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Baseline

Distribution and origin of trace metals in sediments of a marine park (Northern San Jorge Gulf) from Argentina

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ABSTRACT

The Northern San Jorge Gulf (NSJG) was designated Interjurisdictional Coastal Marine Park "Patagonia Austral" in 2008 with the objective of conserving biodiversity and natural resources. Metals released to the environment can be accumulated by organisms and can be toxic in some cases, making it necessary to evaluate their presence and biological risk. This study examined concentrations of Fe, Mn, Zn, Cu, Cr, Ni, Cd and Pb in intertidal sediments of the NSJG, and was the first study of its kind to be conducted in this area. Concentrations of all metals fell below biological risk levels. Anthropogenic enrichment was only found for Ni around the Aristizábal lighthouse and was attributed to the frequent oil spills that impact this particular area.

1. Introduction

The Northern San Jorge Gulf (NSJG) is one of the most productive marine coastal areas of Patagonia. It has an extensive development of seaweeds and benthic invertebrate communities, with places for spawning and rearing of fish as well as reproduction of birds and marine mammals (Yorio, 2001). In 2008, authorities created the National Law N° 26.446, the Interjurisdictional Coastal Marine Park "Patagonia Austral" (ICMPPA), to conserve biodiversity and natural resources in this area.

The main environmental threat of this ecosystem comes from oil spills associated with the production and transportation of oil within San Jorge Gulf on the Atlantic coast of Chubut and Santa Cruz provinces. This area is one of the most important crude oil fields in Argentina. After extraction, petroleum is transported by sea from the port of Comodoro Rivadavia towards the North of the country. Previous studies on Patagonian coasts not only reported high hydrocarbon concentrations in loading and unloading sites (mainly in Cordova creek and Comodoro Rivadavia port), but also around the Aristizábal lighthouse in the ICMPPA, away from the port (Commendatore and Esteves, 2007; Commendatore et al., 2000). This was attributed to oil spills transported towards the Park by ocean currents and wind action. Oil spills undergo physical, chemical, and microbiological changes. Biodegradation in marine sediments can alter the mobility and bioavailability of the trace metals present in oil, such as Ni, V, Cd, Cr, Cu, Fe, Pb, Mn, and Zn (Dell'**Anno** et al., 2009). Unlike hydrocarbons, trace metals do not undergo biodegradation process, which favors their persistence in the environment, as well as their bioaccumulation and potential damage to organisms. This study presents the first data of trace metals levels in the coastline surface sediments from NSJG.

Sediment samples were collected in summer 2009/2010 from 22 locations between 44°46′S; 065°41′W and 45°22′S; 067°05′W (Fig. 1). At each site, 20 subsamples were collected manually with acrylic cores of 45 mm internal diameter and 30 cm in length (upper 10 cm) every 3 m and along the low tide line. Subsequently, they were mixed in a composite sample, which was stored in a single polyethylene bag at −20 °C.

Before analysis, the sediments were dried at 60 °C and carefully homogenized. The content of total organic matter was determined by loss of weight after calcination at 450 °C for 4 h. Particle size distribution was determined by sieving through plastic meshes: gravel (>2 mm), sand (between 63 µm and 2 mm), and silt–clay (<63 µm). For metal analysis, the bulk dried sediment was manually sieved through a 2-mm plastic mesh to remove coarser material and debris. Two replicates of 1 g of each sample were digested using 10 ml of aqua regia and evaporated in hot plate to near dryness. The digests were cooled to ambient temperature and transferred into a 25-ml flask and to final volume with 5% nitric acid. This method obtained the pseudo-total concentrations of Fe, Mn, Zn, Cu, Ni, Cd, Pb, and Cr (MacGrath and Cunliffe, 1985; ISO, 1995). The extracts were analyzed in an Atomic Absorption Spectrometer using N_2O/acetylene flame for Cr and air/acetylene flame for other metals. Two blanks were run with each set of 12 samples

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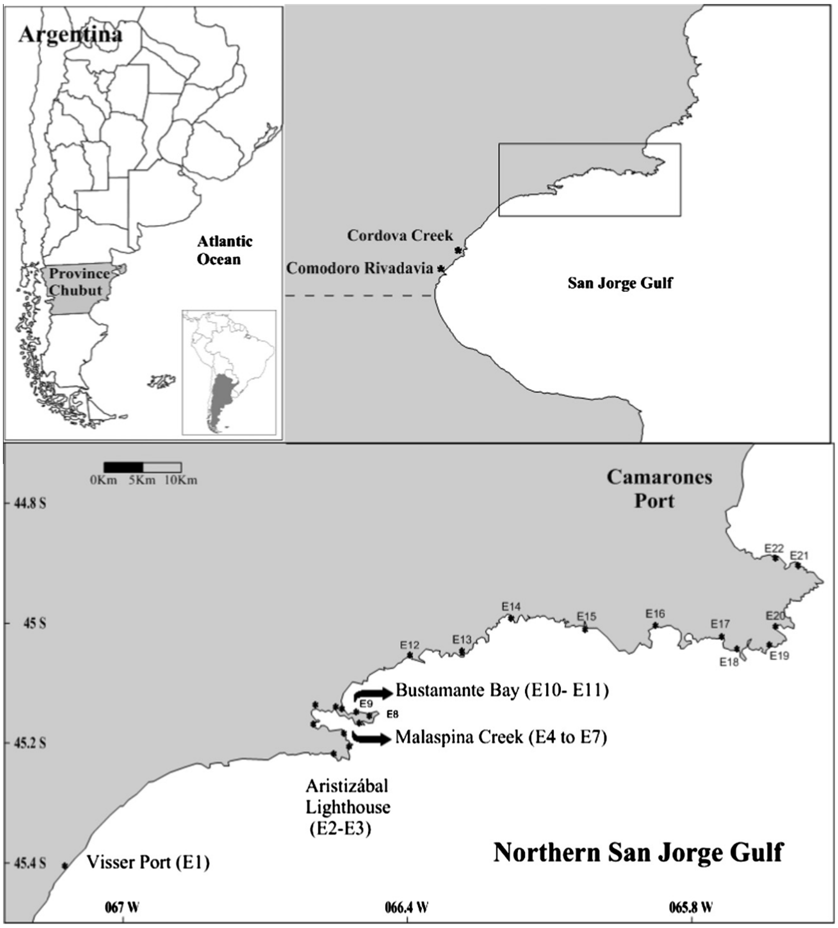

Fig. 1. Sampling sites along the coast of NSJG.

and reagents of analytical grade were used in every case. The results are reported as $\mu g\ g^{-1}$ of dry weight of sediment, except for Fe, which is expressed as $mg\ g^{-1}$. Variation coefficients tested for five replicates of the same sample were <10% for all metals. The detection limits and recovery percentages from PACS-2 Marine Sediment Reference Materials are shown in Table 1. Spearman correlations were performed to assess the relationships between the metals.

The samples were composed mainly of sand-sized particles, >50% (Table 2). The highest proportions of finest material (9.75–36.04%) were observed in Stations E4–E7 (located in Malaspina creek) and E22 (4.68%) (Sara creek). Both the creeks are semi-enclosed and low-energy ecosystems, hydrodynamically favorable for the deposition of suspended particles. On the other hand, stations E1 (Visser port), E2 and E3 (Aristizábal lighthouse), and E11 (Bustamante bay) showed gravel-sandy sediments.

Table 1
Detection limits and recovery from reference material (PACS-2 Marine Sediment) expressed in $\mu g\ g^{-1}$ dry weight.

Element	Detection limits ($\mu g\ g^{-1}$)	Certified concentration ($\mu g\ g^{-1}$)	Obtained concentration ($\mu g\ g^{-1}$)	Recovery (%)
Fe	2.5	40,900	30,863	75
Mn	0.63	440	252	57
Zn	0.25	364	362	99
Cu	0.63	310	294	95
Ni	2.5	39.5	35.2	89
Cd	0.25	2.11	1.95	93
Pb	5.0	183	176	96
Cr	2.5	90.7	56.8	63

Organic matter content varied between 0.23 and 3.5% (Table 2). The highest values (1.87–3.50%) were measured in Malaspina creek, which are in agreement with the highest content of fine material, followed by stations near Aristizábal lighthouse (0.71–1.25%), despite their high gravel level and low fine content.

Concentrations of Fe were the highest at all sites (1.22–15.72 $mg\ g^{-1}$), followed by Mn (23.5–298.7 $\mu g\ g^{-1}$), Zn (7.9–46.5 $\mu g\ g^{-1}$), Ni (<2.5–20.8 $\mu g\ g^{-1}$), Cr (<2.5–13.3 $\mu g\ g^{-1}$), and Cu (<0.63–6.98 $\mu g\ g^{-1}$). Pb was detected only in two stations: E7 (5.36 $\mu g\ g^{-1}$) and E20 (5.48 $\mu g\ g^{-1}$), with values very close to the detection limit (5.0 $\mu g\ g^{-1}$). The Cd concentrations were always undetectable (<0.25 $\mu g\ g^{-1}$) (Table 2). These metal concentrations are within the range or even below those reported for other coastal environments of Patagonia with low or without anthropogenic impact (Amin et al., 1996; Harvey and Gil, 1988; Mohamed, 2008).

To analyze the probable sources of metals, we performed correlation analysis among them. The only metal that did not show significant correlation with any other was Ni, unless the stations E2 and E3 were removed (Table 3). Fe and Mn, in general, are considered not to be affected by anthropogenic loads; thus, the metals statistically associated with them were assumed to be of natural origin. In that sense, the relatively high Ni values measured at E2 and E3 were therefore believed to be of anthropogenic origin. Since Ni is a known component of oil, the relatively high levels noted in sediments from these sites could be reflective of oil spills that frequently impact the area (Commendatore and Esteves, 2007; Commendatore et al., 2000).The existence of anthropogenic Ni

Table 2
Type of sediment, organic matter content (OM) (%) and metals concentrations (μg g^{-1} dry weight, except for Fe, mg g^{-1}).

Site	Type of sediment	OM	Fe	Mn	Zn	Cr	Cu	Ni	Pb	Cd
1-Visser port	Gravel sandy	0.38	10.14	298.7	26.4	5.4	1.86	4.9	<5.00	<0.25
2-Aristizabal lighthouse	Sand	1.25	1.89	52.5	12.8	2.9	0.75	20.8	<5.00	<0.25
3-Aristizabal lighthouse	Gravel sandy	0.71	1.22	43.1	8.3	<2.5	<0.63	12.8	<5.00	<0.25
4-Malaspina creek	Sand silty	1.87	5.71	63.0	17.7	6.5	1.24	3.1	<5.00	<0.25
5-Malaspina creek	Sand silty	3.50	15.72	262.4	46.5	12.5	6.98	8.5	<5.00	<0.25
6-Malaspina creek	Sand silty	2.31	5.77	61.2	23.9	6.7	1.62	2.7	<5.00	<0.25
7-Malaspina creek	Sand silty	1.94	14.47	196.4	44.4	13.3	4.61	8.4	5.36	<0.25
8-Piojo port	Sand	0.32	1.55	23.5	8.6	2.7	<0.63	<2.5	<5.00	<0.25
9-Gravina peak	Sand	0.62	2.84	52.3	10.2	4.0	<0.63	4.1	<5.00	<0.25
10-Bustamante bay	Sand gravely	0.50	1.92	27.4	10.5	2.8	<0.63	<2.5	<5.00	<0.25
11-Bustamante bay	Gravel sandy	0.32	2.70	38.5	7.9	4.2	0.66	<2.5	<5.00	<0.25
12-Ezquena peak	Gravel sandy	0.26	2.89	54.1	19.8	3.6	0.97	<2.5	<5.00	<0.25
13-Tafor peak	Sand gravely	0.46	2.81	53.0	11.0	4.7	<0.63	<2.5	<5.00	<0.25
14-Ranch San Miguel	Sand	0.29	5.47	86.2	16.6	5.7	0.75	<2.5	<5.00	<0.25
15-Melo port	Sand	0.60	2.81	43.1	10.7	5.0	<0.63	<2.5	<5.00	<0.25
16-Arredondo bay	Sand	0.33	3.36	49.9	9.9	4.4	<0.63	<2.5	<5.00	<0.25
17-Cayetano bay	Sand	0.51	3.03	44.8	10.9	3.9	0.72	<2.5	<5.00	<0.25
18-Huevo bay	Sand gravely	0.29	3.44	63.0	21.5	2.7	0.79	2.9	<5.00	<0.25
19-front Islas Leones	Sand	0.45	3.93	91.1	23.9	<2.5	<0.63	4.1	5.48	<0.25
20-San Gregorio bay	Sand gravely	0.23	5.35	89.7	31.3	4.0	0.91	<2.5	<5.00	<0.25
21-Sara creek	Sand silty	0.42	5.16	88.3	18.2	6.4	1.12	<2.5	<5.00	<0.25
22-School culture 721	Sand	0.44	6.50	90.0	21.2	5.7	0.87	<2.5	<5.00	<0.25

Table 3
Spearman correlation coefficients.

Metal	Fe	Mn	Zn	Cr	Cu
Mn	0.88*				
Zn	0.84*	0.90*			
Cr	0.77*	0.64*	0.51*		
Cu	0.81*	0.74*	0.82*	0.71*	
Ni	−0.15	−0.01	−0.07	0.14	0.4
Ni (after removing E2–E3)	0.64	0.79*	0.67	0.50	0.83*

* $p < 0.05$.

contribution was corroborated after obtaining the enrichment factors (EF) with respect to crustal Earth concentrations, according to the following equation:

$$\mathrm{EF} = [(\mathrm{M/Fe})\mathrm{sample}]/[(\mathrm{M/Fe})]\mathrm{crust}$$

This equation takes into account the relationship between the concentration of a metal (M) and Fe in the sample and the same relationship in the crust (natural background level) (Nikolaidis et al., 2010; Kamau, 2002; Alomary and Belhadj, 2007). There is no accepted pollution ranking system or categorization of degree of pollution based on the enrichment factor methodology. Nikolaidis et al. (2010) have proposed five contamination categories for EF: <2 minimal enrichment, 2–5 moderate enrichment, 5–20 significant enrichment, 20–40 very highly enriched, and >40 extremely highly enriched. For Zn some values were close to 2 (moderate enrichment). Only for Ni in stations E2 and E3, EF was >5 and <20 (significant enrichment) (Fig. 2).

With the aim of evaluating probable risk to the organisms, we used the NOAA, the Canadian, and the USEPA criteria (Table 4). The NOAA has set two guidelines: ERL (Effect Range Low) and ERM (Effect Range Medium), which refer to the incidence of adverse effects on the biota (Long et al., 1995). All the concentrations measured in this study were far below the ERL (20.9 μg g^{-1}), except for Ni in Aristizábal lighthouse very closed (20.8 μg g^{-1}). The Canadian Council of Ministers of the Environment (2002) has established the ISQG (Interine Sediment Quality Guidelines), which refer to "neartotal" trace metal extraction methods (mild digestions), similar to that used in this study (e.g., aqua regia, nitric acid or hydrochloric acid). Our results are far below these guidelines for all metals. The EPA refers to a set of methods for the evaluation of metals in sediments, including partial extraction and total extraction. The values found in the NSJG are within the range established by USEPA (1977) for no contaminated sediments.

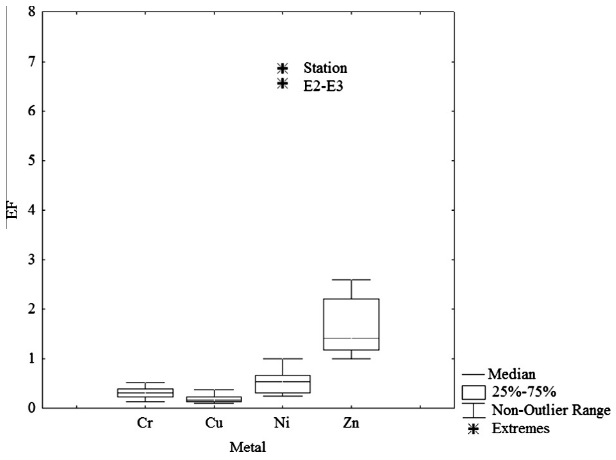

Fig. 2. Enrichment factors (EF). Pb was detected only rare occasion and Cd were always undetectable.

Table 4
Comparison with guidelines (expressed in μg g^{-1}).

	Zn	Cu	Cr	Ni	Cd	Pb
NSJG	7.92–46.53	<0.63–6.98	<2.5–13.34	<2.5–20.8	<0.25	<4.98–5.48
ERL	150	34	81	20.9	1.2	46.7
ERM	410	270	370	51.6	9.6	218
ISQGs	124	18.7	52.3	–	0.7	30.2
USEPA	90	25	25	20	–	40

We conclude that the concentrations of the trace metals analyzed in the sediments from the ICMPPA are not of biological risk and have predominantly natural origin. A possible anthropogenic contribution was only detected for Ni around Aristizábal lighthouse, which may be related to the crude oil spills that historically occur in loading buoys and along the tanker routes, and which is then carried to the Northern coast of the Gulf by currents and wind action. To our knowledge, there is no other important human source of Ni within the Park, and therefore, its monitoring would be a complement for tracking hydrocarbon pollution. Further studies are necessary to corroborate this hypothesis.

The growth of petroleum activities within San Jorge Gulf could not only increase Ni, but also other metal concentrations. For that reason, this research provides valuable reference information for management purposes and future scientific studies.

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