Oceanographic Processes Driving Low Oxygen Conditions Inside Patagonian Fjords

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30 Abstract

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The dissolved oxygen (DO) levels of oceanic coastal ocean waters has have decreased over the last decades owing in part because of to the increase in surface and subsurface water temperature caused by climate change, the reduction of ocean ventilation, and the increase in stratification and eutrophication. In addition, biological and human activity in coastal zones, bays, and estuaries has contributed to the acceleration of current oxygen loss. The Patagonian fjord and channel system is one world region where low DO water (LDOW, 30%–60% oxygen saturation) and hypoxia

conditions (<30% oxygen saturation, 2 ml L⁻¹ or 89.2 µmol L⁻¹) is observed. An *in-situ* data set of hydrographic and biogeochemical variables (1507 stations), collected from sporadic oceanographic cruises between 1970 and 2021, was used to evaluate the mechanisms involved in the presence of LDOW and hypoxic conditions in northern Patagonian fjords. Results denoted two main areas with LDOW (e.g., Puyuhuapi Fjord Jacaf channel, Comau Fjord, and the Reloncaví estuarine system) extending from 25 400 m depth. Simultaneously Furthermore, and hypoxia was recorded in the Puyuhuapi Fjord, Jacaf Channel, and Quitralco Fjord. Quitralco registered the lowest values of DO (9.36 µmol L⁺ and 1.6% oxygen saturation) of the entire Patagonian fjord system. Areas of LDOW and hypoxia coincidinged with the accumulation of inorganic nutrients and the. Water mass analysis confirmed the contribution of presence of salty and poor-water Equatorial equatorial subsurface water mass in the advection of the LDOW to only the Puyuhuapi Fjord and Jacaf Channel. In addition, in Puyuhuapi Fjord, hypoxic conditions occurred when the community respiration rate (6.6 g C m⁻²d⁻¹) exceeded the gross primary production estimate (1.9 g C m⁻²d⁻¹) possibly due to the increased consumption of DO during the use of both autochthonous and allochthonous organic matter. -The role of biological activity in oxygen reduction was evident in the dominance of community respiration over gross primary production. This study elucidates the physical and biogeochemical processes contributing to hypoxia and LDOW in the northern Patagonian fjords, highlighting the significance of performing multidisciplinary research and applying of numerical model.—combining observational and modeling work. This approach underscores the importance of a holistic understanding of the subject, encompassing both real-world observations and -insights provided by modeling techniques.

1 Introduction

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Hypoxic conditions and low dissolved oxygen water (LDOW)_have expanded globally over the last decade along coastal waters and oceans (Schmidtko et al., 2017; Breitburg et al., 2018). The origins of the hypoxia and LDOW are attributed to natural and anthropogenic processes. Remineralization of organic matter, weak circulation, extended residence time, and stratification were reported a natural processes (Rabalais et al., 2010; Bianchi et al., 2010). In contrast, water eutrophication was documented as one of the main anthropogenic processes. While hypoxia is mostly attributed to anthropogenic processes, such as eutrophication (Díaz et al., 2001; Conley et al., 2009; Meire et al., 2013)_, LDOW and deoxygenation occurs most prominently in the open ocean as a combination of natural and anthropogenic forcing (Oschlies et al., 2018; Garcon et al., 2019). Therefore, for decades, the scientific community has been paying close attention to this issue because of the expected impacts on the survival, abundance, development, growth, reproduction, and behavior of the most important taxonomic groups at different stages of their life cycles, such as mollusks, crustaceans, and fish (Sampaio et al., 2021, Ekau et al., 2010; Batiuk et al., 2009; Vaquer-Sunyer yand Duarte, 2008; Breitburg et al., 1997; Díaz and Rosenberg, 1995; Andrewartha and Birch, 1986; Davis, 1975), which could also affect all services provided to humans (Laffoley and Baxter, 2019).

Some examples of the impact of LDOW on biological behaviors are changes in the composition of benthic communities in prolonged periods of DO<4.2 ml L⁻¹ (Hoos, 1973); negative impact on the growth and abundance of cod (3.6 ml L⁻¹; 70%), the limit of the distribution of sardine larvae (2.6 ml L⁻¹; 50%), the distribution of jellyfish (1.6 ml L⁻¹; 30%), the decrease of the abundance, swimming capacity and filtration of copepods (0.52 ml L⁻¹; 10%),

described by Ekau et al., (2010). Additionally, oxygen deficiency affects the growth rate and feed conversion efficiency, and in some species, even increases the concentration of toxic substances (Davis, 1975). In a Patagonian fjord used for recreational fishing of rainbow trout (*Salmo gairdneri*), values under 50% saturation caused a reduction in swimming speed (Jones, 1971b) and altered respiration and metabolism (Kutty, 1968a). In the case of coho salmon (*Oncorhynchus kisutch*), a commonly farmed species, a growth rate proportional to the oxygen level was observed for saturations between 40% and 80% (Herrmann, 1958), and the hypoxia modulated the transcriptional immunological response (Martinez et al., 2020). Finally, Pérez–Santos et al. (2018) reported habitat reduction of microzooplankton in a Patagonian fjord (Puyuhuapi Fjord) due to the presence of hypoxic conditions at depths below 100 m.

Throughout the world's oceans, there are areas in which the dissolved oxygen (DO) is significantly lower than in well-oxygenated areas (such as <20 μ M, ~ 0.4 mg L⁻¹, or 0.31 ml L⁻¹ as shown by Breitburg et al., (2018). These areas are known as oxygen minimum zones (OMZs). OMZs result from organic matter degradation, weak water circulation, long residence times, and weak ventilation (Fuenzalida et al., 2009). The major ocean OMZs are located in the Eastern South Pacific, the Arabian Sea, the Bay of Bengal (Indian Ocean), the West Bering Sea, and the Gulf of Alaska, covering approximately 8% of the total ocean or approximately 30 million km² (Paulmier and Ruiz-Pino, 2009; Fuenzalida et al., 2009).

Along the Perú Chile coastline, the Eastern South Pacific (ESP) OMZ extends poleward, decreasing in strength and size to the south near the Patagonian fjord system (Silva et al., 2009) Along the Peru-Chile coastline, the Eastern South Pacific (ESP) Oxygen Minimum Zone (OMZ) extends poleward. As one moves southward, it gradually diminishes in both size and strength until it approaches -the Patagonian fjord system (Silva et al., 2009). Recently, Linford et al. (2023) demonstrated poleward transport of hypoxic and LDOW of the Equatorial Subsurface water mass (ESSW) alongside the Patagonian region. As ESSW (originated in the Equatorial region) moves south, it passes throughout the OMZ, carrying oxygen-poor water (2–3 ml L⁻¹)(89 - 134 μM) with high nitrate concentration (20–30 μM) and elevated salinity (34.9) (Silva et al., 2009). Studies of water masses inside Patagonian fjords and channels have detected the presence of ESSW only in the northern region, between 41° S and 45° S. This water mass enters the northern Patagonia region via the Guafo mouth (Figure 1b), a deep channel with a depth of 150–200 m and width of 35 km (Sievers and Silva, 2008; Pérez-Santos et al., 2014; Schneider et al., 2014). ESSW is one of the main causes of hypoxia and LDOW inside Patagonian fjords (e.g., Puyuhuapi Fjord and Jacaf Channel). Nevertheless, these conditions are also found in other areas where sills block the pass of ESSW, e.g., the Reloncaví system (Reloncaví Fjord and Reloncaví Sound), Aysén, Comau, and Quitralco fjords (Figure 1) (Silva and Vargas, 2014; Linford et al., 2023; Díaz et al., 2023).

Regarding other processes favoring hypoxia and LDOW inside Patagonian fjords, Silva (2008) proposed those biological processes that include the consumption of DO, such as respiration and the remineralization of organic matter. A high load of organic matter (autochthonous and allochthonous) in the water column and sediments increases DO consumption during microbial community respiration, contributing to the LDOW content in most of the Patagonian fjord headwaters (Castillo et al., 2016) as well as higher community respiration rates than primary production (Montero et al., 2011; Montero et al., 2017a). The main contributor to the increase of allochthonous organic matter is the river supplies, mainly during late winter and early spring, owing to the dominance of ice melt over

precipitation during the winter season. The highest river discharges in the region are found in the Puelo, Petrohue, and Cochamo Rivers in the Reloncaví Fjord, the Cisne River in the Puyuhuapi Fjord, and other freshwater contributions from small rivers in the northern Patagonian fjords (Castillo et al., 2016; Schneider et al., 2014). Additionally, weak deep ventilation and long residence times in fjord waters are assumed to promote a reduction in the DO concentration (Schneider et al., 2014; Silva and Vargas, 2014).

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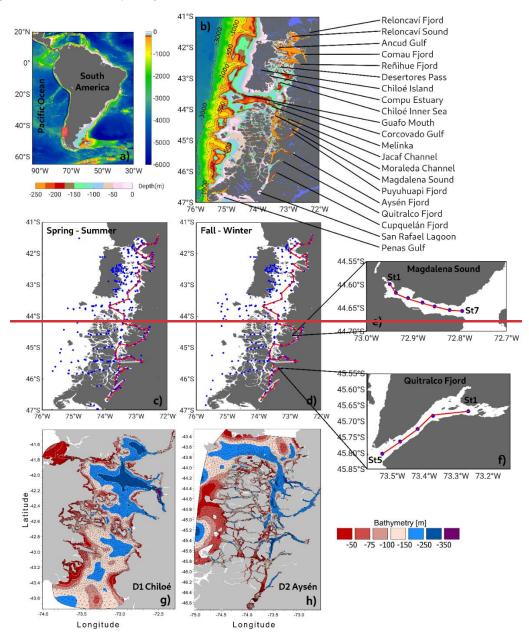
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Weak deep ventilation and long residence times in fjord waters are also assumed to promote a reduction in the DO concentration (Schneider et al., 2014; Silva and Vargas, 2014).

Finally, most published manuscripts hypothesize and discuss the processes favoring hypoxia and LDOW inside Patagonian fjords without showing any evidence, particularly that based on g in situ data and fieldwork experiments. The Patagonian fjords ecosystem is under substantial continued economic pressure due to salmon aquaculture and other economic activities (Billi et al., 2022). The northern Patagonian fjords (Figure 1b, 1c) reported half of the national production and a significant number of salmon concessions (Billi et al., 2022). A risk analysis carried out in this region established that the Reloncaví estuarine system, and the Comau, Puyuhuapi, Quitralco, and Cupquelan fjords are regions with an especially elevated level of risk for the development of harmful algal blooms (HABs) and eutrophication events, owing to the nutrients input by the intense aquaculture of salmon (Soto et al., 2021). Nevertheless, environmental studies on salmon farming have shown that this economic activity has a

geographically limited impact, because most nutrients are quickly recycled by biological processes in the water column (Soto and Norambuena, 2004).



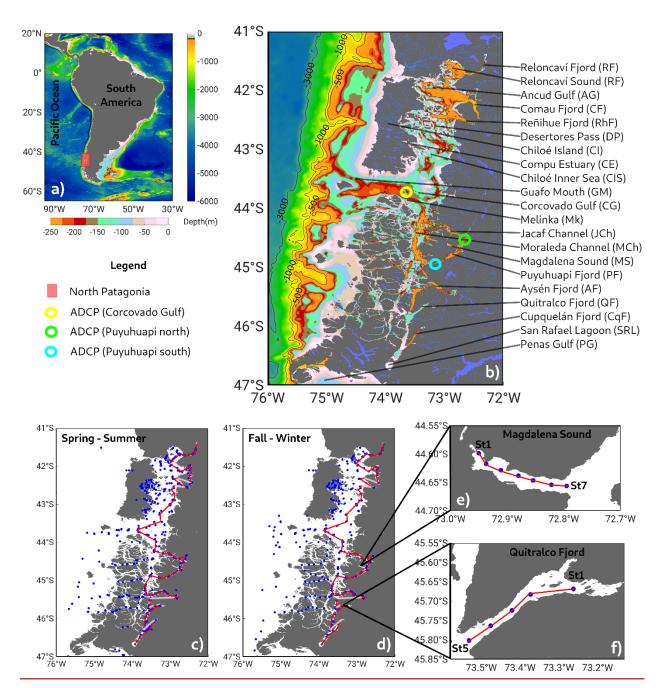


Figure 1. (a) Map showing the study area in the (b) northern region of Patagonian fjords. Color bars represent bathymetric features from ETOPO2. (c, d) Sampling stations during the spring-summer and fall-winter seasons. Red lines in (c, d) represent along-fjord transects <u>carried outused</u> to describe vertical features of hydrographic-chemical stations from Figure 2, 4, and 5. Data was collected on sporadic cruises, from 1970–2021 (see Table 1). (e, f) Details of Magdalena Sound and Quitralco Fjord sampling stations. (g, h) High-resolution model domain includes the northern Patagonia inner sea and is denoted as D1_Chiloé, while D2_Aysén covers the southern section. Bathymetry <u>used</u> was

based on an SHOASHOA (acronym for its Spanish name, Servicio Hidrográfico y Oceanográfico de la Armada de Chile) nautical chart from the Chilean Navy.

Another meaningful impact of salmon production is the increase in allochthonous organic matter load, which, when combined with the high production of autochthonous organic matter by phytoplankton, favors a decrease in DO in the water column and sediments (Quiñones et al., 2019). Salmon farming supplies allochthonous dissolved substrates through the dissolution of organic particles derived from feces and uneaten feed (Wang et al., 2012). This organic material is considered highly degradable (Nimptsch et al., 2015; Montero et al., 2022), promoting enhanced rates of heterotrophic bacterial activity (e.g., bacterial production (BP) and extracellular enzymatic activity (EEA) (Montero et al., 2022).

The main goal of this study was to analyzee the processes contributing to hypoxia and LDOW in northern Patagonia, such as ESSW advection, DO consumption during the use of organic matter (community respiration), biogeochemical processes, deep-water ventilation, and residence times of water inside fjords. A combination of the An in-situ dataset, primary production experiments, and modeling results of -2000 profiles of hydrographic chemical variables was were used to describe the seasonal distribution of water masses and their relationship with biogeochemical processes. Primary production experiments and the output of a 3D hydrodynamic model were utilized to demonstrate the occurrence of other processes promoting low oxygen conditions in the northern Patagonian fjords.

2. Materials and Methods

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2.1 Hydrographic and chemical data

A total of 1507 stations were used to describe northern Patagonia's hydrographical and chemical processes; 593 stations were sampled during the fall-winter seasons and 914 during the spring-summer seasons (Table 1). Most temperature and salinity records were obtained using a CTD (Conductivity, Temperature, and Depth profiler) instrument (e.g., SBE19 plus, SBE15, and AML Metrec XL). When SEBBE CTDs were used, data were processed according to the manufacturer's protocol and software (SBE Data Processing). When using AML CTD, the raw data underwent-a quality control, eliminating records out of range according to historical CTD data (Pérez-Santos et al., 2014; Pérez-Santos et al., 2021; Linford et al., 2023), after which the data were averaged every 1 m. Additionally, membrane and optical sensors (e.g., SBE 43 and Optode 4831) together with the Winkler method have been used to obtain DO data (Strickland and Parsons, 1968). Experiments were conducted to validate the CTD-DO data with the Winkler method showing satisfactory results and high statistical correlation (R² ranging 0.92–0.99, Figure not included).

Figures 1b and 1c show the station positions during fall-winter and spring-summer. The absolute salinity (S_A in gkg⁻¹) and conservative temperature (Θ in °C) were calculated using the Thermodynamic Equation of Seawater 2010 (TEOS-10) (IOC et al., 2010). In TEOS-10, absolute salinity represents the spatial variation in the composition of seawater, considering the different thermodynamic properties and gradients of horizontal density in the open ocean. Conservative temperature is similar to potential temperature but represents the heat content of seawater with greater precision.

A temperature/salinity (TS) diagram was constructed based on the conservative temperature and absolute salinity values, which was used to identify and quantify the water masses in the Patagonian fjords using only the salinity criteria proposed by Sievers (2008) and Sievers and Silva (2008). In Patagonian fjords, the density features of the water column are dominated by the vertical/horizontal distribution of the salinity rather than the water temperature, justifying the use of salinity in the identification of water masses (Aiken 2012; Pérez-Santos et al., 2014). -According to this classification, Estuarine Water (EW, 0-31-4 g kg⁻¹) originates was detected in the surface layer owing to the water supply from rivers and summer time glacier melting. Below the EW, a Modified Subantarctic Water (MSAAW, salinity 31-33 g kg⁻¹) layer is located from the mixing of the EW with the Subantarctic Water (SAAW, salinity 33-33.8 g kg⁻¹). was found, with salinities values ranging 31-33 g kg⁻¹. The MSAAW originated from mixing of the EW and Subantarctic Water (ESSW) layer mass represents was identified, with salinity values higher than 33.8 g kg⁻¹. The ESSW was localized near the bottom of the Puyuhuapi Fjord and Jacaf Channel (Linford et al., 2023).

The long-term seasonal means were calculated using the Data Interpolation Variational Analysis (DIVA) gridding software developed by the University of Liege (http://modb.oce.ulg.ac.be/mediawiki/index.php/DIVA). The DIVA software was used to analyze and interpolate datasets via an optimal interpolation method, which considers the coastline and bathymetry of the study area; the calculations were executed on a finite element mesh adapted to the study area gridding domains (Troupin et al., 2010). Additionally, the DIVA results were graphically displayed using the Ocean Data View software (https://odv.awi.de).

 Table 1. Oceanographic campaigns carried out in Patagonian fjords and channels.

Expeditions	Date	Season	Stations	Measurements
HUDSON	06/03-01/04, 1970	Summer	112	(Temperature, Salinity)* + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-01	18/10-04/11, 1995	Spring	99	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, NO2, Si; bottle) + pH(bottle)
CIMAR-04-I	28/09-09/10, 1998	Spring	31	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-07-I	07-21/07/2001	Winter	49	CTD + O2(bottle-Winkler)
CIMAR-07-II	13-25/11/2001	Spring	51	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-08-I	06-20/07/2002	Winter	51	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-08-II	16-24/11/2002	Spring	39	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-09-I	09-23/08/2003	Winter	58	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-09-II	07-20/11/2003	Spring	55	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-10-I	26/06-31/08, 2004	Winter	49	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-10-II	12-23/11/2004	Spring	63	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-11-I	18-25/07/2005	Winter	78	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-11-II	11-21/11/2005	Spring	80	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)
CIMAR-12-I	10-19/07/2006	Winter	32	CTD + O2(bottle-Winkler) +Nutrients (PO4, NO3, Si; bottle)
CIMAR-12-II	04-12/11/2006	Spring	40	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)

CIMAR-13-I	27/07-07/08, 2007	Winter	42	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)		
CIMAR-13-II	02-12/11/2007	Spring	46	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)		
CIMAR-17	17/10-14/11, 2011	Spring Fall-	195	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)		
CIMAR-18	01/06-04/07, 2012	Winter	98	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)		
CIMAR-19	04-16/07/2013	Winter	70	CTD + O2(bottle-Winkler) + Nutrients (PO4, NO3, Si; bottle)		
CHEPU-IFOP	05-17/08/2017	Winter	22	CTD + O2(optic)		
CIMAR-24	26/09-16/10, 2018	Spring	37	CTD + O2(bottle-Winkler) + Nutrients (NO3; bottle)		
CHEPU-MR-I	06-08/06/2018	Fall	12	CTD + O2(optic)		
CHEPU-MR-II	11/10/2018	Spring	2	CTD + O2(optic)		
PN-I (IFOP)	13-25/11/2020	Spring	32	$CTD + O2(optic) + Nutrients \ (PO4, NO3, NO2, Si; bottle) + pH, Tur, Fluor \ (optic)$		
PN-II (IFOP)	24/02-04/03, 2021	Summer	32	$CTD + O2(optic) + Nutrients \ (PO4, NO3, NO2, Si; bottle) + pH, Chl-a, Tur, Fluor \ (optic)$		
PN-III (IFOP)	28/07-10/08, 2021	Winter	32	$CTD + O2(optic) + Nutrients \ (PO4, NO3, NO2, Si; bottle) + pH, Chl-a, Tur, \ Fluor \ (optic)$		
593 Fall-Winter + 914 Spring-Summer = 1507 stations						

^{*}Temperature and salinity were measured with a reversing thermometer and inductive salinometer respectively.

2.2 Primary production, community respiration, bacterial production, and phytoplankton community.

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During the spring-summer period of 2020–2021 and summer of 2022, nine *in situ* experiments were conducted to measure gross primary production (GPP) and community respiration (CR) in some fjords of northern Patagonia (Table 2). Water samples were obtained from three depths (2, 10, and 20 m depth) at each sampling station. GPP and CR rates were estimated from changes in dissolved oxygen (DO) concentrations observed during *in situ* incubation of light and dark bottles (Strickland, 1960). Water from the Niskin bottles was transferred into 125 mL (nominal volume) borosilicate bottles (gravimetrically calibrated) using a silicone tube. Five time-zero bottles, five light bottles, and five dark bottles were used at each incubation depth. Water samples were collected at dawn and incubated throughout the entire light period (approximately —8—9 h). Time-zero bottles were fixed at the beginning of each experiment, whereas the light and dark incubation bottles were attached to the surface-tethered mooring system. The samples were incubated at the depths from which they were collected. Additionally, we presented GPP and CR values from February 2009 in Figure 9, which have been previously published by Montero et al. (2011).

Dissolved oxygen concentrations were determined according to the Winkler method (Strickland and Parsons, 1968), using an automatic Metrohom burette (Dosimat plus 865) and automatic end-point detection (AULOX Measurement System). Daily GPP and CR rates were calculated as follows: $GPP = (mean [O_2] light bottles - mean [O_2] dark bottles)$; $CR = (mean [O_2] time zero bottles - mean [O_2] dark bottles)$. The GPP and CR values were converted from oxygen to carbon units using a conservative photosynthetic quotient of 1.25 (Williams and Robertson, 1991) and a respiratory quotient of 1.

A total of five bacterial production (BP) experiments were performed during the same period as mentioned above (Table 2). Experiments were conducted using the same water samples collected for the *in situ* GPP and CR incubation experiments. The BP estimates were based on the incorporation of leucine into proteins using the microcentrifugation method (Smith and Azam, 1992). Briefly, a blank and three samples (1.5 mL) were taken from

each sampling depth and incubated with L-[3,4,5-³H]-leucine (123.8 Ci mmol⁻¹, 40 nM final concentration) in the dark for 1 h. After incubation, samples were extracted with 100% trichloroacetic acid (TCA), rinsed with 5% TCA, and centrifuged at 13500 rpm twice for 15 min before removal of the supernatant. Liquid scintillation cocktail Ecoscint (1 mL) (National Diagnostic) was added to each sample. The samples were counted for dpm using a Packard (Mod. 1600 TR) liquid scintillation counter. Discrete depth estimates of the GPP, CR, and BS rates were integrated to 20 m using the trapezoidal method.

For analyses of the phytoplankton community, water samples were collected from four discrete depths (2, 4, 10, and 20 m) using a 5 L Niskin bottle. Samples were stored in 120 mL clear plastic bottles and preserved in 1% Lugol's iodine solution (alkaline). From each sample, a 10 mL subsample was placed in a sedimentation chamber and allowed to settle for 12 h (Utermöhl, 1958) prior to identification at 40× and 100× under an inverted microscope (Carl Zeiss, Axio Observer A.1). Finally, taxonomic descriptions from Tomas (1997) were used to identify phytoplankton composition.

Table 2. *In situ* experiments were carried out in Patagonian fjords and channels. Gross primary production (GPP), community respiration (CR), and bacterial secondary production (BSP) from in situ experiments in northern Patagonian fjords and channels.

Fjord region	Date	Season	Measurements			
	(mm-dd-yyyy)		$(g C m^{-2}d^{-1})$			
			GPP	CR	BSP	GPP:CR
*Reloncaví	02/27/2009	Summer	3.83	3.31	-	1.16
Compu	10/03/2020	Spring	1.22	0.92	0.06	1.32
Quitralco	11/17/2020	Spring	1.41	2.66	0.05	0.53
Camou	12/12/2020	Spring	0.12	1.67	0.15	0.07
Puyuhuapi	01/21/2020	Summer	1.89	6.64	0.25	0.28
Reloncaví	01/14/2021	Summer	2.60	1.90	0.58	1.37
Compu	03/19/2022	Summer	1.25	0.76	-	1.64
Quitralco	02/28/2022	Summer	0.73	1.71	-	0.42
Camou	03/16/2022	Summer	0.56	1.12	-	0.50
Puyuhuapi	01/20/2022	Summer	2.18	2.55	=	0.85

^{*}Data were taken from Montero et al. (2011).

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2.3 Biogeochemical variables and analysis

Biogeochemical-variable datas were collected in November 2020 (Expedition PN-I IFOP, Table 1). The water samples were obtained by filtering seawater collected (1–2 L) using a 25-mm diameter, GF/F filter pre-combusted with a 0.7 μ m pore diameter. Suspended particulate matter (SPM, μ g L⁻¹), was determined by gravimetry using the weight difference between the dried filter and the same filter before filtration (Grasshoff et al., 2009). Particulate organic carbon (POC, μ mol L⁻¹), total nitrogen (TN, μ mol L⁻¹), stables carbon (δ ¹³C, %) and nitrogen (δ ¹⁵N, %) isotopes were obtained following the method described by Verardo et al., (1990), with modifications by Barrera et al., (2017) and Díaz et al., (2023), and measured at the Stable Isotope Facility at the Pontifical Catholic University of

245 Chile by using an elemental analyzer (EA Flash 2000 Thermo Finnigan), interfaced to a continuous flow isotope ratio mass spectrometer (IRMS Delta V Advantage).

The stable carbon isotope composition of organic carbon (δ^{13} C) can vary depending on its origin, with values ranging from -23 to -19% for carbon sources such as marine phytoplankton (Fry and Sherr, 1989; Harmelin-Vivien et al., 2008) and values closer to those of terrestrial organic matter (-30 to -26%) for other sources (Fry and Sherr, 1989). By analyzing the carbon isotopic composition of organic carbon, it is possible to differentiate carbon between different sources and estimate their contributions. We calculated the relative importance of allochthonous and autochthonous organic matter with two-source endmember mixing models (Bianchi, 2007). The importance of autochthonous marine and allochthonous terrestrial fractions were was calculated based on the following equation:

$$\%POC_{allo} = \frac{(\delta^{13}C_s - \delta^{13}C_m)}{(\delta^{13}C_t - \delta^{13}C_m)} 100\%$$

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where $\delta^{13}C_s$ is the isotopic composition of a sample, $\delta^{13}C_m$ is the marine endmember from more oceanic stations (-13.447 %), and $\delta^{13}C_t$ terrestrial is the riverine/lake endmember values for POC (-42.933 %) as proposed for this area by González et al., (2019). The resulting %POC_{allo}, represents the relative contribution of allochthonous (terrestrial) organic carbon to the overall organic carbon pool. Higher values indicate a more significant influence of terrestrial organic carbon, while lower values suggest a higher proportion of autochthonous (marine) organic carbon (González et al., 2019). The carbon: nitrogen ratio was also calculated as a proxy for the organic matter pool (Barrera et al., 2017).

Dissolved inorganic nutrients (NO₃⁻, NO₂⁻, PO₄³⁻, and Si(OH)₄) were analyzed from 15 mL seawater samples, stored at -20 °C in HDPE bottles, using a Seal AA3 Autoanalyzer according to the methodology described by Grasshoff et al., (1983) and standard methods for seawater analysis (Kattner and Becker, 1991). Chromophoric Dissolved Organic Matter (CDOM) plays a crucial role in understanding the optical properties and biogeochemical processes in aquatic ecosystems (Stedmon and Nelson, 2015). It is an important component of dissolved organic matter (DOM) that absorbs light in the visible spectrum (ultraviolet and blue wavelengths) and fluoresces at longer wavelengths (Stedmon and Nelson, 2015). CDOM was determined by fluorometry using quinine sulfate dihydrate (μgL⁻¹ QSU) diluted in 0.1 N sulfuric acid at a specific wavelength (Ex/Em = 350/450 nm) as standard in a Trilogy Turner Design fluorometer and CDOM module (Kim et al., 2018).

2.4 Satellite images

Sentinel-2 level 1 images were downloaded from the Copernicus Open Access Hub (https://scihub.copernicus.eu/) for specific dates and regions, as shown in Table 3. The chosen dates correspond to periods of high discharge of freshwater from the continent. Using ACOLITE v 20220222.0 (https://odnature.naturalsciences.be/remsem/software-and-data/acolite, (Vanhellemont and Rudick, 2018), we calculated the satellite suspended particulate matter (SSPM) following Nechad et al. (2016). These data have a spatial resolution of 10 m and allow the resolution of the small-scale distribution of suspended particulate matter SSPM within the narrow channels and fjords of the region.

Table 3. Dates and regions of the Sentinel-2 datasets analyzed.

Date	Region
17 March 2017	Puyuhuapi Fjord
09 May 2017	Reloncaví Sound and Fjord
06 April 2018	Comau Fjord
09 June 2022	Quitralco Fjord

2.5 Marine current registered with ADCP

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In the study region, three mooring systems were deployed in the Corcovado Gulf and Puyuhuapi Fjord. In each mooring, a Teledyne RD Instruments (TRDI) and a WorkHorse-300 kHz Acoustic Doppler Current Profiler (ADCP) were installed with the transducers facing downward. The instruments were configured with 1-m cell size and 1 h ensembles. The moorings covered the period from January to December 2016, with the ADCP sensors moored between 40 and 100 m. The ADCP provides the current magnitude and direction (in Earth coordinates); thus, the current vector is decomposed into zonal (u) and meridional (v) components. The basic and standard protocol of quality control was applied to identify outliers and low-quality data following the methodology suggested by TRDI. To obtain the mean pattern of the zonal and meridional components of the currents, they were filtered using a low-pass cosine-Lanzcos filter of 121 weight and 40 h half-power.

The currents were rotated following the main axis of the Guafo channel and Puyuhuapi Fjord (Figure 1), thus implying that in Guafo, currents were rotated 14° south of east whereas in Puyuhuapi south currents were rotated 36° north of the east and in Puyuhuapi north the axis was rotated 22° east of north. Following those rotations, the contours of the time series of the along-channel/fjord components are shown in Figure 11.

2.6 Circulation model

To gain a better understanding of the physical forcing related to the DO dynamics, we used the hydrodynamic model MIKE 3 FM), which solves continuity, momentum, temperature, and salinity transport equations using the finite volume method (DHI, 2019). In this study, two high resolution model domains include the North Patagonian inner sea named D1_Chiloé (41.3° S - 43.7° S) and D2_Aysén, with an area from 43.6°S to 46.8° S (Figures 1d, 1e). The MIKE 3 model, maintaining the same configuration, has a track record of previous validation and application to investigate the physical aspects of HABs (Díaz et al., 2021, Mardones et al., 2021) as well as other oceanographic processes (Pérez Santos et al., 2021, Soto Riquelme et al. 2023). It has also been utilized for studying sub domains within this Patagonian region (Pinilla et al., 2020; Díaz et al., 2021).

The time frame for the modeling process extended over six years, from 2016 to 2021. The use of two overlapping domains, specifically D1_Chiloe and D2_Aysen was influenced by computational capacity, resulting in a staggered development over time, from 2016 onwards. Initially, the D1_Chiloe domain was developed, followed by the D2_Aysen domain. The model configuration for both domains assumes a hydrostatic variant of the MIKE 3 model, with vertical discretization executed via hybrid coordinates: surface based sigma coordinates and z level coordinates in the bottom layers. The model included 55 layers for D1_Chiloe and 40 layers for D2_Aysen, which were utilized to accurately depict stratification, focusing on the highest resolution in the upper water column (approximating ~ 1m near the surface). Horizontal eddy viscosity was characterized using the Smagorinsky model (Smagorinsky, 1963), while the vertical viscosity was incorporated through the κ c turbulence scheme, which solves the transport equations

for both turbulent kinetic energy (κ) and turbulent dissipation rate (ε) (Rodi, 1984). Bathymetry was based on SHOA nautical chart soundings (horizontal resolution of 500 meters), and a digital elevation model was constructed using the natural neighbor method (Sibson, 1981). This domain was discretized using triangular elements of different sizes. The highest resolution was observed in coastal, narrow, and shallow areas, with an average element size of ~300 m, whereas the spatial resolution near the boundary was ~1000 m.

Atmospheric forcings, such as wind stress and heat fluxes over the sea surface, were introduced using spatially and temporally varying fields from the Weather Research and Forecasting (WRF) atmospheric model (Skamarock et al., 2008), development by Instituto Fomento Pesquero (IFOP), named in this manuscript as WRF IFOP. The WRF IFOP model, with its superior spatial resolution of 3 km compared to global models, enables a more accurate representation of the complex fjord topography. The performance of the WRF IFOP model was evaluated as described by Pinilla et al. (2020). Soto Riquelme et al. (2023) evaluated the performance of the WRF IFOP model near the Guafo Mouth and confirmed its effective correlation with meteorological stations in at area. Notably, their results revealed a high correlation with atmospheric pressure (R=0.99), accompanied by significant correlations for wind direction: R=0.81 for the east west component and a more robust correlation of R=0.94 for the north south component (Soto Riquelme et al., 2023).

Freshwater sources were identified through the FLOW IFOP hydrological model, which employs precipitation and temperature—series—data—from—the—CR2MET—(Climate—Resilience—2—Meteorological)—gridded—product (http://www.cr2.cl/datos productos grillados/). Using this data, characterized by a spatial resolution of 5 × 5 km, enables the simulation of runoff and the calculation of daily discharge series. Based on FLOW IFOP estimates, the average annual freshwater discharge entering the D1_Chiloé domain during the 2016—2021 period was approximately 2545 m³-s¹-, while for the D2_Aysén domain, it was approximately 3126 m³-s¹-. The performance of the FLOW IFOP model at the gauged river stations of the Chilean Water Authority can be accessed at http://chonos.ifop.cl/flow/. Furthermore, the correlations for the three main rivers in these regions—Puelo, Palena, and Aysén, Table S1, Fig. S1 were found to be 0.88, 0.76, and 0.87 respectively (see Fig. S2 in the supplementary material).

The water levels at the open boundary were set using harmonic analysis (Pawlowicz et al., 2002), based on a regional barotropic model data (Pinilla et al., 2012). The performance of water levels at seven locations (Table S1, Fig. S1) is presented as supplementary material (Table S2, Figure S3). The results demonstrate robust correlations between the sea level at different stations, with minimum correlations ranging from 0.93 to 0.97 (Table S2). Additionally, they exhibited an appropriate amplification of amplitude particularly in the northern area of this domain (Puerto Montt and Comau fjord) (Figure S3).

The flow data at the boundaries were set to zero in our hydrodynamics model, leading to internal balance in the current dynamics within the model domain across both spatial and temporal scales. The performance of the current data within the models contrasted with the ADCP data from different mooring points (Figure S1, Table S1), as shown in the supplementary material (Figures S4 and S5). The hydrodynamic model current was evaluated against the current velocities gathered by the ADCP. An empirical orthogonal function analysis (Thomson and Emery, 2014) was performed on the currents (both observed and modeled) to discern if the model could accurately depict the dominant

modes of variability identified with the observations. Similar analyses have been previously performed to assess the suitability of hydrodynamic models in Patagonia (Pinilla et al., 2020, Soto Riquelme et al., 2023).

Mode 1 plus Mode 2 accounted for over 95% of the variance in the model, whereas they accounted for approximately 86% of it in the observations, except in the Quitralco fjord, with a 77% variance observed in the model and 62% in the ADCP (Figure S4). The distribution of these percentages of variance between the model and the ADCP was correlated with an R-value of 0.96, as shown in Figure S5, which highlights the distinctiveness of the Quitralco fjord. On the other hand, the spatial vertical structures of Modes 1 and 2 between the model and the ADCP data were identical, generally showing agreement in barotropic structures, two layer baroclinic structures, and even three layer structures, as observed in the Quitralco fjord (Figure S4). Though the model is not without flaws, our analysis suggests an agreement between the modes of variability, further implying a proficiency of the model in representing the processes vital to water transport in different locations.

The temperature and salinity boundary conditions were derived from CTD profiles obtained during CIMAR FIORDOS oceanographic cruises (Guzman and Silva 2002; Silva and Guerra 2004; Valdenegro and Silva 2003; Carrasco and Silva 2010). The performance of temperature time series and salinity fields within the model are presented as Supplementary Material. The model demonstrated commendable alignment in replicating the annual temperature cycle at various depths and locations (Table S1, Figure S1), generally exhibiting R values above 0.78. An exception was observed in the Moraleda Channel at a depth of 120 m, where a lower R value (0.28) was recorded (Figures S6 and S7).

To assess the water masses present within the fjords, salinity was employed as a key parameter. High salinity waters (>33.5 g kg⁻¹), associated with SAAW and ESSW ocean masses, enter the deep layer of the Guafo mouth, traverse the Corcovado Gulf, and end their journey in the deep layers of the Puyuhuapi Fjord and Jacaf Channel. A reduction in salinity, indicative of Estuarine Water (EW), is also observed due to the melting of ice from the San Rafael Lagoon. The model's task was to accurately depict the arrival of specific salinity categories inside the fjords and channels (see Figure S8 in the Supplementary Material). Although the 34 g kg⁻¹ isohaline is not visually present within the model domains, we believe the model successfully replicates the spatial structure, which suggests that the processes controlling salinity transport within the fjords were successfully incorporated. While the model may not perfectly replicate these processes, it does allow us to understand the fundamental physical transport mechanisms at play.

The MIKE 3 FM hydrodynamic model data were used to calculate the flushing time via a conservative tracer. According to Takeoka (1984) and Monsen et al. (2002), flushing time is defined as the time required for the total mass of a material within a specific area such as a fjord, sound, or bay to be reduced by a factor of e⁻¹ (approximately 37%) (Prandle, 1984). The interior and exterior of the area were assigned initial concentration values of 1 and 0, respectively. Over the course of the simulation, the original water mass of the basin was incrementally replaced with inputs from open boundaries and rivers. This variable symbolizes the proportion of original water in each element within the area of interest at a given time, thereby, facilitating the identification of less flushed areas within the modeled basins (Andrejev et al., 2004). The final values were derived from a temporal average from 2016 to 2021, and a vertical average was calculated from 50 m to the bottom, which represents the area that typically displays the lowest oxygen

values. In the present study, the flushing time was implemented in the Ecolab module of the MIKE 3 FM for every fjord within D1_Chiloé and D2_Aysén.

The MIKE 3 FM hydrodynamic model data was utilized in calculating the flushing time via a conservative tracer. According to Takeoka (1984) and Monsen (2002), flushing time is defined as the time required for the total mass of a material within a specified area—such as a fjord, sound, bay, etc.—to be reduced by a factor of e⁺ (approximately 37%) (Prandle, 1984). The interior and exterior of the area were assigned initial concentration values of 1 and 0 respectively. Over the course of the simulation, the original basin's water mass was incrementally replaced with inputs from open boundaries and rivers. This variable symbolizes the proportion of the original water in each element within the area of interest at a given time, thereby facilitating the identification of less flushed areas within the modeled basins (Andrejev et al., 2004). Furthermore, the final values are derived from a temporal average from 2016 to 2021 and a vertical average was calculated from 50m to the seabed—the zone typically displaying the lowest oxygen values. In the present study, the flushing time was implemented in the Ecolab module of the MIKE 3 FM for every fjord within D1. Chiloé and D2. Aysén.

2.6 Circulation model

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To enhance our understanding of the DO dynamics' and physical factors, we utilized the MIKE 3 FM hydrodynamic model. This model employs the finite volume method to solve continuity, momentum, temperature, and salinity transport equations (DHI, 2019). This study focuses on two high-resolution model domains: D1_Chiloé (41.3° S to 43.7° S) and D2 Aysén (43.6°S to 46.8° S) (Figures S1a, S1b).

The D1_Chiloe and D2_Aysen models are part of the 'CHONOS' Initiative (Reche et al. 2021), available at chonos.ifop.cl. This platform offers an open-access oceanographic database, primarily tailored for environmental applications. Led by the Instituto de Fomento Pesquero (IFOP) and supported by the Undersecretariat for Fisheries and Aquaculture of the Chilean Government, this system guides decisions concerning aquaculture in southern Chile. Moreover, this oceanographic database, grounded in the D1 and D2 domains, has been used in studies on harmful algal blooms (Mardones et al. 2021; Diaz et al., 2021), larval fish dispersion (Landaeta, 2023), and overarching marine circulation dynamics (Soto Riquelme et al. 2023; Perez Santo et al. 2019). -The modeling process was conducted over a period of six years, from 2016 to 2021. Owing to computational constraints, the development began with the D1_Chiloe domain, subsequently followed by D2_Aysen. Both domains employed a hydrostatic variant of the MIKE 3 model. Vertical discretization was implemented using hybrid coordinates, combining sigma and z-level systems. The bathymetry was sourced from the Nautical chart soundings provided by the Chilean Navy (www.shoa.cl).

For atmospheric forcing, we used the Weather Research and Forecasting (WRF) model from the 'CHONOS' Initiative. This version provides a refined 3-km spatial resolution, tailored for the complex topography of the fjords. Its efficacy was previously described by Soto-Riquelme et al. (2023), who specifically evaluated its performance near the Guafo Mouth, finding significant correlations with local meteorological stations, especially particulary in atmospheric pressure (R=0.99) and wind (R=0.87).

Freshwater sources were identified through the FLOW-IFOP hydrological model, which employs precipitation and temperature series data from the CR2MET gridded product (http://www.cr2.cl/datos-productos-

grillados/). Using these data, characterized by a spatial resolution of 5 × 5 km, enables the simulation of runoff and the calculation of daily discharge series. Based on FLOW-IFOP estimates, the average annual freshwater discharge entering the D1 Chiloé domain during the 2016–2021 period was approximately 2545 m³ s⁻¹¬. Conversely, while for the D2 Aysén domain, it was approximately 3126 m³ s⁻¹. The performance of the FLOW-IFOP model at the gauged river stations of the Chilean Water Authority can be accessed at http://chonos.ifop.cl/flow/ and in the Supplementary Material.

Water levels at the open boundary were established using harmonic analysis (Pawlowicz et al., 2002), based on data from a regional barotropic model (Pinilla et al., 2012). TFor temperature and salinity boundary conditions were compiled from CTD profiles, collected during the CIMAR FIORDOS oceanographic cruises (Guzman and Silva 2002; Silva and Guerra 2004; Valdenegro and Silva 2003; Carrasco and Silva 2010). Finally, boundary flow data wasere set to zero, ensuring an internal balance of current dynamics within the model domain over-both temporally and spatially. both time and space.

For an in-depth understanding of the configuration and model validation, kindly refer to the Supplementary Material (Figures S1–S8).

2.7 Flushing time calculation

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The MIKE 3 FM hydrodynamic model data were used to calculate the flushing time via a conservative tracer. According to Takeoka (1984) and Monsen et al. (2002), flushing time is defined as the time required for the total mass of a material within a specific area such as a fjord, sound, or bay to be reduced by a factor of e⁻¹ (approximately 37%) (Prandle, 1984). The interior and exterior of the area were assigned initial concentration values of 1 and 0, respectively. ThroughtoutOver the course of the simulation, the original water mass of the basin was incrementally replaced with inputs from open boundaries and rivers. This variable symbolizes the proportion of original water in each element within the area of interest at a given time, thereby, facilitating the identification of less flushed areas within the modeled basins (Andrejev et al., 2004). The final values were derived from a temporal average from 2016 to 2021, and a vertical average was calculated from 50 m to the bottom, which represents the area that typically displays the lowest oxygen values. In the present study, the flushing time was implemented in the Ecolab module of the MIKE 3 FM for every fjord within D1_Chiloé and D2_Aysén.

3 Results

3.1. Long-term annual mean of hydrographic-chemical parameters

The long-term annual means include all data sets presented in Figures 2a and 2b (location and detailed information are presented in Figures 1c,d and Table 1). This section scrutinizes the behavior of conservative temperature, absolute salinity, DO, and inorganic nutrients. The long-term seasonal mean of conservative temperature (CT) denoted warmer water in the northern region $(41.5^{\circ}-43^{\circ} \text{ S})$ during both seasons, between the Desertores Pass and the Reloncaví Fjord (Figure 2c-d). In contrast, cold waters were observed in the deep layer of the Puyuhuapi Fjord and Jacaf Channel, but colderand the coldest water was registered in San Rafael Lagoon. This location also had the lowest absolute salinity $(S_A=15-21 \text{ gkg}^{-1})$, indicating the presence of EW owing to the contribution of the ice melting

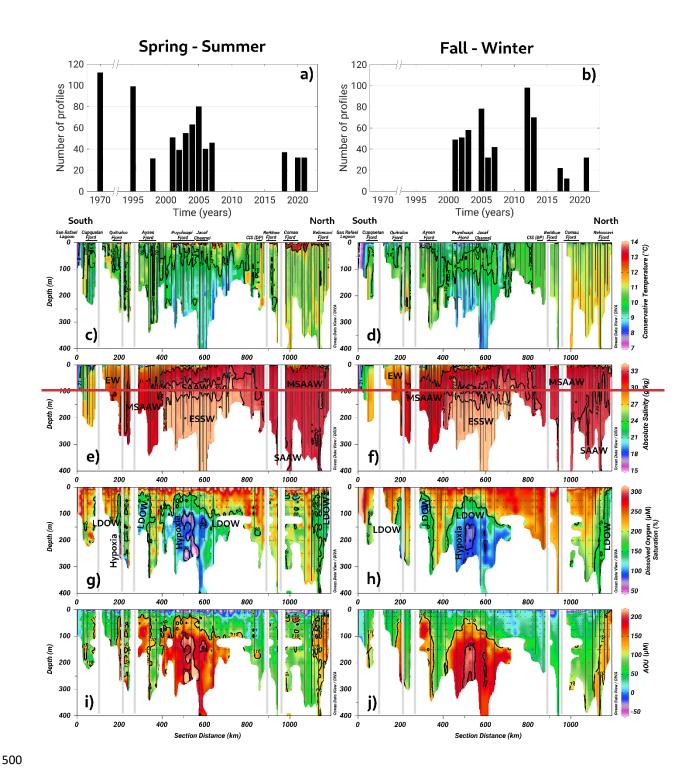
from the San Rafael Lagoon and rivers discharges (Figure 2e-f). In this area, EW moved from south to north and mixed with the SAAW, contributing to the origin of the MSAAW, as was observed in the vertical-horizontal salinity distribution. Moreover, EW was also observed in the northern domain of the study area, especially at the surface layer in the Reloncaví system and the Comau and Reñihue fjords, contributing to the formation of the MSAAW. In this region, the origin of EW was mainly attributed to the freshwater supply from river discharge. We identified two different sources favoring the presence of EW and formation of the MSAAW Therefore, we identified two different sources of EW that led to the formation of the MSAAW: 1) The combination of ice melting from the San Rafael Lagoon with river discharge in the southern region and 2) the freshwater supply by river discharge in the northern region. Both sources contributed to the difference in conservative temperature observed in the MSAAW.

Finally, ESSW enters the deep layer of the Guafo mouth, crosses the Corcovado Gulf, and ends its travel at the deep layers of the Puyuhuapi Fjord and Jacaf Channel. During the fall-winter season, a slight reduction in ESSW distribution was observed (Figure 2e–2f). In the area contained by the ESSW, low DO (LDOW) and hypoxic waters were observed, but LDOW was registered at Reloncaví Fjord, where ESSW was not observed (Figure 2g–h).

In general, the Chiloé Inner Sea showed a homogenized water column, mainly during the fall-winter seasons, in which high DO values (267–312 μmol L⁻¹) and oversaturated waters (DO Saturation >< 100% DO Saturation) were registered. In addition, high DO records were measured in the San Rafael Lagoon, between the Aysén and Puyuhuapi fjords, and in the Corcovado Gulf (Figure 2g-h). Additionally, more extensions of the hypoxic conditions and LDOW were registered during the spring summer seasons Furthermore, a larger area with hypoxic conditions and LDOW was recorded during the spring-summer seasons (Figure 2g-2h) compared to the autumn-winter period. (Figure 2g-2h). Apparent oxygen utilization showed higher values (2-200 μmol kg⁻¹) in areas where LDOW and hypoxia were detected (Figure 2i i).

Table 4 details the statistical characteristics of the water masses identified in this study. Furthermore, Figure 3 shows a TS diagram representing the quantification of water masses, which highlights the dominance of the MSAAW, with 60.96% and 54.67% proportions during the spring summer and fall winter seasons, respectively. The SAAW was the second dominant water mass, with 15.25% and 22.64% proportions, followed by the EW. Finally, the ESSW showed the smallest proportion, with 10.77% and 11.15% values. The ESSW was generally characterized by cold, salty, and poor DO water when compared to those of the EW, MSAAW, and SAAW (Table 4 and Figure 3).

The quantification of water masses through a TS diagram (Figure 3) highlights the dominance of the MSAAW, with proportions of 60.96% and 54.67% during the spring-summer and fall-winter seasons, respectively. Following closely, the SAAW was the second dominant water mass, with proportions of 15.25% and 22.64%. The EW came next, and finally, the ESSW displayed the smallest proportion, with values of 10.77% and 11.15%. It¹ is worth noting that ESSW was-generally characterized by cold, salty, and poor dissolved oxygen (DO) content in comparison to the EW, MSAAW, and SAAW, as detailed in Table 4.



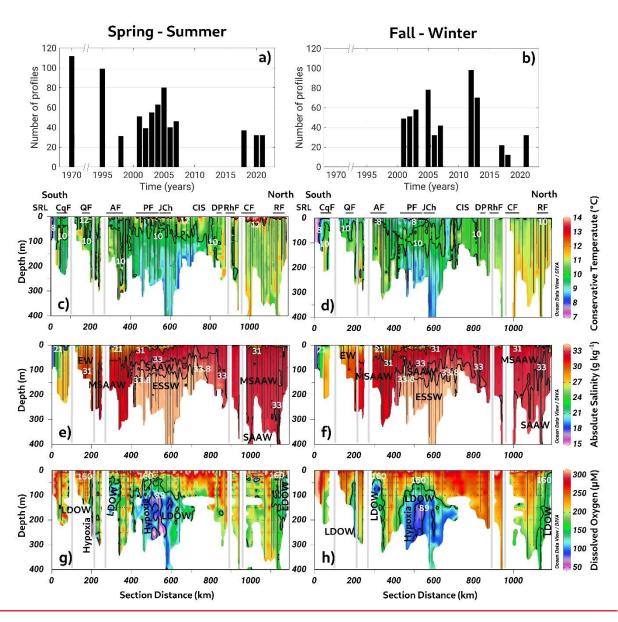


Figure 2. (a, b) Time series of <u>conductivity</u>, <u>temperature</u>, <u>and depth (CTD)</u> profiles used to compute seasonal averages. Long-term seasonal means of (a_-b) conservative temperature, (c_-d) absolute salinity, and (e_-f) dissolved oxygen collected along a vertical section in the northern Patagonian fjord during the fall-winter and spring-summer seasons. See Figure 1b for the acronymous in (c) and (d).

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Table 4. Statistical characteristics of the water masses identified in the northern Patagonian fjords.

Salinity criteria		Spring-Summer				Fall-Winter			
(Sievers and Silva,		Campaigns				Campaigns			
2008)									
	Salinity	Water	CT <u>(°C)</u>	$S_A (g kg^{-1})$	DO	Water	CT <u>(°C)</u>	$S_A (g kg^{-1})$	DO
Water	range	masses	Mean	Mean	(µmol L ⁻¹)	masses	Mean	Mean	(µmol L ⁻¹)
masses	$(g kg^{-1})$	(%)	Stda	Std	Mean-Std	(%)	Std	Std	Mean-Std
EW	0-31	12.64	10.29	27.92	245.25	11.92	9.70	28.75	238.02
			± 1.1	±4.7	± 65.8		± 0.8	±3.4	± 56.8
MSAAW	31-33	60.96	10.64	32.44	197.11	54.67	10.55	32.34	231.82
			± 0.5	± 0.5	± 46.2		± 0.6	± 0.5	± 37.6
SAAW	33-33.8	15.25	10.49	33.25	196.03	22.64	10.85	33.19	208.34
			± 0.6	± 0.2	±41.9		± 0.6	±0.2	± 46.1
ESSW	33.8>	11.15	9.12	34.11	109.57	10.77	9.27	34.13	114.77
			± 0.4	±0.1	±32.6		±0.5	±0.1	±36.0

^aStd: standard deviation.

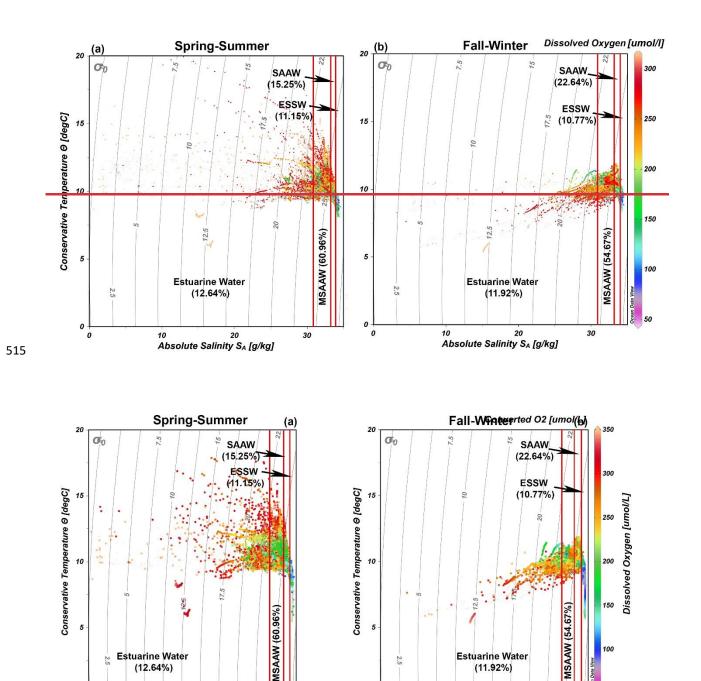


Figure 3. Temperature/salinity (TS) diagram with dissolved oxygen records showing the representation of water masses identified during (a) spring-summer and (b) fall-winter seasons in the northern Patagonian fjords. The dataset utilized in the TS diagram is described in Table 1.

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Absolute Salinity SA [g/kg]

10 20 Absolute Salinity S_A [g/kg]

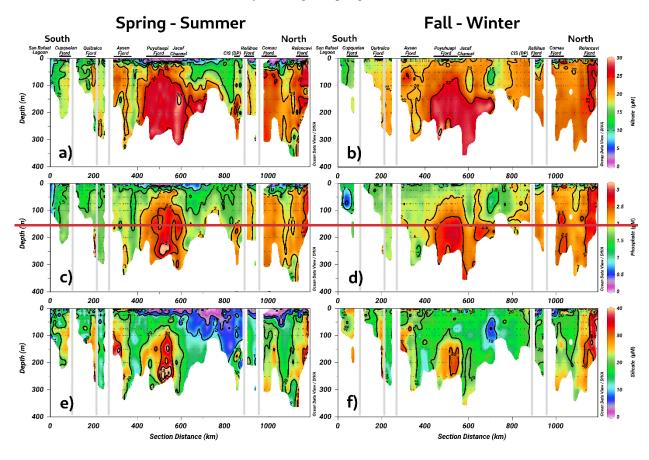
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As <u>previously</u> shown in Fig. 2, the Puyuhuapi Fjord and Jacaf Channel were regions where high-salinity and hypoxic-LDOW waters were registered. In addition, a high concentration of inorganic nutrients was observed in the subsurface layer at a depth of 50 mt at depths greater than 50 m (Figure 4). In the Puyuhuapi Fjord and the Jacaf

Channel, between 100-300 m depth, nitrate (Figure 4a), phosphate (Figure 4c), and silicic acid (Figure 4e) range from $25-30~\mu M$, $2-3~\mu M$, and $30-50~\mu M$, respectively. A second area with high inorganic nutrients was detected in the Reloncaví system, in which the highest absolute values of surface silicic acid were registered during the fall-winter season (e.g., $210~\mu M$). Comparing seasonal concentrations, the fall-winter season showed the highest abundance in the water column. However, the absolute maximum nitrate (Figure 4b), phosphate (Figure 4d), and silicic acid (Figure 4f) values were recorded in the subsurface layer during the spring and summer seasons.



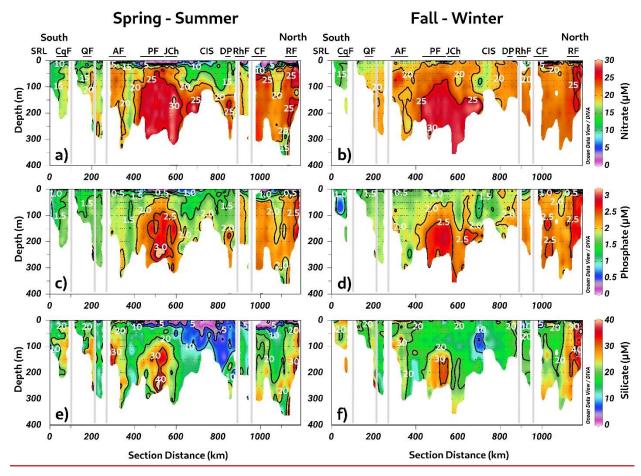


Figure 4. Long-term seasonal mean of inorganic nutrients. (a, b) Nitrate, (c, d) phosphate, and (e-f) silicate collected along a vertical section in the northern Patagonian fjord system during fall-winter and spring-summer seasons.

The calculation of the Brunt-Väisälä frequency (BVF), a variable used to identify mixed/stratified regions, evidenced a permanent mixing of the water column in the Chiloé inner sea (BVF≤<10 cycl h⁻¹) (Figure 5a–b). Furthermore, the homogenization of physical (e.g., conservative temperature and absolute salinity) and chemical (e.g., DO oxygen and inorganic nutrients) variables was observed in these regions. On another sideIn contrast, stratified water (between 2 and 10 m depth) was detected during spring-summer inside the fjords, e.g., Cupquelan, Quitralco, Aysén, Puyuhuapi, Comau, and Reloncaví, showing values over BVF>50 cycl h⁻¹ that coincided with the lower salinity (Figure 5a). The main drivers of the stratification in the northern Patagonian fjords depended on the freshwater supply by rivers and precipitations affecting the surface. The highest river flow relies on the melting of ice that occurs during the spring, but during the fall and winter, rivers flow is also increased due to the precipitation regime. Additionally, stratification enhanced in summer because of the increase in solar radiation, making the spring-summer season the period where the absolute maximum stratification was registered (e.g., ~100 cycl h⁻¹) (Figure 5a).

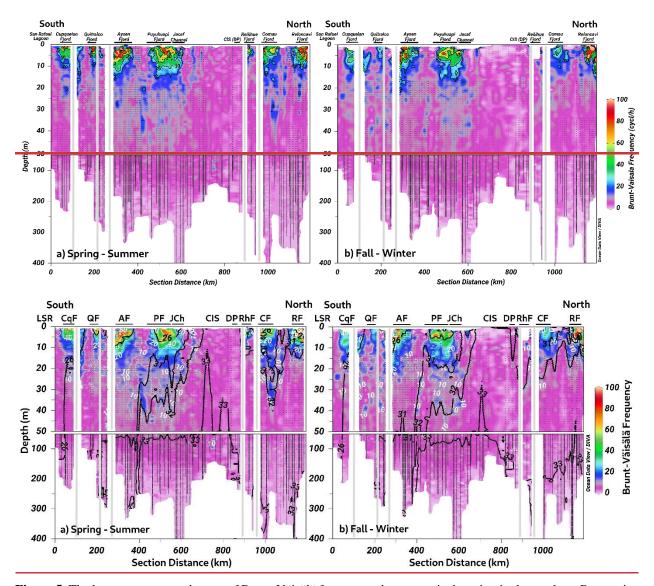


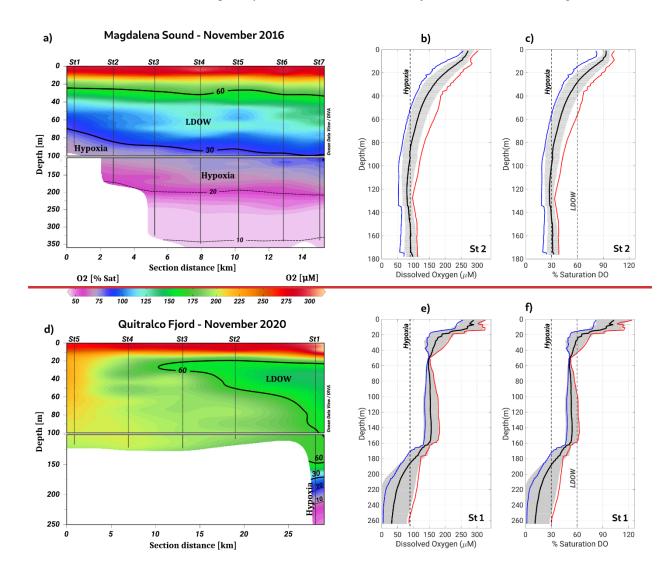
Figure 5. The long-term seasonal mean of Brunt-Väisälä frequency along a vertical section in the northern Patagonian fjords during the (a) spring-summer, and (b) fall-winter seasons. The white and black contour lines denote the Brunt-Väisälä and absolute salinity values.

3.32. DO and chlorophyll-a features from sporadic oceanographic cruises

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The analysis of hypoxia and LDOW conditions in the northern Patagonian fjord system highlighted the presence of two areas with water bodies with these characteristics: the Puyuhuapi-Jacaf and Reloncaví regions. Moreover, Magdalena Sound (44.6° S, 72.9° W), located between the Puyuhuapi Fjord and the Jacaf Channel (Figure 1), showed the shallowest hypoxia over the entire northern Patagonian fjords. At this location, a 30% DO saturation isoline was observed at a depth of 70 m, with the LDOW reaching a depth of approximately 20 m (Figure 6a–c).



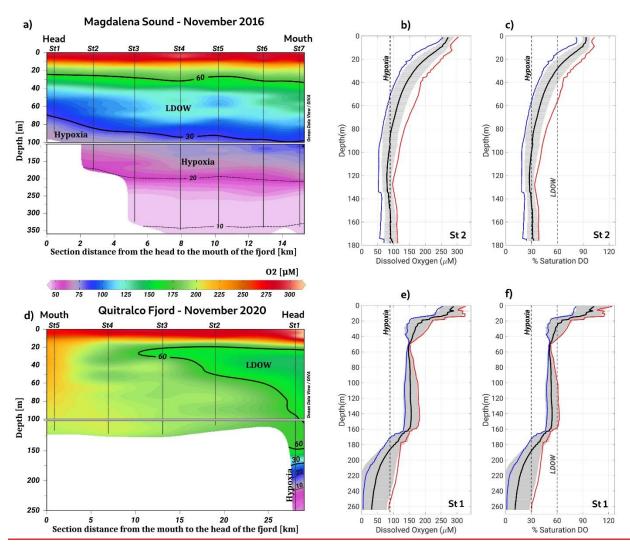


Figure 6. Vertical section of dissolved oxygen along (a-c) Magdalena Sound and (d-f) Quitralco Fjord during November 2016 and November 2020, respectively. In (b, c, e, f), red, black, and blue lines represent the absolute maximum, average, and minimum values of DO, respectively. Grey horizontal lines show the standard deviations calculated using 16 profiles for Magdalena Sound and 3 profiles for the Quitralco Fjord.

The chlorophyll-a (Chl-a) data collected during two oceanographic campaigns (Figure 7a) denoted high concentrations of Chl-a in the Reloncaví Fjord, the Puyuhuapi Fjord, and the Jacaf Channel (Figure 7b, 7c) where LDOW and hypoxia conditions were registered. The Chl-a values observed during the winter season in the Reloncaví Fjord were exceptionally high (32.8 mg m⁻³)-, which discussed in Section 4. This observation is scrutinized in the discussion section. Regardless, in general, the winter season of August 2021 showed a deficiency lack of Chl-a in the southern part of the study area (Figure 7c). The vertical distribution of the Chl-a data described before earlier was obtained through a statistical analysis between the fluorescence data from CTD (every 1-m depth) and the in-situ Chl-a samples from discrete levels (i.e., 0, 5, 10, 15, 25, and 50 m) (Figure 7d_-, 7e).

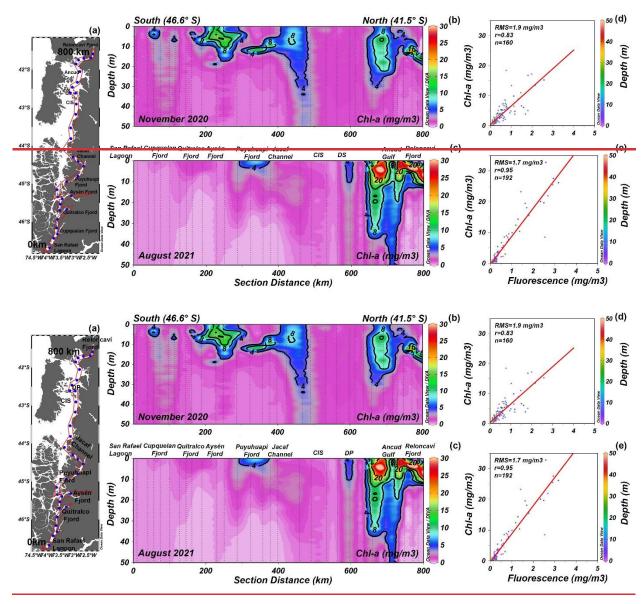


Figure 7. (a) Distribution map of the stations. Vertical distribution of chlorophyll-a (Chl-a) obtained during (b) November 2020 and (c) August 2021 in the northern Patagonian fjords. (d and e) Statistical relationship between the fluorescence data from CTD and in-situ Chl-a samples. In (d and e) RMS is the root mean square, and n is the number of data points used to obtain the R-values, and red lines represent the lineal tendency fit -in (b and c) CIS is Chiloé Inner Sea and DP is Desertores Pass.

3.23. Rates of primary production, community respiration, and bacterial production

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The GPP and CR estimates obtained in our sampling campaigns agreed well with the measurements reported in previous studies for the Patagonian fjords during the productive period (Iriarte et al., 2007; Montero et al., 2011; Montero et al., 2017a). The GPP and CR rates showed a weak coupling, with most experiments indicating that less oxygen is produced than consumed (Figure 8a). Thus, most fjords exhibited heterotrophic metabolism (GPP:CR <1)

in the surface layer (0–20 m) during the study period (Figure 8b). The highest rates of GPP in terms of oxygen (18.6 to 41.02 mmol O_2 m⁻³ d⁻¹) were mainly recorded in the upper 5 m of the water column, whereas the lowest values (0 to 17.6 mmol O_2 m⁻³ d⁻¹) were observed between 10 and 20 m depth (Figure 8c to, 8j). CR rates did not show a definite vertical pattern, registering highest (23.3 to 76.3 mmol O_2 m⁻³ d⁻¹) and lowest (0 to 12.3 mmol O_2 m⁻³ d⁻¹) values throughout the water column (0–20 m) (Figure 8c to, 8j).

Throughout the study period in different fjords, integrated GPP and CR rates (down to 20 m) ranged from 0.1-2.6 g C m⁻² d⁻¹ and from 0.8-6.6 g C m⁻² d⁻¹, respectively, (Figure 9, Table 2). Neither rate showed significant differences (p > 0.05) between spring-summer 2020–2021 (Figure 9a) and summer of 2022 (Figure 9b). Although there were no significant differences (p > 0.05) between GPP values recorded from different fjords in both study periods (Figure 9a_3, 9b), Comau Fjord showed the lowest rates of GPP (0.1 to 0.6 g C m⁻² d⁻¹) whereas Puyuhuapi and Reloncaví fjords showed the highest values (1.9 to 2.6 g C m⁻² d⁻¹). In the case of CR, the highest rates were recorded in Puyuhuapi Fjord (2.2 to 6.6 g C m⁻² d⁻¹) and the lowest in Comau Fjord (0.8 to 0.9 g C m⁻² d⁻¹) (Figure 9a, 9b). The phytoplankton composition in the study area showed a similar pattern to the GPP values, highlighting maximum abundances on the surface and minimal abundances at a depth of 20 m (data not shown). In addition, Comau Fjord showed the lowest abundances (66×10^3 cell L⁻¹) whereas Reloncaví Fjord showed the highest concentrations of phytoplankton ($1,227 \times 10^3$ cell L⁻¹).

Estimated rates of BSP ranged between 0.05 and 0.6 g C m⁻² d⁻¹ within the study area and were positively and significantly correlated with GPP values (Figure 9, Table 2). The percentage of GPP utilized by bacteria ranged

from 3% to 56%, except in Comau Fjord, where a higher utilization percentage (151%) was recorded, suggesting that more organic carbon is consumed than is produced locally.



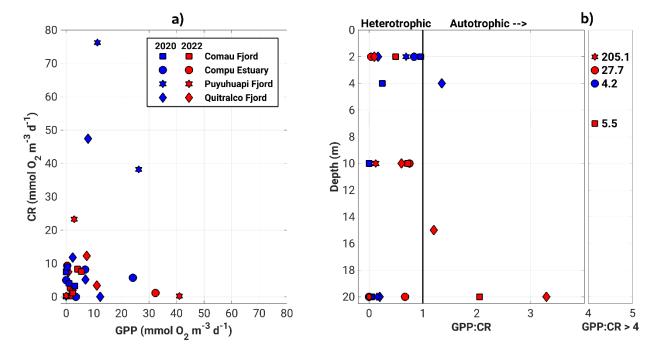
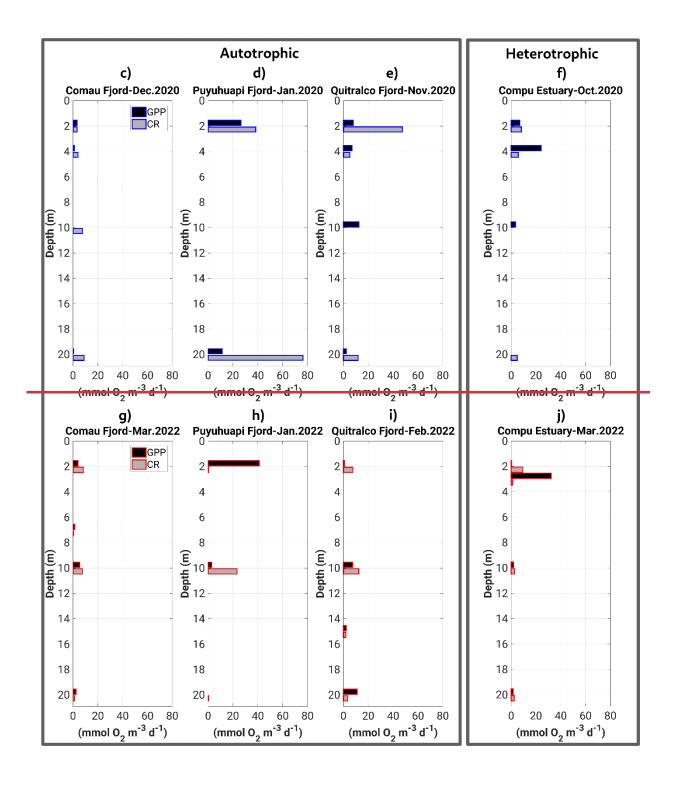


Figure 8. (a) Relationship and (b) vertical patterns of all datasets from the GPP and CR. (c-j) represents the vertical distribution of GPP and CR obtained during experiments of primary production on (c-f) spring-summer of 2020–2021, and (g-j) summer of 2022. GPP: Globalross primary production, and CR: community respiration.



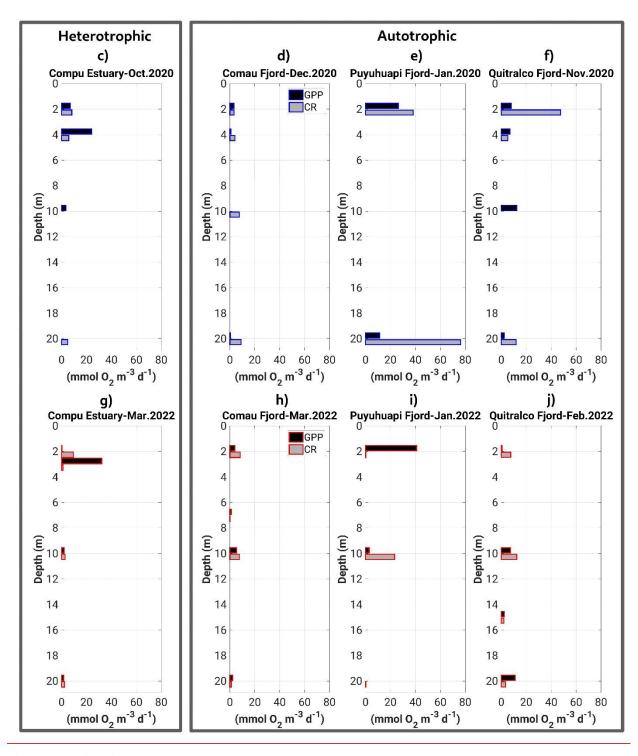


Figure 8. Continued.

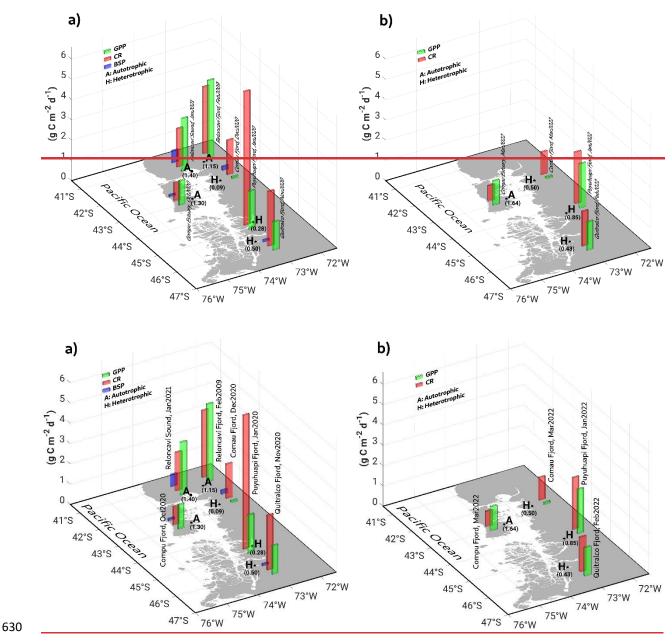


Figure 9. *In-situ* experiment of primary production during (a) spring-summer of 2020–2021, and (b) summer of 2022, covering some fjords in the northern Patagonian fjord system. GPP: Grosslobal primary production, CR: Community respiration, BSP: Bacterial secondary production. Results shown from Reloncaví Fjord in (a) were extracted from Montero et al., (2011).

3.34. Satellite image of organic matter supply to fjords

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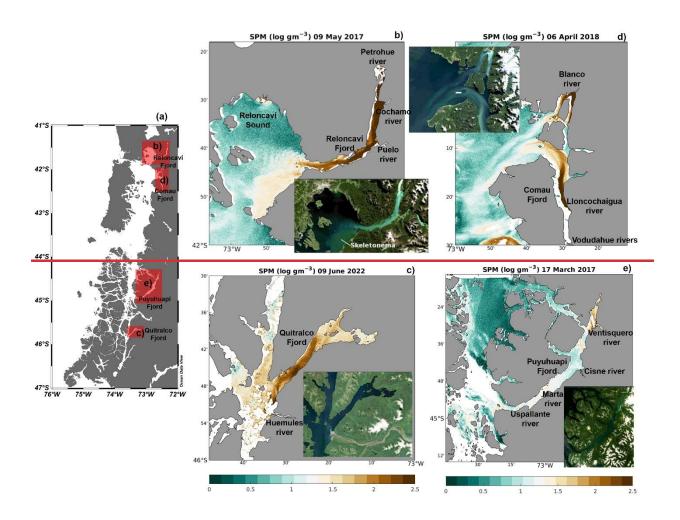
Satellite images show that freshwater inputs into the sea were accompanied by large amounts of suspended sedimentsparticles (Figure 10), possibly acting as a source of allochthonous organic matter, favoring the heterotrophic metabolism reported in the previous section. On May 9, 2017, a large amount of suspended matter flowed into the Reloncaví Sound from its fjord, mainly dominated by three rivers: Petrohue, Cochamo, and Puelo (Figure 10b). In the

southeast part of the Reloncaví Sound, the observed high concentration of sediments suspended particles was accompanied by due to the presence of a diatom bloom (evidenced by greenish waters at the true color images in the southeast part of the Reloncaví Sound), mainly formed by Skeletonema costatum, which attained concentrations of more than 5 million cells L⁻¹ within the fjord (Figure S8not shown). This bloom affected both the eastern part of the Reloncaví Sound and the Reloncaví Fjord. While tThe amount of suspended matter visible in the Sentinel-2 images was generally homogeneously high along the fjords e.g., on June 9, 2022, in the Quitralco Fjord (Figure 10c), and May 9, 2017, in Reloncaví, (Figure 10b). Some examples of this phenomenon, such as the one on However, heterogeneous distribution can also be found (e.g. on April 6 2018 on Comau Fjord, Ffigure 10d), suggesting the influence April 6, 2018, on Comau Fjord (Figure 9d), show a very heterogeneous distribution of suspended sediments particles within the fjord, suggesting the influence of the currents in the distribution of waters rich in sediment. On this date, waters flowing from the river Blanco in the northern part of the fjord's mouth were whitish in color, indicating carbonate rich sediments. Water flowing into this fjord from the south, principally from the Lloncochaígua and Vodudahue rivers, has a more brownish color, indicating a higher quantity of organic matter. At the Quitralco Fjord (Figure 10c), SSPM suspended sediments from Rio de los Huemules (at 73.30° E 45.54° S, the brown riverbed is clearly visible in the natural color insert) appeared to propagate within the fjord, affecting the water clarity along the entire fjord. Inspection on other dates (not shown) revealed high variability in the direction of the river outflow, sometimes entering the fjord (and staying there for extended periods), and sometimes being directed towards the south. Finally, the Puyuhuapi Fjord also registered a high signal from SSPMsuspended sediments due to river discharge; for example, the Vestiquero River was located at the fjord head (Figure 10e). Other rivers, such as the Cisnes, Marta, and Uspallante, could also influence the supply of allochthonous organic matter to the Puyuhuapi Fjord, contributing to a decrease in DO and hypoxia. However, the cloud cover does not allow for better satellite images.

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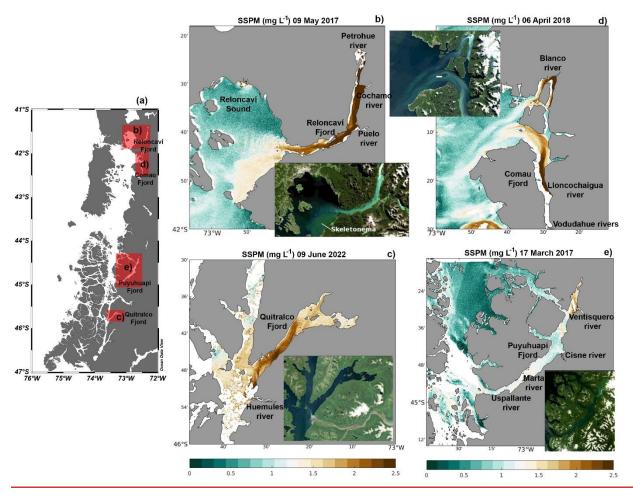


Figure 10. (a) Map showing the study sites. <u>Satellite Ssuspended particulate</u> matter as measured by Sentinel 2 on (b) Reloncaví Sound, (c) Quitralco Fjord, (d) Comau Fjord, and (e) Puyuhuapi Fjord.

3.45. Biogeochemical variables

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We observed different signals of SPM (Figure 11b) along a latitudinal transect conducted from north to south in the northern Patagonian fjords (Figure 11a). Specifically, significant increases in SPM were registered in Cupquelán Fjord (~ 7 mg L⁻¹) and at the surface layer of the mouths of the Comau and Aysén Ffjords (~ 6 mg L⁻¹). Furthermore, smaller areas with values of SPM> 3 mg L⁻¹ were found at the subsurface layer of the Quitralco and Aysén fjords. in the southern region, the SPM levels were high at the subsurface layer (50_-150 m) from San Rafael Lagoon to Jacaf Channel, with maximum values exceeding 4 mg L⁻¹, except in Quitralco Fjord, which showed values close to 2 mg L⁻¹. Similar conditions were observed in the transition zone between the Puyuhuapi Fjord and Jacaf Channel. In the northern central region, within the Chiloé Inner Sea_and the subsurface layer of the Comau and Reloncaví fjords, SPM values were minimal. In the northern area, a small subsurface core near Comau Fjord and the Reloncaví system exhibited an increase in SPM. Along the water column, characteristic cores were found in the inner

channels south of the study area, between 45° S and 47° S. Other deep but less intense cores (<3 mg L⁻¹) were located in the Inner Sea of Chiloé and Reloncaví system.

The percentage of allochthonous organic carbon (%POC_{allo}) exhibited an irregular distribution in the southern area, with surface minimums under 30% at the mouths of the Quitralco, Aysén, and Puyuhuapi fjords (Figure 11c). In the northern area, the Comau Fjord and Reloncaví Sound presented low %POC_{allo} values. Along the water column, %POC_{allo} appeared to increase with depth, reaching values of approximately 70%, except in the Inner Sea of Chiloé, where it was under 50%. The C:N ratio exhibited a discernible reduction with increasing depth along the water column in the broader study area, encompassing the Chiloé Inner Sea region and extending to the Reloncaví Fjord. Although a similar C:N ratio trend was observed in both Chiloé and Reloncaví, the predominant feature is not a uniform 'depth-dependent decrease' but rather an overall modest vertical gradient, ranging from 6–9. Furthermore, despite their comparable low C:N ratios, Chiloé and Reloncaví have differing CDOM concentrations, isotopic compositions, and POC allocations. Specifically, the Chiloé Inner Sea and Reloncaví Fjord exhibit analogous patterns of minimum C:N ratios (6-9). In addition, the subsurface regions of the Puyuhuapi and Aysén fjords register absolute maximum values (C:N>14), as depicted in Figure 11d.

The C:N ratio showed more homogeneous values at the surface layer (C:N<8) (Figure 11d) but increased from a 50 m depth until the seabed (C:N>12), especially in the region between the San Rafael Lagoon and the Jacaf Channel, coinciding with the high SPM region presented in Figure 11b. In the Chiloé Inner Sea, the C:N ratio decreased along the water column (from surface to the seabed).

The isotopic signal of the carbon (ỗ™¹³C) increased in the same sites where %POC_{allo} decreased, with values ranging from −25‰ to −15‰ (Figure 11e). At the subsurface layer, ỗ™¹³C signal became lighter than that in the surface. An exception was observed in the Chiloé Inner Sea and the transition zone between the Aysén Fjord and San Rafael Lagoon, where the C:N ratio coincidentally decreased. In the region extending from the southern Chiloé Inner Sea to Aysén Fjord, elevated levels of the isotopic signal of nitrogen (ỗ™¹⁵N) enrichment were observed, primarily at the surface and subsurface levels (Figure 11f). Notably, there was a significant increase in nitrogen values, with some exceeding 9%; particularly, in the Chiloé Inner Sea, the enrichment extended to depths of 150—200 m.

The first CDOM Notable observations were made regarding the concentrations of CDOM in the Patagonian fjords regiondenoted, with high concentrations throughout the water columns in the north area, spanning from the Chiloé Inner Sea to the Reloncaví system (Figure 11g). Conversely, in the southern area, CDOM concentrations declined, with minimum values as low as 20 µg L⁻¹ of specific UV absorbance between the Jacaf Channel and San Rafael Lagoon, but the absolute minimum was registered in the Comau Fjord. Despite this overall decrease, localized increases in CDOM concentrations were identified in certain fjords, such as Aysén, Quitralco, and the San Rafael Lagoon. These subsurface concentration spikes highlight the spatial variability of CDOM distribution within the fjord system. Moreover, these findings provide valuable insights into the spatial distribution patterns of CDOM in the Patagonian fjords, indicating higher concentrations in the northern region and a decline towards the southern end of

the study area. The localized increases in CDOM concentrations in specific fjords suggest the influence of local processes or inputs contributing to the observed spatial heterogeneity.

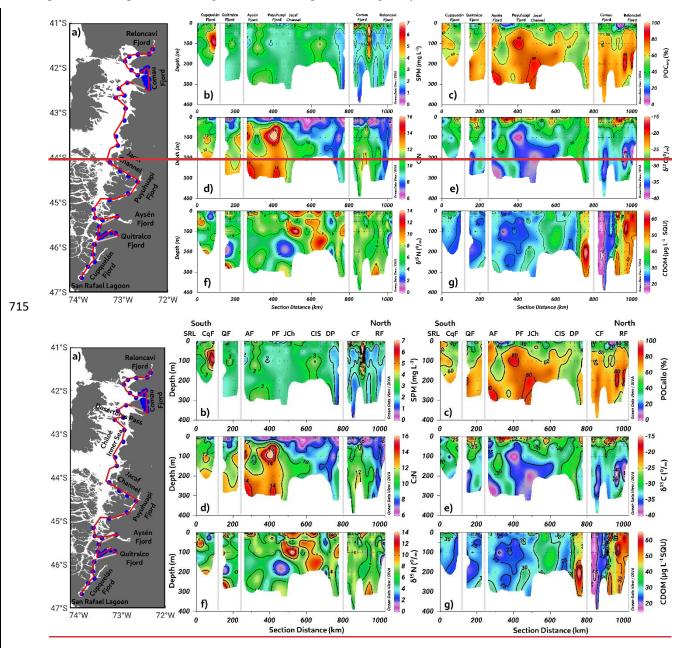


Figure 11. (a) Study area showing transect (<u>stations in blue, transect in red-color</u>) used to biogeochemical study case carried out in November 2020 during Expeditions PN-I IFOP. (b) Suspended particular material (SPM), (c) allochthonous carbon percentage (POC_{allo}), (d) Carbon and nitrogen ratio (C:N), Isotopic signal of (e) δ^{13} C and (f) δ^{15} N, and (g) Chromophoric Dissolved Organic Matter (CDOM).

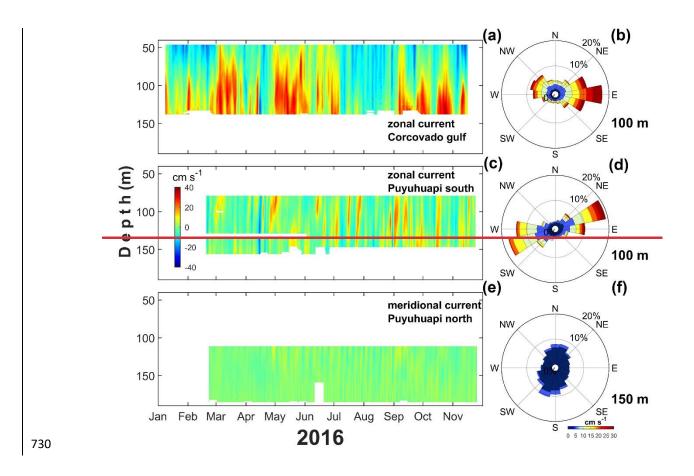
3.56. Circulation regime from ADCP measurements

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The low-frequency deep circulation (> 40 m depth) in the <u>inner sea of the region mooring of the Corcovado</u>

<u>Gulf Chiloe Inner Sea</u>-showed a marked east—west <u>regional gradient direction</u> in the along-channel current amplitude

(Figure 12b). The Corcovado currents were dominated by an eastward flow with a maximum intensity of approximately 30 cm s⁻¹ (Figure 12a-b), whereas at the mouth of the Puyuhuapi Fjord (Figure 12c-d), the maximum current was approximately 10 cm s⁻¹.



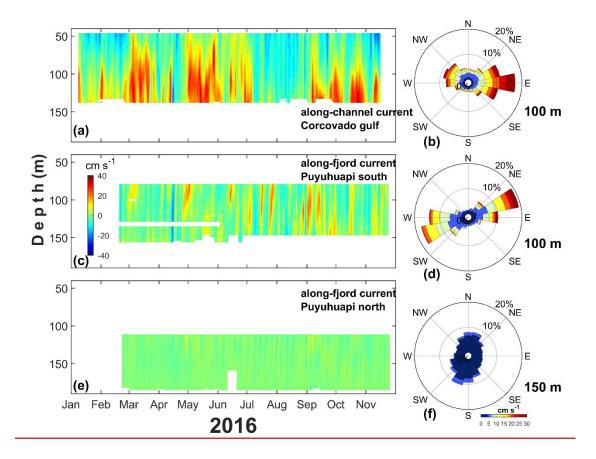


Figure 12. Subtidal deep circulation regimen obtained with ADCP performed in the (a) Corcovado Gulf and in (c, e) southern-northern zone of the Puyuhuapi Fjord from January to November 2016. (b, d, and f) Marine current rose obtained at 100 m (Corcovado Gulf), 100 m (Puyuhuapi south), and 150 m (Puyuhuapi north) depths. <u>Location of moorings shown in Figure 1. In (a and c) the red-blue color represents the eastward-westward currents, and in (e) red-blue color represents northward-southward currents.</u>

The Corcovado currents showed a marked pattern in the 40–70 m layer, which was dominated by westward currents, and short-duration events of approximately 20 cm s⁻¹ were observed throughout the entire time series. This intensestrong westward flow seems to be associated with the austral spring-summer seasons (January–March and November–December 2016); however, a weak (~5 cm s⁻¹) and longer (July–October 2016) westward flow was observed during the austral winter-autumn period. In the layer between 70 and 130 m, eastward (and intensestrong) currents dominated, and there were periods of one to two months with eastward flow during March–April, May–July, and September–December 2016 with currents > 20 cm s⁻¹. The layer between 100 and 130 m showed maximum currents of approximately 40 cm s⁻¹ at the end of October 2016 (Figure 12a).

Puyuhuapi Fjord currents were obtained at the southern mouth (South Puyuhuapi, Figure 12c-d) and middle fjord (North Puyuhuapi, Figure 12e-f. At the mouth of the fjord, low-frequency currents showed short pulses that covered most of the 70–160 m layer; typically, those pulses were eastward without an evident seasonal pattern. A unique low-frequency westward event was observed in mid-April 2016, which was also present in the Corcovado

Gulf. In general, the currents in southern Puyuhuapi were weak (< 10 cm s⁻¹); however, during September and October 2016, eastward events of 20 cm s⁻¹ were observed. In northern Puyuhuapi, most currents were weak (< 10 cm s⁻¹) without a temporally or spatially evident pattern, and the flow tended to be northward and intensified between May and September 2016.

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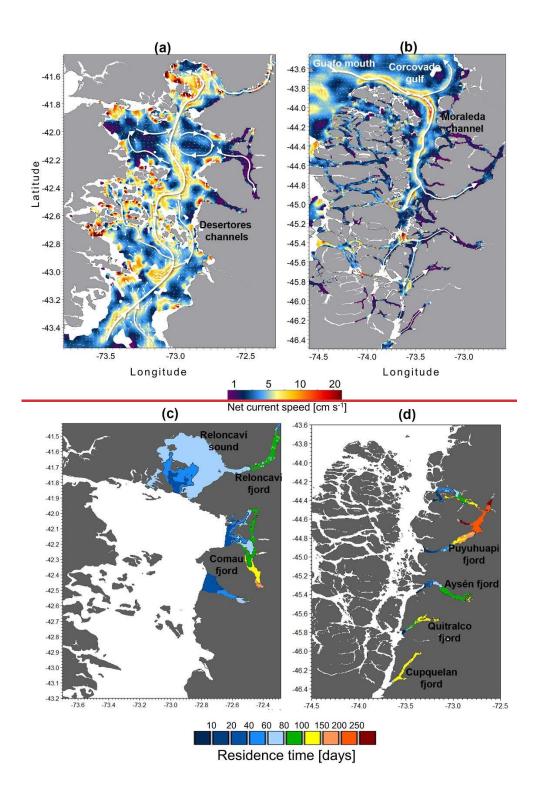
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3.67 Circulation regimen oceanographic model

Deep <u>subtidal</u> currents, <u>defined as subtidal or residual currents</u> (average of 50–300 m) over the three years of simulation, have a relatively large spatial variation (Figure 13a_, 13b). <u>Consequently, tThe</u> model could correlate the most energetic zones in the outer channels with those of lower energy inside the fjords. In general, the exchanges between the fjords and ocean registered high average velocities, that is, the Guafo mouth, Moraleda Channel, Corcovado Gulf, and Desertores Pass, with net current velocities ranging from 10 to 20 cm s⁻¹. In contrast, in the fjords, the average velocity of the deep flow was less than 5 cm s⁻¹. The predominant flow was generally towards the interior of the fjords (Figure 13–a, 13b).

The flushing/residence time calculated for each fjord showed that the sector towards the head of Puyuhuapi Fjord registered the longest retention time (>200 days). In comparison, the shortest times were found in the Reloncaví Sound–Fjord (60–90 days), except for the Reloncaví Fjord head, which reached values close to 100 days (Figures 13c and 13d). Comau Fjord showed relatively high values, which increased from north to south mouth to head. In the central part of Comau Fjord, the residence time ranged from 90 to 120 days, whereas at the fjord head, it ranged from 150 to 190 days. Meanwhile, the Aysén Fjord showed residence time values lower than 120 days, which were higher towards the fjord head, whereas the Quitralco Fjord reported 150 days at the fjord head and 100 days at its central part. Finally, the Cupquelán Fjord exhibited greater homogeneity throughout the fjord, with relatively high values ranging from 120 to 150 days. Most studies reported a spatial gradient of water retention, with the highest values found near the fjord's head. The areas of longer residence time coincided with the region of LDOW and hypoxia (Figures 13e–f).

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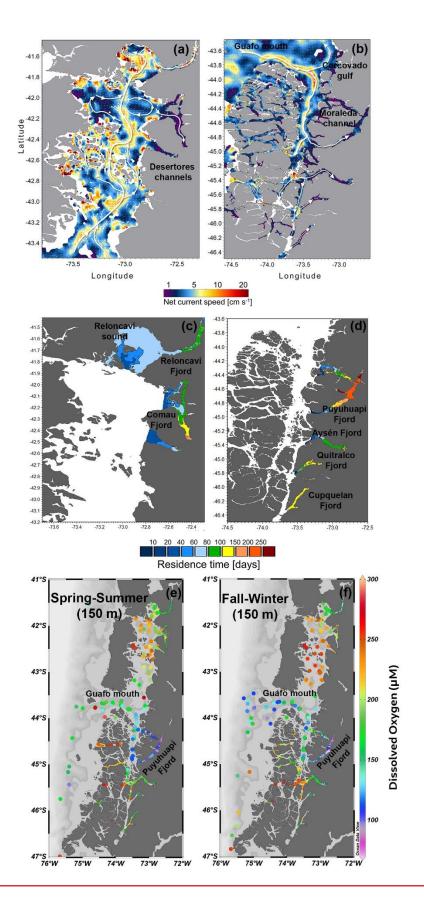


Figure 13. (a, b) Map showing the deep currents regime in the northern Patagonian fjords. The deep current was defined as subtidal currents calculated as the average of currents from 50–300 m depth. (c, d) The residence time was calculated for each fjord of the northern Patagonian fjord. (a-d) Data were obtained from the hydrodynamic model MIKE 3 FM developed by IFOP. (e, f) Horizontal distribution of dissolved oxygen at a level of 150 m during spring-summer and fall-winter. Data and bathymetry are plotted in color dots and gray.

4. Discussion

Oceanographic research in the Patagonian fjords started in 1995 with CIMAR-fjords project, supported by the Chilean Navy. As an oceanographic sampling strategy, Patagonia was divided into three zones, e.g., northern (41°–47° S), central (47°–53° S), and southern (53°–55.8° S) Patagonia, and the frequency of the cruises were primarily seasonal (Sievers, 2008). Moreover, someother oceanographic cruises, such as the Hudson expedition in 1970, occurred in this zone (Table 1). The data collected through the CIMAR projects allowed us to understand the main physical (water mass quantification) and chemical (e.g., dissolved oxygen and inorganic nutrients) processes impacting this fjord system, such as the hypoxic conditions due to the influence of the ESSW (Sievers, 2008; Sievers and Silva, 2008; Silva, 2008; Silva and Vargas, 2014; Schneider et al., 2014; Pérez-Santos et a., 2014). Furthermore, some studies about biological processes that include the consumption of DO, such as respiration and the remineralization of organic matter, have also contributed to understanding the processes that favor hypoxia and DO depletion (Montero et al., 2011; 2017; Iriarte et al., 2018). Additionally, the development of hydrodynamic models helped to determine the areas where the water age was significantly high, for example, the Puyuhuapi Fjord (Pinilla et al., 2020), and where stronger mixing and stratification occurred (Ruiz et al., 2021). ThisOur study scrutinized all the natural processes contributing to the presence of water under hypoxic conditions and LDOW in the northern Patagonian fjords, as discussed in the next section.

4.1 Water masses proprieties properties and biogeochemical processes in northern Patagonian Fjords

Recent and historical hydrographic data collected from the Patagonian fjords, especially in the northern area, confirmed the presence of analogous water masses detected previously by the Hudson oceanographic cruise in 1970. EW, MSAAW, SAAW, and ESSW were recorded from the surface layer to the bottom (to a depth of approximately 500 m) (Figure 2 and Figure 3). Similar patterns were recognized in terms of the vertical-horizontal distributions, highlighting the location of the salty-hypoxic/-LDOW and nutrient-rich waters associated with the ESSW in the Jacaf Channel and Puyuhuapi Fjord (Figures 2 and 4). This water mass enters Patagonia by the within the subsurface layers via the Guafo mMouth and moves south throughout the Moraleda Channel to end at the Puyuhuapi Fjord and Jacaf Channel (Linford et al., 2023). On the other hand In contrast, the EW dominated in the southern area due to freshwater input from the San Rafael Lagoon and rivers discharge, which is characterized by oxygenated waters due to its high solubility and recent contact with the atmosphere. Finally, SAAW and MSAAW covered the entire study area (Figure 2), as reported by Siever and Silva (2008), Schneider et al., (2014), Pérez-Santos et al., (2014), and Pinilla et al., (2020).

The absence of stratification was observed throughout the year in the Chiloé Inner Sea (Figure 5). In this area, both physical and biogeochemical variables showed homogeneous values from the surface layer to the bottom (Figures 2 and Figure 4), indicating the presence of MSAAW (originating from mixing the SAAW with the EW). Furthermore, the calculation of the buoyancy frequency and potential energy anomalies using the output from the oceanographic model demonstrated that more robust mixing occurred in the Chiloé Inner Sea (Ruiz et al., 2021). This explains the importance of this area for DO ventilation and redistribution in the northern Patagonian fjords.

Water masses in northern Patagonia have unique physicochemical properties (Sievers and Silva, 2008; Silva, 2008; Silva and Vargas, 2014; Schneider et al., 2014; Pérez-Santos et al., 2014). In the case of northern Patagonian fjords, EW is rich in silicie acid silicate (Figure 4f) because of the riverine supply (Silva and Vargas, 2014), with characteristic the high spatial variability in silicate pulses at the surface layer that changes throughout the year due to the organisms' consumption (Montero et al., 2011), as observed in northern Patagonia, including the Chiloé Inner Sea (Figure 4).

The SAAW is strongly connected with the estuarine water masses (MSAAW and EW), and the ESSW interacts with it, as shown in this study (Figures 2 and 3). Organic matter degradation processes occurred inside the fjords, mainly in terms of nitrogenous compounds being remineralized. These processes increase the nutrient pool that is originally transported by oceanic water and are responsible for the high accumulation of nitrate and phosphate registered in the subsurface layer of the Puyuhuapi Fjord and Jacaf Channel (Figure 4).

Inside the fjords, where low salinity from high river discharge dominated, a persistent halocline/pycnocline/stratified water column developed; therefore, deep-water ventilation by vertical mixing and diffusion with the oxic surface layer was limited (Figures 2–5). These conditions favored the occurrence of LDOW zones in the fjords, where stratification and particulate organic matter input were higher than at the mouths (Figure 10). Thus, DO consumption was favored owing to organic matter degradation in the Reloncaví, Comau, Puyuhuapi, Aysén, and Quitralco fjords (Figure 2), as was reported for the Milford Sound in New Zealand (Stanton, 1984), Framvaren Fjord in Norway (Yao and Millero, 1995), Lower St. Lawrence Estuary in Canada (Lefort, 2012), and Rivers Inlet in British Columbia (Jackson et al., 2022).

A latitudinal transect from north to south in the study area revealed distinct signals of SPM within the fjords (Figure 11b). Although SPM concentrations generally fell within expected ranges, there was significant variability, with values ranging from 0.5 to 500 mg L⁺(Muñoz et al., 2014; Pryer et al., 2020). A noteworthy pattern of increased SPM levels below the surface was observed at the fjord mouths, particularly in the southern part of the study area (Figure 11b). This finding suggests that fjord mouth outlets play a crucial role in particulate organic matter accumulation, potentially that originating from terrestrial sources. Furthermore, the high SPM values observed in the southern region indicate substantial contributions of allochthonous material, which may be influenced by factors such as river discharge, sediment resuspension, and glacial activity (Gonzalez et al., 2010). A more detailed analysis of SPM distribution revealed irregular patterns in the percentage of allochthonous organic matter (%POC_{allo}). At the mouths of the Quitralco, Aysén, and Puyuhuapi fjords, a subsurface minimum indicated relatively low terrestrial organic matter inputs as was reported by (Gonzalez et al., (2010)). The low-level input of organic matter could be attributed to limited river contributions or the autochthonous organic material production rate coinciding with nutrient

depletion and increased DO (Holding et al., 2017). In contrast, areas such as the Jacaf Channel and the Chiloé Inner Sea exhibited higher contributions of %POC_{allo}, indicating a more significant influence of allochthonous sources. Further, the increase in %POC_{allo} with depth highlights the importance of vertical transport and sedimentation processes in determining the distribution of organic matter throughout the water column (Figure 11c). Given the notable seasonality in carbon fluxes and fjord system dynamics, as highlighted by Gonzalez et al. (2010), the potential implications extend to the variability of trophic webs and carbon export. Recognizing that these effects are more autonomous from local primary production than open ocean water systems is crucial. The seasonally driven variations in carbon fluxes can significantly influence the intricate interactions within trophic webs and contribute to fluctuations in carbon export processes within the fjord system. Considering that carbon fluxes and the functioning of the fjord system are highly variable depending on the season of the year (Gonzalez et al., 2010), these could potentially affect both the trophic webs and carbon export, which are more independent of local primary production than coastal areas.

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The C:N ratio exhibited spatial variability, with more homogeneous values in subsurface layers shallower than 50 m (Figure 11d). On average, the bulk particulate organic carbon and nitrogen concentrations maintained a C:N ratio of 8.5:1, exceeding the Redfield ratio of 6.6:1 typically observed in phytoplankton biomass within the marine realm (Redfield, 1958). Notably, the southern region exhibited higher C:N ratios, coinciding with areas with elevated SPM levels and increased %POC_{allo}. While the intuitively higher C:N ratio could be attributed to terrestrial sources with a higher carbon-to-nitrogen content, a more plausible explanation could be the increasing trend of the C:N ratio with depth and elevated particulate organic carbon (POC_{allo}), or a combination of both. The observed C:N ratios suggest the influence of microbial remineralization processes and the preferential removal of nitrogen-rich organic matter (Taucher et al., 2020), potentially resulting in a lower POCallo signal. While these higher C:N ratios may be intuitively attributed to terrestrial sources with a higher carbon content relative to nitrogen, a more plausible explanation may be the increasing trend of the C:N ratio with depth. The observed C:N ratios suggest the influence of microbial remineralization processes and the preferential removal of nitrogen rich organic matter (Taucher et al., 2020). The increase of the C:N ratio with depth likely reflects the consumption and degradation of sinking particles by zooplankton and heterotrophic bacteria, resulting in the preferential remineralization of nitrogen (Figure 3) over carbon and the subsequent elevation of the C:N ratio in sinking particles (Tomas et al., 1999; Schneider et al., 2003). The spatial gradients of δ^{13} C have been previously documented in estuarine and continental shelf waters in Patagonian fjords (Silva and Vargas, 2014 Gonzalez et al., 2010; Iriarte et al., 2018). The horizontal-vertical distribution of the isotopic signal of δ^{13} C and δ^{15} N showed substantial variability in the northern Patagonian fjords and, for the first time, reported for the δ^{15} N., but there is no evidence of gradient of nitrogen isotopic signals prior to this study. Nevertheless, *The pronounced phytoplankton bloom (Figure 7b) resulted in an enrichment of δ^{13} C in the upper 50 m of SPM in the upper 50 m (Figure 11e), similar to observations made in other fjords around the world (Remeikaite-Nikiene et al., 2017). The isotopic carbon signals revealed an increase in δ^{13} C values where %POC_{allo} decreased, indicating a shift towards a more depleted isotopic signature. This suggests the predominance of marine-derived organic carbon in areas with lower inputs of allochthonous material (Kumar et al., 2016). Moreover, the lighter carbon isotopic signals observed with depth suggest isotopic fractionation processes associated with remineralization and the preferential utilization of more labile organic carbon by heterotrophic bacteria (Muñoz et al., 2014; Kuliński et al., 2014).

The seasonal distribution of Chl-a evidenced the phytoplankton activity along the northern Patagonian fjords, especially during spring, 2020 (Figure 7). However, in the winter of 2021, a phytoplankton bloom was registered in the Reloncaví Fjord and Ancud Gulf. Pérez-Santos et al., (2021) reported the occurrence of high Chl-a and an increase of phytoplankton in the Reloncaví Sound during middle and late winters (August and September, 2017–2020) due to changes in the water column conditions, e.g., stratification started when salinity decreased owing to the increase of river discharge mainly caused by early start of the ice melting. The stabilization of the water column is one of the main factors triggering primary production in the Patagonian fjords (Pérez-Santos et al., 2021). The isotopic earbon signals revealed an increase in 8¹³C values where %POC_{allo} decreased, indicating a shift towards a more depleted isotopic signature. This suggests the predominance of marine derived organic earbon in areas with lower inputs of allochthonous material (Kumar et al., 2016). Moreover, the lighter carbon isotopic signals observed with depth suggest isotopic fractionation processes associated with remineralization and the preferential utilization of more labile organic earbon by heterotrophic bacteria (Muñoz et al., 2014; Kuliński et al., 2014).

Elevated levels of nitrogen enrichment were primarily observed in the surface layer of the region extending from the southern Chiloé Inner Sea to the Aysén Fjord, indicating the influence of nitrogen inputs from sources such as river discharge, atmospheric deposition, and biological activity (Velinsky and Fogel, 1999). The significant increase in nitrogen values, particularly in the Chiloé Inner Sea, suggests the presence of enhanced nitrogen cycling and retention processes within this fjord system. This increase could result from the degradation of organic nitrogen with depth, where isotopically light $\delta^{15}N$ is preferentially released from the organic matrix, leaving behind isotopically heavier residual $\delta^{15}N$ (Saino and Hattori, 1980, 1987; Altabet, 1988). Similarly, the enrichment of $\delta^{15}N$ in SPM suggests that primary production mainly originates from autochthonous sources in some regions of the fjords (Figure 11). The horizontal–vertical distribution of the isotopic signal of $\delta^{13}C$ and $\delta^{15}N$ showed substantial variability in the northern Patagonian fjords. Our results strongly suggest that this variability was driven by biological processes, as was demonstrated by Savoye et al. (2003). TheyIn this work, the authors found that the co-variation of $\delta^{13}C$ and $\delta^{15}N$ reflects the seasonal succession of phytoplankton species due to seasonal changes in abiotic factors, such as temperature and nutrient concentration.

Silva and Vargas (2014) identified an LDOW zone near the fjord heads (<178 μmoL L⁻¹), attributed to a significant influx of allochthonous particulate organic matter from local rivers (Figure 10). Nevertheless, the observed organic material mixture resulted in relatively lighter isotopic values of particulate organic matter than those expected for an autochthonous organic matter pool (Figure 711). Regardless, the input of organic matter (autochthonous or allochthonous) to the deep layer increased DO consumption through respiration, overwhelming the oxygen supply from horizontal advection (Figures 8 and 9).

The distribution of CDOM in the Patagonian fjords reveals distinctive patterns, as depicted in Figure 11. Notably, elevated CDOM concentrations were observed in the northern region, likely stemming from increased terrestrial inputs, heightened microbial activity, and prolonged CDOM residence times (Figure 13). This phenomenon aligns with observations in fjords within the northern hemisphere (Mannino et al., 2008). Conversely, the southern region displays lower CDOM concentrations, indicative of diminished dissolved terrestrial inputs and potentially more efficient removal processes. The proposal that localized CDOM concentration peaks within specific fjords signify the

influence of local processes, including freshwater inputs, glacier melting, or biological production (Mannino et al., 2008), contributes significantly to the spatial heterogeneity of CDOM distribution in Patagonian fjords.

The distribution of CDOM displayed distinct patterns within the Patagonian fjords (Figure 11). Higher CDOM concentrations were observed in the northern region and were attributed to factors such as greater terrestrial inputs, increased microbial activity, and longer residence times (Figure 13) of CDOM in these fjords (Mannino et al., 2008). In contrast, the southern region exhibited lower CDOM concentrations, indicating a decrease in dissolved terrestrial inputs and potentially more efficient removal processes. Localized increases in CDOM concentrations within specific fjords suggest the influence of local processes, such as freshwater inputs, glacial melting, or biological production, contributing to the heterogeneity of CDOM spatial distribution (Mannino et al., 2008).

4.2. Mechanisms driving hypoxia and LDOW in northern Patagonian fjords

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As discussed in the previous section, one of the principal mechanisms involved in the origin of hypoxic conditions in some areas of the northern Patagonian fjords was attributed to the advection of the ESSW from the Pacific Ocean to Patagonia. Recently, Linford et al. (2023) demonstrated the poleward advection of water with lower DO values by the ESSW that was transported by the Perú Chile Undercurrent (PCUC). The passage of this water mass into the northern Patagonian fjord system was detected in a DO time series from a mooring system installed at the Guafo mouth. Moreover, as shown in Figure 2, extreme hypoxic conditions were registered in the Quitralco Fjord, where ESSW was not delivered absent (Figure 6d-f).

In the Quitralco Fjord, the DO concentration was mainly governed by the biological processes of oxygen production and consumption during photosynthesis and respiration, respectively. The primary production experiments conducted in this fjord (Figures 8 and Figure-9) showed higher values of community respiration than the primary production of DO (Table 2). In addition, the oceanographic model showed a less intense deep net current, allowing a residence time of water between 100–150 days (Figure 13). Furthermore, satellite images provide evidence of of a high concentration highly of suspended sediments along the Quitralco Fjord due to river discharge (Figure 10). Regarding Magdalena Sound, the shallower hypoxia observed there (70 m depth) could be explained by the occurrence of the local upwelling produced when westerly winds blow across the mountains, as was reported for the Comau Fjord by Crosswell et al., (2022) and Díaz et al., (2023), and to a temperate Canadian Fjord (Jackson et al., 2023). A shallower hypoxia (10–20 m) was also registered in Clayoquot Sound, British Columbia, mainly attributed to the local processes, such as, DO consumption during the organic matter degradation, enhanced by upwelling conditions (Rosen et al., 2022).

photosynthesis (i.e. through oxygen production) and is primarily depleted through respiration/remineralization (e.g. oxygen consumption), as well as by the physiochemical properties of water (Zhang et al., 2010); therefore, in many oceanic environments, the GPP and CR rates tend to be tightly coupled. In general, the production of oxygen occurs through photosynthesis in the surface waters (euphotic zone) and oxygen consumption occurs through respiration and remineralization in the entire water column. Consequently, surface waters usually contain high concentrations of oxygen as a result of photosynthesis and atmospheric exchange, whereas concentration decreases in deeper waters

(Pitcher et al. 2021). However, iIn coastal waters or fjord ecosystems, owing to the high amount of organic matter (autochthonous and allochthonous) available in the water column, a greater amount of oxygen is consumed (Jackson et al., 2022) during microbial respiration (Robinson, 2019), thus dominating heterotrophic processes over autotrophic processes. Nevertheless, seasonal and spatial differences can also be observed in the dominance of these processes, as well as within a temporal scale they may have an irregular or persistent occurrence in the water column. This study recorded high CR rates (greater than GPP), indicating heterotrophic metabolism, where more oxygen was consumed than produced (Figure 8). Nevertheless, Puyuhuapi Fjord, Reloncaví Fjord, and Compu estuary –showed high oxygen production values (GPP >20 mmol O₂ m⁻³ d⁻¹) within the 2 to 4 m layer at least in one of the two sampling periods (Figure 8), suggesting a greater uptake than release of CO₂ due to the high surface primary production rates during the spring-summer period at surface waters of some Patagonian fjords (Torres et al., 2011). A recent global assessment of CO₂ uptake from estuaries, including tidal systems and deltas, lagoons, and fjord-fjords reported that fjords ecosystems can reduce 37% of CO₂ anthropogenic emissions (Rosentreter et al., 2023). DO and organic matter are produced only in the well-lit upper ocean but can be consumed throughout the water column. Therefore, in areas of high surface production and slow resupply of oxygen at depth (compared to the rate at which oxygen is respired), DO concentrations may be reduced to hypoxic levels at depth. Nevertheless, sporadic deepwater renewal was observed close to the bottom (160–180 meters) in Puyuhuapi Fjord owing to the inflow of dense salty water above the sill favoring the ventilation of the intermediate layer and inhibiting the occurrence of deep anoxia conditions (Pinilla et al., 2020), as was also reported by Jackson et al., (2022) in Rivers Inlet, British Columbia, and on the west coast of the Vancouver Island (Thomson et al., 2017).

However, tThe first map of residence time in the northern Patagonian fjord showed a coincidence of the area where a high residence time was reported (100–250 days, Figure 13) with the depleted oxygen region, for example, hypoxic and LDOW areas (Figure 213). The hydrodynamic model and derived calculations are helpful tools for explaining the oxygen distribution and patterns in the northern Patagonian fjord system.

5. Conclusions

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Since the beginning of oceanographic research in the Patagonian fjords (1970), hypoxia and LDOW have been reported along the water column. A dataset of hydrographic-biogeochemical parameters, *in-situ* experiments of primary production/community respiration, satellite-suspended particulate mattersediments, and the output of a hydrodynamic model allowed for a holistic evaluation the first time the scrutinization of the oceanographic and biogeochemical processes contributing to hypoxia and LDOW in Patagonian subsurface waters. The influence of the ESSW was recognized as one of the first drivers of this phenomenon. This water mass transported poleward poorly oxygenated waters that entered the northern Patagonian fjords through the Guafo mouth and moved southward through the Moraleda and Jacaf channels and the Puyuhuapi Fjord. The distribution of the ESSW inside the northern Patagonian fjords coincides with the most extensive zone of the LDOW records. However, the hypoxic conditions registered in this zone were also attributed to the high rate of DO consumption during community respiration processes, owing to the entrance of allochthonous organic matter (natural and/or anthropogenic) to the fjords. Additionally, the results from marine currents derived from ADCP measurements and the hydrodynamic model

demonstrated a weak water circulation and a long residence time leading to slow contributing to the reduction of deepwater ventilation, resulting in a drop in DO level, and finally, the occurrence of hypoxic conditions. The Quitralco Fjord also reported hypoxic conditions showing the absolute minimum of DO with 9.36 μmol L⁻¹ and 1.6% oxygen saturation. ESSW was not observed in this area. Therefore, the presence of hypoxic water in the deep layer of Quitralco was attributed to weak deep-water circulation and a long residence time, together with a high rate of DO consumption by community respiration and a higher supply of allochthonous organic matter due to river discharge. Similar processes favoring LDOW were registered at the Aysén, Comau, and Reloncaví fjords, but in the Reloncaví systems, marine currents and residence time were significantly higher than in other fjords. The presence of LDOW in the Reloncaví systems responded mainly to biological processes, e.g., DO consumption during community respiration by phytoplankton and remineralization by bacteria. The analyses of the processes contributing to hypoxic conditions and LDOW in the water column of northern Patagonian fjords allowed for the identification of the main causes leading tofavoring oxygen loss in each fjord investigated. The results provide the environmental information needed to contribute to the sustainable management of the northern Patagonian fjord under anthropogenic activities and climate change scenarios. In addition, it provides significant information for understanding the life cycle of marine species that inhabit Patagonian fjords. Finally, our study provides valuable insights into the relationship between hypoxia, low oxygen processes, the origin of organic carbon, isotopic signals of carbon and nitrogen, the C:N ratio, and the presence of CDOM in the Patagonian fjords. These findings highlight the complex interactions between terrestrial and marine processes and emphasize the role of fjords as potential sites for hypoxia and the accumulation of organic matter. Understanding these relationships is crucial for accurately assessing the impact of low oxygen processes and carbon cycle dynamics in fjord ecosystems and their contribution to the global carbon cycle. Further research is needed to elucidate the mechanisms driving these patterns and their implications for the functioning and resilience of fjord ecosystems against continuous environmental changes.

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Data availability. All data sets used in this manuscript can be requested from the corresponding author.

Author contributions. PL: study design, data analysis, and manuscript leader. IPS: study design, collection, and analysis of physical oceanographic data, and manuscript leader. PM: study design, collection, and analysis of primary production data. PD: study design, collection, and analysis of physical-biological oceanographic data. CA: collection, and analysis of primary production data. EP: developed of oceanographic model and analysis of physical oceanographic data. FB: collection, and analysis of biogeochemical data. MC: analysis of marine current data. AA: study design, collection, and analysis of satellite data. MA: collection and analysis of marine current data. GS: study design, collection, and analysis of physical oceanographic data. CP: edition and analysis of satellite data. CS: collection, and analysis of biogeochemical data. PN: collection, and analysis of biogeochemical data. GM: collection of physical, biological, and biogeochemical data. RA:

collection of physical, biological, and biogeochemical data. JSM: processing and analysis of model data for resident time. CSR: validation hydrodynamics model. All authors contributed to the writing of the manuscript.

1035 Competing interests. The authors declare that they have no conflict of interest.

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