Gonzalez et al., 1998, 2000; Marín and Olivares, 1999; Escribano and Hidalgo, 2000). This bay is protected from the direct influence of the dominant S-SW winds, which also induce upwelling events. Its geomorphological configuration turns Mejillones Bay into a sedimentary basin where biogenic debris and organic matter derived from biological productivity are deposited, as are the lithogenic particles carried bayward by the S-SW winds (Vargas, 2002). Primary productivity in the bay measured 1070 g C m⁻² y⁻¹ (Marín et al., 1993). Dissolved oxygen

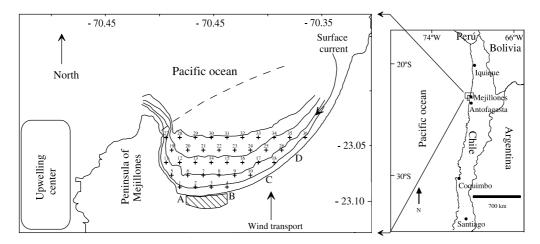


Fig. 1. Schematic map of the study area showing the sampling stations and the idealized location of the upwelling center. Dashed lines correspond to thermal front proposed by Marín et al. (2003). A is the aquaculture farm; B is the fishmeal industry; C is the thermoelectric industry; D is a mineral exportation port (in function since 2003). Bathymetry is showed by 25 m depth lines.

(DO) profiles measured over the annual cycle have shown that, at depths greater than 50 m, the bay comes under the influence of the OMZ (Morales et al., 1996; Valdés, 1998; Escribano, 1998; Valdés et al., 2004), which strongly restricts the presence of benthic fauna (Zúñiga, 1974; Zúñiga et al., 1983; Páez et al., 2001). These factors have favored the accumulation and subsequent preservation of laminated diatomaceous sediments enriched in organic matter, which constitute an exceptional record of high resolution paleoceanographic reconstructions (Ortlieb et al., 1994, 2000; Valdés, 1998; Vargas, 1998; Valdés et al., 2000, 2001; Páez et al., 2001; Vargas, 2002; Valdés et al., 2003, 2004).

The industrial activities around Mejillones Bay are located in a small harbor at the southern extreme of the basin. From the beginning of the 20th century, industrial development focused on fishery and nitrate mining-related activities. These included significant activity by a railway train factory during the first half of the 20th Century. At present, the most important industrial activities are related to aquaculture, thermoelectric generation and fisheries (Fig. 1); their impact on the marine ecosystem is unknown until now. The Mejillones Bay coastal zone and marine area are of high environmental interest due to increasing urbanization and the construction of an important harbor for exporting minerals and other products from the Atacama Desert region.

This paper examines the content and spatial distribution of the chemical and mineralogical composition of the Mejillones Bay superficial sediments in order to (1) provide fundamental data for understanding the natural behavior of heavy metals in this coastal ecosystem and (2) make an environmental base line available with which to evaluate the impact of the increasing urbanization and industrial activities around the bay.

2. Materials and methods

2.1. Sampling

A total of 36 surface sediment samples were collected from Mejillones Bay with a mini box core sampler (225 cm²) during a June 2000 cruise aboard the R/V Purihaalar (University of Antofagasta) (Fig. 1).

The first 0.5 cm taken from the surface of the box core samples was divided into four sub samples for analyzing heavy metals, minerals, total organic carbon, and grain size distribution. A plastic spoon was used to minimize contamination. No contact with the edge of box core happened during the sub sampling procedure. Immediately after collection, the sediment samples were placed in a polyethylene bag and preserved at a low temperature. The samples were then dried at 40 °C to a constant weight, homogenized and powdered using an agate mortar.

2.2. Analytical procedures

Vanadium (V), Molybdenum (Mo), Cadmium (Cd), Nickel (Ni), Manganese (Mn), Zinc (Zn), and Aluminum (Al) concentrations, expressed in mg kg⁻¹ of dry sediment, were analyzed with the AAES flame technique. The powered samples were digested an airproof Teflon bomb with a 3 step procedure. Firstly, 10 ml of HNO₃ was used to eliminate organic matter. Second $1 \ ml \ of \ HClO_4$ was used and then $0.5 \ ml \ of \ HF$ was added, to remove silicates (Zwolsman et al., 1996; Cho et al., 1999). In the metal analysis procedure, certain samples were selected for standard additional experiments to assess the possibility of matrix effects; none were observed. Analyses of blank samples, duplicate samples, and standard reference materials (PACS-1 K1A OR6 and MESS-1 K1A OR9 of National Research Council, Canada) were periodically performed, resulting in good agreement ($\pm 5\%$).

Minerals were determined and quantified using the FTIR method. This analysis performed in transmission mode allowed the quantification of the concentration of lithic minerals, carbonates and amorphous silica. The method, including its confidence and precision, is fully described in Bertaux et al. (1998). FTIR spectra were measured on a 300 mg of a preparation of bulk sediment mixed with KBr, and then compared with reference mineralogical spectra. Quantities are expressed as wt% of total dry sediment. A precision of $\pm 1\%$ has been estimated for each individual determination (Bertaux et al., 1998). Grain size analyses were performed with a laser technique using a Malvern "Masterizer" at the laboratory of the Université Bordeaux I. The calcium carbonate content was determined using a Bernard calcimeter. Total Organic Carbon (TOC), expressed as a percentage of dry sediment, was estimated using 100 mg of dry sediment by Rock-Eval 6 programmed pyrolysis methods, according to Lafargue et al. (1998).

All results were used to create contouring surface maps with the Surfer software package, using Shepard's interpolation method (Renka, 1988).

3. Results and discussion

3.1. TOC, grain size and mineral distribution

The mean TOC measured in superficial sediments was 4.8%, and range of variation was 0.3–8.5%. The TOC's spatial distribution is shown in Fig. 2; a rise toward the bay's deeper zones is apparent. The inverse correlation between the organic matter content and mean grain size in superficial bay sediments (Table 1) corresponds to a typical observation along coastal margins (Keil et al., 1994; Keil and Cowie, 1999). Hydrodynamic processes induce the accumulation of

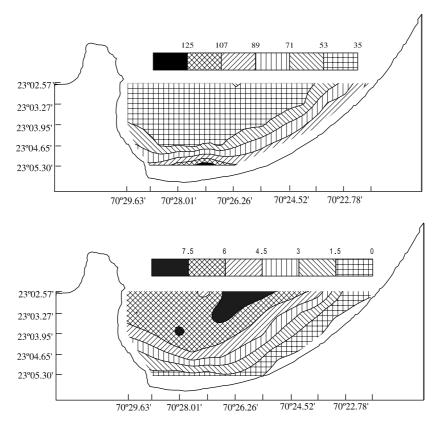


Fig. 2. Spatial distribution of mean grain size (µm) (up) and TOC (%) (down) in surface sediments from Mejillones Bay.

Table 1
Pearson's coefficient correlations for all geochemical parameters measured in Mejillones Bay surface sediments

| | Cd | Zn | Mn | Mo | Ni | V | Al | Deep | TOC | Grain size | Carbonates | Quartz | Feldspars |
|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------------|------------|--------|-----------|
| Cd | | | | | | | | | | | | | |
| Zn | 0.53 | | | | | | | | | | | | |
| Mn | 0.04 | 0.62 | | | | | | | | | | | |
| Mo | -0.03 | 0.03 | -0.01 | | | | | | | | | | |
| Ni | 0.93 | 0.67 | 0.2 | 0.07 | | | | | | | | | |
| V | 0.66 | 0.47 | -0.03 | 0.43 | 0.72 | | | | | | | | |
| Al | -0.1 | 0.53 | 0.63 | 0.23 | 0.05 | -0.01 | | | | | | | |
| Deep | 0.69 | 0.00 | -0.27 | -0.33 | 0.56 | 0.22 | -0.38 | | | | | | |
| TOC | 0.93 | 0.57 | 0.1 | -0.08 | 0.91 | 0.57 | -0.09 | 0.69 | | | | | |
| Grain size | -0.87 | -0.58 | -0.06 | -0.05 | -0.83 | -0.67 | 0.07 | -0.47 | -0.83 | | | | |
| Carbonates | 0.58 | 0.57 | 0.46 | -0.12 | 0.51 | 0.22 | 0.23 | 0.18 | 0.48 | -0.62 | | | |
| Quartz | -0.94 | -0.61 | -0.04 | -0.06 | -0.93 | -0.72 | 0.06 | -0.61 | -0.94 | 0.91 | -0.47 | | |
| Feldspars | -0.92 | -0.59 | -0.02 | -0.09 | -0.93 | -0.73 | 0.1 | -0.55 | -0.94 | 0.9 | -0.42 | 0.98 | |
| | | | | | | | | | | | | | |

Significant values (p < 0.05) are shown in bold.

fine sediments associated with organic matter in zones characterized by lower hydrodynamic energy or a more efficient absorption of organic matter over the greater net surface area characteristic of fine sediments.

The organic matter accumulated in Mejillones Bay sediment is a result of high biological productivity associated with upwelling events (Rodriguez et al., 1991; Marín et al., 1993; Marín and Olivares, 1999). Palynofacies microscopic analyses (organic fraction isolated from silicate and carbonate) were carried out on sedi-

mentary short cores retrieved from the bay; amorphous organic matter (AOM), as agglomerates of remains without an identifiable shape, were the dominant species (Valdés et al., 2003, 2004). This type of material commonly originates from the abundant phytoplanktonic biomass generated during upwelling events (Ramanampisoa et al., 1992; Habib et al., 1994). The high organic matter content in the superficial sediments of Mejillones Bay can further be associated with the efficient preservation process driven by the sea bottom's

persistent hypoxic conditions (Valdés et al., 2000, 2004; Valdés and Ortlieb, 2001).

The surface sediment grain-sizes vary from middlegrain sands (lower depths) to silt (mud) toward the bay's center (>50-70 m deep). The spatial distribution of the mean grain size is shown in Fig. 2. Two sedimentary provinces are clearly distinguished in the study area (between 15 and 100 m deep): (i) a shallow water zone (15– 55 m deep) characterized by fine sand, with a progressive decrease toward greater depths, and (ii) silty organic mud in the bay's central zone (55–100 m deep). This agrees with results from previous work that indicate the dominance of fine and very fine sand in basin's shallow zones and an increasing percentage of muddy facies toward its deeper zones (Ramorino and Muñiz, 1970; Zúñiga et al., 1983). The spatial distribution of the mean grain size is closely associated with the basin's bathymetry and geomorphology. Greater slopes and greater mean grain sizes are found at deeper zones on the western side, as opposed to the gentle slopes characteristic of the basin's southern and eastern margins (Vargas, 2002).

Quartz, feldspars (albite and oligoclase), and carbonates (calcite, aragonite) are present in the surface sediments of Mejillones Bay. Feldspars and quartz are the dominant terrigenous species, averaging 21% and 11% respectively, of the superficial sediment's content. The mineral's spatial distribution is closely associated with the bathymetry; contents in shallow zones are high (toward the littoral area), decreasing progressively toward the bay's deeper zones (Fig. 3). The significant inverse correlation between minerals and water depth supports this observation (Table 1). Moreover, the significant positive correlation between quartz and feldspar contents and mean grain size (Table 1) confirms the visual observation that the sandy fraction characteristic of the bay's shallower zones corresponds to terrigenous material. Unpublished oceanographic results from hydrological measurements within the bay suggest that the spatial distribution of the sedimentary facies may also be influenced by hydrological factors, such as local oceanic circulation (cyclonic gyre), littoral currents, and the regional S-SW wave trend.

Although the calcium carbonate content averages 13%, a more important central band running east-west is centered between 50 and 75 m water depth (Fig. 3). This distribution correlates significantly with a high abundance of benthic foraminifer tests (calcareous shelled protozoa) at similar depths within the bay (Páez, 2004), suggesting that the calcium carbonate concentration in superficial sediments is controlled by the abundance of such biogenic debris.

3.2. Geochemistry and distribution of total metals

Averages, ranges, and standard deviations of heavy metal concentrations in superficial sediments are summarized in Table 2. From major to minor concentrations, the analyzed metals are: Al, Mn, Mo, V, Zn, Cd and Ni. Table 2 also shows the average crust values from Martin and Whitfield (1983) as well as the concentrations measured in Mejillones Bay sediment cores (Valdés et al., 2000, 2001). In the first case, Cd is the only metal whose superficial sediment values are high with respect to the average crust concentration. In the second case, superficial sediment values of V, Cd and Al are lower than in core samples. Since the sedimentary core samples represent variations in metal accumulations during the last millennia (Valdés et al., 2000), they correspond to a natural base line, before industrial development.

Sedimentary organic matter may also influence metal concentrations in sediments. The significant positive correlation between organic matter content and Cd, Zn, Ni, and V concentrations is shown in Table 1. Considering the dominant biogenic origin of the bay's sediments, we suggest that the accumulation of heavy metals is closely related to the accumulation of organic matter and biogenic remains, whose levels are influenced by the area's high level of biological productivity.

The analyzed metals present different spatial distribution patterns. Cd and Ni concentrations have similar spatial distributions, both closely related to the basin's bathymetry (r > 0.69 and 0.56, respectively, p < 0.05) (Fig. 4). Lower concentrations occur in the shallower zones of the southeastern part of the bay, in accordance with the dominant sandy quartz and feldspar facies. A similar spatial distribution pattern, although not statistically significant, can be observed for the V concentration. The spatial distribution of Zn, Mo and Mn do not show a regular distribution pattern, and no correlation with deep was observed (Table 1). A central band, characterized by higher contents of Mn and Zn, can be distinguished crossing the bay (Fig. 4). This distribution is similar to carbonate band, and significant correlation was founded between them. In case of Mn, which presents a significant correlation with Al but not with mean grain size, its distribution is probably dependent on the redox condition within the sediment column (Cho et al., 1999). For example Lee et al. (1992) explained the poor relationship between Mn content and the mean grain size of the sediments present in the South Eastern Yellow Sea, in terms of early diagenetic mobilization within the sediment column. The Cd, Ni, V, and Zn concentrations correlate significantly with TOC.

The spatial distribution of Mo shows two zones where values are high: one in the southern area, off the town of Mejillones, and the other on the northern boundary of the study area. Lower values can be observed on the eastern side of the bay (Fig. 4). Mo is a conservative metal, only affected by physical–chemical factors (Libes, 1992; Brown et al., 1994; Adelson et al., 2001). There may be some influence of circulation upon its distribution. Unpublished data of temporal variabil-

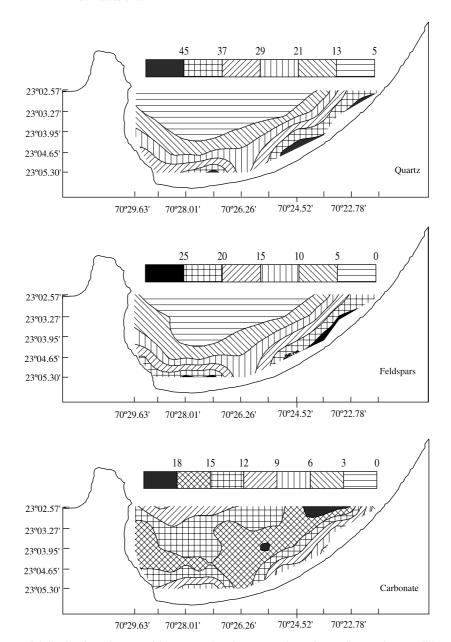


Fig. 3. Spatial distribution of quartz, feldspars, and carbonate (%) in surface sediments from Mejillones Bay.

Table 2 Mean, range and standard deviation of metal concentrations in the 36 surface sediment samples from Mejillones Bay; from sediment cores (Valdés et al., 2000; Valdés and Ortlieb, 2001); and from the earth's crust (Turekian and Wedepohl, 1963; Martin and Whitfield, 1983)

| Metal | This stu | dy | | Sedime | Average | | |
|-------|----------|----------|-------|--------|---------|-------|--|
| | Mean | Range | S.D. | Mean | Range | crust | |
| Cd | 21.9 | 3–38 | 11.1 | 38 | 20–60 | 0.3 | |
| Zn | 29.7 | 10-62 | 12.5 | 18 | 11-30 | 127 | |
| Mn | 93.8 | 20-138 | 24.4 | 46 | 28-73 | 720 | |
| Mo | 50.5 | 10-118 | 28.2 | 51 | 28-72 | _ | |
| Ni | 20.6 | 2-36 | 10.4 | 40 | 19-73 | 49 | |
| V | 43.9 | <1–97 | 26.5 | 134 | 120-155 | 97 | |
| Al | 3321 | 715-4910 | 854.9 | 2.1 | 1-3 | 6.93 | |

All values given in mg kg^{-1} , except for Al in sediment core and average crust, which are in %.

ity of Mo in surface waters of Mejillones show an intense rise in Mo concentrations during periods of high productivity, when vertical and horizontal circulation are intensified by upwelling events. Al showed a high concentration zone in the southwest of the bay, and its distribution correlates negatively with depth (Table 1). In both cases, problems of contamination cannot be discarded (and must be studied in the future) because in the zone where Mo and Al showed high concentrations, domestic waste effluent is present.

3.3. Enrichment Factors

The trace metals accumulated in the bay's marine sediments may have two sources: detrital clastic debris and

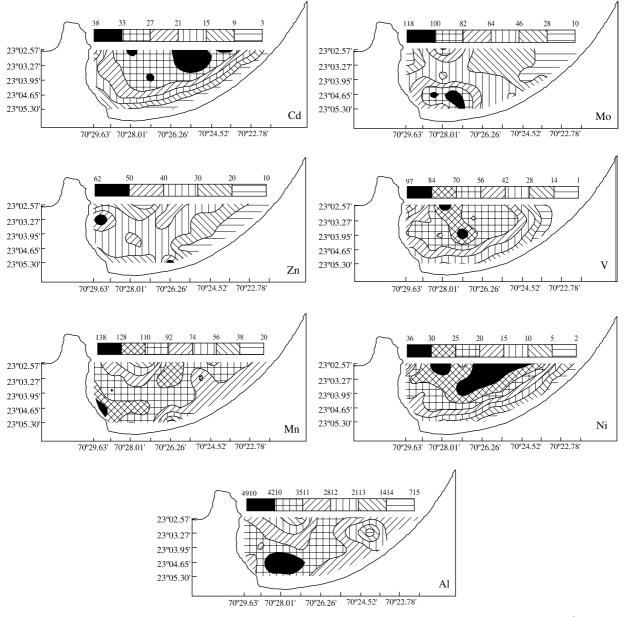


Fig. 4. Spatial distribution of analyzed metals in surface sediments from Mejillones Bay. Concentration in mg kg⁻¹.

dissolved seawater forms (Dean et al., 1997). The significant inverse correlation between quartz and feldspars and Cd, Zn, Ni, and V concentrations, as well as the absence of a correlation with Mn and Mo concentrations (Table 1), suggests that terrigenous minerals are not the principal source of the heavy metals in the bay's sediments. The metal content in marine sediments depends on the grain size distribution, since the increased specific surface of finer sediments favors adsorption processes (Cauwet, 1987). The significant negative correlation observed between mean grain size and Cd, Zn, Ni, and V concentrations (Table 1) indicates a relationship between the metals' accumulation and the bay's hydrodynamic conditions, which may themselves be closely

related to the spatial distribution of the mean grain size. Effectively, for all cases, the average metal concentration was higher in zones characterized by muddy facies, and probably associated with reduced circulation in the basin. A normalization procedure using Al for the metal concentrations permitted the variation to be compensated—for in both textural and composition characteristics (Jenne et al., 1980; Schropp et al., 1990). Moreover, according to Nolting et al. (1999) and Selvaraj et al. (2004), this method is a powerful tool for regional comparison and evaluating the anthropogenic input of trace metals in the sediments; the method can also be applied to determine Enrichment Factors (EFs). Table 3 presents the mean values of calculated EFs for the studied

Table 3
Enrichment Factors with respect to crustal average and background level (sediment core in Table 2), in surface sediments of Mejillones Bay

| Metal | Mean | Min. value | Max. value | Std. dev. | | | | | |
|----------------------------------|-------|------------|------------|-----------|--|--|--|--|--|
| Crustal average | | | | | | | | | |
| Cd | 1963 | 260 | 9440 | 1802 | | | | | |
| Zn | 5.2 | 1.9 | 17.6 | 2.8 | | | | | |
| Mn | 1.6 | 0.3 | 5.9 | 1.2 | | | | | |
| Ni | 10.1 | 1 | 39.6 | 7.9 | | | | | |
| V | 11.1 | 0.2 | 43.5 | 10.1 | | | | | |
| Background level (sediment core) | | | | | | | | | |
| Cd | 4.3 | 0.6 | 20.9 | 4 | | | | | |
| Zn | 11.2 | 4.1 | 37.5 | 6.1 | | | | | |
| Mn | 108.1 | 24.5 | 489 | 69 | | | | | |
| Ni | 3.7 | 0.4 | 14.7 | 2.9 | | | | | |
| V | 2.4 | 0.1 | 9.5 | 2.2 | | | | | |

metals with respect to crustal averages; the equation $EF = (\text{metal/Al})_{\text{sediment}}/(\text{metal/Al})_{\text{crust}}$ was used. EFs close to one indicate a crustal origin of the metal, whereas EFs over 10 denote non-crustal sources. In order to evaluate the surface metal concentration with respect to natural background levels, all metal data are also subjected to EF calculations using the concentration of metals in the sediment core (Valdés and Ortlieb, 2001); in Mejillones Bay, these are preindustrial levels. This assumption is based on the fact that laminated sediments, such as those of Mejillones Bay, preserve their vertical composition, providing a representation of the environmental conditions at the moment of sedimentation. Moreover, the actual sedimentation rate in the center of Mejillones Bay is 156 cm ky⁻¹ (Vargas et al., 2004), indicating that the 0.5 cm surface sediments sampled in this work represent, more or less, the 3 years of sedimentation prior to sampling in 2000. Furthermore, the metal content in the sediment core used for this discussion corresponds to a vertical section of between 15 and 70 cm sediment depth; clearly, this section's values are preindustrial.

All EFs measured in surface sediment are greater than the crustal average. Only Mn had a value close to 1 (mean 1.64) (Table 3), which could indicate some crustal origin for this metal. In the other cases (Cd, Zn, Ni, V) the results indicate a metal source other than lithogenic debris. The EFs for Cd (mean 1963) are particularly high, which could be interpreted as a situation of contamination, but when we consider the background level EFs, the scenario is quite different. For example, Mn had the higher EF value (mean 108), whereas Cd decayed significantly towards 4 (Table 3). Considering that all metal concentrations in surface sediments (except Mn) are within or lower than the ranges recorded in the sediment core (preindustrial values) (Table 2), it is difficult to assume a contamination problem in Mejillones Bay. For this reason, the natural variation in environmental conditions of Mejillones Bay could possibly explain, at least in part, how the EFs relate to the background level.

Cd, Ni, V, Zn, and Cu are normally recognized as redox-sensitive metals and their concentration in marine sediments is influenced by the intensity of the water column's hypoxic conditions (Calvert and Pedersen, 1993; Rosenthal et al., 1995; Dean et al., 1997; Morford and Emerson, 1999; Bostick et al., 2000; Zheng et al., 2000; Morford et al., 2001; Russell and Morford, 2001). According to Valdés et al. (2004) the highly hypoxic conditions characterizing the water column below the oxycline in Mejillones Bay explain the high concentrations of all these metals detected in the sediments of the basin's central part, which agrees with the high organic matter content in the same samples. In fact, the bottom oxygenation during winter 2000 (Fig. 5) shows a close relationship with all these redox-sensitive metals, especially with Cd and Ni. Both of these metals registered the highest concentrations in the most depleted DO zone ($<0.05 \text{ ml l}^{-1}$). An intensification of hypoxic conditions during the last centuries in Mejillones was

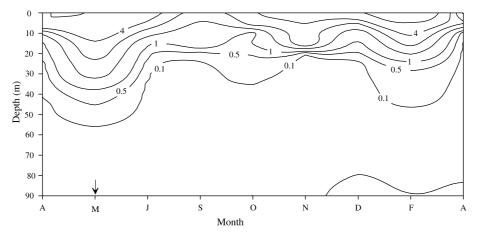


Fig. 5. Vertical distribution of dissolved oxygen in Mejillones Bay, during an annual cycle. The month of sampling is highlighted.

Table 4
Factor analyses (after Varimax rotation) showing the contribution of statistically dominant variables measured in this study

| Parameters | Factor | | | | | |
|-------------------------|--------|--------|--------|--|--|--|
| | 1 | 2 | 3 | | | |
| TOC | 0.948 | -0.178 | -0.110 | | | |
| Cd | 0.926 | 0.054 | -0.025 | | | |
| Zn | 0.550 | -0.433 | 0.426 | | | |
| Mn | -0.000 | -0.350 | 0.910 | | | |
| Mo | 0.007 | -0.070 | -0.055 | | | |
| Ni | 0.943 | -0.050 | 0.156 | | | |
| V | 0.674 | 0.018 | 0.044 | | | |
| Al | -0.060 | -0.943 | 0.304 | | | |
| Carbonates | 0.385 | -0.109 | 0.257 | | | |
| Grain size | -0.852 | 0.076 | -0.010 | | | |
| Quartz | -0.979 | -0.026 | 0.004 | | | |
| Feldspars | -0.973 | -0.066 | 0.015 | | | |
| Variance (%) | 51.5 | 10.5 | 10.1 | | | |
| Cumulative variance (%) | 51.5 | 62.0 | 72.1 | | | |

proposed by Valdés et al. (2000, 2004) based on different proxies evaluated in sediment cores of this bay.

3.4. Factor analysis

Factor analysis was used to identify the parameters that control trace metal distributions in the Mejillones Bay surface sediments (Loring, 1991; Selvaraj et al., 2004). Table 4 shows the Varimax rotation factor matrix results. Three factors explain 72.1% of the total variance in the 36 sediment samples analyzed. Factor 1 accounts for 51.5% of the total variance and group TOC and all the trace metals except Mn and Mo. This indicates that organic flux through the water column is an efficient mechanism for non-detrital metal export to the bay's bottom sediments. Another group, made up by lithogenic minerals and grain size, presents high negative loading and represents the influence of hydraulic transport in the littoral zone and aeolian transport from land to the bay's center.

Factor 2 explains 10.5% of the total variance and is characterized by strong negative loading of Al and moderate Mn and Zn, indicating some degree of continental influence, especially of Mn, which was present in the bottom sediments of Mejillones Bay. This agrees with the EF results, according to the crustal average. Factor 3 accounts for 10.1% of the total variance and shows a strong positive loading of Mn and moderate Zn, indicating an association between Zn with Mn oxides, which could explain, at least in part, the accumulation mechanism of this metal in bottom sediments.

4. Summary and conclusions

The geochemical and mineralogical compositions of surface marine sediments from the Mejillones Bay were

studied through the analysis of 36 samples. The spatial distribution of lithogenic minerals (quartz and feldspars) probably reflects the influence of hydrodynamic processes in the littoral zone and the input of aeolian material into the bay's central zone. The spatial distribution of calcium carbonate concentrations in these sediments can be explained by their association with abundant foraminifers. The high level of sedimentary organic matter can be explained by the strong influence of marine biological productivity associated with the local upwelling cell.

The high concentrations of heavy metals in the Mejillones Bay surface sediments may be associated with the flux of organic matter and the water column's persistent strong hypoxic environmental conditions. These metal concentrations are within the natural range for marine sediments and provide a base line for studying the impact of future industrial activities in this basin.

In spite of the relationship between mean grain size and metal concentration in Mejillones Bay, the main factors controlling the spatial distribution of the superficial sediments are probably (1) oceanic biological productivity and (2) the spatial distribution of the accumulation rates, which is most likely associated with the basin's hydrological conditions. The first factor controls the type and quality of the organic matter and the second the accumulation and preservation of sedimentary components.

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