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Redox conditions in a coastal zone of the Humboldt system (Mejillones, 23° S). Influence on the preservation of redox-sensitive metals

- Jorge Valdés^{ac}
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Abstract

The distribution of, Co, Mo, Zn, Ni, Cd, U, Cu, Mn, V, Al, Fe, Ti, Total Organic Carbon (TOC) and Total Sulfur (TS) was studied in surface sediments accumulated at the upper limit of the oxygen minimum zone in the northern Humboldt Current (Mejillones Bay), using samples taken during two cruises in May 2002 and October 2004. The time series of dissolved oxygen revealed a seasonal fluctuation of the upper limit of the oxygen minimum zone into the bay.

Similar bathymetric distribution curves of the metals measured in the two studied periods in the OMZ off northern Chile suggest that the factors responsible for this distribution are persistent over time. Authigenic metal content was calculated using lithogenic background by determining Metal/Al ratio from local aeolian dust, instead of average shale values, which are classically used for background correction. This more precise assessment allows examination of the source–sink relation of each metal in this coastal zone. Mo preserved in the bottom sediments originates from seawater and accumulates via particulate shuttle, whereas Cd is pre-concentrated in biodebris. Ni, Mn, V and Fe show a combined behavior.

Sulfate reduction is not the most important mechanism affecting metal accumulation in Mejillones Bay, probably due to the presence of *Thioploca*, which inhibits the pyrite formation and the metal-sulfide reaction.

We propose the use of the authigenic Mo/U ratio and a preliminary statistical model to reconstruct the levels of paleoxygenation in the subsurface waters of Mejillones Bay, by analyzing the same metals measured throughout the sedimentary sequences (and using the same statistical procedure), at least to identify extreme variations of the OMZ in this bay of northern Chile.

Keywords

- Redox sensitive metals;
- Oxygen minimum zone;
- Humboldt Current;
- Mejillones Bay;
- Chile

1. Introduction

Oxygen-poor marine environments are widely distributed in the oceans, mainly as a consequence of the mesoscale circulation of oxygen-poor waters and the high rates of organic matter decomposition (Diaz, 2001 and Helly and Levin, 2004). Environments with oxygen

concentrations permanently below 0.5 mL L^{-1} are called oxygen minimum zones (OMZs) and are distributed worldwide between 10 and 1300 m depth (Levin, 2003).

One such OMZ is located along the western border of South America and is part of the Humboldt Current System (HCS). This OMZ is associated with Equatorial Subsurface Waters that are transported southward by the Peru–Chile Subsurface Current. The extension and depth of the OMZ vary from north to south; it is more coastal and shallower toward the northern part of the HCS (Pizarro et al., 2002). The presence of upwelling centers generates high fluxes of organic matter that consumes dissolved oxygen as it decomposes, thereby enhancing the development of OMZs. Such is the case of Mejillones del Sur Bay (23° S), where high productivity rates (up to $1070 \text{ g C m}^{-2} \text{ y}^{-1}$); generate an OMZ beginning at approximately 50–60 m depth depending on the season of the year (Marín and Olivares, 1999 and Escribano and Hidalgo, 2000). These factors have favored the accumulation of diatomaceous sediments, rich in organic matter, and with minimal signs of bioturbation (Vargas et al., 2004; Valdés et al., 2009). As a result, the sedimentary records present a high potential for paleo-ocean-climatic reconstruction, (Ortlieb et al., 2000, Vargas et al., 2007, Valdés et al., 2008, Caniupán et al., 2009 and Díaz-Ochoa et al., 2011).

In the places where an OMZ intercepts the sea floor, the composition of the accumulated material changes noticeably due to suppression of the diagenetic processes mediated by dissolved oxygen (Levin, 2003 and Quiroga et al., 2005). This situation may have an important effects on organic and inorganic substances reaching the bottom sediments, because any changes (natural or anthropogenic) in the condition of subsurface oxygenation influence the deposition/remobilization balance, changing the concentration of substances in the sediments and in the water column.

Many metals are affected by the availability of oxygen in the water column, remaining in solution or precipitating as water-insoluble complexes, when the dissolved oxygen changes (Pailler et al., 2002). This feature makes metals excellent markers for oxygen deficient conditions, whether to assess current deposition environments or to reconstruct paleo-oxygenation conditions on different time scales (Morford et al., 2001 and Sainz and Ruiz, 2006). However, the use of metals as markers of past and present conditions requires understanding the geochemical response of these metals to different environmental parameters. Thus, OMZs constitute an attractive environment for studying the influence of bottom water oxygenation on the accumulation of metals in the sediments. This work describes the seasonal variability of the OMZ along the north coast of the Humboldt Current and explains the dynamics affecting the presence of a number of metals in the sediments deposited on and within the OMZ of this system.

2. Methodology

The distribution of oxygen in the water column was measured monthly with a CTD profiler (Sea Bird 19 plus) between April 2000 and October 2004 at an oceanographic station located in the center of Mejillones Bay (Fig. 1A).

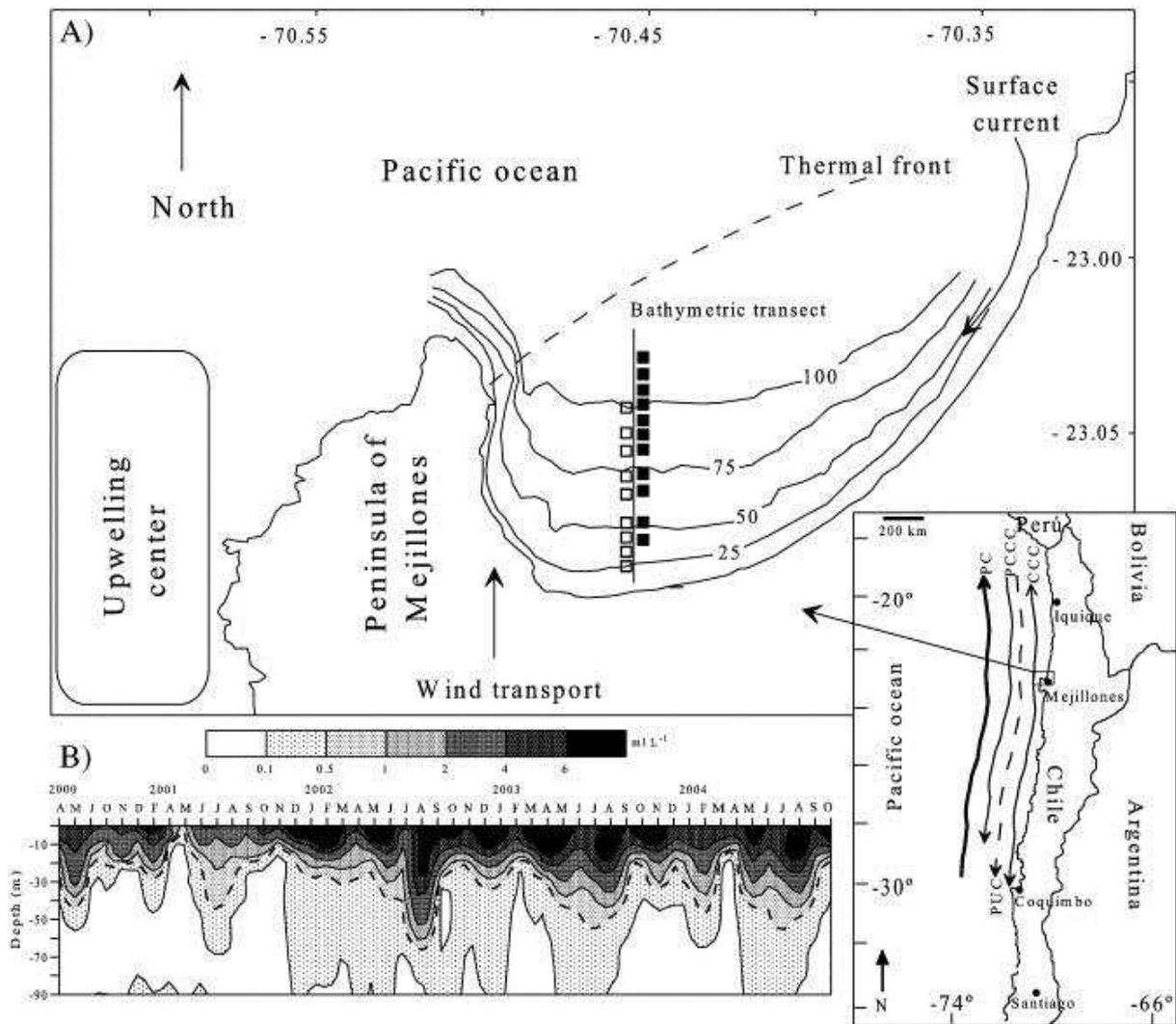


Fig. 1. : A) Mejillones del Sur Bay, its main oceanographic characteristics, and the sampling transect in the center of the bay are shown (White squares correspond to 2002 and black squares correspond to 2004). Bathymetry is showed each 25 m depth. PC is Peru Current, PCCC is Peru–Chile Counter Current, PUC is Peru Under Current, CCC is Chile Coastal Current. B) Monthly dissolved oxygen variability in the water column between 2000 and 2004 in Mejillones Bay. Dashed line represents the position of OMZ (oxygen $< 0.5 \text{ mL L}^{-1}$).

In May 2002 and October 2004, we collected eleven and nine samples, respectively, of surface sediments along a bathymetric transect between 20 and 120 m depth (Fig. 1). The sampling was done using a 225 cm^2 mini boxcore sampler. The surface layer of the sediment (0.5 cm) was removed from the samples with a plastic spatula. All samples were stored in plastic bags at a low temperature for transport to the laboratory. They were later dried at 40°C until reaching a constant weight. Finally, the samples were subjected to a sequence of attacks with acids in order to dissolve them and extract the metals. For this, we first used a combination of HNO_3 (65% Normapure) and HF (40% Normapure), placing the samples in an ultrasound bath for 10 m. After they cooled, the samples were placed on a heating plate at 150°C for 3 h. Later, a solution of HF (40% Normapure) and HClO_4 (70–72% Merck) was added. Finally, at the same temperature, an HNO_3 (65% Normapure) attack was added and

then repeated once in order to evaporate all the acid from the samples. The resulting material was brought to 25 mL with HNO₃.

Both major (Ti, Al, Fe) and minor elements (Mn and V) were measured with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES Liberty 200, Varian) using external calibration. Other minor elements (Co, Zn, Mo, Ni, Cu, U) were measured with Inductively Coupled Plasma Mass Spectrometry (ICP-MS Ultramass, Varian) using external calibration. The Cd content was determined in an atomic absorption spectrophotometer (Shimadzu 6300) using the flame technique. The analytical procedure was controlled by the routine replicate analysis, target material, and MESS-3 certified reference material (Canadian National Research Council). The analytical validation data to support the suitability and efficiency of the analytical techniques applied to determine the metal content in the sedimentary samples used herein, showed accuracy with a relative error that did not exceed 5% in any case.

The Total Organic Carbon (TOC), which expresses the quantity of organic content as a percentage of bulk sediment, was analyzed using Rock-Eval 6 programmed pyrolysis (Lafargue et al., 1998), while the Total Sulfur (TS) was determined using an induction furnace (LECO, USA), both expressed as percentage of total dry sediment.

Several methods of data analysis were used to evaluate and identify the factors responsible for the presence of these metals in the bottom sediments. The statistical analysis was performed using a one-way ANOVA applied to those metals measured in both campaigns. A Kolmogorov–Smirnov normality test was previously applied and the homogeneity of variance was examined with an F test. For cases that showed significant differences ($\alpha = 0.05$), the data were transformed by Log(x). Moreover, we applied a principal component analysis with the data obtained in 2002. Both analyses were performed with Minitab 14 computer software.

3. Results and discussion

3.1. The OMZ in a coastal upwelling environment off northern Chile

Off northern Chile, the OMZ is generally distributed between 100 and 500 m (Escribano et al., 2004). However, in environments with high biological productivity, the upper limit of the OMZ moves closer to the surface due to the consumption of oxygen caused by the decomposition of organic matter. In Mejillones Bay, the vertical distribution of oxygen measured between April 2000 and October 2004 reveals seasonal variability of the OMZ, which is shallower in summer and deeper in winter (Fig. 1B). This time showed that during 2000–2001, the water column was dominated by a low level of dissolved oxygen condition throughout the year. After that and until 2004, the OMZ experienced seasonal oxygen fluctuations (Fig. 1B). The first period could correspond to the development of a La Niña event in the area, as documented by Cantillanez et al. (2005) and Vega et al. (2005) through an analysis of the sea surface temperature along the coast of Mejillones Peninsula (outside the bay area, Fig. 1A). During El Niño events, the opposite situation occurs in the bay; the OMZ deepens beyond 80 m, leaving almost the entire bottom of the bay with unusually high dissolved oxygen levels (Escribano et al., 2004).

At 30 m depth, the oxygen content in the water column decreases considerably, generating poor oxygenation conditions throughout the study period. In normal years, the average OMZ begins at 40 m depth. These data show that, although the OMZ position fluctuates in time,

beyond 60 m depth the sediments generally accumulate under low dissolved oxygen conditions.

3.2. Lithogenic vs. authigenic fractions in Mejillones marine sediments

Table 1 shows the descriptive statistics of the metals measured in Mejillones Bay. In the case of Mo, Ni, Cd, V, Al, Mn and U (only in the case of 2004), the concentration found in the Mejillones surface sediments is a function of the depth of the water column (Fig. 2). The presence of these metals in this coastal environment is determined by the origin of each metal and the conditions prevailing in the depositional environment.

Table 1.

Descriptive statistics of the metals measured in Mejillones Bay. S.D. = standard deviation. Shale concentrations (average shales) according to Wedepohl, 1971 and Wedepohl, 1991 and aeolian dust of Pampa Mejillones (mean values), are also indicated. Concentration in mg kg^{-1} , except for Al, Fe and Ti which are in %.

Metal	Mean	Range	S.D.		Aeolian dust Pampa Mejillones	Average shales
Co	4.9	3.1–6.4	0.9	4.7		19.0
Mo	69.8	14.2–112.7	30.4	0.6		1.3
Ni	39.4	9.6–73.6	18.3	13.2		68.0
Cd	40.9	17.5–57.3	12.6	0.2		0.3
U	9.7	5.9–16.6	3.3	3.5		3.0
Cu	246.9	78.9–368.9	111.5	19.4		45.0
Mn	197.4	132.8–319.0	50.3	342.7		850.0
V	140.6	61.6–211.6	49.9	54.8		130.0
Zn	51.2	39.0–71.1	10.6	38.9		95.0
Al	2.4	1.5–4.9	0.9	5.8		8.9
Fe	1.5	0.8–1.8	0.4	1.3		4.7
Ti	0.2	0.1–0.2	0.0	0.2		0.5

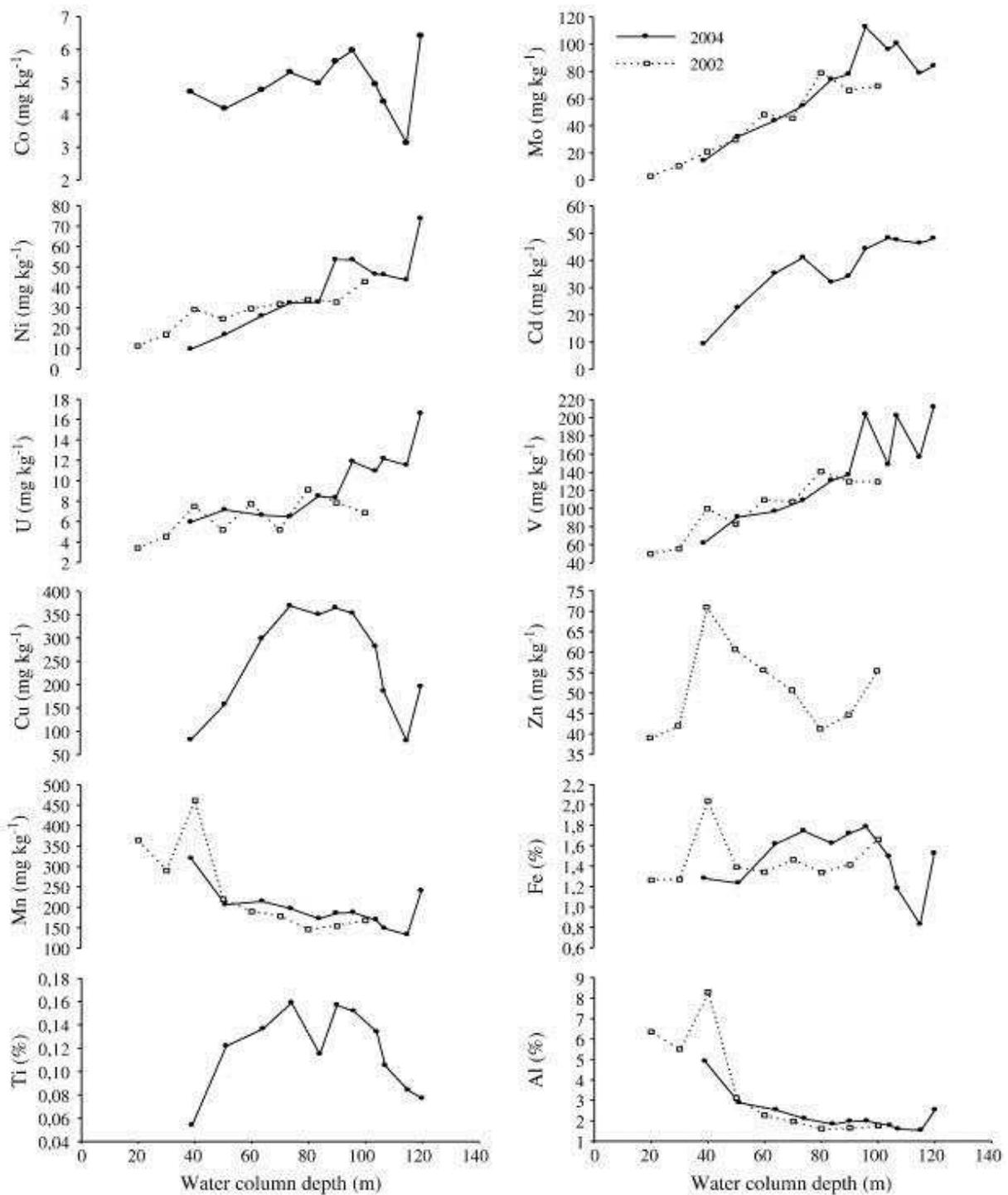


Fig. 2. : Concentrations of metals in the bottom sediments of Mejillones Bay in two sampling periods. White squares correspond to 2002 and black circles correspond to 2004.

The material present in the bottom sediments can be continental source (lithogenic) or marine source (non-lithogenic). The calculation of non-lithogenic content of several metals in marine sediments, using average shale and/or crust metal concentrations may result in negative values (Böning et al., 2005). This problem can be solved using local metal/Al ratios, representative of the principal source of metals to the marine environment under study, as was made by Böning et al. (2009) in central Chile marine sediments. The authors determined the Metal/Al ratio for the riverine suspended material collected close to the mouth of the Bio-Bio River, the

most important carrier of the particulate and dissolved matter entering the coastal zone, to study the trace elements signature of the marine sediments at 36° S (Chile).

In Mejillones Bay, the principal source of lithogenic material is “Pampa Mejillones” (P_{mej}) (Fig. 1A), where the southward wind is the exclusive carrier of particulate material entering to the coastal zone. This situation was corroborated by Flores et al. (2009) who found a direct relation between the horizontal particle flux toward Mejillones Bay and the regional south–southwest winds, especially during spring and summer. For this reason we collected suspended material in two aeolian traps located in “Pampa Mejillones” (Fig. 1A) (see details of methodology in Flores et al., 2009), in order to measure the Metal/Al ratio of this material ($Metal/Al_{P_{mej}}$) and use it to differentiate the authigenic and lithogenic metal contents preserved in marine sediments of Mejillones Bay.

The result shows that, with the exception of Mo and U, $Metal/Al_{P_{mej}}$ ratios are significantly lower than $Metal/Al_{shale}$ ratio (Table 2). These results are similar to those found by Böning et al. (2009) at 36° S, and confirm the idea that local Metal/Al ratio provides the best estimate of the lithogenic metal fraction of the coastal zone of Chile.

Table 2.

Metal/Al ratios of average shale (Wedepohl., 1991) and Pampa Mejillones materials (10^{-4}).

Metal/Al Average shale Pampa Mejillones

Ni/Al	7.65	2.54
Mo/Al	0.15	0.11
Cd/Al	0.02	0.04
V/Al	14.70	10.58
Mn/Al	95.40	66.15
Fe/Al	5309.34	2547.49
Ti/Al	0.08	0.03
Co/Al	2.15	0.91
Cu/Al	5.09	3.74
Zn/Al	10.80	7.52
U/Al	0.42	0.67

Mejillones Bay is located off the coast of the driest desert on Earth. As consequence of this, the contribution of lithogenic detritus to the bottom sediments is restricted to material transported by the wind. The flux of lithogenic detritus reaches up to $6 \text{ mg cm}^{-2} \text{ yr}^{-1}$, which represents no more than 20% of the bottom sediment (Vargas et al., 2007). The prevailing wind in Mejillones Bay is south–southwest, so the effect of wind transport on the material that is finally deposited on the bottom sediments should decrease toward the mouth of the bay.

Al is the most abundant lithogenic metal in the Earth's crust, being a primary constituent of aluminosilicates (Dean et al., 1997). Titanium is a relatively concentrated refractory metal in continental rocks (Yarincik et al., 2000a and Yarincik et al., 2000b). In Mejillones, the distribution of Al in the surface sediments has high values in the shallowest coastal zone (with

a maximum of 8.5%) and low values toward the deepest zone ($\approx 1.5\%$) (Fig. 2). In contrast, Ti showed low values at the extreme points of the bathymetric sampling transect ($\approx 0.05\%$) and high values in the middle zone (a maximum of 0.16% at 70 m deep) (Fig. 2). Nameroff et al. (2002) indicate that this metal tends to be enriched in the quartz fraction of marine sediments. In Mejillones, the quartz present in surface sediments is inversely related to the depth of the water column (Valdés et al., 2005); however, this pattern was not observed in the Ti distribution.

For most sedimentary deposits, Al is considered a good indicator of the aluminosilicate fraction of the sediments, because it is not affected by diagenesis (Morford and Emerson, 1999; Piper and Perkins, 2004). However, there are some instances when Al should not be used for normalization. For example, in marine sediments with a detrital fraction lower than 3–5% (which is not the case of Mejillones sediments) and a relative excess of aluminum compared to other detrital elemental proxies such as titanium, the excess of Al may have been scavenged as a hydroxide coating on biogenic particles (Yarincik et al., 2000a and Yarincik et al., 2000b; Kryc et al., 2003a), and could also result from authigenic clay-mineral formation (Timothy and Calvert, 1998). Nevertheless, such instances are fairly uncommon (Tribovillard et al., 2006).

For this reason, Al could be considered as markers of continental contributions (Brown et al., 2000). Thus, it is possible to use it in order to estimate the fraction of terrigenous material existing in the marine sediments according to the formula proposed by Murray and Leinen (1996):

$$\% \text{terrigenous} = (A_{\text{sample}} / Al_{\text{PMej}}) * 100$$

where “PMej” corresponds to the concentration of this metal in the suspended material of Pampa Mejillones. According to these results, the input of terrigenous material into the Mejillones Bay is about 44%, being the biogenic material the dominant fraction of the bottom sediments (Valdés et al., 2004; Valdés et al., 2009). The continental matter present in the Mejillones marine sediments is mainly quartz and feldspars, whose distribution (associated with bathymetry) is high in shallow areas and decreases toward deeper zones (Valdés et al., 2005). These results suggest that the aeolian contribution, favored by the southward winds, and the coastal erosion are factors that mainly influence the sedimentary composition of the littoral zone and they have less influence toward the pelagic zone (Fig. 3A).

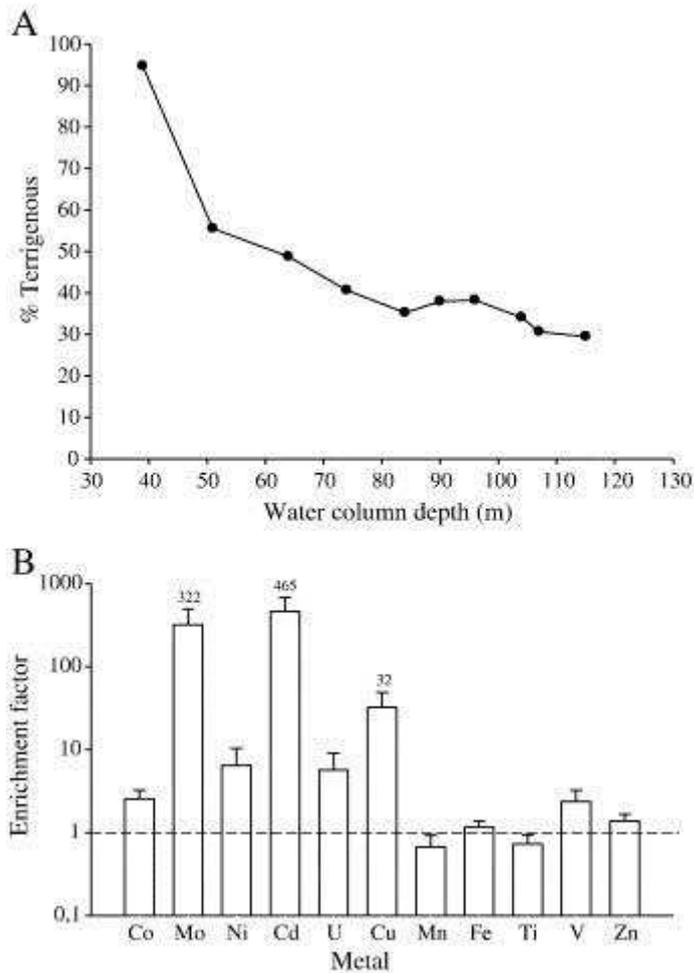


Fig. 3. : A) Content of terrigenous material in marine sediments of Mejillones calculated according to formula (1). B) Enrichment factor of metals analyzed in surface sediments of Mejillones Bay, calculated according to formula (2).

3.3. Trace metal source/sink relations in Mejillones Bay

Despite the proportion of terrigenous material in the marine sediments of Mejillones, which is less than 50%, the presence of metals in this bay could possibly be explained by a variable proportion of lithogenic material that can generate a dilution effect of the trace elements in the sediments. Therefore, we calculated the Enrichment Factor as a way to assess the proportion of metal that is in excess with respect to the lithogenic background (Pampa Mejillones). For this, we applied the formula described by Tribovillard et al. (2006):

equation(2)

$$EF = \frac{(X/Al)_{\text{sample}}}{(X/Al)_{P_{\text{Mej}}}}$$

where X is the metal analyzed and the P_{Mej} values are given in Table 1. If the EF is higher than 1, then the metal analyzed is enriched with respect to the base values. If the EF is less

than 1, then the metal is less abundant with respect to the base values. In general, values close to 1 are expected to identify a lithogenic source. The marine sediments of Mejillones show a high enrichment in Cd, Cu and Mo ($EF > 10$), a slight enrichment of Ni, U, Co, V and Zn, depletion in Mn and Ti, and a background level in case of Fe (Fig. 3B). These results are higher than reported by Böning et al. (2009) at 36° S (Chile). Particularly, the EF of Cd and Mo in Mejillones sediments is very high, close to that found in Peru coastal zone Böning et al. (2004). The Cd concentration measured in Mejillones sediments significantly exceeds reports for other coastal areas (Morford and Emerson, 1999, Bostick et al., 2000, Russell and Morford, 2001 and Morford et al., 2001). However, the concentrations measured in this study are within the ranges reported in previous works using different measurement techniques (Valdés et al., 2003, Valdés et al., 2005 and Valdés, 2004). The high biological productivity, the high biogenic flux through the water column and the low oxygen levels at the bottom (possibly anoxic sediments) that characterize this bay, are factors that explain the high content of Cd in these marine sediments.

We used the $metal/Al_{PMej}$ to calculate the non-lithogenic metal content in marine sediment of Mejillones Bay, according to Böning et al. (2009)

equation(3)

$$Metal_{excess} = metal_{sample} - (metal/Al_{PMej} * Al_{sample}).$$

Any significant metal excess in sediments must be related to metal availability in seawater or metal preconcentration in plankton/particles and associated preservation processes (Böning et al., 2004). In order to test whether trace metals are related to availability in seawater or preconcentration in biodebris we plotted some $metal_{excess}$ contents of sediments of Mejillones (this study) vs. seawater contents reported by Valdés et al. (2008) for this same bay. We use the model proposed by Böning et al., 2004 and Böning et al., 2009 for metals accumulated within and below the OMZ in the Peruvian, Namibian and Chilean coastal zone, which separates metals related to a seawater source from those related to a biodebris source. The authors use this model to test whether excess TE contents are related to TE availability in seawater or TE preconcentration in biodebris, plotting average excess TE contents of Chilean upwelling sediments (ChileXS) vs. seawater concentrations. In case of Mejillones Bay, the results show that Mo clearly displays a seawater source, whereas Cd is related to a biodebris source. In contrast, V, Ni and Mn are related to both sources of metals in Mejillones Bay (Fig. 4). Fe has shown a different behavior, and escape to the model proposed by Böning et al. (2009), probably due to this metal is very close to the background level, as shown by the Enrichment Factor (Fig. 3B). The Mo behavior is similar those exhibited in central Chile (Böning et al., 2009) and Peru coastal areas (Böning et al., 2004), which suggests that the seawater source of this metal is a characteristic of coastal bottom sediment of the entire Humboldt system, whereas the biodebris source of Cd is more evident only for the northern section of the Humboldt system (Böning et al., 2009).

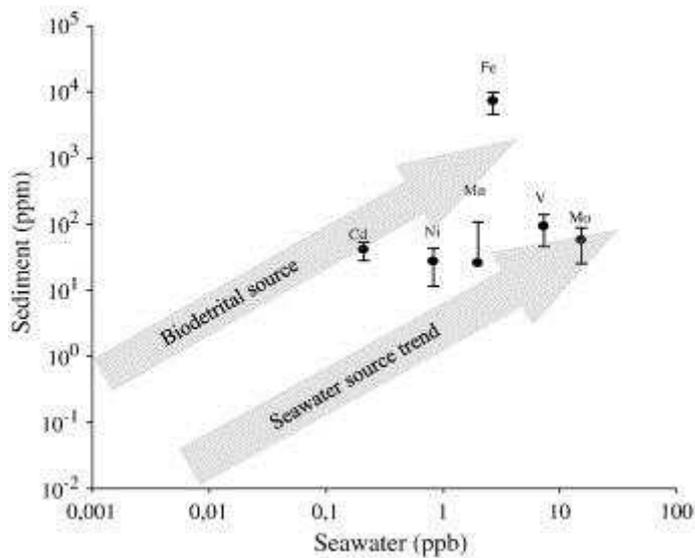


Fig. 4. : Average metal concentration in seawaters (Valdés et al., 2008) versus non-lithogenic metal (according formula 3) in Mejillones Bay. Arrows represent seawater and biodeutral source, defined by Böning et al., 2004 and Böning et al., 2009.

3.4. Factors influencing the metal distribution in Mejillones Bay

In most cases, the metal concentrations showed a gradient associated with the bathymetry of the bay (Fig. 2). The concentrations of Mo, Ni, Cd, U, and V increased toward the deepest zone, whereas Mn and Al showed an opposite gradient. In all cases, these trends were similar in both sampling periods, suggesting a constant behavior of the factors that determine the accumulation of metals in the bottom sediments.

In order to evaluate the differences in the content of metals accumulated within and outside of the OMZ of the bay, we applied a one-way analysis of variance (ANOVA) to Enrichment Factor of those metals measured in both campaigns. For this, the limit of the OMZ (dissolved oxygen = 0.5 mL L^{-1}) was established according to the time series analyzed herein. The results indicate that the Mo, Ni, U, V and Mn concentrations collected above the OMZ differ significantly from those collected within the OMZ. In the first four cases, the concentrations were significantly higher within the OMZ whereas, in the other case, the concentration was lower. Only Fe showed no significant differences between both environments (Table 3).

Table 3.

One-way ANOVA test for Enrichment Factor of metals measured in both campaigns over and within the Mejillones Bay OMZ. Significant values are highlighted ($p < 0.05$).

	Mo	Ni	U	Mn	V	Fe
<i>F</i>	16.15	18.67	15.01	60.81	10.93	0.00
<i>p</i>	0.001	0.000	0.001	0.000	0.004	0.967

The metals present in the marine environment can reach the bottom sediments by adsorption onto the particles that fall through the water column and by direct precipitation of dissolved chemical forms in the seawater (Tribovillard et al., 2006). Highly biologically productive environments generate an elevated flux of particles toward the bottom sediments that increases the scavenging of chemicals (including metals) present in the water column. The Punta Angamos upwelling center (Fig. 1A) and the development of upwelling shadows within the bay (Marín et al., 2003) generate high rates of biological productivity in surface waters, with values reaching $1070 \text{ g C m}^{-2} \text{ y}^{-1}$ (Marín et al., 1993). Moreover, the thermal front developed at the mouth of the bay (Fig. 1A) as a result of the upwelling shadow (Marín et al., 2003) increases the stability and retains the particles within this coastal system, generating a flux of biogenic material that is finally deposited in the bay. This flux not only scavenges the metals present in the water, but also carries the metals incorporated in the organic remains, several of which (i.e. Cd, Cu, Ni, Fe, Zn) are used by primary producers as micronutrients essential for various physiological processes (Billler and Bruland, 2013). On the other hand, all the metals analyzed in this study except for Al and Ti are regarded as redox-sensitive, meaning that the oxygenation level of the sea environment affects the exchange of these metals between the sediments and the water column (Morford et al., 2001 and Sainz and Ruiz, 2006). Mn and Fe tend to accumulate in the bottom sediments under oxic conditions, whereas the other metals accumulate in the sediments under dysoxic/anoxic conditions (Tribovillard et al., 2006).

At the water–sediment interface, metals are exchanged through a redox gradient that depends on the penetration of oxygen, the availability of free sulfides, and the mass accumulation rate (MAR) (Böning et al., 2009). The TOC contents in the Mejillones sediments are high and follow the same tendency as the metals were analyzed, while the TS contents are very low (but have a tendency similar to that of the metals). As results, the TS–TOC ratio is far below that which characterizes marine sediments (Fig. 5) (Bernier and Raiswell, 1983). Even so, in Mejillones, Valdés et al. (2004) showed that sulfate reduction, despite its low intensity, is a function of the metabolizable organic matter that reaches the marine floor. Although the presence of pyrite in the sediments of Mejillones (Valdés et al., 2004) indicates the existence of a co-precipitation of metals due to the reaction of Fe with free sulfide (Huerta-Diaz and Morse, 1992), the lack of correlation between the metals recorded in the sediments of this bay and the Sulfate Reduction Index (SRI), which indicates the relationship between metabolizable organic matter and sulfate reduction (Betrand and Lallier-Verges, 1993) (Fig. 6), suggests that pyrite formation is not the primary mechanism explaining the exchange of metals at the water–sediment interface. It is possible that the abundant presence of the macrobacterium *Thioploca* in this area of the Chilean coast (Gallardo, 1977) inhibits the formation of pyrite and/or metal sulfide due to the macrobacterium's capacity to reoxidize free sulfides (Ferdelman et al., 1997; Böning et al., 2009).

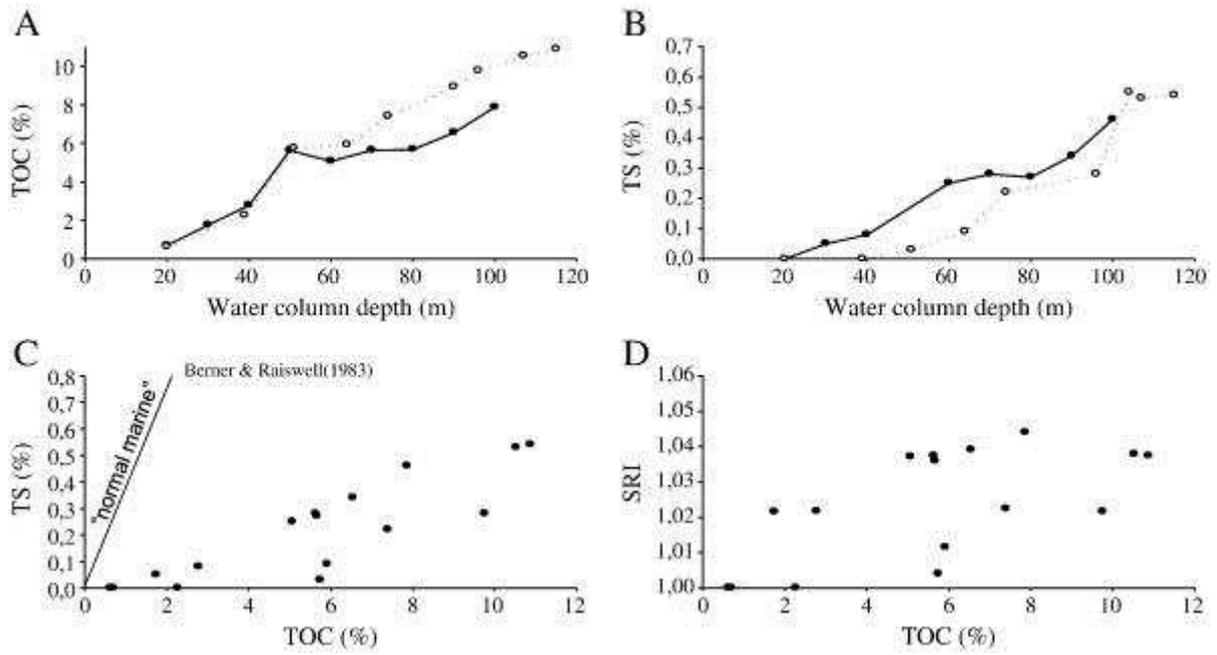


Fig. 5.

Total Organic Carbon (A) and Total Sulfur (B) vs. water depth; TS (C) and SRI (D) vs. TOC in marine sediments of Mejillones Bay. SRI calculated according Bertrand and Lallier-Verges (1993). See text for details.

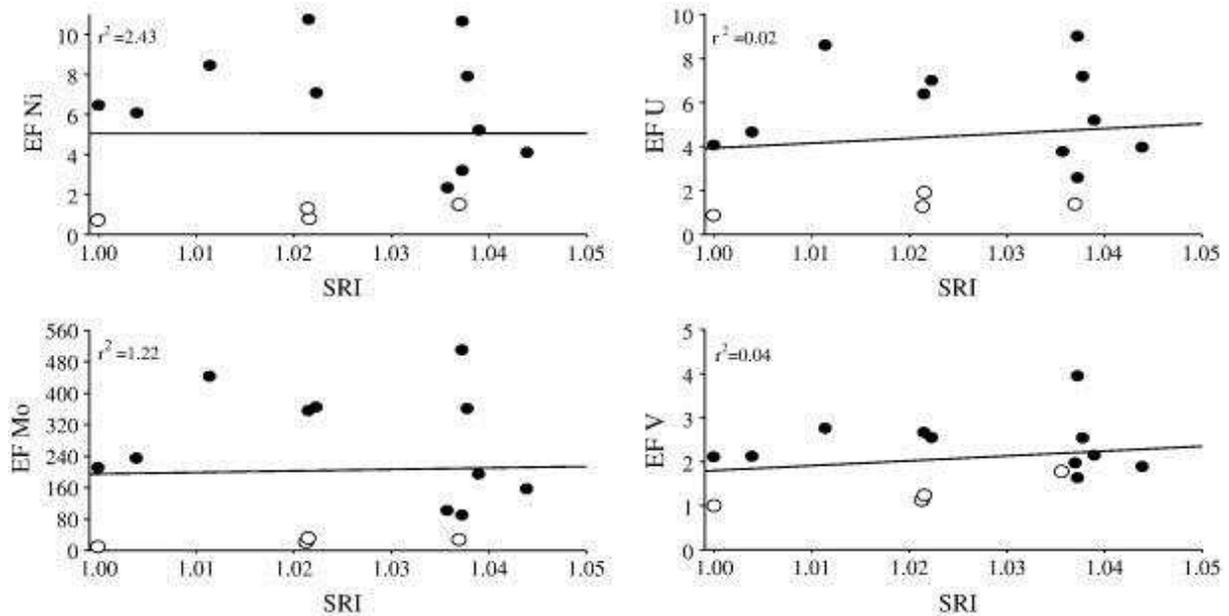


Fig. 6.

SRI (Sulfate Reduction Index, according Bertrand and Lallier-Verges, 1993) vs. some metals (Enrichment Factor) in Mejillones Bay. White circles correspond to samples outside the OMZ, and black circles correspond to samples within the OMZ.

In any case, once the metals have been incorporated into the sediment, they may return to the water column through diagenetic processes that release the metals that have been adsorbed and incorporated by biogenic material into the interstitial water, allowing them to mobilize and escape into the water column. Furthermore, changes in the oxygenation levels can re-dissolve these metals, returning them to the water column (Nameroff et al., 2002 and Böning et al., 2005).

3.5. Trace metal sediment contents as proxies of redox conditions in Mejillones Bay

The accumulation of certain trace metals in sediments is directly controlled by redox conditions through either change in redox state and/or speciation (McKay et al., 2007). In particular, redox-sensitive and/or sulfide-forming elements are commonly used as paleoenvironmental proxies because they may become strongly enriched in sediments accumulated under low-oxygen and/or sulfidic water mass condition (Tribovillard et al., 2011).

Discerning redox conditions typically means determining whether conditions are oxidizing or reducing; in this paper we shall refer to the following redox gradation: oxic ($O_2 > 2 \text{ mL L}^{-1}$)–suboxic ($2 \text{ mL L}^{-1} < O_2 < 0.2 \text{ mL L}^{-1}$)–anoxic ($O_2 < 0.2 \text{ mL L}^{-1}$) (Tyson and Pearson, 1991). Anoxic conditions may be nonsulfidic or sulfidic; in the latter case, they are also called euxinic when hydrogen sulfide occurs within the water column (Tribovillard et al., 2006).

Bottom water oxygen concentration in sediments of Mejillones Bay decrease rapidly toward the deeper zone, where concentrations less than 0.3 mL L^{-1} (even $< 0.2 \text{ mL L}^{-1}$) prevail year round (Fig. 1B). In a previous study, Valdés et al. (2009) demonstrated that the composition and structure of sediments display a spatial trend that is in agreement with the principal zones of bottom oxygenation (annual mean condition) identified in this bay. The authors identified two principal zones in the bay; the oxic coastal zone ($O_2 > 1 \text{ mL L}^{-1}$) where most of the metabolizable organic matter is degraded within the water-column and/or in the sediment–water interface, and the dysoxic hemipelagic zone ($0.1 < \text{mL L}^{-1}$), located deeper than 65 m, where a better preservation of metabolizable and non-metabolizable compounds happens.

A low oxygen concentration, combined with the high organic carbon content of the sediments, probably creates an anoxic condition below the sediment–water interface. This situation may explain the high metal contents and their correlation with the depth, which suggests that some metals could be used as proxies of redox conditions of present and past environments of this coastal system.

3.5.1. A statistical approach

To determinate the relation between the content of metals in surface sediments and the factors that influence their presence in bottom sediments of Mejillones Bay, a Principal Component Analysis (PCA) was applied.

Principal Components Analysis (PCA) is an exploratory, multivariate, statistical technique that can be used to examine data variability. It is frequently applied to environmental data, where complex inter-relationships between variables are difficult to identify and visualize (Reid and Spencer, 2009). Multivariate techniques can consider a number of factors which control data variability simultaneously (Boruvka et al., 2005). In simple terms PCA is a data reduction technique whereby new variables (principal components or factors) are calculated

from linear combinations of the original variables. The first principal component, or factor, accounts for the greatest variability in the data, and there can be an infinite number of new factors with each accounting for less data variability than the previous (Webster, 2001). Factor loadings are correlation coefficients between the original variables and factors and are frequently used in the literature to investigate the processes that control data variability. Factor scores indicate how strongly individual samples are associated with each of the factors, and thus can be used to investigate similarity between samples, where samples with a similar composition will have similar scores and may therefore have similar contaminant sources and/or behavior.

Environmental applications of PCA are varied and widespread and the technique has been applied to surface and around waters (e.g. Chen et al., 2007 and Kuppusamy and Grirdhar, 2006), soils (e.g. Boruvka et al., 2005 and Zhang, 2006), sediments (e.g. Spencer, 2002 and Reid and Spencer, 2009) and biota (e.g. Yawei et al., 2005).

This analysis, conducted with the metals measured in both years, in the case of Mejillones Bay, indicates that the first two components explain 86.4% of the total variance, showing three groups of variables. The first group includes Al and Mn, while the second group includes Ni, Mo, V, and U. The position of these both groups on the PC1 axis suggests the influence of the deep of water column and the availability of dissolved oxygen of bottom waters on the metals preserved in the bay's sediments. Al and Mn come from continental contributions, and they are characterized by lower concentrations with greater water depths (Fig. 2). By other hand, Ni, Mo, V and U increase their content as the depth increases (and, therefore, the bottom oxygen decreases) (Fig. 2). Thus, these metals exhibit a behavior typical of redox-sensitive metals. The third group includes only Fe; this metal did not show any tendency that would allow us to identify the degree of influence of the bottom oxygenation on its concentrations. This behavior suggests that some other mechanisms must explain its presence and bathymetric distribution in the sediments of Mejillones Bay.

The data suggest that the first component of this analysis (PC1, with 65.2% of the variance) is related to the bathymetric distribution of the samples, which is equivalent to the dissolved oxygen gradient in the waters adjacent to the marine floor. Therefore, and considering the weight of PC1, it is possible to establish a correlation between both variables. Thus, when graphing this PC1 versus dissolved oxygen, we can see a significant exponential fit of the data with ($r = 0.71$) and two groups of points, one of them representing samples collected in the shallow zone of the bay that do not fall on the curve and another representing samples collected in the deeper zone of the bay, where anoxic conditions prevail (Fig. 7). Because PC1 combines the effect that the level of oxygenation has on all the metals measured in the bottom sediments, a PC1 derived from the analysis of metals in sediments core can be used as a predictive model (using the equation of the curve included in Fig. 7) for determining the oxygenation level of the subsurface waters in the bay, at least within the range of data effectively measured herein and in which the curve presents a better fit (dissolved oxygen $< 0.5 \text{ mL L}^{-1}$). Therefore, values of PC1 that range from -3 to 3 and were derived from the analysis of the metals in sediment cores could indicate conditions of deposition within the OMZ. This preliminary model suggests that it is feasible to reconstruct the levels of paleoxygenation in the subsurface waters of Mejillones Bay by analyzing the same metals measured throughout the sedimentary sequences (and using the same statistical procedure), at least to identify extreme variations of the OMZ in this bay of northern Chile.

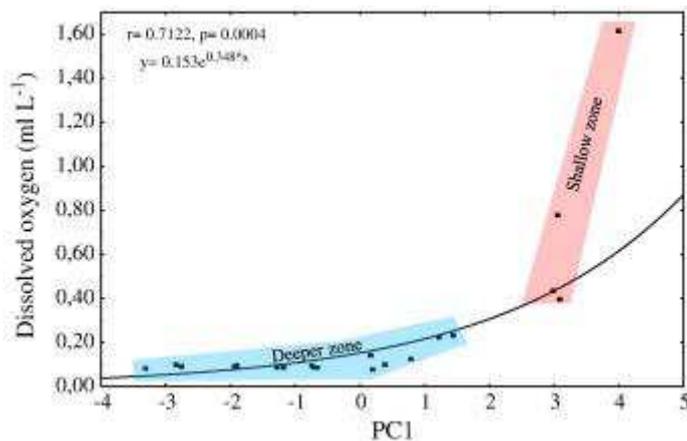


Fig. 7. : PC1 versus dissolved oxygen in Mejillones Bay. PC1 generated with metals measured in both sampling years. Mathematical model may be used to reconstruct paleoxygenation of bottom waters in this bay (see text).

3.5.2. Mo-U relationship

In the marine environment, Mo is a conservative metal found in the form of Mo (VI). The conservative molybdate anion can transition to a particle reactive thiomolybdate anion (MoO_4^{2-} to $\text{MoO}_4-x\text{Sx}^{2-}$, $x = 1-4$) in the presence of H_2S (Helz et al., 1996). Thiomolybdates are effectively scavenged from the aqueous phase (Helz et al., 2004). In the sediments, this metal is related to the diagenesis of Mn (Morford and Emerson, 1999). Many studies have shown that anoxic sediments are rich in Mo (1993; Morford and Emerson, 1999, Adelson et al., 2001 and McManus et al., 2006). In Mejillones, the Mo ranged from 0 mg kg^{-1} at 20 m depth (dissolved oxygen ca. 1 mL L^{-1}) to more than 100 mg kg^{-1} at 100 m depth (dissolved oxygen $< 0.1 \text{ mL L}^{-1}$) (Figs. 1A and 2). These values are higher than others record along the southern Chilean coast (41° and 36°) influenced by the OMZ (McManus et al., 2006 and Böning et al., 2005), but similar to previous measurements performed in Mejillones Bay (Valdés, 2004).

The stable form of uranium in oxygenated waters is U(VI). The main process for removing this metal from the water column is the diffusion of $(\text{UO}_2(\text{CO}_3)_3)^{4-}$ to the sediments (Morford and Emerson, 1999 and Morford et al., 2001). In sediments, uranium can be adsorbed or precipitated as $(\text{U(VI)O}_2)_{(s)}$ at the Fe remobilization limit (Crusius et al., 1996). The sediments deposited under oxygen-poor waters tend to accumulate U either by direct diffusion from the sediment-water interface or by the effect of the biogenic flux (Morford et al., 2001). Mejillones sediments have U concentrations of between 3 mg kg^{-1} at 20 m depth (dissolved oxygen ca. 1 mL L^{-1}) and 16 mg kg^{-1} at 120 m depth (dissolved oxygen $< 0.1 \text{ mL L}^{-1}$). These values are higher than those reported by McManus et al. (2006) for the OMZ sediments in southern Chile (41° S). The distribution of U in the sediments of Mejillones shows a gentle slope up to 80 m that then increases strongly toward the deepest zone (Fig. 3). Tribovillard et al. (2006) suggest that the enrichment of U in marine sediments strongly depends on the oxygen concentration at the sediment-water interface. This relation would explain why, in Mejillones, the concentration of U tends to increase significantly at depths greater than 80 m, where the bottom waters are dysoxic (and the sediments probably anoxic) all year round (Fig. 1A).

In oxic marine sediments both U and Mo are released from solid phase by bioturbation of the sediment, and only approximately 20 to 70% of the metals delivered to the sediment are retained in authigenic phases (Morford et al., 2001). On the other hand, in anoxic marine sediments there is no evidence of post-depositional remobilization of U and Mo (Morford et al., 2001). Although post-depositional redistribution of Mo and U has the capacity to alter the primary depositional concentration and concentration ratios of these metals, different studies provide no evidence to suggest any systematic differences in their remobilization potential (Colley and Thomson, 1985; Thomson et al., 1995; McManus et al., 2006 and Algeo and Tribovillard, 2009).

In the marine environment both metals are present in low concentrations in plankton, exhibit a conservative behavior under oxic conditions, and have residence times of 450 ky for U and 780 ky for Mo (Algeo and Tribovillard, 2009). By these reasons both metals have nearly uniform concentrations in the ocean, with a seawater Mo/U molar ratio of 7.53 ± 0.25 in the Pacific Ocean (Millero, 1996). This ratio has been used by Algeo and Tribovillard (2009) to characterize the modern redox condition of several marine environments of the eastern tropical Pacific. The authors indicate that in environments with suboxic bottom waters the U_{auth} enrichment tends to exceed that of Mo_{auth} resulting in sediments $(Mo/U)_{auth}$ ratios less than that of seawaters, whereas in environments with bottom waters increasingly reducing and at least occasionally sulfidic, the rate of accumulation of Mo_{auth} increases relative to that U_{auth} , resulting in sediment $(Mo/U)_{auth}$ ratios equal or higher than that of seawater. Those trends are characteristics of unrestricted marine setting, like the Mexican Margin, the Peru shelf and others zones of the eastern tropical Pacific (Algeo and Tribovillard, 2009). Bottom sediments with strong enrichment of Mo_{auth} relative to U_{auth} reflect the operation of a metal-oxyhydroxide particulate shuttle that increases the export of Mo to the sediments. As a consequence of this, the $(Mo/U)_{auth}$ ratios are generally much greater (3 to 10 times than SW molar ratio), as observed in the Cariaco Basin (Tribovillard et al., 2011).

Sediments of Mejillones Bay exhibit a well-defined Mo_{auth} – U_{auth} covariation trend (Fig. 8), as reported in other coastal zones of the eastern Pacific characterized by low-oxygen conditions in subsurface waters (Algeo and Tribovillard, 2009). Local covariance trends of authigenic Molybdenum (Mo_{auth}) and Uranium (U_{auth}) and their respective enrichment factors (EFs) define a uniform $(Mo/U)_{auth}$ ratio of ≈ 2 –3 times the Mo/U molar ratio of seawater. Mo_{auth} is enriched relatively to U_{auth} by a factor of 8:1 to 11:1, suggesting accelerated transport of Mo to the seafloor by a particulate (Mn) transport mechanism that would have required frequent fluctuations between suboxic and moderately sulfidic water column conditions. This interpretation is supported by results of the metal source model of Bóning et al. (2004) that indicate a seawater origin to Mo preserved in bottom sediments of Mejillones Bay (Fig. 4). The $(Mo/U)_{auth}$ ratio defines a trend roughly parallel to the seawater ratio, but ranging between 2 and 22, and most of the samples show values 3 times higher than the seawater molar ratio (Fig. 8), indicating that Mo_{auth} enrichment is higher than U_{auth} enrichment. As shown in the case of the statistical approach (Fig. 7) these results display a trend characterized by samples (red circles in Fig. 8) representing the shallow zone of the bay (more ventilated) and with $(Mo/U)_{auth}$ close to the seawater ratio, and the rest of the samples representing the deeper zone (anoxic condition) and with $(Mo/U)_{auth}$ about 3 times higher than the seawater ratio. The fact that the $(Mo/U)_{auth}$ ratio correlates with the water depth in Mejillones, suggests that the bathymetric transect studied in this bay represents the evolution of suboxic benthic redox conditions prevailing in the shallow zone, toward anoxic (and eventually sulfidic) condition prevailing in the deeper zone, which is characteristic of unrestricted marine settings (Tribovillard et al., 2011). This interpretation agrees with those of Valdés et al. (2009)

concerning the spatial distribution of organic matter in bottom sediments of this bay. Also, this trend is similar to those reported for continental sediments of Peru (Algeo and Tribovillard, 2009), indicating that sediment–water interface of Mejillones Bay has anoxic conditions and suggesting that the $(\text{Mo}/\text{U})_{\text{auth}}$ ratio is a potential proxy to study the paleoredox evolution of bottom environment of this coastal zone of the Humboldt system.

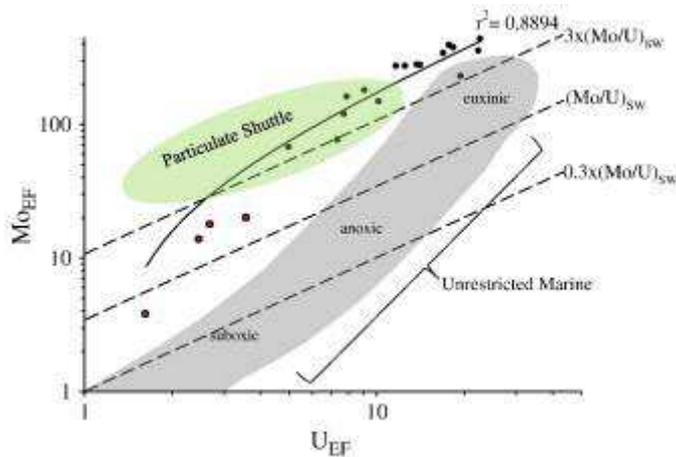


Fig. 8. : Mo_{EF} versus U_{EF} for Mejillones Bay. Solid Line shows main trend in dataset and dashed line shows Mo/U molar ratios equal to the seawater value ($1 \times \text{SW}$) and to fractions thereof ($0.3 \times \text{SW}$, $3 \times \text{SW}$). Gray and green zones represent the principal redox conditions, and Mo and U accumulations mechanisms (see texts for details) (Adapted from Tribovillard et al., 2011). Red circles correspond to samples outside the OMZ and black circles correspond to samples within the OMZ.

4. Conclusions

In Mejillones Bay, the OMZ begins at 40–60 m water depth, and as a consequence of this situation, most of the bottom sediments are under the influence of oxygen-depleted waters.

The lithogenic fraction of metals found in marine sediments of this bay is best evaluated using local Metal/Al ratio (Aeolian dust of Pampa Mejillones) than the classic contents of geological formations such as shales or continental crust.

The similarity in the bathymetric distribution curves of the metals measured in the OMZ of northern Chile suggests that the factors responsible for this distribution are persistent over time.

Mo preserved in bottom sediments originates from seawater and accumulates via particulate shuttle across the sediment–water interface, whereas Cd is pre-concentrated in biodebris. The other metals show a combined behavior. Geochemical reactions occurring in the interstitial water release these metals and, depending on the oxygenation conditions, these metals can redissolve and return to the water column or form insoluble compounds that are preserved in the bottom sediments.

Sulfate reduction is not the most important mechanism on metal accumulation in Mejillones Bay, probably due to the presence of *Thioploca*, which inhibits pyrite formation and metal-sulfide reactions.

We propose the use of the $(\text{Mo}/\text{U})_{\text{auth}}$ ratio and a preliminary statistical model to reconstruct the levels of paleoxygenation in the subsurface waters of Mejillones Bay, by analyzing the same metals throughout the sedimentary sequences (and using the same statistical procedure), at least to identify extreme variations of the OMZ in this bay of northern Chile.

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