Environmental and Sustainability Indicators 22 (2024) 100373

Contents lists available at ScienceDirect

Environmental and Sustainability Indicators

journal homepage: www.sciencedirect.com/journal/environmental-and-sustainability-indicators

Metals and metaloid preserved in marine sediments of an industrial complex of central Chile. Environmental assessment using different background values

Jorge Valdés Saavedra[a,*], Eduardo Quiroga[b]

[a] *Laboratorio de Sedimentología y Paleoambientes, Instituto de Ciencias Naturales A. von Humboldt, Facultad de Ciencias Del Mar y de Recursos Biológicos, Universidad de Antofagasta, Av. Universidad de Antofagasta 2800, Antofagasta, Chile*

[b] *Escuela de Ciencias Del Mar, Facultad de Ciencias Del Mar y Geografía, Pontificia Universidad Católica de Valparaíso, Chile. Av. Altamirano 1424, Valparaíso, Chile*

ARTICLE INFO

Keywords:
Metals
Marine sediments
Marine pollution
Chile

ABSTRACT

This work examines the distribution of metals(oid) in coastal sediments of the Concon-Quintero industrial complexes (central Chile), and evaluates the environmental condition of this zone, using some environmental indexes and different global and local background values.

The Index of geoaccumulation and the Enrichment Factor were different depending on the background values used to calculate them. Only Mo and Pb, simultaneously show both an enrichment, and some degree of pollution problem, with all backgrounds utilized. Three of the four background values used in this work to calculates the Pollution Load Index suggests a polluted condition of the bottom environment. The spatial distribution, the results of environmental indices and the comparison with local environmental legislation suggests that Pb is introduced to the marine system by industrial activities. The result of both, SQG and m-ERM-Q suggest that metals preserved in the sediments are a threat to the benthic life, especially in the Concon-Ritoque zone, where the highest values were recorded.

These results suggest a notorious influence of the Aconcagua river on the metal accumulation in the coastal zone.

1. Introduction

The occupation of coastal zones around the world not only has transformed the natural landscape, but also represents a strong pressure on the capacity of natural systems to assimilate the high amount of waste derived from human activities. Particularly, the industrialized complexes located near or within residential zones represent a threat to natural ecosystems and human health, even more in countries where the environmental legislation remains conditioned by economic factors (Bellas et al., 2020; Di Cesare et al., 2020; Tonne et al., 2021).

Chile has a mining tradition that has promoted economic growth, but generally without a strict protection of the natural environment and/or public health. This development model has transformed the natural landscape, generating a concentration of human population and economic activities in specific geographic areas, particularly in coastal zones where industries of different nature coexist with human settlements without clear boundaries to protect their health. Central Chile concentrates 50.7 % of the population and an intense industrial activity (www.OECD.org/chile/). The Concon-Quintero Industrial Complex (CQIC), located at 32° 50′ S, is one of the most populated and industrialized coastal zones of Chile, with more than 60 years of industrial activity (Pastene et al., 2019). Here, three coastal systems are possible to identify (Fig. 1). In the northern zone, Quintero bay has 38,000 inhabitants living in town and sharing the coastal zone whit industries related mainly to copper mining (smelting and refinery), energy power plants, cement production, chemical plants and fuel storage (Muñoz et al., 2019). In the southern zone, Concon is a little coastal town with 42,000 inhabitants and different industries of oil refinery, fuel storage, energy power plants, metallurgy, and others. Ritoque, located between these two bays, is a touristic coastal zone with a marine area administered by an artisanal fishermen's organization, whose aim is to develop the management, culture and marketing of benthic organisms (Pastene et al., 2019).

The main geographic feature of this coastal zone is the presence of

---

* Corresponding author.
E-mail addresses: jorge.valdes.saavedra@uantof.cl (J.V. Saavedra), eduardo.quiroga@pucv.cl (E. Quiroga).

https://doi.org/10.1016/j.indic.2024.100373
Received 27 November 2023; Received in revised form 28 February 2024; Accepted 29 February 2024

different types of freshwater inlets. Two estuaries, Campiche in Quintero and Mantagua in Ritoque and one river, Aconcagua in Concon, connect the continent and their human activities with the marine zone (Pastene et al., 2019), which can eventually be recorder in the bottom sediments as a signal of pollution. This is the case of the Aconcagua River basin, where important agricultural and mining activities are developed. This basin has an area of 7200 km^2 with a total population of 732,000 people, and it hosts El Soldado and Andina mining complexes in the central valley and Andean zone, respectively. Besides, a copper smelter at Chagres, and other smaller mines are distributed throughout the basin (Aguilar et al., 2011; Gaete et al., 2017; Neaman et al., 2020).

Although the industrial activities are highly linked to the metal accumulation in marine environmental matrices, scarce investigations about the assessment of ecological and health risks have been carried out in these environments (Samhouri et al., 2019; Tian et al., 2020; Varol et al., 2020). In Chile, the studies conducted in Mejillones (Valdes et al., 2005; Valdés, 2012), Antofagasta (Valdés et al., 2015), Bio region (Salamanca et al., 2019), mouth of the Itata river (Chandía and Salamanca., 2012), Caldera, Chañaral and others bays (Valdés and Tapia, 2019) have been focused on metals baseline in sediments. All these studies considered the enrichment of metals in sediments as evidence of contamination using spatial and temporal measurements, Sediment Quality Guidelines, and different environmental indexes (see Hübner et al., 2009, and references cited therein).

In this context, the main concern is that the use of environmental indexes to evaluate the impact of pollutants in the ocean requires background reference values, which are not always available at local scale. In general, most of the studies all around the world use backgrounds defined as global reference values like those proposed by Turekian and Wedepohl (1961), Taylor and McLennan (1985), Rudnick and

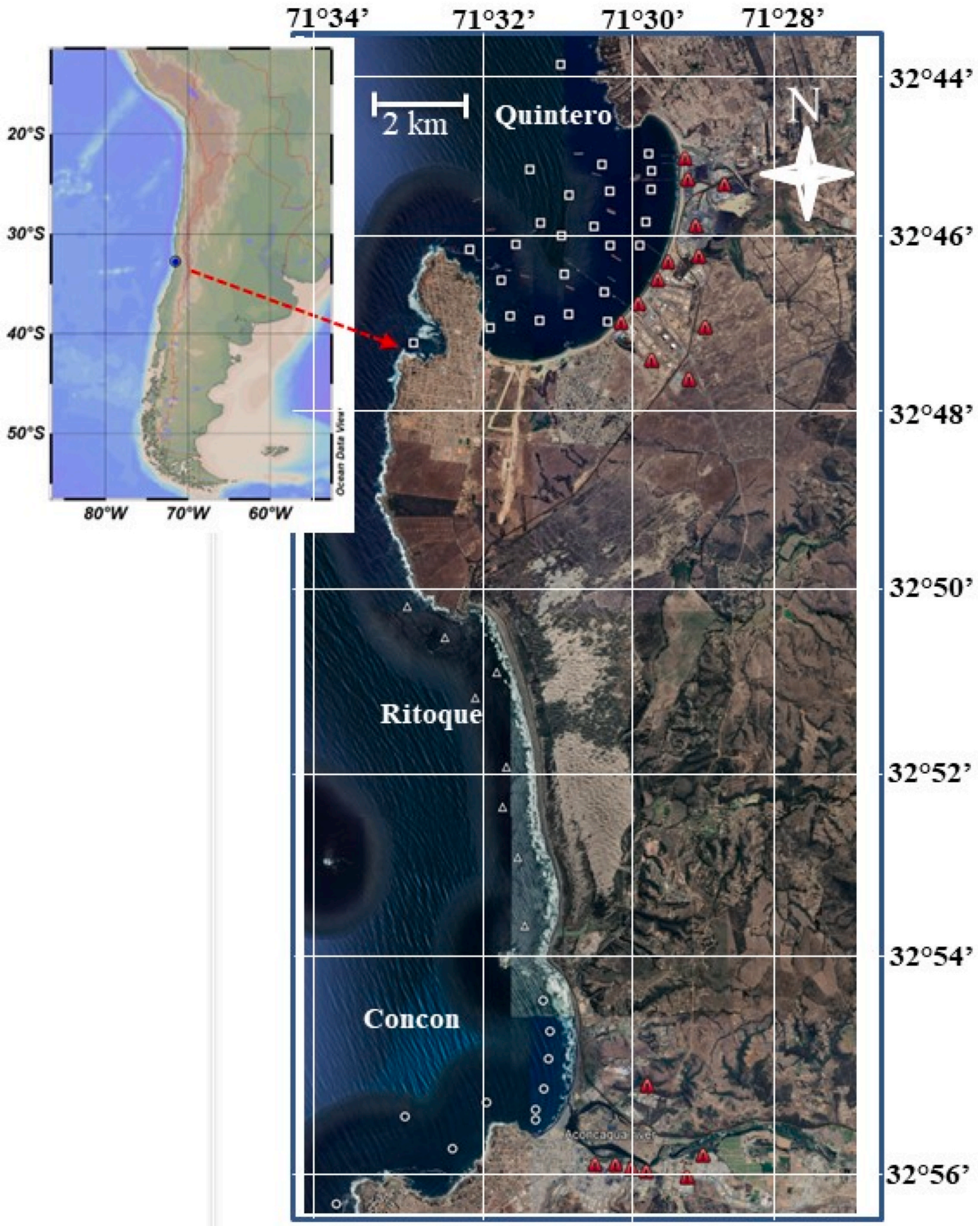


Fig. 1. Study zone in central Chile. White circles, triangle symbols and square symbols indicate sampling point in Concon, Ritoque and Quintero, respectively. Red triangles indicate location of industries in the zone. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Gao (2003). The problem is that these values do not always have a good representation at local scale due to the high variability of the geological formation, which is also the parent source of material deposited in the marine environment.

The coastal zone of central Chile has been the object of environmental studies that have shown the critical situation and the threat to ecological and human health (Rivera et al., 2019). In general, all these studies have been focused on the presence and distribution of heavy metals released by mining activities and preserved in soil, vegetation and aquatic sediments, and their toxic effect for benthic organisms (Pizarro et al., 2010; Aguilar et al., 2011; Gaete et al., 2017; Muñoz et al., 2019).

In the marine environment of CQIC, studies have been focused on the content and distribution of inorganic and organic substances in bottom sediments. Parra et al. (2015) showed that Cu, Zn, As and Pb accumulated in the marine sediments of Quintero bay are most likely associated with the copper smelter located in this coastal zone, while Pastene et al. (2019) assessed the sedimentary organic matter sources (anthropogenic, terrestrial, or marine) by means of stable isotopes and geochemical proxies (Total Organic Carbon/Total Nitrogen and Chlorophyll-a/TOC). The researchers concluded that a substantial fraction of this organic matter in Quintero Bay is anthropogenic, from industrial and domestic wastewater sources, even when the coastal environment has a high capacity for natural remediation due to factors like topography and circulation that favors the dispersion and assimilation of OM. Recently, Oyarzo-Miranda et al. (2020) developed an *in vitro* experiment concluding that the seawaters of Quintero bay have highly negative effects on individual development of seaweed populations (*Lessonia spicata*), which suggests a long-term negative impact on the community structure of these coastal marine areas. Finally, Castillo et al. (2023) demonstrated that metals present in the shellfish *Concholepas concholepas* captured and commercialized in Quintero bay, are a threat to human health.

Even though the scientific knowledge of the coastal ecosystem of central Chile has increased during the last decades, there is still a lack of environmental information that incorporates the analysis of the temporal and spatial dimensions, and the effects of the natural and anthropogenic substances on the marine ecosystems and human health. In this context, the goals of this work are (i) to analyze the spatial distribution of metals(oid) in marine coastal sediments of one of the most industrialized zones of Chile, and (ii) to apply different environmental indicators, based on different background reference values, to assess the ecological risk in coastal environments.

2. Materials and methods

A total of 43 sediment samples were collected in 2017, between 5 m and 50 m water depth in the coastal zone of Concon, Ritoque and Quintero (Fig. 1). A detailed description of the sampling methodology and the grain-size and Total Organic Matter (TOM) analysis is given in Pastene et al. (2019). The metals analysis was carried out at LASPAL laboratory (University of Antofagasta), in the <63 μm fraction of sediment. This fraction is commonly associated to contaminant metal(loid)s in marine sediments (Fukue et al., 2006). After sieving, 400 mg of marine sediments were digested in a MARS-X microwave digester (ICEM model 350) with a mixture of 10 mL HNO_3 + 1 mL $HClO_4$ + 0.5 mL HF, according the US-EPA 3052 procedure (US EPA, 1996). The concentrations of Cd, Ni, Zn, Cu, V, As, Mo, Fe, Al, and Pb were analyzed in a PerkinElmer ICP-OES OPTIMA 8300.

The accuracy and precision of the methods were evaluated using the marine sediment MESS-3 standards, certified by the National Research Council, Canada. According to close correlation between the data of this study and the certified value, the isobaric interferences for the studied elements were negligible (Table S1, Supplementary material). Spatial distribution of metal(oid)s in surface sediment was performed with the software Ocean Data View 5.2.1 version, using DIVA gridding routine, because this interpolations method considers coastlines and bathymetry features to structure and subdivide the domain on which estimation is performed (Schlitzer, 2020).

Four indexes and a Sediment Quality Guideline were used to evaluate the environmental condition and risk for marine organisms of coastal zones near the CQIC.

The Enrichment Factor (EF; Eq. (1)), that assesses the proportion of the metal(loid)s that is in excess with respect to the lithologic background was calculated according to Tribovillard et al. (2006):

$$EF = \left(\frac{M}{X}\right)_{sample} \div \left(\frac{M}{X}\right)_{background} \qquad \text{Equation 1}$$

where M is the analyzed metal(loid), and X is the level of a normalizer element that in this case was Fe (Reimann and de Caritat, 2005; Mil-Homens et al., 2013; Wan et al., 2015). The results were interpreted according to Essien et al. (2009) and Larrose et al. (2010): $0.5 < EF < 1.5$, the metal(loid)s may be derived entirely from crustal materials or natural weathering processes, $EF > 1.5$ indicate an important proportion of non-crustal contributions and/or unnatural weathering processes (e.g., anthropogenic effects).

The geoaccumulation index (I_{geo}; Eq. (2)) was calculated according to Müller (1979):

$$I_{geo} = log_2 \frac{c_n}{1.5 \times B_N} \qquad \text{Equation 2}$$

where C_n is the current element concentration and B_n is the background concentration. The results of I_{geo} were classified according to the contamination scale proposed by Müller (1979), that indicates Not polluted (I_{geo} <0), Not polluted to moderately polluted ($0<I_{geo}\leq1$), Moderately polluted ($1< I_{geo}\leq2$), Moderately to heavily polluted ($2< I_{geo}\leq3$), Heavily polluted ($3< I_{geo}\leq4$), Heavily to extremely polluted ($4< I_{geo}\leq5$), Extremely polluted ($I_{geo}>5$).

Additionally, the Pollution Load Index (PLI), that measure the effect of a mixture of metals, was used to determine the integrated pollution status of the combined toxic groups at sampling stations. The PLI was calculated following Bhuiyan et al. (2010), using the nth root of the product of n contamination factors (CFs) for the tested metal(loid)s (Eq. (3)):

$$PLA = (CF_1 \times CF_2 \times CF_3 \times \bullet\bullet\bullet \times CF_n)^{\frac{1}{n}} \qquad \text{Equation 3}$$

where CF_n is the contamination factor of metal(loid) n (CF = current metal(loid) concentration/metal(loid) background concentration). The PLI values were interpreted in two ways: polluted (PLI >1) and unpolluted (PLI <1) (Tomlinson et al., 1980; Harikrishnan et al., 2017).

In all calculation procedures, the concentration of 4 background values were used to evaluate which source best reflects the chemical composition of the marine sediments in the studied areas. This was done because values traditionally used, such as that of the continental crust correspond to global geological references that usually do not represent exactly the evaluated local area. For this reason, local and global baseline reference values were used. These baseline concentrations correspond to (i) local background, (ii) Sedimentary rocks (Turekian and Wedepohl, 1961), (iii) Upper Continental Crust (Rudnick and Gao, 2003) and Upper Continental Crust (Taylor and McLennan, 1985) (Table 1). Local background corresponds to 6 geological soil samples collected in the surrounding continental area of Quintero bay (more than 7 km away from coastal zone, and protected of the influence of the prevailing winds) that was analyzed by the same method used in the case of marine sediment samples.

The adverse effects produced by polluted sediments on aquatic organisms were evaluated using the Sediment Quality Guideline (SQG) procedure (Long et al., 1995; MacDonald et al., 2000; Birch and Taylor, 2000; Crane, 2003). The SQG assessment showing chemical concentrations in the 19th percentile are known as effects range—low (ERL), and those in the 50th percentile are referred to as effects range—median

Table 1
EF and I_{geo} with different background values. See Methodology in order to identify the corresponding category. BRV stands for background reference value (mg kg^{-1}). UCC stands for Upper Continental Crust. BRV values correspond to mean concentrations.

Metal	UCC[a]			Local background			Shale, Sedimentary rock[b]			UCC[c]		
	BRV	EF	I_{geo}	BRV	EF	I_{geo}	BRV	EF	I_{geo}	BRV	EF	I_{geo}
Cu	25	15.5	0.2	24.2	0.8	0.3	45	11.7	−0.6	28	20.1	0.1
Zn	71	1.4	−3.4	4.1	1.2	0.7	95	1.4	−3.8	67	2.1	−3.3
Pb	16	29.4	1.1	10.2	2.3	1.3	20	31.7	0.8	17	39.8	1.0
Cd	0.1	161.9	3.6	0.84	0.9	0.5	0.3	72.8	2.0	0.09	259.0	3.8
Ni	50	3.3	−2.0	6.71	1.2	0.9	68	3.3	−2.5	47	5.0	−1.9
V	110	2.4	−2.5	22.48	0.6	−0.2	130	2.8	−2.7	130	3.0	−2.7
Mo	1.5	71.9	2.4	3.2	1.6	1.4	–	–	–	1.1	141.5	2.9
As	1.5	31.1	1.4	2.66	0.9	0.4	13	4.8	−1.9	4.8	14.0	−0.5
Al	8.04	0.4	−5.0	0.2	0.4	0.6	8	0.56	−4.99	15.4	0.3	−5.9

[a] Taylor and McLennan (1985).
[b] Turekian and Wedepohl. (1961).
[c] Rudnick and Gao. (2003).

(ERM) (Long et al., 1995). Considering this classification, three ranges of chemical concentrations in which adverse effects are rarely observed (<ERL), occasionally observed (≥ERL and <ERM), and frequently observed (>ERM) (McCready et al., 2006) were identified.

Based on the SQG procedure, the Ecological Risk Assessment (ERA) (Long and MacDonald, 1998) was used to evaluate the hazardousness of the contaminated sediments considering the mean ERM quotient (m-ERM-Q). The m-ERM-Q represents the effects of multiple anthropogenic contaminants, and it is calculated according to Trifuoggi et al. (2017) by Eq (4):

$$m - ERM - Q = \frac{\sum_{I-1}^{Q}\left(\frac{C_I}{ERM_I}\right)}{n} \qquad \text{Equation 4}$$

where C_I is the concentration of the measured metal(loid) I, ERM_I is the ERM value of metal(oid) i, and n is the number of metal(oid)s. The results were interpreted according Long and MacDonald (1998): m-ERM-Q < 0.1 indicates a 9% probability of toxicity, 0.1 ≤ m-ERM-Q < 0.5 denotes a 21% probability of toxicity, 0.5 ≤ m-ERM-Q<1.5 indicates a 49% probability of toxicity, and 1.5 ≤ m-ERM-Q correspond to 76% probability of toxicity.

The concentrations of As, Cu, Ni, Pb and V were compared with threshold concentrations defined in the Secondary Environmental Quality Standard for the Protection of Waters and Sediments of Quintero-Bay (Ministerio del Interior y Seguridad Pública, 2021), that is the first environmental regulation established in Chile for the protection of a coastal marine zone.

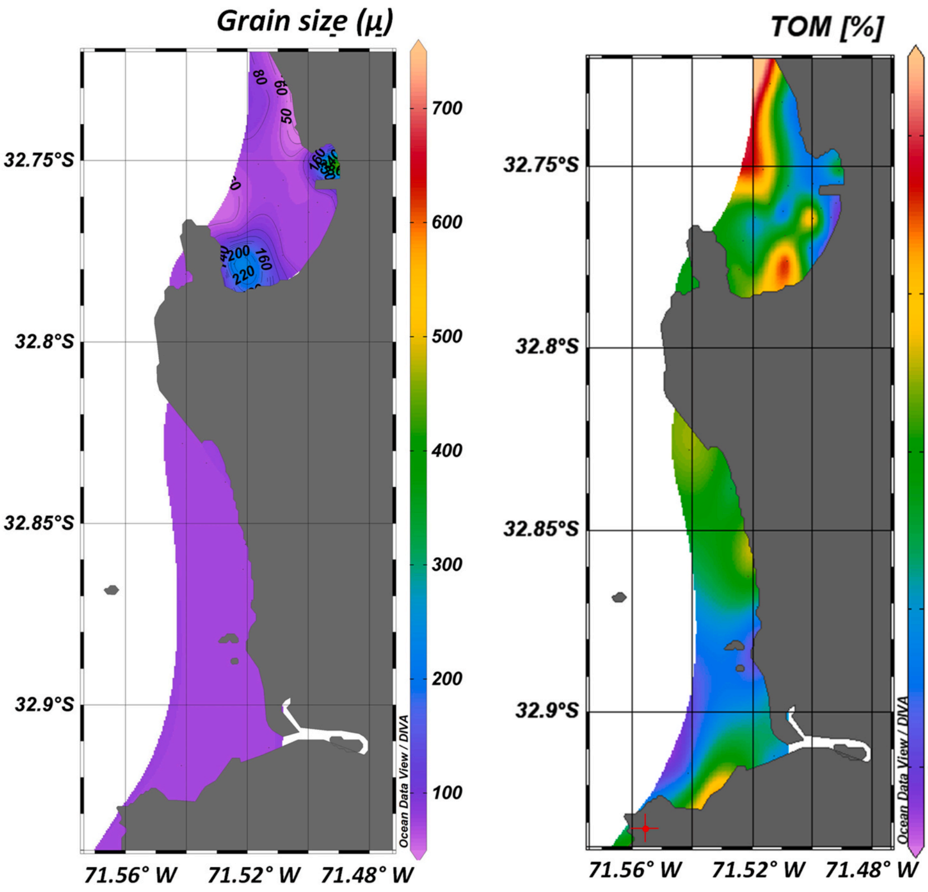


Fig. 2. Spatial distribution of grain size and Total Organic Matter in surface sediments of CQIC.

In order to explore the spatial environmental variability in the distribution of metals (oid) in surface sediments of the study area, a Principal Component Analysis (PCA) was used to search for associations between the sampling stations and geochemical variables. For this analysis, a non-transformed correlation matrix was used (Jongman et al., 1987), considering 1000 bootstrap iterations to obtain confidence intervals ($p < 0.05$). In addition, a Spearman rank correlation analysis was performed to look for relationships among sediment variables (TOM and heavy metal concentrations). Heavy metal variables were transformed to $\mathrm{Log}_2\,(x+1)$, meanwhile TOM (%) was transformed to arcsine ($\sqrt{x}/100$) (Zar, 2010; Pastene et al., 2019). All statistical analyses were performed using PAST v4.30 (Hammer et al., 2001).

3. Results and discussion

3.1. Spatial distribution of metals and Arsenic in marine sediments

Marine sediments of CQIC were formed by homogeneously sized particles. Most of the zone was dominated by material of mean particle size <63 μm, belonging to a very fine sand. Only two sectors in Quintero bay have thicker material (up to 220 μm) corresponding to fine sand (Fig. 2). In general, in aquatic systems, particle size has a significant influence on the capacity of the sediment to adsorb metals due to specific surface area, establishing an inverse correlation between particle size and metal content (Kim et al., 2017), situation that must be considered when the sediment presents a heterogeneous granulometry. However, the fact that the sediments of the study zone are represented mostly by one Wentworth category (very fine sand), allows discarding particle size as a factor influencing the spatial variability of metals. Therefore, in this study the effect of grain size was normalized using only the <63 μm fraction to measure metal content.

The order of abundance of major elements was Fe > Al, while for minor elements it was Pb > Cu > V > Ni > Mo > Zn > As > Cd (Fig. S1, Table S2, Supplementary material). Comparing the three studied zones, Quintero has the highest mean concentration of V, while Ritoque exhibits the highest mean concentration of Cd, Ni, Al and Mo. The other metals recorded the highest mean concentration in Concon (Fig. 3), even when Pb content was similar along the three studied zones (Fig. 3).

In Chile, the studies of metals in marine sediments of industrial zones are scarce, making it difficult to compare environments with similar conditions. Four bays of northern Chile (Mejillones, San Jorge, Chañaral and Caldera) and two bays of southern Chile (San Vicente and Talcahuano) with recent and past industrial activities were studied using similar methods and analytical approaches (Valdes et al., 2005; 2010; Valdés, 2012, Valdés and Castillo, 2014; Valdés and Tapia 2019; Aguirre-Martínez et al., 2009). These studies were used to compare our results and to evaluate the environmental condition of CQIC (Fig. 4). Of the 7 coastal zones with similar industrial activities along the Chilean coast, the CQIC had the lowest concentration of Cu, Zn, Cd, Ni, V, Mo and As, while in the case of Pb, CQIC was the third and in the cases of Fe and Al it was the first, but comparing only two and four bays, respectively (Fig. 4). In the case of Cu, the high content found in Talcahuano bay is remarkable, because in this bay there are no port services (like loading and/or storage) for mining. However, the samples taken by Aguirre-Martínez et al. (2009) in this bay (and San Vicente) were collected closer to the port sector, where the pollution by different sources is most plausible. This situation, and a high temporal variability in the environmental conditions can explain the differences with the values reported by Ahumada (1992) for San Vicente bay. On the other hand, San Jorge and Chañaral bays have current and historical evidence of contamination, respectively. In San Jorge, the principal port activity is the storage and loading of Cu, Zn and Pb minerals (Valdés et al., 2010), while the Chañaral bay was, during five decades, the destination of the mine tailings from a company located 170 km east of the coast where tailings were dumped (Valdés and Tapia., 2019). In the case of Pb, San Jorge bay has been historically affected by stockpiles in the city port (Tapia et al., 2018), that explains the highest concentration found in its marine sediments. However, San Vicente and CQIC also show high Pb concentrations (second and third, respectively), probably due to both these bays having similar chemical and fuel industries. In general, these types of industries as well as the vessel painting, generate liquid wastes with high content of Cu, Pb, Zn and Fe (Ahumada, 1992) that accumulate in marine sediments of the coastal zone. The cases of Fe and Al, in which CQIC showed the highest concentrations (even when only two and four bays were compared, respectively), probably can be associated to the continental supply, due to the rivers transport, because these two metals are associated to the lithogenic fraction of marine sediments (Wan et al., 2015).

The comparison between these 7 industrial coastal zones showed that the CQIC is not the environment with the highest metal content in marine sediments. This preliminary conclusion may suggest the idea that the zone has no pollution problems. But the wide picture of the zone shows that the problems associated with human health have been more studied, concluding that atmospheric pollution is the principal concern from the human viewpoint (Muñoz et al., 2019). This situation may hide the problems associated with marine environments, as well as for benthic organisms and fishery and recreational activities developed in the zone. It is important to point out that this comparative analysis between Chilean industrial bays must be taken with caution because it is based only on the similarities of anthropic activities developed therein. Other natural sources of variability, like geography, geological formations, exposition of the coast line, presence of rivers, hydrography, climate, Etc., may influence the sedimentological processes, making it difficult to make a correct comparison. For this reason, the environmental analysis must be set at a local scale, taking into consideration natural and anthropic factors and, when it is possible, local baseline and local background values of metals under evaluation.

Metals in marine sediments displayed different spatial patterns of distribution in the coastal zone of CQIC. The distribution of most of the metals preserved in the sediment of Concon, showed the influence of the Aconcagua river discharge. Al, As, Cu, Ni, V and Zn recorded high concentration in sediments deposited in front of the Aconcagua river mouth, while Fe and Cd showed patches of low concentration in this zone (Figs, 5). The Aconcagua basin, historically and currently, has been occupied by mining and agricultural activities, and the river has become a carrier to organic and inorganic wastes. Different studies suggest that the high concentration of Hg, Cr and Cu found in waters and sediment along the Aconcagua river are related to mining and agriculture activities developed in the basin (Pizarro et al., 2010; Gaete et al., 2017). Aguilar et al. (2011) concluded that the high Cu concentration (up to 700 mg kg^{-1}) in agricultural soils of the Aconcagua basin, most likely resulted from either modern or former mining activities. In this context, the patches of high concentration of As, Cu, Ni and V found in the mouth of the Aconcagua river are a solid evidence of its influence on the composition of the marine sediments, and that other metals, besides those reported previously, may also be released in the river before reaching the coastal marine zone. The location of the industries in Concon and Quintero and the influence of freshwater discharges of the Aconcagua river are the principal factors controlling the metal accumulation in sediment of the coastal marine environment. In Quintero bay, the industries are located along the coastline, and the outfalls of many of them discharge into the bay, while in Concon, the industries are located inland, along the shore of the Aconcagua river (Fig. 1). The influence of rivers as contamination carriers has been documented in other coastal zones around the world (Pastene et al., 2019; Yang et al., 2020; Liu et al., 2020; Lu et al., 2020).

An important factor to evaluate the distribution of pollutants in marine environments is the coastal currents, which can be influencing the sediment transport in the study area. Unfortunately, local hydrographic studies in the CQIC are limited. In central Chile (33°S), studies based on lagrangian current meters and simulations have shown a coastal circulation dominated by the Chilean Coastal Current (CCC), an

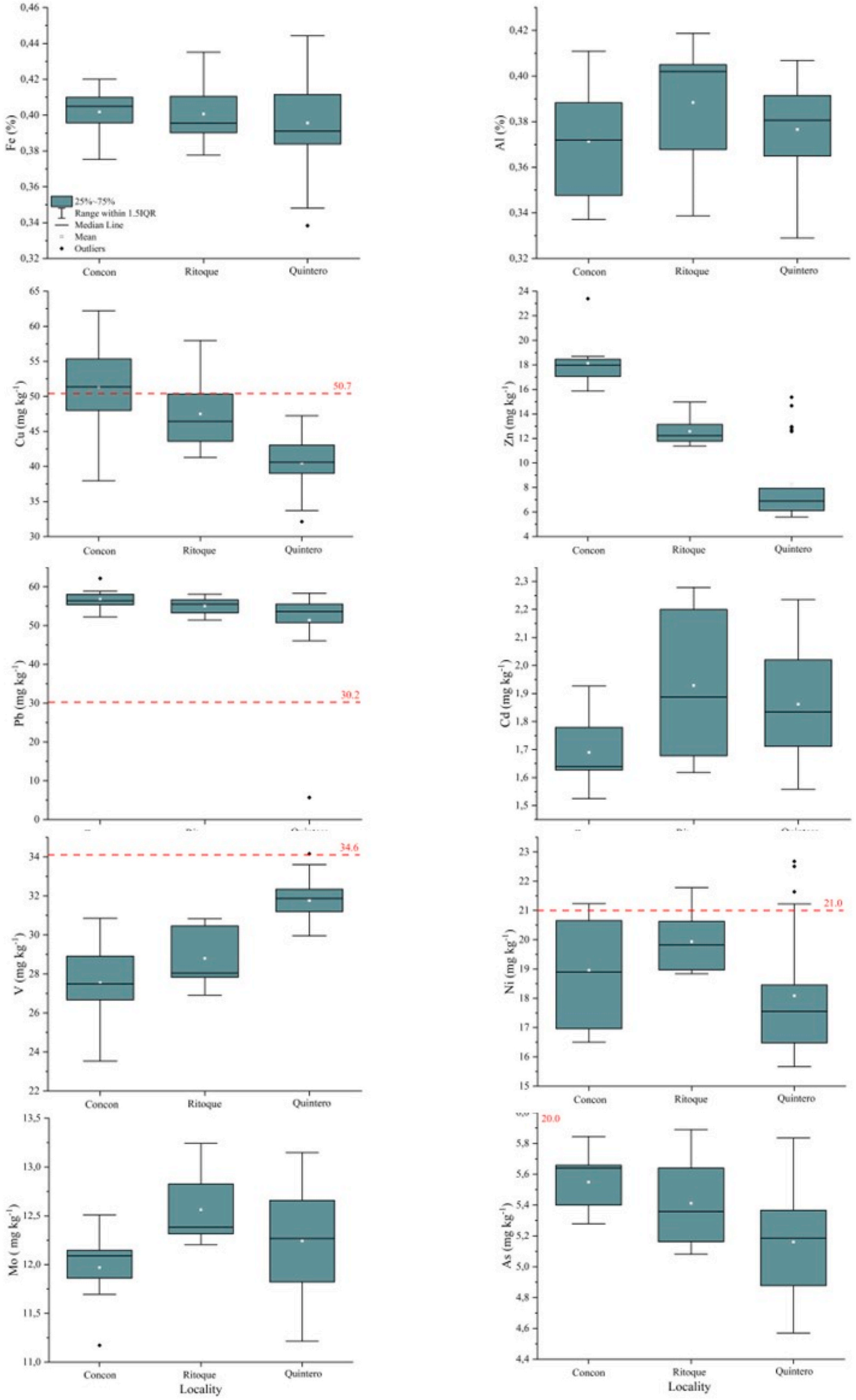
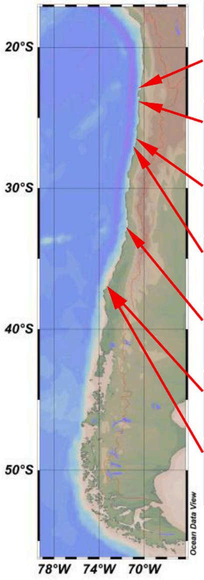


Fig. 3. Box-plots of metals analyzed in surface sediments of three coastal zones of central Chile. The mean concentration (Blue point), standard deviation (black line), interquartile range (light blue box) and the outliers (asterisk) are shown. Dashed line represents the threshold concentrations defined in the Secondary Environmental Quality Standard for the Protection of Waters and Sediments of Quintero-Bay (Ministerio del Interior y Seguridad Pública, 2021). These values are also indicated in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Bay	Cu	Zn	Pb	Cd	Ni	V	Mo	As	Fe	Al
Mejillones[1]	106.0	59.0	19.7	11.9	31.8					
San Jorge[1]	244.4	41.9	182.3		30.2	51.3	66.0	16.6	0.3	0.3
Chañaral[1]	421.4	31.6	43.0	29.7	22.3	72.2		13.7		0.4
Caldera[1]	105.8	60.2	32.6		21.7	112.7				0.1
CQIC[2]	44.3	11.3	53.3	1.8	18.7	30.2	12.3	5.3	0.4	0.4
Talcahuano[3]	512.1		50.5	12.7						
San Vicente[3]	109.8 29.4	81.8	68.1 12.0	2.3 2.4	67.2					

[1] Valdés et al. (2005. 2010); Valdés (2012); Valdés & Castillo (2014); Valdés & Tapia (2019)

[2] This study

[3] Aguirre-Martinez et al. (2009); Ahumada (1992). Up and down, respectively.

Fig. 4. Map of Chilean coastal zones with analysis of metals in sediments, and the mean concentrations reported in the respective studies.

equatorward surface flux driven by persistent upwelling-favorable winds (Aiken et al., 2008). This circulation pattern controls the dynamic of the sediment transports (and eventually, pollutants) accumulated in the Concon area, which also are transported northward, and it can be influencing the characteristics of material deposited in the Ritoque area. Indeed, the homogeneous grain size distribution observed in Concon-Ritoque area (Fig. 2), and the high concentration of all metals, except Zn (Fig. 5) in the Aconcagua river mouth suggest that coastal circulation is important to characterize the distribution of pollutants associated to industrial activities. The case of Pb is evident, because, even when Ritoque has no industries, this metal was distributed homogeneously in both, Concon and Ritoque areas (Fig. 5). On the other hand, the Quintero bay must be considered as an independent unit, due to its geographic orientation. Into the bay, some studies show a circulation model dominated by the wind and tides, with a main flux entering from the north, and exiting by the south (Escobar, 1971), mostly during summer, and an inverse pattern during winter (IFOP, 2016). The grain size distribution in the Quintero bay (Fig. 2) agreed with this hydrodynamic pattern, because the north and south zones accumulate a thicker sediment (150–200 μm), which suggests an environment of high energy. In general, it is assumed that the transport of natural and/or anthropogenic material as well as their dispersion and final disposition are related to textural characteristics of the sediments (Sánchez et al., 2019; Ming et al., 2019). In our study area, the Spearman correlation analysis showed that Al and Fe are not correlated with minor elements that suggests that lithogenic source is not the main factor controlling the metals(oid) supply to the marine environment (Table S3, Supplementary material). On the other side, there is a negative correlation between Pb and %TOM ($r = -0.32$, $p < 0.05$) (Table S2, Supplementary material). Although, some studies show that organic matter (principally in form of dissolved organic carbon) is an efficient carrier of soluble Pb in surface waters (Landre et al., 2009; Dawson et al., 2010; Plach and Warren, 2012), and the pH play a significant role on the anionic organo-Pb complex in bottom sediment (El Bilali et al., 2002), the negative correlation found in the sediments of CQIC, is unclear and need further studies to explain it. Positive correlations between metals(oid), as in the cases of Cu and Zn, Pb, Ni, As, suggest that the same mechanism is responsible of its accumulation in the bottom sediments. It is important to note that processes like adsorption, precipitation, diffusion, chemical reactions, and biological activities influence directly or indirectly the effect of fine sediment transport and organic matter on heavy metal distribution in bottom sediments (Sreekanth et al., 2015; Bui et al., 2019), resulting in different types of correlations between metals and metals-organic matter.

All these factors influence the final accumulation of different metals in marine sediments. In the case of the CQIC the PCA result suggests a segregation between the three studied zones based on the dominant metals in each of them (Fig. 6). The two principal components explain the 50,1% of the variance of the data, and correlates the V, Cd, Fe and Mo content with Quintero, while Pb, Cu, As and Zn are correlated with Concon, that in concordance with the concentrations and spatial distribution of these metals in the coastal zone (Figs. 3 and 5).

The industrial activities developed in Quintero bay have been pointed out as responsible for many and recurrent environmental problems recorded in the marine and continental surrounding zone (Pastene et al., 2019), and it is necessary to identify the source of these pollution and to apply measures to prevent human health damage of the population living around this bay. It is known that more scientific information is necessary to support the decision-making of the Chilean environmental and health authorities. Unfortunately, environmental studies are scarce and generally with a low spatial and temporal resolution. Even when the composition of the aquatic sediments is more stable than other environmental matrices, the spatial and temporal dimensions are critical to evaluate the real condition of coastal ecosystems. In this context, this study can be used to evaluate temporal changes in the metal content of marine sediments of Quintero bay, comparing it with a previous work developed by Parra et al. (2015). These authors evaluated the spatial distribution of Cu, Zn, Pb, Ni, V and As in sediments, using samples taken before 2015, while the present work analyzed samples collected in 2017. The content of these metals in both periods shows remarkable differences (Fig. S2, Supplementary material). While Cu, Zn, V and As decrease their concentration, Pb and Ni increase. Natural factors such as resuspension of bottom sediments by currents and storms, and/or anthropic factors such as ships movement, changes in productive processes or production of local industries, and especially, sediments dredging, that is a common technique used to facilitate the harbor activities, can explain this temporal variability. In any case, the most efficient strategy of environmental evaluation must be supported by a more continuous monitoring of marine sediments, to understand and differentiate between the natural and anthropic factors that influence the variability of metal content, which is valid for any parameter and environmental matrix.

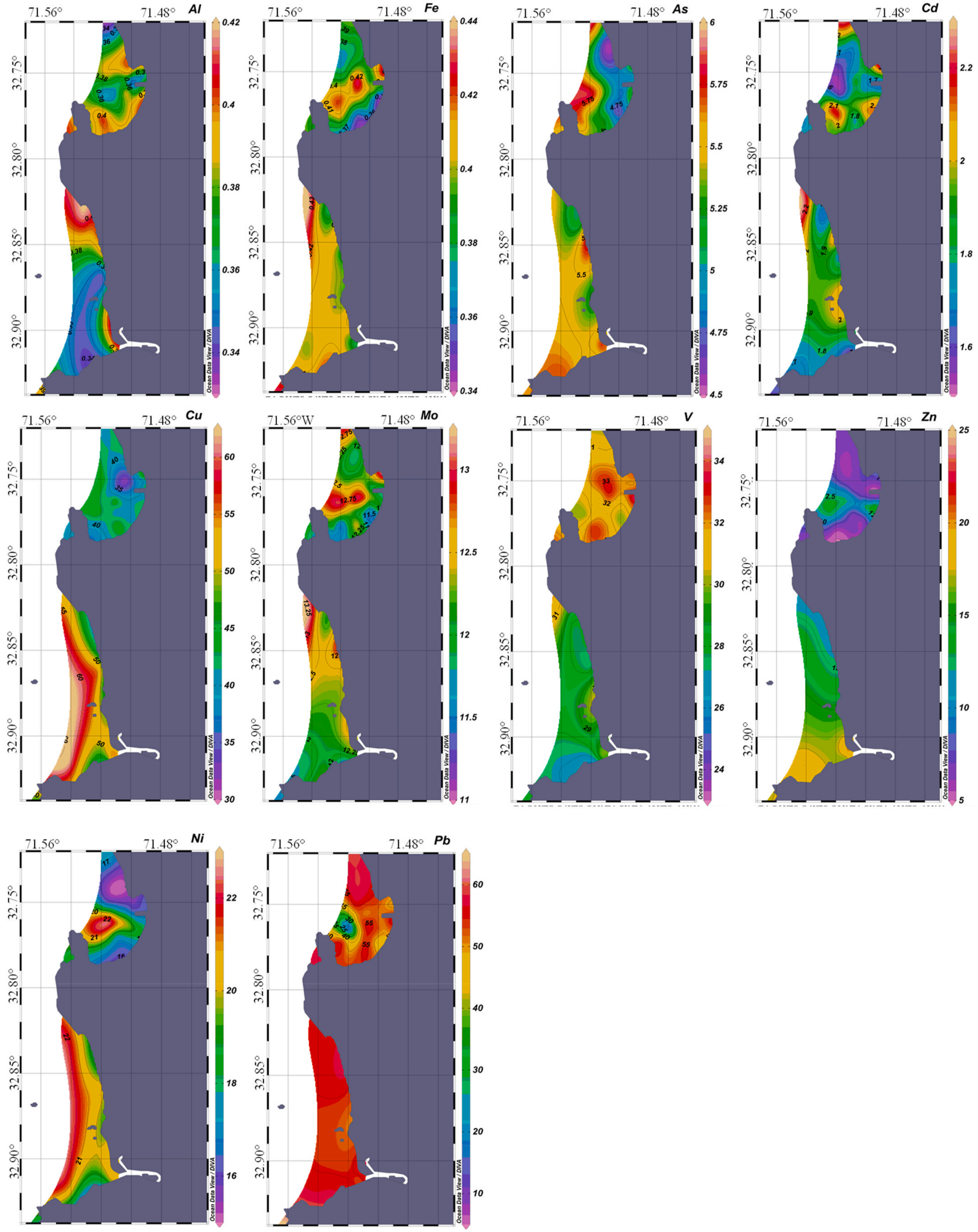


Fig. 5. Spatial distribution of metals/oid and in marine surface sediments of CQIC.

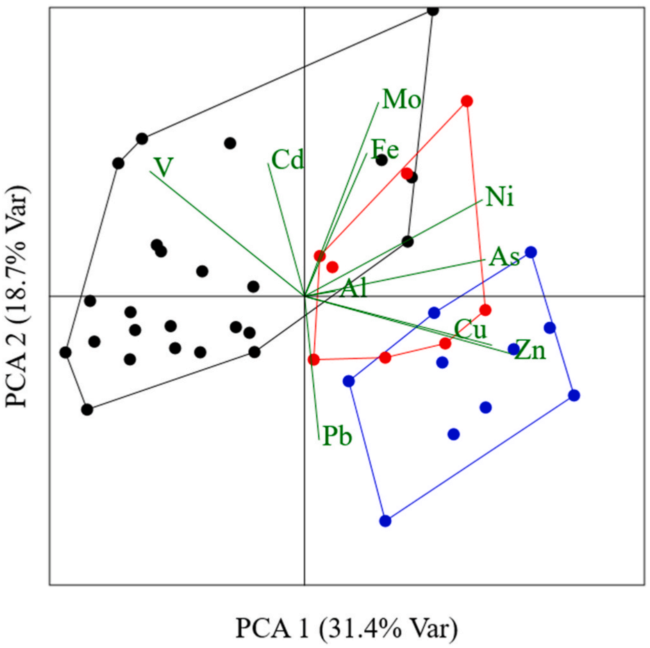


Fig. 6. Principal Component Analysis diagram of metals analyzed in surface sediments of CQIC. Black circles, red circles and blue circles are associated to Quintero, Ritoque and Concon zones, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.2. *Environmental assessment*

All the metals analyzed in this work are linked to different anthropogenic activities. The industries that significantly contribute metals to aquatic systems are mining, agriculture (pesticides, fungicides, fertilizers), thermal power plants, oil refineries, paints, pulp and paper, among many others (Rivera et al., 2019). In the study zone all industrial activities developed on the coast, and in the Aconcagua basin, are potential sources of metals to the marine environment. However, it is difficult to establish a link between a specific industry and a metal and its fingerprint found in marine sediments. For this reason, the environmental evaluation must be done considering all the industrial activities located near the coast, as a whole, and as the principal responsible for the eventual contamination problems detected in marine organisms, waters and sediments. Enrichment Factor, Geoaccumulation Index and Pollution Load Index, are commonly used to evaluate the increase of metals in bottom marine sediments (Harikrishnan et al., 2017; Christophoridis et al., 2019; Alharby et al., 2023, and references therein). However, all these indexes were formulated to compare the current with the pristine condition, that are not always available for the environments under evaluation. This is the case of Chile, a country with a fast economic and industrial growth, but still with a scarce knowledge of the structure and functionality of its natural ecosystems, especially those related to coastal marine environments where most of the Chilean population is located.

Pristine condition is related to pre-industrial metal concentration, during which only natural factors, like scavenging and supply from the surrounding land, are responsible for the metal accumulation in bottom marine sediments (Wang et al., 2013; Sharifuzzaman et al., 2016). Considering that all metals are naturally present in marine waters, the continental supply, either by rivers and/or wind transport are the main factors that must be considered during the pre-industrial period. At the current period, and in zones with human activities, the anthropogenic factors could be responsible for an important fraction of metals incorporated in the marine environments. All these factors must be considered to evaluate correctly eventual pollution processes identified in natural environments. The continental supply corresponds to lithogenic fraction found in surrounding geological formations, whose minerals contain metals as part of its structure, while anthropic sources correspond to different industrial activities that eliminate metals by water and air, which finally can be incorporated into the marine environment (Apitz et al., 2009; Nour et al., 2022; Al-kahtany et al., 2023). In this context, the Enrichment Factor and the Geoaccumulation Index do not always evaluate the same situation. The first of them can indicate the increase of metals compared with the lithogenic background, that could be the result of natural and/or anthropogenic factors. The second one, although it can use the lithogenic background as reference metal values, evaluates pollution processes directly. For this reason, it is very important to clearly define the background values used to calculate these indexes. The use of lithogenic background that represents the metal content in the geological formation, assumes that this is the natural content found in marine sediments, and any increase of metal in the sediments is due to unnatural factors. However, other physic-chemical and biological processes occurring in the water column, like changes in water masses (and properties therein), scavenging, oxygenation, productivity, Etc., can influence the final metal content in bottom marine environments (Apitz et al., 2009; Rigaud et al., 2011). In this context, the values of Enrichment Factor above 1.5 (see methodology) may indicate natural or anthropic source of metals, and must be considered with caution. This is especially important when it uses the Geoaccumulation Index, because the interpretation is based on a contamination scale. On the other hand, the use of pre-industrial values to calculate the environmental indexes, incorporates all the factors responsible for the final metal content in marine sediments, and seems to be more appropriate to evaluate pollution processes, either, with the Enrichment Factor and/or Geoaccumulation Index. However, the main problem is that pre-industrial values of metals (and any substance) are not available in practically any Chilean coastal environment. Some approaches have been developed to define pre-industrial values, using aquatic sediment records (paleoenvironmental studies), statistical procedures (that need many data), and metal contents in sediments of similar environments to those under evaluation, but without anthropogenic activities, which is uncommon and scarce (Birch, 2017; Valdés and Tapia, 2019; Valdés et al., 2023). Unfortunately, none of these possibilities are available for the marine environment of the CQIC, which is an urgent topic to solve. For this reason, in this study, it was used as background values, the metal concentrations measured in soil samples collected in the continental zone around the CQIC (see Methodology), and values of global geological formation proposed by Turekian and Wedepohl (1961), Taylor and McLennan (2004) and Rudnick and Gao (2003), to evaluate the environmental condition of the CQIC marine bottom environment. This approach allows to compare and analyze the effect of different background values on the final environmental interpretation.

Of the 9 metals used to calculate the environmental indexes, only Pb and Mo showed the same trend with all background values used to calculate it. These both metals showed some enrichment and pollution problem with all background values (EF > 1.5 and $I_{geo} > 0$; Table 1). The EF of Pb fluctuates between 2.3 and 39.8, while the EF of Mo fluctuates between 1.6 and 141.5 (Table 1). The I_{geo} of Pb fluctuates between 0.8 (Not polluted to moderately polluted) and 1.3 (Moderately polluted) while in the case of Mo the I_{geo} fluctuates between 1.4 (Moderately polluted) and 2.9 (Moderately to heavily polluted) (Table 1). In general, the results showed notorious differences in each metal when different background values were used to calculate the EF and I_{geo}. None of the background values gave equivalent results between EF and I_{geo}, simultaneously for all metals analyzed in the study zone (Table 1). In general, the background values from geological formation defined at global scale overestimates the results of the environmental indexes, particularly in the case of the EF. This is notorious in the case of Cd, which fluctuates between 0.9, calculated with the local background, and 259, calculated with the background proposed by Rudnick and Gao (2003) (Table 1).

Valdés and Tapia (2019) carried out a similar exercise using different background values to evaluate the environmental condition of some bays of northern Chile. The authors concluded that the most realistic result was obtained when the EF and the I_{geo} were calculated using background values from near coastal sediments, but without industrial activities, an aspect that may be the next challenge for the CQIC marine environment. For instance, and considering that it is difficult to accurately assess the metal pollution in sediment using a single method, we propose to use a mixture of them as the best approach. Fig. 7 displays the distribution of metals in an I_{geo} v/s EF diagram using the 4 background reference values considered in this study. The results show that Mo and Pb, simultaneously show both an enrichment in the sediment, and some degree of pollution problem, with all backgrounds utilized. This approach supports the conclusion that the bottom coastal sediments of CQIC are polluted at least with these 2 metals. Note that Pb not only is high in the sediments, but it is homogeneously distributed throughout the study zone (Fig. 6), suggesting that industries located in Concon and Quintero besides coastal water circulation are the main responsibles of this situation.

Recently, the environmental regulation that establish the threshold of some chemical parameters in waters and sediments of Quintero bay was incorporated in the Chilean legislation (Ministerio del Interior y Seguridad Pública, 2021). This is the first officialized regulation oriented to protect a coastal marine ecosystem in Chile. Five metals were considered in this environmental regulation; As, Cu, Ni, Pb and V. In the CQIC, only Pb measured in the sediments was higher than threshold, in the three study zones, while mean Cu concentration was higher only in Concon (Fig. 3). In the case of Pb, the spatial distribution, the results of Ef and I_{geo}, and the comparison with the quality regulation, are strong evidences that the study zone is polluted with this metal.

Even though the individual evaluation of metals preserved in marine sediments is a common routine, different studies suggest that the impact of metals on bottom environments needs to be evaluated considering the combined effect of many of them, because the impact is not a linear response to the sum of the metals (Yang et al., 2020). For this reason, the Pollution Load Index was used in this study to evaluate this combined effect on coastal sediments of the CQIC. Of the four background values used to calculate the PLI, only those of Turekian and Wedepohl (1961), suggest no pollution problem due to the metals analyzed (Fig. 7). The other three backgrounds suggest that the combination of these metals preserved in the sediments generate a polluted condition of the bottom environment of the CQIC, especially in the case of PLI calculated with local background values (Fig. 7).

The fact that the marine sediments of the study zone are polluted by some metals, generates the necessity to evaluate the impact of this condition on benthic organisms. To do this, Sediment Quality Guidelines have been established in different countries (Long et al., 1995; Ankley et al., 1996; MacDonald et al., 2000). However, in Chile, this is a pending topic, and in absence of national guidelines, the reference values proposed by Long et al. (1995) must be used. Six metals were evaluated, three of them (Ni, Zn and As) show values mostly < ERL suggesting that adverse effects are rarely observed (Table 2). On the other hand, the values of Cu, Pb and Cd were almost totally between ERL and ERM, indicating that adverse effects are occasionally observed

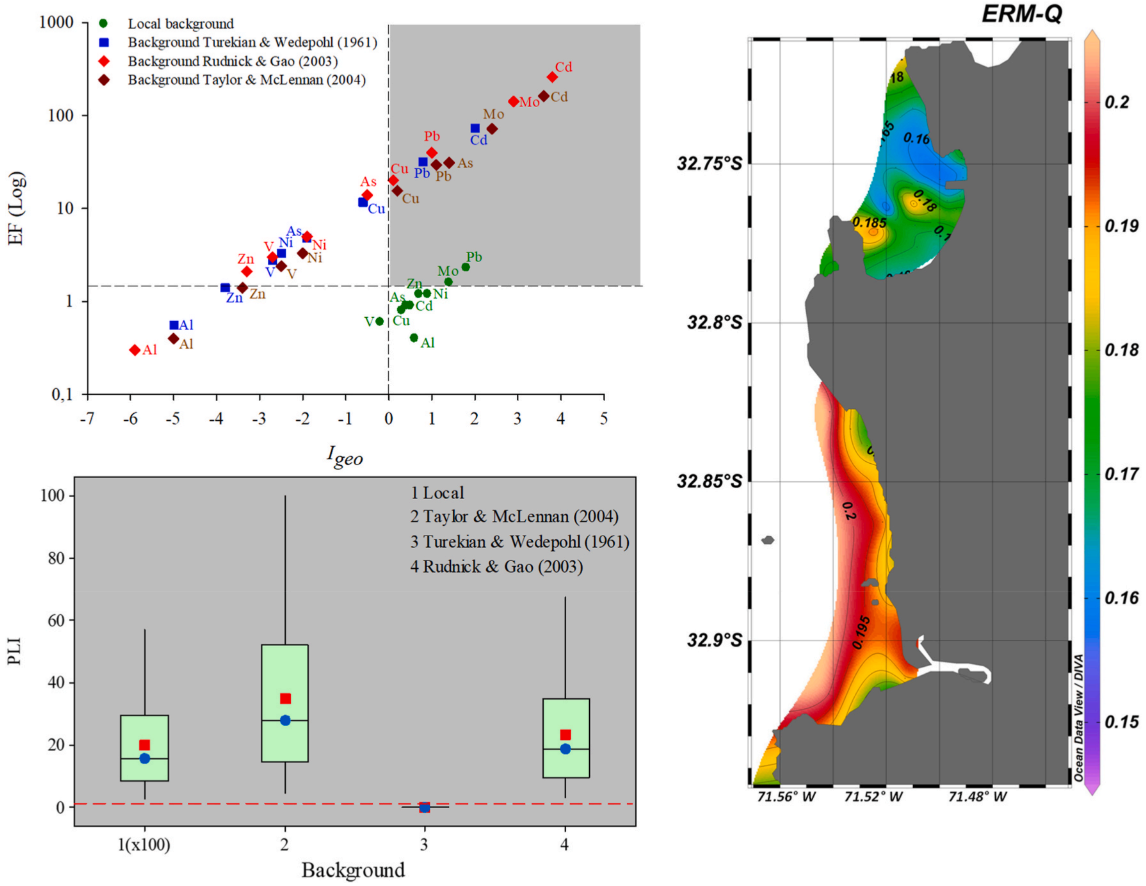


Fig. 7. Results of Environmental indexes used in this study. Up left panel is I_{geo} vs EF graph of the metals analyzed in surface sediments of CQIC, calculated with four background reference values (note that Mo indexes were calculated only with 3 background values). Dashed lines indicate reference values that separate enrichment condition (EF) and pollution condition (I_{geo}). Down left panel is Pollution Load Index for the surface sediments of CQIC, calculated with four background reference values. The red dashed line indicates the boundary between “no pollution” (<1) and pollution problem (>1). Right panel is Potential Ecological Risk Index for the sediments of CQIC. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Distribution of samples in the ranges established by the SQG according to the analyzed metal concentrations (in mg kg^{-1}) in coastal sediments of Concon-Quintero industrial complex, central Chile.

Metal	Mean concentration	Sediment Quality Guideline[a]		% of samples within ranges of the Sediment Quality Guideline		
		ERL	ERM	< ERL	>ERL and <ERM	> ERM
Cu	44.33	34	270	4.55	95.45	0.00
Ni	18.69	20.9	51.6	100	0	0
Zn	11.32	150	410	100	0	0
Pb	53.29	46.7	218	4.55	95.45	0
Cd	1.84	1.2	9.6	0	100	0
As	5.30	8.2	70	100	0	0

(Table 2). Even though this method uses reference values defined for other coastal zones (another urgent challenge for our country), it is noticeable that the case of Pb agrees with the conclusion of the environmental indexes which indicates that the coastal sediments of the CQIC are polluted by this metal, and now, they represent a threat for benthic life.

The presence of heavy metals in marine sediments, above natural levels, may alter the normal development of benthic ecosystems. For this reason, it is necessary to evaluate the levels of metals in the marine environments and the impact of these pollutants on such ecosystems. The Ecological Risk Assessment (m-ERM-Q) is a useful tool commonly used in studies of the impact of metals present in marine sediments (e.g., Tian et al., 2020). In the CQIC, the m-ERM-Q values fall in the range of 0.1–0.2 (Fig. 7C), suggesting a toxicity probability of 21%. These values are similar to other Chilean industrial bays like San Jorge, Mejillones and Caldera (See Fig. 4 for location), where the m-ERM-Q was less than 0.5 (Valdés and Tapia, 2019), even when the concentration of some metals (Pb, Cu, Zn, Ni, Cd) in the CQIC was less than those recorded in such bays (Fig. 4). Studies about heavy metal concentration have shown differences between local and international reference values used to evaluate the ecological risk, and point out the importance of the development of site-specific SQGs, which are based on various toxicity tests on local biota, to support the characterization of sediments and their impact on benthic organisms (Birch and Hogg, 2011; Vallius, 2015; Moreira et al., 2017; Rivera et al., 2019; Valdés and Tapia, 2019). Due to the limited information on local reference values, this is still the best approach to analyze eventual pollution processes of marine environments due to heavy metals and their risk. Indeed, the results of both, SQG and m-ERM-Q suggest that metals preserved in the sediments of the study zone are a threat for the benthic life, and although the results of the m-ERM-Q indicate the same probability of toxicity (21%), it is notorious that the Concon-Ritoque zone showed the highest values (Fig. 7), suggesting a higher risk for the marine organisms inhabiting this area. This is an important issue because Concon and Ritoque, especially the last one, are also touristic zones where the artisanal fishermen organizations have a management area to produce, caught and sell fish and shellfish for human consumption.

4. Conclusions

The Concon-Quintero Industrial Complex has historically recorded pollution episodes that threatened the human population inhabiting the zone, while the risk for the marine ecosystem has been evaluated partially during the recent past.

In this study, the results of the Index of geoaccumulation and the Enrichment Factor were different depending on the background reference values used to calculate it (three international and one local). Only Mo and Pb, simultaneously show both an enrichment in the sediment, and some degree of pollution problem, with all backgrounds utilized. However, the Pollution Load Index suggests that the combination of all metals preserved in the sediments generate a polluted condition of the bottom environment of the CQIC, with three of the four background values used. The spatial distribution af Pb, the results of Ef and I_{geo}, and the comparison with the threshold established in the environmental legislation of Quintero Bay, suggest that the study zone is polluted with this metal.

Finally, the results of both, SQG and m-ERM-Q suggest that metals preserved in the sediments of the study zone are a threat for the benthic life, especially in the Concon-Ritoque zone, where the highest values were recorded.

This study suggests that a combined approach of different indexes is a realistic way to assess the environmental condition of this industrial coastal zone. However, the identification of local background values (defined with comparable analytical methodology) and biological thresholds are important topics to develop in coastal systems of Chile.

Even though the studied zone is not the environment with the high metal content in marine sediments of the Chilean coast, the kind of industries, the distribution pattern of metals in the marine ecosystems and the environmental indexes suggest an enrichment of some metals and, particularly, a notorious influence of the Aconcagua river on the metal accumulation in the coastal zone.

Funding statement

1200390 FONDECYT grant.
039.421/2017 PUCV/DII grant.
MINEDUC-UA project, cod. ANT 22991.

CRediT authorship contribution statement

Jorge Valdés Saavedra: Writing – original draft, Supervision, Funding acquisition, Formal analysis. **Eduardo Quiroga:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research was partially funded by 1200390 FONDECYT Grant. We thank to Department of Research (No. PUCV/DII 039.421/2017) and the Laboratorio de Oceanografía y Bentos (LOBOS) from Pontificia Universidad Católica de Valparaíso (PUCV), Chile, for providing additional funds. We deeply thank M. Pastene, C. Vasquez, F. Gallardo, Maritza Malebrán and Sue Ellen Vega for their assistance in field and laboratory works. This work was partially done by Jorge Valdés Saavedra into visit at the University of Vigo, supported by MINEDUC-UA project, code ANT 22991.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.indic.2024.100373.

References

Aguilar, R., Hormazábal, C., Gaete, H., Neaman, A., 2011. Spatial distribution of copper, organic matter and ph in agricultural soils affected by mining activities. J. Soil Sci. Plant Nutr. 11 (3), 125–145.

Aguirre-Martínez, G., Rudolph, A., Ahumada, R., Loyola, R., Medina, V., 2009. Toxicidad no específica en sedimentos portuarios, una aproximación al contenido de contaminantes críticos. Rev. Biol. Mar. Oceanogr. 44 (3), 725–735.

Ahumada, R., 1992. Patrones de distribución espacial de Cr, Ni, Cu, Zn, Cd, y Pb, en sedimentos superficiales de bahía San Vicente, Chile. Rev. Biol. Mar 27 (2), 265–282.

Aiken, C., Castillo, M., Navarrete, S., 2008. A simulation of the Chilean Coastal Current and associated topographic upwelling near Valparaíso, Chile. Continent. Shelf Res. 28, 2371–2381. https://doi.org/10.1016/j.csr.2008.05.006.

Alharby, T., Nour, H., Al-kahtany, K., Giacobbe, S., El-Sorogy, A., 2023. Sediment's quality and health risk assessment of heavy metals in the Al-Khafji area of the Arabian Gulf, Saudi Arabia, 82. Environmental Earth Sciences, p. 471.

Al-kahtany, K., Nour, H., El-Sorogy, A., Alharby, T., 2023. Ecological and health risk assessment of heavy metals contamination in mangrove sediments, Red Sea coast. Mar. Pollut. Bull. 192, 115000.

Ankley, G., Di Toro, D., Hansen, D., Berry, W., 1996. Technical basis and proposal for deriving sediment quality criteria for metals. Environ. Toxicol. Chem. 15, 2056–2066.

Apitz, S., Degetto, S., Cantaluppi, C., 2009. The use of statistical methods to separate natural background and anthropogenic concentration of trace elements in radio-chronologically selected surface sediments of the Venice Lagoon. Mar. Pollut. Bull. 58, 402–4014.

Bellas, J., Hylland, K., Burgeot, T., 2020. Editorial: new challenges in marine pollution monitoring. Front. Mar. Sci. 6, 820. https://doi.org/10.3389/fmars.2019.00820.

Birch, G., Taylor, S., 2000. The use of size-normalization procedures in the analysis of organic contaminants in estuarine environments. Hydrobiologia 431, 129–133.

Birch, G., Hogg, T., 2011. Sediment quality guidelines for copper and zinc for filter-feeding estuarine oysters? Environ. Pollut. 159, 108–115.

Bhuiyan, M., Parvez, L., Islam, M., Dampare, S., Suzuki, S., 2010. Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. J. Hazard Mater. 173 (1–3), 384–392.

Birch, G., 2017. Determination of sediment metal background concentrations and enrichment in marine environments – a critical review. In: Science of the Total Environment 580, pp. 813–831.

Bui, V.H., Bui, M.D., Rutschmann, P., 2019. Advanced numerical modeling of sediment transport in gravel-bed rivers. Water 11, 550. https://doi.org/10.3390/w11030550.

Castillo, A., Valdés, J., Marambio, Y., Figueroa, L., Letelier, L., Carcamo, F., 2023. Metal (loid)s content in Concholepas concholepas (Mollusca) and human health assessment in a coastal environmental sacrifice zone, central Chile (∼32∘S). Mar. Pollut. Bull. 197, 115738.

Chandía, Ch, Salamanca, M., 2012. Long-term monitoring of heavy metals in Chilean coastal sediments in the eastern South Pacific Ocean. Mar. Pollut. Bull. 64 (10), 2254–2260.

Christophoridis, C., Bourliva, A., Evgenakis, E., Papadopoulou, L., Fytianos, K., 2019. Effects of anthropogenic activities on the levels of heavy metals in marine surface sediments of the Thessaloniki Bay, Northern Greece: spatial distribution, sources and contamination assessment. Microchem. J. 149, 104001.

Crane, M., 2003. Proposed development of sediment quality guidelines under the European Water Framework Directive: a critique. Toxicol. Lett. 142, 195–206.

Dawson, J.J.C., Tetzlaff, D., Carey, A.M., Raab, A., Soulsby, C., Killham, K., Meharg, A.A., 2010. Characterizing Pb mobilization from upland soils to streams using ^{206}Pb/^{207}Pb isotopic ratios. Environ. Sci. Technol. 44, 243–249.

Di Cesare, A., Pjevac, P., Eckert, E., Curkov, N., Sparica, M.M., Corno, G., Orlic, S., 2020. The role of the metal contamination in shaping microbial communities in heavily polluted marine sediments. Environ. Pollut. 265, 114823 https://doi.org/10.1016/j.envpol.2020.114823.

El Bilali, L., Rasmussen, P.E., Hall, G.E.M., Fortin, D., 2002. Role of sediment composition in trace metal distribution in lake sediments. Appl. Geochem. 17, 1171–1181.

Essien, J., Antai, S., Olajire, A., 2009. Distribution, seasonal variations and ecotoxicological significance of heavy metals in sediments of Cross River Estuary mangrove swamp. Water Air Soil Pollut. 197, 91–105.

Escobar, J., 1971. Corrientes dentro de la bahía de Quintero. Cepal, Santiago, Chile, pp. 25–38.

Fukue, M., Yanai, M., Sato, Y., Fujikawa, T., Furukawa, Y., Tani, S., 2006. Background values for evaluation of heavy metal contamination in sediments. J. Hazard Mater. 136, 111–119.

Gaete, H., Álvarez, M., Lobos, G., Soto, E., Jara-Gutiérrez, C., 2017. Assessment of oxidative stress and bioaccumulation of the metals Cu, Fe, Zn, Pb, Cd in the polychaete *Perinereis gualpensis* from estuaries of central Chile. Ecotoxicol. Environ. Saf. 145, 653–658.

Hammer, O., Harper, D.A.T., Ryan, P.D., 2001. PAST: paleontological statistic software package for education and data analysis. Paleontología Electrónica 4 (1), 1–9.

Harikrishnan, N., Ravisankar, R., Chandrasekaran, A., Suresh Gandhi, M., Kanagasabapathy, K.V., Prasad, M.V.R., Satapathy, K.K., 2017. Assessment of heavy metal contamination in marine sediments of east coast of Tamil nadu affected by different pollution sources. Mar. Pollut. Bull. 121, 418–424.

Hübner, R., Astin, K., Herbert, R., 2009. Comparison of sediment quality guidelines (SQGs) for the assessment of metal contamination in marine and estuarine environments. J. Environ. Monit. 11 (4), 713–722. https://doi.org/10.1039/b818593j.

IFOP, 2016. Determinación de los impactos en los recursos hidrobiológicos y en los ecosistemas marinos presentes en el área de influencia de los derrames de hidrocarburos de bahía Quintero, V Región. Informe Final Subsecretaría de Pesca y Acuicultura, pp. 155–246.

Jongman, R., Ter Braak, C., van Tongeren, O., 1987. Data Analysis in Community and Landscape Ecology. PUDOC, Wageningen.

Kim, B., Friedmann, J., Ferreira, P., Rosemberg, J., Miyoshi, C., Mahiques, M., Lopes, R., 2017. Use of a chemometric tool to establish the regional background and assess trace metal enrichment at Baixada Santista e southeastern Brazil. Chemosphere 166, 372–379.

Landre, A.L., Watmough, S.A., Dillon, P.J., 2009. The effects of dissolved organic carbon, acidity and seasonality on metal geochemistry within a forested catchment on the Precambrian Shield, central Ontario, Canada. Biogeochemistry 93, 271–289.

Larrose, A., Coynel, A., Schäfer, J., Blanc, G., Massé, L., Maneux, E., 2010. Assessing the current state of the Gironde Estuary by mapping priority contaminant distribution and risk potential in surface sediment. Appl. Geochem. 25, 1912–1923.

Liu, M., Hea, Y., Baumann, Z., Zhanga, Q., Jing, X., Mason, R.P., Xie, H., Shen, H., Chen, L., Zhang, W., Zhang, Q., Wang, X., 2020. The impact of the Three Gorges Dam on the fate of metal contaminants across the river–ocean continuum. Water Res. 185, 116295 https://doi.org/10.1016/j.watres.2020.116295.

Long, E., Macdonald, D., Smith, S., Calder, F., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manag. 19, 81–97.

Long, E., Macdonald, D., 1998. Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. Hum. Ecol. Risk Assess. 4 (5), 1019–1039. http://www.tandfonline.com/loi/bher20.

Lu, Q., Bai, J., Zhang, G., Wu, J., 2020. Effects of coastal reclamation history on heavy metals in different types of wetland soils in the Pearl River Delta: levels, sources and ecological risks. J. Clean. Prod. 272, 122668 https://doi.org/10.1016/j.jclepro.2020.122668.

MacDonald, D., DiPinto, L., Field, J., Ingersoll, C., Long, E., Swartz, R., 2000. Development and evaluation of consensus based sediment effect concentrations for polychlorinated biphenyls. Environ. Toxicol. Chem. 19, 1403–1413.

McCready, S., Birch, G., Long, E., 2006. Metallic and organic contaminants in sediments of Sydney Harbour, Australia and vicinity -A chemical dataset for evaluating sediment quality guideline. Environ. Int. 32, 455–465.

Mil-Homens, M., Costa, A.M., Fonseca, S., Trancoso, M.A., Lopes, C., Serrano, R., Sousa, R., 2013. Natural heavy metal and metalloid concentrations in sediments of the Minho River estuary (Portugal): baseline values for environmental studies. Environ. Monit. Assess. 185, 5937–5950.

Ministerio del Interior y Seguridad Pública, 2021. Aprueba anteproyecto de las normas secundarias de calidad ambiental para la protección de las aguas marinas y sedimentos de la bahía de Quintero-Puchuncaví. Diario Oficial 43.066, 1–7.

Ming, L., Dejiang, F., Naishuang, B., Xueshi, S., Yuana, T., 2019. Impact of water-sediment regulation on the transport of heavy metals from the Yellow River to the sea in 2015. Sci. Total Environ. 658, 268–279. https://doi.org/10.1016/j.scitotenv.2018.12.170.

Moreira, L., Ícastro, I., Hortellani, M., Sasaki, S., Taniguchi, S., Petti, M., Fillmann, G., Sarkis, J., Bícego, M., Costa-Lotufo, L., Abessa, D., 2017. Effects of harbor activities on sediment quality in a semi-arid region in Brazil. Ecotoxicol. Environ. Saf. 135, 137–151.

Muñoz, A., lock-Barría, K., Sheppard, P., Aguilera-Betti, I., Toledo-Guerrero, I., Christie, D., Gorena, T., Gallardo, L., González-Reyes, A., Lara, A., Lambert, F., Gayo, E., Barraza, F., Chávez, R., 2019. Multidecadal environmental pollution in a mega-industrial area in central Chile registered by tree rings. Sci. Total Environ. 696, 133915 https://doi.org/10.1016/j.scitotenv.2019.133915.

Müller, G., 1979. Schwermetalle in den sedimenten des Rheins-Veranderungen seitt 1971. Umschan 79, 778–783.

Neaman, A., Valenzuela, P., Tapia-Gatica, J., Selles, I., Novoselov, A., Dovletyarova, E., Yáñez, C., Krutyakov, Y., Stuckey, J., 2020. Chilean regulations on metal-polluted soils: the need to advance from adapting foreign laws towards developing sovereign legislation. Environ. Res. 185, 109429 https://doi.org/10.1016/j.envres.2020.109429.

Nour, H., Alshehri, F., Sahour, H., El-Sorogy, A., 2022. Evaluation of sediment and water quality of Ismailia Canal for heavy metal contamination, Eastern Nile Delta, Egypt. Regional Studies in Marine Science 56, 102714.

Oyarzo-Miranda, C., Latorre, N., Meynard, A., Rivas, J., Bulboa, C., Contreras-Porcia, L., 2020. Coastal pollution from the industrial park Quintero bay of central Chile: effects on abundance, morphology, and development of the kelp Lessonia spicata (Phaeophyceae). PLoS One 15 (10), e0240581. https://doi.org/10.1371/journal.pone.0240581.

Parra, S., Bravo, M., Quiroz, W., Querol, X., Paipa, C., 2015. Distribution and pollution assessment of trace elements in marine sediments in the Quintero Bay (Chile). Mar. Pollut. Bull. 99, 256–263. https://doi.org/10.1016/j.marpolbul.2015.07.066.

Pastene, M., Quiroga, E., Hurtado, F., 2019. Stable isotopes and geochemical proxies in marine sediments as indicators for anthropogenic impact: a case of study in coastal environments of Central Chile (33°S). Mar. Pollut. Bull. 142, 76–84. https://doi.org/10.1016/j.marpolbul.2019.03.005.

Pizarro, J., Vergara, P., Rodríguez, J., Valenzuela, A., 2010. Heavy metals in northern Chilean rivers: spatial variation and temporal trends. J. Hazard Mater. 181, 747–754. https://doi.org/10.1016/j.jhazmat.2010.05.076.

Plach, J., Warren, L., 2012. Differentiating natural organic matter roles in freshwater floc and bed sediment lead dynamics. Chem. Geol. 304 (305), 97–105.

Reimann, C., de Caritat, P., 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Sci. Total Environ. 337, 91–107.

Rigaud, S., Radakovitch, O., Nerini, D., Picon, P., Garnier, J., 2011. Reconstruction historical trends of Berre lagoon contamination form surface sediments datasets: influences of industrial regulations and anthropogenic silt inputs. J. Environ. Manag. 92, 2201–2210.

Rivera, C., Quiroga, E., Meza, V., Pastene, M., 2019. Water quality and heavy metal at the El Yali wetland complex (Central Chile): an environmental assessment of a

RAMSAR site. Mar. Pollut. Bull. 145, 499–507. https://doi.org/10.1016/j.marpolbul.2019.06.054.

Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. Treatise on Geochemistry 3, 1–64.

Salamanca, M., Chandía, Ch, Hernández, A., Vargas, F., 2019. First long-term record of halogenated organic compounds (AOX, EOX, and PCDD/F) and trace elements (Cd, Cr, Cu, Fe, Hg, Pb, Ni, and Zn) in marine biota of the coastal zone of south central Chile. Mar. Pollut. Bull. 146, 442–453.

Samhouri, J., Ramanujam, E., Bizzarro, J., Carter, H., Sayce, K., Shen, S., 2019. An ecosystem-based risk assessment for California fisheries co-developed by scientists, managers, and stakeholders. Biol. Conserv. 231, 103–121. https://doi.org/10.1016/j.biocon.2018.12.027.

Sánchez, A., Shumilin, E., Rodríguez-Figueroa, G., 2019. Sediment transport patterns inferred from grain size trends and trace metal dispersion near the Santa Rosalía mining district, Gulf of California. Sediment. Geol. 380, 158–163. https://doi.org/10.1016/j.sedgeo.2018.12.006.

Schlitzer, R., 2020. Ocean Data View. https://odv.awi.de.

Sharifuzzaman, S.M., Rahman, H., Ashezuzzaman, S.M., Islam, M.M., Chowdhuyr, S.R., Hossain, M.S., 2016. Heavy metals accumulation in coastal sediments. In: Hasegawa, H., et al. (Eds.), Environmental Remediation Technologies for Metal Contaminated Soils. https://doi.org/10.1007/978-4-431-55759-3_2.

Sreekanth, A., Mrudulrag, S.K., Cheriyan, E., Sujatha, C.H., 2015. Trace metal enrichment and organic matter sources in the surface sediments of Arabian Sea along southwest India (Kerala coast). Mar. Pollut. Bull. 101, 938–946.

Tapia, J., Valdés, J., Orrego, R., Tchernitchin, A., Dorador, C., Bolados, A., Harrod, C., 2018. Geologic and anthropogenic sources of contamination in settled dust of a historic mining port city in northern Chile: health risk implications. PeerJ 6, e4699. https://doi.org/10.7717/peerj.4699.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: its Composition and Evolution, vol. 312. Blackwell, Oxford.

Tian, K., Wu, Q., Liu, P., Hu, W., Huang, B., Shi, B., Zhou, Y., Kwon, B., Choi, K., Ryu, J., Khim, J.S., Wang, T., 2020. Ecological risk assessment of heavy metals in sediments and water from the coastal areas of the Bohai Sea and the Yellow Sea. Environ. Int. 136, 105512 https://doi.org/10.1016/j.envint.2020.105512.

Tomlinson, D.C., Wilson, J.G., Harris, C.R., Jeffrey, D.W., 1980. Problems in the assessment of heavy metals in estuaries and the formation pollution index. Helgol. Mar. Res. 33, 566–575.

Tonne, C., Adair, L., Adlakha, D., Anguelovski, I., Belesova, K., Berger, M., Brelsford, C., Dadvand, P., Dimitrova, A., Giles-Corti, B., Heinz, A., Mehran, N., Nieuwenhuijsen, M., Pelletier, F., Ranzani, O., Rodenstein, M., Rybski, D., Samavati, S., Satterthwaite, D., Schöndorf, J., Schreckenberg, D., Stollmann, J., Taubenböck, H., Tiwari, G., van Wee, B., Adli, M., 2021. Defining pathways to healthy sustainable urban development. Environ. Int. 146, 106236 https://doi.org/10.1016/j.envint.2020.106236.

Tribovillard, N., Algeo, Th, Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. Chem. Geol. 232, 12–32.

Trifuoggi, M., Donadio, C., Mangoni, O., Ferrara, L., Bolinesi, F., Nastro, R., Stanislao, C., Toscanesi, M., Di Natale, G., Arienzo, M., 2017. Distribution and enrichment of trace metals in surface marine sediments in the Gulf of Pozzuoli and off the coast of the brownfield metallurgical site of Ilva of Bagnoli (Campania, Italy). Mar. Pollut. Bull. 124, 502–511.

Turekian, K., Wedepohl, K., 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull. 72, 175–192.

US EPA, 1996. SW-846 Test Method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices. EPA, p. 20.

Valdes, 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. Mar. Pollut. Bull. 50, 1558–1568.

Valdés, J., Román, D., Guiñez, M., Rivera, L., Morales, T., Ávila, J., Cortés, P., 2010. Distribution and temporal variation of trace metal enrichment in surface sediments of San Jorge Bay, Chile. Environ. Monit. Assess. 167, 185–197.

Valdés, J., 2012. Heavy metal distribution and enrichment in sediments of Mejillones Bay (23° S), Chile: a spatial and temporal approach. Environ. Monit. Assess. 184, 5283–5294.

Valdés, J., Castillo, A., 2014. Evaluación de la calidad ambiental de los sedimentos marinos en el sistema de bahías de Caldera (27°S), Chile. Latin American Journal of Aquatic Research 42 (3), 497–513.

Valdés, J., Román, D., Guiñez, M., Rivera, L., Ávila, J., Cortés, P., Castillo, A., 2015. Trace metal variability in coastal waters of San Jorge Bay, Antofagasta, Chile: an environmental evaluation and statistical approach to propose local background levels. Mar. Pollut. Bull. 100, 544–554.

Valdés, J., Tapia, J., 2019. Spatial monitoring of metals and as in coastal sediments of northern Chile: an evaluation of background values for the analysis of local environmental conditions. Mar. Pollut. Bull. 145, 624–640.

Valdés, J., Ortlieb, L., Sifeddine, A., Castillo, A., 2023. Human-induced metals accumulation in sediments of an industrialized bay of northern Chile. An enrichment and ecological risk assessment based on preindustrial values. Mar. Pollut. Bull. 119, 114723.

Vallius, H., 2015. Quality of the surface sediments of the northern coast of the Gulf of Finland, Baltic Sea. Mar. Pollut. Bull. 99, 250–255.

Varol, M., Canpolat, Ö., Eriş, K., Çağlar, M., 2020. Trace metals in core sediments from a deep lake in eastern Turkey: vertical concentration profiles, eco-environmental risks and possible sources. Ecology and Environmental Safety 189, 110060. https://doi.org/10.1016/j.ecoenv.2019.110060.

Wan, S., Toucanne, S., Clift, P.D., Zhao, D., Bayon, G., Yu, Z., Cai, G., Yin, X., Révillon, S., Wang, D., Li, A., Li, T., 2015. Human impact overwhelms long-term climate control of weathering and erosion in southwest China. Geology 43, 439–442.

Wang, S.L., Xu, X.R., Sun, Y.X., Liu, J.L., Li, H.B., 2013. Heavy metal pollution in coastal areas of South China: a review. Mar. Pollut. Bull. 15 (1–2), 7–15. https://doi.org/10.1016/j.marpolbul.2013.08.025, 76.

Yang, H.J., Jeong, H.J., Bong, K.M., Jin, D.R., Kang, T., Ryu, H., Jong, H.H., Yang, W.J., Jung, H., Hwang, S.H., Na, E.H., 2020. Organic matter and heavy metal in river sediments of southwestern coastal Korea: spatial distributions, pollution, and ecological risk assessment. Mar. Pollut. Bull. 159, 111466 https://doi.org/10.1016/j.marpolbul.2020.111466.

Zar, J.H., 2010. Biostatistical Analysis, fifth ed. Prentice Hall, Upper Saddle River, NJ.M, p. 944.