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Research Article

Dissolved trace metals in the water column of Reloncaví Fjord, Chile

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ABSTRACT. We analyzed the concentration of dissolved trace metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb) in the water column of Reloncaví Fjord. Sampling was performed during the CIMAR 12 Fiordos cruise in 2006. A total of 36 passive samplers or DGTs (diffusion gradient in thin films) were anchored at four stations along the longitudinal axis of the fjord. The DGTs were deployed at three depths per station and left there for 48 h. The metal contents on each thin film were analyzed using inductively coupled plasma atomic emission spectroscopy. Concentrations were highest in the surface layer at the head of the estuary, which is directly influenced by Petrohué River. Characteristic sequences of the studied metals were defined in the area with the greatest continental influence ($Z_{(5-25\text{ m})} = \text{Cu} > \text{Mn} > \text{Fe} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd} > \text{Co}$) and in the area with a marine or coastal influence ($Z_{(5-25\text{ m})} = \text{Fe} > \text{Cu} > \text{Mn} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd} > \text{Co}$). A similar metal sequence was found in the deepest layer: $Z_{(40\text{ m})} = \text{Fe} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Cr} > \text{Co}$. The passive sampling technique using DGTs to determine dissolved trace metals in the sea water provided robust information on the concentrations of the ten metals analyzed.

Keywords: dissolved metals, passive samplers, fjords, southern Chile.

Metales trazas disueltos en la columna de agua en el fiordo Reloncaví, Chile

RESUMEN. Se analiza la concentración de metales trazas disueltos (Cd, Co, Cr, Cu, Fe, Mn, Ni y Pb), en la columna de agua del fiordo Reloncaví. El muestreo se realizó durante la campaña CIMAR 12 Fiordos, 2006. Para ello se fondeó en cuatro estaciones y en tres profundidades, un total de 36 muestreadores pasivos o DGT (láminas de gradiente de difusión) a lo largo del eje longitudinal del fiordo, durante 48 h. El contenido de metales en cada lámina fue analizado mediante espectroscopía de emisión atómica con acoplamiento inductivo de plasma. Las mayores concentraciones se observaron en la superficie de la columna de agua, en la cabeza del estuario, directamente influenciada por el río Petrohué. Se definió para el área una secuencia de los metales estudiados característica, para la zona de mayor influencia continental: $Z_{(5-25\text{ m})} = \text{Cu} > \text{Mn} > \text{Fe} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd} > \text{Co}$ y para la zona de influencia marina o costera: $Z_{(5-25\text{ m})} = \text{Fe} > \text{Cu} > \text{Mn} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd} > \text{Co}$, observándose una secuencia semejante para los metales analizados en la capa de mayor profundidad: $Z_{(40\text{ m})} = \text{Fe} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Cr} > \text{Co}$. La técnica de muestreo pasiva, con DGTs, para la determinación de metales traza disueltos en agua de mar, permitió obtener información robusta de las concentraciones de los diez metales analizados.

Palabras clave: metales disueltos, muestreadores pasivos, fiordos, sur de Chile.

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INTRODUCTION

Baselines of metals are established to determine the natural concentrations and ranges of variations for these elements or compounds, in order to elucidate any changes that may be produced and to identify

them as natural enrichment or pollution (Regnier & Wollast, 1993; Salamanca & Jara, 2003; Navarro *et al.*, 2006). Trace metals include a highly toxic group that requires monitoring. These metals are most easily absorbed and bioaccumulated by living organisms when the metals are in their dissolved (ionic) form.

Sea water contains low concentrations ($\mu\text{g L}^{-1}$ or ng L^{-1}) of most metals in solution. Their solubility depends on the solvent characteristics and the solubility constant for each element, which determines its proportionality and abundance. These can be studied both in the water column and in interstitial waters (Davison *et al.*, 1991, 1994, 1997, 2000; Zhang & Davison, 1995; Fones *et al.*, 1998; Pizarro *et al.*, 2001).

Metal concentration in sea water can be modified regionally through volcanic activity, meteorization and/or erosion of the detritus phases of the rocky basement, and fluvial contribution (Humbord *et al.*, 1997). Although rivers transport small amounts of dissolved metals, these can alter the natural proportions in local sea water by dilution or enrichment of some major and minor cations (Ca, Na, B, Mg, Ba, etc.) (Libes, 2009).

The variability of metal concentration in water is highly uncertain, due to the fact that samples are obtained through instantaneous sampling. At present, a wide gamut of continuous recording systems is available for physical, biological, and chemical measurements. However, the study of the chemistry of dissolved metals is highly complex, involving difficulties of sampling (*i.e.*, obtaining, transporting, storing, and pre-treating the samples), low concentrations (near the detection limit of the analytical equipment) of dissolved ions in this environmental matrix, and the risk of contamination. Every stage of such research offers the potential for sample contamination and the possibility of altering the results of the analytes under study (González *et al.*, 2004).

The fjords of southern Chile are highly dynamic systems, whether due to their dimensions, morphology, tidal activity, and/or important freshwater contributions from the continent. The input of freshwater stratifies the water column, creating a low salinity surface layer and resulting in the dynamics of estuarine behavior (Silva *et al.*, 1998; Dávila *et al.*, 2002; Sievers & Silva, 2008). A fast-moving surface layer moves out of the basin and a slower, deep layer moves inward to the head (Salinas & Hormazábal, 2004; Cáceres & Valle-Levinson, 2004; Valle-Levinson *et al.*, 2007). This generates changes in the physical and chemical variables of the water column (Sievers, 2008; Silva, 2008), particularly organic matter contents, temperature, pH, Eh, and/or ionic strength, amongst others.

Dissolved trace metal information for the Chilean coastal waters has been scarcely reported on the scientific literature, and only for few metals (Jara & Salamanca, 2003; Valdés *et al.*, 2006; Ahumada *et al.*, 2008). The first information on dissolved metal

contents in the fjords of southern Chile was obtained in 1995, with the beginning of the CIMAR Fjords Program. The analytic difficulties did not allow to make the analyses in all cruises to the fjords areas. The present work analyzed the dissolved fraction of eight elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb), determining their vertical distribution and variability along the Reloncaví Fjord water column. A passive sampling technique was used in which devices with diffusion gradients in thin film (DGT) were anchored at different depths in the water column for a known period of time (48 h) in order to produce the *in situ* pre-concentration of the metal ions.

Study Area

Reloncaví Fjord is located at $41^{\circ}38'22''\text{S}$, $72^{\circ}22'40''\text{W}$, and has a west-east orientation (Fig. 1). This fjord averages 56 km in length and 3 km in width, with a water surface area of $\sim 170 \text{ km}^2$. The first third of the estuary (nearest to the head) is 20 to 100 m deep, dropping rapidly to 150 m in the second third and 400 m in the last third; the depth at the mouth is $\sim 450 \text{ m}$. The interior tides fluctuate between 6 and 7 m at syzygies tides and are as much as $\sim 1 \text{ m}$ lower during quadrature (León, 2005; Valle-Levinson *et al.*, 2007). Local winds blow from the south (southeast and southwest) in spring and summer and from the north in autumn and winter (Molinet *et al.*, 2003).

The fjord has three important tributaries – the Petrohué River at the head ($Q = 278 \text{ m}^3 \text{ s}^{-1}$) the Cochamó river ($Q = 20 \text{ m}^3 \text{ s}^{-1}$) and Puelo river ($Q = 670 \text{ m}^3 \text{ s}^{-1}$) in the middle – as well as other, smaller tributaries (Anuario Estadístico de Chile, 2007) (Fig. 1). Sediment grain size is mostly silt-mud (63%) and clay (37%) at the head, silt in the central part, and silt and fine sand with a high percentage of fine sand (48%) near the mouth. Organic matter contents in the fjord fluctuate between 5.1 and 6.9% (Pineda, 2009; Silva *et al.*, 2009). Important salmon and mussel farming activities are developed along the fjord coastline, and mollusks are also harvested from natural banks.

MATERIALS AND METHODS

Sampling was performed during the oceanographic CIMAR 12 Fjords cruise in October 2006, on board the “AGOR Vidal Gormaz” of the Chilean Navy. The experimental design of sampling considered four stations and 36 passive samplers or DGTs (diffusion gradient in thin films) (Davison, 2000; Pizarro *et al.*, 2001; Richir *et al.*, 2011). The four stations were located along the longitudinal axis of the fjord, from its head to its mouth (Fig. 1). For this, we prepared

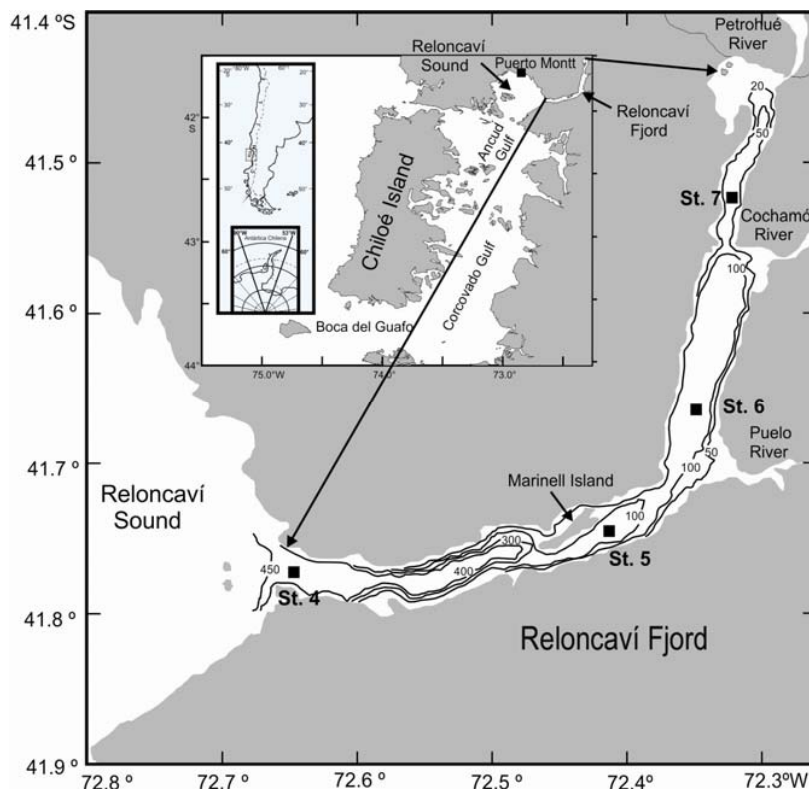


Figure 1. Geographic location of the Reloncaví Fjord and positions of the DGT anchoring stations during the CIMAR 12 Fjords cruise in October 2006.

Figura 1. Ubicación geográfica del Estuario Reloncaví y posicionamiento de las estaciones de anclaje de los DGT, durante el crucero CIMAR 12 Fiordos en octubre 2006.

and dropped anchor lines having a dead weight at the bottom, a subsurface buoy, and a surface buoy (Fig. 2a). Three unit of DGTs were inserted in a plate (Fig. 2b), and then three plates were located along the anchor line at three different sampling depths i.e., surface (5-10 m), mid-water (25-35 m), and deep water (40-50 m).

The deployment and recovery operations were done according to Neshyba & Fonseca (1981), and a Zodiac boat was used for anchoring the four lines between 9 and 11 October 2006. The DGTs were left in place for 48 h and reference data of salinity and temperature were obtained with a CTD, at each station during the anchoring and when DGTs were recovered (Madrid & Zayas, 2007). CTD data was used in the computation of metal concentrations.

The anchoring at station 4 was lost due to bad weather conditions. Only three stations were completed successfully, stations 5, 6 and 7. Station 7 covered the first fourth of the fjord length at its head; station 6 covered the second fourth (the Cochamó and Puelo rivers empty into this section) and station 5 covered the third fourth of the fjord length.

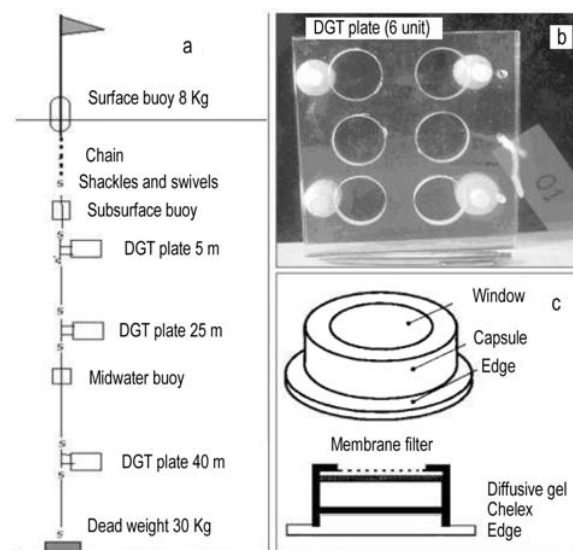


Figure 2. a) Diagram of DGT set-up and anchoring, b) plate detail, c) DGT capsule.

Figure 2. a) Diagrama de anclaje de los DGTs, b) detalle de una placa, c) cápsula de un DGT.

Each plate contained three thin sheets or DGTs, which were considered to be replicates per depth (Fig. 2b). The DGTs were recovered, removed (Fig. 2c), washed with MilliQ water, and stored individually in labeled Ziploc® bags at 4°C until their analysis. The analytical determination of the 8 metals in the sea water, *i.e.*, Fe, Mn, Cd, Co, Cr, Cu, Ni, Pb, was done using atomic emission spectroscopy with inductively coupled plasma (AES-ICP) in clean laboratories of the University of Portsmouth (UK).

These data were tabulated, and the statistical software package Statistica version 6.0 (StatSoft. Inc., 2001) was used for their statistical description.

RESULTS

Table 1 shows the results of the average concentration of the metals in solution measured at three of the sampling stations. The study shows that the surface layer of the water column at the head of the estuary (St. 7) was directly influenced by contributions from the Petrohué River, with a temperature of 10°C and salinity < 20 psu. The water column showed strong vertical stratification and, below 20 m depth, temperatures of 12°C and higher salinity (28 psu) than in the surface layer were found. In the central part of the fjord, despite contributions from the Cochamó (St. 7) and Puelo (St. 6) rivers, temperatures were near 12°C at the surface and 10.5°C at 40 m. Salinity was 28 psu, at station 7, increasing along a gradient with depth until reaching 32 psu at surface salinity near station 5.

Data showed that most of the metals studied (Cd, Co, Cr, Cu, Mn, Ni, Pb) were higher in the surface layer (5 m) at the head of the fjord (St. 7), which is influenced by the Petrohué River. The only exception to these findings was Fe. The concentration of metals at the head of the estuary was ~5 times greater than the rest of metals, showing a decreasing gradient towards the mouth.

The Cochamó and Puelo rivers enter the fjord around St. 7 and 6, respectively, but did not have the same effect on metal concentrations. Instead, these rivers contributed to dilute rather than increase metal concentrations. This suggests that the behavior of the metals is different along the longitudinal axis of the fjord. Likewise, metal concentrations in the intermediate water layer (25 and 35 m depth), which had intermediate salinity values, were lower than in the upper and deeper layers, as found at all three stations (Table 1).

DISCUSSION

The main forcing factors in the Reloncaví Fjord are freshwater contributions (Petrohué, Puelo, Cochamó rivers), tidal differences (6-7 m), and strong local winds. These factors result in high variability within the fjord in terms of the spatial and temporal distribution of physical, chemical, and biological properties of its waters (Silva *et al.*, 1998; Dávila *et al.*, 2002; Salinas & Hormazábal, 2004; Cáceres & Valle-Levinson, 2004; Valle-Levinson *et al.*, 2007). Given this context, it was decided to use a passive technique that would allow to obtain an *in situ* concentration of the dissolved metals over a 48 h time period. The disadvantage of this system is the high probability of losing the anchor lines, as it occurred at the station four at the mouth of the estuary.

In terms of absolute abundance, Co, Cr, and Cd showed the lowest concentrations in all the stations sampled at the estuary. The concentrations of Cu and Mn were higher than other metals in the surface layer at the head of the fjord, showing a characteristic abundance sequence pattern. The concentration of Fe increased towards the fjord mouth and as well as in depth.

The temperature and salinity were used to identify the thickness of the stratified layer in the fjord (Table 1). The upper 25 m correspond to a layer of estuarine influence with salinities between 22-30 psu. The deeper layer corresponds to a layer of marine influence, with salinity near 30 psu and reaching 32 psu at the mouth of the fjord (St. 4). This vertical salinity gradient was observed in all the stations and a horizontal gradient was observed from the head of the fjord to its mouth. Given the relative abundance of metals and the stratification of the fjord, we defined areas of concentration distribution.

The metal concentrations in the deep layer were lower than in the surface one, but higher than in the intermediate layer, with the exception of Fe, which was first in abundance at 40 m depth. This concentration distribution, allowed to identify two groups according to their relative abundance:

1. The area of continental influence covered the fjord's first quarter (St. 7). The sequence at the surface (5 and 25 m) was $Z_{(5-25\text{ m})} = \text{Cu} > \text{Mn} > \text{Fe} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd} > \text{Co}$ and at depth (40 m) was $Z_{(40\text{ m})} = \text{Fe} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Cr} > \text{Co}$.
2. The area of marine influence included two quarters at the center of the estuary (St. 5 and 6). The sequence at the surface (5 and 25 m) was $Z_{(5-25\text{ m})} = \text{Fe} > \text{Cu} > \text{Mn} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd} > \text{Co}$ and at depth (40 m) was $Z_{(40\text{ m})} = \text{Fe} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Cr} > \text{Co}$.

Table 1. Average of salinity and of dissolved metals concentrations at the different depths along the longitudinal axis of the Reloncaví Fjord during the CIMAR 12 Fiordos cruise in October 2006.**Tabla 1.** Promedios de salinidad, temperatura y concentración de metales disueltos en diferentes profundidades a lo largo del eje longitudinal del fiordo Reloncaví, durante el crucero CIMAR 12 Fiordos, octubre 2006.

Coastal Stations	Depth (m)	Salinity (psu)	Temperature (°C)	Cd ($\mu\text{g L}^{-1}$)	Co ($\mu\text{g L}^{-1}$)	Cr ($\mu\text{g L}^{-1}$)	Cu ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)	Ni ($\mu\text{g L}^{-1}$)	Pb ($\mu\text{g L}^{-1}$)
St. 7	5	24.124	12.15	0.57	0.07	0.83	28.07	2.58	6.32	2.56	2.19
	25	32.183	10.95	0.03	0.01	0.03	0.41	0.18	1.47	0.36	0.10
	40	32.196	10.89	0.17	0.02	0.10	4.00	14.04	5.49	0.49	0.80
St. 6	15	22.478	12.05	0.07	0.03	0.51	3.48	29.45	1.66	1.84	0.67
	35	32.185	11.00	0.07	0.02	0.06	0.96	6.28	1.80	1.19	0.21
	50	32.203	10.82	0.41	0.05	0.37	7.49	29.93	9.13	1.85	2.09
St. 5	5	27.632	12.35	0.09	0.04	0.26	3.24	16.34	1.88	1.52	0.55
	25	32.184	11.25	0.04	0.02	0.08	1.15	7.45	2.14	0.85	0.23
	40	32.265	10.80	0.17	0.05	0.23	2.59	31.46	2.43	1.31	0.68

The sequences pattern of metals abundances in the deep layer (40 m) were similar in both of these areas (continental and marine influence). Dissolved Fe was the most abundant element for the area, in which salinity was higher and velocity lower in this deep layer, which circulates towards the head of the estuary (Salinas & Hormazábal, 2004; Cáceres & Valle-Levinson, 2004).

Table 2 shows the whole column average data for the continental or estuarine area and for the marine influence or coastal area (the fjord empties into the Interior Sea of Chiloé). The greater concentrations of Cu in the area of continental influence (less salty) could be associated with the formation processes of hydroxides colloids or soluble complexes in this area, which has higher pH (differences of pH from freshwater to seawater).

The concentrations of Ni and Cu in the sediments indicate a risk zone at the head of the fjord (St. 7), unlike the situation observed in the water column.

Finally, for comparative purposes and reference, it is presented the concentration values for dissolved metals reported by other authors at different sites (Table 3). The values of Cd, Co, Cr, Mn, Ni, and Pb found in the Reloncaví Fjord were near to or lower than those found in the other sites studied. Nonetheless, the concentrations of Cu, were greater in the surface layer at the stations near the head of the fjord, and Fe was more concentrated towards the mouth and in the deeper parts of the fjord. The marked differences in the concentrations of Cu suggest an additional input of these metals from the continent.

Table 2. Average concentration of dissolved metals ($\mu\text{g L}^{-1}$) that characterize the continental influence area (CI) and the marine influence area (MI) in the Reloncaví Fjord during the CIMAR 12 Fiordos cruise in October 2006. SD: standard deviation, CV: coefficient of variation**Tabla 2.** Promedio de concentración de metales disueltos ($\mu\text{g L}^{-1}$) que caracterizan el área de influencia continental (CI) y el área de influencia marina (MI) en el fiordo Reloncaví, durante el crucero CIMAR 12 Fiordos, octubre 2006. SD: desviación estándar, CV: coeficiente de variación.

Metals		Cd ($\mu\text{g L}^{-1}$)	Co ($\mu\text{g L}^{-1}$)	Cr ($\mu\text{g L}^{-1}$)	Cu ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)	Ni ($\mu\text{g L}^{-1}$)	Pb ($\mu\text{g L}^{-1}$)
Zone CI (Estuarine)	Mean	0.349	0.066	0.414	10.82	6.127	4.429	1.136	1.034
	SD	0.165	0.037	0.309	12.28	5.607	2.118	1.011	0.868
	CV	47.28	55.92	74.58	113.5	91.51	47.82	89.04	83.98
Zone MI (Coastal)	Mean	0.14	0.04	0.25	3.15	20.15	3.17	1.43	0.74
	SD	0.13	0.01	0.16	2.16	10.63	2.68	0.36	0.63
	CV	88.30	33.51	63.64	68.61	52.76	84.38	25.11	85.51

Table 3. Concentration of dissolved trace metals reported at different marine sites. nd: non detected.**Tabla 3.** Concentración de metales trazas disueltos, registrados en diferentes localidades marinas. nd: no detectado.

Trace metal	Concentration in seawater	References
Cd	nd-7.1 $\mu\text{g kg}^{-1}$	Beltrame <i>et al.</i> 2009
	0.01-010 $\mu\text{g L}^{-1}$	Hatje <i>et al.</i> 2003
	0.011-0.38 $\mu\text{g L}^{-1}$	Baeyens <i>et al.</i> 1998
Co	0.5 $\mu\text{g kg}^{-1}$	Libes 2009
	0.3-6.1 nM	Fang & Lin 2002
Cr	2.82-6.79 $\mu\text{g kg}^{-1}$	Vásquez <i>et al.</i> 1998
	nd-5.86 $\mu\text{g kg}^{-1}$	Botté <i>et al.</i> 2008
Cu	0.65-13.40 $\mu\text{g kg}^{-1}$	Vásquez <i>et al.</i> 1998
	0.25-3.2 $\mu\text{g L}^{-1}$	Baeyens <i>et al.</i> 1998
Fe	nd-3.49 $\mu\text{g kg}^{-1}$	Botté <i>et al.</i> 2008
Mn	1.03-53.04 $\mu\text{g kg}^{-1}$	Fang & Lin 2002
Ni	0.18-1.61 $\mu\text{g kg}^{-1}$	Hatje <i>et al.</i> 2003
Pb	0.013-3.29 $\mu\text{g kg}^{-1}$	Mendiguchía <i>et al.</i> 2007
	0.04-1.5 $\mu\text{g L}^{-1}$	Baeyens <i>et al.</i> 1998

CONCLUSIONS

The dissolved metal concentrations were high for Cu, Mn and Fe, and low for Co, Cr, and Cd. Moreover, the concentrations were the greatest in the surface layer of the water column and at the head of the fjord, a lower-density area due to the influence of the Petrohué River.

The dissolved metal abundances revealed a characteristic sequence for the area of continental influence ($Z_{(5-25\text{ m})} = \text{Cu} > \text{Mn} > \text{Fe} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd} > \text{Co}$) different from that of the area of marine or coastal influence ($Z_{(5-25\text{ m})} = \text{Fe} > \text{Cu} > \text{Mn} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd} > \text{Co}$). The two areas shared a similar sequence in the deep layer: $Z_{(40\text{ m})} = \text{Fe} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Cr} > \text{Co}$.

The use of DGTs devices for sampling and the AES-ICP analyses shown to be adequate; its results were not significantly different from those obtained by DPASV with HMDE. Thus, our data are consistent with the values that fluctuate according to the characteristics and dynamics of the sampling site.

The passive samplers (DGTs) allowed to determine dissolved trace metal contents in the water column in an area of high variability and to obtain robust information on the concentrations of the ten metals analyzed.

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