

Distribution and temporal variation of trace metal enrichment in surface sediments of San Jorge Bay, Chile

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Abstract Cu, Pb, and Hg concentrations were determined in surface sediment samples collected at three sites in San Jorge Bay, northern Chile. This study aims to evaluate differences in their spatial distribution and temporal variability. The highest metal concentrations were found at the site “Puerto”, where minerals (Cu and Pb) have been loaded for more than 60 years. On the other

hand, Hg does not pose a contamination problem in this bay. Cu and Pb concentrations showed significant variations from 1 year to another. These variations seem to be a consequence of the combination of several factors, including changes in the loading and/or storage of minerals in San Jorge Bay, the dredging of bottom sediments (especially at Puerto), and seasonal changes in physical–chemical properties of the water column that modify the exchange of metals at the sediment–water interface. Differences in the contamination factor and geoaccumulation index suggest that pre-industrial concentrations measured in marine sediments of this geographical zone, were better than geological values (average shale, continental crust average) for evaluating the degree of contamination in this coastal system. Based on these last two indexes, San Jorge Bay has a serious problem of Cu and Pb pollution at the three sampling locations. However, only Cu exceeds the national maximum values used to evaluate ecological risk and the health of marine environments. It is suggested that Chilean environmental legislation for marine sediment quality—presently under technical discussion—is not an efficient tool for protecting the marine ecosystem.

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Introduction

Coastal marine systems are influenced by heavy anthropogenic pressure, since most human activities are concentrated along the coast. The geography of Chile augments this situation, not only because of the location of urban centers along the coast, but also because the sea is the principal route for exporting industrial products from the entire national territory.

Pollutants are input into the ocean mainly through domestic sewage and harbor and industrial activities. As a result, large extensions of the world's coastal areas are contaminated. Management and conservation strategies require an understanding of ecosystem behavior. Unfortunately, scientific knowledge on marine pollution is patchy, constituting a major obstacle for introducing effective management strategies for pollution control (Shahidul and Tanaka 2004).

Contaminating substances in coastal zones include persistent organic pollutants, nutrients, oils, radionuclides, pathogens, heavy metals, etc. (Cobelo-García and Prego 2004). Many studies have focused on heavy metal contents in marine systems (Pekey et al. 2004; Alagarsamy 2006; Buccolieri et al. 2006; McCready et al. 2006; and others). All metals present in the marine environment are found in dissolved and particulate forms. Many of these trace metals are classified as micronutrients because they are essential for phytoplankton growth (Libes 1992). The concentration of these metals can vary due to changing inputs and/or seasonal effects involving biological, geochemical, and physical interactions (Hatje et al. 2001).

Marine sediments can be sensitive to pollution monitoring (Atgin et al. 2000) because they are the most important reservoir for metals and other pollutants in aquatic systems. The problem is that heavy metals also have natural sources that reach the coastal zone through the same biogeochemical pathways as the anthropogenic sources. The combination of these factors complicates the understanding of heavy metal spatial and temporal distribution patterns (Salamanca et al. 2000).

San Jorge Bay (Fig. 1) is located at 23.5° S, on the boundary of the Atacama Desert. At this

latitude, the linearity of the northern Chilean coast is interrupted by two bay systems: one oriented to the north (Mejillones) and another oriented to the south (San Jorge). Local oceanographical conditions are controlled by the influence of the Humboldt Current, one of the most productive systems in the world (Strub et al. 1998). The principal characteristic at this latitude is the permanent upwelling cell (Punta Angamos) that supports important pelagic fisheries (Strub et al. 1998). This area borders one of the world's most arid regions, and continental input to the ocean is restricted to minimal atmospheric transport of lithogenic particles (Vargas 2002). For this reason, upwelling seems to be one of the most important natural processes influencing the chemical composition of the water column and bottom sediments.

The city of Antofagasta, the most important urban center in northern Chile, is located on San Jorge Bay. Founded in 1866, Antofagasta currently has a population of 345,000 and its principal commercial activity is the loading onto ships of minerals (mainly copper) produced in this region. The bay has two ports: one at "Coloso" (Fig. 1), where concentrated copper has been loaded since 1991, and the other at "Puerto" (Fig. 1), where copper, lead, and other products have been loaded since 1943. The bay also has three oil-loading terminals and one effluent for the discharge of domestic waters after a secondary treatment (Fig. 1).

Very few efforts have been made to understand the environmental conditions of San Jorge Bay. Rather, studies tend to focus on oceanographic topics like temperature pattern variability and seasonal growth of marine copepods (Escribano et al. 1995), phytoplankton ecology (Rodríguez and Escribano 1996), physical–biological interactions (Escribano et al. 2002), surface circulation (Escribano et al. 2004), plankton behavior (Castilla et al. 2002), and Cu, Pb, and Zn distributions in near-shore waters (Salamanca et al. 2000).

In this work, we studied the distribution of Cu, Pb, and Hg in the marine sediment, considering spatial differences (three different sites in the bay) and temporal variability (2 years). Moreover, we used different approaches to eval-

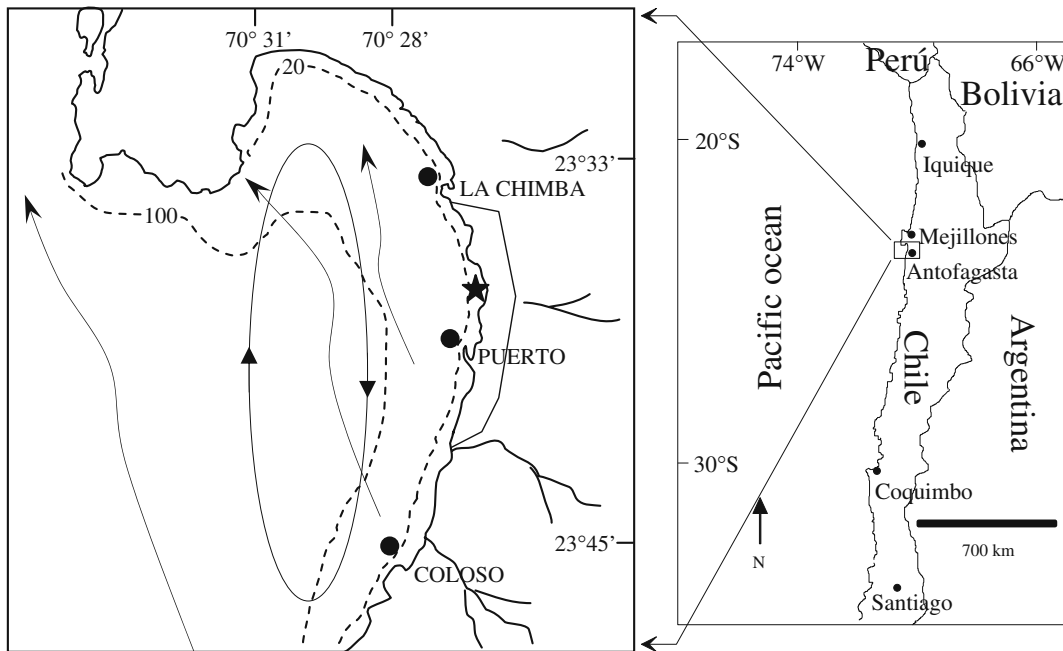


Fig. 1 Location of sampling stations (*black points*) in San Jorge Bay. Major oceanographic characteristics are indicated. *Dashed lines* correspond to bathymetry. *Arrows*

represent surface circulation patterns and the cyclonic gyre according to Escribano et al. (2002). *Stars* indicate the location of domestic effluents and oil-loading terminals

uate the environmental conditions of this coastal system.

Materials and methods

Sample collection

Two oceanographic cruises were done in San Jorge Bay: one at the end of winter 2003 and another at the end of summer 2004. During each cruise, samples of surface sediments for metal analyses were collected with a Van Veen bottom dredge sampler at three points in the bay: from north to south, La Chimba, Puerto, and Coloso (Fig. 1). All the material used in sampling and sample storage was treated with nitric acid. Sampling and the marine field work were done using standard operating procedures (Cooper and Rees 2002); due to the intrinsic manipulation required for such studies, we implemented the most rigorous precautions in order to keep the samples contamination-free.

Analytical procedure

Cu, Pb, and Hg were determined in the particle size fraction (<63 μm) of the marine sediments because this fraction is nearly equivalent to the material carried in suspension, the most important system for sediment transport (Salomons and Förstner 1984).

For Cu and Pb analyses, 400–600 mg of homogenized dry fine fractions of sediments and MESS-2 (marine sediment, NRC-CNRC) standard reference material were accurately weighed, placed in Teflon digestion bombs, and subjected to a chemical attack with 12 mL of aqua regia, 4 mL of Perhydrol (H₂O₂ to 30%), and 4 mL of perchloric acid, all reagents of special quality for trace element analysis. Once the evolution of the gases was completed, the bombs were closed and placed in a ceramic oven with an internal temperature probe and external temperature control; a rigorous heating program was applied for 2 h until reaching 150°C. Once the bombs had cooled, the residuals were eliminated by filtration

Table 1 Analytical validation of the techniques for the Cu, Pb, and Hg analyses in marine sediments

Element	Technique	RSD ^a (± %)	RE ^b (± %)	C _L ^c (ng/ml)
Cu	FAAS	1.1	0.7 (MESS-2)	2.7
Pb	FAAS	3.1	1.2 (MESS-2)	1.5
	HHPN – FF – AAS	2.5	3.5 (MESS-2)	1.0
Hg	CVAAS	5.0	1.5 (MESS-2)	0.1

For techniques see “[Analytical procedure](#)” chapter

^aRelative standard deviation

^bRelative errors

^cDetection limit

through glass microfiber Whatman GF/F filters and the acid solution samples were introduced into 100-mL flasks, completing the volume with 1 M nitric acid. The “analytical blanks” were also prepared by this procedure. The metal measurements were made using flame atomic absorption spectrometry (FAAS; Jones and Laslett 1994) and hydraulic high-pressure nebulization flame furnace atomic absorption spectrometry (HHPN-FF-AAS; Román et al. 2003; Ghaedi et al. 2005, 2006a, b) on a GBC 909 PBT atomic absorption spectrometer (Australia), applying multiple standard addition methodology.

For the Hg analysis, 600 mg of sediments were introduced into Teflon bombs and subjected to a chemical attack with 6 mL of nitric acid and 6 mL of sulfuric acid. Once the gas evolution was concluded, the bombs were closed and put inside the ceramic oven, where they underwent a rigorous heating program for 2 h until reaching 140°C. Once the bombs had cooled, the residuals were eliminated by filtration through glass Whatman GF/F microfiber filters and then the acid solution samples were introduced into 25-mL flasks, completing the volumes with deionized water. When it was necessary to make dilutions, a mixed solution of 2 M in HNO₃ and 2 M in H₂SO₄ was used. Blanks and MESS-2 marine standard reference material were used to carry out analytical quality control measurements. The Hg measurements were performed by CVAAS (Welz and Melcher 1985; Jones and Laslett 1994; Ghaedi et al. 2006a, b) at 253.7 nm HCl in the factor extended height peak signal on a GBC 909 PBT atomic absorption spectrometer coupled with the standard GBC HG-900 mercury generator. Multiple standard addition methodology was applied. The Hg additions were made from a diluted solution prepared from Hg (II) Titrisol, Merck ampoule. Moreover, 5% Sn (II) chloride in 3 M HCl was used as a reducing agent; this was

Table 2 Descriptive statistics of metal concentrations (mg kg⁻¹) measured in coastal sediments of San Jorge Bay

Metal	Year	Statistical parameters	Coloso	Puerto	Chimba
Cu	2003	Range	109.6–230.4	520.2–1212.1	
		Mean	155.27	856.9	70.3
		SD	37.7	280.6	
	2004	Range	194.2–507.9	867–3166.6	379–841.8
		Mean	316.2	2321.7	587.6
		SD	96.9	921.5	200.9
Pb	2003	Range	19.2–82.9	209–421	
		Mean	47.6	321.15	44.1
		SD	23.4	69.1	
	2004	Range	11.6–105.1	38.6–68.4	9.69–73.2
		Mean	58.6	56.6	32.09
		SD	39.01	10.2	24.25
Hg	2003	Range	0.337–0.605	0.226–0.606	
		Mean	0.48	0.404	0.54
		SD	0.1	0.15	
	2004	Range	0.259–0.799	0.437–1.069	0.373–1.21
		Mean	0.51	0.82	0.66
		SD	0.19	0.19	0.36

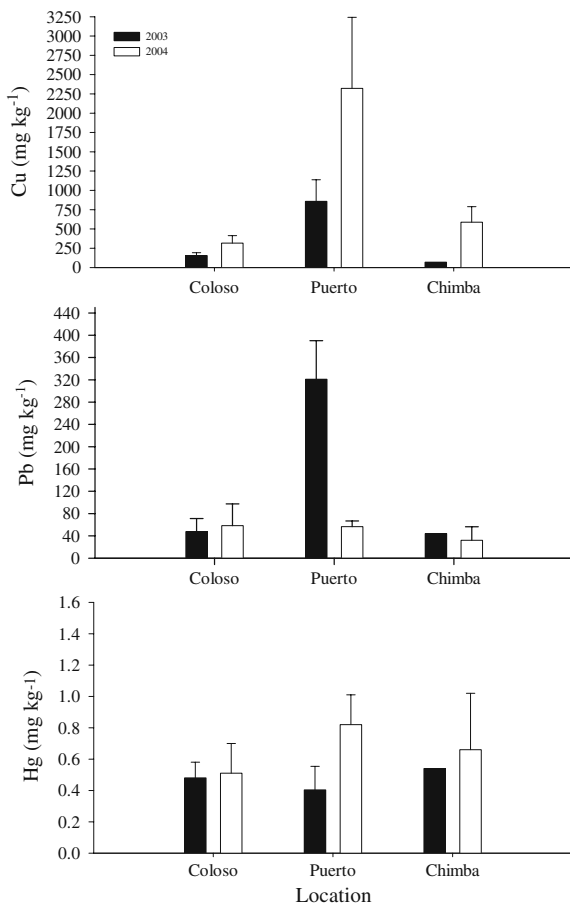


Fig. 2 Mean trace metal concentrations in the surface sediments of San Jorge Bay for both sampling cruises. Standard deviations are shown

prepared from SnCl₂·2H₂O ACS reagent suitable for mercury determinations and HCl.

Table 1 shows the analytical validation data to support the suitability and efficiency of the analytical techniques applied to determine the Cu, Pb, and Hg in the sedimentary samples used herein. Detection limits were calculated in accordance with IUPAC criteria (Winefordner and Long 1983; Currie 1999).

Results were analyzed with a one-factor ANOVA test ($\alpha = 0.01$), after examining the homogeneity of variance and removing heterogeneity by a Log ($x + 1$) transformation. For this analysis, we used the statistical program Minitab 14.

Table 3 ANOVA test for each cruise, comparing the sampled sites

Cruise year		Cu	Pb	Hg
2003	<i>F</i>	49.1	121.37	0.97
	<i>p</i>	0.000	0.000	0.343
2004	<i>F</i>	26.94	1.43	2.7
	<i>p</i>	0.000	0.269	0.097

Only Coloso and Puerto were compared in 2003. $p < 0.01$

Results and discussion

Trace metals in San Jorge Bay

Copper

The range of Cu in the San Jorge Bay sediments was between 70 mg kg⁻¹ and 3,167 mg kg⁻¹ (Table 2). The average values at Coloso, Puerto, and Chimba were 236 mg kg⁻¹, 1,589 mg kg⁻¹, and 364 mg kg⁻¹, respectively. The concentration was higher in 2004 than in 2003. The highest concentrations of Cu were found at the Puerto site in both years (Fig. 2). The ANOVA test showed significant differences ($p < 0.01$) in Cu content when comparing sampling sites in each year (Table 3) and when comparing different years in the cases of Coloso and Puerto (Table 4). Temporal variations of Cu content in the Coloso and Puerto sediments may be related to higher loading activities and/or dredging activities of bottom sediments (especially at the Puerto site). Also, the higher organic matter flux through the water column in summer (Escribano et al. 2004) could play an important role in the precipitation of Cu.

The mean Cu concentration for San Jorge Bay was 774 mg kg⁻¹, which is significantly higher than in similar environments along different coasts of the world (Table 5). Other subtidal environments in Chilean harbors with important industrial activities registered maximum Cu concentrations of

Table 4 ANOVA test for each sampled site, comparing both years

Site		Cu	Pb	Hg
Coloso	<i>F</i>	19.97	0.28	0.25
	<i>p</i>	0.000	0.607	0.624
Puerto	<i>F</i>	13.7	85.73	15.26
	<i>p</i>	0.004	0.000	0.003

Table 5 Comparison of the metal levels (mg kg⁻¹ dry weight) in surface sediments from different coastal environments, average shale, continental crust, and sediment cores from Mejillones (pre-industrial levels)

Location	Cu	Pb	Hg	Depositional environment	Reference
San Jorge Bay ^a	774.1	94.2	0.59	Subtidal	This study
San Jorge Bay ^a	37.8	–	–	Sandy beach	Lepez et al. (2001)
San Vicente Bay ^a	27.7	17.4	–	Subtidal	Salamanca et al. (1988)
Concepción Bay ^a	41.0	40.1	–	Subtidal	Salamanca et al. (1988)
Chañaral Beach ^a	1659	21.2	–	Sandy beach	Ramirez et al. (2005)
Izmit Bay, eastern Marmara Sea	89.4	94.9	–	Subtidal	Pekey et al. (2004)
Izmir Bay, eastern Aegean Sea	–	–	0.312	Subtidal	Kontas (2006)
Kastela Bay, Adriatic coast	–	–	2.85	Subtidal	Kljaković-Gaspic et al. (2006)
Average shales ^b	45	20	1.4		Turekian and Wedepohl (1961)
Continental crust ^b	75	8	0.08		Taylor (1972)
Sediment core (Mejillones Bay) ^{a,b}	53.5	4.7	0.3		Unpublished data

^aChilean coast^bBackground level

41 mg kg⁻¹ (Salamanca et al. 1988). Particularly, a study conducted by Lepez et al. (2001), also in San Jorge Bay but on the sandy beaches of this coastal environment, recorded only 38 mg kg⁻¹ (Table 5). Differences in metal contents between sand (beach environment) and mud fractions (subtidal environment) are expected, because the latter has more affinity with metals due to its more equivalent surface of particles. However, the beaches of Chañaral Bay (350 km south of San Jorge) showed a mean concentration of 1,659 mg kg⁻¹ (Ramirez et al. 2005), which is significantly higher than that registered for the sandy beaches (Lepez et al. 2001) and even subtidal environments (this study) of San Jorge Bay.

Copper found in the coastal marine sediments of this bay is related principally to mining activities, especially at the Puerto site, which is the principal and oldest Cu loading site of the bay.

Lead

The mean Pb concentration in San Jorge Bay was 94 mg kg⁻¹, ranging between 9 mg kg⁻¹ and 421 mg kg⁻¹ (Table 2). Differences in lead concentrations between sites were significant only in 2003 (ANOVA, $p < 0.01$, Table 3), and only Puerto showed significant differences ($p < 0.01$) in Pb content when comparing both years of sampling (Table 4). Whereas the values of Pb content at Coloso and Chimba were similar for both years,

the Pb content at Puerto decreased drastically from 1 year to the next (from 321 mg kg⁻¹ in 2003 to 57 mg kg⁻¹ in 2004; Fig. 2). This could be due to the change in the Pb storage location; originally at Puerto, this was moved 30 km inland at the end of the 1900s. As in the case of Cu, dredging activities of bottom sediments (especially at Puerto) may be an important factor in the changes in the Pb concentrations observed in the bay's marine sediments. However, we cannot discard a seasonal effect such as the remobilization of sediments into the water column due to changes in the physical-chemical properties of the sediment-water interface. A definitive explanation of this occurrence requires further studies.

San Jorge Bay registered higher concentrations than other Chilean bays, comparing both subtidal and sandy beach environments (Table 5). In San Jorge Bay, specifically at the Puerto site, Pb concentrate has been stored and loaded for more or less 30 years, which explains the levels of this metal found in the bottom sediments.

Mercury

The mean concentration of Hg increased from 2003 to 2004 at the three sites studied (Fig. 2): at Coloso from 0.48 to 0.51 mg kg⁻¹, at Puerto from 0.4 to 0.82 mg kg⁻¹, and at Chimba from 0.54 to 0.66 mg kg⁻¹ (Table 2). No significant differences in Hg content were found between

sites in both years (ANOVA, $p < 0.01$, Table 3) and only Puerto showed significant differences in Hg concentrations when comparing 2003 and 2004 (Table 4). In general, the subtidal environment of San Jorge Bay presented similar Hg concentrations as the other bays in the world, which range between 0.02 mg kg^{-1} and 2.85 mg kg^{-1} (Table 5). The highest Hg concentration in Table 5 is from Kastela Bay (Adriatic Sea), where mercury contents in the sediments varied widely ($0.143\text{--}11 \text{ mg kg}^{-1}$) in association with industrial waste from a chlor-alkaly plant that closed 15 years ago but is still a source of contamination (Kljaković-Gaspic et al. 2006).

Differences in Hg concentrations between years can be attributed to sediment remobilization due to seasonal differences in the physical and chemical characteristics of the water column. The most common mercury species in the marine environment are Hg^{+2} compounds dissolved and bound to suspended matter and mercury (II) associated with humic matter and sulfide (Wallschläger et al. 1998). Only 74% of the deposited mercury is retained in the sediments (Horvat et al. 1999) and one of the reasons for this situation is the redox condition of the bottom waters (Beldowski and Pempkowiak 2003). In San Jorge Bay, the winter biological productivity is low and the water column becomes more oxygenated whereas in summer, the biological productivity and consequent flux of organic matter to the sea bottom increases and the water column becomes less oxygenated (Escribano et al. 2004), altering the redox condition of the sediment–water interface. Hence, we suggest that in summer, Hg in the water column is bound to organic matter and carried efficiently to the bottom sediments, increasing the mercury concentration, as found in this study.

Assessment of sedimentary conditions related to trace metal contents

Pre-industrial metal concentrations

Normally “average shale” values (Turekian and Wedepohl 1961) or “continental crust average” abundances (Taylor 1972) are used as background

concentrations (Pekey et al. 2004; Buccolieri et al. 2006; Alagarsamy 2006). In this work, we used these concentration references as well as pre-industrial metal values measured in the bottom sediments of Mejillones Bay, which is located 50 km north of San Jorge Bay (Fig. 1). Both bays are located in the same continental geological formation (Vargas 2002) and, thus, are subjected to the same continental influence in the marine sedimentation process. Previous studies have demonstrated that laminated marine sediments are preserved in Mejillones Bay (Ortlieb et al. 2000; Valdés 2004; Vargas et al. 2007) without signs of vertical mixing. Signal preservation in sediments like those of Mejillones Bay are the best source of pre-industrial levels of all substances allowing the reconstruction of ancient sedimentary conditions with high chronological certainty (Sainz and Ruiz 2006). In this case, we used values of metal concentrations measured at the base (below 20 cm) of a sediment core (Table 5); given a sedimentation rate of 156 cm ky^{-1} (Vargas et al. 2007) and considering that human occupation in this bay began in the early twentieth century (Panadés et al. 1995), these metal concentrations represent the pre-industrial condition (before 1872).

Contamination factor

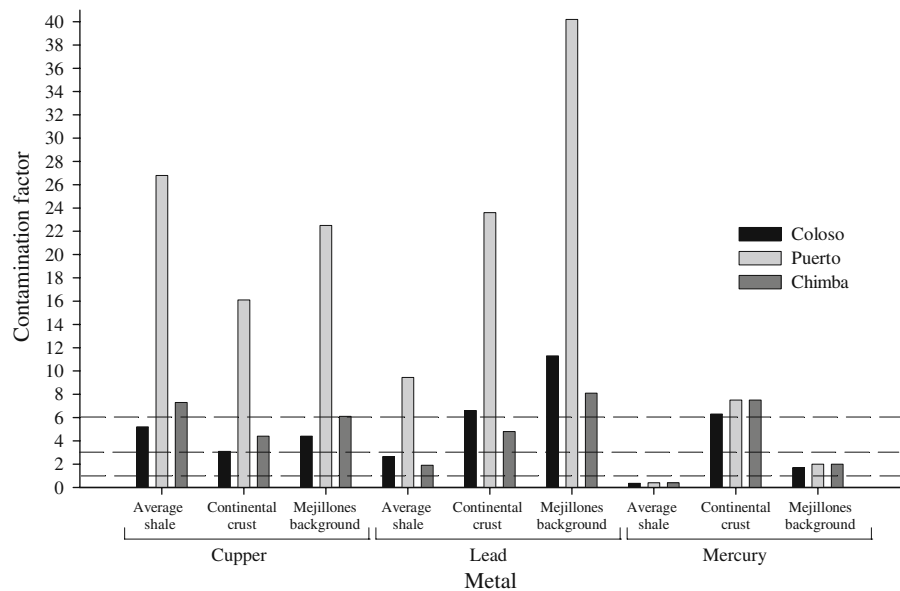
To describe the contamination of a given toxic substance in a basin, Håkanson (1980) proposed the contamination factor (C_f), which is expressed as:

$$C_f = C_o / C_b$$

where C_o is the mean content of the substance in the sample and C_b is the background level value for the substance. The evaluation of this factor uses the following terminology: $C_f < 1$ low contamination; $1 \leq C_f < 3$ moderate contamination; $3 \leq C_f < 6$ considerable contamination; $C_f \geq 6$ very high contamination.

Results of C_f for the three metals measured in San Jorge Bay are shown in Fig. 3. In the case of Cu, all the sampling sites showed similar trends of environmental conditions when we used the three different pre-industrial reference values. Chimba

Fig. 3 Contamination factor (C_f) by metal and location, calculated according to three background levels. Dashed lines represent reference values according to the following terminology: $C_f < 1$ = low contamination; $1 \leq C_f < 3$ = moderate contamination; $3 \leq C_f < 6$ = considerable contamination; $C_f \geq 6$ = very high contamination



and especially Puerto showed sediments with very high Cu contamination; Puerto had the highest concentration for all of San Jorge Bay. In the case of Coloso, the C_f indicated that the sediments were considerably contaminated by Cu.

The three approaches used to calculate the C_f for Pb showed differences between the sites studied in the bay. Only Puerto showed the same environmental condition regardless of the methodological approach used, evidencing high contamination by Pb. Given the Mejillones background level, all three sites showed very high Pb contamination.

The C_f of Hg differed according to the pre-industrial levels. Whereas, in the case of the Mejillones background level, all the sites presented moderate contamination, in the case of the C_f based on the continental crust, the three sites showed very high Hg contamination. However, in the case of the average shale background level, the three sites showed low contamination.

Index of geoaccumulation

The geoaccumulation index (I_{geo}) is usually used to evaluate possible sediment enrichment by metals. This index was proposed by Müller (1979) in order to determine and define metal contamina-

tion in aquatic sediments by comparing current concentrations with pre-industrial levels. The formula used for the calculation is:

$$I_{geo} = \log_2 (C_n / 1.5 B_n)$$

where C_n is the measured content of element n in the sediment and B_n is the geochemical background value of metal n . A factor of 1.5 represents possible variations in the background values for a given metal in the environment, as well as very small anthropogenic influences (Buccolieri et al. 2006). Sediment quality was evaluated according to the I_{geo} classification proposed by Müller (1979), which is shown in Table 6.

Table 6 Description of sediment quality according to I_{geo} classification (Müller 1979)

I_{geo}	I_{geo} class	Description of sediment quality
>5	6	Extremely contaminated
4–5	5	Strongly to extremely contaminated
3–4	4	Strongly contaminated
2–3	3	Moderately to strongly contaminated
1–2	2	Moderately contaminated
0–1	1	Uncontaminated to moderately contaminated
<0	0	Uncontaminated

The I_{geo} for San Jorge sediments based on three pre-industrial concentration values (Table 5) is shown in Fig. 4. The three approaches used to evaluate the environmental condition in terms of the Cu levels in San Jorge Bay sediments showed similar trends at all the sites. Elevated I_{geo} values (class 3 and 4) identified at Puerto indicated strongly contaminated (Cu) surface sediments, whereas contamination at Coloso was low. On the other hand, in the case of Pb, all the sampling sites showed different environmental conditions depending on the pre-industrial reference values used to calculate the I_{geo} . According to the Mejillones background value, all the sites showed a high degree of Pb contamination. Moreover, in all cases, Puerto was found to be moderately to strongly contaminated (I_{geo} of Pb). When using the average shale reference values, the I_{geo} for Hg indicated that the three locations were uncontaminated. However, the other two approaches showed moderate to strong contamination at all three sites.

National and international sediment quality guidelines

Normally, each country enacts its own legislation related to environmental management, partly due to environmental heterogeneity but mostly to

the individual country’s degree of development, which may result in more restrictive laws to protect the health of natural environments.

In this study, we used the sediment quality guidelines (SQG) to evaluate the environmental condition of the bottom sediments of San Jorge Bay. The SQG is a numerical approach developed to provide tools for assessing the biological significance of individual chemical substances (Mucha et al. 2003). The chemical concentrations indicated in the SQG that correspond to the 10th and 50th percentiles of adverse biological effects were called the effects-range-low (ERL) and effects-range-medium (ERM), respectively (Long et al. 1995). Based on this classification, it is possible to distinguish three ranges of chemical concentrations: adverse effects that were observed rarely (<ERM), occasionally (values between ERL and ERM), and frequently (>ERM; McCreedy et al. 2006). However, these values can only be used for screening approaches or in weight-of-evidence methods (Pekey et al. 2004), as they are only two points on a continuum of bulk chemical concentrations in the sediments that roughly relate to sediment toxicity (O’Connor 2004).

According to the ERM values for Cu, Pb, and Hg of Canada, Australia, and the USA, along with the equivalent Chilean legislation (presently in the phase of technical discussion), we evaluated

Fig. 4 Geoaccumulation index by metal and location calculated according to three background levels. *Dashed lines* represent reference values (see Table 6 for details)

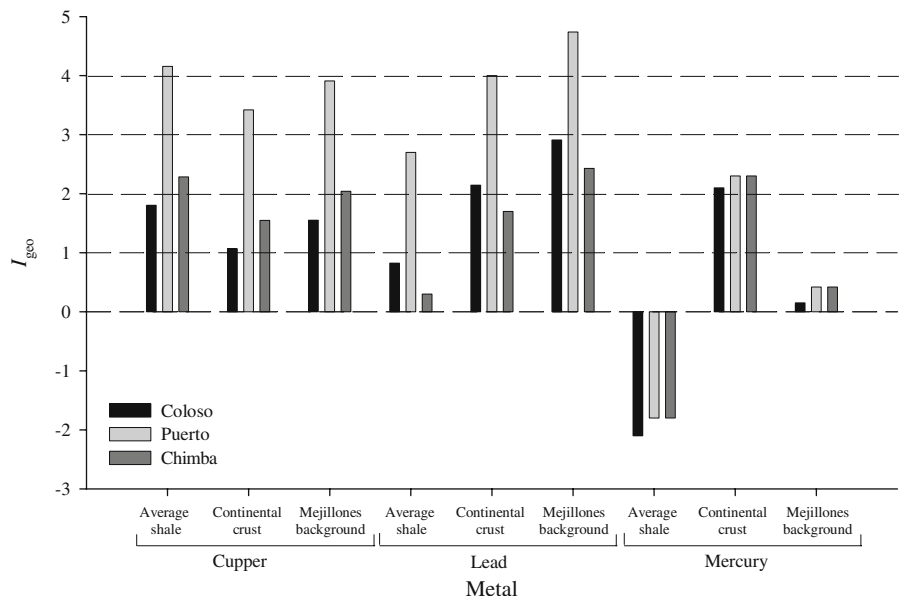
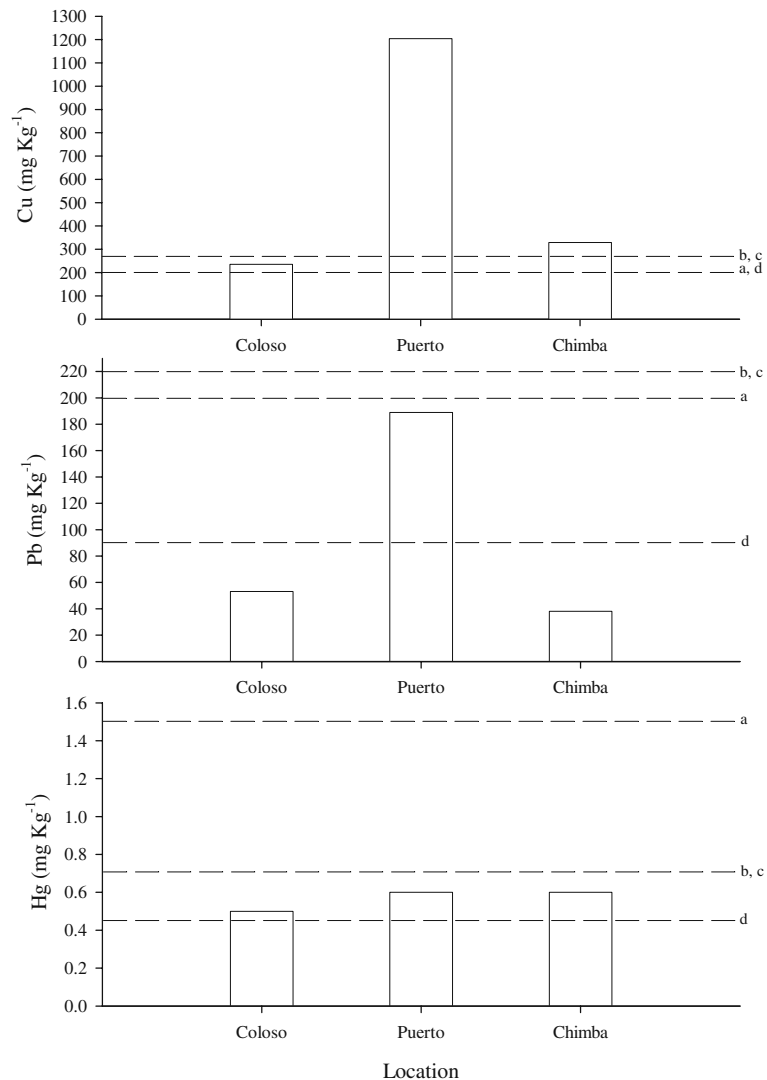


Fig. 5 Metal concentrations in the surface sediments of San Jorge Bay, measured in this study. *Dashed line* corresponds to standard concentrations in marine environments used by different environmental legislations; *a* is the effect-range-medium (ERM of 200 mg kg⁻¹ for Cu, 200 mg kg⁻¹ for Pb, 1.5 mg kg⁻¹ for Hg) indicated in the Chilean legislation (Universidad de Playa Ancha 2002), *b* is the ERM (270 mg kg⁻¹ for Cu, 218 mg kg⁻¹ for Pb, 0.71 mg kg⁻¹ for Hg) indicated in the Australian legislation (McCready et al. 2006), *c* is the ERM (270 mg kg⁻¹ for Cu, 220 mg kg⁻¹ for Pb, 0.71 mg kg⁻¹ for Hg) indicated in the USA legislation (Long et al. 1995), and *d* is the maximum probable effect level (PEL, equivalent to ERM; 197 mg kg⁻¹ for Cu, 91.3 mg kg⁻¹ for Pb, 0.49 mg kg⁻¹ for Hg) indicated in the Canadian legislation (Canadian Council of Ministers of the Environment 1999)



the environmental condition of the three sampling points in San Jorge Bay (Fig. 5). In the case of Cu, values at Puerto and Chimba were higher than the ERM, evidencing contamination problems and probable adverse biological effects. On the other hand, Cu concentrations at Coloso were only higher than the ERM of the Chilean and Canadian SQG. Pb concentrations were higher than the ERM only at Puerto and in terms of the Canadian SQG, whereas Hg exceeded the ERM only for the Canadian SQG at all sampling sites in San Jorge Bay. Note that whereas only Cu exceeded the Chilean SQG at the Puerto site, Cu, Pb, and Hg exceeded at least one ERM, indicating

that this site is contaminated by all three metals analyzed in this work.

Conclusions

The study of Cu, Pb, and Hg in the surface sediments of San Jorge Bay showed significant differences at the three sampling sites analyzed. Puerto had the highest concentrations, associated with the historic loading of metals for more than 60 years. Cu concentrations in this bay were superior to the subtidal environments of other bay systems, whereas Pb was in the concentration range

measured in different contaminated bays. Hg concentrations were lower than the values reported in other bays.

The high temporal variability of metal concentrations (especially Cu and Pb) observed herein seems to be a consequence of a combination of different factors, such as changes in loading and/or mineral storage in San Jorge Bay, dredging activities of bottom sediments (especially at the Puerto site), and seasonal changes in physical and chemical properties of the water column that modify the exchange of metals at the sediment–water interface.

Noteworthy differences were found in the pollution indicators used in this work (C_f , I_{geo}) depending on the pre-industrial values used for the calculations. We suggest using the pre-industrial concentrations of Mejillones Bay rather than the geological values (average shale, continental crust) to evaluate the degree of contamination in this coastal zone. Using this indicator, San Jorge Bay presented serious pollution problems by Cu and Pb at the three sampling sites studied.

When comparing Chilean environmental legislation for marine sediment quality (presently under discussion) with other international standards, the former seems to be less restrictive because only Cu exceeded the maximum values used to evaluate ecological risk and the health of marine environments.

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