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THEMATIC ISSUE

A global record of particulated metals on the southwestern Atlantic shelf (Argentine Sea)

Diana Mariel Villagran[1] · Melisa Daiana Fernández Severini[1] · Daniela María Truchet[1,2] · Matias Nicolás Tártara[1] · Jorge Eduardo Marcovecchio[1,3]

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Abstract
The Argentine Sea (Southwestern Atlantic) is one of the most productive ecosystem in the Southern Hemisphere. Research on metals in this region is scarce or null. In this study, we evaluated the concentrations of some metals in the suspended particulate matter (SPM), to provide baseline data that would enable us to understand the role of the SPM in the transport of metals in the Argentine Sea. Sampling was carried out during the austral summer 2016 at 20 stations distributed in the Argentine Sea. Surface seawater samples were collected and then filtered by vacuum through Millipore® HAWP 04,700 filters (0.45 µm). The samples were acid-digested (HNO_3 and $HClO_4$, 5:1) and the metal concentrations were determined with ICP-OES Optima 2100 DV (Perkin Elmer). Significant spatial variations were detected due to the extension of the study area, with the highest levels of metals in the stations next to large urban centers (Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn: 13.9, 154.9, 48.7, 54,470, 7646, 49.2, 58.6 and 509.5 µg g^{-1} d.w. respectively), which was supported by the nMDS and Cluster analyses. According to PCA analysis, two groups of metals that could have similar behavior were stablished: one group integrated by Cu, Zn, Pb and Ni, and the other group integrated by Cr, Fe and Mn. Metals that act as micronutrients and the toxic ones were present in all the sampling stations, highlighting the need to reinforce the study of these elements in this extensive and productive area of the South Atlantic Ocean.

Keywords Heavy metals · Suspended Particulate Matter · Argentine Sea · Urban centers · Pollutants · Micronutrients

Introduction

Continental shelves are an essential link between the land and ocean since they modulate the transfer of materials. To quantify the processes occurring at this interface, one of the fundamental issues is to understand the biogeochemistry of trace metals in the oceans. Moreover, the supply and removal of trace metals in coastal oceans have a direct influence on the structure of the oceans ecosystems and their productivity (Charette et al. 2016).

A global representation of reported profiles shows that the Mediterranean Sea, North Atlantic Ocean, North and Eastern Pacific Ocean, and the Weddell Sea are the areas where metals have been most studied, while the South Indian, South Pacific Oceans and Southwestern Atlantic Ocean have been seldom studied or are unexplored altogether for some metals (Gonzalez et al. 2012). Particularly, the Argentine Sea is part of the Southwestern Atlantic Ocean and there is no information about the particulate metals in this area. This ecosystem is one of the widest in the world—with an area of 1.2 million km^2—and one of the most productive and complex in the Southern Hemisphere (Palma et al. 2008; Lutz et al. 2010; Matano et al. 2010). It supports high phytoplankton productivity with several ecosystem services (Martinetto et al. 2019) and important commercial fisheries, such

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✉ Diana Mariel Villagran
dianavillagran88@gmail.com

1 Instituto Argentino de Oceanografía (IADO), Universidad Nacional del Sur (UNS)-CONICET, Camino La Carrindanga Km7, 8000 Bahía Blanca, Argentina

2 Departamento de Biología, Bioquímica y Farmacia, Universidad Nacional del Sur, San Juan 630, B8000 Bahía Blanca, Argentina

3 Universidad Tecnológica Nacional (UTN-FRBB), 11 de Abril, 8000 Bahía Blanca, Argentina

as hake (*Merluccius australis, Merluccius hubbsi*), squid (*Illex argentinus*) and shrimps (*Pleoticus muelleri, Artemesia longinaris*) (Bezzi et al. 2000; Acha et al. 2004; Carreto et al. 2016; Carranza et al. 2017; Martinetto et al. 2019) that adds economic value to this ecosystem and sustains the livelihoods of many families of small-scale artisanal fishers (Truchet et al. 2019; Truchet and Noceti 2020). Hence, the determination of metals in the water column gives information about their bioavailability, which helps understand changes in productivity or evaluate potential risk for biota. These issues become essential for the management and conservation of marine ecosystems.

Heavy metals originate from natural sources, mainly from the weathering of soil and rocks, erosion, forest fires, and volcanic eruptions, but also from extensive human activities (Yao et al. 2016). They are continuously introduced to the marine environments through riverine runoffs, wastewaters and aeolian processes. In coastal systems, metals can be introduced in the dissolved phase and rapidly sorbed to particles, or can also be introduced directly in the particulate form. Then, in the water column, the metals associated with suspended particulate matter (SPM) can be incorporated into deposited sediments, and being available for organisms (Stecko and Bendell-Young 2000). Most of the heavy metals have a high affinity to this fraction due to their high ratio surface/volume (Showell and Gaskin 1992; Sanders and Riedle 1998). Other crucial properties of the SPM are their reactivity, mobility, as well as the high nutritional value that make these particles fundamental to the transfer of chemical constituents between the water, food web and bed sediments in aquatic environments (Turner and Millward 2002; Severini et al. 2018). Also, the mobility and fate of heavy metals are affected by the complex dynamics of the coastal water which include variations in physical, chemical and biological parameters (De Machado et al. 2016).

On the other hand, heavy metals play a fundamental role in the biological cycles of the ocean (Jenssen 2011; González et al. 2012). Some of them are considered micronutrients (i.e., iron, manganese, nickel and copper) since they act as co-factors of many enzymes and can control the growth and metabolism of phytoplankton—the primary producers—(Morel and Price 2003; Boyd et al. 2007; Moore et al. 2013; Twining et al. 2015) and other organisms at the bottom of the food webs (Monserrat et al. 2007; Truchet et al. 2020). However, other metals (i.e., lead, cadmium, and chromium) can be toxic for the biota even in a small-dose response (Da Silva and Williams 2001) due to their ability to bioaccumulate and their persistence in aquatic ecosystems (Van Vuuren et al. 1999; Censi et al. 2006; Ley-Quiñónez et al. 2011). In this sense, across a large extension of coastal areas of the Argentine Sea, many authors have reported the bioaccumulation of heavy metals in marine invertebrates (Severini et al. 2009, 2013; Giarratano et al. 2010, 2011; Bertrand et al. 2016; Buzzi et al. 2017; Marinho et al. 2018; Villagran et al. 2019; Truchet et al. 2020) and marine fish (Authman et al. 2015; La Colla et al. 2017, 2018). Also, worldwide information has addressed adverse effects of metals in marine animals, such as erratic swimming of fishes (Bhat and Vamsee 1993), hyperglycemic stress (Lorenzon et al. 2000), induction of oxidative stress and oxidative damage (Kim et al. 2014; Lompré et al. 2019) and inhibition of reproduction (Yi et al. 2019).

Therefore, taking into account the lack of information about metals in one of the most productive ecosystems in the Southern Hemisphere and the importance of these elements in the biogeochemical cycles of the oceans, the main objective of this study is to provide baseline data on the levels of particulate Cd, Cu, Pb, Zn, Mn, Ni, Cr and Fe to elucidate the role of the SPM in the transport of essential and toxic metals to this sea.

Materials and methods

Study area

The Argentine Sea (34°–55° S and 56°–68° W), also known as the Patagonian Shelf Large Marine Ecosystem (PSLME) (Heileman 2009), cover an extensive area of about 1.2 million km^2 along the Southwestern Atlantic (South America), from the La Plata River to the southern Patagonian and Tierra del Fuego (Fig. 1a). The continental shelf is one of the widest in the world, and two distinct boundary currents influence it: The Malvinas Current, that circulates northward carrying cold nutrient rich and the relatively freshwater of sub-antarctic origin, and the Brazil Current, that circulates southward, carrying warmer, nutrient-poor and saltier waters (Piola et al. 2000; Palma et al. 2008; Matano et al. 2010; Marrari et al. 2017). These currents flow in opposite directions and meet, in average, at 36° S (Acha et al. 2004), in a region known as the Brazil–Malvinas Confluence, which is one of the most energetic globally (i.e., Chelton et al. 1990; Garzoli 1993; Piola and Matano 2001). These currents and the association with several shelf and shelf-break fronts controlled by the strong winds, large-amplitude tides and freshwater discharges, makes this ecosystem one of the most productive in the world (150–300 gcm^{-2} year^{-1}) (Acha et al. 2004; Romero et al. 2006; Matano and Palma 2008; Palma et al. 2008; Matano et al. 2010; Marrari et al. 2017; Martinetto et al. 2019).

Phytoplankton shows a high heterogeneity in biomass and community structure with a maxim of chlorophyll-*a* associated with different taxonomic groups, especially diatoms, dinoflagellates and the picoplankton fraction represented by *Synechococcus* sp (Lutz and Carreto 1991; Garcia et al. 2008; Sabatini et al. 2012; Segura et al. 2013).

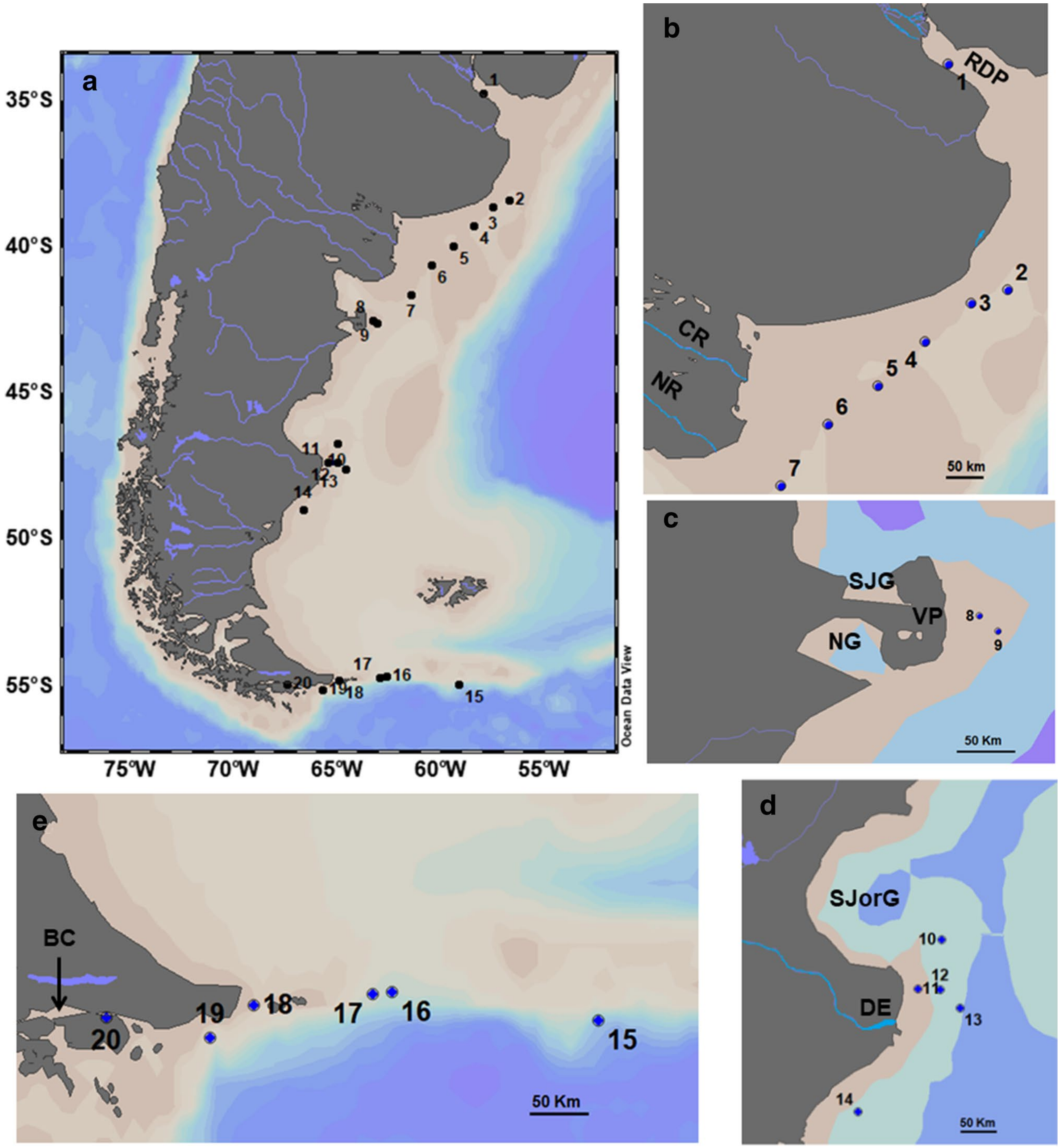

Fig. 1 Study area. **a** Locations of the sampling sites in the Argentine Sea; **b** Buenos Aires area, location of stations 1, 2, 3, 4, 5, 6 and 7; **c** Valdés Peninsula area, locations of stations 8 and 9; **d** Santa Cruz area, locations of stations from 10, 11, 12, 13 and 14; **e** Tierra del Fuego area, locations of stations from 15, 16, 17, 18, 19 and 20

The zooplankton community shows a high abundance of calanoid copepods, chaetognaths, salps and hydromedusa (Heileman 2009; Dutto et al. 2019). Also, the PSLME supports significant seabirds and marine mammals communities as well as invertebrates and is particularly rich in fisheries resources (Favero et al. 2003; Veit 2008; Elías et al. 2011; Mandiola et al. 2015; Bigatti and Signorelli 2018).

This study was carried out in four areas of the PSLME that here have been called in practical terms as Buenos Aires

(BA), Valdés Peninsula (VP), Santa Cruz (SC) and Tierra del Fuego (TF).

The BA (Fig. 1b) extends from the Río de la Plata Estuary (RDP) to the area called El Rincón. The RDP is an extensive, shallow, and microtidal coastal–plain estuary that receives freshwater from the second-largest South American basin (a surface of 35,000 km^2 and with a freshwater runoff of 16,000–28,000 $m^3\ s^{-1}$) (Bilos et al. 1998; Auad and Martos 2012) and it is characterized by a strong vertical stratification (Acha et al. 2004). Meanwhile, El Rincón is characterized by vertical homogeneity due to tidal forcing, and a coastal front separating diluted coastal water, coming from the Negro and Colorado rivers (960 $m^3\ s^{-1}$ total average discharge), and shelf waters (Acha et al. 2004). Large urban centers are located in this area, as an example, 14.8 million people live in Buenos Aires city and its metropolitan area (AMBA) laying on the RDP while ~ 800,000 people live in Mar del Plata city (~ 400 km south of Buenos Aires city). This area also supports a wide range of industries, including chemical industry, oil refinery, textile industries, tourism, fishing and agriculture. Hence, it receives permanently agricultural runoff, industrial discharges and mostly untreated sewage effluents (Becherucci and Seco Pon 2014; Pazos et al. 2017; Zorzoli 2017).

The VP (Fig. 1c) presents in spring and summer a thermal mixing front observed between stratified (offshore) waters and a coastal, vertically mixed body of water (Acha et al. 2004). The peninsula is surrounded by San José Gulf, which opens to the north and Nuevo Gulf and the south. Both gulfs are essential calving grounds for the Southern right whale population in the SW Atlantic Ocean (D'Agostino et al. 2017). Nuevo Gulf is much larger than San José Gulf and it hosts the city of Puerto Madryn (~ 100,000 inhabitants), an active port, and industries (including one of the largest aluminum plants in the country). On the other hand, San José Gulf is smaller, has no nearby urban settlements, and it is a protected area with no activities beyond extraction of shellfish by coastal diving (Rosas et al. 2012).

The SC extends from San Jorge Gulf to the Deseado estuary (DE) (Fig. 1d). The San Jorge Gulf is the largest coastal embayment of the Patagonian Shelf, one of the most productive portions of the South Atlantic Ocean (Marrari et al. 2017; Palma et al. 2020). In this gulf, an economically significant fishery (Glembocki et al. 2015) and oil industries—including production, offshore drilling and transit of tankers—are developed (Silwan 2001). Furthermore, regional oil and fishing industries encompass substantial reproductive and foraging grounds of many marine birds and mammals (Torres et al. 2016). It has a shallow-water region (45–75 m depth) near 46° 48′ S, 65° 43′ W, where the formation of the seasonal pycnocline is restricted by intense vertical mixing due to high bottom friction. Besides, during the Southern Hemisphere warm period (October–March), net surface heat flux is positive, sufficient to warm the surface layer of the San Jorge Gulf and give rise to the southern tidal front (Rivas 1994; Rivas and Piola 2002; Carabajal et al. 2018).

On the other hand, the DE is a macrotidal sea inlet with an extensive coastal plain and a reduced freshwater discharge (Piccolo and Perillo 1999). This area has a deep-water port located on the north edge where fishing activities take place and it is also a nature reserve for vulnerable marine fauna (Islas et al. 2004). The Magellan Strait influences the Santa Cruz area since it is introduced as a plume of vertically homogeneous, low-salinity water (~ 33.2) that extends northwards to 42° S (Carabajal et al. 2018; Palma et al. 2020).

Finally, the TF area (Fig. 1e) is located in the southernmost part of the SW Atlantic Ocean and it includes the Beagle Channel (BC) that connects the Pacific and the Atlantic Oceans, hosting a wide range of wildlife and biodiversity. This area is hydrologically complex since the Antarctic and Sub-Antarctic waters converge and interconnect with the Cape Horn Current that enters the continental shelf through the Le Maire Strait in the eastern part of Tierra del Fuego, and the Antarctic Circumpolar Current (Guerrero et al. 1999). The Antarctic Circumpolar Current is highly loaded with nutrients that enter the Argentine shelf and is diluted in part by the freshwater inputs from glacier melting through the Beagle Channel (Guinder et al. 2020). The central urban city in this area is Ushuaia that is the southernmost city of the world with ~ 60,000 inhabitants. In this area, there are also some electronic manufacturing industries and the most crucial port for Antarctic tourism and maritime traffic (Conti et al. 2019).

Sampling, laboratory procedures and data analysis

Sampling was carried out during the austral summer (January 2016), on board the vessel "*Dr. Bernardo Houssay*" that belongs to the Prefectura Naval Argentina (PNA), at 20 stations distributed in the four areas of the PSLME mentioned above (Fig. 1). The BA comprised 7 stations (1, 2, 3, 4, 5, 6 and 7), the VP comprised 2 stations (8 and 9), the SC area comprised 5 stations (10, 11, 12, 13 and 14) and the TF area comprised 6 stations (15, 16, 17, 18, 19 and 20).

Surface seawater samples for SPM were collected, from a nominal depth of 5 m, with a Teflon peristaltic pump attached to a Teflon tube. The sampling and laboratory materials were carefully cleaned with diluted 5% HNO_3 (APHA-AWWA-WEF 1998). 5 L of seawater were immediately filtered on board by vacuum through acid-treated Millipore® HAWP 04,700 filters (0.45 µm) for the determinations of the particulate metals. Finally, all the filters were frozen at − 20 °C until analysis in the laboratory. At the Laboratorio de Oceanografía Química of the Instituto Argentino de Oceanografía (IADO, CONICET-UNS), the filters with the SPM were dried at 50 ± 5 °C until constant weight and weighed in an analytical balance to obtain the dry weights of the samples by difference with the weights of the filters. Subsequently, the filters were acid-digested with HNO_3 (65% purity, Merck) and $HClO_4$ (70% purity, Merck) in a proportion of 5:1 mL, respectively. Then, they were put in a bath of glycerin at 110 ± 10 °C to obtain a sample of about 1 mL. Each of the extracts was carefully transferred into a graduated tube and completed with HNO_3 0.7% until a final 10 mL volume. For the treatment blanks, the same digestion procedure was performed for filters without particles. All the samples were analyzed in duplicate and the metal concentrations were determined with ICP-OES Optima 2100 DV (Perkin Elmer).

The method detection limits (MDL) for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were 0.03, 0.05, 0.09, 3.00, 0.23, 0.05, 0.04, and 0.11 µg g^{-1}, respectively. In addition, for each metal, the limit of quantification (LOQ) was calculated, which is the lowest concentration that can be determined with an acceptable level of repeatable precision and confidence. The LOQ is defined as ten times the standard deviation of the blank (according to IUPAC) and it was estimated as following, for each metal previously mentioned: 0.01, 0.19, 0.3, 9.82, 0.76, 0.17, 0.14 and 0.37 µg g^{-1}.

For the analytical quality control, reagent blanks, certified reference materials (CRMs [Certified Reference Material BCR-414 (No 509), IRMM, Geel, Belgium]) and analytical grade reagents (Merck) were used. The recovery percentages for all metals in CRM were higher than 90%.

To evaluate the associations between metals and the concentrations of SPM, two statistical analyses were performed with InfoStat V2016 software (Universidad Nacional de Córdoba, Argentina): Spearman correlation between the particulate metals and SPM concentrations, and a principal component analysis (PCA) between the metals. Also, a cluster analysis (Bray–Curtis similarity) and a non-metrical multidimensional scaling (nMDS) using Bray–Curtis similarity were employed to analyze the similarity between the metal loadings of the sampling stations and to determine internally similar groups between them. These two analyses were conducted with the Primer 6 software (Clarke and Gorley 2006).

Results

The SPM concentration did not show a remarkable spatial variation (Fig. 2), except for station 1 (corresponding to RDP) that showed a peak of 63.8 mg L^{-1}. Other stations with relatively high levels of SPM were station 14 in the SC (11.4 mg L^{-1}), station 20 in TF (10.5 mg L^{-1}), and station 9 in VP (10.2 mg L^{-1}). On the other hand, the sites with relatively low SPM levels were 2 in BA (4 mg L^{-1}), 19 in TF (5.1 mg L^{-1}), 3 in BA (5.2 mg L^{-1}) and 16 in TF (5.4 mg L^{-1}).

Regarding the concentration of metals, the mean concentrations and ranges of all metals are summarized in Table 1. Overall, the particulate metals showed a wide spatial variation (Fig. 3). The highest concentrations of Mn, Ni, Cr and Fe were found at station 1 (7646, 49.2, 48.7 and 54,470 µg g^{-1} dry weight respectively), the highest values of Cu, Pb and Zn were found at station 2 (154.9, 58.6 and 509.5 µg g^{-1} d.w., respectively), whereas the highest concentration of Cd was found at station 4 (13.9 µg g^{-1} d.w.). On the other hand, Pb was below the MDL (0.04 µg g^{-1}) in eleven of the twenty stations (7, 8, 9, 10, 12, 14, 15, 17, 18, 19, and 20), and Ni values were below the MDL (0.05 µg g^{-1}) in fourteen of the twenty stations (4, 5, 6, 7, 8, 9, 12, 13, 14, 15, 17, 18, 19 and 20).

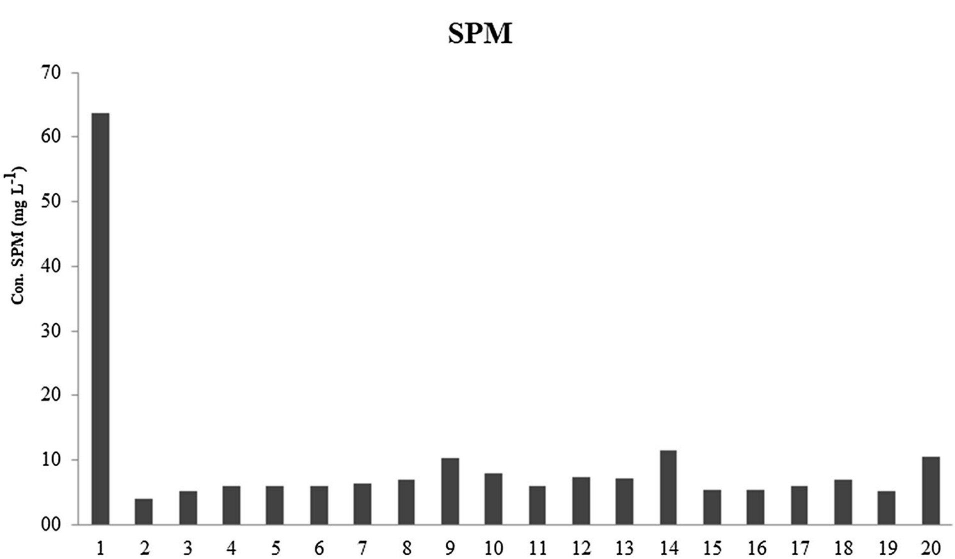

Fig. 2 Distribution of suspended particulate matter (SPM) concentrations (mg L^{-1})

Table 1 Summary of means and ranges of particulate heavy metals in the Argentine Sea (μg g^{-1} dry weight)

	Cd	Cu	Pb	Zn	Mn	Ni	Cr	Fe
Min	0.9	15.4	< MDL	< MDL	7.9	< MDL	< MDL	263
Max	13.9	154.9	58.6	509.5	764.6	49.2	48.7	54,470
Mean	2.6	36.1	14.5	94.4	91.7	20.6	10.2	4166
SD	± 2.8	± 31	± 21.5	± 158.8	± 166.7	± 21.4	± 10.6	± 11,876

Min minimum concentration, *Max* maximun concentration, *Mean* mean concentration

SD standard deviation, < *MDL* values below the method detection limit

According to each area, the BA showed relatively high concentrations of all the metals, especially at stations 1 and 2. The VP showed relatively high concentrations of Cu, Mn and Cr (station 8); the SC presented relatively high values of Cd, Cu, Zn and Ni, whereas the TF showed relatively high concentrations of Cd, Zn, Mn and Cr (Fig. 3).

The Spearman correlations between heavy metals and the SPM are shown in Table 2. Significantly positive correlations were found between Pb and Zn, Ni, Cr and Fe, whereas Ni correlated positively with Cu, Mn and Cr, and negatively with Cd. Cr correlated positively with Cu, Zn, Fe and Cu, and Fe correlated positively with Mn. SPM concentrations only correlated negatively with Cd.

With almost 60% of similitude, the cluster analysis (Fig. 4a) clustered together all the stations except for station 1 (RDP). Stations 2, 3 and 16 showed more similarity between them, as well as 10, 9 and 13. The other stations were grouped with almost 85% of similitude. The nMDS (Fig. 4b) exhibited the same pattern and determined three groups (80% similarity) including a group with station 1 (RDP), another one with 2, 3 (BA) and 16 (BC), while the remaining stations grouped sites corresponding to the south of BA, VP, SC and TF.

The results of the PCA of metals in SPM are shown in Fig. 5. The two first components (F1 and F2) explained 89.3% of the total variability. Cu, Zn, Pb and Ni are clustered together and contributed to F1 and F2 with high positive loadings. On the other hand, Cr, Fe and Mn are clustered together and contributed to F1 with high positive loadings and F2 with significant negative loadings.

Discussion

The spatial distribution of SPM concentrations along the study area showed some fluctuations according to the location of the sample. The stations located far from the coast presented the lowest concentrations of SPM, while the stations near to the coast presented the higher ones. In coastal areas, sediments and seston are suspended in the water column either in a state of exchange with bed sediments and intertidal flats (Jonge and Beusekom 1995). The origin of SPM and associated organic material in these environments could come from autochthonous primary production of pelagic and benthic algae, erosion and sedimentation of channel beds, intertidal flats, and salt marshes (de Jonge 2000). External sources like the particulate matter derive from freshwater runoff, water mass intrusion from the open sea, and accumulation of mud from the coast (Velegrakis et al. 1997) also contribute to the SPM pool.

On the other hand, SPM concentrations at sea are very variable: minimum concentrations have been observed in oligotrophic areas of the open ocean (1 μg L^{-1} or even lower), while in coastal waters, the concentrations can exceed 50 mg L^{-1} (Helmers 1996), as is the case of the RDP.

The concentration of particulate metals in the Argentine Sea shows a wide spatial variation, which might be expected in a very complex and large area with more than 4000 km of coastline. Overall, all the metals, except for Pb and Ni, were detected at all the sampling sites.

The BA presented the highest levels of all the heavy metals, especially the stations 1 and 2. The highest concentrations of Mn, Ni, Cr and Fe were found at station 1—located on the mouth of the RDP—with a corresponding relatively high value of SPM that was between 6 and 16 orders of magnitude above the concentrations of the rest of the stations. The riverine runoffs might explain these high concentrations from RDP, since about 160 million tons of sediment are discharged into this estuary every year with SPM concentrations between 10 years 1000 mg L^{-1} (FREPLATA RLA 99/G31 2005). This sediment load is composed of 56% silt, 28% clay and 16% sand, and 90% of the load is transported in suspension (Drago and Amsler 1988; Amsler 1995). According to a study about the hydro-sedimentological dynamics of the Río de la Plata (Proyecto FREPLATA RLA 99/G31), the finest sediments carried by this river are the primary source of transportation of various types of pollutants, mainly heavy metals, towards the estuarial environment. In the zone of maximum turbulence (ZMT), accumulation occurs in the bottom of the sediments and, consequently, of their contaminants, associated by physical–chemical flocculation processes. Then these sediments are resuspended by turbulent processes mainly induced by tidal currents, waves and wind. Dredging activities can also participate in the resuspention of bottom sediments and contribute to the metal pool in the SPM. However, no significant

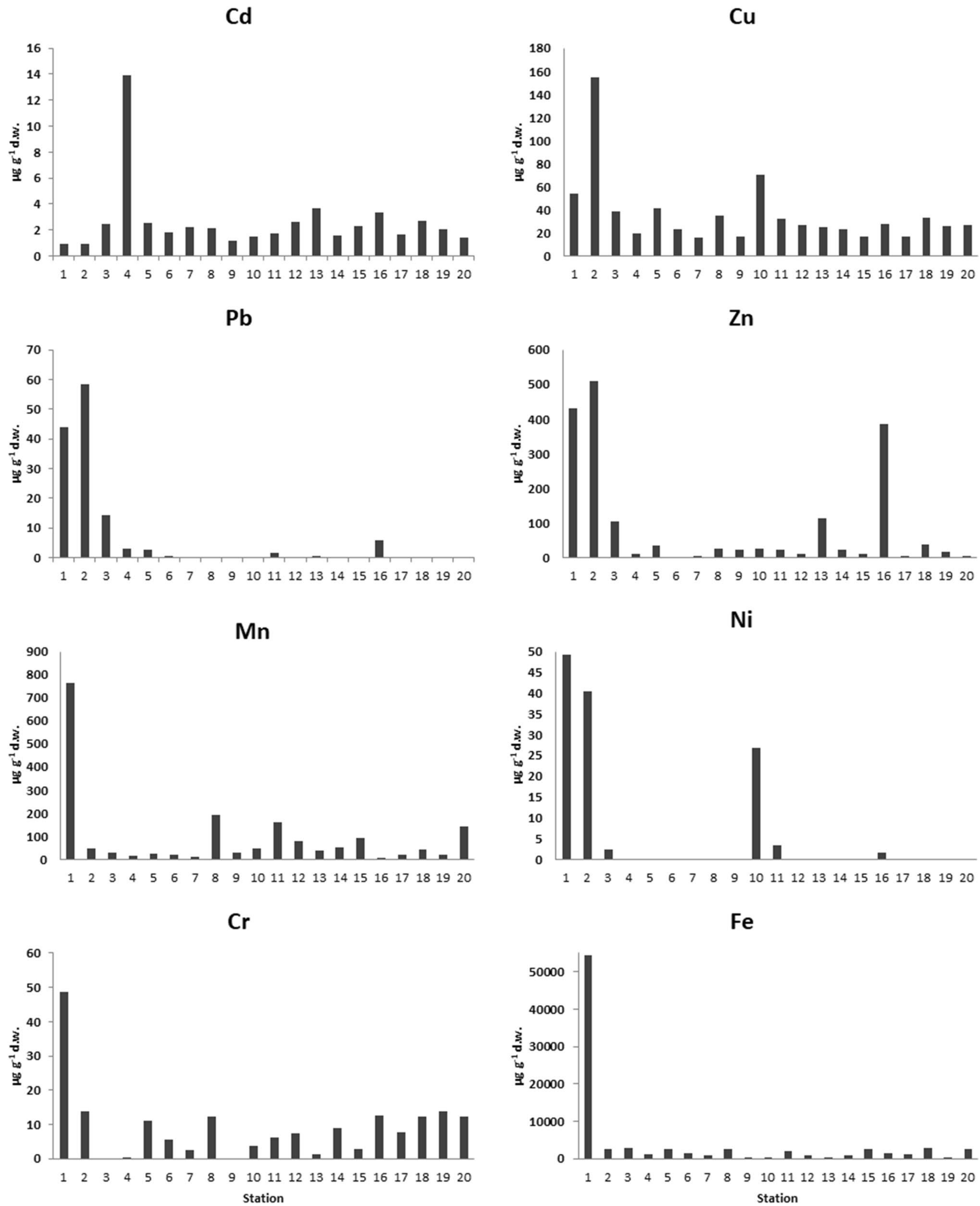

Fig. 3 Spatial distribution of heavy metals (µg g^{-1}dry weight) in the suspended particulate matter (SPM) in the Argentine sea

Table 2 Spearman correlation matrix

	Cd	Cu	Pb	Zn	Mn	Ni	Cr	Fe	SPM
Cd	1								
Cu	−0.16	1							
Pb	−0.4	**0.7**	1						
Zn	−0.02	**0.75**	**0.64**	1					
Mn	−0.42	0.42	0.27	0.15	1				
Ni	**−0.89**	**0.77**	**0.6**	0.43	**0.77**	1			
Cr	−0.43	**0.58**	**0.71**	**0.52**	0.22	**0.6**	1		
Fe	−0.03	0.43	**0.73**	0.3	**0.44**	0.43	**0.48**	1	
SPM	**−0.47**	−0.13	−0.42	−0.21	0.39	0.41	−0.03	−0.3	1

R critic (threshold value of the correlation coefficient to declare a correlation *r* as significant with an error probability of 5%) = |0.44|

Significant correlations are shown in bold ($p = 0.05$)

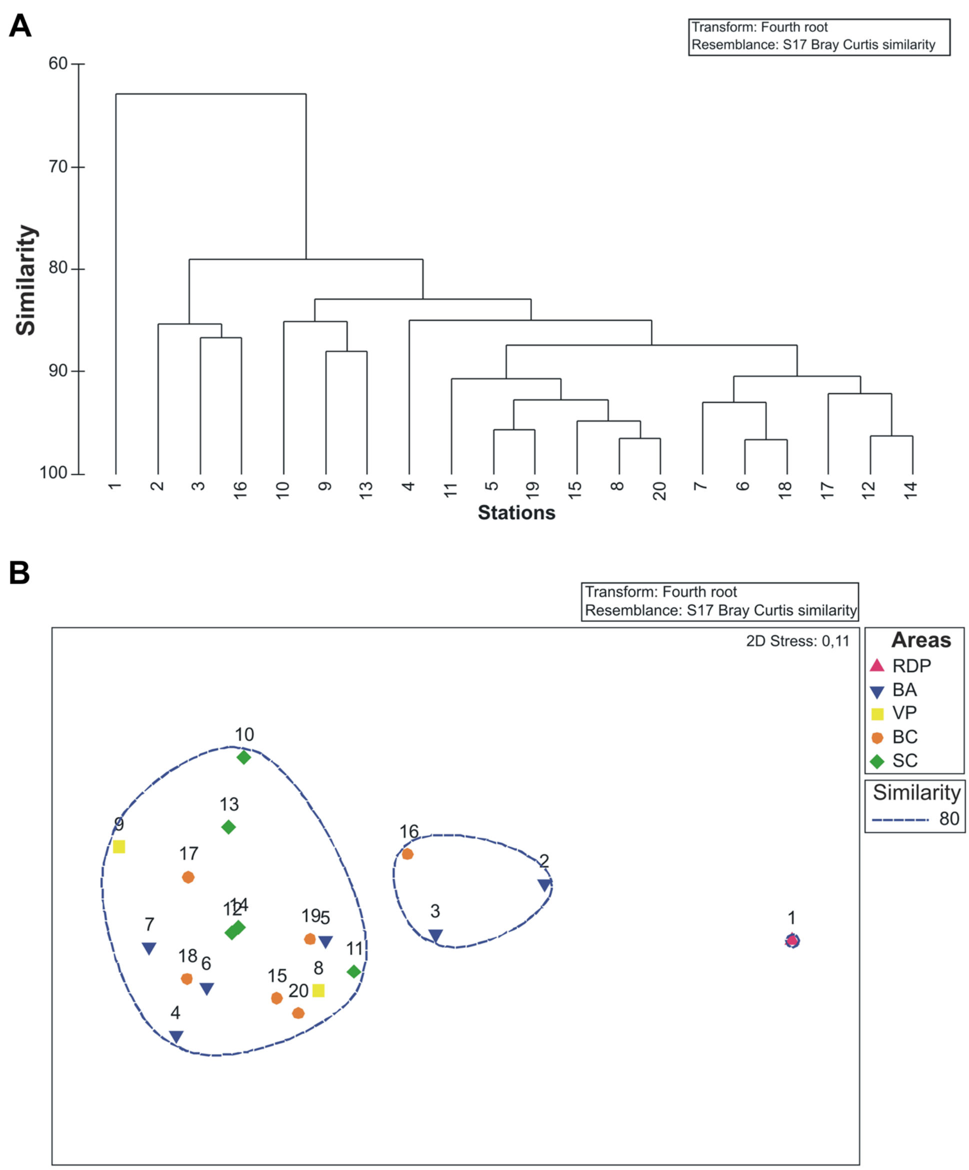

Fig. 4 **a** Cluster analysis based on the Bray–Curtis similarity between the particulate metals of the sampling stations **b** non-Metrical Multidimensional Scaling (nMDS) (Bray–Curtis similitude) between the total particulate metal loading of the sampling stations of the different areas. *RDP* Río de la Plata Estuary, *BA* Buenos Aires, *VP* Valdés Península, *BC* Beagle Channel in Tierra del Fuego (TF), *SC* Santa Cruz

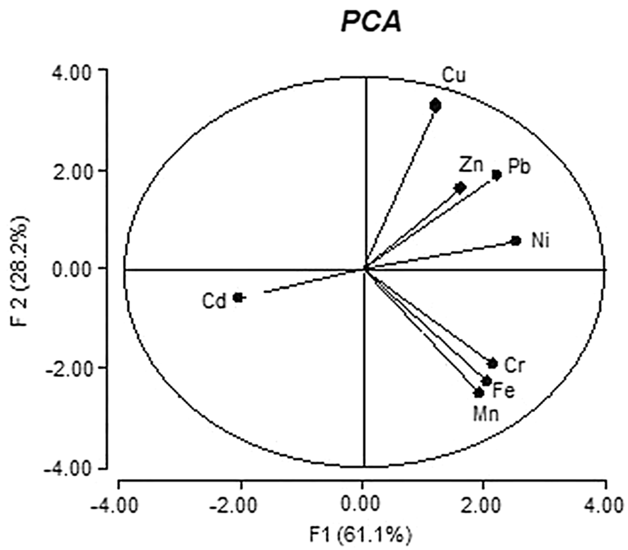

Fig. 5 Principal component analysis (PCA) loading plots of heavy metals

correlations were found between these metals and the SPM. It is important to remark that Buenos Aires city, the capital city of Argentina and the largest city in the country, and its metropolitan area (AMBA) are located along the coast of the RDP, which together concentrates 40% of the country's population. In these areas, most of the sewage waters are untreated before being discharged into the Río de la Plata (Lombardi et al. 2010; Zorzoli 2017), and they also contain around 60% of the chemical, rubber and plastic industries, and 46% of the textile, leather and footwear industries in the country (INDEC 2005). Moreover, the second economically important ports of Argentina are here. Thus a high degree of urbanization and industrialization affects this area and generates inputs of contaminants—including nutrients, organic matter, metals (mainly Cr and Pb), pesticides, hydrocarbons, suspended solids, and pathogenic agents (Licursi and Gómez 2013).

According to Zorzoli (2017), the heavy metal inputs in the RDP are indirect since the industrial effluents are discharged into the different tributaries that flow into the estuary. Some studies have reported concentrations of heavy metals in the water, SPM, sediments and several fish in the Río de La Plata (Bilos et al. 1998; Marcovecchio 2003; Ronco et al. 2001, 2008; Lombardi et al. 2010; Avigliano et al. 2015; Zorzoli 2017; Muniz et al. 2019). Bilos et al. (1998) found higher levels of particulate Cu and Cr than those recorded in this study, but similar levels of Mn, which probably implies that the concentration of Mn might have persisted over time (Table 3). Avigliano et al. (2015) reported values of Pb, Cd and Zn for the dissolved phase above the recommended levels based on the Argentinean National Guidelines for the Aquatic Biota Protection (ANGABP) and for the Canadian Guidelines for the Aquatic Biota Protection, and high concentrations of Pb in the muscle of silverside (*Odontesthes bonariensis*), a human-consumed species. On the other hand, Zorzoli (2017) reported lower mean values of Cd, Cu and Pb in dissolved phase and sediments and higher mean values of Cr in sediments. Meanwhile, Muniz et al. (2019) found lower mean levels of all metals in the sediments in the Montevideo coastal zone (Uruguay) (Table 3) and suggest that this area of the RDP can be considered from low to mildly polluted by metals. From all this data, it is suggested that the RDP is a metal contamination hotspot, and it is highly probable that the particulate and dissolved metals might reach the bottom sediments and become absorbed by them. Also, they could be bioaccumulated by the biota, causing enzymatic dysfunctions and with risks for human health in those commercial and consumed species.

South of BA, station 2 showed the highest levels of Cu, Pb and Zn, but the lowest levels of SPM concentrations and there was no significant correlation between these variables. This sampling station is close to Mar del Plata, which has more than half a million inhabitants, being the most populated coastal city in Argentina (CIEM 2010; Pon and Becherucci 2012). This city also supports a wide range of industries, including tourism, fishing, and cereal industries with large cargo ships sailing its shores. Moreover, it is considered the oldest and most popular seaside resort in the country (Juárez and Mantobani 2006), receiving between 2 and 3 million tourists during the summer months (December–March) (Bouvet et al. 2005; Pon and Becherucci 2012). Mar del Plata is also the most important commercial fishing harbor of the country. In this context, Marcovecchio et al (2006) found two primary sources of heavy metals: Mar del Plata harbor and the area affected by the treatment plant for the urban and industrial sewage disposal of the city.

At the north of the station 2, it is located Mar Chiquita Coastal Lagoon, an estuarine environment with an area of ~ 60 km^2 and a drainage basin of 10,000 km^2 characterized by intensive agricultural activities, that is connected to the sea through an elongated inlet channel of approximately 6 km (Marcovecchio et al. 2006). Beltrame et al. (2009) reported higher levels of particulate Cu, Pb and Zn for this lagoon than those found in our study (Table 3). Hence, if the relative proximity of this lagoon to the sampling station is considered (~ 50 km,) it could be suggested that the Mar Chiquita lagoon has significant influence through underground transport of particulate metals to the ocean.

Still, in BA, station 4 presented the highest concentration of Cd. This metal was the only one that correlated negatively with SPM concentrations. This result could indicate that low concentrations of SPM were favorable for the enrichment of metals in the particulate phase. The possible reason is that the particle size is generally smaller in a low concentration of SPM and shows a stronger absorption capacity for

Table 3 Concentrations of heavy metals in different matrices in Argentine Sea and in other world seas

References	Study area	Matrix	Cd	Cu	Pb	Zn	Mn	Ni	Cr	Fe
This study	Rio de la Plata Estuary	SPM ($\mu g\ g^{-1}$)	0.9	53.84	43.85	430.2	764.6	49.18	48.5	54,470
Avigliano et al. (2015)	Rio de la Plata Estuary	Dissolved ($\mu g\ L^{-1}$)	0.32 ± 0.00		2.48 ± 0.04	81.2 ± 13.0	25.6 ± 0.50	3.97 ± 0.74	1.17 ± 0.21	681 ± 14,000
Bilos et al. (1998)	Rio de la Plata Estuary	SPM ($\mu g\ g^{-1}$)		7.4–109			525–1341		75–408	
Muniz et al. (2019)	Rio de la Plata Estuary (Uruguay)	Sediments ($\mu g\ g^{-1}$)	0.76 ± 0.40	31.21 ± 7.53	20.23 ± 4.50	75.77 ± 26.24	207 ± 65	12.00 ± 5.46	33.54 ± 8.26	29,225 ± 15,995
Zorzoli (2017)	Rio de la Plata Estuary	Dissolved ($\mu g\ L^{-1}$)	0.29	7.0	5.5				11.4	
Zorzoli (2017)	Rio de la Plata Estuary	Sediments ($\mu g\ g^{-1}$)	0.35	18.8	18.2				80.0	
This study	Mar Chiquita Lagoon	SPM ($\mu g\ g^{-1}$)	0.94	154.9	58.55	509.5	46.48	40.33	13.67	2462
Beltrame et al. (2009)	Mar Chiquita Lagoon	SPM ($\mu g\ g^{-1}$)	< MDL—58.64	< MDL—22,921	< MDL—342	< MDL—16,922	1947–2415	< MDL—16,327	< MDL—60	48.71—54,684
This study	San Jorge Gulf	SPM ($\mu g\ g^{-1}$)	1.52	69.9	< MDL	26.57	46.67	26.77	3.77	262.8
Marinho and Esteves (2013)	San Jorge Gulf	Sediments ($\mu g\ g^{-1}$)		< MDL—6.98	< MDL—5.48	7.9–46.5	23.5–298.7	< MDL—20.8	< MDL—13.3	1,220 – 15,720
This study	Beagle Channel	SPM ($\mu g\ g^{-1}$)	1.42	26.37	< MDL	4.93	140.7	< MDL	12.15	2569
Duarte et al. (2011)	Beagle Channel	Sediments ($\mu g\ g^{-1}$)	1.05 ± 0.61	13.17 ± 5.86	20.04 ± 13.27	108.63 ± 51.60				22,470 ± 8850
Gaiero et al. (2002)	Patagonian Rivers	Sediments ($\mu g\ g^{-1}$)		22.0 ± 8.0	21.0 ± 8.0	84.0 ± 13.0	945.0 ± 201.0	19.0 ± 5.0	53 ± 14.0	53 ± 14.0
Demina and Nemirovskaya (2007)	White Sea	SPM ($\mu g\ g^{-1}$)	0.02–2.69	0.18–72.4	0.24–319.4	39.0–612.5	2.52–84.8	0.04–49.4		60.0–3316.3
Prego et al. (2013)	Northeast Atlantic Ocean	SPM ($\mu g\ g^{-1}$)	3.6–5.8	9–44	1.0–3.8	7–54		0.6–4.0		975–4050

pollutants in water body (Zhang et al. 2018). This is one of the reasons of the particle concentration effect (p.c.e.) (Benoit and Rozan 1999). Another of the causes of this effect is that the SPM is heterogeneous and can exist in morphologically complex forms, and trace components can dominate surface composition if they occur as coatings on more abundant substances. As a consequence, SPM possesses a variety of complexation sites characterized by a range of stabilities with various metals, with sites with lower constants (weak sites) and more abundant than those with higher constants (strong sites). If reversible reactions are assumed, at equilibrium, metals should occupy the strongest available sites. Thus, at low sorption densities, metals would occupy the few strongest sites, whereas at high values of sorption densities, metals are complexed at progressively weaker sites. In this sense, periods of high SPM would be associated with greater dissolved metal concentrations and lower partition coefficients.

In VP, relatively high concentrations of Cu, Mn and Cr were detected, especially at station 8. Previous studies on trace metals in different matrices, such as sediments, seston, algae, invertebrates and marine mammals, are available for the San José Gulf and Nuevo Gulf (Harvey and Gil 1988; Gil et al. 1989, 2015; Rosas et al. 2012; Giarratano et al. 2014) but not for the external zone of the peninsula. In the present study, it was considered that there is a tidal mixing front in VP, a thermal front observed in spring and summer, that defines the boundary between stratified (offshore) waters and a coastal, vertically mixed body of water which could have an effect on the fraction of the particulate metals. The front is formed because the stratification of shelf waters is induced by surface warming during spring and summer periods, and the mixing of the coastal water is forced by vertical shear induced by tidal currents at particular topographic shoals southeast and northeast of the peninsula (Acha et al. 2004). Even more, the tidal energy drives the lower layer—rich in nutrients—towards the well-lit upper layer, creating the optimal conditions for phytoplankton blooms and zooplankton (Derisio 2012). The structure of the front is maintained until autumn when stratification of shelf waters decays (Acha et al. 2004). So, it is possible that the concentration of heavy metals changes over the seasons due to the dynamic of this front.

The SC showed relatively high levels of Cd, Cu, Zn and Ni, although the latter metal was only detected at stations 10 and 11. During the austral spring–summer, a southern tidal front takes place in the San Jorge Gulf: a tongue that comes from the Magellan Strait of vertically homogeneous, low-salinity water that extends northwards that comprises the vertically homogeneous portion of the front, and in contrast, mid-shelf waters that are stratified during the warm period and comprise the vertically stratified portion of the front (Matano and Palma 2008). Carabajal et al. (2018) have revealed that the front has a dynamically complex three-dimensional frontal structure. It exhibits a horizontal subsurface intrusion from the mixed region to the pycnocline of the stratified side that is rich in nutrients, and which possibly causes a subsurface chlorophyll-*a* peak. The relatively high concentration of some particulate metals in SC could suggest that those nutrient-rich waters are also rich in metals that are essential for the phytoplankton (e.g., Cu and Zn), which is why there is an increase in primary production that causes the chlorophyll-*a* peak described by these authors. However, more studies on the availability of the essential metals for the phytoplankton and their seasonal variation are necessary to corroborate this hypothesis. In this sense, some studies detected essential and toxic heavy metals in Seaweeds in the northern and central parts of the San Jorge Gulf (Muse et al. 1999; Perez et al. 2007), revealing that heavy metals are available for the planktonic organisms. On the other hand, Marinho and Esteves (2013) detected higher levels of Pb, Mn, Cr and Fe, and lower levels of Ni and Zn in the sediments than those reported in the particulate fraction of our study in the north of the San Jorge Gulf (Table 3), indicating that the distribution of heavy metals in this is area is subject to spatial and seasonal variation.

Relatively high values of Cd, Zn, Mn and Cr were detected in TF, whereas Pb and Ni were only found at station 16. Some studies have reported heavy metals in invertebrates, the dissolved phase and sediments in several coastal sites of the Beagle Channel and Ushuaia Bay (Conti et al. 2011, 2012, 2019; Duarte et al. 2011; Giarratano et al. 2010, 2011), but to our knowledge, there are no metal records in the sector of the shelf that belongs to this area. Higher levels of Pb, Zn, and Fe, and lower levels of Cd and Cu have been reported in the sediments of the BC (Duarte et al. 2011) (Table 3), than in the particulate fraction in the present study. The Antarctic Circumpolar Current enters the Argentinian shelf as the Malvinas Current highly loaded with nutrients (Amin et al. 2011), and, therefore, the relatively high concentration of some particulate heavy metals in this area suggests that this current is also enriched with heavy metals, especially those considered as micronutrients (e.g., Cu, Zn, Mn). This means that possibly the micronutrients have similar behavior to the nutrients, but the data collected in this study are insufficient to corroborate this hypothesis.

The cluster analysis defined three groups of stations but utterly different from the areas proposed in this study. The only coincidence was that station 1 did not join any of these groups, which reinforces the idea that the RDP is a heavy metals contamination hotspot. Meanwhile, the nMDS formed three groups, including the station belonging to RDP formed a distinct group, the northern sites 2 and 3 of BA and the station 16 of BC. This could be explained by the anthropogenic disturbances from these areas that include large urban settlements with untreated sewage waters, industrial and port activities.

Group three included the southern stations of BA, VC, SC and the remnants of TF in BC. The physical, geological and oceanographic variables are different over the area from the last group (Martinetto et al. 2019); therefore, studies covering more significant numbers of stations along the PSLME are necessary to elucidate the spatial distribution of heavy metals and the SPM loadings.

According to the PCA analysis, it was possible to establish two groups of heavy metals: on the one hand Cu, Zn, Pb and Ni, and on the other hand Cr, Fe and Mn. This could suggest that the metals that conform to these two groups have similar behavior. Cd was not associated with any of these groups and was the only metal that showed a negative correlation with the concentration of SMP, meaning that possibly Cd has a different behavior from the rest of the metals in the Argentine sea. The group of Cr, Fe and Mn is generally associated with each other. Under reducing conditions, Cr(VI) may convert to Cr(III), which is insoluble, strongly adsorbed onto solid surfaces (Loyaux-Lawniczak et al. 2001), Cr(VI) can be removed from solution naturally by reductants such as aqueous Fe(II), dissolved humic acids, and Fe(II)-bearing minerals. Moreover, Cr(III) is oxidized into Cr(VI) in sediments or suspended particulate spontaneously by manganese oxide (MnO_2) (Jobby et al. 2018). Nevertheless, it is necessary to carry out more detailed studies to assess the real behavior of each metal. Also, the presence of Ni and Pb below the MDL in almost all stations may indicate that these metals could be associated with other phases, such as the dissolved and sedimentary, rather than the particulate.

Comparing with the baseline data on sediments of pristine Patagonian rivers proposed by Gaiero et al. (2002), higher values of Cu, Zn and Ni were found in our study. These authors concluded that the South Atlantic coastal areas located in the nearby outlets of rivers, such as the Negro, Chico and Santa Cruz, receive around 90% of the total trace metals produced by the Patagonian rivers. High proportions of metals are transported to the ocean in the suspended load, and evidence indicates that Fe oxides and organic matter are essential phases controlling their distribution in the non-residual fraction of sediments. However, in some rivers (especially the Colorado, Coyle and Gallegos), the dissolved load might play an important role in delivering Ni, Cr, Co, Pb and Cu to the coastal areas in a biologically available form. Therefore, most of the pollutants that are released to the marine system become associated with the suspended matter and bottom sediments, with high risks to the biota.

Finally, in comparison with other worldwide works, we found higher mean levels of particulate Cd, Cu, Pb, Zn Ni, and Fe than those reported by Prego et al. (2013) in the Northeast Atlantic Ocean, and higher levels of particulate Cu, Pb, Mn and Ni than in the study carried out by Demina and Nemirovskaya (2007) in the White Sea.

Conclusions

This framework provides novel, baseline data of particulate metals and the suspended particulate matter from a scarcely explored region of the Southwestern Atlantic Ocean. Large spatial variations were detected due to the extension of the area that is influenced by different factors, like weather, various shelves and shelf-break fronts, riverine runoff, and different anthropogenic pressures. The highest concentration of heavy metals was found at the station located in Río de la Plata estuary, a station influenced by anthropogenic activities like large urban centers, ports and industries. Statistical analysis showed that this station differs from the rest of the stations, and, therefore, it is possible to define it as a hotspot of heavy metals pollution.

Two groups of heavy metals were detected: one of them is integrated by Cu, Zn, Pb and Ni, and the other one is integrated by Cr, Fe and Mn, indicating that the metals that integrate each group have different behaviors. Cd is not part of either of these groups since it may have completely different behavior. However, to understand the real behavior of each metal in the Argentine sea, it is necessary to carry out more studies that involve other matrices, such as dissolved phases and the sediments. It was not possible to establish a spatial pattern in the study area, which might be due to some gaps in the sampling stations. Hence, to elucidate the spatial distribution of heavy metals, it is necessary to generate more information that covers a more significant number of stations along the Argentine Sea, including seasonal and oceanographic data.

Some essential metals (Fe, Mn, Zn and Cu) were detected in all the sampling sites indicating that these micronutrients are available for primary producers. Along with essential elements, some toxic metals (Cd and Cr) were also detected in all the stations. We consider that integral studies about heavy metals in different matrices are necessary to fulfill the gaps in knowledge of the biogeochemical cycles of heavy metals in the Argentine Sea. Finally, it is necessary to continue studying the role of metals as micronutrients and their trophic transfer from primary producers to consumers throughout the food web, which are critical to evaluate the productivity and ecological cycles for the conservation of the biodiversity of the coastal and shelf areas in the Southwestern Atlantic.

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