

5.3. Oxic-reducing conditions in the interstitial waters of the austral Chilean channels and fjords

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The development of a variety of economic activities along a coastline may increase the organic and nutrient loads entering the interior channels and fjords. The effects of deforestation, erosion, changes in land use from native forests to cultivable and livestock pasture lands, mining activities (Ahumada, 1998), liquid industrial wastes, and sewage from shoreline communities can alter the quality of a water body, its trophic or nutrient environment, and its habitats. Intensive aquaculture such as salmon farming in low-circulation channels and fjords may also reduce dissolved oxygen concentrations due to the proliferation of microalgae and the accumulation of organic matter in the seabed (Henderson *et al.*, 1997).

The Chilean channels and fjords are characterized by the presence of dissolved oxygen throughout the water column (Silva *et al.*, 1997). This contrasts with the anaerobic conditions found at the water/sediment interface and even in overlying waters of some fjords in the Northern Hemisphere such as Saanich Inlet in Canada (Presley *et al.*, 1972) and the Framvaren (Landing & Westerlund, 1988) and Nordåsvannet (Müller, 2002) fjords in Norway.

Silva *et al.* (1997) found minimum dissolved oxygen concentrations below 4 mL·L⁻¹ at depths exceeding 100 m in the Jacaf and Puyuguapi-Ventisquero channels, Boca del Guafo, the southern sector of Golfo Corcovado, and Canal Moraleda; in Canal Puyuguapi, the minimum was 1.5 mL·L⁻¹. These same authors indicated that the waters with low dissolved oxygen levels are remnants of the subsurface equatorial dissolved oxygen minimum that are advected into the interior channels from the adjacent oceanic zone.

The continuous oxygenation of the fjords suggests that autochthonous organic detritus from

the plankton biomass is broken down and oxidized in aerobic conditions, whereas the allochthonous land-based organic matter entering the channels and fjords is apparently refractory, being deposited in the sedimentary stratum. There are at least three lines of evidence supporting this hypothesis. First, Silva *et al.* (1997) recorded concentrations near 2.5 mL·L⁻¹ at the head of Fiordo Aysén, which implies that the more labile terrigenous organic matter was oxidized in the waters of Río Aysén before entering the estuarine zone. Secondly, a $\delta^{13}\text{C}$ analysis of the surface sediments from Bahía Aantilada (at the head of Fiordo Aysén) revealed that almost 90% of the organic content originated in terrestrial vegetation (Pinto & Bonert, 2005). Thirdly, the main lipid component of the sediment matrix at the head of Fiordo Aysén was a homologous series of aliphatic hydrocarbons with more than 23 carbons (Pinto & Bonert, 2005) representing biomarkers of leaf detritus from terrestrial plants (Kolattukudy, 1976).

Given the system's thermodynamic characteristics (Froelich *et al.*, 1979) and the high concentrations of sulfate in the seawater (28 mM), the process of organic matter degradation rapidly consumes the dissolved oxygen in the interstitial waters and the sulfate reduction process takes on a significant role when the organic carbon content deposited in coastal surface sediments is higher than 1.5%. However, the presence of manganese oxides and mainly colloidal iron oxides (iron oxyhydroxides) precedes, in terms of Gibbs free energy, the sulfate ion as a terminal electron acceptor (Froelich *et al.*, 1979; Canfield, 1989). These minerals, derived from terrestrial erosive processes, are transported by rivers to the coastal zone where they are reduced to Mn(II) and Fe(II) during bacterial dissimilative processes in suboxic/anoxic conditions (+50 to -50 mV redox potential) (Froelich *et al.*, 1979). Thus, the reduction of iron and manganese produces their

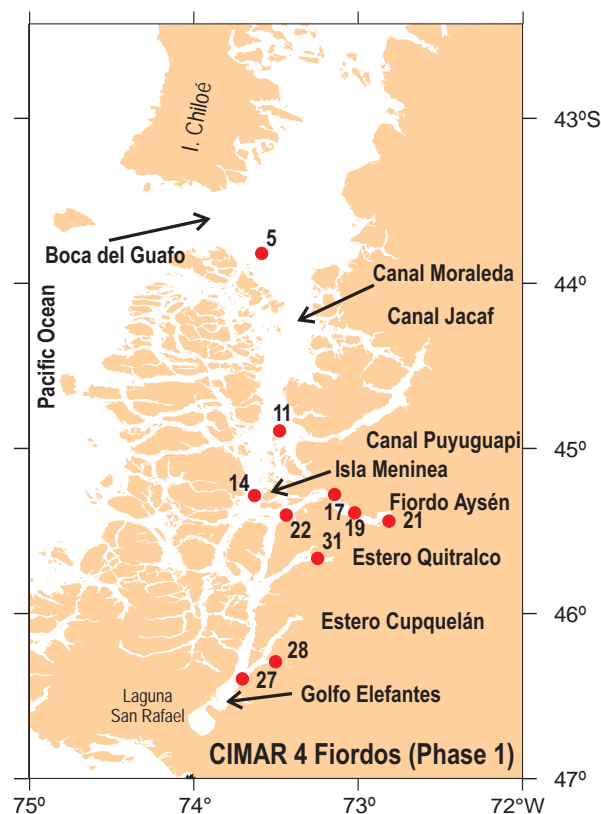


Figure 1: Geographic position of the stations used for sediment sampling to determine reduced iron and manganese in interstitial waters.

remobilization from the solid to the aqueous phase in the interstitial sediment water, resulting in subsurface maxima in coastal water Fe(II) and Mn(II) profiles (Pinto & Rivera, 2003).

During the CIMAR 4 Fjords cruise, the interstitial waters from diverse channels and fjords (Fig. 1) were sampled in order to determine Fe(II) and Mn(II) profiles produced by the degradation of organic matter in surface sediments. These profiles exhibited different patterns, showing the diversity of environments that can be found in the seabeds of interior channels and fjords. The highest concentrations of reduced iron were observed in Fiordo Aysén, with values higher than 1,500 μM in Bahía Acantilada (Pinto & Rivera, 2006). Not only were the concentrations high at this station, the position of the maximum was also observed at the water/sediment interface here, suggesting the absence of dissolved oxygen from the first centimeter of sediments. This indicates that the system's capability to oxidize organic matter in aerobic conditions is at a critical point.

Increased anthropogenic activity along the shoreline of Saguenay Fjord, Canada, seems to be causing similar results. Whereas the fjord's water column remains oxygenated, the reductive capacity of the sediments is such that the oxygen is totally used in the first millimeters of the sediment (Louchouart *et al.*, 1997). Mucci & Edenborn (1992) detected hydrogen sulfide (H_2S) in the interstitial waters near the water/sediment interface as a product of the anaerobic degradation of organic matter via sulfate reduction. An independent lignin analysis of these sediments (Louchouart *et al.*, 1997) demonstrated the presence of mainly gymnosperm (conifer) bark debris, which the authors associated with increased solid waste disposal from nearby cellulose plants.

Natural conditions and waterbody dynamics determine the magnitude and type of effect that an increased organic load could have on a water resource. At present, little information is available in this area and seasonal measurements are necessary in order to determine whether higher contributions of organic detritus to the bottom produce anoxia at the water/sediment interface, leading to permanent modifications in the benthic diversity.

A series of biological and physical processes and mechanisms such as bioturbation, bioirrigation, tidal currents, winds, and advective processes, as well as the quality of land-based organic matter generally appear to favor the aeration of the water column in the channel and fjord area (Rojas & Silva, 2003). Nonetheless, these characteristics can be transitory or permanently overridden at some sites. Interior water systems receive a significant contribution of freshwater and terrestrial organic matter that may vary seasonally, resulting in more variable carbon and nutrient flows than found in open coastal systems.

Fe(II) and Mn(II) profiles are reliable geochemical tools that are able to unequivocally delimit a redoxcline in the interstitial waters of recent sediments (Van Capellen & Wang, 1996). Iron and manganese cycles are tied to the sulfur cycle via sulfate reduction (Sorensen & Jorgensen, 1987), which is an important mechanism in the degradation of the organic matter in the sediments off the Chilean coast (Thamdrup & Canfield, 1996).

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