Influences of riverine and upwelling waters on the coastal carbonate system off Central Chile and their ocean acidification implications

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Abstract A combined data set, combining data from field campaigns and oceanographic cruises, was used to ascertain the influence of both river discharges and upwelling processes, covering spatial and temporal variation in dissolved inorganic carbon (DIC) and aragonite saturation state. This work was conducted in one of the most productive river-influenced upwelling areas in the South Pacific coast (36°S). Additionally, further work was also conducted to ascertain the contribution of different DIC sources, influencing the dynamics of DIC along the land-ocean range. Six sampling campaigns were conducted across seven stations at the Biobio River basin, covering approximately 200 km. Three research cruises were undertaken simultaneously, covering the adjacent continental shelf, including 12 sampling stations for hydrographic measurements. Additionally, six stations were also sampled for chemical analyses, covering summer, winter, and spring conditions over 2010 and 2011. Our results evidenced that seaward extent of the river plume was more evident during the winter field campaign, when highest riverine DIC fluxes were observed. The carbonate system along the river-ocean continuum was very heterogeneous varying over spatial and temporal scales. High DIC and pCO2 were observed in river areas with larger anthropogenic effects. CO2 supersaturation at the river plume was observed during all campaigns due to the influence of low pH river waters in winter/spring and high-pCO2 upwelling waters in summer. δ13C DIC evidenced that main DIC sources along the river and river plume corresponded to the respiration of terrestrial organic matter. We have linked this natural process to the carbonate saturation on the adjacent river-influenced coastal area, suggesting that Ωaragonite undersaturation in surface/subsurface waters is largely modulated by the influence of both river discharge and coastal upwelling events in this productive coastal area. Conditions of low Ωaragonite might impact negatively physiological traits for marine organisms, such as bivalves, gastropods, and crustaceans. Therefore, local populations from river-influenced sites could be inherently more tolerant to ocean acidification than organisms living in regions with lower Ωaragonite variability.

1. Introduction

A total of 30% of the total marine primary productivity represents approximately ~0.3 Pg C y−1 or ~20% of the net-annual open-ocean CO2 uptake [Wollast, 1991]. This process occurs in continental shelves and slopes [Takahashi et al., 2009] and generates the deposition of ~50% of the total deposition of calcium carbonates (CaCO3) [Gattuso et al., 1998, 2015]. Given the low spatial/temporal heterogeneity observed in open ocean, changes in the seawater carbonate chemistry can be fairly accurately predicted by using standard CO2-carbonic acid system chemical equations for any potential scenario of anthropogenic CO2 emissions [Joos et al., 2011]. However, in the coastal domain, surface waters are commonly exposed to levels in partial pressure of CO2 (pCO2) higher than expected at equilibrium with the atmosphere [Hofmann et al., 2011; Yu et al., 2011], which is mostly associated to both biological processes (e.g., daily time cycles of photosynthesis and respiration) [Shamberger et al., 2011] and two important oceanographic processes: riverine discharges and coastal upwelling events [Cao et al., 2011].
Atmospheric CO₂ is sequestered into terrestrial systems through photosynthesis and weathering reactions and, together with mineral materials, is transported by rivers as dissolved inorganic carbon (DIC) to the ocean [Cao et al., 2011]. This riverine DIC accounts for almost 40% of the total fluvial carbon inputs to the coastal ocean [Ludwig et al., 1996] and also affects the pCO₂ levels [Huang et al., 2015]. The fluvial export of terrestrial alkalinity is also the predominant source of oceanic alkalinity and a key regulator of the CaCO₃ saturation state in the ocean [Raymond and Cole, 2003]. In fact, most freshwater discharges has lower pH in comparison with oceanic waters, mostly because the combination of high DIC and pCO₂ originating from respiration of natural and anthropogenic organic matter, which might result in aragonite-undersaturated river-influenced areas [Salisbury et al., 2008; Zhai et al., 2015]. In coastal upwelling events result in low pH/high pCO₂ subsurface waters rising to the surface, and consequently, decreasing the pH of upwelling-influenced coastal areas [Feely et al., 2008]. This condition could also result in undersaturated subsurface waters with respect to aragonite, implying a natural acidification condition not expected to occur in the ocean until 2050 [Orr et al., 2005]. Considering the high physical/chemical variability in short temporal and spatial scales of both upwelling and river discharges [Cao et al., 2011], a more detailed description of the carbonate system in these regions is required. The need to evaluate the impact of these natural processes on pCO₂ and CaCO₃ saturation state (i.e., Ωaragonite) not only provides valuable understanding on the processes which could affect marine calcifiers inhabiting these coastal regions [Waldbusser and Salisbury, 2014] but also provides the scientific basis for defining control conditions in ocean acidification experiments for these coastal areas [Reum et al., 2014].

In addition to river runoff and coastal upwelling, there may be other additional sources that could be affecting DIC to surface coastal waters. For instance, the dissolution of carbonate rocks along the river basin, atmospheric CO₂ dissolution, and biogenic CO₂ resulting from bacterial respiration of marine terrestrial organic matter, can all contribute to DIC pool in river-influenced coastal waters [Brunet et al., 2009]. Isotopic tools could be, therefore, useful to identify the contribution of different DIC sources driving changes in the carbonate system along the river and in the adjacent coastal domain [Bouillon et al., 2003]. In river plume waters, the respiration of terrestrial organic matter and weathering of carbonate minerals may influence δ¹³C-DIC, which results in an isotopically depleted pool compared to oceanic DIC [Brutemark et al., 2009]. In contrast, the pulses of low pH and high pCO₂ acidic waters during coastal upwelling provide an additional DIC pool for biological productivity. In fact, δ¹³C-DIC is often used as a tracer of upwelling strength [Sheu et al., 1996].

The coastal area of Central Chile is seasonally affected by intense spring/summer upwelling events [e.g., Sobarzo and Djurfeldt, 2004], with higher pCO₂ levels around the edge of the continental shelf, which in turn results in strong across-shore pCO₂ gradients [Torres et al., 2011]. Furthermore, the Biobío River is one of the highest sources of fresh water along the South Pacific coast; it is considered to be an important source not only of nutrients, silicic acid, and trace metals [Sánchez et al., 2008] but also of dissolved organic carbon (DOC) and DIC [Vargas et al., 2013a]. There is a lack of understating on the water column carbonate chemistry of temperate river-estuary-coastal ocean continuum systems that has rarely been investigated along South American coasts. Increasing the knowledge of DIC sources, particularly from rivers and coastal upwelling events (and their modulation), is important for a better understanding of global biogeochemical cycling in eastern boundary systems. This research examines via a combination of field campaigns and oceanographic cruises on how the combination of river discharges and coastal upwelling processes may influence spatial and temporal variation in DIC and Ωaragonite. This work also aimed to determine how different DIC sources could influence the dynamics of DIC along the land-ocean range. This information is very valuable to understand how the carbonate system is influenced in one of the most productive coastal upwelling areas along South Pacific coast.

2. Material and Methods

2.1. Study Area

This study was carried out in the Biobío River basin and its adjacent coastal upwelling area, located off Central Chile in the Southern Pacific Ocean (36°S) (Figure 1a). The Biobío River is Chile’s second longest river, and the Biobío basin is Chile’s third largest watershed (24,260 km²). In its lower reaches, it passes through agricultural land, towns, cities, and industrial areas [Karrasch et al., 2006]. The Biobío River is also one of the most polluted watersheds in Chile [Focardi et al., 1996], where ~83% of the Chilean pulp production takes place. Mean daily
flow rates range between 120 and 8500 m$^3$s$^{-1}$. The hydrological regime is strongly influenced by a maximum flow rate during the rainy season in winter (June–July) and a minimum flow rate during summer (February–March), with medium levels in spring due to ice melting [Barra et al., 2001]. The runoff from this river supplies significant amounts of silicate, nitrate, phosphate, DOC, and DIC as well as traces metals to the coastal ocean [Pérez et al., 2015]. The adjacent coastal area is influenced not only by the seasonally variable river flow but also by intense seasonal coastal upwelling events [Sobarzo et al., 2007]. The seasonal

Figure 1. (a) Study area in Chile, including location of the sampling stations along the Biobio River basin and the adjacent coastal ocean. Chemical measurements were made at all river stations (open square), whereas in the coastal ocean they were estimated only for some selected stations (open circle). Hydrographic data were collected at all river-oceanic stations (open square). (b) River flow (shaded area) and Ekman transport (line) for the study period during 2011. Grey shaded areas represent the days on which the field sampling took place at the coastal ocean. Positive (negative) values of Ekman transport represent offshore (onshore) transport of coastal water. (c) MODIS true color images for the sampling periods during summer, winter, and spring 2011. The MODIS imagery and salinity contours should be analyzed with caution as the field sampling took several days on each season, whereas MODIS images are the best images (less cloudy) for a single day of each sampling period. However, these represent typical contrasting river plume conditions, especially in winter and spring. No river flow data were available between late February and early April 2011.
variation of winds and runoff creates two distinct modes of oceanographic conditions, a highly productive summer upwelling season and a winter downwelling season with a thick surface layer to which maximum riverine freshwater flows are added [Sobarzo et al., 2007]. In the present study, we sampled seven stations along the Biobío River, covering almost 200 km and including two stations located at the mouth of two important tributaries (Laja River, Stn 1 and Vergara River, Stn 5; Figure 1). Almost simultaneously, we conducted three research cruises on the adjacent continental shelf, including 12 sampling stations for hydrographic measurements and 6 stations for chemical analyses (Table 1). Six sampling campaigns along the river basin were conducted between late December 2010 and early December 2011, representing summer, winter, and spring conditions, and for each seasonal condition a 3 day cruise was conducted (Table 1). Finally, an observing program between July 2011 and June 2012 was also conducted at the Biobío River mouth (Stn 7), and freshwater samples were collected for pH, DIC, and δ¹³C-DIC measurements.

2.2. Water Sampling and Hydrography

Dates for each sampling campaign are shown in Table 1, including all physical, chemical, and biological measurements taken at each site.

In the river, surface samples (10 L from the upper 1 m depth) were collected from the central channel of the river. Considering the high energy levels of the river upstream and the reduced depth in the lower reaches (<2 m depth), we did not collect depth-integrated water samples. Temperature and conductivity were measured immediately before water sampling using WTW (issenschafftlich-Technische Werkstätten GmbH) meters, whereas pH was measured spectrophotometrically. Subsamples were taken for dissolved organic carbon (DOC; 30 mL) and dissolved inorganic carbon (DIC; 30 mL), including their δ¹³C signatures.

During the oceanographic cruises in the adjacent ocean, temperature and salinity were recorded from near the bottom to the surface using a SeaBird SBE-19 plus conductivity-temperature-depth (CTD) equipped with a Wetstar fluorometer. Water samples for chlorophyll a (Chl a, 1 L) were collected at 2, 10, 20, and 50 m depths with 10 L Niskin bottles. Samples for DIC (40 mL) and DOC (30 mL) and their δ¹³C signatures were collected only at 2, 5, 10, and 20 m depth. Chlorophyll measurements (Chl a) from the river and vertical profiles from the adjacent ocean were conducted with a Fluorprobe sensor (bbe-Moldaenke, Kiel, Germany) [Beutler et al., 2002]. Chlorophyll measurements with this equipment were calibrated by contrasting with analysis by fluorometry (Turner Design TD-700), using acetone (90% vol/vol) for the pigment extraction of discrete samples according to standard procedures [Parsons et al., 1984].

All these environmental variables were studied within the context of the seasonal variability of river flow, wind (derived Ekman Transport), and MODIS (Moderate Resolution Imaging Spectroradiometer) true color imagery identifying the turbid signature of the Biobío River plume. The signature of river plumes has been

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aData not analyzed for summer campaign.
commonly detected and quantified using the normalized water-leaving radiance at 555 nm (nLw555) in coastal waters [e.g., Nezlin and DiGiacomo, 2005]. In the coastal region off Central Chile, nLw555 data have been demonstrated to be a good proxy for mapping turbid river plumes, and its maximum signature is coherent with the green brownish color of the turbid plumes in the area [Soldias et al., 2012]. L1A MODIS files were obtained from NASA web site (http://oceancolor.gsfc.nasa.gov/) and processed following high-resolution procedures to produce enhanced true color images at 250 m spatial resolution. The processing procedure was carried out combining bands 1 (red), 4 (green), and 3 (blue) and using SeaDAS (SeaWIFS Data Analysis System) software [Franz et al., 2006].

Daily river flow data were obtained from the Direccion General de Aguas, Chile (www.dga.cl), between winter 2010 and summer 2011. Moreover, wind data were obtained from a coastal meteorological station (36°42.28′S, 73°06.73′W), which is located next to the river mouth. Ekman transport was computed using the meridional component of wind stress, following Smith [1968]. The seasonal variability of river flow and Ekman transport during the study period are presented in Figure 1.

2.3. Basic Chemical and Isotopic Analyses

pH in seawater samples was measured spectrophotometrically using the nonpurified indicator m-cresol purple (pH: total scale, pH7) [Clayton and Byrne, 1993]. pH7 calculations were performed according to Mosley et al. [2004] and Clayton and Byrne [1993] for salinity < 30 practical salinity unit (psu) and salinity > 30 psu, respectively, with the molar absorptivity ratios from Clayton and Byrne [1993]. On occasion, pH7 was also compared with estimates determined using an Orion 3 Ross combined pH electrode, which was calibrated against three traceable pH buffers (pH4.01, 7.00, and 10.01). The estimated analysis error for this analysis was estimated as <0.009 pH for acid waters (pH ~ 7.2) and 0.006 pH for surface waters (pH ~ 8), and measurements was regularly calibrated against a Reference Material from M. DeGrandpre of the University of Montana. For dissolved organic carbon (DOC) and δ13C-DOC, a 30 mL subsample was collected with a sterile syringe and filtered through a Swinex containing a GF/F filter of 0.7 μm, precombusted for 4–5 h at 450°C. The samples were collected directly in 40 mL Glass 200 Series I-CHEM® vials, preventing the formation of any bubbles. For dissolved inorganic carbon (DIC) and its δ13C signature, a 40 mL subsample was collected with a sterile syringe and filtered through a Swinex containing a filter of 0.2 μm and poisoned with HgCl2 to halt biological activity. The septa of vials were exchanged for butyl rubber septa to prevent diffusion of CO2. Samples were refrigerated at 5°C until fast shipment for analysis.

Prior to analysis, DOC samples were bubbled with CO2-free nitrogen for 7 min to ensure complete removal of DIC. All samples were run on an OI Analytical total inorganic carbon-total organic carbon (TIC-TOC) Analyzer Model 1030, first run to determine the parts per million carbon organic/inorganic concentration then for the δ13C isotope. The TIC-TOC analyzer was interfaced to a Finnegan Mat Delta Plus isotope ratio mass spectrometer for analysis by continuous flow. Data were normalized using internal standards. The analytical precision was 1.8% for the quantitative measurements of DIC and DOC and ±0.2‰ for the isotopes. Analyses were conducted in the G.G. Hatch Isotope Laboratories at the University of Ottawa, Canada.

2.4. Estimation of Other Carbonate System Parameters

pH and DIC data were applied to the program CO2SYS [Pierrot et al., 2006] to calculate aragonite saturation state (ΩAragonite) and other carbonate parameters (e.g., pCO2). We have used pH7 and DIC measurements for pCO2 estimates, since it is well known that contribution of noncarbonate anions may overestimate river alkalinity estimates, which cannot directly contribute to pCO2 [Hunt et al., 2011]. The dissociation constants for carbonic acid (K1 and K2) were those of Mehrbach et al. [1973] refit by Dickson and Millero [1987] for salinities between > 30 psu, [Millero, 2010] for estuarine waters between 1 and 30 psu, and Dickson [1990] for freshwater samples in the middle and upper river sampling stations. KHSO4 was determined by Dickson [1990] for both freshwater and seawater samples.

3. Results

3.1. Hydrography

The Biobio River outflow presented typical values according to its annual cycle: minimum during summer, maximum values in winter, and decreasing progressively through the spring season (Figure 1b). Note that
the wintertime sampling occurred right after a peak in river flow. Contrasting upwelling and river flow conditions existed in all three seasons of study, including, an upwelling-dominated summertime, a downwelling-dominated wintertime with increased freshwater flow into the coastal ocean, and a combined upwelling-moderate river flow regime in spring (Figure 1b).

The selected MODIS images show a larger turbid plume in winter, whereas a contrasting turbid plume is barely identified near the river mouth in spring and summer (Figure 1c). The overlaying surface salinity contours are coherent with typical plume patterns-lower salinities (<25 psu) in the downstream direction (south in this case) from the river mouth in winter and a low salinity (~32 psu and lower) plume extended offshore in spring (Figure 1c). The seaward extent of the river plume was more evident during winter field campaign (Figure 2). As typical at this latitude, surface Chl a concentration was relatively low during winter season (<3 μg Chl a L⁻¹), whereas the highest Chl a concentration occurred during the spring campaign, with maximum concentration (>20 μg Chl a L⁻¹) associated to the river plume at Stn 4 (Figure 3c).

### 3.2. pH, DIC, and δ¹³C-DIC Temporal and Spatial Variations Along the River and the Adjacent Coastal Ocean

A river-ocean transect along the Biobío River and the upper (<20 m depth) adjacent water column revealed a large pH spatial heterogeneity (i.e., from approximately 6.902 up to 8.315 units). Typically, pH values were lower along the river basin than in the coastal ocean, especially at Stns 1 and 2 near to tributaries (i.e., Laja River). At the adjacent coastal ocean, pH values in surface waters of the river plume area were lower (<7.6 units) during periods of maximum river discharge in winter and associated to subsurface waters (>10 m depth) during upwelling events in the region of the Biobío River canyon in summer (Figure 2). The surface spatial distribution of pH in the river-influenced coastal ocean evidenced the influence of freshwater
discharge by decreasing oceanic pH to levels < 7.650 in the river plume area, in comparison to more oceanic stations (7.950–8.150) (Figures 3d–3f). The conditions at the river plume changed during spring, when pH at the river plume was > 8.15, mostly associated to a dense algal biomass (>20 μg Chl a L⁻¹) associated to Stn 4 during this upwelling event (Figures 3c and 3f).

DIC concentrations ranged from 250 to 1100 μmol kg⁻¹ along the Biobío River and some of the tributaries (Figures 2 and 4a). DIC concentrations presented a general decreasing trend as river flow (Q) increased (Spearman rank; \( r^2 = -0.406, p < 0.05 \) with the highest DIC concentration during spring/summer months. In general terms, lowest DIC concentrations were recorded from samples collected in winter (Figure 3a)

Figure 3. Surface spatial distribution of (a–c) chlorophyll (Chl a), (d–f) pH (pHT), (g–i) \( \delta^{13} \)C\(_{\text{DIC}} \) (‰), (j–l) pCO\(_2 \) (μatm), and (m–ñ) aragonite saturation state (\( \Omega_{\text{arag}} \)) during summer, winter, and spring campaigns.
and at the upper sector (Figure 3b), whereas DIC increased and pH decreased (pH = 6.921–7.121) downstream as a result of tributary and floodplain inputs in the midportion (Spearman rank; $r^2 = 0.47$, $p < 0.01$). Higher concentrations of DIC in the adjacent coastal ocean were observed in denser subsurface waters below 10 m depth (Figure 2). There was a positive and significant correlation between DIC concentration and salinity ($r^2 = 0.650$, $p < 0.05$; Figure 5).

DIC composition ($\delta^{13}$C$_{DIC}$) reflects the potential sources of inorganic carbon along the riverine system. For measured field pH$_T$ of 6.802 to 8.211, DIC will comprise varying proportions of CO$_2$(aq) and bicarbonate (HCO$_3$). In the upper river $\delta^{13}$C$_{DIC}$ ranged from −5 to −10‰ with a progressive depletion to −10 up to −16‰ at the middle and lower portion (Figures 2 and 6), especially during winter periods (Figure 2). High DIC concentration and depleted $\delta^{13}$C$_{DIC}$ in some stations of the midportion of the river and associated to tributary inputs reflect the dominance of organic matter respiration (Figures 2 and 6). When using data along all the river basin and the adjacent coastal ocean, $\delta^{13}$C$_{DIC}$ was positively correlated (statistically significant) with $\delta^{13}$C-DOC (Spearman rank; $r^2 = −0.61$, $p < 0.01$) (Figure 7).

The influence of the riverine DIC in the adjacent coastal ocean was more evident during winter periods, when a surface lens of brackish waters with $\delta^{13}$C$_{DIC}$ values of −2 up to −4‰ extended from the river mouth until Stn 6 (>10 nm from the coast) (Figure 2) and northward in the surface layer as the river plume moves (Figure 3h), which is also evident in the turbid river plume observed by MODIS image (Figure 1). During spring and summer, the $\delta^{13}$C$_{DIC}$ signal in the upper water column at the adjacent coastal ocean ranged from +3 to −1‰ (Figure 2), and the influence of more depleted $\delta^{13}$C$_{DIC}$ from riverine contribution was only evident in surface waters and close to the river mouth (Figures 3g–3i). In subsurface waters, lower $\delta^{13}$C$_{DIC}$ than the surface ones are typical of upwelling waters (i.e., due to the oxidation of $\delta^{13}$C$_{DIC}$-depleted organic matter sinking from the surface), which

![Figure 4](image4.png)

**Figure 4.** (a) Relationship between river flow (Q, m$^3$ s$^{-1}$) and dissolved inorganic carbon (DIC, μmol kg$^{-1}$) along Biobío River during summer, winter, and spring periods and (b) DIC (μmol kg$^{-1}$) and pH$_T$ during the whole sampling periods for the upper, middle, and lower Biobío River.

![Figure 5](image5.png)

**Figure 5.** Relationship between salinity (psu) and dissolved inorganic carbon (DIC, μmol kg$^{-1}$) in the river-influenced coastal upwelling area.
averaged between 1 and 3‰ (Figure 6). Furthermore, the relationship between DIC concentration and δ¹³CDIC both in the surface and subsurface layer (Figure 6) suggest a degassing of CO₂ all over the river-influenced coastal ocean.

The calculated pCO₂ along the river-ocean continuum was generally higher than the atmospheric equilibrium varying between 1000 and 5000 μatm (Figures 3 and 8). Highest pCO₂ values were observed in some stations at the midportion of the river basin, in the more anthropogenically influenced areas at Stn 5 (Vergara River, near a domestic sewage plant) and Stn 2 (i.e., near a pulp-mill industry), as well as at Stns 6 and 7, close to more urbanized areas (i.e., Santa Juana village and Concepcion city, respectively) (Figure 2).

Surface distribution of pCO₂ at the adjacent coastal area (Figures 3j–3l) evidenced high values >1000 μatm associated to the coastal area and river mouth area (Stns 4 and 13) during all field campaigns. The vertical cross sections indicate that during spring and summer campaigns, subsurface waters with low pH (7.523–7.612) and high pCO₂ (>1000 μatm) ascends to the surface, i.e., upwelling of corrosive waters supersaturated in CO₂. In contrast, during winter periods the surface brackish lens of low pH, depleted δ¹³CDIC, and high pCO₂ (Figure 2) suggests the influence of riverine DIC on the spatial distribution of pCO₂ observed during winter (Figure 3k).

The results of the monthly time series station at the Biobío River mouth (Stn 7) showed that lowest river pH (7.625–7.639) was observed during early winter (June–July) and late spring (November) (Figure 9). δ¹³CDIC ranged throughout the year mostly between /C₀9 and 11.5‰, with an extremely depleted δ¹³CDIC value of approximately −15‰ during May, which was also associated to the minimum DIC concentration during the observing period (Figure 9).

### 3.3. Aragonite Saturation State in the River-Influenced Coastal Upwelling Area

The physicochemical properties of the river plume and/or coastal upwelling events, or the combination of both processes, determined different vertical structures in terms of Ωaragonite Values in the upper water column. During almost all field campaigns the upper 20 m depth associated to the river plume (Stn 4) were undersaturated (<1), especially during summer and winter. The upwelling of subsurface corrosive waters (Ωaragonite < 1) was evident during spring and summer campaigns, whereas during winter, undersaturation was more evident in the upper water column due to the effect of the river freshwater discharge (Figure 2). Surface areas occupied by brackish waters resulting from the sediment and freshwater outflow of the Biobío River (Figure 1) displayed distinguishable low Ωaragonite especially during summer and winter campaigns, whereas in summer the river plume weakened (Figures 3m–3ñ). Considering the low freshwater flow during summer months, the slope of isolines of Ωaragonite during
summer suggests that the surface expression in $\Omega_{\text{aragonite}}$ undersaturation might be the result of subsurface waters elevated through the Biobío submarine canyon located cross to the shelf west of the mouth of the Biobío River [Sobarzo et al., 2001]. A relationship between $\delta^{13}$CDIC and $\Omega_{\text{aragonite}}$, as well as salinity and $\Omega_{\text{aragonite}}$ (Figure 10), can provide evidence regarding the main processes (river versus upwelling) driving CaCO$_3$ saturation state on this river-influenced coastal upwelling area, relative to global drivers, such as ocean acidification. Low salinity waters (<32.5 psu) typically were undersaturated with respect to aragonite, and the $\delta^{13}$CDIC signal suggests that depleted riverine DIC ($\delta^{13}$CDIC = 0–6‰) is one of the main drivers of this undersaturation. Nevertheless, $\Omega_{\text{aragonite}}$ undersaturation also occurred in high salinity waters (>34 psu), which typically evidenced $\delta^{13}$CDIC-upwelling values, which are lower than that of surface ocean water, in a range from 2 to 4‰ lowering the $\delta^{13}$C of surface DIC during upwelling. In consequence, $\delta^{13}$CDIC values evidenced the influence of both river discharge and upwelling events on the $\Omega_{\text{aragonite}}$ undersaturation of the upper water column in this coastal upwelling area.

4. Discussion
4.1. Spatial and Temporal Variability Along the River-Ocean Continuum

The present study shows the large spatial and temporal heterogeneity in the carbonate system along a river-ocean continuum system in Central Chile and the contrasting conditions in the adjacent coastal ocean, depending on the relative influence of river discharges versus coastal upwelling events. Despite this large heterogeneity, our results of DIC and pCO$_2$ along the river were in the mean range for different riverine systems worldwide [e.g., Brunet et al., 2005; Cai et al., 2008; Wachniew, 2006]. Lower DIC concentrations were observed in the upper river section (Stn 3) close to the Andes Mountain, which might result from the algal uptake in a dam reservoir located near to the sampling stations (<20 km). Nevertheless, we also need to consider the reduced DIC contribution from rock weathering, due to carbonate rocks that are less abundant close to the Andes Mountain [Thiele et al., 1998].

Despite this significant riverine DIC flux, DIC concentrations along the river were typically lower than those observed in the adjacent coastal ocean, thus evidencing a lower buffering capacity (500–1500 μmol kg$^{-1}$) as also evidenced with the low pH observed, especially in the river midportion (pH = 7.0–7.8). Moreover, the acid neutralizing capacity in river basins with a significant influence of volcanic rocks, such as Biobío River, lacks buffering capacity [Kalff, 2002], and this is an important factor influencing riverine CO$_2$ outgassing [Cai et al., 2008]. Riverine and estuarine ecosystems are typically significant source of CO$_2$ to the atmosphere, with pCO$_2$ in
is observed (DIC flux = 0.8 t d⁻¹; river flow = 1536.7 m³ s⁻¹). However, the highest values of pCO₂ are in summer, and supersaturation at the river plume area is observed during all field surveys because the interaction between decomposition of riverine material and the effect of upwelled high-CO₂ waters, as observed in other eastern boundary systems (e.g., California) [Feely et al., 2008]. However, on occasion the near-field river plume area can be considered as autotrophic because of the input of riverine nutrients or those associated to the upwelling of subsurface waters from offshore. For instance, in spring, maximum chlorophyll concentration (>20 μg Chl L⁻¹) was observed at the Stn 4, where also higher pH and low pCO₂ was observed. Gan et al. [2010] have demonstrated for a similar river-influenced coastal upwelling area at the northern South China Sea, which enhanced primary productivity on the shelf that was induced by the large nutrient supply from the river plume and also from the coastal upwelling. Nevertheless, river plumes are highly dynamic and difficult to quantify and generalize in terms of pH and CO₂ fluxes, and that is one of the reasons by which they are not included in previous synthesis of global coastal water CO₂ fluxes [e.g., Cai et al., 2006; Laruelle et al., 2010].

4.2. Sources of DIC Along the River-Ocean Continuum

The organic geochemical processes of temperate rivers in South America are still poorly understood. In general terms, the source of riverine DIC can be divided into three different categories: (1) carbonate dissolution, which results in a wide spectrum of δ¹³C_DIC, depending on the source of carbonate and on the dissolving acid [Zeng et al., 2011] but typically is in a mean range from −18 to −7‰, (2) atmospheric CO₂ invasion, with δ¹³C_DIC of −5 to −3‰ [Raymond et al., 2004], and (3) CO₂ derived from respiration of terrestrial organic matter, which is in the range of −23 to −14‰ [Raymond et al., 2004; Zhang et al., 1995]. As expected, it is extremely difficult to identify the amount of DIC derived from each source, but considering the longitudinal trend observed in δ¹³C_DIC along the Biobío River during the present study, it is possible to identify some processes controlling the riverine and oceanic-adjacent DIC pool. In the upper river section, δ¹³C_DIC of −5 to −10‰ clearly suggest a combination between DIC produced by rock weathering and H₂CO₃ produced by the dissolution of atmospheric CO₂, which yields δ¹³C_DIC more enriched. Ralco and Pangue reservoirs by damming Biobío River in the upper section have a long hydrographic residence time, which might enhance the exchange of CO₂ between river and atmosphere, which in turn draws riverine pCO₂ nearly to the atmospheric CO₂. This process can be also responsible for the high δ¹³C_DIC observed at this river section, since invasion of atmospheric CO₂ might enrich the isotopic DIC signature of the reservoir waters flowing down to the midportion [Alin et al., 2008]. In contrast, at the middle and lower reaches, the respiration of terrestrial organic matter appears to be the dominant DIC source. Indeed, in a previous study at the lower section of Biobío River, Pérez et al. [2015] suggested that HCO₃⁻ results during river plume area are considered during all field surveys because the interaction between decomposition of riverine material and the effect of upwelled high-CO₂ waters, as observed in other eastern boundary systems (e.g., California) [Feely et al., 2008]. However, on occasion the near-field river plume area can be considered as autotrophic because of the input of riverine nutrients or those associated to the upwelling of subsurface waters from offshore. For instance, in spring, maximum chlorophyll concentration (>20 μg Chl L⁻¹) was observed at the Stn 4, where also higher pH and low pCO₂ was observed. Gan et al. [2010] have demonstrated for a similar river-influenced coastal upwelling area at the northern South China Sea, which enhanced primary productivity on the shelf that was induced by the large nutrient supply from the river plume and also from the coastal upwelling. Nevertheless, river plumes are highly dynamic and difficult to quantify and generalize in terms of pH and CO₂ fluxes, and that is one of the reasons by which they are not included in previous synthesis of global coastal water CO₂ fluxes [e.g., Cai et al., 2006; Laruelle et al., 2010].

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mostly from both soil CO$_2$ and carbonate dissolution. The significant correlation between $\delta^{13}$C$_{\text{DIC}}$ and $\delta^{13}$C$_{\text{DOC}}$ also suggests the occurrence of similar processes associated to DOC and DIC production along the river. Destabilization of aged soil DOC due to anthropogenic activities, such as urbanization and agricultural development in this river midportion, might be responsible for DOC and DIC release [Petrone et al., 2011; Sickman et al., 2010].

Our results support the idea that terrestrial DIC can be exported to the coastal ocean within a narrow coastal band (<20 km), depending on the river plume dynamic driven by wind regime, tidal, and upwelling circulation. During spring and winter periods, riverine DIC export in surface waters, depending on the local forcing (i.e., river discharge versus coastal upwelling). During summer and winter campaigns, practically, the whole upper 20 m depth of the near-field plume area was undersaturated (<1), mostly driven by the influence of low pH high pCO$_2$, riverine waters. The opposite effect was observed during the spring field sampling, when the slope of the isolines of pH, pCO$_2$, and $\Omega_{\text{aragonite}}$ suggested the upwelling of subsurface corrosive waters from below the upper 20 m depth layer, despite the Ekman transport was relatively low (<1 m$^2$s$^{-1}$) during the spring field sampling. However, the high productivity during spring (i.e., as suggested by the high Chl $a$ concentration; > 20 $\mu$g L$^{-1}$) dropped pH levels in the surface river plume waters, and pCO$_2$ was reduced from approximately 1000 to 250 $\mu$atm.

Low $\Omega_{\text{aragonite}}$ values have been recently reported around different estuarine and river plume environments [e.g., Salisbury et al., 2008, 2009; Wallace et al., 2014]. In our study, as suggested by the isotopic analysis, HCO$_3^-$ resulting from the soil respiration along the watershed is exported to the adjacent continental shelf in the Arauco Gulf and might drop $\Omega_{\text{aragonite}}$ in the near 5–10 km from the coast. As a consequence of these drivers, inner shelf water $\Omega_{\text{aragonite}}$ values were reduced relative to the offshore as a consequence of the input of riverine low pH and alkalinity. Recently, Pérez et al. [2015] in a year-round study carried out in the river mouth and adjacent coastal area of five watersheds along central-Southern Chile, have shown that rockshy sites influenced by the effect of Biobío River plume might experience $\Omega_{\text{aragonite}}$ values < 1 during summer and autumn, mostly associated to freshwater discharges with low pH/high DIC. Because river water is low in carbonate concentration relative to the ocean, depressions of CaCO$_3$ acting cumulatively with the global ocean acidification effect [Salisbury et al., 2008]. Therefore, the flux of riverine corrosive waters might have significant implications for marine calcifiers inhabiting river-influenced coastal sites. Low $\Omega_{\text{aragonite}}$ has been demonstrated to impact negatively the calcification and growth of the Chilean mussel Mytilus chilensis [Duarte et al., 2015] and the larval ingestion rate of the Chilean gastropod Concholepas concholepas [Vargas et al., 2013b]. Moreover, Aguiera et al. [2013] have shown that low-pH freshwater discharge might impair the reproductive outcome in the neritic copepod Acartia tonsa in Southern Chile. Other marine organisms, such as macroalgae, phytoplankton, planktonic larval stages, clams, oysters, crabs, and especially other benthic organisms, might also experience similar effects under low pH/low $\Omega_{\text{aragonite}}$ conditions. Nevertheless, Duarte et al. [2015] and Vargas et al. [2014] have also shown that local populations of marine invertebrates from river-influenced sites could be inherently more tolerant to ocean acidification (OA) events than organisms that live on regions with a lower pCO$_2$ variability. Similarly, organisms living in upwelling regions may be acclimatized and adapted to extremes in ocean chemistry [Hofmann et al., 2011].
However, this high variability may mean that the organisms inhabiting in river-influenced and upwelling regions are already operating at the limits of their physiological tolerances. Thus, future OA may drive the physiology of these marine organisms up to the edge in their tolerance range. In consequence, this simplistic view disregards that other relevant processes such as species acclimation, adaptation, and selective breeding may also operate leading to uncertainties about biological responses of species in a future low Ω/high pCO2 ocean.

Similar interactions between upwelling and riverine discharges have been reported for other coastal areas such as Northern Gulf of Mexico [Keul et al., 2010] and the South China Sea [Cao et al., 2011]. Given the different isotopic signature of DIC associated to river plume brackish waters in comparison to high salinity upwelled waters, there may be potential to use the relationship between salinity and δ13C_DIC to discriminate different local drivers of acidification processes. Unfortunately, oxygen concentrations were not assessed in a very rigorous fashion during our oceanographic cruises, in order to establish the relationship between oxygen and Ω_{aragonite} values. It is well known that the acidification of coastal systems is a phenomenon that displays a high degree of temporal and spatial coherence with oxygen levels [Melzner et al., 2013].

Many studies have shown that anthropogenic CO2 emissions are a principal driver of alterations in marine carbon chemistry [e.g., Doney et al., 2009; Orr et al., 2005]. However, here we have shown that the carbonate system along a river basin and its adjacent coastal ocean, where many species of marine organisms inhabit, can be affected by the interactive effect of both upwelling events and riverine plumes waters [e.g., Borges and Gypens, 2010; Duarte et al., 2013]. Our results support the idea that considering the high variability in the carbonate system in river-influenced coastal upwelling areas relative to open ocean environments, OA experiments that use organisms from these coastal environments and that rely on IPCC future atmospheric CO2 scenarios to setup control and acidified treatments may inadequately replicate actual carbonate chemistry conditions that fail to reflect realistic future OA conditions.

5. Conclusions

This study has contributed with newly acquired information to detect how significant river discharges, and coastal upwelling events may influence spatial and temporal variation in DIC and Ω_{aragonite} and how different DIC sources (δ13C_DIC) may also influence the dynamics of DIC along the land-ocean continuum, influencing the carbonate system of highly productive coastal upwelling area of Central Chile. The main conclusions of our study are outlined below.

Carbonate system along the river-ocean continuum showed a large spatial and temporal heterogeneity. Isotopic analysis of DIC (δ13C_DIC), evidenced that main DIC sources along the river, corresponds to a combination between DIC produced by rock weathering and H2CO3 produced by the dissolution of atmospheric CO2 in the upper river section, whereas at the middle and lower reaches, the respiration of terrestrial organic matter appears to be the dominant DIC source. A gross estimation of riverine DIC fluxes to coastal ocean evidences that maximum fluxes were observed during the winter season when the highest river flow is observed. However, CO2 supersaturation at the river plume area is observed during all field campaigns because of the interaction between decomposition of riverine material and the effect of upwelled high CO2 waters.

Our results highlight the importance of terrestrial DIC exported to the adjacent coastal ocean, where physical processes related to the buoyant river plume dynamic and upwelling intensity determine their spatial distribution. The influence of both river discharge and coastal upwelling can drive CO2 outgassing as well as Ω_{aragonite} undersaturation in surface/subsurface waters during all the periods considered in our study, with potential implications for acclimation and/or adaptation of local biota to a high pCO2 conditions.

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