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The Pacific-Atlantic connection: Biogeochemical signals in the southern end of the Argentine shelf

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ABSTRACT

The Cape Horn Current transports low-salinity waters from the SE Pacific Ocean into the Atlantic, which are transported further north by the Malvinas current. Biogeochemical signals of this connection were studied by characterization of dissolved organic matter (DOM) by determination of dissolved organic carbon (DOC), fluorescent dissolved organic matter ($FDOM_c$), and DOM humification index (HIX). Further, inorganic nutrients, salinity, temperature, stable isotopic composition of particulate organic nitrogen ($\delta^{15}N$) and chlorophyll *a* (Chl*a*) were measured in the southern end of the Argentine shelf in March 2012. Three water types were characterized: waters of the Beagle Channel (BCW), coastal waters (CW) and oceanic waters (OW). Highest values of ammonium, DOC, $FDOM_c$ and HIX were found in BCW, the lowest in OW, suggesting that terrigenous input is a main source of ammonium and refractory carbon, which is supported by a highly significant inverse correlation of these parameters with salinity. In turn, lowest concentrations of nitrate, silicate and phosphate were found in BCW and CW, and highest in OW, with highly significant correlations of these nutrients with salinity, indicating the contribution of the saltier, nutrient-rich Antarctic Circumpolar Current (ACC) to the Pacific-Atlantic connection system. In general there was an inverse distribution pattern between Chl*a* and those nutrients contributed by the ACC, which is consistent with the transition from coastal waters to the low-silicate, high-nitrate, low-chlorophyll, iron-limited setting of the Subantarctic oceanic waters north of the Polar Front. In contrast, in the low-salinity, internal BCW, high values of ammonium, DOC, HIX and FDOM indicate continental inputs, likely including iron complexes, which could have led to the observed high Chl*a* values. $\delta^{15}N$ values were positive in the study region, and same as ammonium, reached a maximum in the inner part of the BCW, declining towards OW. This does not support a previous assumption that rainfall on the SE Pacific could be the source of ammonium and hence explain negative $\delta^{15}N$ values previously found in the northern Drake Passage. The highly significant inverse correlations of ammonium, $FDOM_c$, HIX, and DOC with salinity suggest that continental runoff rather than wet deposition is an important source of ammonium and DOM in the Pacific-Atlantic connection.

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1. Introduction

The Southwest Atlantic embraces a high diversity of ecologic, hydrographical and biogeochemical systems. Despite this heterogeneity, organic matter properties show distinct differences between the northern and southern shelf (Lara et al., 2010), with environments defined by differences in nutrient regimes and bacterioplankton abundances (Alder and Franzosi, 2004).

The southern end of the Argentine shelf is part of the Patagonian Cold Estuarine System. This Pacific–Atlantic connection is of particular interest for its hydrological diversity and is interconnected by the Cape Horn Current, which transports low-salinity water from the Southeast Pacific (Acha et al., 2004), and continues as the Malvinas Current (Longhurst, 1998), a source of nutrient-rich Subantarctic waters to the Argentine shelf (Silva and Neshiba, 1979).

North of the Polar Front are the Subantarctic, "low-silicate, high-nitrate, low-chlorophyll", waters (LSiHNLC, Dugdale and Minas, 1995). South of the Polar Front are the Antarctic water masses, high in nutrients and called the true "high-nutrient, low-chlorophyll" region (HNLC). A steep silicate gradient is found between both sectors (Brzezinski et al., 2005), which together with iron availability, influences growth conditions and distribution of phytoplankton in the Southern Ocean (Franck et al., 2000 and references therein). Several large-scale iron-fertilization experiments indicate that micronutrient concentration alone cannot explain the responses of phytoplankton to changing environmental conditions. Instead, micronutrient bioavailability, determined by their chemical speciation (Boye et al., 2001), is

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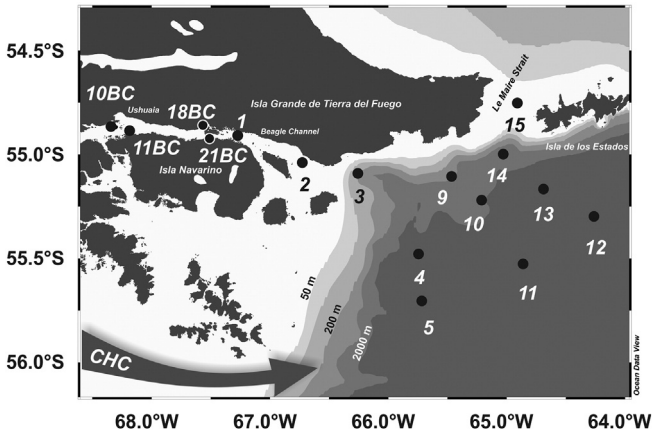


Fig. 1. Location of surface sampling stations in the southern end of the Argentine shelf in late summer 2012. CHC: Cape Horn Current.

among the most important parameters. However, the chemical identity of the organic complexes is almost completely unknown and imposes a principal challenge to the field of marine chemistry.

Little information is available about the dynamics of inorganic nutrients, dissolved and particulate organic matter in this sector of the Patagonian Cold Estuarine System. A previous study (Lara et al., 2010) reported a general increase of ammonium from about 0.25 μM at 48°S to 1.5 μM at 55°S in the beginning of April, together with a consistent, concomitant increase of nitrate and decline of the relative amount of heavy stable nitrogen isotope ($\delta^{15}N$) in seston. While the nitrate source was ascribed to the Antarctic Circumpolar Current (ACC), it was speculated that the origin of the higher ammonium values and the reason for the steeply declining $\delta^{15}N$ values at ~55°S could be partly related to an input of isotopically light ammonium by rainfall (Paerl and Fogel, 1994) in the SE Pacific (Acha et al., 2004). Although the contribution of ammonium to dissolved inorganic nitrogen and to its average $\delta^{15}N$ might be low, Rönner et al. (1983) found in the Scotia Sea that even at high nitrate concentrations, primary production in the austral summer subsisted predominantly on ammonium. Thus, if isotopically light ammonium derived from the large freshwater input in the SE Pacific is actively taken up by phytoplankton in the southern end of the Argentine shelf, this isotopic signal might be detected in its biomass as low $\delta^{15}N$ values.

Following the same reasoning as for ammonium, it could be expected that a significant fraction of the dissolved organic matter (DOM) in waters of the Patagonian Cold Estuarine System is derived from a rainfall-related source in the SE Pacific, e.g. continental runoff. Hence, DOM composition in this estuarine-oceanic system could be the result of the combination of compounds of terrigenous and autochthonous origin.

The identification of DOM sources and its diagenetic state represents a challenging task. Yet, a bulk characterization of DOM can be approached by sensitive and relatively straightforward techniques such as molecular fluorescence spectroscopy (Coble, 1996). A main group of substances in DOM that can be characterized by its fluorescence properties (FDOM) is the fraction of humic-like components ($FDOM_c$). These complex, stable substances with refractory characteristics can contribute to a large extent to dissolved organic carbon (DOC) in marine systems (Benner et al., 1992; Burdige and Zheng, 1998; Middelboe et al., 1995). The characteristics of this DOM can be also evaluated by different indices derived from its fluorescence characteristics, e.g. by the humification index HIX (Senesi et al., 1991; Zsolnay et al., 1999; Ohno, 2002) which gives information about complexity and diagenetic maturity of humic DOM based on its structure.

The distribution of terrigenous DOM, its role in the DOC pool, primary production and microbial food web will be influenced by the particularly complex hydrographical and nutrient regimes of the study zone and is therefore of particular interest for the understanding of the biogeochemical patterns in the Pacific-Atlantic connection and Northern Drake Passage (Lara et al., 2010).

In view of this, a main goal of this study was to examine the effects of the Pacific-Atlantic connection on the biogeochemical patterns in the southern end of the Patagonian Cold Estuarine System. Particularly the origin of relatively high ammonium concentrations and their possible relationship to the low $\delta^{15}N$ values reported in the Atlantic sector of this system has been a focus. In this context, the characterization and quantification of different types and amounts of DOM were used as tracer of continental inputs. A specific issue to be addressed was the role of DOM on phytoplankton distribution in the Subantarctic high-nutrient, low-chlorophyll region. To our knowledge this is the first report on information about these parameters reported for the marine southernmost tip of South America.

2. Materials and methods

2.1. Study area and sampling

Sampling was carried out during the late austral summer in March 2012 at 15 stations distributed in three sectors between 64°–68°W, and 54.75°–55.75°S (Fig. 1). The Beagle Channel connects the Pacific and the Atlantic in W-E direction (Balestrini et al., 1998; Speroni et al., 2003) and included four stations (Sta. 10CB, 11CB, 18CB, 21CB). In the southern coastal and shelf area of Tierra del Fuego seven stations (Sta.1, 2, 3, 9, 13, 14, 15) were situated between the external sector of the Beagle Channel and the Le Maire Strait. The third area is located in a north sector of the Subantarctic Front, embracing five stations (Sta. 4, 5, 10, 11, 12).

Surface water samples were collected between 3 and 10 m depth with Niskin bottles attached to a rosette with a CTD (Sea Bird model 911 plus with General Oceanic rosette) that provided depth, salinity and temperature data. The sensors were calibrated with a final precision of 0.05 in salinity and 0.02 °C in temperature. There were no significant differences in temperature and salinity in the first 10 m of the water column. One to two litre water samples were filtered on board through GF/F filters (Whatman, precombusted at 450 °C, 3 h). Filtrates were divided in three aliquots. For the determination of fluorescence properties, water was kept in precombusted glass vials at 4 °C in the darkness. Aliquots for nutrients analysis were poisoned with $HgCl_2$ and stored at 4 °C in 50 mL acid-washed PE bottles for later analyses (Kattner, 1999). For the determination of DOC, 10 mL seawater were transferred to precombusted glass ampoules (450 °C, 4 h) and acidified to pH 2 with concentrated phosphoric acid (20%, v/v). Filters with particulate material were stored frozen at −20 °C.

2.2. Analysis of dissolved components

2.2.1. Inorganic nutrients and DOC

Nitrate, nitrite, ammonium (all in μM N), silicate (μM Si) and phosphate (μM P) were determined according to seawater standard methods (Kattner and Becker, 1991). DOC was measured by high temperature catalytic oxidation in a TOC analyser (TOC-VCPN, Shimadzu) followed by quantification of CO_2 by non-dispersive linearized infrared gas analysis. A solution of potassium hydrogen phthalate was used as calibration standard (Skoog et al., 1997).

2.2.2. Fluorescence properties of DOM: $FDOM_c$ and HIX

Spectral properties of DOM were determined with a Shimadzu RF-5301 spectrofluorometer with a 150 W xenon lamp and a 1 cm quartz cell. Milli-Q water was used as reference and the intensity of the Raman peak was regularly checked.

An estimation of dissolved terrigenous humic substances was carried out at the wavelengths proposed by Coble et al. (1990) (humic-like fluorophore in the visible region "Peak C", Ex/Em: 325/443 nm, $FDOM_c$). The results were expressed in quinine sulphate equivalent units, converted with the signal at Ex/Em: 350/451 nm of quinine sulphate dehydrate standard dissolved in H_2SO_4 0.05 M and the equivalence 1 QSU = 1 $\mu g \cdot L^{-1}$ (Coble, 1996; Coble et al., 1998; Muller et al., 2008; Ghervase et al., 2010; Para et al., 2010).

HIX was calculated after Zsolnay et al. (1999) and Ohno (2002) as the ratio H/L of two spectral region areas from the emission spectrum scanned for excitation at 254 nm. These two areas are quantified between emission wavelengths 435 nm and 480 nm for H, and between 300 nm and 345 nm for L. When the degree of aromaticity increases, the H/L ratio and hence HIX, increase. This corresponds to a shift in maximum fluorescence intensity from shorter to longer wavelengths associated with an increasing number of highly substituted aromatic nuclei and/or with conjugated unsaturated systems of high molecular weight (Senesi et al., 1991).

2.3. Analysis of particulate matter

2.3.1. Determination of chlorophyll a and $\delta^{15}N$

Photosynthetic pigments were extracted with 90% acetone for 24 h in the darkness at −20 °C. Chlorophyll *a* (Chl*a*) was determined by fluorimetry after Holm-Hansen et al. (1965) with a Shimadzu RF-5301 at Ex/Em: 460/671 nm, using as standard pure Chl*a* from *Anacystis nidulans*.

Filters for the determination of stable isotopes, carbon (C) and nitrogen (N) content were dried at 50 °C for 4 h and kept at room temperature in a desiccator until analysis. Analysis of stable C and N isotopes was carried out with a Thermo Finnigan Delta Plus mass spectrometer coupled to a Flash EA 1112 elemental analyser. GF/F filters containing POM were put in silver vials, acidified with 0.1 N HCl to remove inorganic C, dried 12 h at 50 °C and completely oxidised in the elemental analyser by flash combustion at temperatures above 1000 °C under pure O_2. The isotope composition of N_2 and CO_2 was analysed by mass spectrometry. Samples were analysed in duplicate including an internal standard and a blank every four samples. The amount of isotope for each sample was within the analytical linearity range. The relative standard deviation (as coefficient of variation) between the duplicates never exceeded 3%. Results were normalised to the Pee Dee Belemnite (PDB) (Fry and Sherr, 1984) and atmospheric N_2 standards calculating isotope ratios (R), given as ‰ deviation from the standard value ($\delta^{13}C$ and $\delta^{15}N$) where:

$$R = {}^{13}C/{}^{12}C \text{ or } {}^{15}N/{}^{14}N; \text{ and}$$
$$\delta‰ = \left(\left(R_{sample}/R_{standard}\right) - 1\right) \times 1000$$

The isotope ratios were determined with the international standards from the International Atomic Energy Agency (Vienna): IAEA-N1 and IAEA-N2 were used for ^{15}N, NBS 22 and USGS-24 for ^{13}C, and peptone as internal standard. Only $\delta^{15}N$ values are discussed in this work; $\delta^{13}C$ data will be reported elsewhere.

2.4. Data analysis

Statistical data processing was carried out with the software PAST 2.17c. Relationship between parameters was tested using the Pearson correlation coefficient.

3. Results and discussion

A summary of the data obtained in different zones of the Pacific-Atlantic connection is given in Table 1, including average and standard deviation values.

3.1. Hydrography

The collected data and their patterns were consistent with previous reports from the internal and external sectors of the Beagle Channel cited below, basically associated with transitions between the characteristics of the Cape Horn and the ACC. In general, water temperature decreased from the Beagle Channel towards the Subantarctic Front. Salinity was lower in the Beagle Channel and the coastal zone of Tierra del Fuego compared to the north sector of the Subantarctic Front.

Based on temperature, salinity and bathymetric data, the study area was divided in three waters types (Fig. 2):

(1) Waters of the Beagle Channel (BCW), with temperatures between 8 and 9 °C, low salinities (<30) and depths <50 m. These characteristics were associated with those of the Cape Horn Current, with temperatures >7 °C and salinities <34 due to a high precipitation regime in the zone of the Chilean fjords and ice melting in Southern Patagonia (Acha et al., 2004; Antezana, 1999; Lara et al., 2010; Almandoz et al., 2011; Candel et al., 2013; Biancalana et al., 2014).

(2) Coastal waters (CW), from the external BCW to the Le Maire Strait, with a range of temperatures between 7 and 8 °C, salinities between 31.1 and 33.8, and depths from 32 to 1700 m. The wide ranges of salinity, temperature and depths in the CW point to the connection and transition between the water masses from the Cape Horn Current and the ACC (Acha et al., 2004; Krock et al., 2015).

(3) Oceanic waters (OW), with high salinities (>34) and depths (1093–2285 m) and low temperatures (<7 °C) (Fig. 2), derived from the Northern Drake Passage (Bianchi et al., 1982; Guerrero and Piola, 1997; Piola et al., 2010; Krock et al., 2015).

3.2. Distribution and relationship between inorganic nutrients and salinity

Surface concentrations of nitrate, silicate and phosphate (Fig. 3A, B, C) showed a clear gradient with highest concentrations in OW (nitrate: 19.8 ± 0.6 μM, silicate: 3.2 ± 0.2 μM, phosphate: 1.3 ± 0.1 μM) and lowest values in BCW (nitrate: 7.9 ± 0.3 μM, silicate: 2.1 ± 0.23 μM, phosphate: 0.8 ± 0.1 μM. In CW and OW, these nutrients presented a decreasing trend from SE to NW. This is consistent with the results

Table 1
Summary of data obtained in different zones of the Pacific-Atlantic connection. Average values of dissolved inorganic nutrients (in μM); NO_3^- (nitrate), $Si(OH)_4$ (silicate), PO_4^{-3} (phosphate), NH_4^+ (ammonium); DOC (dissolved organic carbon, μM), $FDOM_c$ (fluorescent dissolved organic matter, QSU), HIX (humification index), Chl*a* (chlorophyll *a*, μg L^{-1}), $\delta^{15}N$ (stable nitrogen isotopic composition, ‰). BCW: Beagle Channel Water, CW: coastal water, OW: ocean water. Number of samples: n. Values in brackets: standard deviation.

Zone	n	Diss. matter							Partic. matter	
		NO_3^-	$Si(OH)_4$	PO_4^{-3}	NH_4^+	DOC	$FDOM_c$	HIX	Chl*a*	$\delta^{15}N$
BCW	4	7.90 (0.34)	2.05 (0.27)	0.77 (0.06)	2.89 (0.69)	68.93 (5.96)	1.12 (0.25)	1.79 (0.17)	1.53 (1.21)	7.19 (0.85)
CW	6–7	11.97 (3.07)	2.05 (0.24)	0.99 (0.08)	1.19 (0.61)	57.55 (7.04)	0.55 (0.26)	1.01 (0.39)	0.46 (0.04)	5.23 (2.16)
OW	5	19.76 (0.59)	3.23 (0.22)	1.31 (0.07)	0.52 (0.09)	54.12 (5.33)	0.28 (0.06)	0.70 (0.37)	0.17 (0.06)	2.82 (0.83)

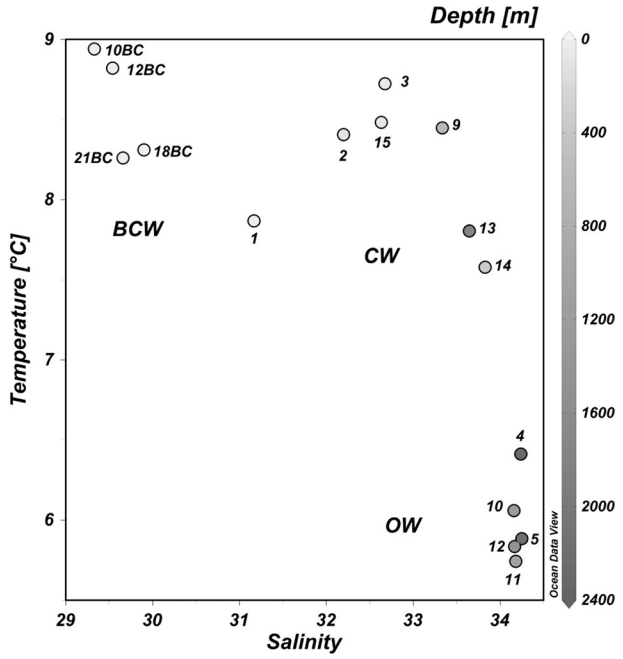


Fig. 2. Division of the study area in three waters types based on surface temperature and salinity, and bathymetric data. BCW: Beagle Channel Waters; CW: coastal waters; OW: oceanic waters.

reported by Silva (2008) from a cruise from Desolada Bay (SE Pacific) to Cape Horn. In BCW, nutrient concentrations were generally lower compared to those reported for summer and autumn in the west sector of the Beagle Channel (Amin et al., 2011; Duarte et al., 2011). In its eastern sector, concentrations were similar to those from Almandoz et al. (2011); Silva (2008), and Gil et al. (2011). Oppositely, ammonium was distributed inversely as the other nutrients, increasing its concentrations from OW (0.5 ± 0.1 μM) to BCW (2.9 ± 0.7 μM) (Fig. 3D). Values were similar to those reported by Gil et al. (2011) and Lara et al. (2010), but higher than in Biancalana et al. (2014).

There were two main distribution patterns of inorganic nutrients. On the one side, there was a highly significant positive correlation between salinity and the concentrations of nitrate, silicate and phosphate ($r = 0.90$, $r = 0.65$, $r = 0.91$, $n = 15$, $p < 0.01$, respectively), indicating the saltier ACC as main source of these nutrients. On the other side, the highly significant inverse correlation between ammonium and salinity ($r = -0.94$, $n = 15$, $p < 0.0001$) (Fig. 4), suggests an input of this nutrient by continental runoff/rainfall via Cape Horn Current/Beagle Channel.

3.3. Distribution and relationship between $FDOM_c$, HIX, DOC and salinity

The fluorophore "C" corresponding to $FDOM_c$ was identified in all samples. $FDOM_c$ is associated with highly degraded terrigenous humic material, and its intensities showed a decreasing trend from BCW (0.84–1.36 USQ) to values ranging 0.21–0.37 USQ in OW (Fig. 4). The fluorescence intensities of $FDOM_c$ and the values of the HIX index (0.27–2.02) were similar to those reported by Para et al. (2010) for the coastal surface waters of the Northwestern Mediterranean Sea but lower than those measured in the Gironde Estuary by Huguet et al. (2009).

$FDOM_c$ followed the same distribution pattern as ammonium. These parameters correlated highly significantly ($r = 0.95$, $n = 15$, $p < 0.0001$), suggesting that both have a common origin. Further, the fact that both, $FDOM_c$ and ammonium presented a highly significant inverse correlation with salinity ($r = -0.92$, $n = 15$, $p < 0.0001$), indicates that the main source of these parameters is the freshwater input

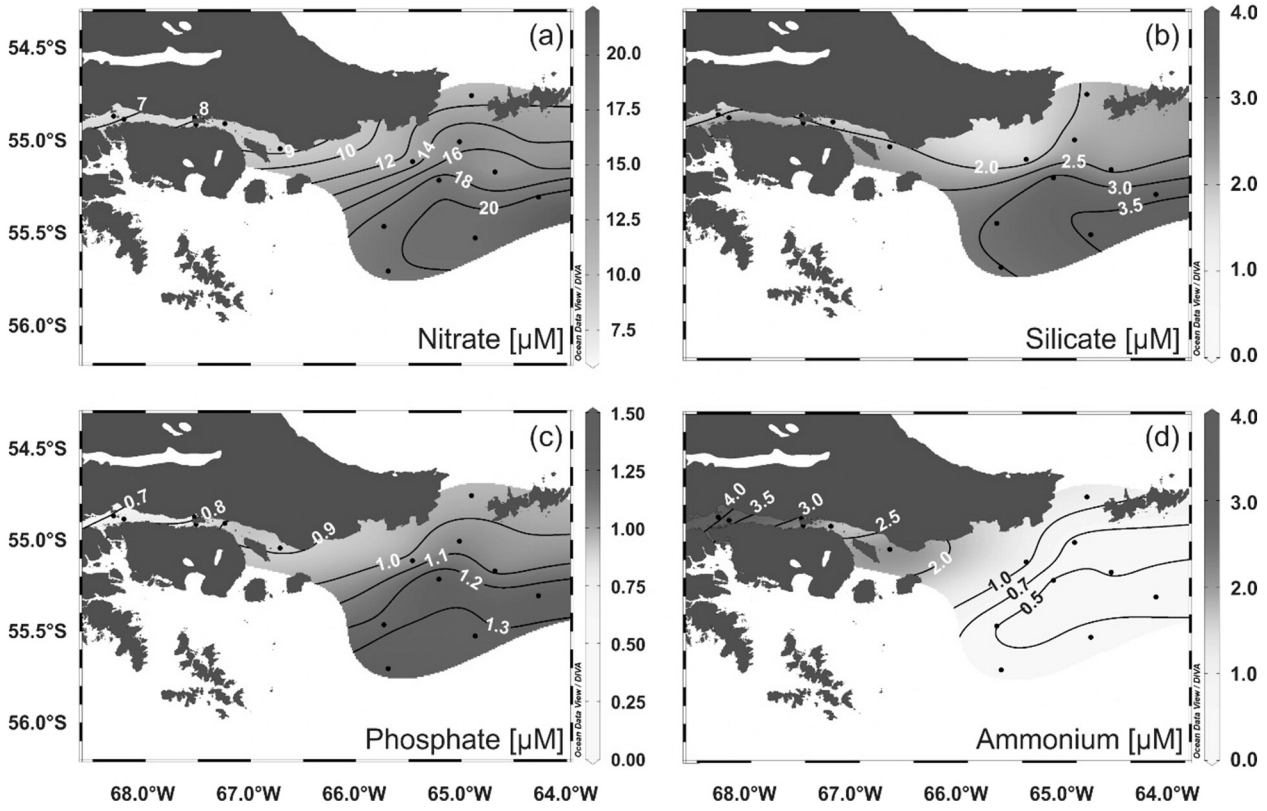


Fig. 3. Distribution of inorganic nutrients in surface waters of the study zone.

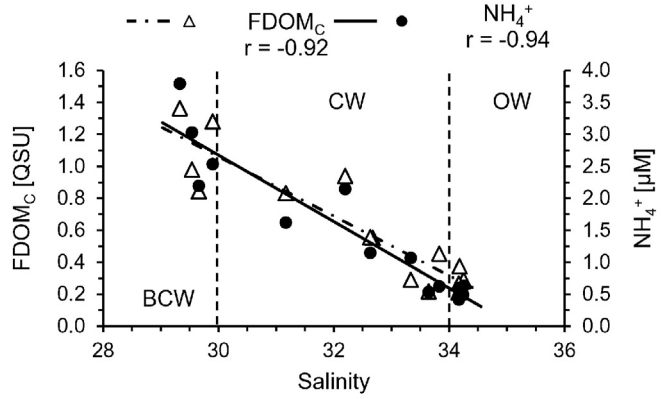


Fig. 4. Relationships of fluorescent dissolved organic matter ($FDOM_c$) and ammonium (NH_4^+) with salinity in surface waters of the study zone. BCW: Beagle Channel Waters; CW: coastal waters; OW: oceanic waters.

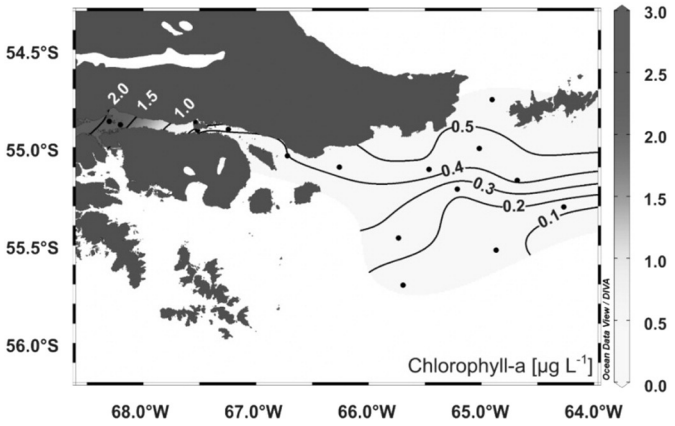


Fig. 6. Distribution of chlorophyll *a* in surface waters of the study zone.

in the southern end of the Pacific-Atlantic Patagonia. A lower, yet still highly significant correlation ($r = 0.82$, $n = 15$, $p < 0.001$) was also obtained between ammonium and the HIX index, whose distribution and characteristics are discussed below.

The HIX index presented a similar trend as DOC, decreasing from highest values in BCW (2.02) to a minimum in OW (0.27). Highest DOC values (77 μM C) occurred in BCW with a decreasing trend towards OW (46 μM C) (Fig. 5). This analogous distribution was reflected in a highly significant correlation between DOC and HIX ($r = 0.70$, $n = 15$, $p < 0.01$).

This implies a significant contribution of terrigenous carbon with refractory characteristics to the DOC pool in the Pacific-Atlantic connection, where the decrease of these parameters with increasing salinity reflects the dilution of the continental input with OW.

Besides the effect of dilution with low-DOM water masses, the observed values and distribution gradients of $FDOM_c$ and HIX might be partly the result of the photochemical decomposition of chromophoric DOM (Vahatalo and Wetzel, 2004). Thus, a fraction of terrigenous $FDOM_c$ could be eliminated by photobleaching from BCW to OW. Notwithstanding, (i) the marked SW-SE gradient, (ii) the fact that in BCW the highest $FDOM_c$, HIX and DOC occurred at the lowest salinity values and (iii) the highly significant inverse correlation with salinity, reinforce the postulated input of refractory carbon to the zone of the Pacific-Atlantic connection by runoff from southern Chilean fjords, main source of freshwater to the Cape Horn Current, and likely also from Tierra del Fuego streams.

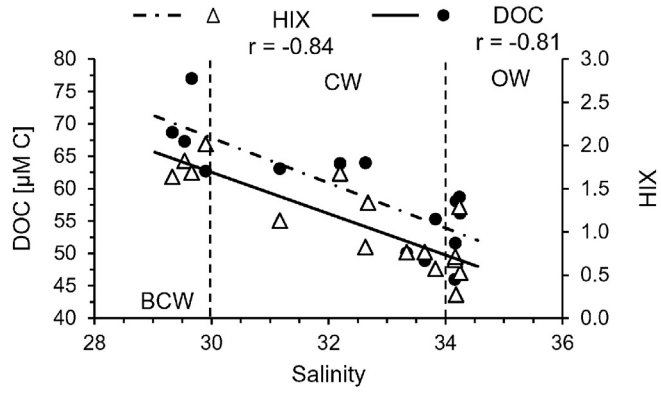


Fig. 5. Relationships of dissolved organic carbon (DOC) and humification index (HIX) of dissolved organic matter with salinity in surface waters of the study zone. BCW: Beagle Channel Waters; CW: coastal waters; OW: oceanic waters.

3.4. Distribution and relationships among Chla, $\delta^{15}N$ and nutrients

Chl*a* values (0.34–2.87 μg L^{-1}) and trends were comparable to those previously reported by Biancalana et al. (2012, 2014) in the same zone and season, with a decreasing tendency to the east of the Beagle Channel. Highest Chl*a* concentrations were found in BCW (2.9 μg L^{-1}) and CW (0.5 μg L^{-1}), gradually decreasing to a range of 0.1–0.3 μg L^{-1} in OW (Fig. 6), similar to those reported by Lara et al. (2010) in this sector in late summer.

There was inverse distribution pattern between Chl*a* and those nutrients contributed by the ACC (nitrate, silicate and phosphate, Fig. 3A, B, C), which is consistent with the general "low-silicate, high-nitrate, low-chlorophyll" setting of the Subantarctic oceanic waters north of the Polar Front (LSiHNLC; Dugdale and Minas, 1995). In contrast, the high Chl*a* values in the internal part of BCW suggest an influence of continental input of ammonium and DOM and phytoplankton activity.

The values of $\delta^{15}N$ in suspended particulate matter varied between 8.0‰ and 1.9‰, with a decreasing gradient in approximately SE direction from higher values in BCW and CW towards OW (Fig. 7). This trend could be part of a larger scale pattern reaching consistently negative $\delta^{15}N$ values in the northern Drake Passage between 56° and 58°S as reported by Lara et al. (2010) (Fig. 7, SE sector).

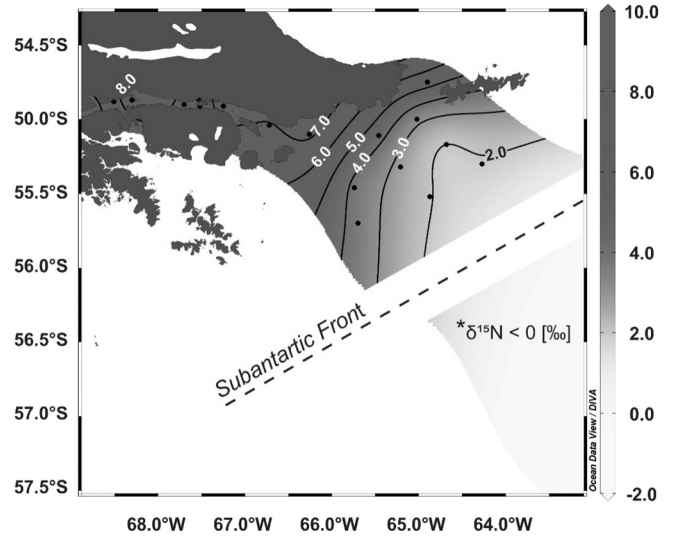


Fig. 7. Distribution of $\delta^{15}N$ of suspended particulate organic matter in surface waters of the study zone. *$\delta^{15}N$ values from Lara et al. (2010).

There was a highly significant inverse correlation between $\delta^{15}N$ and nitrate ($r = -0.90$, $n = 15$, $p < 0.0001$) in the study region. This reflects the active uptake of nitrate by phytoplankton and hence an increased incorporation of the isotopically heavier fraction of this nutrient as its concentration decreases towards the high-Chl*a* sector in BCW, resulting in a ^{15}N-enriched POM. Yet, it is not known to what extent the high ammonium concentrations in BCW could have contributed with their own isotopic signature to the overall $\delta^{15}N$ values in POM.

Although $\delta^{15}N$ generally decreases with increasing nitrate concentration, phytoplankton preference for ammonium can influence the isotopic signature to a significant extent, even at high nitrate settings. For example, Lourey et al. (2004) reported $\delta^{15}N$ values from about 0 to −4‰ near the Polar Front in summer, in relation to the production of low ^{15}N-POM by summertime ammonium uptake. Thus, there may be a transition system from decreasing positive $\delta^{15}N$ values from BCW to OW, to negative values in waters of the Subantarctic and Polar Fronts. This might be partly associated to different sources of ammonium, from allochthonous, continental runoff in the SE Pacific, and eventually Tierra del Fuego, to autochthonous nitrogen regeneration in the Drake Passage, even in a setting of high nitrate concentrations (Lara et al., 2010). Although the low $\delta^{15}N$ values might be also associated to biological fixation of atmospheric N_2, this is unlikely since the density of cyanobacteria is generally low in the whole Drake Passage and in the Southern Ocean (Alder and Franzosi, 2004, 2005). Lara et al. (2010) further hypothesized that the southwards increase of ammonium values in the Cold Estuarine Zone on the Argentine Shelf, together with decreasing POM-$\delta^{15}N$ values reaching consistently negative values in the northern Drake Passage could be at least partly produced by the entrance into the Argentine Shelf of isotopically light ammonium from wet deposition in the SE Pacific. After Paerl and Fogel (1994), $\delta^{15}N$ of ammonium in rainfall can cover a wide range of negative values. However, in this study all POM-$\delta^{15}N$ values were positive and >1‰, reaching maxima in the sector with the highest ammonium values. Thus, it is unlikely that wet deposition could be a significant ammonium source in this region.

4. Conclusions

In the southern end of the Argentine shelf, the investigated biogeochemical signals of the Pacific-Atlantic connection presented following trends: Among the dissolved components, ammonium and the organic carbon with terrigenous characteristics showed a spatial distribution strongly influenced by the freshwater input from the SE Pacific through the connection with the Atlantic driven by the Cape Horn Current and likely also from continental sources in Tierra del Fuego. In turn, nitrate, phosphate and silicate distribution in the region showed a strong influence from the contribution of saltier, nutrient-rich ACC waters.

The distribution of Chl*a* and of stable nitrogen isotopes presented patterns associated with a two-end member mixing: on the one side, BCW waters rich in ammonium, chlorophyll and dissolved organic matter probably providing ligands that could make micronutrients such as iron available for primary producers. On the other side, nutrient-rich, chlorophyll-low waters of the Southern Ocean produced the dilution of those signals, and a consequently decreasing gradient towards SE. The positive values of $\delta^{15}N$ and the highly significant correlations between ammonium, $FDOM_c$ and the HIX index in the studied sector seem to preclude a significant input of ammonium to the Atlantic through wet deposition in the SE Pacific, which is rather derived from continental runoff. Probably only the determination of $\delta^{15}N$ in the different dissolved nitrogen species, in addition to POM- $\delta^{15}N$, can help further clarify the dynamics of inorganic and organic nutrients in this complex region, tracking ammonium input from Chilean waters through the Cape Horn Current into the Southwest Atlantic.

The patterns resulting from this study stress the high biogeochemical and ecological significance of the Beagle Channel and its external zone, in its intermediate position between the Pacific and Atlantic Oceans and its proximity to the Subantartic Front and the Antartic Circumpolar Current (Knox, 1994; Brandt et al., 1997; Gambi and Mariani, 1999; Ríos et al., 2003).

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