**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 deployed 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 (Z¹ = Cu > Mn > Fe > Ni > Pb > Cr > Cd > Co) and in the area with a marine or coastal influence (Z¹ = Fe > Cu > Mn > Ni > Pb > Cr > Cd > Co). A similar metal sequence was found in the deepest layer: Z¹ = Fe > Mn > Cu > Pb > Ni > Cd > Cr > Co. The passive sampling technique using DGTs to determine dissolved trace metals in the seawater provided robust information on the concentrations of the ten metals analyzed.

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

**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 (µg 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 (Humbold 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 analyses 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 Fiordos 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°38′22″S, 72°22′40″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 ~170 km². 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 ~450 m. The interior tides fluctuate between 6 and 7 m at syzygies tides and are as much as ~1 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 m³ s⁻¹) the Cochará River (Q = 20 m³ s⁻¹) and Puelo river (Q = 670 m³ 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 Fiordos 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