

3.2 Dissolved oxygen, pH, and nutrients in the austral Chilean channels and fjords

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Information on dissolved oxygen and nutrients in the water column of the austral Chilean channels and fjords prior to the beginning of the CIMAR Program in 1995 was limited. The first results for this area came from the Swedish expedition Lund University-Chile (1948-1949) carried out between Puerto Montt and Canal Moraleda (Brattström & Dahl, 1951) and the Canadian Expedition Hudson Chile 70 (March 1970), which covered most of the channels between Puerto Montt and Seno Almirantazgo (Pickard, 1971). Later, Vargas (1983) studied the area between Boca del Guafo and Canal Pulluche, whereas Sievers & Prado (1994) analyzed Fiordo Aysén during four seasonal cruises carried out in 1991 and 1992. Information on the Strait of Magellan and the Magdalena, Cockburn, Brecknock, Ballenero, Brazo Norte, and Beagle channels, was obtained by the foreign cruises onboard the OGS Explora (October-November 1989) and R/V Víctor Hensen (November 1994) and analyzed by Celio (1991), Panella et al. (1991), and Antezana (1999). The North American Piquero cruise (January-February 1969) provided results for the oceanic waters adjacent to Chile's austral fjord and channel sector (Silva, 1978; Silva & Neshyba, 1979/1980). Thus, until 1995, the channel and fjord areas, as well as their adjacent oceanic waters, were studied mainly by foreign cruises and a large number of channels and fjords were, in oceanographic terms, left unexplored.

The CIMAR Program provided a chemical characterization of the interior waters of this extensive geographic area by intensively measuring and sampling dissolved oxygen content, pH, phosphate, nitrate, and silicate in the water column and some adjacent rivers. This information was obtained from three zones: the northern zone, between Puerto Montt and Laguna San Rafael (CIMAR 1 Fiordos) (Silva *et al.*, 1997; Prado-Fiedler, 2000), the central

zone, between Golfo de Penas and Strait of Magellan (CIMAR 2 Fiordos) (Sievers *et al.*, 2002; Silva & Calvete, 2002), and the southern zone, between Strait of Magellan and Cape Horn (CIMAR 3 Fiordos) (Valdenegro & Silva, 2003) (Fig.1). The characteristics and vertical distribution of the dissolved oxygen content, pH, phosphate, nitrate, and silicate are described herein.

In general terms, the water column consists of two layers: a well-oxygenated (5-8 mL·L⁻¹; 90-130 % saturation) surface layer (30-50 m thick) with high pH (8.0-8.3) and a deep layer (75 m to the bottom) in which the dissolved oxygen, in most of the channels, decreases gradually to concentrations of 3-4 mL·L⁻¹ (40-50 % saturation) and pH values are low (7.4-7.7). A sharp vertical gradient occurs between these two layers, with dissolved oxygen and pH rapidly decreasing with depth, generating an oxycline and a pHcline of variable intensity.

Dissolved oxygen and pH are lowest in the deep parts of the channels and fjords that begin on or very close to the continental edge. In the northern zone, dissolved oxygen (< 4.0 mL·L⁻¹; < 60 % saturation) and pH (7.6) are lowest in the Comau, Quitralco, Cupquelán, Moraleda, Jacaf, and Puyuguapi channels, Seno Ventisquero, and Fiordo Aysén. In the central zone, low dissolved oxygen and pH are found in the Fallos, Baker, Troya, Steffen, and Estero Las Montañas channels, Seno Iceberg, and on both sides of the Angostura Inglesa. Because dissolved oxygen concentrations do not drop below 5.0 mL·L⁻¹ nor pH below 7.7 in the deep layer of any of the oceanic channels throughout the study area (except Canal Fallos) or in the continental channels and fjords located between Seno Unión (51° 10' S) and Cape Horn (56° S), these waters are considered to be well ventilated.

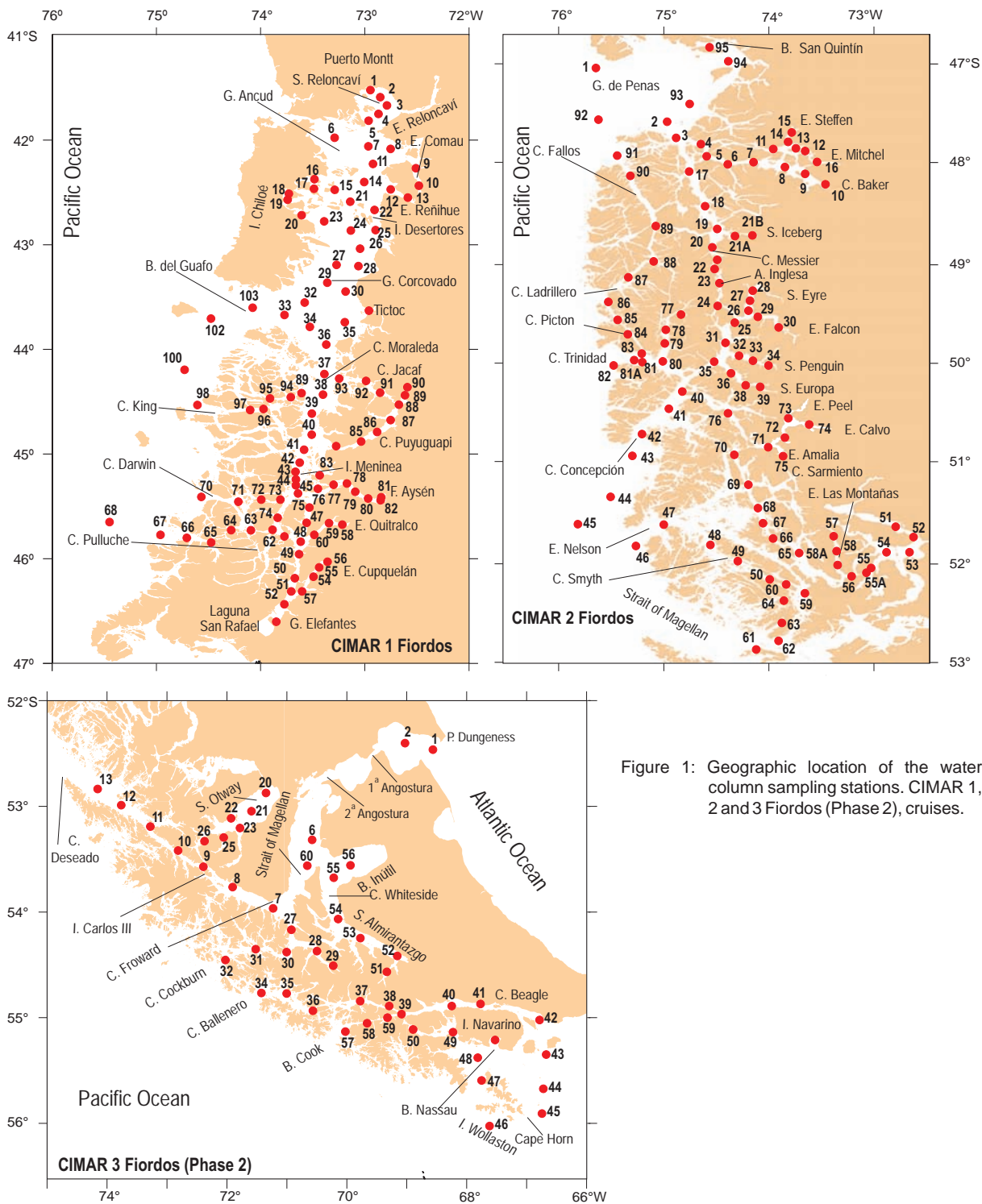


Figure 1: Geographic location of the water column sampling stations. CIMAR 1, 2 and 3 Fjords (Phase 2), cruises.

Of all the austral channels and fjords, the deep zone of Canal Puyuguapi is the least oxygenated and most acid, with dissolved oxygen around $2.0 \text{ mL}\cdot\text{L}^{-1}$ and pH around 7.4. Therefore, anoxic conditions are not found in the water column of any of Chile's austral channels or fjords.

In general, phosphate and nitrate present a two-layer vertical structure. The surface layer (30-50 m thick) has low nutrient concentrations (0-0.8 μM phosphate, 0-8 μM nitrate) and the deep layer (> 75 m) has high nutrient concentrations (1.2-2.4 μM phosphate, 12-24 μM nitrate). These two layers are separated by a sharp vertical gradient, in which phosphate and nitrate increase rapidly with depth, generating a phosphatecline or nitratecline of variable intensity.

Phosphate and nitrate concentrations are generally highest in the deep parts of most of the channels and fjords that begin at or very near the continental edge, and are associated with low dissolved oxygen and pH values. In the northern zone, high nutrient values (> 2.0 μM phosphate, >20 μM nitrate) are found in the Comau and Reñihue estuaries; Moraleda, Jacaf, and Puyuguapi channels; Seno Ventisquero; and Fiordo Aysén. In the central zone, in the channels Fallos, Baker, Troya, and Steffen; Seno Iceberg; and at both sides of the Angostura Inglesa. Of all the austral channels and fjords, phosphate (2.8 μM) and nitrate (24 μM) concentrations are highest in the deep part of Canal Puyuguapi, where they are associated with the area's lowest dissolved oxygen concentrations ($\sim 2.0 \text{ mL}\cdot\text{L}^{-1}$).

Information on ammonium, only available for the northern zone (Prado-Fiedler, 2000), reveals a three-layer structure. Ammonium concentrations are low (< 0.5 μM) in the surface layer (0 to 20-30 m) and high (0.5-2.5 μM) in the sub-surface layer (25-100 m); concentrations in the deep layer are low (< 0.2 μM) and, in many cases, below the detection limit. At times, the sub-surface maximum is not observed or is very weak, resulting in a quasi-homogeneous vertical structure.

The vertical structure of silicate resembles that of phosphate and nitrate, with low concentrations (0-8 μM) in the surface layer and high concentrations (8-24 μM) in the deep layer. These two layers are separated by a vertical gradient in which silicate increases rapidly with depth, generating a silicocline of variable intensity.

Nonetheless, a sizeable number of channels, fjords, sounds, and gulfs (Reloncaví, Ancud, Comau, Reñihue, Puyuguapi, Ventisquero, Aysén, Quitraco, Cupquelán, Moraleda, Baker, Mitchell, Steffen, Sarmiento) receive significant fresh water contributions from rivers or glaciers. In these cases, a thin surface layer (~ 2 -5 m) with high silicate concentrations (20-100 μM) is detected, giving rise to a three-layer structure. Below this high silicate surface layer there is a 2 to 5-m-thick layer with a silicate minimum (4-10 μM), a remnant of the oceanic surface minimum. Below this shallow minimum, silicate concentrations are again high in the deep layer.

An analysis of phosphate and nitrate sources indicates that these come mainly from the sea, since fresh waters from rivers, rain, and glacial melting are poor in these nutrients (0-1.2 μM phosphate, 0-2 μM nitrate). However, fresh waters from rivers are rich in silicate (40-150 μM) and make an important contribution to the surface layer.

In spite of the general two –and occasional three– layer structures (such as found for ammonium and silicate) described above, phosphate, nitrate, and silicate tend to fluctuate at depth and their increments toward the bottom are not always constant. These fluctuations depend on the action of physical forcings and biogeochemical processes in the water column. Physical forcings include advection of fresh waters from rivers, rain, or melting into marine waters with higher or lower nutrient concentrations, advection of low nutrient sea waters from the adjacent ocean, and turbulent mixing due to wind and tides. The biogeochemical processes include biological production and consumption by photosynthesis, respiration, organic matter decomposition (remineration), the dissolution of silicate shells, and clay regeneration, among others.

The physical forcings and biogeochemical processes that affect the vertical distribution of dissolved oxygen, pH, and nutrients can act independently or in combination (Table I).

These physical forcings and biogeochemical processes generate characteristic vertical structures in the water column. Silva *et al.* (1997) and Silva & Calvete (2002) grouped these structures, creating a typology that can be used to identify the presence of the respective forcings or

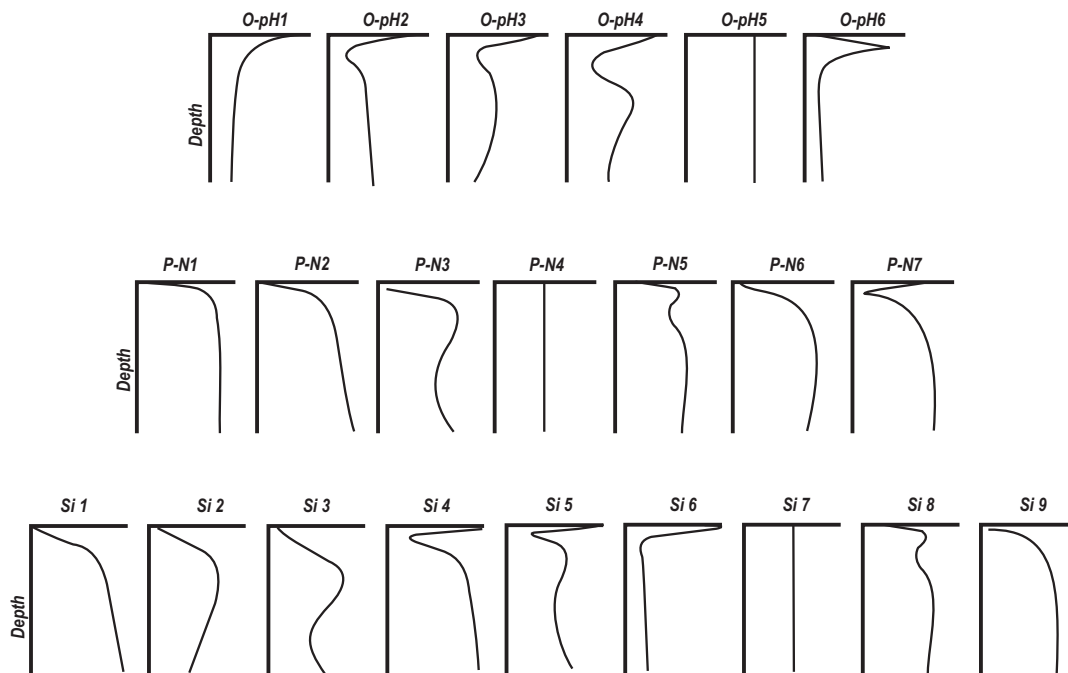


Figure 2: Diagram of the different types of vertical structures of dissolved oxygen and pH (O-pH), phosphate and nitrate (P-N), and silicate (Si) (adapted from Silva *et al.*, 1997 and Silva & Calvete, 2002).

processes by merely comparing a given station's vertical profile with a typical profile (Fig. 2).

Dissolved oxygen and pH generally present similar variations and are grouped in five structure types (O-pH1 to O-pH5); a sixth type is valid only for pH (pH6). In general, phosphate and nitrate are also similar. These nutrients are classified in six structure types (P-N1 to P-N6), with a seventh type that is only valid for phosphate (P-7). Silicate structures are grouped in nine types (Si1 to Si9). No structure types are established for ammonium, since information is not available for the entire channel and fjord area.

Ocean-atmosphere exchanges and photosynthetic processes result in high surface layer values for all the O-pH structure types. If limited to only physical forcings, surface dissolved

oxygen concentrations would be, in general, near saturation. Nevertheless, at some stations, concentrations are greater than $8 \text{ mL}\cdot\text{L}^{-1}$ for oxygen and over 8.0 pH. These values are attributed to greater photosynthetic activity, which increases the oxygen concentration and decreases carbonic anhydride, thus increasing the pH.

The decreased depth of the O-pH1 structure corresponds to organic matter decomposition that consumes dissolved oxygen and releases carbonic anhydride, thereby decreasing the pH. In the O-pH2 structure, the decreased depth is a response to organic matter decomposition combined with the advection of more oxygenated, more acid waters into the deep part of the channel, generating a higher subsurface minimum.

Table I. Summary of the principle physical forcings and biogeochemical processes that affect the vertical distribution of dissolved oxygen, pH, and nutrients in the austral channels and fjords (taken from Silva *et al.*, 1997).

Dissolved oxygen	pH	Phosphate – Nitrate	Silicate
O ₂ production and consumption by organisms.	CO ₂ production and consumption by organisms.	Biological consumption for the formation of organic matter.	Biological consumption for the production of exoskeletons.
Ocean-atmosphere gaseous O ₂ exchange.	Ocean-atmosphere gaseous CO ₂ exchange.	Advection of fresh water with low phosphate and nitrate concentrations.	Advection of fresh water with high silicate concentration.
Advection of sea water with higher or lower O ₂ concentration.	Advection of sea water with higher or lower pH.	Advection of sea water with higher or lower phosphate and nitrate concentrations .	Advection of sea water with higher or lower silicate concentration.
Vertical mixing produced by the wind.	Vertical mixing produced by the wind.	Vertical mixing produced by the wind.	Vertical mixing produced by the wind.
O ₂ consumption through organic matter remineralization.	CO ₂ production due to organic matter remineralization.	Phosphate and nitrate increase due to organic matter remineralization.	Dissolution of biogenic silicate shells.

The O-pH3 structure responds to the same forcings and processes as the previous structure but, in this case, the advection of more oxygenated and less acid waters occurs at an intermediate depth within the channel, generating a sub-surface minimum, a concave structure at intermediate depths, and another deep minimum. The O-pH4 structure is representative of the oceanic stations. Here, the subsurface minimum is associated with poorly oxygenated, more acid Equatorial Subsurface Waters (150-350 m) and the intermediate maximum with more oxygenated and less acid Intermediate Antarctic Waters (400-1,200 m).

The O-pH5 structure has a characteristic deep mixed layer produced by the wind forcing; in some shallow areas (50-100 m), this layer can reach the bottom. Thus, the dissolved oxygen content and acidity of the water column are homogenized and the water column is more ventilated. In the pH6 structure (Baker and Steffen channels), the variation of pH in the upper layer differs from that of oxygen, generating a surface pH minimum. This is attributed to the advection of more oxygenated, more acid fresh waters from Río Baker.

For all the P-N structures, phosphate and nitrate concentrations in the surface layer are low due to phytoplankton consumption during photosynthesis and the contribution of nutrient-poor fresh waters from rivers, rain, and melting. On occasion, surface nutrient concentrations can become depleted in association with supersaturations of dissolved oxygen (> 120 %) and more basic pH values (> 8.2).

Increased phosphate and nitrate concentrations in the deep layer of the P-N1 structure are due mainly to the remineralization of organic matter, which releases these nutrients, and the presence of waters with marine origins. In the case of the P-N2 structure, the constant increase in nutrients towards the bottom is associated with the advection of external high nutrient marine waters to the channel's deep layer.

The P-N3 structure is representative of the oceanic stations. In these areas, the sub-surface maximum is associated with remnants of Equatorial Subsurface Waters (150-350 m) with greater nutrient concentrations and an intermediate maximum, and Antarctic Intermediate Waters (400-1,200 m) that are comparatively poorer in nutrients. The P-N4 structure is a result of

a deep mixing layer, produced by wind forcing that, in some shallow areas (50-100 m), can reach the bottom, causing homogenized nutrient contents in the water column.

The increased nutrient contents in the deep layer of the P-N5 structure are explained in function of organic matter decomposition, which releases nutrients, in association with the advection of waters that are comparatively poorer in nutrients at intermediate depths and that generate a maximum at the sub-surface layer, a relative minimum in the intermediate layer, and an absolute maximum in the deeper layer. The forcings and processes that affect the P-N6 structure are similar to those of the P-N5 structure; however, in the former case, the advection occurs at the deepest level.

The P7 structure (Baker and Steffen channels) does not have similar nitrate fluctuations in its upper portion and the observed surface phosphate maximum is attributed to the input of fresh waters from Río Baker, high in phosphate but low in nitrate.

Surface silicate concentrations are low in structures Si1 to Si3, Si8, and Si9 because of the presence of low silicate surface marine waters and the consumption of phytoplankton with silicate structures, such as diatoms. Structures Si4 to Si6 have high surface silicate concentrations, which are explained by mixing with fresh waters, rich in silicate, from adjacent rivers and glaciers.

The increased silicate concentration in the deep layer of the Si1 structure is due mainly to the dissolution of biogenic silicate structures, which release this element, and the presence of sea waters with higher silicate contents. In the Si2 structure, increased nutrients at the intermediate depths are associated with the advection of external waters that were richer in silicate.

The Si3 structure is representative of the oceanic stations. Here, the sub-surface maximum is associated with Equatorial Subsurface Waters (150-350 m) that have higher nutrient contents and the intermediate maximum is associated with Intermediate Antarctic Waters (400-1,200 m) that are comparatively poorer in nutrients. In the Si4 structure, the forcings and processes are similar to those of Si1. However, in this case, the upper

maximum is due to the contribution of silicate by fluvial waters and causes the change in the surface layer structure.

The forcings and processes of the Si5 structure are similar to those of Si4. Waters that are comparatively poorer in silicate enter at intermediate depths, where they cause a relative minimum, which is followed by a deep maximum. In the Si6 structure, silica contributions from rivers are high and the effect of the oceanic minimum on the surface layer is very low; this structure does not have a sub-surface minimum, as do Si4 and Si5, but shifts immediately to a more homogeneous deep layer with lower concentrations than are found in the surface layer.

In structure Si7, as with P-N4 and O-pH5, a deep mixed layer is observed. This is due to the wind forcing that, in some shallow zones (50-100 m), pushes the mixed layer to the bottom, thereby homogenizing the water column's silicate content. The Si8 structure, like the P-N5 structure, is explained in function of the decomposition of organic matter that releases nutrients and the dissolution of silicate structures that is associated with the entrance of waters that are comparatively poorer in silicate at the intermediate level. This generates a subsurface maximum, a relative intermediate minimum, and a deep maximum.

Finally, the Si9 structure consists of a surface minimum and a deep layer with quasi-homogeneous contents that seem not to be affected by the entrance of waters either richer or poorer in silicate.

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