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Short Communication

Characterization of Baker Fjord region through its heavy metal content on sediments (Central Chilean Patagonia)

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ABSTRACT. The spatial distribution of heavy metals content (Ba, Cd, Cu, Pb, Sr and Zn) in sediments of the Baker Fjord and surrounding channels in the central region of the Chilean fjords (47°45'S, 48°15'S) is analyzed. The aim of the study was characterized the patterns of abundance and distribution of these metals in surface sediments. The area corresponds to a poorly studied zone with low human activity. Distribution patterns would be influenced by rainfall conditions (local erosion), fluvial (continental sediments carried by rivers), glacier (glacier flour) and estuarine circulation. Cluster analysis allows differentiation among the sampled sites and group with similar characteristics. Finally, the concentrations found were contrasted with average values of metamorphic rocks and show with some certainty that the values found for calendar for this area and the greatest concentrations are the result of natural enrichment.

Keywords: heavy metals, unpolluted sediments, fjords, Patagonia, Chile.

Caracterización de la región del fiordo Baker en relación al contenido de metales pesados en los sedimentos (Patagonia Central de Chile)

RESUMEN. Se analiza la distribución espacial del contenido de metales pesados (Ba, Cd, Cu, Pb, Sr y Zn) en sedimentos del Fiordo Baker y canales aledaños, en la región central de los fiordos patagónicos chilenos (47°45'S, 48°15'S). El objetivo del estudio fue caracterizar los patrones de abundancia y distribución de estos metales en los sedimentos superficiales. La zona corresponde a un área escasamente estudiada con baja actividad antrópica. Los patrones de distribución estarían influenciados por condiciones pluviales (erosión local), fluvial (sedimentos continentales arrastrados por los ríos), glaciar (harina de glaciar) y circulación estuarina. El análisis de conglomerados permite establecer diferencias entre los sitios muestreados y agruparlos con características semejantes. Finalmente, las concentraciones encontradas fueron contrastadas con valores promedios de rocas metamórficas y muestran con cierta certidumbre, que los valores encontrados corresponden a los naturales para esta zona y las concentraciones mayores son producto de enriquecimiento natural.

Palabras clave: metales pesados, sedimentos no contaminados, fiordos, Patagonia, Chile.

The Baker Fjord is located in the extreme north-eastern zone of the Central Chilean Patagonian Fjords (~48°00'S), in between the Northern and Southern Patagonian Ice Field Glaciers. The basin of the Baker Fjord disrupts the continuity of these two glacier systems, and it receives inflow from the Baker (870 $m^3 s^{-1}$) and Pascua (574 $m^3 s^{-1}$) rivers. This fjord is also influenced by marine waters coming from the Gulf of Penas generating a two layer estuarine circulation system (Pickard, 1971; Sievers & Silva, 2006).

The scarce population of this region (0.1 inhabitants km^{-2}; INE, 2012) minimizes the possible influence of human activity in the area. Therefore the fjord sediment's metal content should be representative of

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concentrations due to erosion and the natural lixiviation of the rocks that form the geological landscape (Ospina-Alvarez *et al.*, 2014). The first study concerning sediment metal composition of Baker Fjord area was performed in 1997 during the research cruise CIMAR 2 Fiordos (Ahumada & Contreras, 1999; Ahumada, 2006). In this study the metal content was analyzed only at three oceanographic stations, generating a limited amount of information. In 2009 during the CIMAR 14 Fiordos cruise, new sediment samples were taken at seven oceanographic stations, with the objective of characterizing its surface sediment through the analysis of its metal content. Specific aims were to identify areas of enrichment and the patterns of distribution of six metals (Zn, Ba, Cu, Sr, Pb and Cd) and its association with adjacent continental basins. The sampling was performed on board the research vessel R/V "AGOR Vidal Gormaz" between October 27th and November 26th 2009, where seven oceanographic stations were sampled with a box corer (box size 30x30x40 cm) (Fig. 1). From each box corer, 4 to 6 subsamples were taken with a 30 cm long PVC tube of 10 cm in diameter.

The samples were sealed with PCV lids to keep them humid and stored in a freezer until their physical and chemical analyses, at the Laboratorio de Oceanografía Química of Universidad Católica de la Santísima Concepción (UCSC). From each subsample, the upper 3 cm of the sediment were extracted and divided in four portions or quarters. One was used to analyze sediment texture and the second quarter was used to analyze total organic material (TOM). Texture was determined by means of the wet method and sieved according the Udden Wentworth grain-size scale (Fütterer, 2000). The TOM content was gravimetrically determined using the weight loss-on-ignition method (Mook & Hoskin, 1982) burning the dry sediment subsample in a furnace at a temperature of 450ºC.

The third subsample quarter was used for the metal analysis and the last one was kept as a reference sample. These subsamples were dried and crushed in an agate mortar until very fine dust. 0.5 g were extracted and subjected to acid digestion (HNO_3, HF, and $HClO_4$), which was carried out in covered Teflon cups at 70ºC until the samples were dry. The residue was dissolved in 10 mL of HCl Suprapur® (Merck) and gauged to 25 mL using Milli-Q (EMD Millipore). Following this, 50 µL of the acid fraction were analyzed using thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) in a GBC 902 atomic absorption spectrophotometer (González *et al.*, 2004). For metal determinations, MESS-3 Certified Reference Materials were used.

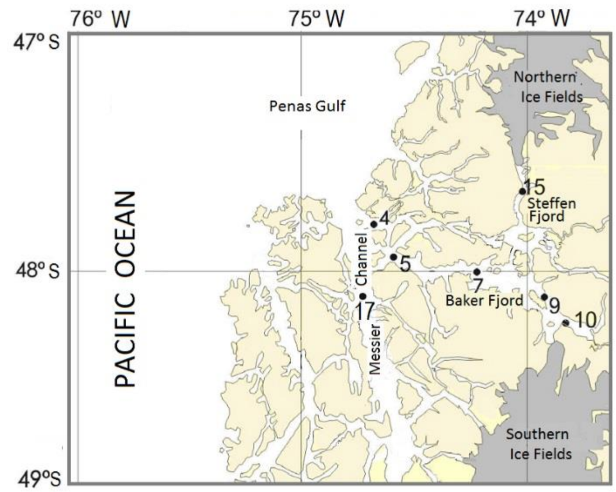

Figure 1. Position of sampling sites used within the area of study.

Once the analytic data was obtained, the geoaccumulation index (Igeo) was computed according to Müller (1979):

$$Igeo = \log_2 (Cm/1.5\ Bn)$$

where: Cm = experimentally measured mean concentration; Bn = background superficial sediments, using the baseline value previously established by Ahumada (2006) for this central fjord region, *i.e.*, Ba = 649.7 µg g^{-1}; Cu = 18.0 µg g^{-1}; Pb = 27.6 µg g^{-1}; Sr =155.8 µg g^{-1}; and Zn = 102.5 µg g^{-1}.

The enrichment factor was calculated according to Chester (2003):

$$FE = (CExp\ m / CExp\ n) / (CBn\ m / CBn\ n)$$

where: CExp*m= experimentally measured concentration; CExp*n= experimentally measured concentration of the standardization element; CBn*m = base line (background) concentration of the metal; and CBn*n = background concentration of the standardization element.

The geoaccumulation index (Table 1) and enrichment factor (Table 2) were conceptually defined for the sake of interpretation.

The relation between metals and sample sites was analyzed through bilateral Pearson correlations ($P < 0.0001$). A dendrogram was used for the exploratory analysis of characteristic patterns of distribution, and a multivariate analysis was applied to group the sampling sites considering their metal concentrations and spatial dispersion.

Table 3 lists the characteristics of the collected sediments, and it is possible to observe that five of the sampling site had a depth of more than 300 m.

Table 1. Scale and concepts used for interpreting the values obtained by the geoaccumulation index (Igeo). Source: Modified from Ahumada (2006).

Igeo scale	Igeo interval	Concept
0	Igeo ≤ 0.0	Pristine or unaltered.
1	0.0 < Igeo ≤ 1.1	Uncontaminated or slightly altered.
2	1.1 < Igeo ≤ 2.1	Slightly or moderately contaminated.
3	2.1 < Igeo ≤ 3.1	Moderately to highly contaminated.
4	3.1 < Igeo ≤ 4.1	Highly to extremely contaminated.
5	4.1 < Igeo ≤ 5.0	Extremely contaminated.
6	Igeo > 5.0	Requires remediation studies.

Table 2. Scale and concepts used for interpreting total values of metal concentration obtain through the application of the enrichment factor (EF). (Modified from Lawson & Winchester, 1979).

Intervals of EF	Source or origin of metal
0.0 < EF ≤ 1.5	Product of erosion from parent rock.
1.5 < EF ≤ 3.0	Enriched through sedimentary processes: soft sediment, organic material, inorganic precipitates.
3.0 < EF ≤ 6.2	Enriched from external sources.
EF > 6.2	Contamination through human activities.

Table 3. Grain-size of sediments (*i.e.*, texture) determined by the Udden Wentworth (U-W) scale, including soil moisture (SM) and total organic material (TOM).

Site	Depth (m)	1.00-0.50 mm (%)	0.51-0.25 mm (%)	0.26-0.12 mm (%)	0.13-0.06 mm (%)	< 0.07 mm (%)	Texture (U-W)	Color	SM (%)	TOM (%)
4	550	3.20	1.63	4.50	11.72	74.82	VFS-Sil	Grey	---	4.9
5	505	0.02	0.03	0.07	0.90	98.32	Sil-Cla	Grey-Brown	43.21	5.6
7	706	0.07	1.45	0.67	0.36	97.40	Sil-Cla	Grey-Brown	50.80	5.1
9	401	0.05	2.17	1.04	0.49	96.26	Sil-Cla	Grey-Brown	45.65	3.5
10	278	0.12	1.07	9.82	20.57	67.45	VFS-Cla	Dark Grey	35.09	2.7
15	108	0.00	0.00	0.00	0.00	100.00	Sil-Cla	Grey-Brown	37.26	2.6
17	938	0.00	0.00	0.00	0.00	100.00	Sil-Cla	Grey-Green	38.50	3.7

The collected sediment was predominated by grey silt-clayed sediment (>95%). Two sites (4 and 10) were an exception to this tendency, with presence of coarse, fine and very fine sand (> 25%). TOM content fluctuated between 2.6 and 5.6, with higher values towards the oceanic zone. The color of the sediment varied from clear grey to a clear grey/brown and until a dark grey (Table 3).

The metals analytical results were averaged and shown in Table 4. Relative abundance metals values, were the same for all sampled fjords and sites, with the following order: Ba > Sr > Zn > Pb > Cu > Cd. The exception to this was found for Steffen Fjord, where Sr was found in greater concentration than Ba.

Table 5 shows the co-variation of the metal concentrations, which was calculated through the Pearson correlation coefficient (r). Zn presented a significant positive correlation with Ba, Cu, and Pb, and a significant negative correlation with Sr ($P < 0.0001$). Moreover, a positive correlation was observed between Cu and Pb ($P < 0.0001$). Concentrations of Sr and Cd were dominant at inland sites, suggesting a more continental origin, whereas Ba and Zn were dominant at sampling sites with coastal influence.

Patterns of distribution and abundance of metal contents in sediments were examined through cluster analysis, with the aim of establishing the sources of origin and the compositions associated with the areas of influence conditions. The results estimated considering three Euclidean distances (Fig. 2) allowed us to distinguish three basins. The head of the Steffen Fjord basin which is influenced by the Steffen Glacier (site 15), which originates from the Northern Patagonian Ice Field; the mouth of the Baker Fjord which correspond

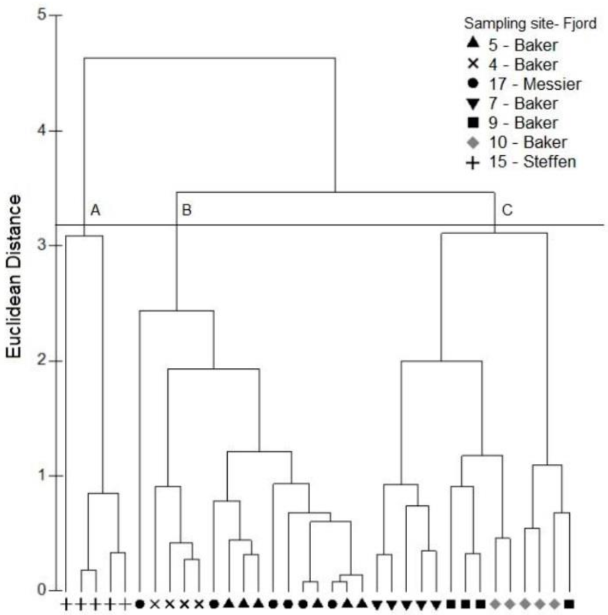

Figure 2. Dendrogram of sampling sites from the Baker area, establishing relations of similarity where A) head of Steffen Fjord, B) mouth of Baker Fjord, and C) head of the Baker Fjord.

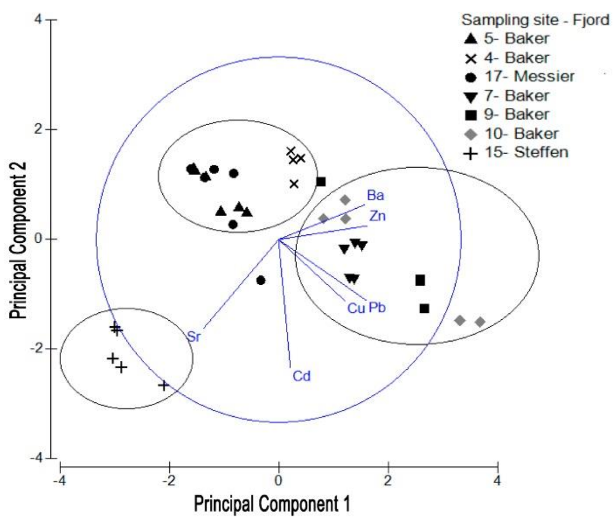

Figure 3. Spatial grouping pattern for the metal contents of the Baker area.

to a confluence zone of estuarine and marine waters (sites 4, 5, and 17); and the head of the Baker Fjord influenced by the Pascua River fresh water drainage (sites 6, 9, 10).

In order to confirm the patterns inferred through the cluster analysis, a new classification analysis was performed (Fig. 3).

This analysis confirmed the previous observations and defined the same spatial groups. (*i.e.*, sites 15 (Steffen), 4 (Baker), and 10 (Baker), located towards

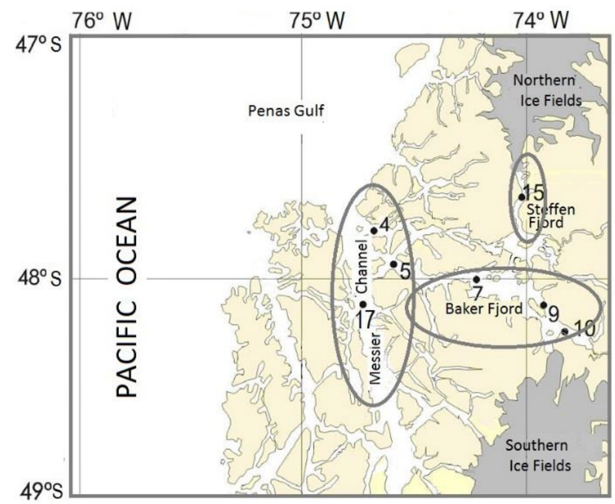

Figure 4. Grouping pattern of sampling sites according to sediment analysis of metal content and correlations.

the extreme boundary of the studied area, while sites 9 (Baker) and 7 (Baker) were close to the influence of site 10, and sites 5 (Baker) and 17 (Messier) were under the influence of site 4 (Baker). These results reflect the coastal influence that extends towards the Messier Fjord (site 17). Site 15 showed the greatest distance and was influenced by the Steffen Glacier, which is part of the Northern Patagonian Ice Fields, is active, and is in retreat. Site 10 and those associated with it were influenced by the Pascua River.

The segregation established by the distribution patterns of the metals, as corroborated by the performed statistical tests and the geographic grouping of sampling sites (Fig. 4), would allow for making associations between distribution and local processes.

The computation of the Igeo index of the studied metals using the Ahumada´s (2006) base line values, give results less than 0, which corresponds to natural concentrations found in unaltered areas (Table 6). The calculated value for Sr (Igeo = 1.71) was obtained from the Steffen Fjord and is an exception to the pattern observed for other sites. This would indicate that the accumulation of fine sediments is due to the Steffen Glacier (Table 4).

The calculated EF values (Table 7) showed values less than 1.5. Those EF vales would confirm that metal concentrations in the sediments are originated from metals released from the parent rock.

When comparing the obtained average concentration values (Table 4) with averages from existing literature (Table 8), it appears that values for Zn could be associated with averages for basalts and shale (Libes, 1992). In turn, Cu and Pb content appear close to contents from granite, basalt, and shale, while, the content of Cd would be closest to shale due to its low concentration and high variance.

Table 4. Averaged concentrations of metals in fjord´s sediments (Unit ug g^{-1}, dw).

Fjord	Site	Ba	Sr	Zn	Pb	Cu	Cd
Baker	4	669.5	112.5	89.3	23.5	16.5	0.2
Baker	5	501.0	300.0	87.2	17.4	14.0	0.2
Baker	7	627.6	213.4	106.2	31.4	25.2	0.3
Baker	9	657.5	197.0	125.0	33.5	27.3	0.4
Baker	10	584.0	215.4	136.4	32.2	29.6	0.3
Steffen	15	321.0	764.0	62.8	20.4	19.6	0.4
Messier	17	501.0	300.0	89.8	17.4	15.0	0.2

Table 5. Bivariate correlations (r) of metal content from the Baker Fjord. ***$P < 0.0001$, **$P < 0.001$, *$P < 0.01$.

Metal	Coeff./Sig.	Zn	Ba	Cu	Sr	Pb	Cd
Zn	r	1.000	0.627***	0.648***	-0.675***	0.718***	-0.069
	P		0.000	0.000	0.000	0.000	0.694
Ba	r		1.000	0.290	-0.870***	0.694***	0.058
	P			0.090	0.000	0.000	0.739
Cu	r			1.000	-0.151	0.685***	0.187
	P				0.387	0.000	0.282
Sr	r				1.000	-0.417**	0.338**
	P					0.013	0.047
Pb	r					1.000	0.482**
	P						0.003
Cd	r						1.000
	P						

Table 6. Geoaccumulation index (Igeo) values calculated from averaged data of each sampling site.

Fjord/channel	Site	Igeo Zn	Igeo Ba	Igeo Cu	Igeo Sr	Igeo Pb	Igeo Cd
Baker (n = 6)	5	-0.81	-0.96	-0.90	0.36	-1.20	-0.75
Baker (n = 5)	7	-0.53	-0.64	-0.08	-1.13	-0.38	-0.25
Baker (n = 4)	9	-0.29	-0.56	-0.04	-0.28	-0.30	-0.21
Baker (n = 5)	10	-0.17	-0.74	-0.15	-0.12	-0.36	-0.43
Messier (n = 6)	17	-0.77	-0.96	-0.79	0.36	-1.23	-0.88
Steffen (n = 5)	15	-1.28	-1.50	-0.42	1.71	-1.00	0.12

Table 7. Calculated values for the enrichment factor (EF).

Fjord/channel	Site	FE Zn	FE Ba	FE Cu	FE Sr	FE Pb	FE Cd
Baker (n = 6)	5	1.10	0.96	0.52	2.40	0.81	1.10
Baker (n = 5)	7	0.73	0.68	0.91	0.96	0.94	0.84
Baker (n = 4)	9	0.79	0.66	0.99	0.80	0.79	0.84
Baker (n = 5)	10	0.80	0.54	1.06	0.83	0.70	0.67
Messier (n = 6)	17	1.01	0.89	0.56	2.20	0.74	0.94
Steffen (n = 5)	15	0.55	0.44	0.72	4.39	0.67	1.50

The observed enrichment (*i.e.*, site 15, Steffen Fjord) would be due to the dynamic conditions and influences of specific zones (Glacial silt, see Table 3). Müller (1979) suggested increases up to 50% over the baseline for unaltered values (*i.e.*, the calculation algorithm for Igeo). Using this, it is possible to postu-

Table 8. Concentration values (dw µg g^{-1}), for comparative purposes, of metals reported in the existing literature for different marine localities. (1) Chester, 2003; (2, 3) Libes, 1992; (4*) Ahumada, *et al.* (2008); (4**) Silva, *et al.* (2009); (5) Ahumada *et al.* (2008); (6) This study; (7) Loring & Asmund (1996); (8 y 9) Prego & Cobelo-García, 2003.

Metal	Rock	Basalt	Granite	North Patagonia Fjords	Central Patagonia Fjords	Central Patagonia This study	East Greenland	Rias Gallegas	Unpolluted sediment
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Ba	445	840	330	435,7 *	649.7	607.9	s/d	s/d	s/d
Sr	278	100	470	260,2 *	155.8	207.7	s/d	s/d	s/d
Zn	127	s/d	s/d	60.1 **	102.5	108.8	89.0	100	20-100
Cu	32	10	90	36.6 **	18.0	22.5	46.0	14	5-25
Pb	16	s/d	s/d	9.3 **	27.6	27.6	19.0	45	5-25
Cd	0.2	s/d	s/d	0.18 **	0.27	0.3	0.11	0.15	0.01-0.2

late that the present study area presented concentration values corresponding to the accumulation of glacier erosion and natural lixiviation of the rocks that form the geological landscape. The relative abundance of metals according to geological zone was found to be Ba > Sr > Zn > Cu > Pb > Cd, with concentrations of Ba = 552 µg g^{-1}; Sr = 300 µg g^{-1}; Zn = 100 µg g^{-1}; Cu = 22 µg g^{-1}; Pb = 25 µg g^{-1}; and Cd = 0.3 µg g^{-1} (Table 4). These values concur with the abundance and distributions patterns reported by Ahumada & Contreras (1999) and Silva *et al.* (2009) for the northern Patagonian fjords an compared with references values (Table 8).

The Baker study area was characterized by relatively homogeneous concentrations and with a variability derived from local specific processes, as determined through geological composition, and from processes related to glacier erosion, natural lixiviation, fluvial influences, and from advection derived from estuarial circulation.

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