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Factors influencing the characteristics and distribution or surface organic matter in the Pacific-Atlantic connection

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ABSTRACT

The present work reports the first data set on particulate organic carbon (POC) and nitrogen (PON), and the high-resolution modelling of their stable isotope variability in the Patagonian Cold Estuarine System (PCES), with focus on particulate organic matter (POM) origin and distribution in dependence on physical, chemical and biological parameters. POC, PON, stable carbon ($\delta^{13}C$) and nitrogen isotopes ($\delta^{15}N$), dissolved organic nitrogen, phaeopigments, diatom, dinoflagellate and heterotrophic bacteria (HB) abundance are reported for 17 stations in different waters masses in the southern end of the Argentine shelf in late summer 2012. Most parameters denote clear differences between Beagle - Magellan Water (BMW), Subantarctic Shelf Water (SSW) and Subantarctic Water (SAW). POC and PON decreased from maxima in BMW to intermediate values in SSW and minima in SAW. There was a highly significant correlation among POC, PON and fluorescence indicators of diagenetic maturity of dissolved humic matter. This, together with the inverse correlations of salinity with POC and PON, and the wide range of C:N ratios indicate that POM in the study area is partly derived from terrestrial runoff, superimposed by autochthonous components from plankton of different life stages. HB abundance was significantly correlated with POC and dissolved organic matter (DOM), likely reflecting a resource control of HB and a significant contribution of bacterial biomass to POM in the nanoparticle fraction. The direct relationship between HB and dissolved humics suggests bacterial uptake of DOM fractions otherwise considered refractory.

POM complexity was reflected in a wide variation of $\delta^{13}C$, despite the narrow temperature range of this region. The variability of stable isotopes of POC could be accounted for by a model with a degree of detail hitherto not reported in the literature. A multiple regression including C:N ratio, ammonium and the quotient between log abundance of diatoms, dinoflagellates and HB explained 92% of $\delta^{13}C$ variance, mostly produced by ammonium. Despite the strong effect of ammonium on $\delta^{13}C$, $\delta^{15}N$ variability was largely explained by a strong inverse relationship with the fraction of unutilized nitrate, suggesting dominance of nitrate uptake. However, the proportion of presumably isotopically heavier ammonium derived from continental runoff in the marine $\delta^{15}N$-POM pool is unknown and requires investigation of the isotopic composition of dissolved inorganic nitrogen in the PCES.

The presented new information and its comparison with data from other sectors of the Argentine shelf constitute a contribution to an approach for the understanding of the organic matter dynamics that can be potentially expanded to the entire Southwest Atlantic.

1. Introduction

A sound understanding of the driving forces of dissolved (DOM) and particulate organic matter (POM) variability is essential to improve the current knowledge of carbon and nitrogen dynamics, particularly where continental and oceanic inputs occur in hydrographically complex environments. On a global scale, the amount of carbon in DOM in seawater is 20 times higher than in POM (Sharp, 1973). POM comprises living and non-living matter, including microalgae, bacteria, detritus, fecal pellets, and clays (Volkman and Tanoue, 2002). The pool of non-living POM is about 10 times higher than plankton biomass and is dominated by complex organic molecules that are difficult to decompose (Benner and Kaiser, 2003).

Alteration of POM by microbes is particularly important in estuaries, where it represents a significant source of nutrients for adjacent coastal ecosystems (Mayer et al., 1988; Rabalais et al., 1996). DOM also plays a key role in bacterial production and microbial food web processes in coastal ecosystems (Azam and Hodson, 1977). It acts as a substrate supporting heterotrophic bacterial (HB) activity (Carlson, 2002 and

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references therein). The factors controlling its transfer, production, removal and accumulation in estuarine environments have therefore both biogeochemical and ecological significance. Determining organic matter sources (McCallister et al., 2006a, 2006b), and the factors regulating its production, consumption and transformation in coastal and oceanic waters is critical for improving our knowledge on the biogeochemical cycles in complex estuarine environments.

In this context, the Patagonian Cold Estuarine System (PCES), in the southern end of the Argentine shelf, is particularly relevant for its hydrographic complexity, high biologic productivity, freshwater inputs, and as link between oceans, particularly when trying to understand the main biogeochemical mechanisms and the sources of biogenic carbon (C) and nitrogen (N). The PCES is part of the Pacific–Atlantic system interconnected by the Cape Horn current, which transports low-salinity water from the Southeast Pacific (Antezana, 1999; Acha et al., 2004), and continues as the Malvinas Current (Longhurst, 1998), which delivers oceanic nutrient-rich Subantarctic Waters (SAW) to the Argentine shelf (Silva and Neshiba, 1979).

Studies on the biogeochemical dynamics of organic matter in the Southwestern Atlantic are scarce, and the spatio-temporal variability of bulk POM and DOM is largely unknown. In fact, to date there are few available publications addressing tracers of suspended POM, such as stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopes (Lara et al., 2010), dissolved organic carbon (DOC) and fluorescent DOM (Garzón-Cardona et al., 2016) in Argentine shelf and adjacent oceanic waters. The latter work stressed the importance of continental runoff on the productivity of waters of the Beagle Channel, focusing on the sources of ammonium and DOC of this system. It also tested the hypothesis that ammonium derived from wet deposition or continental runoff could explain negative $\delta^{15}N$ values reported for this area in previous studies (Lara et al., 2010), but did not further investigate the sources of isotopic variability. Based on the interaction of Subantarctic waters with freshwater inputs from the SE Pacific, and relationships between DOM fluorescence properties and inorganic nutrient distributions (Garzón-Cardona et al., 2016) described a zonation of the region in Beagle Channel, coastal and oceanic waters.

The complexity of this environmental setting allows the assumption that properties of the water masses also play a major role in the characteristics of POM. Thus, the current study has two main objectives: first, the zonal characterisation of POM properties as dependent on physical and chemical parameters, and second, the understanding of the isotopic variability of organic matter in the region.

To our knowledge, the present work reports the first data set of particulate organic carbon (POC) and nitrogen (PON) distribution in the PCES, with focus on POM origin and distribution, as well as the modelling of its isotopic variability ($\delta^{13}C$ and $\delta^{15}N$). For this purpose, plankton size fractions were studied taxonomically and functionally; and the influence of oceanographic properties, chlorophyll, DOM features and inorganic nutrient concentration patterns reported by Garzón-Cardona et al. (2016) were also included in this analysis.

2. Materials and methods

2.1. Study area and sample collection

During the austral autumn, from March 27th to April 14th 2012, surface water samples were collected on board of *F/B* Don Pedro and *R/V* Puerto Deseado during the expedition IADO 0312 and PATAGONIA AUSTRAL-2012. For clarity, we used in this work an ordinal numbering for the seventeen sampling stations covering the Beagle-Drake geographical area (Fig. 1). Water depths ranged from 80 m in the inner part of the Beagle Channel to 2300 m in the open ocean. At all stations, continuous temperature and salinity (CTD) profiles were recorded.

An aliquot of 250 mL of sea water from the Niskin bottle samples from each station was fixed with acidic Lugol's iodine solution for determination of total plankton community composition and quantitative analyses. Diatoms and dinoflagellates cells were enumerated with a phase contrast Leica DMIL LED inverted microscope according to the procedures described by Utermöhl (1958). Subsamples of 50 mL were settled for 24 h in a composite sedimentation chamber. Additionally, plankton samples were collected by vertical net tows through the upper 20 m of the water column with a 20 mm-mesh Nitex net of 60 cm diameter. An aliquot of 100 mL of net sample was fixed with acidic Lugol's iodine solution for diatoms and dinoflagellates taxonomic analysis.

For picoplankton abundance determination, 3 mL of surface seawater sample were preserved with 1% paraformaldehyde + 0.05% glutaraldehyde (final concentration), frozen and stored at −20 °C. The samples were later thawed, stained with SYBR-Green I (SYBR-I, 1:30 dilution of commercial stock; Invitrogen, USA; lex λ 495 nm, lem λ 525 nm) diluted in dimethyl sulfoxide (DMSO, Merck, Germany) (Marie et al., 2005). Ten microliters of fluorochrome was added to 1 mL of bacterial sample. Samples were incubated in the dark for 15 min at room temperature. Cell counts were performed with a flow cytometer (A40, Apogee Flow Systems, UK) equipped with an argon laser (488 nm). Cells were counted following Marie et al. (2005). Briefly, HB were detected by their signature in a plot of side scatter (SSC) *versus* green fluorescence (FL1). Autotrophic picoplankton (AP) was detected by direct fluorescence in a plot of SSC *versus* red fluorescence (FL3).

2.2. Biogeochemical bulk parameters

POM and DOM samples were obtained from surface water between 3 and 10 m using Niskin bottles. Mostly 3 L of each sample was passed through 200 μm mesh to remove large zooplankton, filtered (max. 300 mbar) using precombusted (4 h, 450 °C) glass fiber filters (GF/F, Whatman). The nominal 0.7 μm pore-size of GF/F filters was the operational limit for separating POM from DOM in this study. The filtered water was kept frozen (−20 °C) until determination of DOM fluorescence and dissolved organic nitrogen (DON) concentration.

POC, PON, stable C and N isotope ratio analyses were carried out with a mass spectrometer (Delta Plus, Thermo Finnigan) coupled to CN Analyser Eurovector EA3000 element analyzer according to Verado et al. (1990). Inorganic C was removed by acidification with 0.1 HCl and dried again at 50 °C. Accuracy was checked and tolerances corrected by measuring internal standards and automated baseline correction after a set of five samples, with analytical precision CN analyses ≤ 1.0%. Results were normalized to the Pee Dee Belemnite (PDB) (Fry and Sherr, 1984) and atmospheric N_2 standards calculating isotope ratios (R) (Eq. (I)), given as ‰ deviation from the standard value $\delta^{13}C$ and $\delta^{15}N$ (Eq. (II)), with the analytical precision ≤ 0.5‰.

$$R = \frac{{}^{13}_{0}C}{{}^{12}_{0}C} \; or \; \frac{{}^{15}_{0}N}{{}^{14}_{0}N} \; and, \tag{I}$$

$$\delta(‰) = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right]^{*} 1000 \tag{II}$$

Pigment extraction on duplicate filter samples was performed in 10 mL 90% acetone during 24 h at 4 °C in darkness. After acidification with 0.1 N HCl phaeopigments were quantified by fluorometry (Holm-Hansen et al., 1965).

Dissolved inorganic nutrients (nitrate, nitrite, phosphate, silicate and ammonium), were determined spectrophotometrically with an autoanalyzer (Evolution III, Alliance Instruments) according to standard methods for seawater analysis (Kattner and Becker, 1991; Garzón-Cardona et al., 2016). DOC and total dissolved nitrogen (TDN) was quantified in duplicate by high temperature catalytic oxidation and subsequent non-dispersive infrared spectroscopy and chemoluminescence detection (TOC-VCPN, Shimadzu), (Koroleff, 1983) and substracting inorganic nitrogen species previously determined by Garzón-Cardona et al. (2016),