ARTICLE IN PRESS

Progress in Oceanography xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Progress in Oceanography

journal homepage: www.elsevier.com/locate/pocean

Hypoxia in Chilean Patagonian Fjords

Nelson Silva [a,*], Cristian A. Vargas [b]

[a] Escuela de Ciencias del Mar, Pontificia Universidad Católica de Valparaíso, PO Box 1020, Valparaíso, Chile

[b] Aquatic Ecosystem Functioning Lab (LAFE), Department of Aquatic System, Faculty of Environmental Sciences & Environmental Sciences Center EULA Chile, Universidad de Concepción, Concepción, Chile

ARTICLE INFO

Article history:
Available online xxxx

ABSTRACT

Chilean Patagonia is one of the largest estuarine systems in the world. It is characterized by a complex geography of approximately 3300 islands, a total surface area of 240,000 km^2, and 84,000 km of coast line, including islands, peninsulas, channels, fjords, and sounds. The Chilean Patagonia Interior Sea is filled with a mixture of sea, estuarine, and fresh waters, and is characterized by a two layer vertical general circulation. Dissolved oxygen (DO) conditions in these fjords were analyzed based on historic salinity, dissolved oxygen and nutrient data from 1200 oceanographic stations. Horizontal advection of adjacent well oxygenated Subantarctic Waters (5–6 mL L^{-1}) was the mayor source of DO in the deep layers of the Interior Sea. Incoming DO was consumed by the respiration of autochthonous and allochthonous particulate organic matter, as ocean water flows towards the continental fjord heads, reaching near-hypoxic (2–3 mL L^{-1}) or hypoxic levels (<2 mL L^{-1}). As DO declined nutrient concentrations increased towards the fjord heads (from ~1.6 μM PO_4^{-3} and ~16 μM NO_3^- to ~2.4 μM PO_4^{-3} and ~24 μM NO_3^-). Overall, DO conditions in the Interior Sea were mostly the result of a combination of physical and biogeochemical processes. In all eastern channels and fjords, a low DO zone developed near the fjord heads (<4 mL L^{-1}) as a result of larger allochthonous particulate organic matter inputs transported by local rivers. This enhanced organic matter input to the deep layer increased DO consumption due to respiration and overwhelmed the oxygen supplied by horizontal advection. Out of the 90 Chilean Patagonian gulfs, channels and fjords analyzed, 86 systems were oxic (>2 mL L^{-1}) and four hypoxic (<2 mL L^{-1}), but only at their heads. None were found to be anoxic (0 mL L^{-1}). We found these DO conditions to be permanent features of the Chilean Patagonia Interior Sea.

Introduction

The coastal oceans are arguably one of the most important ecosystems on Earth and bear the brunt of the negative effects of human activities on the ocean. The presence of low water column DO concentrations can be a natural condition in many semi-closed coastal systems, such as estuaries and fjords, given their topographic characteristics. This environmental condition, known as hypoxia (DO < 2 mL L^{-1}; Diaz and Rosenberg, 1995), may be produced naturally by the DO consumption associated with high inputs of autochthonous and/or allochthonous organic matter (Zhang et al., 2010). The slow water renewal of semi-closed basins also favors DO consumption due to organic matter degradation (Gray et al., 2002). This situation commonly occurs under the presence of shallow constriction-sills in deep fjords and channels, which slow down or impede deep water circulation (Pickard, 1963, 1971). Anthropogenic activities may also provide additional inputs of organic matter and/or nutrients, which mostly are transported through river basins, or discharged directly into a water body as urban or industrial drainage. Aquaculture is one of such anthropogenic activities, and involves the direct discharge of organic by-products, such as non-consumed food pellets or feces, which may also contribute to generating hypoxic conditions (Holmer et al., 2005; Mulsow et al., 2006; Burt et al., 2012). Hypoxic conditions, and to a greater extent, anoxic conditions, both in deep waters and sediments, can lead to damage for marine biota inhabiting such areas (Kramer, 1987; Breitburg, 2002; Gray et al., 2002). Recently, such areas have been referred to as "dead zones" in the literature (Díaz and Rosenberg, 2008). Dead zones are present worldwide (Díaz, 2001), including some estuaries and fjords (Stanton and Pickard, 1981; Fenchel et al., 1990), and also large areas, such as the Gulf of Mexico, the Baltic Sea and the Black Sea (Zhang et al., 2010).

The Chilean Patagonian Fjords is one of the largest estuarine systems in the world with currently low levels of anthropogenic activity due to the relatively low population density (≈2 inhabitants km^{-2}) and most large towns/cities (Puerto Montt: 176,000

* Corresponding author. Tel.: +56 (32) 2274266.
E-mail address: nsilva@ucv.cl (N. Silva).

http://dx.doi.org/10.1016/j.pocean.2014.05.016
0079-6611/

inhabitants; Punta Arenas: 131,000 inhabitants; Castro: 40,000 inhabitants, Puerto Natales: 20,000 inhabitants; Puerto Aysén: 17,000 inhabitants) are located along the shoreline. Coyhaique, the third largest town in the area (50,000 inhabitants), is located about 120 km from the Aysén Fjord on the border of the Simpson River (116 $m^3 s^{-1}$; Niemeyer and Cereceda, 1984), which is a tributary of the Aysén River. The urban contribution of organic matter appears to be highly localized since there are few cities (i.e., 6 towns/cities 17,000–170,000 inhab.), with large spatial separations between them (500–1000 km).

The main commercial activities in the area are fisheries, aquaculture, and tourism, of which aquaculture is the most important. During 2011 a total of 895 fish and shellfish aquaculture centers were operating, with a total fish and mollusk production of 955,042 ton y^{-1} (SERNAPESCA, 2013). The large quantities of salmon and mollusk farming by-products (uneaten food and/or feces) might have a measurable influence on surface sediment's organic matter content, and therefore on the DO content, due to its consumption during its degradation. Nevertheless, according to Holmer et al. (2005) on Canadian salmon farms, the contribution of organic matter from salmon cages only reaches surface sediments within a 50–100 m perimeter. By means of dispersion models, Cromey and Black (2005) and Stucchi et al. (2005) obtained similar results. An analysis of the effects produced by Chilean salmon farming on the Chiloé–Aysén marine environment concluded that the effects seem to be restricted to the salmon cage shadow, with no broader impact on the ecosystem (Soto and Norambuena, 2004).

The Chilean Patagonian Fjords have only been the subject of oceanographic research during the past 20 years (Silva and Palma, 2008), and the current knowledge on the oceanographic processes associated with water circulation, water and sediment biogeochemistry, and marine biological productivity remains limited. The aims of this study are to perform a comprehensive analysis of water column DO in the Chilean Patagonian Fjords, to define their DO conditions (oxic: $O_2 > 2$ mL L^{-1}; hypoxic: <2 mL L^{-1}; anoxic: $O_2 = 0$ mL L^{-1}) and to infer the processes which may explain these conditions.

Materials and methods

Survey area

The Chilean Patagonia Inland Sea (CPIS) is made up of hundreds of inner channels, sounds, gulfs, and fjords, located between the Reloncaví Fjord and Cape Horn (Fig. 1). It was formed through glacial erosion and tectonic sinking of longitudinal valleys during the Pleistocene (Borgel, 1970; Clapperton, 1994), which were then later filled with seawater from the adjacent South Pacific Ocean during the Holocene sea level rise. Thus, the confluence of the seawater and freshwater from rainfall, continental rivers, and glacial melting along the eroded continental border, gave rise to one of the largest estuarine areas in the world. Chilean Patagonia covers an area of approximately 250,000 km^2, with 84,000 km of coastline (continental coastline plus the coastlines of some 3300 islands) (Silva and Palma, 2008). In the CPIS, there are several shallow constriction-sills (0.5–10 km wide; 50–100 m depth), which segment the bathymetry forming isolated deep micro-basins (200–1300 m), and restricting free deep water flow (Fig. 2a, b, e, and f; Sievers and Silva, 2008). The main ones included in this paper are: Desertores, Meninea, Kirke and Carlos III (Fig. 2).

The precipitation in this study area ranges from 1000 to 7000 mm y^{-1} on the western side of the Andes (Niemeyer and Cereceda, 1984). The major fluvial inputs are found in the continental fjords, coming mainly from the larger rivers Petrohué, Puelo, Yelcho, Aysén, Baker and Pascua (Fig. 1; and Table 2), which have nivo-pluvial regimes and respective average annual flows of 284, 676, 363, 628, 1011 and 690 $m^3 s^{-1}$ (DGA, 1988; Niemeyer and Cereceda, 1984; Ríos de Chile, 2013). The discharges from these rivers constitute the major source of freshwater and allochthonous organic matter to the CPIS. The vegetation in this area is predominantly evergreen forest made up mainly of species from the *Nothofagaceae* family (Huiña-Pukios, 2002; Rodriguez et al., 2008).

General water circulation follows a two layer estuarine flow pattern (Sievers and Silva, 2008) with water exchange between the CPIS and the adjacent Pacific Ocean mainly through several narrow and shallow passages located along the adjacent oceanic coastline between the Chacao Channel and Cape Horn (Fig. 1). Occasionally, and associated with wind effects (Caceres et al., 2002) and/or nonlinear tidal effects (Valle-Levinson et al., 2007), a general three layer circulation pattern has also been observed: a thin surface ocean-ward flowing layer, a thick intermediate inward flowing layer, and a thin bottom ocean-ward flowing layer.

Sampling and analyses

Between 1995 and 2012 the Chilean "Cruceros de Investigación Marina en Areas Remotas" program (CIMAR), conducted 16 cruises in the CPIS. Those field campaigns included the sampling of 1161 oceanographic stations, distributed between the Reloncaví Fjord and Cape Horn (Fig. 1, and Table 1). At these stations continuous temperature and salinity records were obtained with a Seabird CTD. Water samples at standard depths for DO and nutrients were taken with a 25 Niskin-Rosette system, between the surface and 10–50 m above the seafloor. All oceanographic stations were performed at the center of the channel or fjord.

The DO was measured according to the Carpenter (1965) technique. Nutrient samples (phosphate, nitrate and nitrite) were stored in acid-cleaned high density plastic bottles (60 mL) and the analyses were done at the Biogeochemical Laboratory of the Pontificia Universidad Católica de Valparaíso by means of a nutrient autoanalyzer according to Atlas et al. (1971). DO saturation values were estimated based on Weiss (1970) algorithm. During CIMAR Fiordos 1, 2 and 3 cruises, pH measurements were performed according to DOE (1994).

At some stations of the CIMAR Fiordos Cruise 15, water samples for nitrous oxide measurements were taken and stored in glass vials (20 mL), which were fixed with 50 µL of $HgCl_2$ and sealed without air bubbles trapped inside. The nitrous oxide analyses were performed at the Oceanographic Laboratory of the Universidad de Concepción by means of a gas chromatographer (VARIAN 3380 with an electro capture detector ^{63}Ni) and the headspace technique according to Mc Ailiffe (1971). Of all the stations that were sampled for nitrous oxide, only one station performed in Almirante Montt Gulf, was included in this study. In this station, called station "P", a CTDO-nutrient cast was performed every 3 h, during a 24-h cycle.

We concentrated our oceanographic analysis on salinity (as a flow tracer *proxy*), DO and nutrients (phosphate and nitrate). Temperature, together with salinity, was used to compute DO saturation and pH was used in the discussion of oceanographic characteristic of station "P". Vertical sections only include depths down to 400 m, which is the most variable portion of the water column. However, in the general circulation schematics, full sections are shown to represent the size and bathymetry of different fjord micro-basins.

From all CIMAR cruises (Table 1), six cross-sections were chosen as being representative of the oceanographic conditions in terms of salinity, DO, phosphate and nitrate. Each of them extended from the adjacent oceanic zone, to the fjord head. For the northern zone, the selected sections were: Boca del Guafo to the Reloncaví Fjord (Section 1); Boca del Guafo to the Puyuguapi Fjord (Section 2); and Boca del Guafo to the Aysén Fjord (Section 3). The central zone

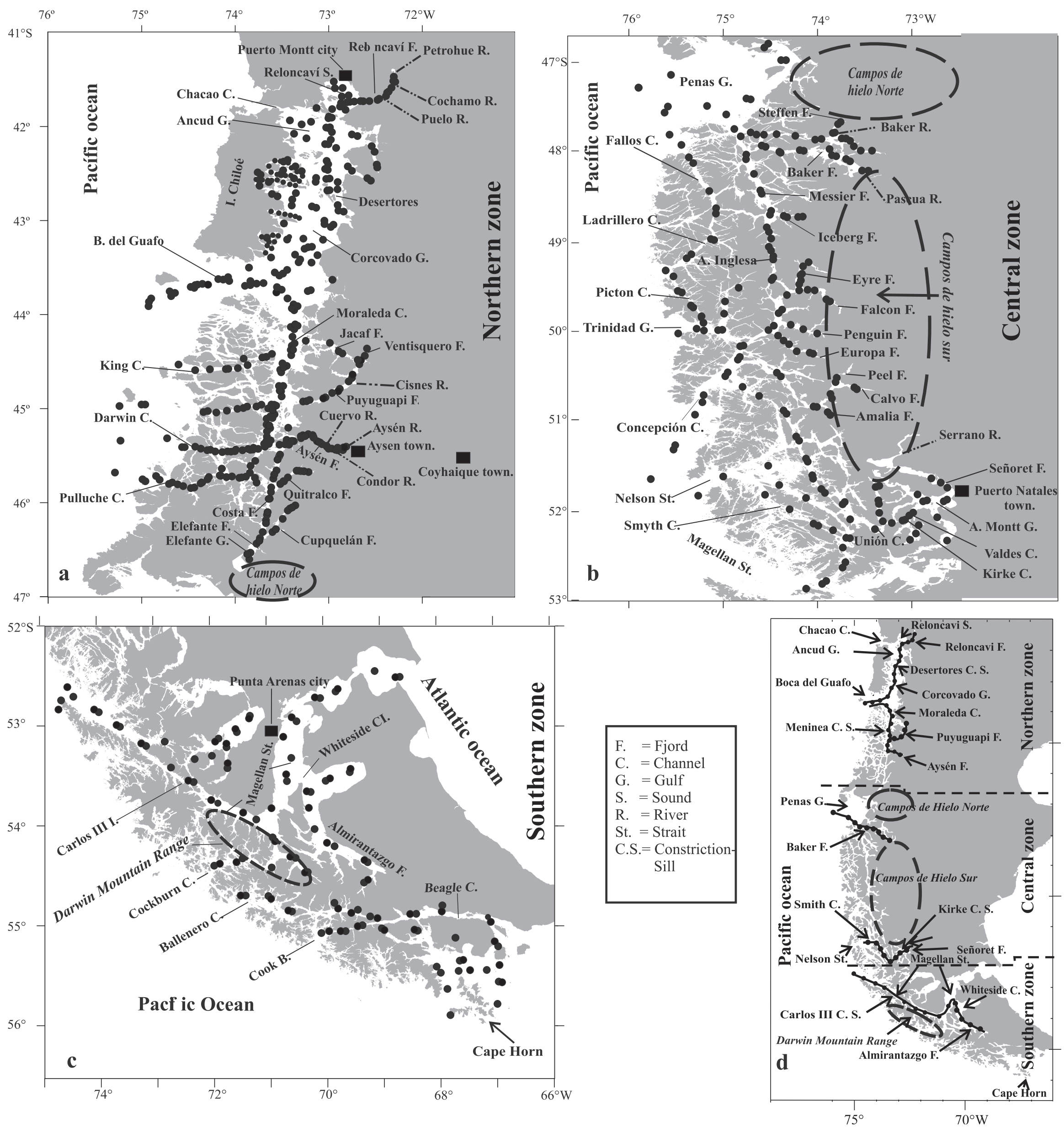

Fig. 1. Station positions for CIMAR Fiordos 1–18 oceanographic cruises in Chilean Patagonia. (a) Northern zone, (b) Central zone, (c) Southern zone and (d) six selected oceanographic sections to analyze vertical water circulation, salinity, dissolved oxygen, phosphate and nitrate distribution.

sections were: Penas Gulf to the Baker Fjord (Section 4); and the Nelson Strait to the Señoret Fjord (Section 5). The southern zone section was: the Magellan Strait to the Almirantazgo Fjord (Section 6) (Fig. 2).

Results

Salinity, DO and inorganic macro-nutrients in the Northern Patagonian Zone

The Chilean Northern Patagonian Zone includes several of the major rivers characterized by low dissolved inorganic phosphate and nitrate content (Table 3). In the Reloncaví Fjord, the Petrohué, Cochamó and Puelo Rivers discharge into its upper half (combined annual mean flow: 968 $m^3\ s^{-1}$; Table 2; and Fig. 1a). The Puyuguapi Fjord receives, in its middle section, freshwater inputs from the Cisnes River (annual mean flow: 233 $m^3\ s^{-1}$; Table 2; and Fig. 1a). The upper third of the Aysén Fjord, receives freshwater inputs from the Aysén, Condor and Cuervo Rivers (combined annual mean flow: 813 $m^3\ s^{-1}$; Table 2; and Fig. 1a). Within these fjords, freshwater mixes with Subantarctic Waters (SAAW) flowing towards the fjord head, generating a thin layer of estuarine water.

The thin surface estuarine water layer (i.e. 20–30 m), with low salinity (2–25), high DO (6–8 mL L^{-1}) and low nutrient content (0.1–0.8 μM PO_4^{-3}; 1–8 μM NO_3^-), flows towards the ocean from its formation area (Figs. 2a–c, 3a–h, and 4a–h). As the estuarine water flows ocean-ward it progressively increases in salinity and nutrient content, but experiences a slight decrease in DO content, until they reach typical oceanic values at the Boca del Guafo (32.5–33.5; 6–7 mL L^{-1}; 0.8–1.2-μM PO_4^{-3}; 8–12 μM NO_3^-).

The subsurface layer (30–130 m) of oceanic SAAW, with high salinities (32.5–34.0) and nutrients (~1.2–1.6 μM PO_4^{-3}; 12–20 μM NO_3^-) but with medium DO content (4–6 mL L^{-1}; ~63–97% sat.), flows into the interior micro-basins, through the Boca del Guafo. As the SAAW flows towards fjord heads, it mixes progressively with the outflowing fresher estuarine water, changing by

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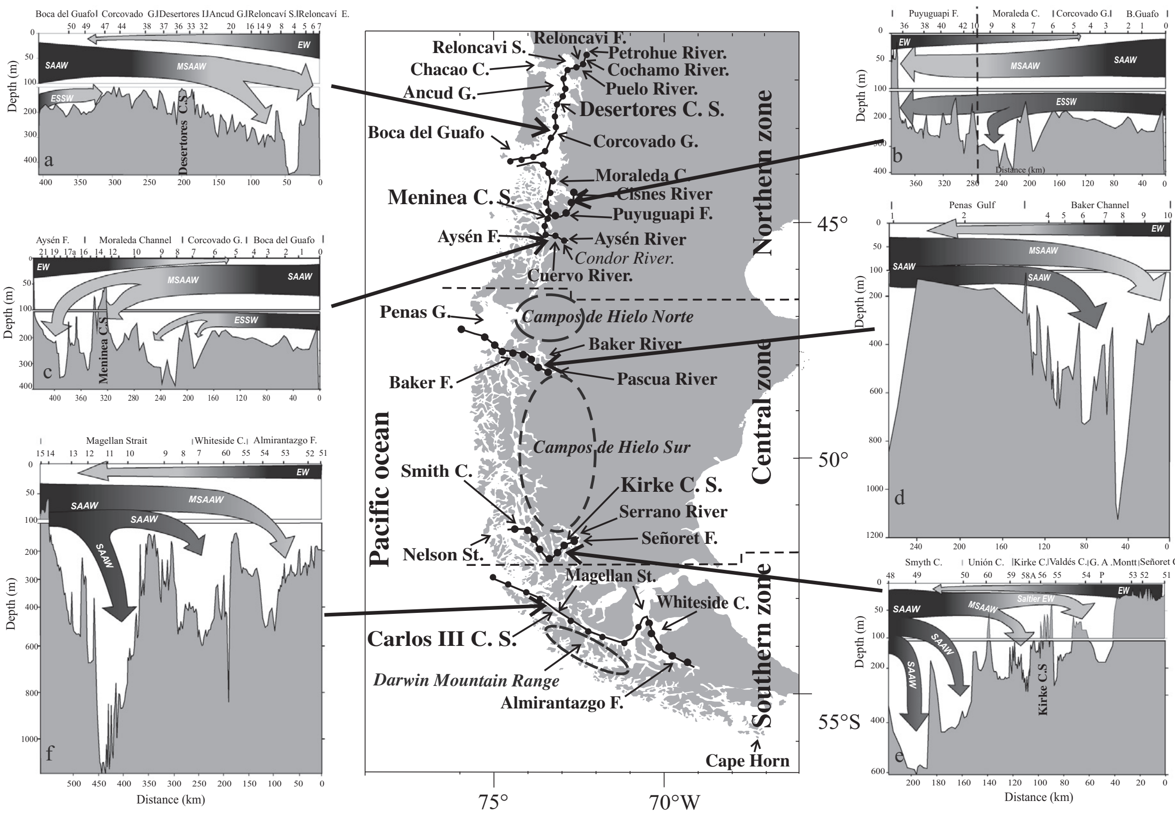

Fig. 2. Vertical water circulation in six selected sections. (a) Boca del Guafo–Reloncaví Fjord section, (b) Boca del Guafo–Puyuguapi Fjord section, (c) Boca del Guafo–Aysén Fjord, (d) Penas Gulf-Baker Fjord section, (e) Smith Channel-Señoret Fjord section and (f) Magellan Strait-Almirantazgo Fjord section. SAAW = Subantarctic Water, ESSW = Sub Surface Equatorial Water, MSAAW = Modified Subantarctic Water and EW = Estuarine Water.

Table 1
CIMAR Fiordos oceanographic sampling: Cruises (CF), Ships (VG = AGOR Vidal Gormaz or AM = B/I Abate Molina), dates, seasons, area, zone, number of stations performed.

Cruise	Date	Season	Area	Zone	# Stations
C1F (VG)	18 October–15 November 1995	Spring	41°30′–46°40′S	Northern	101
C2F (VG)	14 October–9 November 1996	Spring	47°25′–52°45′S	Central	109
C3F (VG)	9–22 October 1998	Spring	52°19′–55°58′S	Southern	51
C4F-1 (VG)	26 September–9 October 1998	Spring	43°35′–46°32′S	Northern	51
C4F-2 (VG)	25 February–8 March 1999	Sumer	43°35′–46°32′S	Northern	37
C7F-1 (VG)	7–21 July 2001	Winter	43°30′–46°40′S	Northern	42
C7F-2 (VG)	12–27 November 2001	Spring	43°30′–46°40′S	Northern	42
C8F-1 (VG)	1–26 July 2002	Winter	43°47′–45°43′S	Northern	53
C8F-2 (VG)	15–28 November 2002	Spring	43°47′–45°43′S	Northern	47
C9F-1 (VG)	5–25 August 2003	Winter	43°47′–45°42′S	Northern	38
C9F-2 (VG)	3–21 November 2003	Spring	43°47′–45°42′S	Northern	33
C10F-1 (VG)	21–31 Ago 2004	Winter	41°31′–43°49′S	Northern	49
C10F-2 (VG)	12–23 November 2004	Spring	41°31′–43°49′S	Northern	50
C11F-1 (VG)	16–27 July 2005	Winter	41°40′–43°48′S	Northern	70
C11F-2 (VG)	11–21 November 2005	Spring	41°40′–43°48′S	Northern	71
C12F-1 (VG)	9–22 July 2006	Winter	41°30′–43°48′S	Northern	23
C12F-2 (VG)	4–12 November 2006	Spring	41°30′–43°48′S	Northern	31
C13F-1 (VG)	27 July–7 August 2007	Winter	43°65′–46°26′S	Northern	32
C13F-2 (VG)	2–12 November 2007	Spring	43°65′–46°26′S	Northern	35
C14F (VG)	27 October–26 November 2008	Spring	46°50′–50°09′S	Central	62
C15F (VG)	17 October–10 November 2009	Spring	50°07′–52°45′S	Central	48
C16F (AM)	20 October–13 November 2010	Spring	52°39′–55°39′S	Central	34
C17F (AM)	16 October–14 November 2011	Spring	41°25′–43°49′S	Southern	21
C18F (AM)	17 June–4 July 2012	Spring	43°65′–46°26′S	Northern	31
				Total	1161

dilution into Modified Subantarctic Water (MSAAW), which has been defined as having intermediate salinities (31–33; Sievers and Silva, 2008). Remnants of oceanic SAAW, and the recently formed MSAAW, fill the Corcovado Gulf in the central part of the Northern Patagonian Zone. From this gulf, a branch of the MSAAW flow northwards to Reloncaví Fjord and another branch flows southwards to the Puyuguapi and Aysén Fjords (Fig. 2a–c). The northward flowing MSAAW branch, with salinities around 32.5, is able to flow over the Desertores Constriction-Sill (100–120 m depth), filling the Ancud Gulf, the Reloncaví Sound and the Reloncaví Fjord, whose head is located 400 km from the Boca del Guafo (Fig. 3a).

Table 2
The flows of Chilean Patagonian rivers mentioned in this paper.

Zone	Fjord	River	Mean annual flow (m^{-3} s^{-1})	Combined mean annual flow (m^{-3} s^{-1})
Northern	Reloncaví	Petrohué	284[a]	Reloncaví = 968
	Reloncaví	Puelo	676[a]	
	Reloncaví	Cochamó	20[b]	
	Aysén	Aysén	628[b]	Aysén = 678
	Aysén	Cóndor	50[c]	
	Aysén	Cuervo	135[a]	
	Puyuguapi	Cisnes	233[a]	
Central	Baker	Baker	1011[a]	Baker = 1701
	Baker	Pascua	690[a]	
	Ultima Esperanza	Serrano	63[a]	Ultima Esperanza = 184
	Ultima Esperanza	Grey	120[a]	
Southern	Estrecho Magallanes	San Juan	19[a]	

[a] Dirección General de Aguas (1988).
[b] Niemeyer and Cereceda (1984).
[c] Ríos de Chile (2013).

Table 3
CIMAR Fiordos river sampling: season, mean phosphate and nitrate concentrations, sampled zone, number of cruises and number of samples analyzed.

Zone	River	Season	# Cruises	Phosphate (μM)	Nitrate (μM)	# Samples
Northern	Puelo	Winter	3	0.18	1.2	6
		Spring	4	0.28	0.3	5
	Petrohué	Winter	3	0.26	0.3	5
		Spring	3	0.22	0.2	5
	Cochamó	Spring	2	0.21	0.2	3
		Winter	–	–	–	–
	Aysén	Winter	3	0.11	0.6	7
		Spring	4	0.13	0.6	8
	Cóndor	Winter	4	0.06	0.7	8
		Spring	4	0.13	0.3	9
	Cuervo	Winter	4	0.14	0.1	8
		Spring	4	0.19	nd	9
	Cisne	Winter	3	0.20	0.6	5
		Spring	3	0.07	0.3	5
Central	Baker	Spring	1	0.43	1.2	4
	Pascua	Spring	1	nd	0.5	4
Southern	Serrano	Spring	1	nd	0.8	2

Nd = non-detected.

From the stand point of DO and nutrients, the deep layer of the Boca del Guafo–Reloncaví Fjord section, does not display a horizontal continuum of deep DO and nutrient content along the section axis (Fig. 3b–d), as it does for salinity (Fig. 3a). As the MSAAW deep layer flows inland, towards Reloncaví Fjord, its DO decreases from ~5 mL L^{-1} (~75% sat.) to ~3 mL L^{-1} (~47% sat.) and its nutrients increase from ~1.6 μM PO_4^{-3} and ~16 μM NO_3^- to ~2.4 μM PO_4^{-3} and ~24 μM NO_3^- at its head.

The southern MSAAW branch flows into the Moraleda Channel, up over the Meninea Constriction-Sill (60 m depth), and then its deeper portion (60–150 m) turns eastward up towards the Puyuhuapi Fjord head, located at 380 km from the Boca del Guafo (Figs. 2b and 3e). As the MSAAW deep layer flows inland, along the Moraleda Channel up the Puyuguapi Fjord, its DO decreases continuously from ~5 mL L^{-1} (~75% sat.) to ~3 mL L^{-1} (~47% sat.) and its nutrients increase from ~1.6 μM PO_4^{-3} and ~16 μM NO_3^- to ~2.4 μM PO_4^{-3} and ~24 μM NO_3^- at the Puyuguapi Fjord head (Fig. 3f–h).

Although the deeper portion of the MSAAW (~60–150 m depth) is not able to flow further south of the Meninea Constriction-Sill (60 m depth), the upper portion of MSSAW (~30–60 m depth), with salinities of around 31, intermediate concentrations of DO and nutrients (5–6 mL L^{-1} ~76–94% sat.; 1.2–1.6 μM PO_4^{-3} and 12–16 μM NO_3), does flow south over the sill, sinking and filling the western end of the Aysén Fjord micro-basin (Fig. 4a–d). As the sinking MSAAW flows eastwards, the DO content diminishes to concentrations below 2.5 mL L^{-1} (<35% sat.) and nutrients increase to concentrations higher than 2.4 μM PO_4^{-3} and 24 μM NO_3^- at the Aysén Fjord head (Fig. 4b–d). This generates a contrasting situation between the deep water from the northern Moraleda micro-basin (high salinities 33–34; low DO < 4 mL L^{-1}; and high nutrients >2 μM PO_4^{-3}, >20 μM NO_3^-) with the southern Aysén micro-basin (low salinities 31; high DO > 4 mL L^{-1}; and low nutrient content <1.6 μM PO_4^{-3}; <16 μM NO_3^-), (Fig. 4a–d).

The remnants of Equatorial Subsurface Water (ESSW), with high salinity (33.9–34.2), low DO (<4 mL L^{-1}; <63% sat.) and high nutrient content (~2.0 μM PO_4^{-3}; ~24 μM NO_3^-), flow into the CPIS through the Boca del Guafo filling the deep layer (>150 m) of the Corcovado Gulf. From here, they flow northwards the Desertores Constriction-Sill and to the south up to the Meninea Constriction-Sill, not been able to overflow them (Figs. 3a–d and 4a–d). These topographic obstacles constrain ESSW to the deep central zone of the Northern Patagonian Zone. As the ESSW flows through the Moraleda Channel towards the Puyuguapi Fjord, DO decreases from <4 mL L^{-1} (<63% sat.) to <2 mL L^{-1} (<31% sat.) and nutrients increase from >2.4 μM PO_4^{-3} and >24 μM NO_3^- to >2.8 μM PO_4^{-3} and >26 μM NO_3^- at the Puyuguapi Fjord head (Fig. 3f–h). A similar situation occurs in the Jacaf Fjord, located east of the Moraleda Channel (Fig. 1). The eastern end of the Jacaf Fjord joins the Puyuguapi Fjord head, with low DO and high nutrient content (not shown).

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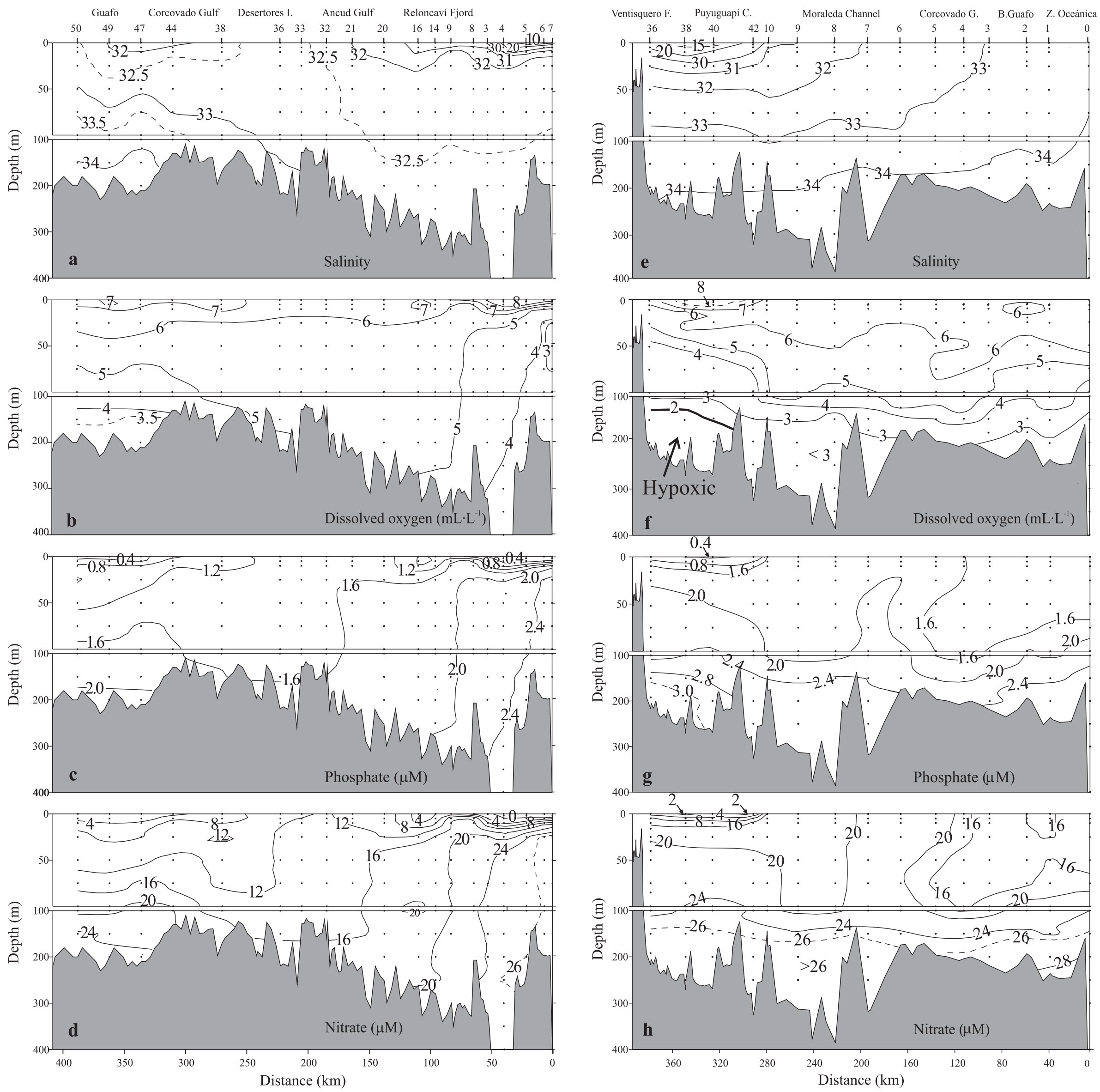

Fig. 3. Vertical distributions: (a) salinity, (b) dissolved oxygen, (c) phosphate, (d) nitrate for Boca del Guafo–Reloncaví Fjord section; (e) salinity, (f) dissolved oxygen, (g) phosphate, (h) nitrate for Boca del Guafo–Puyuguapi Fjord section.

ESSW is not present in the adjacent zone to Patagonian Archipelago, south of the Boca del Guafo, due to mixing with surface SAAW, and Antarctic Intermediate Water (AAIW) (Silva et al., 2009). Thus, ESSW is neither found in the Central nor in the Southern Patagonian micro-basins.

Salinity, DO and inorganic macro-nutrients in the Central Patagonian Zone

The Central Patagonian Zone includes two largest rivers in Chilean Patagonia (Baker and Pascua Rivers, Table 2), and two mayor Southern Hemisphere Glaciers (Campos de Hielo Norte and Campos de Hielo Sur; Fig. 1). These Central Patagonian Rivers are also characterized by low nutrient content (Table 3), and a combined total annual mean 1701 $m^3\ s^{-1}$; Table 2; and Fig. 1b) into the vicinity of the Baker Fjord head. Campos de Hielo Norte drains its glacier melt into the Steffen Fjord, which is connected to the Baker Fjord head. The Serrano River collects glacial melt from the Torres del Paine Glaciers and from the southern tip of the Campos de Hielo Sur. The Serrano River, which receives inputs from the Grey River (combined annual mean 183 $m^3\ s^{-1}$; Table 2; and Fig. 1b), drains into the Ultima Esperanza Fjord and then into the Señoret Fjord.

A thin surface estuarine water layer (20–30 m) of low salinity (5–25), high DO (6–7 $mL\ L^{-1}$) and low nutrient content (not detected –0.8 μM PO_4^{-3}; not detected –8 μM NO_3^-) flows towards the ocean (Fig. 5a–d). As the estuarine water from the Baker and Señoret Fjords flows towards the Penas Gulf and Nelson Strait respectively, it increases progressively in salinity to 33–34, and in nutrient content to ~1.2 μM PO_4^{-3} and ~8 μM NO_3^-. Nevertheless, the DO content remains similar along the sections (~7 $mL\ L^{-1}$) (Figs. 4e–h and 5a–d). As in the Northern Patagonian Zone, the estuarine water ocean-ward flow occurs not only through the Penas Gulf and Nelson Strait, but also through several shallow and narrow channels along the western side of the Patagonian Archipelago, such as the Fallos, Ladrillero, Tirnidad, and Concepción Channels (Fig. 1b).

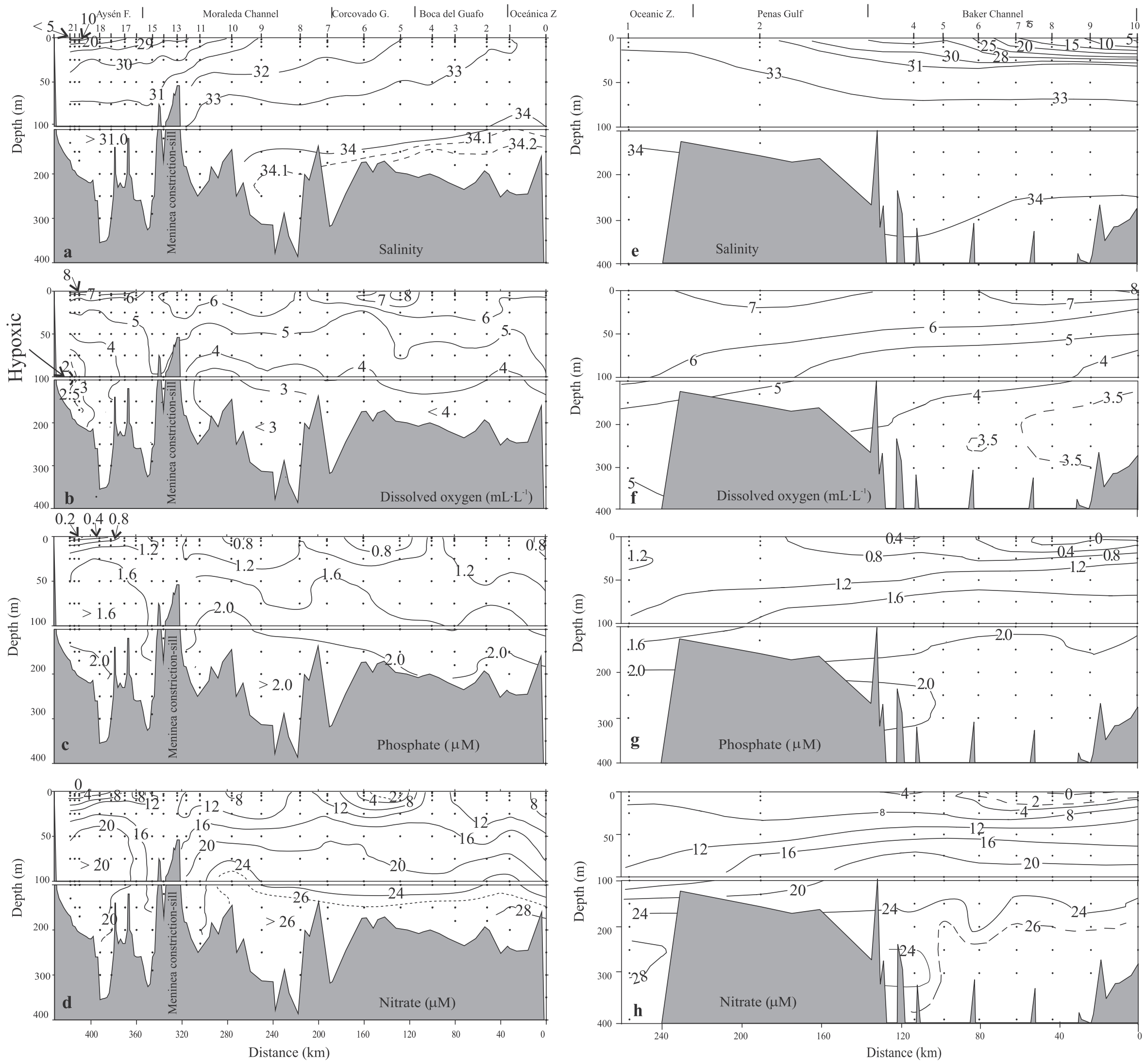

Fig. 4. Vertical distributions: (a) salinity, (b) dissolved oxygen, (c) phosphate, (d) nitrate for Boca del Guafo–Aysén Fjord section; (e) salinity, (f) dissolved oxygen, (g) phosphate, (h) nitrate for Penas Gulf-Baker Fjord section.

Under the surface layer (30–130 m), SAAW flows into the CPIS basins mainly through the Penas Gulf, towards Baker Fjord, and through the Nelson Strait, towards Smyth Channel, mixing progressively with the outflowing estuarine water, generating MSAAW (Figs. 2d, e, 4e, and 5a).

In the Baker Fjord section, SAAW fills most of the Baker micro-basin deep layer (from 50 to 75 m to the bottom) and MSAAW makes up only a subsurface layer between 25 and 75 m depth (Fig. 2d). As the SAAW from the Penas Gulf flows freely inwards along the Baker Channel, its surface layer mixes with the outflowing estuarine water thereby transforming into MSAAW with DO concentrations decreasing from ~6 mL L^{-1} (~85% sat.) to ~3.5 mL L^{-1} (~53% sat.) and its nutrient concentrations increase from ~1.2 µM PO_4^{-3} and ~12 µM NO_3^- to ~2 µM PO_4^{-3} and ~24 µM NO_3^- at the Baker Fjord head, located 240 km from the Penas Gulf (Fig. 4f–h).

In the Smyth Channel-Señoret Fjord section, SAAW fills most of the Smyth Channel micro-basin deep layer (from 100 m to the bottom). MSAAW makes up only a subsurface layer between 50 and 100 m depth in the Smyth Channel, but lies between 50 m and the bottom in the Unión-Kirke Channels. None of these water masses flow into the Almirante Montt Gulf or the Señoret Fjord. As the SAAW and MSAAW from the Nelson Strait flow inwards along the Smyth Channel, their DO and nutrient concentrations remain stable (~5–6 mL L^{-1} ~70–91% sat.; ~1.2–1.6 µM PO_4^{-3} and ~12–16 µM NO_3^-; Fig. 5b–d). The Kirke Constriction-Sill (~40 m depth) does not allow the MSAAW to flow further East, towards the Almirante Montt Gulf-Señoret Fjord micro-basin. More saline (22–26), well-oxygenated (5–6 mL L^{-1} ~68–84% sat.) and medium nutrient content (0.8–1.2 µM PO_4^{-3}; 8–12 µM NO_3^-) estuarine water flows over the Kirke Constriction-Sill and sinks, filling the Valdes Channel-Almirante Montt Gulf micro-basin (Fig. 5b–d). In this inner micro-basin (~200 m deep), the DO decreases from ~6 mL L^{-1} (~78% sat.) to <0.3 mL L^{-1} (<7% sat.), and nutrients increase from ~0.8 µM PO_4^{-3} and ~8 µM NO_3^- at 50 m, to >2.8 µM PO_4^{-3} and >20 µM NO_3^- between 50 and 150 m (Fig. 5b–d).

Similarly to the Meninea Constriction-Sill, there are contrasting differences either side of the Kirke Constriction-Sill: at comparable depths, there are high salinities (32), high DO (>4 mL L^{-1}) and low nutrient content (<1.6 µM PO_4^{-3}; <16 µM NO_3^-) to the west, and low salinities (24), low DO (<4 mL L^{-1}) and high nutrient content (>1.6 µM PO_4^{-3}; >16 µM NO_3^-) to the east (Fig. 5a–d).

At station "P", seven temperature, salinity, DO and nutrient vertical profiles show a decreasing trend in DO with depth, and increasing phosphate, nitrate and nitrous oxide with depth. Nitrite

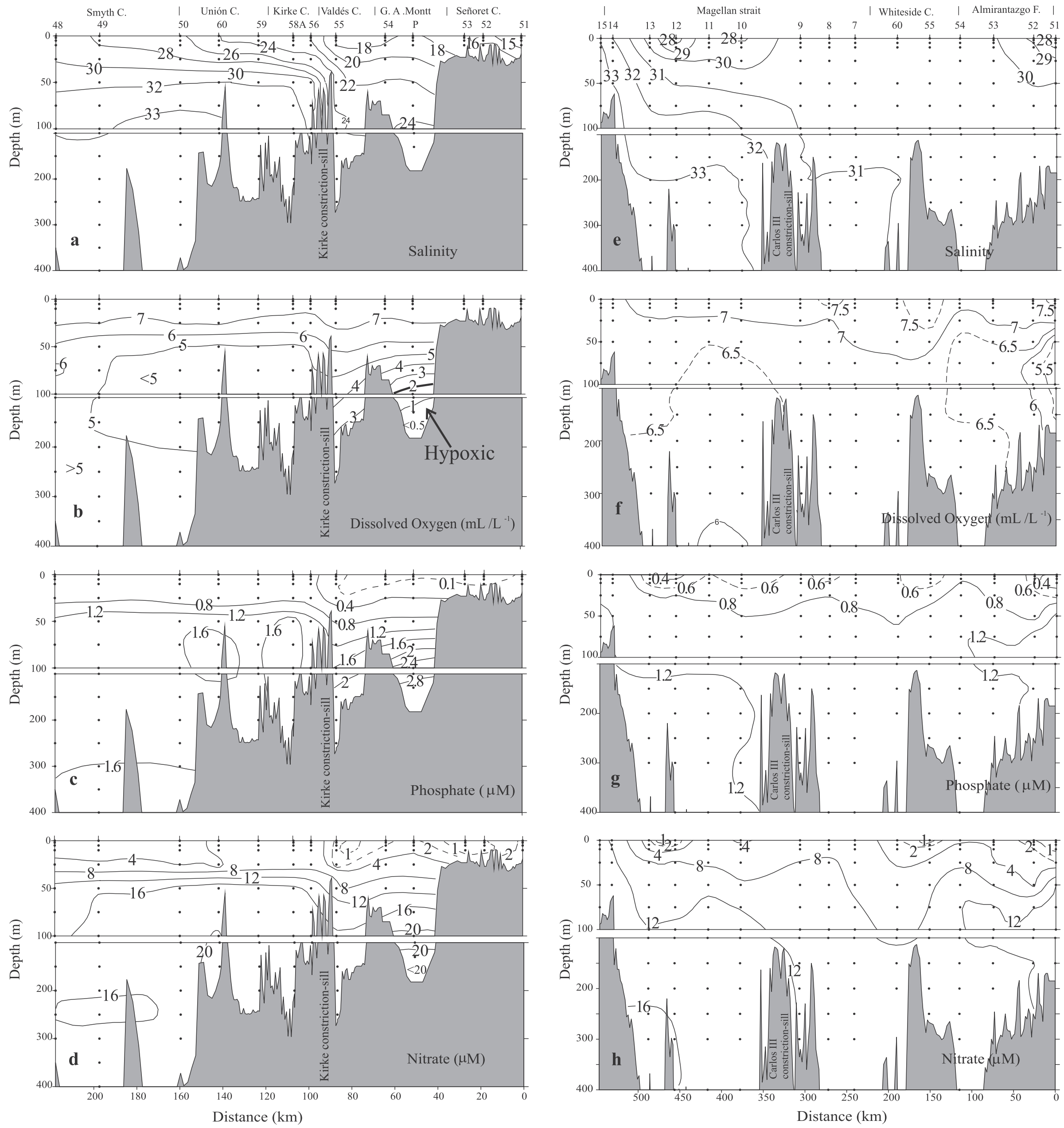

Fig. 5. Vertical distributions: (a) salinity, (b) dissolved oxygen, (c) phosphate, (d) nitrate for Smith Channel-Señoret Fjord section; (e) salinity, (f) dissolved oxygen, (g) phosphate, (h) nitrate for and (f) Magellan Strait-Almirantazgo Fjord section.

was low within the water column (<0.2 μM). At 150 m depth, DO is extremely low (0.3 mL L^{-1}) this, associated with a sudden decrease in nitrate and nitrous oxide, and an increase in nitrite (Fig. 6).

Salinity, DO and inorganic macro-nutrient in the Southern Patagonian Zone

The Southern Chilean Patagonian Zone has short rivers with small outflows (<20 $m^3 s^{-1}$; San Juan, Azopardo, Lapataia, and Yendegaia Rivers). Freshwater comes mainly from rainfall, which is heavy in the western zone but not in the east (2000–5000 v/s 200–400 mm y^{-1}; DGA, 1988) and from the Darwin Mountain Range Glaciers ice melt. Therefore, the Magellan Strait-Almirantazgo Fjord section does not display a well-developed low salinity layer, as seen in the Northern and Central Patagonian Fjords (Fig. 5e). The surface outflowing estuarine layer (25–30 m) has relatively high salinities (25–30), high DO (7–8 mL L^{-1}), and low nutrient concentrations (non-detected – 0.8 μM PO_4^{-3}; non-detected – 8 μM NO_3^-) (Fig. 5e–h). Due to the morphological configuration of the Magellan Strait (Fig. 1c), the estuarine water formed in the interior part of the Strait, is able to flow towards the west and the Pacific Ocean and to the east and to the Atlantic Ocean.

Below the surface layer, mainly from the western extreme of the Magellan Strait, Pacific Ocean SAAW flows into the Interior Sea micro-basins, mixing progressively with estuarine water to generate MASSW (Figs. 2f and 5e). The SAAW with high salinities (33–34), high DO (>7 mL L^{-1}), and high nutrient content (0.8–1.2 μM PO_4^{-3}; 12–16 μM NO_3^-), fills the Eastern Magellan Strait micro-basin (Fig. 5f–h). The MSAAW with lower salinities (31–32), lower DO (~6.5 mL L^{-1}; ~90% sat.) and lower nutrient content (0.8–1.2 μM PO_4^{-3}; 8–12 μM NO_3^-) than SAAW, flows over the Carlos III Constriction-Sill (~120 m depth), filling the Central Magellan

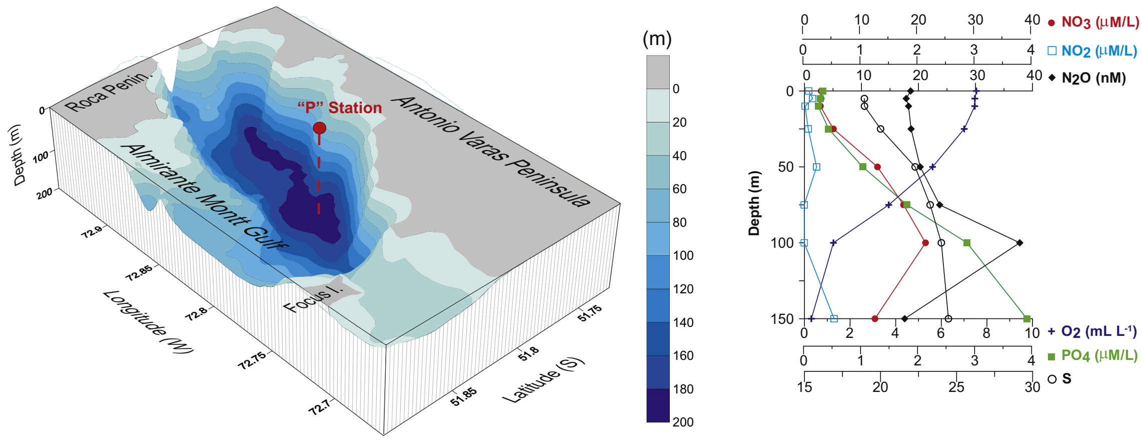

Fig. 6. Bathymetric depression in the Almirante Montt Gulf and vertical profiles for salinity, dissolved oxygen, phosphate, nitrate, nitrite and nitrous oxide at station "P".

Strait micro-basin, and then flowing up to the Almirantazgo Fjord head, located 550 km from the Western Magellan Strait mouth (2f). In the subsurface layer of the Almirantazgo Fjord head (50–150 m), DO decreases (<5.5 mL L^{-1}; <78% sat.) and nutrient concentrations increase (>1.2 µM PO_4^{-3}; >16 µM NO_3^-) (Fig. 5f–h).

Discussion

Hypoxia in Chilean fjords

Hypoxia is an environmental condition that occurs in some coastal and oceanic waters where dissolved oxygen concentrations have dropped to levels, which may negatively affect aquatic life. This condition is present naturally throughout the ocean (Díaz, 2001), and also in some coastal areas such as off northern Chile (Fuenzalida et al., 2009; Silva et al., 2009). Nowadays, hypoxia is increasing rapidly due to anthropogenic perturbations affecting coastal areas, such as urban and/or industrial outflows with high nutrient and/or organic loads released directly into estuaries and/or semi-closed ocean basins (Gray et al., 2002; Zhang et al., 2010). In the Chiloé region of the Northern Patagonian Zone, water pollution is typically associated with salmon farming activities due to the decomposition of uneaten food pellets and salmon feces into coastal waters (Buschmann and Pizarro, 2002). However, most of the physical and chemical perturbations associated with these activities appear to be restricted to the benthic environment, affecting an area no larger than 200–300 m from the farm site (Soto and Norambuena, 2004; Holmer et al., 2005).

As stated previously, hypoxic conditions were defined by Diaz and Rosenberg (1995) as water with DO content lower than 2 mL L^{-1}. Later on, a content lower than 2 mg L^{-1} (1.4 mL L^{-1}) has been widely used as the hypoxia threshold value for marine organisms (i.e. Díaz, 2001; Gray et al., 2002; Hofmann et al., 2011). Since, all the DO data from the Chilean Patagonian Fjords have been published and stored in mL L^{-1} units (Silva, 2008; CENDHOC, 2013), the hypoxia threshold of 2 mL L^{-1} (2.9 mg L^{-1}), was used in our work to distinguish between oxic and hypoxic conditions in the CPIS.

Taking into account all the CIMAR Fiordos dissolved oxygen data (~12,000 measurements) from almost 90 Chilean Patagonian channels, fjords, sounds and gulfs (Fig. 1a–d), we were able to establish where hypoxia is present in the CPIS. This analysis allowed us to identify four hypoxic zones: The Jacaf Fjord, Puyuguapi Fjord and Aysén Fjord heads in the Northern Patagonian Zone (1.1–2.0 mL L^{-1}; Figs. 3f and 4b; Jacaf Fjord, not shown; Table 4), and the Almirante Montt Gulf bathymetric depression in the Central Patagonian Zone (0.3–2.0 mL L^{-1}; Fig. 5b; and Table 4). Almost all other Northern and Central Patagonian Fjord heads display low DO concentrations (2–4 mL L^{-1}), but they are above the hypoxic threshold. All Southern Patagonian Fjord heads presented higher concentrations (4–5 mL L^{-1}) than the Northern and Central Patagonian Fjords, except the micro-basin in the center of Beagle Channel, with 3.5 mL L^{-1} (Not shown). Anoxic zones in the water column were not detected at all.

Sources of hypoxic conditions in Chilean fjords

In surface waters, DO concentrations are the result of a balance between oxygen production (photosynthesis), consumption (respiration) and exchange with the atmosphere, where the latest tends to maintain the DO near saturation, according to temperature and salinity. Below the surface layer, there are several physical and biogeochemical processes that contribute to diminishing DO content and, in extreme situations, to the generation of hypoxic zones (Lefort et al., 2012). At fjord heads, with high river freshwater inputs, a persistent halocline/pycnocline/stratified water column develops; therefore deep-water ventilation by vertical mixing and diffusion with the oxic surface layer is limited. This favors the occurrence of low DO zones at fjord heads, where stratification and particulate organic matter input is higher than at their mouths, and thus favors the consumption of DO due organic matter degradation. This is the case of Milford Sound in New Zealand (Stanton, 1984), Framvaren Fjord in Norway (Yao and Millero, 1995) and the Lower St. Lawrence Estuary in Canada (Lefort et al., 2012), as well as the Reloncaví, Puyuguapi, Aysén and Baker Fjords in southern Chile (Figs. 3a, b, e, f, and 4a, b, e and f).

DO from the isolated deep waters, due to the presence of a permanent pycnocline, can be replenished or ventilated by landward advection of the well oxygenated SAAW or SAAMW (Figs. 2a–e, 3b, f, and 4b and f). Nevertheless, due to the presence of the low-oxygenated ESSW off Boca del Guafo, coastal waters below the 150 m level flow into the Jacaf and Puyuguapi Fjords reducing ventilation capacity, compared with SAAW, favoring the generation of hypoxia at their heads (Figs. 2b and 3f).

In the Northern Patagonian Zone, the presence of the shallow Desertores and Menienea constriction-sills do not allow the low-oxygenated deep ESSW to flow towards the northernmost/southernmost fjord heads. The landward well-oxygenated SAAW subsurface layer off Boca del Guafo, flows over the sills and sinks on the other side due to its higher density, thereby filling and ventilating the Ancud-Reloncaví micro-basins to the north and the Aysén-Costa-Elefantes micro-basins to the south (Figs. 2a–c, 3b, f and 4b). Similar physical processes happen in the Bradshaw and Doubtful Sounds, in New Zealand (Stanton and Pickard, 1981), or the Sagu-

Table 4
Basic statistics on the minimum dissolved oxygen zones and their depth at the head of several Chilean Patagonian Fjords.

Northern Patagonian Fjords and channels					Central Patagonian Fjords and channels					Southern Patagonian Fjords and channels				
Fjord/ channel	Statistics	D.O. ($mL\,L^{-1}$)	Depth (m)	Cruises	Fjord/ channel	Statistics	D.O. ($mL\,L^{-1}$)	Depth (m)	Cruises	Fjord/ channel	Statistics	D.O. ($mL\,L^{-1}$)	Depth (m)	Cruises
Reloncaví	Mean	2.94	145	C10F, C11F, C12F, C17F	Baker	Mean	3..21	235	C2F, C10F	Almirantazgo	Mean	5.43	145	C3F, C16F
	Max.	3.47	185			Max.	3.26	270			Max.	5.53	150	
	Min.	2.16	100			Min.	3.16	200			Min.	2	140	
	# Obs	7	7			# Obs	2	2			# Obs	5.32	2	
	S.D.	0.41	34			S.D.	–	–			S.D.	–	–	
Comau	Mean	3.88	233	C1F, C10F, C11F	Iceberg	Mean	3.87	113	C2F, C14F	Agostini	Mean	5.81	120	C3F, C16F
	Max.	4.6	300			Max.	4.26	150			Max.	6.32	140	
	Min.	3.2	200			Min.	3.48	75			Min.	5.30	100	
	# Obs	4	4			# Obs	2	2			# Obs	2	2	
	S.D.	0.58	47			S.D.	–	–			S.D.	–	–	
Reñihue	Mean	4.86	217	C1F, C10F	Eyre	Mean	4.56	100	C2F, C14F					
	Max.	5.08	300			Max.	4.73	100						
	Min.	4.65	150			Min.	4.38	100						
	# Obs	3	3			# Obs	2	2						
	S.D.	–	–			S.D.	–	–						
Puyuguapi	Mean	1.67	183	C1F, C7F, C9F, C13F, C18F	Calvo	Mean	4.40	301	C2F, C15F					
	Max.	2.19	245			Max.	4.55	352						
	Min.	0.99	150			Min.	4.24	250						
	# Obs	6	6			# Obs	2	2						
	S.D.	0.42	39			S.D.	–	–						
Aysén	Mean	2.02	88	C1F, C4F, C7F, C9F, C13F, C18F	Estero Las Montañas	Mean	3.83	75	C15F					
	Max.	2.48	150			Max.	3.97	75						
	Min.	1.33	50			Min.	3.68	75						
	# Obs	8	8			# Obs	2	2						
	S.D.	0.39	30			S.D.	–	–						
Quitralco	Mean	4.01	42	C1F, C7F, C13F	Puerto Natales	Mean	6.98	13	C2F, C15F					
	Max.	4.31	50			Max.	7.75	20						
	Min.	3.44	25			Min.	6.21	5						
	# Obs	3	3			# Obs	2	2						
	S.D.	–	–			S.D.	–	–						
Cupquelan	Mean	3.63	67	C1F, C7F, C13F	Almirante Montt	Mean	0.29	150	C15F					
	Max.	4.06	100			Max.	0.68	150						
	Min.	3.08	50			Min.	0.18	150						
	# Obs	3	3			# Obs	3	3						
	S.D.	–	–			S.D.	–	–						
Elefantes	Mean	6.01	11	C7F, C13F, C18F	Otway	Mean	6.23	38	C3F, C16F					
	Max.	6.69	20			Max.	6.73	50						
	Min.	5.31	5			Min.	5.73	25						
	# Obs	4	4			# Obs	2	2						
	S.D.	0.57	6			S.D.	–	–						

enay Fjord, Canada (Seibert et al., 1979), where the inner micro-basins are well oxygenated (O_2 ~5–6 $mL\,L^{-1}$). In the Central and Southern Patagonian Zones, the well-oxygenated oceanic SAAW, or MSAAW, fills the adjacent interior micro-basins, thus ventilating those (Figs. 2d–2f, 4f, 5b and f). Moreover, in the Moraleda Channel, and Jacaf and Puyuguapi Fjords, poorly oxygenated ESSW fills deeper layers; in all other Patagonian Channels and Fjords, well-oxygenated SAAW, or MSAAW, fills adjacent micro-basins down to the bottom layers, favoring oxic conditions. This is not the case of some Northern Hemisphere fjords with shallow sills, such as the Lough Ine (Ireland), the Limfjord Fjord (Denmark; Rosenberg, 1980), the Framvaren Fjord (Norway; Yao and Millero, 1995), and the Nitinat Fjord (Canada; Richards et al., 1965). In these fjords, the inflowing oxic seawater does not completely fill the interior micro-basin, as is the case of Chilean fjords, and a stagnant anoxic deep layer is generated due to organic matter degradation and lack of DO replenishment via vertical advection and/or mixing. This restricted vertical circulation, with a stagnant anoxic deep layer, was not observed in any CIPS channels or fjords with sills.

In relation to residence times in the CPIS, unfortunately the published data is scarce. Valle-Levinson et al. (2007), using mass conservation equations, estimate a residence time of 98 days for the Reloncaví Fjord. Calvete and Sobarzo (2011), made an estimation of about 3.5 days for the Aysén Fjord surface water flushing time. Guzman and Silva (2013), using box models estimated a residence time for the Aysén Fjord of 2–3 days km^{-3} at the mouth, 2–3 days km^{-3} at the center and 3–8 days km^{-3} at the head. Therefore, water renewal is slower towards the fjord head, favoring degradation of organic matter and the generation of hypoxic conditions.

In the Smyth-Señoret section, the Kirke Constriction-Sill, the landward well-oxygenated subsurface water flows over the sill,

Please cite this article in press as: Silva, N., Vargas, C.A. Hypoxia in Chilean Patagonian Fjords. Prog. Oceanogr. (2014), http://dx.doi.org/10.1016/j.pocean.2014.05.016

filling the eastern micro-basin and ventilating it (Figs. 2e and 5b). In the Almirante Montt Gulf bathymetric depression (station P; ~200 m deep), DO diminishes rapidly to the lowest concentration ever registered throughout the CPIS (~0.3 mL L^{-1}). This implies that the physical ventilation processes are not enough to replenish the DO consumed by organic matter degradation and a strong DO minimum is generated.

As the well-oxygenated SAAW/SAAMW and the low-oxygenated ESSW, flow landwards to the continental fjord heads, they receive a continuous input of particulate autochthonous organic matter from the surface layer and at their head an allochthonous river input is also added (Silva et al., 2011; Vargas et al., 2011). Both autochthonous and/or allochthonous organic matter introduced into the head of the fjord is either removed via direct photolysis, utilization by decomposers (heterotrophs), and ingestion by grazing organisms or is stored within the fjord ecosystem (e.g. in organisms through the food-web, water, and/or sediments). Previous studies indicate that surface sediments of the Reloncaví, Puyuhuapi and Aysén Fjords have high organic carbon contents (i.e. >3%; Silva and Prego, 2002), where a significant part is supplied by the major rivers (i.e. Puelo, Cisnes, Aysén Rivers). The allochthonous carbon content in these fjords' surface sediments (estimated with $\delta^{13}C$) ranges between 50% and 90%, decreasing to less than 10% towards the oceanic side of the CPIS (Silva et al., 2011; Quiroga et al., 2013). Therefore, the allochthonous particulate matter input to the water column and sediments, and its latter degradation, favors the formation of hypoxia at these fjord heads. Nevertheless, during spring and summer periods primary production in these fjords might increase substantially (González et al., 2010; Montero et al., 2011), and the subsequent production of labile dissolved organic carbon (DOC), may induce rapid carbon turnover by the microbial community, and therefore, respiration may exceed the physical supply rate of DO. This has been observed in many fjord and estuarine ecosystems worldwide. For instance in the Roskilde Fjord (Denmark), Jensen et al. (1990) found phytoplankton biomass to be the single best predictor of variations in DO demand. Similarly, for both the Chesapeake Bay (USA; Smith and Kemp, 1995) and the Urdaibai Estuary (Spain; Iriarte et al., 1996), seasonal relationships between pelagic respiration and phytoplankton production appear to vary along spatial trophic gradients. In fact, during the period of high primary production (spring/summer seasons), in the Reloncaví and Puyuhuapi Fjords, Montero et al. (2011) and Daneri et al. (2012), reported production of labile DOC values ranging from 0.4 to 3.8 gC m^{-2} d^{-1}; and 0.9 to 4.2 gC m^{-2} d^{-1} respectively, which can also lead to consumption of available DO more rapidly than it can be replenished via diffusion or advection, resulting in hypoxia or anoxia.

Even though, the general working hypothesis that allochthonous and autochthonous sources of dissolved organic matter (DOM) and/or particulate organic matter POM on Patagonian fjord have been largely underestimated in their role in fueling hypoxia, this will have to be tested in the future in more focused studies Nevertheless, either from autochthonous and/or allochthonous sources, the aerobic organic matter degradation uses DO as an oxidant, either in the water column or in bottom sediments, lowering its concentration, which in turns introduces additional CO_2, thereby reducing the pH and carbonate saturation state (Figs. 3b–d, f–h, 4b–d and 7). The pH v/s Apparent Oxygen Utilization (AOU) from two lowest DO Puyuguapi Fjord stations, clearly shows the association between hypoxic ($O_2 < 2$ mL L^{-1}, AOU < 4.4 mL L^{-1}) and low pH waters (7.3–7.4), which are also characterized by high phosphate and nitrate concentration released during organic matter respiration (Fig. 7). Decreased pH in deep waters may also have significant implications for demersal and benthic communities inhabiting these hypoxic waters, including negative effects on overall calcification rates for many species, including cold water corals, coccolithophorids, foraminifera, and larval mollusks (Maier et al., 2011; Cai et al., 2011; Vargas et al., 2013). Moreover, the impacts of lowered seawater pH and hypoxia may have synergistic effects on the fjord biota. Given that naturally low DO, carbonate saturation and pH levels in these areas predispose these ecosystems to develop hypoxic corrosive conditions, we put forward that these areas are an ideal natural laboratory for studying the interactions between natural biogeochemical processes and regional to global anthropogenic stressors, such as land use changes and ocean acidification.

The lack of a hypoxic zone in the fjord heads of the Central Patagonian Zone can be explained by lower autochthonous carbon production and/or organic matter input to the water column and the sediments compared with the Northern Patagonian Zone (Silva and Prego, 2002; Silva et al., 2011), despite the Baker River. The freshwater discharges of the Baker River may possibly be the most important source of terrestrial organic matter in the area (Table 2), on the other hand, its more eroded river basin may also provide more sediment but smaller proportions of plant material than other river basins (Vargas et al., 2011). Moreover, this area is heavily influenced by glacier melt water and river discharge loaded with inorganic glacial material or glacier silt (Silva and Prego, 2002; Aracena et al., 2011). Indirect evidence of this is the low total organic carbon content in surface sediment in these fjords, which is due to dilution by the input of glacier silt (Silt + Clay ~ 100%; Corg. <2%; Silva and Prego, 2002). The allochthonous organic carbon content of the sediment in this zone is less than 20% (Lafon et al., this issue). Therefore, even though the DO diminishes landwards due to the degradation of autochthonous

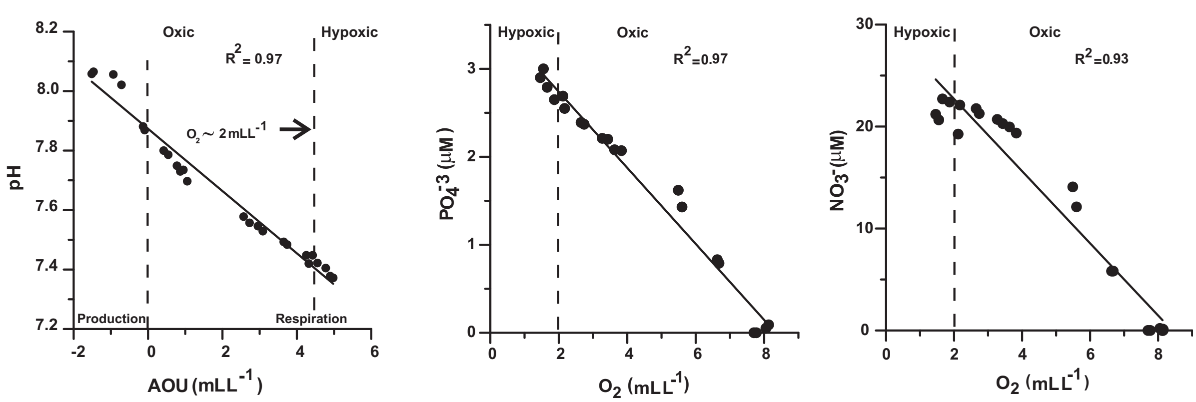

Fig. 7. AOU v/s pH, phosphate v/s dissolved oxygen and nitrate v/s dissolved oxygen for two oceanographic stations sampled at Puyuguapi Fjord. O_2 = 2 mL L^{-1} (Hypoxic threshold) is equivalent to AOU = 4.4 considering T = 10 °C and S = 32.

and allochthonous particulate organic matter, the ventilation due to physical processes is important enough to keep the DO above the hypoxic threshold (Figs. 4f and 5b; and Table 4).

On the other hand, the strong hypoxia in the Almirante Montt Gulf (0.3–2.0 mL L^{-1}), can be explained in terms of low deep water renewal due to a bathymetric depression (~200 m depth), which acts as an isolated pond (Fig. 6) with autochthonous organic matter degradation. Despite the important subsidy of particulate organic carbon from terrestrial sources to the upper water column (1–10 m depth; 80–90% allochthonous carbon; Lafón et al., this issue), the Almirante Montt Gulf surface sediments contain over 80% of autochthonous organic carbon (Lafón et al., this issue) and a total organic carbon content of less than 2% (N. Silva, unpublished data). If DO content in the Almirante Montt Gulf depression is compared with DO content in the Aysén Fjords head (~0.3 v/s ~2 mL L^{-1}) and taking into account that the total organic carbon and allochthonous content of surface sediments in the Almirante Montt Gulf are two and four times lower than in the Aysén Fjord sediments, it is possible to accept the hypothesis that the Almirante Montt deep waters strong hypoxia is the result of low renewal rates due to bathymetric restrictions, rather than the result of a large POM input.

According to Naqvi et al. (2010), as the dissolved oxygen content diminishes downwards to ~0.5 mL L^{-1}, nutrient and N_2O concentrations increase. Below this DO concentration denitrification occurs, diminishing the nitrate and nitrous oxide and increasing the nitrite concentration. In the Almirante Montt Gulf bathymetric depression, due to its strong hypoxia (O_2 < 0.3 mL L^{-1}), nitrate and N_2O diminish and nitrite increases due to denitrification in its deep layer (>100 m; Figs. 5b–d and 6).

The Southern Patagonian Zone has the lowest river inputs of all of Chilean Patagonia (DGA, 1988; Table 2). This Southern Patagonian Zone has reportedly the lowest photosynthetic carbon production (Aracena et al., 2011) and the lowest zooplanktonic biomass (Palma and Silva, 2004) of Chilean Patagonia. The low primary productivity seems to be associated with the reduction in the riverine flux of silicic acid (Aracena et al., 2011; Torres et al., this issue). The total organic carbon content in surface sediments is mostly low (<1%; Silva and Prego, 2002), which in turn is a result of the low autochthonous and allochthonous organic matter inputs to the water column and sediments. Therefore, the Southern Patagonian Zone deep micro-basins are well-oxygenated, with the minimum DO contents well above the hypoxic threshold (Fig. 5f; and Table 4).

The temporal occurrence of oxic/hypoxic conditions can be considered a permanent feature of the Puyuguapi, Jacaf and Aysén fjords, since they have been registered by other CIMAR expeditions, on at least two occasions under different years and during different seasons (Table 4). The Almirante Montt hypoxic condition seems also to be a permanent, feature, due to the gulf topography, even though it has been registered only once.

Conclusions

Our measurements in the Chilean Patagonian Interior Sea allowed us to infer that DO conditions in these waters seems to be mostly the result of physical processes rather than biogeochemical ones. The presence of constriction-sills produces the sinking of well-oxygenated subsurface waters into the adjacent micro-basins, which favors the ventilation of these basins. Without this bathymetric feature, there would be no damming effect and deeper less-oxygenated waters would be able to flow freely landward. These sills do not favor the generation of hypoxic or even anoxic conditions at fjord heads, due to organic matter degradation, as occurs in the Puyuguapi and Jacaf Fjords, where the poorly oxygenated ESSW flows freely towards the fjord's heads. The well-oxygenated SAAW inputs from the continental shelf edge into the Interior Sea allow the Chilean Patagonian Fjords to be mostly oxic. Nevertheless, in all continental fjords a low DO zone does developed, a product of the respiration of autochthonous particulate organic matter (Reloncaví, Comau, Quitralco, Cupquelan, Baker, Iceberg, Eyre, and Las Montañas Fjords; O_2 ~2–4 mL L^{-1}). Moreover, at certain fjord heads, allochthonous organic matter inputs, transported by the local rivers, add to the autochthonous inputs and hypoxic conditions are developed (Puyuguapi, Jacaf, Aysén Fjords; O_2 ~1–2 mL L^{-1}). Bathymetric depressions favor sluggish deep water renewal, which combined with organic matter respiration, contributes to the generation of intense hypoxic zones (the Almirante Montt Gulf; O_2 ~0.3–2.0 mL L^{-1}). Until now, various research expeditions had sampled the water column DO content of the majority of the Chilean fjords, channels, sounds and gulfs and no natural anoxic zones had been detected.

Acknowledgements

This investigation was partially supported by the Comité Oceanográfico Nacional (CONA), Chile, through the CIMAR Fiordos program, who assigned several grants to Prof. Nelson Silva. The authors would like to thank the Captains and crews of AGOR Vidal Gormaz and B/I Abate Molina for their help during the 16 CIMAR Fiordo cruises. We extend our gratitude to Ms. Paola Reinoso who performed most of the DO and nutrient analyses, and to Mr. Reinaldo Rehhof, Mr. Noé Cáceres and Mr. Francisco Gallardo for their valuable help during the ocean and river sampling. We also thank Dr. Laura Farías, Universidad de Concepción (UdeC), for giving us access to the "P" station nitrous oxide data. We also thank the Pontificia Universidad Católica de Valparaíso (PUCV) for its partial support to Prof. N. Silva's staff during their participation in the CIMAR cruises and the Millennium Nucleus Project NC 1200286 "Center for the study of multiple-drivers on marine socio-ecological systems (MUSELS) from the Ministerio de Economia, Fomento y Turismo for additional support to Dr. C.A. Vargas during the final stage of this study. Finally, we want to thank to an anonymous reviewer for his invaluable help to improve our manuscript.

References

Aracena, C., Lange, C.B., Iriarte, J.L., Rebolledo, L., Pantoja, S., 2011. Latitudinal patterns of export production recorded in surface sediments of the Chilean Patagonian fjords (41–551S) as a response to water column productivity. Continental Shelf Research 31, 340–355.

Atlas, E.S., Hager, S., Gordon, L., Park, P., 1971. A practical manual for use of the Technicon Autoanalyser in sea water nutrient analyses. In: Technical Report, Oregon State University, Department of Oceanography, pp. 1–215.

Borgel, R., 1970. Geomorfología de las regiones australes de Chile. Revista Geográfica Chile. Terra Australis 20, 135–140 (in Spanish, with English summary).

Breitburg, D., 2002. Effects of hypoxia, and the balance between enrichment, on coastal fishes and fisheries. Estuaries 25 (4b), 767–781.

Burt, K., Hamoutene, D., Mabrouk, G., Lang, C., Puestow, T., Drover, R., Page, F., 2012. Environmental conditions and occurrence of hipoxia within production cages of Atlantic salmon on the south coast of Newfoundland. Aquaculture Research 43, 607–620.

Buschmann, A., Pizarro, R., 2002. El costo ambiental de la salmonicultura en Chile. Análisis de Políticas Públicas. N 15. Fundación Terram. Santiago, Chile.

Cáceres, M., Valle-Levinson, S.A., Sepúlveda, H., Holderiedc, K., 2002. Transverse variability of flow and density in a Chilean fjord. Continental Shelf Research 22, 1683–1698.

Cai, W.-J., Hu, X., Huang, W.-J., Murrell, M.C., Lehrter, J.C., Lohrenz, S.E., Chou, W.-C., Zhai, W., Hollibaugh, J.T., Wang, Y., Zhao, P., Guo, X., Gundersen, K., Dai, M., Gong, G.-C., 2011. Acidification of subsurface coastal waters enhanced by eutrophication. Nature Geoscience 4, 766–770.

Calvete, C., Sobarzo, M., 2011. Quantification of the surface brackish water layer and frontal zones in southern Chilean fjords between Boca del Guafo and Estero Elefantes. Continental Shelf Research 31 (3–4), 162–171.

Carpenter, J.H., 1965. The Chesapeake bay Institute Technique for the Winkler dissolved oxygen method. Limnology and Oceanography 10, 141–143.

CENDHOC, 2013. Centro Nacional de Datos Oceanográficos, Chile. <http://www.shoa.cl/n_cendhoc/>.

Clapperton, C.M., 1994. The quaternary glaciation of Chile. Revista Chilena de Historia Natural 67, 369–383.

Cromey, C.J., Black, K.D., 2005. Modelling the impacts of finfish aquaculture. In: Hargrave, B. (Ed.), Environmental Effects of Marine Finfish Aquaculture. The Handbook of Environmental Chemistry, Part M, vol. 5. pp. 129–155.

Daneri, G., Montero, P., Lizárraga, L., Torres, R., Iriarte, J.L., Jacob, B., González, H.E., Tapia, F.J., 2012. Primary productivity and heterotrophic activity in an enclosed marine area of central Patagonia (Puyuhuapi channel; 44S, 73W). Biogeosciences Discuss 9, 5929–5968.

DGA, 1988. Balance Hídrico de Chile. Dirección General de Aguas. 35 mapas temáticos, p. 24.

Díaz, R.J., 2001. Overview of hypoxia around the world. Journal of Environmental Quality 2001 (30), 275–281.

Díaz, R.J., Rosenberg, R., 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioral responses of benthic macrofauna. Oceanography and Marine Biology 33, 245–303.

Díaz, R.J., Rosenberg, R., 2008. Spreading dead zones and consequences for marine ecosystems. Science 321, 926–929.

DOE, 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in the sea water; Version 2. In: Dickson, A.G., Goyet, C. (Eds.), ORNL/CDIAC-74.

Fenchel, T., Kristensen, L.D., Rasmussen, L., 1990. Water column anoxia: vertical zonation of planktonic protozoa. Marine Ecology Progress Series 62, 1–10.

Fuenzalida, R., Schneider, W., Garcés-Vargas, J., Braco, L., Lange, C., 2009. Vertical and horizontal extension of the oxygen minimum zone in the Eastern South Pacific Ocean. Deep-Sea Research, II 56, 1027–1038.

González, H.G., Calderón, M.J., Castro, L., Clement, A., Cuevas, L., Daneri, G., Iriarte, J.L., Lizárraga, L., Martínez, R., Menschel, E., Silva, N., Carrasco, C., Valenzuela, C., Vargas, C.A., Molinet, C., 2010. Primary production and its fate in the pelagic food web of the Reloncaví Fjord and plankton dynamics of the Interior Sea of Chiloé, Northern Patagonia, Chile. Marine Ecology Progress Series 402, 13–30.

Gray, J.S., Wu, R.S.S., Or, Y.Y., 2002. Effects of hypoxia and organic enrichment on the coastal marine environment. Marine Ecology Progress Series 238, 249–279.

Guzman, D., Silva, N., 2013. Caracterización físico-química de los canales australes. Modelo geoquímico del Fiordo Aysén. Editorial Académica Española, p. 106.

Hofmann, A.F., Peltzer, E.T., Walz, P.M., Brewer, P.G., 2011. Hypoxia by degrees: establishing definitions for a changing ocean. Deep-Sea Research I 58, 1212–1226.

Holmer, M., Wildish, D., Hargrave, B., 2005. Organic enrichment from marine finfish aquaculture and effects on sediment biogeochemical processes. In: Hargrave, B. (Ed.), Environmental Effects of Marine Finfish Aquaculture. The Handbook of Environmental Chemistry, Part M, vol. 5. Springer-Verlag, Berlin, pp. 181–206.

Huiña-Pukios, 2002. Especies del Género Nothofagus presentes en Chile. <http://www.geocities.com/biodiversidadchile/nothof.htmS>. (visited 16.09.09) (in Spanish).

Iriarte, A., de Madariaga, I., Diez-Garagarza, F., Revilla, M., Orive, E., 1996. Primary plankton production, respiration and nitrification in a shallow temperate estuary during summer. Journal of Experimental Marine Biology and Ecology 208, 127–151.

Jensen, L.M., Sand-Jensen, K., Marcher, S., Hansen, M., 1990. Plankton community respiration along a nutrient gradient in a shallow Danish estuary. Marine Ecology Progress Series 61, 75–85.

Kramer, D.L., 1987. Dissolved oxygen and fish behavior. Environmental Biology of Fishes 18 (2), 81–92.

Lefort, S., Gratton, Y., Mucci, A., Dadou, I., Gilbert, D., 2012. Hypoxia in the Lower St. Lawrence Estuary: how physics controls spatial patterns. Journal of Geophysical Research 117 (C07018), 2012. http://dx.doi.org/10.1029/2011JC007751.

Maier, C., Watremez, P., Taviani, M., Weinbauer, M.G., Gattuso, J.P., 2011. Calcification rates and the effect of ocean acidification on Mediterranean cold-water coral. Proceedings of the Royal Society. Serie B. doi: http://dx.doi.org/10.1098/rspb.2011.1763.

McAuliffe, C., 1971. Gas chromatographic determination of solutes by multiple phase equilibrium. Chemical Technology 1 (1), 46–51.

Montero, P., Daneri, G., González, H.E., Iriarte, J.L., Tapia, F.J., Lizárraga, L., Sanchez, N., Pizarro, O., 2011. Seasonal variability of primary production in a fjord ecosystem of the Chilean Patagonia: implications for the transfer of carbon within pelagic food webs. Continental Shelf Research 31, 202–215.

Mulsow, S., Krieger, Y., Kennedy, R.J., 2006. Sediment profile imaging (SPI) and micro-electrode technologies in impact assessment studies: example from two fjords in Southern Chile used for fish farming. Journal of Marine Systems 62, 152–163.

Naqvi, S.W.A., Bange, H.W., Farías, L., Monteiro, P.M.S., Scranton, M.I., Zhang, J., 2010. Marine hypoxia/anoxia as a source of CH_4 and N_2O. Biogeosciences 7, 2159–2190.

Niemeyer, H., Cereceda, P., 1984. Geografía de Chile: Hidrografía. Instituto Geográfico Militar, Santiago, p. 320.

Palma, S., Silva, N., 2004. Distribution of siphonophores, chaetognaths, euphausiids and oceanographic conditions in the fjords and channels of southern Chile. Deep Sea Research II 51, 513–535.

Pickard, G.L., 1963. Oceanographic characteristics of inlets of Vancouver Island, British Columbia. Journal of Fisheries Research Board of Canada 20 (5), 1109–1144.

Pickard, G., 1971. Some physical oceanographic features of inlets of Chile. Journal Fisheries Board of Canada 28, 1077–1106.

Quiroga, E., Ortiz, P., Reid, B., Gerdes, D., 2013. Classification of the ecological quality of the Aysen and Baker Fjords (Patagonia, Chile) using biotic indices. Marine Pollution Bulletin 68, 117–126.

Richards, F.A., Cline, J.D., Broenkow, W.W., Atkinson, L.P., 1965. Some consequences of decomposition of organic matter in Lake Nitinat, an anoxic fjord. Limnology and Oceanography 10 (Suppl.), R185–R201.

Ríos de Chile, 2013. http://ww2.educarchile.cl/portal.herramientas/nuestros_sitios/bdrios/sitio/rios/rios.htm. (accessed January 2013).

Rodriguez, R., Marticorena, A., Teneb, E., 2008. Vascular plants of Baker and Pascua Rivers, Region of Aysén, Chile. Gayana Botanica 65, 39–70 (in Spanish, with English summary).

Rosenberg, R., 1980. Effect of oxygen deficiency on benthic macrofauna in fjords. In: Freeland, H.J., Farmer, D.M., Lerings, C.D. (Eds.), Fjord Oceanography. Plenum Press, New York, pp. 499–514.

Seibert, G.H., Trites, R.W., Reid, S.J., 1979. Deep water exchange processes in the Saguenay Fjord. Journal Fisheries Research Board of Canada 26, 42–53.

SERNAPESCA, 2013. Servicio Nacional de Pesca y Acuicultura. Anuario 2011. <http://www.sernapesca.cl/index.php?option=com_remository&Itemid=246&func=fileinfo&id=6675>. (visited 10.04.13).

Sievers, A.H., Silva, N., 2008. Water masses and circulation in austral Chilean channels and fjords. In: Silva, N., Palma, S. (Eds.), Progress in the Oceanographic Knowledge of Chilean Inner Waters, from Puerto Montt to Cape Horn. Comité Oceanográfico Nacional – Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile, pp. 53–58. Book on line at <http://www.cona.cl/>.

Silva, N., 2008. Dissolved oxygen, pH, and nutrients in the austral Chilean channels and fjords. In: Silva, N., Palma, S. (Eds.), Progress in the Oceanographic Knowledge of Chilean Inner Waters, from Puerto Montt to Cape Horn. Comité Oceanográfico Nacional – Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile, pp. 37–43. Book on line at <http://www.cona.cl/>.

Silva, N., Palma, S. (Eds.), 2008. Progress in the Oceanographic Knowledge of Chilean Interior Waters, from Puerto Montt to Cape Horn. Comité Oceanográfico Nacional – Pontificia Universidad Católica de Valparaíso, Valparaíso, p. 161. Book on line at <http://www.cona.cl/>.

Silva, N., Prego, R., 2002. Carbon and nitrogen spatial segregation and stoichiometry in the surface sediments of southern chilean inlets (41–56S). Estuarine and Coastal Shelf Science 55, 763–775.

Silva, N., Rojas, N., Fedele, A., 2009. Water masses in the Humboldt Current System: properties, distribution, and the nitrate deficit as a chemical water mass tracer for Equatorial Subsurface Water off Chile. Deep-Sea Research, Part II 56, 1004–1020.

Silva, N., Vargas, C.A., Prego, R., 2011. Land–ocean distribution of allochthonous organic matter in surface sediments of the Chiloé and Aysén interior seas (Chilean Northern Patagonia). Continental Shelf Research 31, 330–339.

Smith, E.M., Kemp, W.M., 1995. Seasonal and regional variations in plankton community production and respiration for Chesapeake Bay. Marine Ecology Progress Series 116, 217–231.

Soto, D., Norambuena, R., 2004. Evaluation of salmon farming effects on marine systems in the inner seas of southern Chile: a large-scale mensurative experiment. Journal of Applied Ichthyology 20, 493–501.

Stanton, B.R., Pickard, G.L., 1981. Physical Oceanography of the New Zealand Fjords. New Zealand Oceanographic Institute, Memoir 88, p. 37.

Staton, B.R., 1984. Some oceanographic observations in the New Zealand Fjords. Estuarine, Coastal and Shelf Science 19, 89–104.

Stucchi, D., Sutherland, T.A., Levings, C., Higgs, D., 2005. Near-field depositional model for salmon aquaculture waste. In: Hargrave, B. (Ed.), Environmental Effects of Marine Finfish Aquaculture. The Handbook of Environmental Chemistry, Part M, vol. 5. Springer-Verlag, Berlin, pp. 157–179.

Torres, R., Silva, N., Reid, B., Frangopulos, M., this issue. Silicic acid enrichment of subantarctic surface water from continental inputs along the Patagonian archipelago interior sea (41°-56°S). Progress in Oceanography.

Valle-Levinson, A., Sarkar, N., Sanay, R., Soto, D., León, J., 2007. Spatial structure of hydrography and flow in a Chilean Fjord, Estuario Reloncaví. Estuaries and Coasts 30 (1), 113–126.

Vargas, C.A., Martínez, R.A., San-Martin, V., Aguayo, M., Silva, N., Torres, R., 2011. Allochthonous subsidies of organic matter across a lake–river–fjord landscape in the Chilean Patagonia: implications for marine zooplankton in inner fjord areas. Continental Shelf Research 31 (4–4), 187–201.

Vargas, C.A., De La Hoz, M., Aguilera, V., San Martin, V., Manríquez, P.H., Navarro, J.M., Torres, R., Lardies, M.A., Lagos, N.A., 2013. CO_2-driven ocean acidification reduces larval feeding efficiency and change food selectivity in the mollusk *Concholepas concholepas*. Journal of Plankton Research. http://dx.doi.org/10.1093/plankt/fbt045.

Weiss, R., 1970. The solubility of nitrogen, oxygen and argon in water and sea water. Deep-Sea Research 17, 721–735.

Yao, W., Millero, F.J., 1995. The chemistry of the anoxic waters in the Framvaren Fjord, Norway. Aquatic Geochemistry 1, 53–88.

Zhang, J., Gilbert, D., Gooday, A.J., Levin, L., Naqvi, S.W.A., Middelburg, J.J., Scranton, M., Ekau, W., Peña, A., Dewitte, B., Oguz, T., Monteiro, P.M.S., Urban, E., Rabalais, N.N., Ittekkot, V., Kemp, W.M., Ulloa, O., Elmgren, R., Escobar-Briones, E., Van der Plas, A.K., 2010. Natural and human-induced hypoxia and consequences for coastal areas: synthesis and future development. Biogeosciences 7, 1443–1467.