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Metals content in surface waters of an upwelling system of the northern Humboldt Current (Mejillones Bay, Chile)

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Abstract

Physical–chemical parameters (temperature, salinity, dissolved oxygen, nutrients, and chlorophyll concentration) of surface waters were used to evaluate the influence of biological and physical processes over the metal concentrations (Cd, Ni, V, Mo, Mn, and Fe) in different periods of a normal annual cycle (June 2002 and April 2003), in Mejillones Bay (23° S), one of northern Chile's strongest upwelling cells. Two points were sampled every 2 months, but statistical analysis of these parameters did not show any spatial differences in surface water composition (annual average) in this bay. The order of total and dissolved metals by abundance (annual mean) in the Mejillones Bay surface waters during the sampling period was Cd<Ni<Mn<Fe<V<Mo.

The surface concentration of metals does not appear to be explained by anthropogenic inputs (at least not during the year of this work), and variability observed in this study appears to be natural. The lack of correlation between physical–chemical parameters and metals could indicate a more complex combination of factors acting on surface concentrations. Moreover, the mixture of water masses and the Oxygen Minimum Zone which characterizes the Mejillones bay should have an important influence on surface distribution of trace metals and can explain the high temporal variability observed in most of the metals analyzed in this work. A two-box conceptual model is proposed to suggest possible influences on metals in surface waters of this coastal ecosystem.

Keywords: Trace metals; Upwelling; Humboldt system; Marine surface water

1. Introduction

The continental margin is a boundary where several sources may affect the chemical characteristics of the water and bring contaminating materials. Of these, the most important are continental sources (atmospheric transport, river runoff), marine (upwelling), and diagenetic exchanges at the water–sediment interface. These sources provide organic and inorganic materials that play an important role in biogeochemical cycles. For example, nutrients and trace metals are essential to the ecosystem, but should be carefully monitored because they are potential contaminants in the coastal environment (Cotte-Krief et al., 2000). In both cases, and in the

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absence of contamination processes, upwelling is the principal source of surface nutrients and trace metals from the deep ocean.

In general, all metals present in marine waters are in dissolved and particulate forms. Many of these trace metals are classified as micronutrients because they are essential for phytoplankton growth. Most are components of the enzyme system, which catalyzes important biochemical reactions such as glycolysis, photosynthesis, and protein metabolism. Partitioning between dissolved and particulate forms of trace metals depends on the physical and chemical conditions of the marine environment and the nature of each metal (Libes, 1992). Moreover, any metal can assume various chemical forms, being able to form a wide variety of ions, compounds, or complexes, or being associated with different mineralogical or organic phases (Grotti et al., 2001). The concentration of these metals can be variable as a consequence of changing inputs and/or seasonal effects involving biological, geochemical, and physical interactions (Hatje et al., 2001).

Knowledge of the biogeochemical cycle of trace metals in coastal environments is needed in order to identify pollution sources and to explore biological and dynamical processes.

This paper aims to study the influence of biological and physical processes over the some metals content in different periods of a normal annual cycle, in surface waters of one the most productive coastal systems of northern Chile.

1.1. Regional setting

The Humboldt Current is one of the most productive systems in the world. In the northern section of this system, many permanent upwelling cells support important pelagic fisheries (Strub et al., 1998). Punta Angamos and Mejillones Bay (Fig. 1) form the most productive upwelling system of northern Chile. Many studies concerning biological and physical characteristics of this system have been developed in recent years, improving our understanding about their response to ocean-climatic variability, principally, El Niño events (Escribano et al., 1998; Gonzalez et al., 1998, 2000; Iriarte et al., 2000; Sobarzo and Figueroa, 2001; Ulloa et al., 2001; Pizarro et al., 2002; Gonzalez et al., 2004; Iriarte and Gonzalez, 2004). This area borders one of the world's most arid regions, and continental input to the ocean is restricted to minor atmospheric transport of lithogenic particles (Vargas et al., 2004). For this reason, upwelling seems to be one of the most important processes influencing the chemical composition of the surface waters. Mejillones Bay is a hotspot of biological productivity. This bay is considered an upwelling shadow system (UPS), which responds with more intense biological productivity due to its internal thermal stability (Marín and Olivares, 1999; Marín et al., 2003). Studies of the Mejillones Bay have been, principally, focused on the structure and composition of marine sediments and their potential for paleo-ocean-climatic reconstructions of the last millennia (Ortlieb et al., 2000;

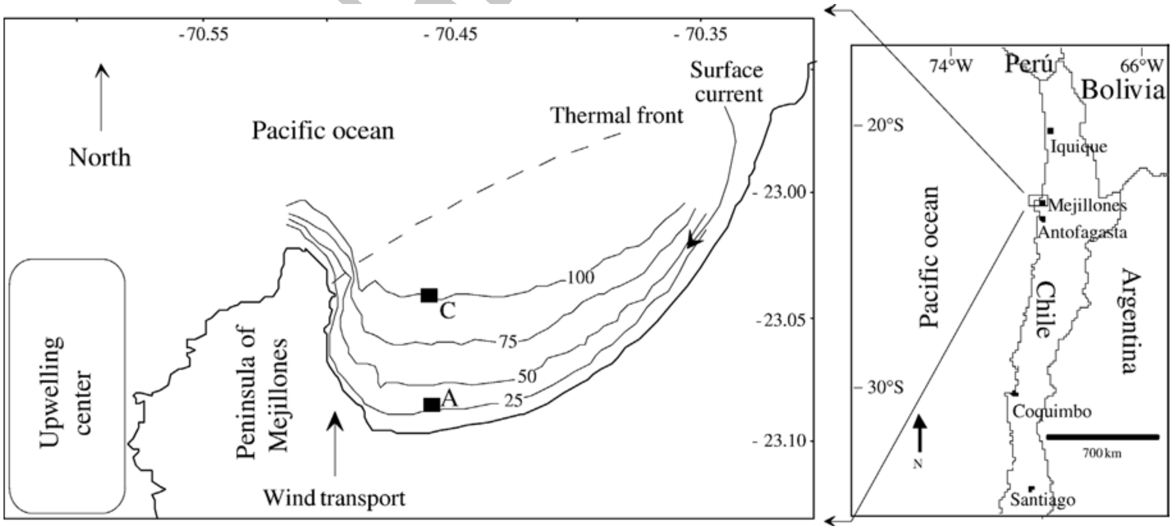

Fig. 1. Oceanographic setting of Mejillones Bay, showing schematic location of upwelling cell and location of sampling stations: A is coastal and C pelagic. Bathymetry's lines each 25 m are showed. The dashed line represents the position of the thermal front, which generates an upwelling shadow (UPS) in Mejillones Bay (Marín et al. 2003).

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Valdés et al., 2000; Valdés and Ortlieb, 2001; Valdés et al., 2003, 2004; Vargas et al., 2004). As part of the latest studies, redox-sensitive metals preserved in sediments have been analyzed in order to calibrate proxies of paleoxygenation (Valdés, 2004) and to asses potential problems of marine contamination derived from intense industrial development in recent years (Valdés et al., 2005).

Industrial activity in the area is represented by aquaculture and the fishmeal industry, power thermoelectric generation, and mineral exports. The real impact of this recent development on the marine ecosystem is still unknown.

2. Materials and methods

2.1. Sample collection

Surface water samples were collected from two sites in Mejillones Bay (Fig. 1), using clean, 5 l inert sampling bottles (Niskin, General Oceanic) hung on stainless steel hydrowire. Between June 2002 and April 2003, samples for nutrients, chlorophyll-*a*, temperature, dissolved oxygen and salinity were collected monthly, while samples for trace metals were collected every 2 months. Samples were stored at low temperatures, in high density polyethylene bottles treated with nitric acid. Temperature, salinity, and dissolved oxygen data were collected with a CTD (Sea Bird, 19 plus) at the same sampling locations.

2.2. Analytical procedures

2.2.1. Trace metals

For dissolved concentrations, the samples were filtered with 0.45 μm Millipore membranes in Nalgene Polisulfone (PSF) systems and acidified to pH 2 with nitric acid. This was done the same day as the collection in a “clean laboratory environment”, inside a laminar flow hood (Labconco, Purifier Class II). The samples were maintained at 4 °C inside the hood. Immediately before the ICP–OES measurements, the samples were acidified to 1 M with HNO_3.

For total concentrations, whole water samples were acidified to pH 2 with nitric acid, and then a 250 ml sub sample was digested with 20 ml of nitric acid at 90 °C in a BOD bottle for 2 h in a stainless steel air forced oven (WTC Binder); the final acidity of this medium was 1 M HNO_3.

Fe and Mo were determined according to the method described by Román et al. (2003). Fe was measured with Hydraulic High Pressure Nebulization, Flame Furnace, Atomic Absorption Spectrometry (HHPN–FF–AAS) before off-line separation and preconcentration with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). Mo was measured with Hydraulic High Pressure Nebulization, Atomic Absorption Spectrometry (HHPN–AAS) before off-line separation and preconcentration with MIBK; afterwards, the sample was acidified to 7 M with HCl.

V and Mn were determined by Inductively Coupled Plasma, Optical Emission Spectrometry (ICP–OES) according to the matrix matching technique, using purified seawater (PSW) (1) for blank measurements and the preparation of the standards for optimization and calibration.

Ni was determined by adsorptive accumulation of the respective complex with dimethylglyoxime at the drop mercury electrode (DME) by Adsorptive Differential Pulse Polarography (AdDPP) (2), and Cd was measured by Potentiometric Stripping Analysis (PSA) in the derivate signal mode (3, 4).

CASS — 4 (coastal seawater) and NASS — 4 (oceanic seawater) certified reference seawater from the Canadian National Research Council (NRC–CNRC) were used to validate the techniques and for quality control of the analytical determinations of Mn, Fe, Ni, Cd, and Mo. Vanadium’s quality control was done with the spiking technique. Purified coastal seawater (PSW) was prepared with an additional solid phase extraction step, using C_{18} 3 M Empore Bakerbond (J. T. Baker) discs (1) to improve the uptake of residual trace metals, and was used for blanks, the ICP–OES calibration matrix, with spikes as a secondary reference material for quality control.

Before each series of ten measurements routine controls of precision and accuracy were done. If, in four consecutive tests, the precision varied from the expected value by 20%, all analytical procedures were reviewed, and any having suspicious measurements were repeated. When the committed relative error was $\geq 15\%$ with respect to the certified value, all the analytical procedures were reviewed, and any suspicions ones were repeated.

All metal concentrations are expressed in $\mu g\ l^{-1}$.

2.2.2. Nutrients and chlorophyll

Water samples for nutrients were filtered through a 0.45 μm membrane filter and concentration was determined using a Spectronic 20D Spectrophotometer, according to methodology proposed by Parsons et al. (1984). Chlorophyll-*a* was measured in a Shimadzu RF-5301 Spectrofluorometer, after filtering samples in the dark through a 0.45 μm membrane filter, following

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Table 1
Descriptive statistics of all parameters measured in this work

Parameter		Mean		SD		Range	
		ST. A	ST. C	ST. A	ST. C	ST. A	ST. C
Temperature (°C)		17.02	17.04	1.79	1.56	14.47–19.92	15.18–20.06
Salinity (psu)		34.79	34.77	0.11	0.10	34.64–34.98	34.65–34.98
Dis. Oxygen (ml l^{-1})		6.40	7.24	2.31	2.02	2.22–10.47	3.20–10.68
Nitrate		2.13	1.04	2.95	1.15	0.06–8.70	0.02–3.66
Nitrite		0.11	0.08	0.14	0.07	0.00–0.46	0.00–0.19
Phosphate		1.40	1.13	0.74	0.49	0.20–2.70	0.30–1.18
Silicate		16.55	17.39	21.86	18.61	0.92–72.60	0.00–50.50
Chlorophyll-*a*		3.2	2.73	2.08	1.68	0.67–6.36	0.24–5.31
V	Total	7.33	7.36	1.91	3.21	4.40–9.23	3.48–12.80
	Dissolved	4.95	3.78	1.47	1.53	3.59–6.61	2.11–6.39
Mn	Total	1.49	1.99	0.73	1.18	0.67–2.54	0.87–4.09
	Dissolved	0.94	1.03	0.31	0.33	0.56–1.32	0.56–1.38
Fe	Total	2.77	2.69	0.41	0.67	2.41–3.51	1.96–3.58
	Dissolved	1.88	1.75	0.58	0.20	1.17–2.41	1.57–2.11
Ni	Total	0.88	0.83	0.05	0.23	0.84–0.98	0.36–0.98
	Dissolved	0.57	0.57	0.23	0.25	0.20–0.88	0.21–0.82
Mo	Total	13.85	15.28	1.79	5.02	11.19–15.36	9.43–21.74
	Dissolved	7.40	10.57	1.88	3.78	4.18–8.97	5.73–15.44
Cd	Total	0.27	0.21	0.30	0.12	0.04–0.80	0.10–0.39
	Dissolved	0.04	0.04	0.04	0.03	0.01–0.11	0.01–0.07

SD = standard deviation; nutrients are expressed in μmol l^{-1}; Chlorophyll is expressed in μg l^{-1}; metals are expressed in μg l^{-1}.

Holm-Hansen et al. (1965). The results of nutrients are reported as μmol l^{-1}; chlorophyll-*a* is reported as μg l^{-1}.

2.3. Statistical analysis

Temperature, dissolved oxygen, salinity, metals, nutrients, and chlorophyll were each analyzed by one-way analyses of variance (ANOVA), to test the significance of spatial and temporal variability. Pearson correlations and cluster analyses were performed to evaluate the relationships between all parameters measured at each station.

3. Results and discussion

3.1. Statistical validation

Descriptive statistics of all parameters measured in both stations in Mejillones Bay are shown in Table 1. The comparison of these results with previous work in this area (Rodriguez et al., 1991; Marín and Olivares, 1999; Marín et al., 2003) indicates that the sampling period corresponds to a normal year, without influence of El Niño event, which drastically changes water column structure in this area.

Table 2
Spatial variability: one-way ANOVA of all parameters measured in Mejillones Bay

	Temperature	Oxygen	Salinity	Chlorophyll-*a*	Nitrate	Nitrite	Phosphate
F	0.000	0.75	0.14	0.31	1.18	0.39	
P	0.977	0.398	0.715	0.588	0.291	0.539	

	Silicate	V_{Total}	Mn_{Total}	Fe_{Total}	Ni_{Total}	Mo_{Total}	Cd_{Total}	$V_{dissolved}$
F	0.01	0.00	0.79	0.06	0.32	0.38	>0.26	1.83
P	0.927	0.986	0.396	0.812	0.587	0.553	0.621	0.206

	$Mn_{dissolved}$	$Fe_{dissolved}$	$Ni_{dissolved}$	$Mo_{dissolved}$	$Cd_{dissolved}$
F	0.27	0.26	0.00	3.39	0.01
P	0.617	0.619	0.963	0.095	0.930

$P<0.05$.

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Table 3
Pearson's Coefficient Correlation of all parameters measured in Mejillones Bay

	Temperature	Oxygen	Chlorophyll	Nitrate	Nitrite	Mn_{tot}	Mo_{tot}	Cd_{tot}
Oxygen	0.53							
Chlorophyll	0.804							
Nitrate	−0.601		−0.651					
Nitrite				0.86				
Phosphate		−0.7						
Silicate		−0.7						
Mn_{tot}			−0.639					
Fe_{tot}	0.822							
Ni_{tot}						0.652		
Cd_{tot}	0.655							
V_{dis}				0.67	0.715			
Mn_{dis}			−0.825			0.832		
Mo_{dis}			0.606				0.598	
Cd_{dis}	0.656							0.699

Only significant values ($P<0.05$) are showed.

The results of the ANOVA showed no significant differences for oceanographic parameters between the two sampling stations (Table 2). In other words, the surface waters of Mejillones Bay, at averaged over a year, present homogeneous spatial conditions for all parameters measured. However, the results suggest some differences related to warm and cold periods which are characteristics of this zone.

Table 3 presents the results of Pearson's Coefficient of Correlation for all parameters measured in this study. In spite of number of parameters measured in this study, significant correlations were found in few cases. Only temperature and chlorophyll correlate with more than two other parameters.

3.2. Oceanographic variability

The annual mean surface temperature, salinity, and dissolved oxygen levels found are characteristic of a normal (non-El Niño) year, whereas the ranges of values reflect seasonality and upwelling events influences.

Considering the results of the ANOVA test, cluster analysis was done with all physical–chemical parameters combining both sampling stations. The result (Fig. 2) showed a clear group formed by temperature, oxygen, and chlorophyll, which present positive and significant correlations, except in case of oxygen and chlorophyll (Table 3). The others parameters didn't showed a clear relationship, but nitrate–nitrite (significant correlation,

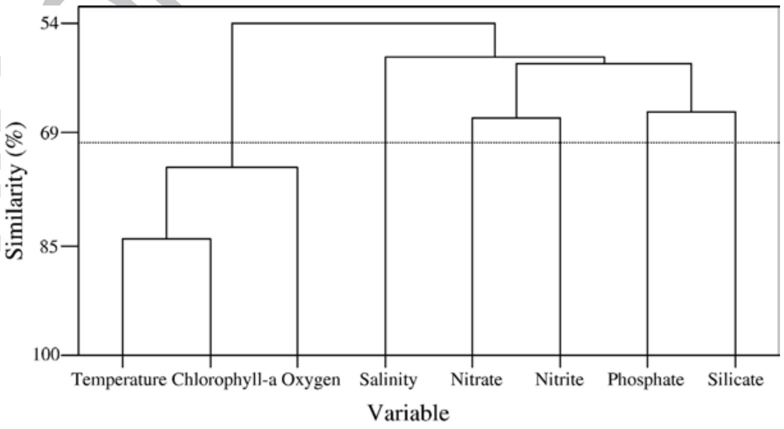

Fig. 2. Single-linkage dendrogram of similitude showing the results of clustering analyses of grouped physical–chemical parameters (not metals). The best line of similitude is shown.

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Table 3), and phosphate–silicate (no significant correlation) suggest some relationship (Fig. 2). Supported in these results we interpret that Mejillones Bay system presents two oceanographic scenarios: one characterized by a low influence of physical processes and rich nutrient surface waters (cold season) and another characterized by strong influences of physical processes coupled to biological factors (warm season), the last one represented in Fig. 2 by group formed by temperature, oxygen, and chlorophyll.

Temperatures ranged between 14.5 °C (winter) and 20.1 °C (summer) and dissolved oxygen between 2.2 ml l^{-1} and 10.7 ml l^{-1} (both in summer; Table 1, Fig. 3). A considerable decrease of these parameters was registered in February. This situation suggests upwelled waters present inside the bay. At this month, it also registered an increase of phosphate (Fig. 3). The negative correlation between dissolved oxygen and phosphate has been used as an indicator of upwelling in this bay (Rodriguez et al., 1991).

During cold season (April–September) nutrients concentration is high because productivity is inhibited due to a lack of radiation. The low intensity of productivity generates low chlorophyll concentrations (Fig. 3). During warm season (October–March), when radiation is optimum, the productivity increases and, consequently, the nutrient concentrations decrease and chlorophyll increases (Fig. 3). A similar pattern, especially between nitrate and chlorophyll, was observed by Rodriguez et al. (1991), during 1987–88.

3.3. Metal content in surface waters

The concentrations of total and dissolved metals at each station are showed in Table 1. As was the case for oceanographic parameters, ANOVA did not show significant differences in metal concentrations between both sampling stations (Table 2). In order of abundance, the total and dissolved trace metals (annual mean) in the surface waters of Mejillones Bay (2002–2003) were Cd<Ni<Mn<Fe<V<Mo.

In general, metals in seawaters can be classified according to their interactive properties with biological and physical–chemical processes. Two groups can be identified: conservative and non-conservative. The first group, including Mo, presents few interactions with the biological cycle and its horizontal and vertical distribution is governed by physical processes such as advection and turbulent mixing (Libes, 1992). The second group, including V, Ni, Cd, Fe, and Mn, is affected by biological processes, whether *via* scavenging and/or biological uptake (Brown et al., 1994). In the latter case, phytoplankton affects the distribution of dissolved metals, using most of them as micronutrients (Gonzalez-Davila, 1995). These intrinsic characteristics of metals must be considered when interpreting this study's results.

3.3.1. Vanadium

The predominant chemical form of V in oxic waters is vanadate, $H_2VO_4^-$ (Morford and Emerson, 1999), whose behavior is mostly conservative with some possible nutrient cycling (Bruland, 1983). Total and dissolved V variability presents a general trend characterized by high concentrations in cold season and low concentrations in warm season, similar to nutrient behavior. The partitioning between the dissolved and particulate phases appears to be relatively constant throughout the year with exception of February in pelagic station (Fig. 3). This situation points to an increase of the particulate form, which could be associated to the influence of upwelled water transported into the bay by onshore advection.

3.3.2. Manganese

Mn is present in oxic waters as MnO_2 (Russell and Morford, 2001). According to Kremling (1985) and Libes (1992), this metal is enriched in coastal surface waters due to a large metal supply from external sources. Variability was more marked for total Mn than for its dissolved form, which could be explained by the presence of particulate Mn in surface waters during periods of high total Mn concentrations (*i.e.* October). According to Schenau et al. (2002), the most important primary source of Mn to the ocean is the product of continental weathering. Valdés et al. (2005) found a significant correlation between this metal and Al in the Mejillones Bay marine sediments, which is a signal of lithogenic input. In Mejillones the continental transport to the ocean is controlled almost exclusively by winds (Vargas et al., 2004). The strongest winds from the south and south-west develops during spring and summer conditions (Escribano et al., 2004) mostly in September–October, which could to explain the increase of particulate Mn registered in October.

3.3.3. Iron

The annual variation of Fe was different at each sampling station. At the coastal station, both total and dissolved iron concentrations were low in winter and increased during spring–summer. On the other hand, the pelagic station showed an opposite trend: high total concentrations during winter and low total concentrations during spring–summer, with constant dissolved

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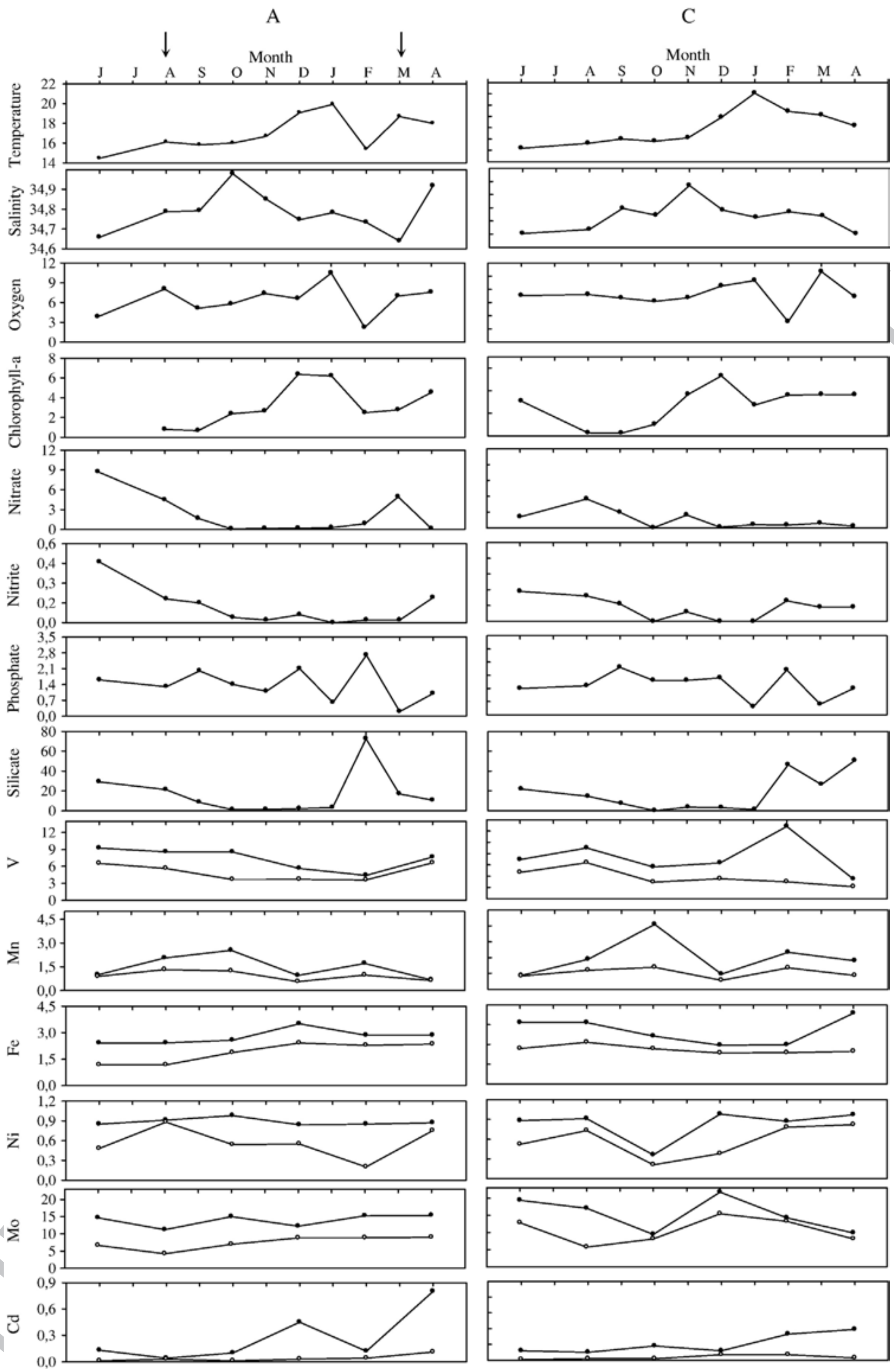

Fig. 3. Surface temporal variability of parameters measured at both Mejillones Bay stations during 2002–2003. Temperature in degrees Celsius; dissolved oxygen in ml l^{-1}; chlorophyll-*a* in µg l^{-1}; nutrients in µmol l^{-1}; metals in µg l^{-1}. Black circle is total metal and white circle is dissolved metal. Arrows indicates satellite image dates (See Fig. 4).

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concentrations year-round (Fig. 3). Martín and Fitzwater (1988) have shown that phytoplankton growth is limited by iron availability, especially in the California and Humboldt Current Systems (Hutchins and Bruland, 1998). However, the lack of correlation between Fe and nutrients and chlorophyll would to indicate that this metal has no relationship with biological factors, at least in this bay. By other hand, Des Combes et al. (1999) indicate that the supply of this metal is governed, principally, by continental input probably in the same way as Mn in Mejillones Bay. However, no significant correlation was found between Fe and Mn (Table 2). In the California Current Johnson et al. (1999) found that Fe was introduced by resuspended bottom sediment during coastal upwelling. A similar mechanism should be acting in Mejillones bay, because the microxic condition of bottom environments (Valdés, 2004) and the persistence of the upwelling should to introduce Fe into the bay from offshore zone.

3.3.4. Nickel

Ni occurs in oxic waters as Ni^{2+} and $NiCl^+$ (Calvert and Pedersen, 1993). At the Mejillones Bay coastal station, total Ni was constant during the entire study period, whereas its dissolved form showed high concentrations during winter and low concentrations during spring–summer. The pelagic station registered a highly variable Ni concentrations, with decay during October and high concentrations before and after this month (Fig. 3). The distribution of Ni is strongly mediated biologically (Kremling, 1985), and its behavior as a micronutrient indicates that it is removed from surface waters by plankton growth (Saager et al., 1992; Morley et al., 1993). It seems like lowest dissolved Ni concentration at station A should be accompanied by a high chlorophyll concentration (Fig. 3), which suggest some influence of biological productivity on Ni behavior.

3.3.5. Molybdenum

Molybdenum (VI) appears in the stable oxidation state in oxic waters and is found as MoO_4^{2-} (Morford and Emerson, 1999; Russell and Morford, 2001; Nameroff et al., 2002). Mo is a conservative metal only affected by physical–chemical factors (Libes, 1992; Brown et al., 1994; Adelson et al., 2001). Because of its conservative nature, it is possible to assume that coastal surface circulation controls the Mo distribution in Mejillones Bay surface waters. Concentrations of dissolved and total Mo were less variable at the coastal than at the pelagic station (Fig. 3), which is closer than upwelling cell (Fig. 1). During warm season the upwelling events are more frequent and intense (Marín et al., 2003), which influence the onshore advection and probably the Mo content in surface waters principally in the pelagic station.

3.3.6. Cadmium

Of all metals measured in this study, Cd had the lowest concentration. The total concentration presented a more marked variability than its dissolved form at both stations (Fig. 3), as a consequence of the variation of particulate Cd in Mejillones Bay surface waters. The typical oceanic Cd distribution presents low or depleted values near the surface (Delgadillo-Hinojosa et al., 2001) and is regulated by marine biogeochemical processes, namely uptake by phytoplankton in surface waters (Abe, 2001). Cd is a nutrient-like metal that presents only one oxidation state in seawater (Cd II) and is found as $CdCl^+$ (Morford and Emerson, 1999; Russell and Morford, 2001; Nameroff et al., 2002). This behavior indicates that Cd has a short residence in surface waters because it is removed rapidly by plankton growth (Calvert and Pedersen, 1993). Temporal Cd variations were associated with chlorophyll-*a* concentration and temperature fluctuation, suggesting that phytoplanktonic biomass production is the principal factor controlling Cadmium concentration in surface waters of Mejillones bay. However, the two highest total Cd values measured in December and April in station A seem too high to be attributed to phytoplankton, because according to Cullen and Sherrell (1999) in a work developed in California Current, the Cd content of marine particles is less than 10 ng l^{-1}. It is possible that upwelled waters transported by onshore advection have some degree of influence in Cd content in Mejillones bay, as account in others coastal environments (Boyle, 1988; Van Geen et al., 1992; Van Geen and Husby, 1996; Takesue et al., 2004).

3.4. Factors controlling seasonal variability of trace metals in Mejillones bay

One possible source of trace metals in Mejillones Bay is the input of lithogenic material. However, Valdés et al. (2000) and Valdés (2004) compared V, Ni, Mo, and Cd with aluminum (a marker of lithogenic sources according to Dean et al. (1997) in marine sediments, without finding any significant correlations). The authors concluded that continental input in the sediments of Mejillones Bay is not the principal source of these trace metals. Moreover, Vargas et al. (2004) indicated that lithogenic debris in the bottom marine sediments of Mejillones Bay represents less than 5% of

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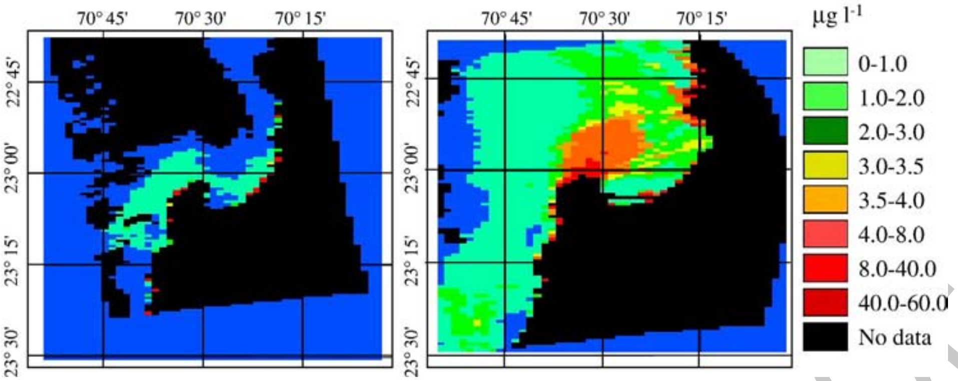

Fig. 4. Satellite image of chlorophyll-*a* in Punta Angamos upwelling system during August 2002 (left) and March 2003 (right).

the total bulk sediments, which suggests that metals in lithogenic minerals transported from the continent to the ocean constitute a minor source in this coastal area. By other hand, Valdés et al. (2005) demonstrated that contamination doesn't explain the concentration of these trace metals in this bay. However, some influence of waste water treatment plant effluent should be considered specially in station A. Even if influenced to some extent by atmospheric inputs and/or contamination processes in the surface waters, the distribution of V, Ni, Cd, and Mo in Mejillones Bay at the moment of sampling, can be broadly and principally accounted by a combination of natural oceanic processes and mechanisms.

Seasonal variability was described by grouping parameters into two general annual periods: the cold (autumn–winter) and warm (spring–summer) seasons. Fig. 4 shows typical satellite images (from EOS Aqua Spacecraft; second and third order polynomic correction process) of chlorophyll-*a* distribution during the cold period (August 28, 2002) and the warm period (February 28, 2003), coincident with the sampling of metals in surface waters. During the cold season low levels of chlorophyll were found in the surface waters of the Punta Angamos upwelling cell and Mejillones Bay (in accordance with chlorophyll measured *in situ*), which indicated that productivity was low during this period. On the other hand, during the warm season, well productive waters are common, with a filament of high levels of chlorophyll displaced to the north-east, generating an upwelling shadow system (UPS) in the bay, as proposed by Marín et al. (2003). Low levels of dissolved oxygen and high levels of phosphate registered during warm season, particularly in February, are characteristic of upwelling events (Fahrbach et al., 1980).

The lack of a similar pattern of temporal variability of metals in both sampling stations seems to be the most important characteristic. This situation could indicate that there is a combination of factors with different temporal variation patterns which influence the presence of metals in surface waters. Based on the area's oceanic characteristics and the results obtained in this study, a conceptual two-box model is proposed to explain the variation of metals in surface waters of this coastal ecosystem (Fig. 5). The two-box model considered in this work was based on the area's UPS interpretation proposed by Marín et al. (2003), which separates the Mejillones Bay from the Punta Angamos upwelling system. The upwelling event of Punta Angamos causes a biological productivity increment into Mejillones bay, and the development of an efficient retention zone of phytoplanktonic organisms (Marin and Olivares, 1999; Escribano et al., 2000). These characteristics are modulated by the "upwelling shadow" condition present in this bay, which is defined as a confined zone of an

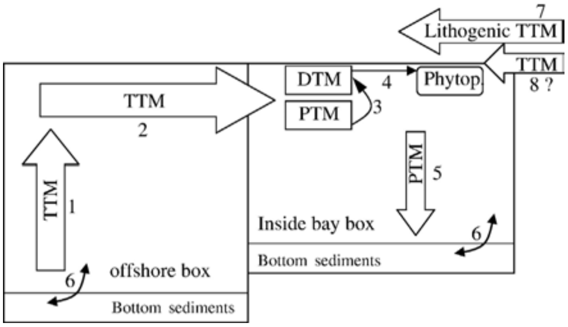

Fig. 5. Conceptual scheme of mechanisms which influence temporal variability of trace metal concentrations in surface waters of Mejillones Bay. TTM = Total Trace Metal; PTM = Particulate Trace Metal; DTM = Dissolved Trace Metal; 1 = offshore deep water upwelling; 2 = onshore advection; 3 = desorption of particulate metals; 4 = phytoplankton uptake; 5 = scavenging; 6 = exchange at sediment–water interface 7 = wind transport; 8 = expected anthropogenic input.

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active coastal upwelling system, whiting which upwelling is less intense (Marin et al., 2001). According to this situation the upwelled waters are transported inside the bay by onshore advection. The upwelling condition founded inside the bay in February, according to PO4 and dissolved oxygen (Fig. 3) represents the spin-up phase of the develop of the upwelling shadow (Marín et al., 2001).

Several studies have shown that coastal surface waters contain higher concentrations of dissolved trace metals (DTM) than open ocean waters (Kremling and Hydes, 1988; Kremling and Pohl, 1989; Muller et al., 1994; Cotté, 1997; Le Gall et al., 1999). The offshore box presents two ways of metal transport: surface circulation entering and vertical circulation *via* the upwelling of deep water, which results in different intensities depending on the wind direction and strength (Strub et al., 1998). Both mechanisms transport water masses with a much defined chemical composition (metals included). For example, in the case of DTM, at a global scale, Martín and Thomas (1994) estimated that the oceanic input would dominate sources for the oceanic margin. Unfortunately, information about the metal composition of marine waters in the Humboldt system is lacking and it was not possible to compare our results with other works. In the inside the bay box, surface metal concentrations result from very low lithogenic input, uncertain industrial contamination processes (a continuing possibility), ingestion by phytoplankton, desorption from particles, and scavenging due to high organic matter production. In this last case, Bacon and Anderson (1982) propose the "reversible scavenging model", in which the settling and regeneration of biogenic particles are important factors in removing trace metals from surface waters in the ocean. These factors are combined with surface water masses present inside the bay. During period of study the water column of Mejillones bay showed a mixture of Subtropical Surface Water (STSW), Subantarctic Surface Water (SASW), and Equatorial Subsurface Water (ESSW), which are commonly observed offshore of Mejillones Bay (Sobarzo and Figueroa, 2001). Considering that the bay have less than 100 m deep, it is convenient to talk about the types of water associated to these water masses. Their original properties are modified by a mixture of processes, and/or due to the atmospheric conditions. The composition of these surface water masses has a temporal and spatial variability that is subject to seasonal atmospheric variations such as solar radiation, wind intensity and a mixture of effects caused by the bay's dynamics and coastal upwelling processes. The features of the water-mass core defined in the oceanographic literature do not correspond to the bay's interior. However, it is possible to recognize these traits in spite of the water mixture. In general terms, it can be said that there is a predominance of the STSW at the surface level. However, this level is also characterized by minimum salinities related to the minimum salinity water levels (MSW) mentioned at Sobarzo and Figueroa's(2001) work corresponding to some type of SASW. This situation should have an important influence on surface distribution of trace metals and can explain the high spatial and temporal variability observed in most of the metals analyzed in this work.

Due to the fact that vertical mixing of water column is an important characteristic in Mejillones bay, another factor that should be considered is the influence of microxic condition of subsurface waters (Valdés, 2004), because all the metals analyzed in this work are redox-sensitive (Morford and Emerson, 1999; Bostick et al., 2000; Brown et al., 2000, Crusius and Thomson, 2000; Hammond et al., 2000; Zheng et al., 2000, Morford et al., 2001; Russell and Morford, 2001). In the shallow zone (between 0 m and 45 m water depth) sediments are deposited under oxic condition. In this zone Ni, V, Cd and Mo are resolubilized during the diagenetic process remaining in solution, while Mn and Fe precipitate to the sediments. Hatje et al. (2001) suggest that Fe is oxidized faster than Mn in natural systems, which indicates that Mn could be transported further away from coast before precipiting in the bottom sediments. In the deeper zone of Mejillones bay prevails a microxic/anoxic sediment–water interface condition which promotes precipitation of Ni, Cd, Mo and V. Fe and Mn remain in solution and are resolubilized during the diagenetic process.

The combination of these mechanisms and temporal variation could explain the complex behavior of these metals in this upwelling system of northern Chile.

4. Conclusions

The temporal distribution of some metals in the coastal waters of the northern Humboldt Current (Mejillones Bay, Chile) has been described in relation to physical–chemical and biological processes.

In Mejillones Bay, nutrients are present year-round in surface waters and are not a limiting factor for high primary productivity. Radiation could be a limiting factor explaining the opposing trend of nutrients and chlorophyll; low radiation in autumn and winter corresponds to high nutrients and low chlorophyll, whereas high radiation in spring and summer corresponds to low nutrients and high chlorophyll.

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The surface concentration of metals does not appear to be explained by anthropogenic inputs (at least not during the year of this work), and variability observed in this study appears to be natural. The lack of correlation between physical–chemical parameters and metals could indicate a more complex combination of factors acting on surface concentrations. It is possible, also, that the temporal variability of metals corresponds to a time scale other than those considered in this study. However, although not significant, a more intense variability in metal concentrations was observed at the pelagic station, which is under the direct influence of the Punta Angamos upwelling cell located off Mejillones Bay.

A two-box conceptual model is proposed to explain the variation of metals in surface waters of this coastal ecosystem. In the offshore box, surface circulation and deep water upwelling transport water masses with different metal contents and different temporal frequencies into the bay. In the inside the bay box, surface metal concentrations result from very low lithogenic input, ingestion by phytoplankton, desorption, and scavenging due to high organic matter production. The development of upwelling events in this area during the sampling period had different effects on each metals and sampling point. Moreover, the mixture of water masses and the Oxygen Minimum Zone which characterize the Mejillones bay should have an important influence on surface distribution of trace metals and can explain the high temporal variability observed in most of the metals analyzed in this work.

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5. Uncited References

Abe and Matsumaga, 1988
Martín and Knauer, 1984
Segovia-Zavala et al., 1998
Takesue and Van Geen, 2002

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References

Abe, K., 2001. Cd in the western equatorial Pacific. Marine Chemistry 74, 197–211.

Abe, K., Matsumaga, K., 1988. Mechanism controlling Cd and PO_4 concentration in Funka Bay, Japan. Marine Chemistry 23, 145–152.

Adelson, J., Helz, G., Miller, C., 2001. Reconstructing the rise of recent coastal anoxia; molybdenum in Chesapeake bay sediments. Geochimica et Cosmochimica Acta 65 (2), 237–252.

Bacon, M., Anderson, R., 1982. Distribution of thorium isotopes between dissolved and particulate forms in the deep sea. Journal of Geophysical Research 83, 2045–2056.

Bostick, B., Fendorf, S., Fendorf, M., 2000. Disulfide disproportionation and CdS formation upon cadmium sorption on FeS_2. Geochemica et Cosmochemica Acta 64 (2), 247–255.

Brown, J., Colling, A., Park, D., Phillips, J., Rothery D., Wright J., 1994. Ocean Chemistry and Deep-Sea sediments. The Open University/Pergamon Eds. Oxford, Great Britain: 133 pp.

Brown, E., Callonec, L., German, Ch., 2000. Geochemical cycling of redox-sensitive metals in sediments from lake Malawi: a diagnostic paleotracer for episodic changes in mixing depth. Geochimica et Cosmochimica Acta 64 (20), 3515–3523.

Bruland, K., 1983. Trace elements in sea-water. In: Riley, J.P., Chester, R. (Eds.), Chemical Oceanography, vol. 8. Academic Press, London, pp. 157–220.

Calvert, S., Pedersen, T., 1993. Geochemistry of recent oxic and anoxic marine sediments: implications for the geological records. Marine Geology 11, 67–88.

Cotté M. 1997. Origines et comportement des métaux disous dans les eaux de la marge Atlantique Européenne. PhD Thesis, University of Paris VI, 210 pp.

Cotte-Krief, M., Guieu, C., Thomas, A., Martin, J., 2000. Sources of Cd, Cu, Ni and Zn in the Portuguese coastal waters. Marine Chemistry 71, 199–214.

Crusius, J., Thomson, J., 2000. Comparative behavior of authigenic Re, U, and Mo during reoxidation and subsequent long-term burial in marine sediments. Geochimica et Cosmochimica Acta 64 (13), 2233–2242.

Cullen, J., Sherrell, R., 1999. Techniques for determination of trace metals in small samples of size-fractioned particulate matter: phytoplankton metals off central California. Marine Geology 67, 233–247.

Dean, W., Gardner, J., Piper, D., 1997. Inorganic geochemical indicators of glacial–interglacial changes in productivity and anoxia on the California continental margin. Geochimica et Cosmochimica Acta 61 (21), 4507–4518.

Delgadillo-Hinojosa, F., Macías-Zamorano, J., Segovia-Zavala, J., Torres-Valdés, S., 2001. Cadmium enrichment in the Gulf of California. Marine Chemistry 75, 109–122.

Des Combes, H., Caulet, J., Tribovillard, N., 1999. Pelagic productivity changes in the equatorial area of the northwest Indian Ocean during the last 400,000 years. Marine Geology 15, 27–55.

Escribano, R., Rodriguez, L., Irribarren, C., 1998. Temperature-dependent development and growth of *Calanus chilensis* Brodsky from northern Chile. Journal of Experimental Marine Biology and Ecology 229, 19–34.

Escribano, R., Rosales, S., Blanco, J., 2004. Understanding upwelling circulation off Antofagasta (northern Chile): a three-dimensional numerical-modeling approach. Continental Shelf Research 24, 37–53.

Please cite this article as: Valdés, J. et al. Metals content in surface waters of an upwelling system of the northern Humboldt Current (Mejillones Bay, Chile). J. Mar. Syst. (2007), doi:10.1016/j.jmarsys.2007.05.006

Fahrbach, E., Brockman, C., Lostanau, N., Urquizo, W., 1980. The northern peruvian upwelling system during the ESACAN experiment. In: Richards, F. (Ed.), Coastal Upwelling, Coastal and Estuarine Science. AGU, Washington D.C., pp. 134–145.

Gonzalez, H., Daneri, G., Figueroa, D., Iriarte, J., Lefevre, N., Pizarro, G., Quiñónez, R., Sobarzo, M., Troncoso, A., 1998. Producción Primaria y su destino en la trama trófica pelágica y océano profundo e intercambio océano-atmósfera de CO2 en la zona norte de la corriente de Humboldt (23° S): posibles efectos del evento El Niño, 1997–98 en Chile. Revista Chilena de Historia Natural 71, 429–458.

Gonzalez, H., Ortiz, V., Sobarzo, M., 2000. The role of faecal material in the particulate organic carbon flux in the northern Humboldt Current, Chile (23° S), before and during the 1997–1998 El Niño. Journal of Plankton Research 22 (3), 499–529.

Gonzalez-Davila, H., 1995. The role of phytoplankton cells on the control of heavy metals concentrations in seawater. Marine Chemistry 48, 215–236.

Gonzalez, H., Giesecke, R., Vargas, C., Pavez, M., Iriarte, J., Santibáñez, P., Castro, L., Escribano, R., Pagés, F., 2004. Carbon cycling through the pelagic foodweb in the northern Humboldt Current off Chile (23° S). Journal of Marine Science 61, 572–584.

Grotti, M., Soggia, F., Abelmoschi, M., Rivaro, P., Magi, E., Frache, R., 2001. Temporal distribution of trace metals in Antarctic coastal waters. Marine Chemistry 76, 189–209.

Hammond, D., Mcmanus, J., Berenson, W., Meredith, Ch., Klinkhammer, G., Coale, K., 2000. Diagenetic fractionation of Ge and Si in reducing sediments: the missing Ge sink and a possible mechanism to cause glacial/interglacial variations in oceanic Ge/Si. Geochimica et Cosmochimica Acta 64 (14), 2453–2465.

Hatje, V., Birch, G., Hill, M., 2001. Spatial variability of particulate trace metals in Port Jackson Estuary, Australia. Estuarine, Coastal and Shelf Science 53, 62–77.

Holm-Hansen, O., Lorenzen, C., Holmes, R., Strickland, J., 1965. Fluorometric determination of chlorophyll. Journal du Conseil - Conseil Permanent International pour l'exploration de la Mer 30, 3.15.

Hutchins, D., Bruland, K., 1998. Iron-limited diatom growth and Si:N uptake ratios in a coastal upwelling regime. Nature 393, 561–564.

Iriarte, J., Gonzalez, H., 2004. Phytoplankton size structure during and after the 1997/1998 El Niño in coastal upwelling area of the northern Humboldt Current System. Marine Ecology Progress Series 269, 83–90.

Iriarte, J., Pizarro, G., Troncoso, V., Sobarzo, M., 2000. Primary production and biomass of size-fractioned phytoplankton of Antofagasta, Chile (23–24° S) during pre-El Niño and El Niño 1997. Journal of Marine Systems 26, 37–51.

Johnson, K., Chavez, F., Friedrich, G., 1999. Continental-shelf sediments as a primary source of iron for coastal phytoplankton. Nature 398, 697–700.

Kremling, K., 1985. The distribution of cadmium, copper, nickel, manganese, and aluminum in surface waters of the open Atlantic and European shelf area. Deep-Sea Research 32 (5), 531–555.

Kremling, K., Hydes, D., 1988. Summer distribution of dissolved Al, Cd, Cu, Mn, and Ni in the surface waters around the British Isles. Continental Shelf Research 8, 89–105.

Kremling, K., Pohl, C., 1989. Studies on the spatial and seasonal variability of dissolved cadmium, copper and nickel in the North-east Atlantic surface waters. Marine Chemistry 27, 43–60.

Le Gall, A., Hydes, D., Statham, P., Morley, H., Hunt, C., 1999. Processes influencing distribution and concentration of Cd, Cu, Mn and Ni at the North West European shelf breaks. Marine Chemistry 68, 97–115.

Libes, S., 1992. An Introduction to Marine Biogeochemistry. John Wiley & Sons, Inc., pp. 15–190.

Marín, V., Olivares, G., 1999. Estacionalidad de la productividad primaria en bahía Mejillones del Sur (Chile): una aproximación proceso-funcional. Revista Chilena de Historia Natural 72, 629–641.

Marín, V., Escribano, R., Delgado, L., Olivares, G., Hidalgo, P., 2001. Nearshore circulation in a coastal upwelling site off the northern Humboldt Current System. Continental Shelf Research 21, 1317–1329.

Marín, V., Delgado, L., Escribano, R., 2003. Upwelling shadows at Mejillones bay (northern Chilean coast): a remote sensing *in situ* análisis. Investigaciones Marinas 31 (2), 47–55.

Martín, J., Knauer, G., 1984. Manganese transport through oxygen minima. Earth and Planet Science Letters 67 , 35–47.

Martín, J., Fitzwater, S., 1988. Iron deficiency limits phytoplankton growth in the north-east Pacific subartic. Nature 331, 341–343.

Martín, J., Thomas, A., 1994. The global insignificance of telluric input of dissolved trace metals (Cd, Cu, Ni and Zinc) to ocean margin. Marine Chemistry 46, 165–178.

Morford, J., Emerson, S., 1999. The geochemistry of redox-sensitive trace metals in sediments. Geochimica et Cosmochimica Acta 63 (11/12), 1735–1750.

Morford, J., Russell, A., Emerson, S., 2001. Trace metal evidence for changes in the redox environment associated with the transition from terrigenous clay to diatomaceous sediment, Saanich Inlet, BC. Marine Geology 174, 355–369.

Morley, N., Statham, P., Burton, J., 1993. Dissolved trace metals in the southwestern Indian Ocean. Deep-Sea Research 40 (5), 1043–1062.

Muller, F., Tranter, M., Balls, P., 1994. Distribution and transport of chemical constituents in the Clyde Estuary. Estuarine, Coastal and Shelf Science 39, 105–126.

Nameroff, T., Balistrieri, L., Murray, W., 2002. Suboxic trace metals geochemistry in the eastern tropical North Pacific. Geochimica et Cosmochimica Acta 66 (7), 1139–1158.

Ortlieb, L., Escribano, R., Follegati, R., Zúñiga, O., Kong, I., Rodríguez, L., Valdes, J., Guzmán, N., Iratchet, P., 2000. Ocean-climatic changes during the last 2,000 years in a hypoxic marine environment of Northern Chile (23° S). Revista Chilena de Historia Natural 73, 221–242.

Parsons, T., Maita, Y., Lalli, C., 1984. A Manual of Chemical and Biological Methods Seawaters Analysis. Pergamon Press, Oxford, United Kingdom, p. 173.

Pizarro, G., Iriarte, J., Montecinos, V., 2002. Mesoscale primary production and bio-optical variability off Antofagasta (23°–24°S) during the transition to El Niño 1997–1998. Revista Chilena de Historia Natural 75, 201–215.

Rodriguez, L., Marin, V., Farias, M., Oyarce, E., 1991. Identification of an upwelling zone by remote sensing and *in situ* measurement. Mejillones del Sur Bay (Antofagasta-Chile). Scientia Marina 55 (3), 467–473.

Román, D., Rivera, L., Morales, T., Ávila, J., Cortés, P., 2003. Determination of trace elements in environmental and biological samples using improved simple introduction in flame absorption spectrometry (HHPN-AAS; HHPN-FF-AAS). International Journal of Environmental Analytical Chemistry 83, 327–341.

Russell, A., Morford, J., 2001. The behavior of redox-sensitive metals across a laminates-massive-laminated transition in Saanich Inlet, British Columbia. Marine Geology 174, 341–354.

Saager, P., De Baarm, H., Howland, R., 1992. Cd, Zn, Ni and Cu in the Indian Ocean. Deep-Sea Research 39 (1), 9–35.

Please cite this article as: Valdés, J. et al. Metals content in surface waters of an upwelling system of the northern Humboldt Current (Mejillones Bay, Chile). J. Mar. Syst. (2007), doi:10.1016/j.jmarsys.2007.05.006

Schenau, S., Reichart, G., De Lange, G., 2002. Oxygen minimum zone controlled Mn redistribution in Arabian Sea sediments during the late Quaternary. Paleoceanography 17 (4), 10–1–10–12.

Segovia-Zavala, J., Delgadillo-Hinojosa, F., Alvarez-Borrego, S., 1998. Cadmium in the coastal upwelling area adjacent to the California–Mexico border. Estuarine, Coastal and Shelf Science 46, 475–781.

Sobarzo, M., Figueroa, D., 2001. The physical structure of a cold filament in a Chilean upwelling zone (Peninsula de Mejillones, Chile, 23° S). Deep-Sea Research 48, 2699–2726.

Strub, P., Mesias, J., Montecinos, V., Rutllant, J., Marchant, S., 1998. Coastal oceanic circulation off western South America. In: Robinson, A., Birnk, K. (Eds.), The Sea. John Wiley, New York, USA, pp. 273–314.

Takesue, R., Van Geen, A., 2002. Nearshore circulation during upwelling inferred from the distribution of dissolved cadmium off the Oregon coast. Limnology and Oceanography 47, 176–185.

Takesue, R., Van Geen, A., Carriquiry, J., Ortiz, E., Godinez-Orta, L., Granados, I., Saldivar, M., Ortlieb, L., Escribano, R., Guzmán, N., Castilla, J., Varas, M., Salamanca, M., Figueroa, C., 2004. Influence of coastal upwelling and El Niño-Southern Oscillation on nearshore water along Baja California and Chile: shore-based monitoring during 1997–2000. Journal of Geophysical Research 109, 1–14.

Ulloa, O., Escribano, R., Hormazabal, S., Quiñónez, R., Gonzalez, R., Ramos, R., 2001. Evolution and biological effects of the 1997–98 El Niño in the upwelling ecosystem off northern Chile. Geophysical Research Letters 28, 1591–1594.

Valdés, J., 2004. Evaluación de metales redox-sensitivos como proxies de paleoxigenación en un ambiente marino hipóxico del norte de Chile. Revista Chilena de Historia Natural 77, 121–138.

Valdés, J., Ortlieb, L., 2001. Paleoxigenación subsuperficial de la columna de agua en la bahía Mejillones del Sur (23° S): Indicadores geoquímicos en testigos de sedimento marino. Investigaciones Marinas 29 (1), 25–35.

Valdés, J., López, L., Lomónaco, S., Ortlieb, L., 2000. Condiciones paleoambientales de sedimentación y preservación de materia orgánica en Bahía Mejillones del Sur (23° S), Chile. Biología Marina y Oceanografía. Revista de Biologia Marina y Oceanografia 35 (2), 169–180.

Valdés, J., Ortlieb, L., Sifeddine, A., 2003. Variaciones del sistema de surgencia de Punta Angamos (23° S) y la Zona de Mínimo Oxígeno durante el pasado reciente. Una aproximación desde el registro sedimentario de la bahía Mejillones del Sur. Revista Chilena de Historia Natural 76, 347–362.

Valdés, J., Sifeddine, A., Lallier-Verges, E., Ortlieb, L., 2004. Petrographic and geochemical study of organic matter in surficial sediments from an upwelling system (Mejillones del Sur bay, northern Chile). Organic Geochemistry 35 (5), 881–894.

Valdés, J., Vargas, G., Sifeddine, A., Ortlieb, L., Guiñez, M., 2005. Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23° S), northern Chile: geochemical and statistical approach. Marine Pollution Bulletin 50, 1558–1568.

Van Geen, A., Husby, D., 1996. Cadmium in the California Current System: tracer of the past and present upwelling. Journal of Geophysical Research 101, 3489–3507.

Van Geen, A., Luoma, S., Fuller, C., Anima, R., Clifton, E., Trumbore, S., 1992. Evidence from Cd/Ca ratio in foraminifera for greater upwelling off California 4,000 years ago. Nature 358, 54–56.

Vargas, G., Ortlieb, L., Pichon, J., Bertaux, J., Pujos, M., 2004. Sedimentary facies and high resolution primary production inferences from laminated diatomaceous sediments off northern Chile (23° S). Marine Geology 211, 79–99.

Zheng, Y., Anderson, R., Van Geen, A., Kuwabara, J., 2000. Authigenic molybdenum formation in marine sediments: a link to porewater sulfide in the Santa Barbara basin. Geochimica et Cosmochimica Acta 64, 4165–4178.

Please cite this article as: Valdés, J. et al. Metals content in surface waters of an upwelling system of the northern Humboldt Current (Mejillones Bay, Chile). J. Mar. Syst. (2007), doi:10.1016/j.jmarsys.2007.05.006