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Degradation capability of the coastal environment adjacent to the Itata River in central Chile (36.5° S)

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Abstract

The response of the coastal ocean influenced by both river discharges and inputs of photosynthetically derived organic carbon product of upwelling, was evaluated by estimating rates of microbial hydrolysis of macromolecules with the goal of estimating the degradation capability of the coastal ecosystem off central Chile.

Extracellular enzymatic hydrolysis in seawater was dominated by aminopeptidase activity on substrate MCA-leu (1.2 to 182 nM h^{-1}), which surpassed that of substrates MUF-glu (0.08–61 nM h^{-1}) and MUF-cel (0.15–6.8 nM h^{-1}), with the fastest rates measured during spring-summer. In riverine waters, extracellular enzymatic hydrolysis remained within the range of 45 to 131 nM h^{-1} for MCA-leu and ca. 20 nM h^{-1} for glucosidic substrates, year-round. Contrary to the observed for the marine water column, surface sediment extracellular enzymatic hydrolysis of MCA-leu (0.04 to 6.13 nmol gdw^{-1} h^{-1}) was in the same order of magnitude as the rates observed for MUF-cel (0.004 to 2.58 nmol gdw^{-1} h^{-1}) and MUF-glu (0.007 to 10.5 nmol gdw^{-1} h^{-1}). Moreover, hydrolysis was characterized by higher rates during winter compared with spring-summer in the coastal and estuarine zone.

The five years of data allowed us to construct a carbon budget for winter and spring-summer in the coastal area adjacent to the Itata River discharge. The comparison of fluxes evidenced a deficit of photosynthetic carbon to fuel extracellular hydrolysis in the water column during both periods (winter 20% and spring-summer 35%). We estimated that the Itata River is a feasible source of dissolved organic carbon, specially during winter, in the form of macromolecules, although non-focal sources may be also significant for the area.

1 Introduction

Although continental shelves (global area $26 \times 10^{12}\,m^2$) sustain high primary production, and estuaries (global area $1.05 \times 10^{12}\,m^2$) are reservoirs of terrestrial primary production transported by rivers, both constitute a small fraction of the global ocean (7.5%, Cai et al., 2010). Although several studies have shown that continental shelves sequester more than 40% of oceanic carbon (Hedges and Keil, 1995; Muller-Karger et al., 2005), there are however uncertainties as to our ability to quantify the exchange of carbon between marine and terrestrial systems (Liu et al., 2000), and difficulties in evaluating the main processes controlling the fate of terrigenous carbon in coastal waters and sediments (Hedges and Keil, 1995). These knowledge gaps have impeded us from determining why most of the terrestrial carbon (ca. 0.25 Pg) transported to the ocean by world rivers every year (Cauwet, 2002) disappears from the reservoir of dissolved organic matter in the ocean (Hedges and Parker, 1976) and marine sediments (Hedges, 2002). Considering the refractory nature of terrestrial carbon (Hedges, 1992), Hedges and Keil (1995) posed the conundrum of the relatively short residence time of terrestrial organic matter compared with the seemingly labile plankton-derived marine organic molecules, pointing to the role of the coastal ocean in processing organic matter (Rabouille et al., 2001).

In coastal upwelling ecosystems, the biological community thrives in an environment of high availability of organic molecules derived from high primary production rates, thus enhancing microbial secondary production (e.g., Quiñones et al., 2010). The coastal ocean in the Humboldt Current System off central Chile at 36.5° S (Fig. 1) is under the influence of seasonal upwelling and associated productivity cycles (Daneri et al., 2000). In this area, coastal upwelling interacts with two seasonal physical processes that modify vertical stratification: the heat balance in the mixed layer during the austral summer, and the fresh water balance during the austral winter due to greater freshwater discharges from the Bio-Bío and Itata Rivers (Sobarzo et al., 2007). The interplay of upwelling and freshwater discharge has a noticeable effect on the chemistry and biology of the water column. For instance, at a site 30 km offshore (COPAS Times Series Coastal Station, www.copas.udec.cl/eng/research/serie/) we observed that biogenic opal from diatom productivity dominates the water column during summer, whereas lithogenic opal predominates during austral winter (Sánchez et al., 2008).

Since the first carbon budget for the Humboldt Current System (Walsh, 1981), several reports have attempted to balance biogeochemical fluxes of the coastal ocean in a variety of environments using different approaches such as trophic transfers (Bernal et al., 1989; González et al., 1998, 2000; Troncoso et al., 2003; Vargas and González, 2004), nutrient balances (Pantoja et al., 2010; Quiñones et al. 2010), and particulate sinking fluxes (González et al., 2000; Pantoja et al., 2004; González et al., 2009). Results from those investigations have revealed overall lower primary production (Montecino et al., 1998; Daneri et al., 2000) than that associated with the heterotrophic activity of microbes (Quiñones et al., 1997; González et al., 1998; Eissler and Quiñones, 1999), and with higher trophic levels (Cubillos et al., 1998). Even though this fundamental discrepancy might be explained by errors due to both experimental approaches and natural variability in ocean processes, excess heterotrophic consumption may be explained by the additional input of carbon into the marine system to fuel the activity of the marine microbial community, as shown for some coastal environments (Chin-Leo and Benner, 1992).

It has been observed that microbial heterotrophic activity is enhanced by the input of organic matter by both phytoplankton production and riverine sources, thus explaining the enhanced microbial consumption rates at the boundaries between river and oceanic waters (Albright, 1983; Kirchman et al., 1989). Only a small fraction of the organic matter pool are monomers capable of being directly transferred to microorganisms for remineralization, thus efficient hydrolysis and utilization of autochthonous and allochthonous biopolymers, such as proteins and carbohydrates, are crucial for sustaining high microbial growth rates and associated degradation of organic matter (Azam, 1998). The extracellular enzymes of aquatic microbes (Chróst, 1991) are key components in the hydrolysis of abundant marine biopolymers. Extracellular hydrolysis is the initial step in carbon mineralization in which organic macromolecules are broken down into smaller substrates capable of being incorporated across the cell membrane of microorganisms (e.g. King, 1986; Chróst, 1991; Hoppe, 1991; Pantoja et al., 1997; Arnosti, 2003), thereby affecting the fate of organic matter in the marine environment (Arnosti, 2011).

In this paper, we undertook the study of the temporal and spatial variability of extracellular enzymatic hydrolysis of carbohydrates and proteins, as a proxy of microbial reworking in the coastal upwelling ecosystem adjacent to the Itata River in central Chile (Fig. 1). We aim to obtaining a deeper understanding of the degradation capability of this coastal area in relation to the carbon sources that fuel heterotrophic consumption. An accurate insight into the magnitude of organic matter reworking of the coastal ocean is needed to understand how the coastal ocean responds to natural and anthropogenic perturbations (Ver et al., 1999; Rabouille et al., 2001).

2 Materials and methods

2.1 Study area

We studied the coastal zone off central-southern Chile (ca. 36.5° S) under the direct influence of the Humboldt Current System (Strub et al., 1998). One of the main features of this coastal system is the occurrence of fertilization events due to upwelling of subsurface nutrient-rich waters into the photic zone during the austral spring-summer (e.g. Ahumada and Chuecas, 1971), which promotes very high primary production rates (Daneri et al., 2000; Montero et al., 2007), and significant commercial fish landings (Quiñones et al., 2010). Upwelling waters also carry low oxygen concentrations thus generating a seasonal suboxic layer below 20 m water depth (Sobarzo et al., 2007).

The thermal structure of the water column during spring and summer is controlled by solar radiation in the top 10 m and upwelling favorable wind stress below 15 m depth, resulting in a stratified surface layer and lower temperature waters under the thermocline.

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During winter, haline stratification is observed in the top layer due to precipitation, enhanced freshwater discharge from the Bio-Bío and Itata Rivers, and downwelling below the thermocline induced by northerly winds (Sobarzo et al., 2007). The coastal ocean receives a noticeable amount of terrigenous material from the adjacent rivers, evidenced by the dominance of lithogenic over biogenic opal during the austral winter (Sánchez et al., 2008) and the presence of lignin phenols in coastal sediments (Schubert et al., 2000).

Observations were carried out in the marine and riverine environments of Central Chile encompassing latitudes from 36°10′ S to 36°7′ S and from 73°10′ W to 72°40′ W surrounding the Itata River mouth (Fig. 1). The Itata River runs for ca. 195 Km and its flux at the mouth is an average of 240 $m^3 s^{-1}$ (Dussaillant, 2009). During December 2009, the submarine outfall disposal for residues from the waste treatment plant of a major pulp mill was installed in December 2009. The pipe is 2 km long, and is located at 30 m depth near sampling station 6 (Fig. 1).

2.2 Water and sediment sampling

We carried out 13 sampling campaigns between 2006 and 2010 covering 6 field observations during the austral spring-summer and 7 in autumn-winter (Table 1) onboard the R/V *Kay-Kay II* (University of Concepción) and small boats for estuarine and river sampling. Twenty-nine locations were visited; 3 river sampling sites, 1 estuarine site, and 25 in the coastal ocean (Fig. 1). Seawater and river samples were collected with Niskin bottles and polypropylene carboys for surface samples, which were used for nutrient, chlorophyll-*a*, protein measurements, and incubations for estimates of rates of primary production and extracellular hydrolysis of proteins and carbohydrates. Water samples were collected at several depths between 1 and 110 m for measurements and incubations. Surface (0–1 and 1–2 cm) sediment samples were collected with a box corer or a Van Veen grab, then stored at 4 °C until arrival at the laboratory to be processed for hydrolysis incubation experiments.

2.3 Water column measurements

Temperature, salinity and oxygen in the water column were recorded with a Sea Bird SBE 19 plus CTD and data were processed with the Ocean Data View 4.3.5 software (Schlitzer, 2010). Water samples for NO_3^- were filtered through 0.7 µm (GFF) and both filtrate and filters were frozen at −20 °C. The filtrate was analyzed for nutrients with the spectrophotometric method of Strickland and Parsons (1972), and filters were split for the determination of chlorophyll-*a* by fluorometry (Parsons et al., l984) and particulate proteins by HPLC. Particulate proteins were analyzed as Total Hydrolyzable Amino Acids by High Pressure Liquid Chromatography coupled to an on-line fluorescence detector set up at 330 nm (excitation) and 450 nm (emission) on a Shimadzu HPLC, fluorescence detector, and autosampler. Subsamples of filters were placed in 2 mL of N_2-purged hydrolysis solution for 1.5 h at 150 °C and neutralized. Aliquots of the neutralized solution were derivatized before injection with *o*-phthaldialdehyde and 2-mercaptoethanol according to Mopper and Lindroth (1982). Separation and quantification of 15 protein amino acids was done in a C18 Kromasil column using a gradient program of 0.025 M sodium acetate and 5% tetrahydrofurane.

Determinations of rates of primary production were carried out at 5, 10, 20, 30 and 40 m depth at Station 14 (Fig. 1) from changes in dissolved oxygen concentrations observed after incubating in situ light and dark bottles (Strickland, 1960). Water from Niskin bottles was transferred to 125-mL borosilicate bottles (gravimetrically calibrated). At each incubation depth, five clear and five darkened bottles were incubated in situ for 8–9 h, attached to a surface buoy mooring anchored to the ocean floor, and then treated with the Winkler reagents. Oxygen concentrations were determined manually according to the Winkler method (Strickland and Parsons, 1972) using an automatic Dosimat Metrohm 665 burette and by visual end-point detection. Oxygen production was converted to carbon units using a photosynthetic quotient of 1.25 and rates calculated as $[O_2]$ after incubation in clear bottles minus $[O_2]$ after incubation in darkened bottles. Discrete primary production rates were integrated for the whole water column. Our data was combined with additional primary production measurements published by Daneri et al. (2000) in the area 35°00′ S to 39°00′ S and 73°00′ W to 75°00′ W from 36 observations from 1989 to 1991.

Estimates of extracellular enzymatic activity were conducted based on duplicate 5 mL-aliquots of seawater, which were incubated in darkness with L-leucine-4-methylcoumarinyl-7-amide (MCA-Leu), methylumbelliferyl-ß-D-cellobiose (MUF-Cel) and 4-methylumbelliferyl-ß-D-glucoside (MUF-Glu) at 10 µM final concentrations (Hoppe, 1983). Fluorescence was measured at time zero, and every two hours for 6 h at 365 nm excitation and 455 nm emission.

Calibration curves were constructed by measuring the fluorescence in seawater with hydrolysis products MCA and MUF at concentrations ranging between 0.03 and 0.5 µM. First order rate constants were calculated from the slope of the plot ln (C_0/C_0-P) vs. time, where C_0 is the initial concentration of the substrate (MCA-leu, MUF-glu, MUF-cel) and P is the concentration of the product (MCA, MUF) at time *t* (Pantoja and Lee, 1994). Actual hydrolysis rates were calculated by multiplying rate constants by C_0. Discrete rates were depth-integrated throughout the water column, and carbon hydrolysis rates calculated using the conversion factor of 72 for MUF-glu and MCA-leu, and 144 for MUF-cel (Hoppe, 1983).

2.4 Surface sediment measurements

Estimates of extracellular enzymatic activity in sediments were carried out in duplicate undisturbed sediment mini-cores containing ~10 mL wet sediment, which were incubated in the dark with MCA-Leu, MUF-Cel, and MUF-Glu at ~50 µM final concentrations (Meyer-Riel, 1986). At time courses 0 and 9 h, the sediment was centrifuged at 3500 rpm for 5 min, and the supernatant was filtered through 0.2 µm Durapore filters and analyzed by fluorescence as before. Calibration curves were determined with pore water, analyzed and expressed as before. Grams of dry sediment were transformed to sediment volume as in Berner (1980).

Primary production rates, hydrolysis rates and hydrolysis in surface sediments were averaged for winter (June to August), and the period spring-summer (September to March).

3 Results

3.1 Physical-chemical and biological characteristics in the coastal area adjacent to the Itata River mouth

Seasonal variability was observed in the vertical distribution of temperature. Thus, during winter cold waters (< 11–12 °C) were homogeneously distributed in the water column (Fig. 2a). In contrast, during spring and summer temperatures higher than 13 °C and a stratified water column were observed (Fig. 2b). Horizontal distribution of temperature showed changes seaward, with the thermocline observed at ~ 10 m at coastal stations and ~ 30 m at offshore stations during the spring-summer period (Fig. 2b). In contrast, during winter temperature remained homogeneously distributed along the gradient (Fig. 2a).

Seasonal variability in salinity was also observed in surface waters with low salinity (28.5–33 psu) recorded during winter in the top ~ 5 m depth, evidencing the influence of freshwater from the Itata River discharge to more than 7 km offshore (Fig. 2c). During spring and summer, salinity was more homogeneously distributed and the influence of freshwater was restricted to surface waters in the top ~ 3 km offshore (Fig. 2d).

Permanent suboxic conditions (< 22 µm) were evidenced below ~ 60 m depth during the entire sampling period (Fig. 2e and f), and although no major temporal changes were observed in oxygen concentrations, during spring-summer the oxycline raised about 20 m in coastal stations (Fig. 2f). That pattern was similar to those observed for temperature (with cold waters reaching about 20 m) indicative of upwelling waters.

The concentration of nitrate ranged between 5 and 20 µm in the top ~ 30 m during winter (Fig. 2g). Below this depth, concentration of nitrate was in the order of 25 µm

(Fig. 2g). Nitrate ranged between 10 and 20 µm in the top 20 m during spring-summer (Fig. 2h). The highest concentrations (∼ 40 µm) of nitrate during the austral spring and summer were observed in bottom waters (Fig. 2h), reaching ca. 20 m depth toward coastal stations, suggesting the effect of seasonal upwelling as described before.

Suspended particulate chlorophyll-*a* showed large differences between the austral winter and spring-summer (Fig. 2). During the latter, values in the range of 10 and $> 30\,\mathrm{mg\,m^{-3}}$ were observed in surface waters (Fig. 2j), while during winter, maximum chlorophyll-*a* only reached values of about $5\,\mathrm{mg\,m^{-3}}$ (Fig. 2i). Along the seaward gradient, the highest concentrations of chlorophyll-*a* were observed within 15 km from the coast in surface waters during spring-summer (Fig. 2j).

Suspended particulate proteins in the water column showed differences in surface waters depending on season, > 2 µm during spring-summer in the upper 20 m, and about 1 µm during winter (Fig. 3). Below 30 m depth, concentrations decreased to ca. 0.5 µm in both winter (Fig. 3a) and spring-summer (Fig. 3b).

3.2 Extracellular enzymatic hydrolysis in the water column from the river to 20 km offshore

Extracellular enzymatic hydrolysis in surface seawater was dominated by aminopeptidase activity (MCA-leu), which ranged from 1.2 to $182\,\mathrm{nM\,h^{-1}}$ and was at least one order of magnitude higher than the activity observed for substrates MUF-glu (0.08–$61\,\mathrm{nM\,h^{-1}}$) and MUF-cel (0.15–$6.8\,\mathrm{nM\,h^{-1}}$) (Fig. 4). Seasonal differences were observed in extracellular enzymatic activity with the highest hydrolysis rates of MCA-leu ($181.9\,\mathrm{nM\,h^{-1}}$), MUF-glu ($61\,\mathrm{nM\,h^{-1}}$), and MUF-cel ($6.8\,\mathrm{nM\,h^{-1}}$) during spring-summer in the coastal area between 0 and 20 km from the coast (Fig. 4b, d and f). During winter, extracellular hydrolysis in the coastal area decreased to values ranging from 1.2 to $56.7\,\mathrm{nM\,h^{-1}}$ for MCA-leu and from 0.08 to $6.9\,\mathrm{nM\,h^{-1}}$ for glucosidic substrates MUF-cel and MUF-glu (Fig. 4a, c, e).

Along the river stations, extracellular enzymatic hydrolysis remained within the range of 40 to $131\,\mathrm{nM\,h^{-1}}$ for MCA-leu and about $20\,\mathrm{nM\,h^{-1}}$ for glucosidic substrates during winter (Fig. 4a, c, e). During summer, hydrolysis of MCA-leu averaged 101 ± 20 nM h^{-1} in the river, 83.3 ± 20 nM h^{-1} in the estuary and 93.5 ± 50.2 nM h^{-1} in coastal waters. During spring-summer extracellular hydrolysis of MCA-leu in riverine waters averaged 96 ± 20 nM h^{-1} and was similar to those observed in coastal waters 93.5 ± 50.2 nM h^{-1}). No major changes in hydrolysis rates were observed between riverine and coastal waters for MUF-glu (Fig. 4c and d), while MUF-cel hydrolysis was higher in river than in coastal waters (Fig. 4e and f).

3.3 Extracellular enzymatic hydrolysis in surface sediments along a river-offshore gradient

Contrary to the observed for the water column, in surface sediments extracellular enzymatic hydrolysis of MCA-leu (0.04 to 6.13 nmol gdw^{-1} h^{-1}) was in the same order of magnitude to those observed for MUF-cel (0.004 to 2.58 nmol gdw^{-1} h^{-1}) and MUF-glu (0.007 to 10.5 nmol gdw^{-1} h^{-1}) substrates (Fig. 5). In addition, seasonality of hydrolysis was characterized by higher rates during winter than in spring-summer in the coastal and estuarine zones (Fig. 5). Extracellular hydrolysis of MCA-leu ranged from 0.04 to 6.13 nmol gdw^{-1} h^{-1} during winter (Fig. 5a), and from 0.24 to 1.97 nmol gdw^{-1} h^{-1} during spring-summer (Fig. 5b). For glucosidic substrates, extracellular hydrolysis during winter ranged between 0.007 and 113.12 nmol gdw^{-1} h^{-1} (Fig. 5c and e) and during spring and summer from 0.05 to 2.2 nmol gdw^{-1} h^{-1} (Fig. 5d and f) in the area adjacent to the Itata River discharge.

No major seasonal changes were observed in extracellular enzymatic hydrolysis in riverine sediments, and the estimated rates were in the low range of those observed for coastal sediments (Fig. 5). Hydrolysis of MCA-leu ranged from 0.07 to 2.3 nmol gdw^{-1} h^{-1} during winter and from 0.11 to 0.38 nmol gdw^{-1} h^{-1} during spring-summer (Fig. 5a and b). For glucosidic substrates, hydrolysis rates ranged from 0.30–0.86 and 0.069–1.7 nmol gdw^{-1} h^{-1} during spring-summer (Fig. 5d and f) and winter (Fig. 5c and e).

The comparison of rates of hydrolysis of MCA-leu over time at a site near the outfall pipe did not show any difference in degradation attributable to the effect of the discharge from the secondary treatment of the pulp mill industry, neither in the water column nor in the surface sediment (Fig. 6).

4 Discussion

4.1 Physical-chemical and biological characteristics in the coastal area adjacent to the Itata River mouth

Temporal changes in hydrographic conditions were observed in the coastal area adjacent to the Itata River reflecting the seasonal variability described for the Humboldt Current System off central-southern Chile (Strub et al., 1998; Daneri et al., 2000; Figueroa and Moffat, 2000; Sobarzo et al., 2007). During spring-summer an increase in surface temperature and a shallow thermocline evidenced a stratified water column (Fig. 2a and b). During this period, cold, nutrient-rich and oxygen-depleted waters reached ca. 20 m depth in the coastal area (Fig. 2), evidencing the influence of upwelling conditions in the vertical structure of the water column. During winter, a low salinity layer along the coastal offshore gradient in surface waters (~ 0–5 m) was observed (Fig. 2c and d), evidencing the influence of the freshwater input from the Itata River. These seasonal changes in hydrographic variability are consistent with previous studies in this coastal ecosystem (Sobarzo et al., 2007) that identified both upwelling events and freshwater influx from the river discharges as the main processes determining the vertical structure of the water column.

As a consequence of the upwelling, high primary production is observed in the coastal ecosystem off central-southern Chile during spring and summer (Daneri et al., 2000; Montero et al., 2007). Our results for the area adjacent of the Itata River mouth showed differences in productivity rates between austral winter (~ $0\,\mathrm{g\,C\,m^{-2}\,d^{-1}}$) and spring-summer ($1.2\,\mathrm{g\,C\,m^{-2}\,d^{-1}}$). These values were in the range of what Daneri et al. (2000) previously measured in the area (Table 2). In addition, higher values of primary production during summer were accompanied by high concentrations of chlorophyll-*a* (Fig. 2j) and particulate proteins (Fig. 3). During winter, photosynthetic production in the coastal ecosystem off Chile decreases (Daneri et al., 2000; Montero et al., 2007), as reflected by chlorophyll-*a* (Fig. 2i) and proteins (Fig. 3) observed in the study area.

4.2 Extracellular enzymatic hydrolysis in seawater and surface sediments

Several patterns in the rates of hydrolysis are observed in this study. First of all, rates of hydrolysis of protein substrates were 4 to 7 times higher than those of carbohydrates in seawater (Fig. 4). This pattern has been previously observed (e.g. Arnosti, 2011) and has been attributed to the preferential mineralization of organic nitrogen with respect to carbon in the marine environment (Lee et al., 2004), and may be supported by more bacterial taxa with transporting genes of amino acids rather than sugars (Poretsky et al., 2009). In estuarine and riverine waters and sediments, we observed that rates of hydrolysis of protein were 5–10 times faster than hydrolysis of carbohydrates (Fig. 4). Within the water column, hydrolysis rates of all substrates were always higher in surface waters (data not shown), as previously shown for other coastal areas such as the Gulf of Genoa, off the Ligurian Coast in the Mediterranean Sea (Misic and Fabiano, 2006), as well as other areas in the upwelling ecosystem of northern Chile (Pantoja et al., 2009). This pattern is attributed to the enhancement of primary production and associated exudation of organics in the photic zone, a trend that has also been observed with amino peptidase activity along a eutrophication gradient in lakes (Chróst and Siuda, 2006). A correlation analysis using Spearman rank order resulted in significant association of water column hydrolysis of all substrates with chlorophyll-*a*, ($p < 0.006$), and of MCA-leu with chlorophyll-*a*, temperature and oxygen ($p < 0.0003$). These results coincide with the general idea of enhancement of hydrolytic activity with substrate availability previously stated. We are however aware that degradation of some substrates may depend on the limitations in microbial ability (Arnosti et al., 2005), and that this is only part of the story.

We observed seasonal differences in activity on glucosidic and protein substrates in river, estuarine and coastal waters (Fig. 4). Hydrolysis of the three substrates was higher during winter in the river and the estuary compared to marine sites, whereas in spring-summer, this pattern was not evident and hydrolysis of MCA-leu and MUF-glu was approximately constant across all environments, showing a decrease in activity of MUF-cel towards marine sites (Fig. 4). For comparison, in a transect from the Sacramento River towards the Central Bay in the northern San Francisco Bay, Murrel et al. (1999) observed generally higher activity of amino peptidase in marine waters, and higher ß-glucosidase activity in river waters. Rates of hydrolysis estimated for the sites located along the Concepcion coast (this study) were comparable to those measured in northern San Francisco Bay. However, our rates of hydrolysis of protein for the Itata River were much lower than those measured by Karrasch et al. (2006) in the nearby Bio-Bío river, and within the range of those estimated for surface waters of the Ottawa, Maumee and Hudson rivers in north America (Sinsabaugh et al., 1997).

An increase in hydrolysis rates of MCA-leu and MUF-glu was observed in coastal waters during spring-summer compared to winter (Fig. 4), probably associated with the enhancement of biological activity in marine waters reflected in an increase in primary production (Table 2), particulate protein (Fig. 3) and chlorophyll-*a* (Fig. 2i and j). Others have found similar trends in hydrolysis along trophic gradients, such as for amino peptidase activity in the Caribbean Sea (Rath et al., 1993) and the Northern Adriatic Sea (Karner et al., 1992). However, organic matter supply may not be the only controlling factor of extracellular enzyme activity since lack of a trend has also been observed between glucosidase activity and organic matter supply in the Northern Adriatic Sea (Karner et al., 1992).

Hydrolysis in surface sediments followed different patterns than those of the water column (Fig. 5), and was within the same order of magnitude as previous measurements in surface sediments in other coastal zones (e.g., Meyer-Reil, 1986; Meyer-Reil, 1987; Mayer, 1989). Hydrolysis rates of MCA-leu, MUF-glu and MUF-cel were higher in the coastal and estuarine sediments than in river sediment during the entire period. Here, hydrolysis of MCA-leu did not dominate, and even some of the fastest rates were those of MUF-glu (Fig. 5). This difference between enzyme activities in the water column and sediment microbes is not unexpected since both environments might have different communities with different enzyme capabilities (Arnosti, 2008).

The temporal pattern in extracellular enzymatic hydrolysis in surface sediments was also different to that observed in seawater, and higher hydrolysis rates were observed during winter compared to spring-summer in coastal sediments (Fig. 5), suggesting that riverine transport of terrestrial organic matter may have enhanced hydrolysis during winter. To support this hypothesis, we had previously observed dominance of particulate lithogenic opal over biogenic during austral winter in the coastal zone (Sánchez et al., 2008).

4.3 Carbon fluxes in the coastal zone adjacent to the Itata River

The coastal ocean is only 7% of the global ocean (Walsh, 1991) but it transfers disproportionately high amounts of carbon and nutrients relative to its surface area. Recent research has determined that several coastal zones (e.g. Baltic Sea, North Sea) are heterotrophic systems, where community respiration surpasses primary production, and therefore net consumption of organic carbon is verified (Thomas and Schneider, 1999; Thomas et al., 2005). This concept implies that the system has to be fueled by alloctonous carbon in order to be sustainable over time.

Considering the fluxes measured in this study and previous reports for primary productivity in the study area (Table 2), we produced a simple carbon budget for winter and spring-summer in the coastal area adjacent to the Itata River discharge (Fig. 7). Depth integrated extracellular enzymatic hydrolysis (ΣMCA-leu + MUF-glu + MUF-cel) was estimated from the average of individual measurements collected during winter and spring-summer (Table 1) in order to generate average profiles of hydrolysis for the coastal zone. During winter, integrated extracellular hydrolysis in the water column averaged 0.6 ± 0.07 g C m^{-2} d^{-1} and during spring-summer it was 5 ± 0.3 g C m^{-2} d^{-1} (Fig. 7). In surface sediments, rates were 0.1 ± 0.1 g C m^{-2} d^{-1} in winter and 0.1 ± 0.04 g C m^{-2} d^{-1} during spring-summer (Fig. 7). Primary production in the study area ranged from 0 to 0.9 g C m^{-2} d^{-1} during winter and 1 to 5.7 g C m^{-2}d^{-1} during spring-summer (Table 2). Our results showed an excess of extracellular hydrolysis in the water column related to primary productivity during both periods (winter 120% and spring-summer 135%; Fig. 7).

Along the coast of central Chile, photosynthetic primary production in the coastal ocean appears unable to provide enough organic carbon for extracellular hydrolysis of macromolecules (Fig. 7). Even during the spring-summer period, when primary production contributes with 82% of plankton carbon, extracellular hydrolysis in the water column was on average ca. 40% higher than photosynthetic carbon production, a similar percentage excess as that observed during winter.

Taking these average rates (Fig. 7) as face values, we can calculate the total production of the area covered by our study (223 km^2, Fig. 1), resulting in the photosynthetic production of 110 tonnes C d^{-1} in wintertime, and 690 tonnes C d^{-1} in the spring-summer period. Likewise, extracellular hydrolysis of proteins and carbohydrates for the area is estimated at 180 and 1140 tonnes C d^{-1} in wintertime and spring-summer, respectively. There is a clear deficit of organic carbon to sustain the observed hydrolysis of macromolecules in the water column, requiring a daily input of ca. 70 (winter) and 400 tonnes C (spring-summer) to fuel the coastal zone from external sources.

Could the required carbon be supplied by the Itata River? Considering the seasonal regime in the river discharge and its impact on biological production (Quiñones and Montes, 2001), and the high levels of lithogenic opal detected in the coastal upwelling ecosystem off central-southern Chile during winter that contrasts with the dominance of biogenic opal in spring-summer (Sánchez et al., 2008), it is highly possible that there is a significant input of organic molecules from freshwater and terrestrial environments. In consequence, we hypothesized that during winter an important input of organics from the river could be supplying the requirement of the heterotrophic community. Although the accurate magnitude of the fluxes and the quality of this organic matter remain unknown, we are in the position of giving a first insight into this process.

Average river fluxes for the period 2007–2008 were 260 and 68 $m^3 s^{-1}$ in winter and spring-summer, respectively (Water Authority Chile, www.dga.cl). The concentration of macromolecular dissolved organic carbon, i.e. molecules of size > 1000D (UDOM) averages 305 µm (3.7 $mg L^{-1}$) in several tributaries to the Amazon River (Hedges et al., 1994). Given the lack of information for the Itata River in Chile, we are considering the value 305 µm as a "good number" to perform our calculations. The multiplication of river flux by UDOM results in the transport by rivers of 24 tonnes $C d^{-1}$ in spring-summer and 90 tonnes $C d^{-1}$ in winter.

The Itata River is a feasible source of dissolved organic carbon, especially during winter, in the form of macromolecules, i.e., carbohydrates and proteins. For the tributaries of the Amazon river, macromolecular carbon constitutes in average 77% of dissolved organic carbon (Hedges et al., 1994), that differs from marine dissolved organic carbon where 25% is of size > 1000 D (e.g. Benner, 2002). However, other sources of carbon on which we have no information are possible as well. For instance, for the South Carolina coast, Goñi and Gardner (2003) estimated that the flux of carbon from the North Inlet through submarine groundwater discharge to the coastal ocean was 0.6 $g C m^{-2} d^{-1}$, within the order of magnitude of our estimates of primary production and hydrolysis of macromolecules in the water column (Fig. 7).

5 Conclusions and perspectives

Our study, which encompassed five years of observations at different times of year in the coastal, estuarine and riverine environments of central Chile, allowed us to obtain a deeper understanding of the degradation capability of this coastal area in relation to carbon sources to fuel heterotrophic consumption. Extracellular hydrolysis of macromolecules is the initial step in the degradation of organic matter, and gives accurate insights into the magnitude of organic matter reworking by the coastal ocean, which is necessary in order to understand how the coastal ocean responds to natural and anthropogenic perturbations.

This study highlights new patterns of hydrolysis such as the differential seasonal response of the water column and surface sediment to hydrolytic activity, and the importance of protein and carbohydrate hydrolysis in river waters, comparable to those of the marine coastal environment.

From our analysis, it is clear that we cannot fully explain the magnitude of production and consumption fluxes to the coastal ocean and transport from the terrestrial environment have to be considered both from focal (rivers) and non-focal (submarine groundwater discharges) sources.

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Table 1. Sampling cruises and samples collected from 2006 to 2010 in the study area.

Area/Cruise	Mo/y	Measurements
Coastal zone (PIMEX 1)	08/2006	O_2, temperature, salinity, nutrients, chlorophyll-a, sediment stable isotopes, primary pro rates
Coastal zone (PIMEX 2)	01/ 2007	O_2, temperature, salinity, nutrients, chlorophyll-*a*, sediment stable isotopes, primary production rates, carbon sinking fluxes, particulate protein, enzymatic hydrolysis.
Coastal zone (PIMEX 3)	08/2007	O_2, temperature, salinity, nutrients, chlorophyll-*a*, sediment stable isotopes, carbon sinking fluxes, particulate protein, enzymatic hydrolysis
River & Estuary	10/2007	O_2, temperature, salinity, nutrients, chlorophyll-*a*, enzymatic hydrolysis
River & Estuary	01/2008	Enzymatic hydrolysis
Coastal zone (PIMEX 4)	04/2008	Primary production rates, carbon sinking fluxes, enzymatic hydrolysis
Coastal zone (PIMEX 5)	06/2009	O_2, temperature, salinity, nutrients, chlorophyll-*a*, enzymatic hydrolysis
Coastal zone (PIMEX 6)	07/2009	O_2, temperature, salinity, nutrients, chlorophyll-*a*, enzymatic hydrolysis
Coastal zone (PIMEX 7)	10/2009	O_2, temperature, salinity, nutrients, chlorophyll-*a*, enzymatic hydrolysis
Coastal zone (PIMEX 8)	01/2010	O_2, temperature, salinity, nutrients, chlorophyll-*a*, enzymatic hydrolysis
Coastal zone (PIMEX 9)	08/2010	O_2, temperature, salinity, nutrients, chlorophyll-*a*, enzymatic hydrolysis
River & Estuary	08/2010	O_2, temperature, salinity, nutrients, chlorophyll-*a*, enzymatic hydrolysis
Coastal zone (PIMEX 10)	10/2010	O_2, temperature, salinity, nutrients, chlorophyll-*a*, enzymatic hydrolysis

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Table 2. Primary production in the upper 40 m of the water column in central-southern Chile according to Daneri et al. (2000), and measurements carried out during this study in January 2007, April 2008, and August 2006.

Month/year	Primary production ($gC\,m^2\,d^{-1}$)
January	5.7
January 2007	1.2
February	1.0
March	2.3
April	1.9
April 2008	0.7
May	1.8
June	0.9
July	0.5
August	0.6
August 2006	0.0
September	4.9
October	3.0
November	6.1
December	2.0

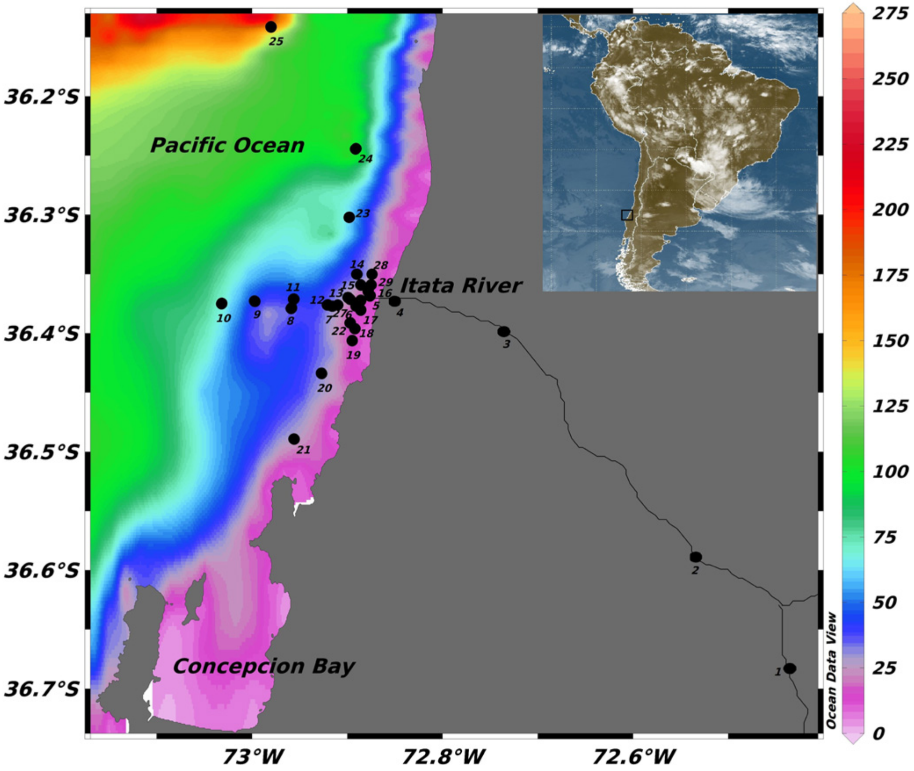

Fig. 1. Study area and location of the sampling stations in the coastal ocean adjacent to the Itata River off Central Chile. Map generated using the software Ocean Data View. Color scale in the ocean represents depth in meters as shown in the bar to the right.

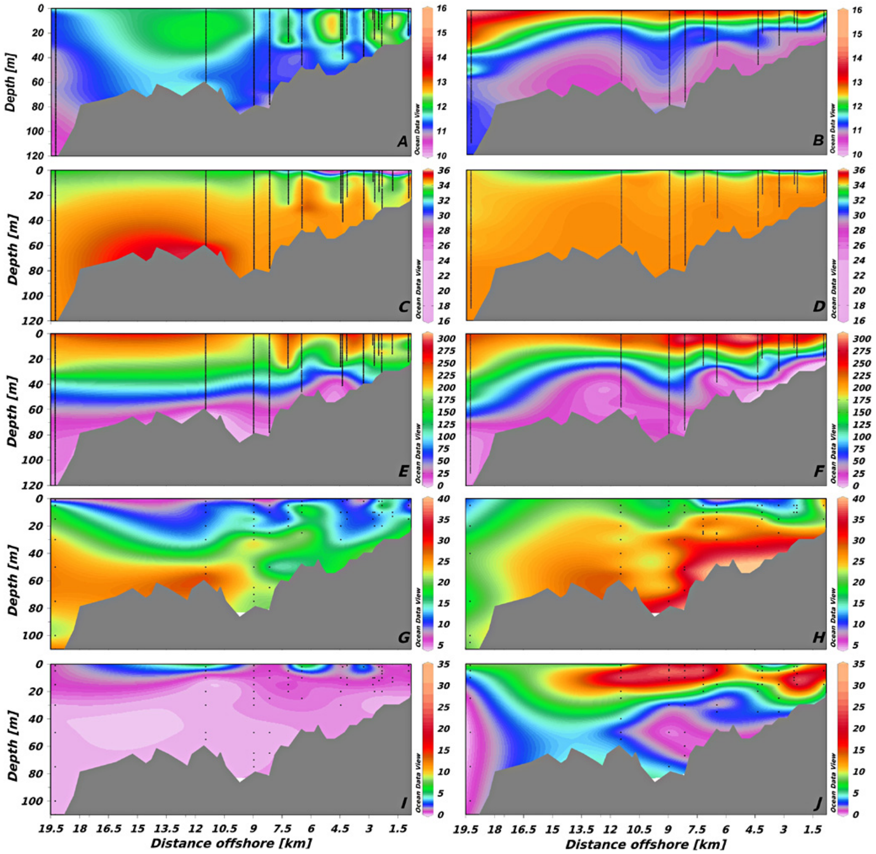

Fig. 2. Cross sections of temperature (°C, panels A, B), salinity (psu, panels C, D), oxygen (µM, panels E, F), nitrate (µM, panels G, H), chlorophyll-*a* (mg m^{-3}, panels I, J) during austral winter (left) and spring-summer (right) panels. x-axis is the distance from the coast. Map generated using the software Ocean Data View.

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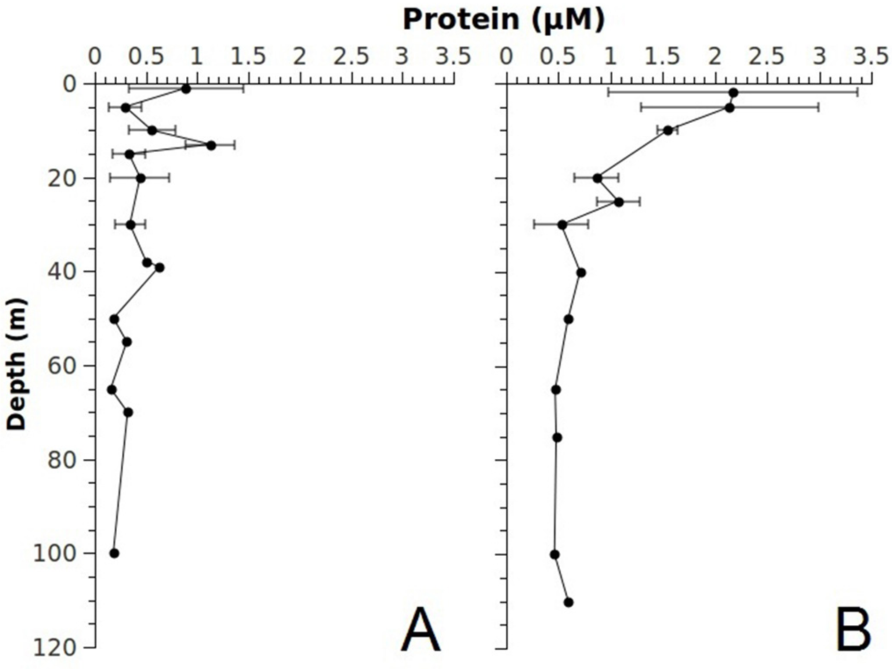

Fig. 3. Suspended particulate protein in the water column (μM) during the austral winter **(A)** and spring-summer **(B)**. Values are average determinations for all sampling sites and depth. Bars are standard deviations.

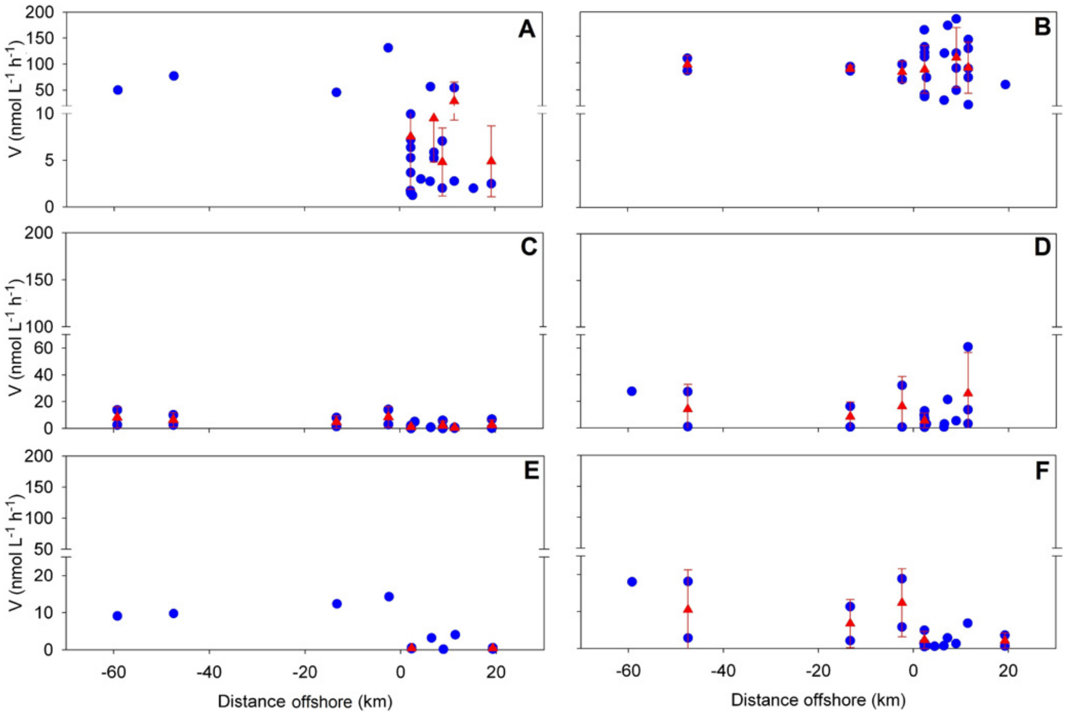

Fig. 4. Enzymatic extracellular hydrolysis of substrates MCA-glu (**A**, **B**), MUF-glu (**C**, **D**), MUF-cel (**E**, **F**) in surface waters during the winter (left panels) and spring-summer (right panels) in relation to distance from the coast (negative distances represent river sampling sites). Rates are in nmol L^{-1} h^{-1}. Blue symbols are discrete values and red symbols are average rates (± SD) when possible.

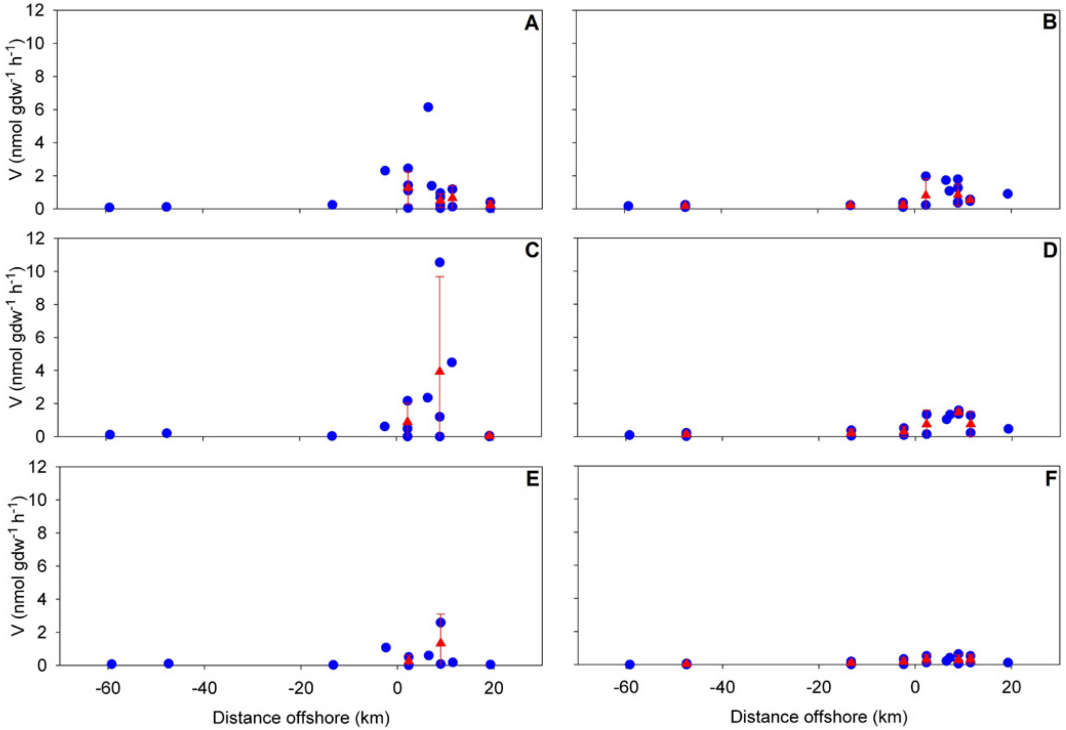

Fig. 5. Enzymatic extracellular hydrolysis of substrates MCA-glu (**A**, **B**), MUF-glu (**C**, **D**), MUF-cel (**E**, **F**) in surface sediment during winter (left panels) and spring-summer (right panels) in relation to distance from the coast (negative distances represent river sampling sites). Rates are in nmol L^{-1} h^{-1}. Blue symbols are discrete values and red symbols are average rates (± SD) when possible.

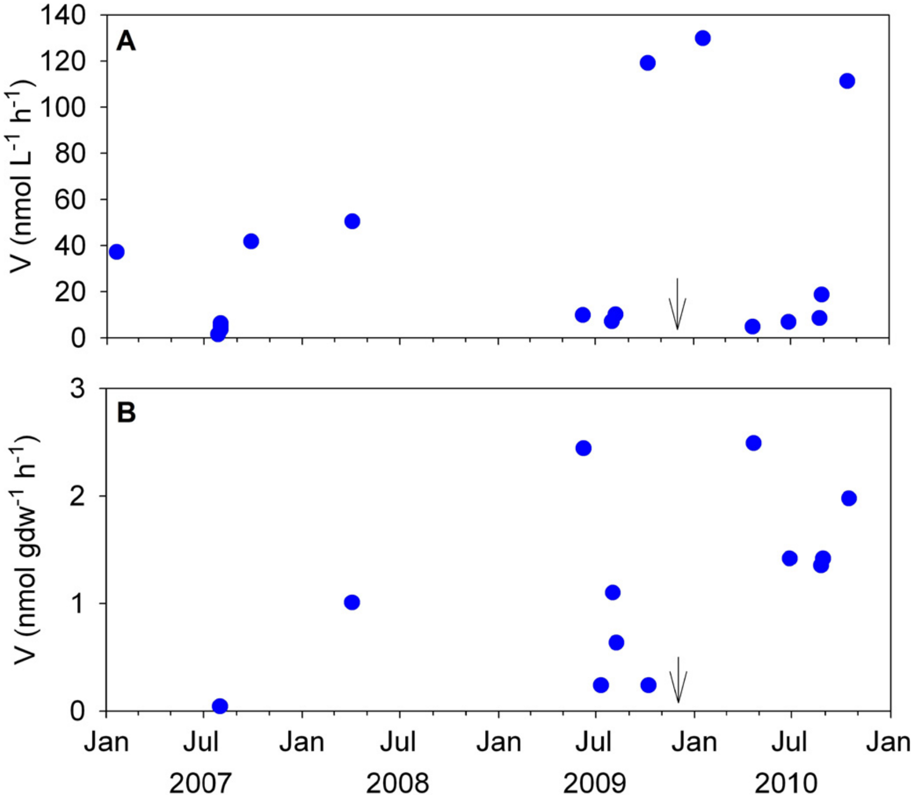

Fig. 6. Hydrolysis rates of MCA-leu in surface water **(A)** and surface sediment **(B)** at sampling station 6 (Fig. 1), where a sewage outfall was installed on December 2009 (vertical arrow).

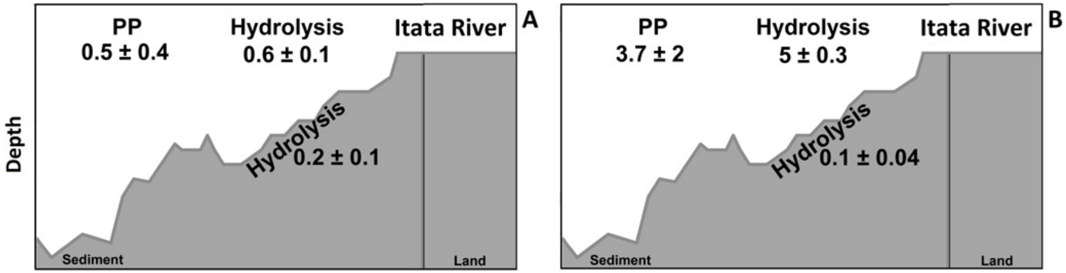

Fig. 7. Average depth integrated rates of primary production, and hydrolysis (ΣMCA-leu + MUF-glu + MUF-cel) in seawater and surface sediment for winter **(A)** and spring-summer **(B)**. Values are presented in $\mathrm{g\,C\,m^{-2}\,d^{-1}}$ ± standard deviation calculated by error propagation calculations.

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