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Contribution of allochthonous organic carbon across the Serrano River Basin and the adjacent fjord system in Southern Chilean Patagonia: Insights from the combined use of stable isotope and fatty acid biomarkers

Alejandra Lafon [a,b], Nelson Silva [c], Cristian A. Vargas [d,*]

[a] Interdisciplinary Center for Aquaculture Research (INCAR), Km 4.5, Coyhaique, Chile
[b] Universidad Austral de Chile, Coyhaique & Doctoral Program in Environmental Sciences, Environmental Sciences Center EULA Chile, Universidad de Concepción, PO Box 160-C, Concepción, Chile
[c] Escuela de Ciencias del Mar, Pontificia Universidad Católica de Valparaíso, PO Box 1020, Valparaíso, Chile
[d] Aquatic Ecosystem Functioning Lab (LAFE), Aquatic System Unit, Environmental Sciences Center EULA Chile, Universidad de Concepción, Concepción, Chile

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ABSTRACT

Chilean Patagonia is characterized by an irregular geography involving many islands, peninsulas, channels, sounds and fjords, that prevent direct interaction between oceanic water masses and freshwater river discharges at the head of the continental fjords. In this paper, we evaluate the potential sources and composition of organic matter along the Serrano River basin and the adjacent channels and fjords in Southern Chilean Patagonia (51–52°S), as well as their importance for marine planktonic organisms. In spring of 2009, evidence of C:N ratio, $\delta^{13}C$, $\delta^{15}N$ and fatty acids composition in particulate organic carbon (POC), surface sediment, soil, plankton, and vegetal tissue, as well some physical and chemical characteristics (i.e. salinity, dissolved oxygen, NO_3^-, NH_4^+, PO_4^{-3}, $Si(OH)_4$), were measured in samples collected during the *CIMAR 14 Fiordos* oceanographic cruise. Significant differences in $\delta^{13}C$-POC were found between the terrestrial and marine environments but not within fjord stations. Along the fjord region, the high C:N ratio and depleted $\delta^{13}C$ values in POC samples suggest that particulate organic matter (POM) in the upper level of the water column (0–10 m depth) is supported by different sources. Terrestrial organic carbon exported by rivers may constitute a significant subsidy, up to 70% based on two end-member mixing model, to the fjord ecosystem. Furthermore, terrestrial carbon might account for a significant percentage of the zooplankton body carbon, estimated both by using isotopic (~24–61%) and fatty acid analysis (~14–61%). Isotopic analyses in marine sediment samples suggest that POC seems to be decoupled from terrestrial-influenced surface sources at the fjord stations, and the contribution of surrounding vegetation seemingly unimportant for carbon export to the benthos. Local hydrographic and geomorphological characteristics might determine the presence of oceanographic frontal zones, which in turn might explain differences in carbon sources found between POM and the surface sediments.

Introduction

Fjords are highly dynamic and complex estuarine ecosystems that act as a zone of interaction between fresh water (lakes, rivers, glaciers) and adjacent coastal systems (McLeod and Wing, 2007; Mayr et al., 2011). These zones may also support many important ecosystem functions, including biogeochemical cycling and movement of nutrients (Silva et al., 2011; Vargas et al., 2011). In order to understand the role of fjords in global biochemical cycles, as well as their vulnerabilities to anthropogenic stressors, the knowledge of different sources of organic matter and their fluctuations is needed. Understanding ecological processes across ecosystems is of growing importance as human interference, such as deforestation, aquaculture, and dam construction, will likely affect climate change with potentially devastating economic and ecological consequences, seriously impairing reciprocal energy exchange among ecosystems (Vargas et al., 2011).

The Chilean Patagonian fjords occur within a large region, from Reloncaví Fjord (41°20′S) to Cape Horn (56°S), which is characterized by about 84,000 km of coast line broken up by the contours of

* Corresponding author. Tel.: +56 41 2204032; fax: +56 41 2207076.
E-mail address: crvargas@udec.cl (C.A. Vargas).

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its multiple islands and peninsulas, and numerous waterways (Silva and Prego, 2002). Formed by erosion, due to the advancement and retreat of glaciers in the last ice age, this study area has a particularly irregular geography (Borgel, 1970–1971), which makes direct communication between water masses of oceanic origin and fresh-river water difficult at the head of the continental fjords. Because fjords are transition areas between rivers and coastal seas, the terrestrial input is usually relatively high in the inner sea area.

Fjords are fed by freshwater discharges from continental runoff, rivers, and glacial tributaries, which are characterized by low nitrate and phosphate, but high silicic acid concentration. However, they are also fed by oceanic Subantartic waters (SAAW) inputs with elevated nutrient concentration (NO_3^- > 12 μM and PO_4: >1 μM) (Silva and Guzman, 2006; Vargas et al., 2008, 2011; Gonzalez et al., 2011). This condition results in an inner fjord region with different hydrographic characteristics that depend on the volume and the source of the freshwater inputs (Silva et al., 2001), which modulate the autochthonous primary production and the contribution of terrestrial allochthonous sources (Vargas et al., 2011). Consequently, the dissolved (DOM) and particulate organic matter (POM) might originate from both the marine primary production and the terrestrial land-plants sources transported by rivers and overland runoff (Sepulveda et al., 2011). For the Chilean fjord region, primary production has been reported as highly seasonal and limited by the amount of light and nutrients (Iriarte et al., 2007; Gonzalez et al., 2011). Nevertheless, some studies in northern Chilean Patagonian fjords have shown strong allochthonous contribution in both POM and surface sediments associated to river-plumes areas or those located at the heads of the fjords (Sepulveda et al., 2011; Silva et al., 2011; Vargas et al., 2011).

A better understanding of the sources and composition of POM may be highly relevant for determining the importance of terrestrial subsidies of POM in fjord ecosystems.

Stable isotopes ($\delta^{13}C$, $\delta^{15}N$) and C:N ratios have been widely used for tracing the source and fate of organic matter in aquatic ecosystems (Canuel et al., 1995; Graham et al., 2001; Mc Callister et al., 2006; Alt-Epping et al., 2007; Liu et al., 2007; McLeod and Wing, 2007). The analysis of $\delta^{13}C$ in POC and surface sediments might indicate the origin of organic matter if the sources have different isotopic signals (Thornton and McManus, 1994). Due to the complexity of organic matter sources in estuarine systems, biogeochemical approaches that use multiple techniques are strongly recommended (Canuel et al., 1997; Hu et al., 2006; Waterson and Canuel, 2008). The application of chemical biomarkers to provide more specific and sensitive information rather than bulk elemental and isotopic techniques has become widespread (Bianchi, 2007). Fatty acids have been used extensively for assessing the sources and fates of organic matter in marine, coastal, and estuarine ecosystems (Mannino and Harvey, 1999; Meziane and Tsuchiya, 2000; Countway et al., 2007; Waterson and Canuel, 2008). In this study, our main objective was to assess the relative contributions of allochthonous (i.e., terrigenous) and autochthonous sources to the POM pool along a gradient from Serrano River Basin to the Nelson Strait, adjacent to the Pacific Ocean, by employing nutrient stoichiometry (N, P, Si:N ratios), isotopic analyses ($\delta^{13}C$), lipid biomarkers (fatty acid composition), and standard measurements of bacterial, protozoan, and phytoplankton carbon biomasses. The results of this study on organic matter reservoirs have been compared with additional measurements in zooplankton organisms, in order to explore the potential utilization of allochthonous OM in the planktonic food webs of this particular Chilean fjord ecosystem. Based on the ultra-oligotrophic nature of Patagonian Rivers, the insignificant riverine autotrophic productivity and their subsequent exportation to the fjord environment we hypothesize that there is a significant contribution (>50%) of allochthonous terrestrial organic matter signature in the POM and in the zooplankton communities inhabiting the surface brackish waters of southern Chilean fjords, which demonstrates a significant terrestrial organic carbon is reaching those fjords.

Methods

Study area

The present study comprises of a large region in Southern Chilean Patagonia (from ~50°50′ to ~52°26′°S), including the Serrano River Basin and the adjacent Última Esperanza-Smyth Fjords (estuarine–marine system), located approximately 50 km SE of the South Patagonian Ice Field (51°S; 72°W, Fig. 1). Sampling was conducted during the course of an austral oceanographic research cruise during the spring of 2009 and during a field survey along the adjacent watersheds (i.e. October, 2009).

The Serrano River basin (SRB) is located within the Torres del Paine National Park (A Biosphere Reserve), which covers an area of approximately 8700 km^2 and is comprised of a complex hydrological system developed east of the Southern Ice Field (Solari et al., 2010). On the western side of the SRB, melt water from the Southern Ice Field makes up a system composed of proglacial lakes feeding many rivers; the Paine River flows into Lake Nordenskjöld, which in turn drains into Lake Pehoe and then into Lake Del Toro. The main outlet of Del Toro Lake is the Serrano River, while the Grey River links up with the Serrano River which flows into the Última Esperanza Fjord (Fig. 1). Most lakes in SRB are characterized by low anthropogenic intervention (Soto et al., 1994) and the large deep lakes (Del Toro, Sarmiento, Pehoe, Nordenskjöld) have been characterized as oligotrophic (Soto and De los Ríos, 2006; De los ríos and Soto, 2009). The terrestrial flora along the basin is mostly dominated by deciduous forest (*Nothofagus* spp., *Drymis winterii*, *Berberis microphylla*, *Maytenus disticha*, *Pernettya pumila*, *Empetrum rubrum*, *Sphagnum magallanicum*) and Patagonian Magellan Steppe (*Festuca gracillina, Stipa humilis, Chilotrichum diffusum, Deschampsia antarctica*) (CADE-IDEPE, 2004).

The Última Esperanza Fjord receives most of its freshwater discharges from the SRB, located on the eastern side of its headwaters and from the Balmaceda and Serrano glaciers on the west (Fig. 1). After reaching the fjord, the estuarine water flows into the Almirante Montt Gulf and to the Pacific Ocean through several inter connected channels such as Kirke, Santa Maria, Union, and Smyth (Fig. 1). The complex bathymetry of this area is characterized by a gradual increase in depth from the east (about 25 m) to the west (600 m). However, in the Kirke Channel, there is a constriction-sill approximately 50 m deep and ~200 m wide, which generates an eastern microbasin (Stn. 55, 54, 53, 52, 51, T1, T2 and T3). The vertical distribution of the water's characteristics (temperature, salinity and σ_t) shows that in general this inlet region is a fairly stratified environment (Silva and Calvete, 2002). The general circulation scheme proposed suggests that the brackish surface water of the estuaries flows outward from Almirante Montt Gulf, while the deeper, more saline water from Smyth and Union Channels flows over the Kirke constriction-sill into Almirante Montt Gulf, filling its basin (Sievers et al., 2002). The population density at the Última Esperanza Province is very low (~3 ind km^{-2}; INE, 2012), but most of the anthropogenic organic matter sources are limited to Puerto Natales town (18,507 inhabitants), some agriculture, tourism, and incipient aquaculture activities.

Hydrography, nutrients and plankton content of biomass

The oceanographic field work, including water, sediment, and marine plankton samples were obtained during the CIMAR 15