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Inter-annual variability of dissolved inorganic nitrogen in the Biobío River, Central Chile: an analysis base on a decadal database along with 1-D reactive transport modeling

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Abstract

Rivers may act as important sinks (filters) or sources for inorganic nutrients between the land and the sea, depending on the biogeochemical processes and nutrient inputs along the river. This study examines the inter-annual variability of dissolved inorganic nitrogen (DIN) seasonal (wet–dry) cycle for the Biobío River, one of the largest and most industrialized rivers of Central Chile (36°45′–38°49′ S and 71°00′–73°20′ W). Long-term water flow (1990–2012) and water quality datasets (2004–2012) were used along with a one-dimensional reactive transport ecosystem model to evaluate the effects of water flow and N inputs on seasonal pattern of DIN. From 2004 to 2012, annual average nitrate levels significantly increased from $1.73 \pm 2.17\,\mu\text{mol}\,\text{L}^{-1}$ (upstream of the river) to $18.4 \pm 12.7\,\mu\text{mol}\,\text{L}^{-1}$ (in the river mouth); while the annual average oxygen concentration decreased from 348 ± 22 to $278 \pm 42\,\mu\text{mol}\,\text{L}^{-1}$ between upstream and downstream, indicating an additional oxygen consumption. Variability in the mid-section of the river (station BB8) was identified as a major influence on the inter-annual variability and appeared to be the site of a major anthropogenic disturbance. However, there was also an influence of climate on riverine DIN concentrations; high DIN production occurred during wet years, whereas high consumption proceeded during dry years. Extremely reduced river flow and drought during summer also strongly affected the annual DIN concentration, reducing the DIN production. Additionally, summer storm events during drought periods appeared to cause significant runoff resulting in nitrate inputs to the river. The total DIN input reaching the river mouth was $0.159\,\text{Gmol}\,\text{yr}^{-1}$, implying that internal production exceeds consumption processes, and identifying nitrification as one of the predominant processes occurring in the estuary. In the following, the impact on the river of DIN increases as a nutrient source, as well as climate and biogeochemical factors are discussed.

1 Introduction

Watersheds provide ecosystem services and rivers are important components that regulate the export of nutrients and other solutes from the land to coastal waters (Scott and Prinsloo, 2008; Palmer et al., 2009). However, human activity in coastal watersheds has affected the provision of ecosystem services by greatly increasing the fluxes of growth-limiting nutrients from land to receiving waters. This trend has increased dramatically in the last few decades as a consequence of climate variability, which has reduced the intensity and duration of rainfall, and land uses changes due to deforestation, industrial settlement, coastal development, forestry, and agriculture activities (EEA, 2010).

Rivers are known to be one of the major sources of dissolved inorganic nitrogen (DIN as mainly nitrate and ammonium) but this input extend depends on various biological factors such as sediment disturbance, nitrate assimilation, denitrification and nitrification processes, among others. For example, rivers act as a sink or nutrient filter for DIN under denitrification conditions when the water column is depleted of oxygen, or in suboxic or anoxic sediments (Lehmann et al., 2004). Conversely rivers act as a source under conditions of nitrification, driven by microorganisms which have a key role in riverine nutrient regeneration (Dahkne et al., 2008).

A large number of studies have contributed to the knowledge base on DIN turnover (Seitzinger, 1988; Seitzinger et al., 2000; Soetaert et al., 2006; Conley et al., 2009), spatial and temporal patterns, relationships between nitrogen sources and sinks in rivers, and concentrations and fluxes (Meybeck, 1982; Seitzinger et al., 1988; Boyer et al., 2002). However, nitrogen variability is still not comprehensively understood. The relevance of inter-annual climatic variation for biogeochemistry of nitrogen has not been fully explored yet, possibly due to the scarcity of time series datasets (Jentsch et al., 2007). Understanding the relation of climatic conditions and large inter-annual variations in DIN concentration are crucial when considering the implications to the fate of DIN in aquatic ecosystems (Stuart et al., 2011). Kaushal et al. (2008) suggested that nitrogen exportation increases during floods (sometimes by orders of magnitude) and decreases during droughts. The relationships between annual runoff and nitrogen exports differ across land uses. In rivers, about 50 % of the nitrogen load is retained in the river mouth or estuaries (Seitzinger, 1988), whereas climatic variations and land use changes can act as potential drivers for substantial increases in nitrate export (Kaushal et al., 2008; Wang et al., 2010).

Recent investigations in the Northern Hemisphere suggest a relationship between nitrate variation and climatic conditions (Cerro et al., 2013; Vegas-Vilarrubia et al., 2012). For instance, in the UK, synchronous trends of variation in nitrate have been related to climatic change (Monteith et al., 2000). Other studies have found strong and consistent signs of El Niño Southern Oscillation (ENSO) in river inflows, nitrate and oxygen contents (Marcé et al., 2010; Vegas-Vilarrubia et al., 2012). Conversely, in the Southern Hemisphere little information is known about temporal DIN variability. It is the case of Chile, where there are some scarce spaced short term studies (Debels et al., 2005; Leniz et al., 2012). Despite valuable results from these studies, they fail to provide a sufficient base of information.

Research in Chile has focused on major problems such as rapid changes in land use, wastewater and industrial discharge, and runoff from areas of intensive deforestation (Echeverria et al., 2006; Aguayo et al., 2009; Sterh et al., 2009). In South-Central Chile this has raised concerns about the effect on hydrological alterations associated with land use changes (Meza et al., 2012) because these can amplify the climate-driven export of nitrate in river catchments (Jordan et al., 2003; Wollheim et al., 2005). Most of the water quality studies in Chilean rivers have focused on characterizing nitrogen concentration dynamics, based on short-term databases which do not incorporated DIN fluxes or budgets (Debels et al., 2005; Pizarro et al., 2010).

The Biobío River is one of the largest hydrological systems located in the Biobío region of Central Chile. It drains into the Pacific Ocean and is strongly threatened by urban and industrial expansion (Valdovinos et al., 2009; Salamanca and Pantoja, 2009; Parra et al., 2012). Studies efforts such as Leniz et al. (2012) found a significant flux of phytoplankton, carbon, and nutrients from the Biobío river mouth to the adjacent coastal ocean during winter and summer of 2009, but there were no long term observations about DIN retention and removal.

As a result, our understanding of DIN concentration dynamics in rivers, and their relations with climatic variations and land use, remains unclear and requires further research in the form of long-term studies. Long-term studies make it possible to track changes in rivers over time, and complements information about the influence of climate in these ecosystems, which are particularly valuable as they provide insights into DIN sources (e.g., nitrification) and sinks (assimilation and burial, denitrification). To integrate long-term data series, reactive transport models (RTMs) provide a quantitative understanding and a mechanistic description of biogeochemical transformations and allow systematic integration of biogeochemical processes (Regnier et al., 2003).

In this study we have gathered water quality and physical parameters collected by the Centro EULA (Parra et al., 2013) during an 8 year period in the Biobío River, and river water discharge samples from the National Water Direction (DGA) of the Ministry of Public Works of Chile over a 22 year period. Based on the premise that over the past years climatic conditions in the watershed have changed (i.e. rainfall intensity), and land use activities have increased (i.e. urban, industrial, agriculture and forestry), we investigated seasonal and inter-annual variations in dissolved inorganic nitrogen (mainly nitrate and ammonium) and oxygen conditions during drought and wet years from 2004 until 2012.

2 Materials and methods

2.1 Study site

The Biobío River has the third largest watershed in Chile with an area of 24 260 km^2. It is located in Central Chile, between 36°45′–38°49′ S and 71°00′–73°20′ W (Fig. 1). It flows for 380 km between the Andes mountain and the Pacific Ocean (Grantham et al., 2013). The river covers approximately 3 % of the total area of the country and is influenced by the temperate climates of the south as well as by the Mediterranean climate of central Chile (Stehr et al., 2008). In this region, rainfall is at its highest during the autumn, winter and spring and precipitation in the Biobío watershed reaches up to 1400 $\mathrm{mm\,yr^{-1}}$. Many authors have reported that anthropogenic stressors, including the alteration of natural water flow patterns through the Pangue (1996) and Ralco (2004) dams, and the diffuse and point source inputs of nutrients, have recently caused detrimental impacts on the system (Karrasch et al., 2006; Stehr et al., 2008; García et al., 2011). The Ralco dam has an annual flow regulation capacity and a storing volume that amounts to 7 % of the mean annual Biobío River discharge. The Pangue and Ralco dams have a total reservoir capacity of $175\times10^6\,\mathrm{m^3}$ and $1222\times10^6\,\mathrm{m^3}$, respectively. The area within the Biobío watershed is important for forestry activities (both pulp mills and exotic species forestry plantations), and contain a major proportion of the Chilean agricultural soils (Stehr et al., 2009). The basin also plays a key role in the national energy supply (hydropower). The Biobío River has a pluvio-nival flow regime, with a very marked difference in discharge near the mouth between dry and wet seasons (the Austral winter wet season is from June to September and the Austral summer dry season is from December to March). A maximum monthly mean discharge of $1823\,\mathrm{m^3\,s^{-1}}$ occurs during July, while a minimum monthly mean discharge of $279\,\mathrm{m^3\,s^{-1}}$ occurs during February. The adjacent coastal area is not only influenced by the river but also by seasonal coastal upwelling events, mainly in spring-summer (Sobarzo et al., 2007).

2.2 River datasets

Long-term water flow (1990–2012) and water quality (2004–2012) datasets are supplied by the National River Monitoring Network of the National Water Direction (DGA) (www.dga.cl), and water quality data (2004–2012) from the EULA Centre from University of Concepcion (Parra et al., 2012). Water quality monitoring from the EULA Center began in 1994, however only the datasets from 2004–2012 have been included in this study over nine continuously monitored EULA sampling stations (see Fig. 1; stations ABB0, BB0, BB1, BB4, BB6, BB7, BB8, BB11 and BB13). Discrete surface water sampling of the river was carried out seasonally during 2004 to 2012. The stations are systematically distributed along the river and main tributaries (sub-basins), covering the continuum from upstream to the river mouth (Fig. 1). Water quality parameters included nitrate, nitrite, ammonium, oxygen, biochemical oxygen demand (BOD). Approximately 72 water samples were collected through manual sampling during the study period. In the laboratory, the water samples were filtered using pre-weighted glass microfiber filter paper (Whatman GF/F 0.7 µm) in order to retain the suspended matter. Each filtered water sample was stored at 4 °C until analysis could be performed as soon as possible not later than one week after filtration. The nutrients concentration was determined by molecular spectrophotometer, Perkin Elmer, model Lambda 25.

Five DGA sampling stations for water quality parameters were selected (DGA1, DGA2, DGA3, DGA4 and DGA 5) and indicated in Fig. 1. Water samples from the river estuary were collected during low tide.

To characterize ENSO periods, we used the Oceanic Niño Index (ONI) downloaded by http://www.cgd.ucar.edu/cas/catalog/climind/Nino_3_3.4_indices.html, ftp://ftp.cpc.ncep.noaa.gov/wd52dg/data/indices/.

2.3 Land use

Land use data was interpreted from Landsat TM satellite imagery. Landsat TM images (2011) of the Biobío river watershed were downloaded from the US Geological Survey, Global Visualization Viewer site (http://glovis.usgs.gov/). ENVI software was used to process the Landsat image. After classification, land uses in the catchments were extracted through buffer tools in ArcGIS, and the result was compared with existing data from the Department of Geography at the University of Concepción, for purposes of corroboration. We identified ten land use classes, our classifications are as follow: (1) forest, (2) water bodies, (3) steppe, (4) scrubland, (5) snow (6), grassland (7), silviculture (8), agriculture (9), and urban. Table 1 characterized the sample sites in the river basin and the related industries in the area.

2.4 Flow data, load calculations and data analysis

Flow data was obtained from DGA and expressed in mega liters (ML) per day and DIN concentrations from EULA, both were used to calculate total load. The total load was calculated for each site and time period using the following formula (UNESCO, 2009):

$$\mathrm{Ld} = \mathrm{Cd} \times \mathrm{Vd} \tag{1}$$

where Ld = observed load of the compound ($\mathrm{t\,d^{-1}}$) for specified day, Cd = concentration of the pollutant for specified day ($\mathrm{\mu mol\,L^{-1}}$), Vd = total volume of discharge ($\mathrm{ML\,d^{-1}}$) for specified day.

2.5 Numerical approach (reactive transport ecosystem model)

To assess the dynamics of DIN in the water (i.e $\mathrm{NO_3^-}$ and $\mathrm{NH_4^+}$), we developed a one dimensional (1-D) reactive transport model for $\mathrm{NO_3^-NO_3^-NO_3^-}$ and $\mathrm{NH_4^+}$ for the last section of the Biobío River (approx. length 80 km). The 1-D reactive transport model was scripted using the open source software R (R Development Core Team, 2009; http://www.r-project.org/). The R package ReacTran (Soetaert and Meysman, 2012) permits the application of the volumetric advective-diffusive transport function in R (Eq. 1):

$$\frac{\partial C}{\partial t} = -\frac{1}{A_x} \cdot \frac{\partial (Q \cdot C)}{\partial x} + \frac{1}{A_x} \cdot \frac{\partial}{\partial x}\left(A_x \cdot E \frac{\partial C}{\partial x}\right) + \text{reaction} \tag{2}$$

where t is time, and x is distance along the river axis; the first term represents transport by the river flow (advection) and the second term represents (turbulent) dispersion. It is assumed that the cross-sectional area (A_x) is constant in time (Alexander et al., 2009), but it varies along the river axis (x). The chemical state variables in the reactive advection dispersion model are described in terms of concentration ($\mathrm{\mu mol\,L^{-1}}$). The reactions comprise two main biogeochemical processes: nitrate removal by denitrification and nitrate regeneration by nitrification. Boundary conditions for nitrate and ammonium were derived from the river database, whereas nitrification and denitrification rates were obtained from literature.

In order to simulate the nitrate, ammonium, oxygen and BOD dynamics in the river flow only the main river, and no tributaries in the catchment, were considered in the model. The modelling was simulated during winter and summer from 2004 to 2012. Representative steady state flow conditions (Q) for the sampling period were assumed in the model in order to focus on the biogeochemical reactions and transformations of nitrate in the river flow. The cross-sectional area (A_x) was estimated from the surface areas at the sampling points and afterwards linearly interpolated. Length axis was defined by the river boundary located upstream (Hualqui) at 0 km and the downstream (river mouth) boundary at 40 km. For modelling purposes we only considered the last six sample collection sites, this is from the mid-section (DGA2) downward to the river mouth (BB13), with six sites (DGA2, DGA3, DGA4, DGA5, BB11 and BB13) collected from DGA and EULA Centre.

The two major reactions in the model are nitrification and denitrification and are calculated by the following chemical reactions:

$$NH_4^+ + 2O_2 \xrightarrow{k1} NO_3^- + 2H^+ + H_2O \qquad \text{(R1)}$$

$$5CH_2O + 4NO_3^- \xrightarrow{k2} 2N_2 + 4HCO_3^- + CO_2 + 3H_2O. \qquad \text{(R2)}$$

2.6 Calibration and validation of the model

Model calibration and verification consisted of testing whether the designed model was able to reproduce qualitatively and quantitatively the observed data (Soetaert and Herman, 2009). During the evaluation step we confronted model predicted outputs against observed data for nitrate, ammonium, oxygen and BOD parameters. Calibration was done using data from 2007 to 2012, while the data from 2004 to 2006 were used to validate the model. We used the Levenberg–Marquardt calibration algorithm, with a non-linear least-squares function objective, to minimize the sum of squared residuals between model and data (Soetaert and Herman, 2009). To run the objective function R program also was used with the minpack.lm package.

3 Results

3.1 River flow and rainfall conditions

Daily flow data from the Biobío River from 1990 to 2012 is shown in Fig. 2a. Yearly average river flow, calculated at the river mouth, varied from 473 to 1469 $m^3 s^{-1}$ during the 22 year period (Fig. 2a). The 25th percentile of the extreme-value distribution was 863 mm yr^{-1}. Six of the 22 year in the dataset had < 863 mm and the 75 % percentile was 1457 mm yr^{-1} (Fig. 2b). Data showed a clear relationship between river flow and rainfall ($r^2 = 0.85$). There was a clear inter-annual variability in river flow related to precipitation anomalies during wet and dry conditions during ENSO events (Fig. 2b). Wet conditions were associated to maximum river flows in 1997 (strong El Niño event) and followed by less intense in 2002. During 2005 and 2006 a high incidence of rainfall was observed during a moderate to weak El Niño event. Major winter precipitation events (1600 mm) were recorded in April of 1997 at the river mouth (Fig. 2c), corresponding to the strong El Niño. Climate data showed an abrupt drop in rainfall after 2006 until 2012, with the exception of La Niña year in 2008, with one of the most extreme rainfall events (108 mm in 24 h) recorded (Fig. 2b and c). Extreme dry conditions accompanied by very low river discharges were observed from 2007 to 2012, also corresponding to La Niña years (Fig. 3). From 2007 onwards, the probability of extreme drought conditions (less than 863 mm rainfall) increased with extreme lows of 108 mm rainfall registered during 2008.

3.2 Spatial water quality trends (entire river course) related to land uses

Concentrations of DIN and water quality parameters varied significantly at different sites across the watershed and at individual sites (Table 2). Nitrate was the most prominent DIN constituent during the time scale analysis. Levels of nitrate upstream (stations ABB0, BB0, and BB1) presented lower mean values between 0.81 and 9.19 μmol L^{-1}. On the contrary, nitrate in stations associated with the river mouth averaged 16 ± 17 μmol L^{-1}. Nitrite and ammonium concentrations in the headwater showed a similar trend, nitrite minimal and maximal values were 0 to 0.13 μmol L^{-1} in stations ABB0, BB0, and BB1. High concentrations of oxygen (always supersaturated) in the headwaters remained above 300 μmol L^{-1}. If we consider that the percentage of oxygen saturation varied inversely against temperature, time series records began high in the upstream areas (ABB0, BB0, and BB1), where temperatures were always low (Table 2). Oxygen values in the mid-section of the river fluctuated between 109 and 375 μmol L^{-1} (stations BB4 and BB7) and decreased between 250 and 284 μmol L^{-1} in the river mouth (between stations BB8 and BB13). In general, BOD$_5$ in the river along the river continuum varied from < 31 to 109 μmol L^{-1}, these values indicate good water quality conditions.

The pH remained fairly constant from the headwater to the mouth; pH was slightly alkaline mostly with values between 7 and 8. Low electrical conductivity values in the upstream and in mid-section were found, however conductivity increased substantially from the station BB7 to the river mouth, from 56 till 3300 μs C^{-1}. Total suspended solids (TSS) did not exhibit clear spatial trend values and generally varied between 3 and 51 mg L^{-1} along the river, with exception of a maximum of 86 mg L^{-1} at the river mouth (BB13). In addition, TSS and nitrate were higher near urban (BB11) and industrial areas (BB8), and in the area of the river mouth (BB11 and BB13).

River stations exposed to draining from silviculture and agricultural land uses had lower nitrate and ammonium concentrations than those subject to draining from urban areas (Fig. 4), but higher nitrate and ammonium levels than river areas draining from forest land uses. Dissolved oxygen was higher in the presence of forest areas (upstream) than urban land use (downstream), and BDO$_5$ showed the highest values in areas with populations related to industrial activities. Approximately 20 % of the land area draining into the Biobío is comprised of urban land areas and approximately 50 %

of agricultural land areas. The remaining area corresponds mainly to silviculture and forest.

3.3 Seasonal water quality trends (entire river continuum)

In general, nitrate, ammonium, BOD_5, conductivity, TSS and oxygen concentrations were higher during winter periods (higher rainfall) of 2004, 2005 and 2006. Mean and SD of water quality parameters during winter and summer periods are shown in Table 2. Average ammonium and nitrate concentrations in surface waters increase more than 3 and 5 times, respectively. Ammonium concentrations remained constant in the headwaters during summer, and slightly increased during winter (i.e. ABB0 to BB0 from 1.1 to 3.3 μmol L^{-1}). Moreover, nitrate, ammonium, and oxygen concentrations showed a clear seasonal trend characterized by higher values during winter and a progressive decrease to minimum values in summer; this continually decreased through the summer. During summer in the river mouth, nitrate concentrations were 16 ± 17 μmol L^{-1} (Fig. 5).

3.4 Temporal and spatial nitrogen and oxygen variations; observed vs. model data

Modelled concentrations of nitrate, ammonium, oxygen and biological oxygen demand in the ultimate 40 km of the Biobío River included both winter and dry seasons for the entire study period and for individual years are shown in Fig. 6. Model simulation showed a reasonable fit against observed data to the overall biogeochemical cycling of nitrogen. Seasonal variations in water volumes influenced nitrate concentration towards the mouth. During the modelled period, the trend of simulated result was consistent with the field data. In Fig. 6, the solid line represents the estimated annual mean nitrate concentration during summer periods which showed to be highly variable. The dotted line represents the annual nitrate concentration during winter periods. At the headwater (0 km, around Hualqui) observed nitrate and ammonium were lower than in the river mouth. The model showed an increase in winter nitrate and ammonium concentrations over time, most evidently in the case of nitrate (Fig. 6). A slight production of NH_4 within the river mouth was observed.

Concentrations of nitrate in winter, during higher river discharges, were higher than those measured during summer. An exception occurred during summer 2008 where the highest nitrate values were observed (Fig. 6); the lowest concentrations of oxygen were recorded during summer. Oxygen levels were relatively constant during both seasons. However, for every modeled year, differences in the mouth of the river were observed. In winter, oxygen values were high, whereas during summer, significant oxygen depletion was detected in the first measured site of the Ralco station, related to minimal oxygen concentrations values ($< 259\,\mu\text{mol}\,L^{-1}$).

The model was used to estimate the nitrate and ammonium production and consumption in the river (Table 3). Most of the nitrate in the estuary was produced/imported from the river (Fig. 6). The majority of the nitrate imported from upstream was partially transported to the estuary.

4 Discussion

Nitrate represents a mobile and biologically reactive fraction of the total N pool that may originate from different sources in a river. Previous studies have suggested that inter-annual and seasonal nitrate variation from rivers in central Chile remain uncertain (Pizarro et al., 2010). The present study found that DIN has spatially and temporally increased in the Biobío River (i.e. three times higher), especially during wet periods and in 2011–2012 during wet events in the summer (Figs. 2c and 6). This suggests that wet periods may increase nitrate leaching and runoff to the river especially in areas with more leaching and runoff potential (Kaushal et al., 2014), and therefore carry an increased nitrate load (Table 3).

4.1 Changes in spatial pattern of DIN along time

As expected, the DIN concentration in the riverine water are generally higher in the lower than in the upper reaches of the river, probably due to the accumulated flux of chemical weathering and runoff from the catchment (Table 2). As shown in Fig. 5, stations located at upper reaches show lower DIN, and BOD values, but higher oxygen levels (Table 2). This distribution is typical of healthy surface water (WHO, 2012). Distributions in the headwaters of the Biobío river watershed are due to vegetation cover in the uplands with dense native forest (Fig. 4), soils with low cation exchange capacities (Stolpe, 2006), and less human impacts (except in the Ralco dam with high DIN values, located at the Ralco station). All these factors contribute to the found low solute concentrations. On the contrary, stations collected from the lower reaches are characterized by higher nitrate values, suggesting important DIN concentration inputs in this part of the catchment. The significant increase of nitrate concentration in the Biobío watershed can also be explained by the increase in forestry (silviculture) and manufacturing activities during the last decade (Habit et al., 2006). Certainly, nitrate concentrations in reaches draining from urban and industrial sub-catchments are higher than those draining from predominantly agricultural sub catchments (Fig. 4). Other studies for the Biobío showed a clear historical increase in nitrate attributed mainly to industrial activity and forestry for the last two decades (Pizarro et al., 2010). At a regional level, the presence of abundant deciduous trees and annual grasses have little capacity to take up nutrients after senescence which allows nutrient pools, especially nitrate, to accumulate up to high levels (Hart et al., 1993; Ahearn et al., 2004). These nutrients are rapidly leached at the beginning of the winter season.

The impact of various land uses on the hydrochemistry of the river can be best observed when the catchment ecosystem is hydrologically connected with local waterways (Aheard et al., 2004; Aguayo et al., 2009). During summer periods when apparently this hydrological connection is not present, the chemistry throughout the watershed varies minimally, but during high precipitation in winter the terrain is connected to the river and a wide fluctuation in chemistry can be observed between the sites in nearly all of the measured constituents (Table 2). Comparing the data from headwater, mid-section and downstream, we can see that each site responds differently to seasonal change. In headwaters (site BB0) the lowest chemical variability is exhibit between seasons for the analyzed parameters. Meanwhile, in the river mouth (site BB13) the highest chemical variability is observed between seasons. Therefore, spatial location within the watershed affects the seasonal variability in hydrochemistry.

4.2 Seasonal and inter-annual variability

Seasonal variations mainly in nitrate and oxygen concentrations in the river, allows the differentiation of DIN levels between winter and summer. We observed that chemical variations in the river are mainly controlled by the high flows. During winter seasons high discharges carrying high concentrations of nitrate, ammonium and oxygen, differ from those during summer periods (Fig. 5). Exceptions occurred during summer 2006 and 2008, where extreme values reaching 30 μmol L^{-1} were observed in the river mouth, and important rainfall events and high river flow were also recorded (Fig. 2b and c, DGA, 2014). Vega-Villarrubia et al. (2012) identified that ENSO, showed highly significant correlations with nitrate concentrations in a Spanish river suggesting that it is a driver of large nitrate inputs to river. Apparently, ENSO extreme negative and positive phases can significantly influence on climatic conditions in Europe, affecting precipitation in spring and autumn (Mariotti et al., 2002), and during winter (Brönnimann et al., 2007; Vega-Villarrubia et al., 2012). The 1990s and 2000s were active ENSO decades, and our results indicated that high rainfall and river flow from 2005 and 2006 (moderate to weak El Niño events) was correlated with nitrate concentrations. We observed a strong correlation ($r = 0.54$) between nitrate concentrations and the ONI indices during the winter and summer of El Niño and Niña and correlate of 0.50 between nitrate concentrations and El Niño (Fig. 7a and b). This suggests that ENSO could influence nitrate concentrations in the Biobío River probably due to the frequent runoff of allochthonous nitrate from the catchment to the river during winter, and occasionally during summer storms. It appears that climatic conditions may play a considerable role in influencing watershed N export (Kaushal et al., 2008).

Some studies have described that sometime during summer an inverse relationship between nitrate concentration and river discharge can be observed (Melack and Sickman, 1995). However rain events after an extended dry season, can produce a solute flushing effect (Ahearn et al., 2004). Apparently, in the Biobío River this flushing effect was observed principally during summer 2008 (Fig. 5). These rainfall events can generate leaches of nitrate-rich water from the soil horizons into the main river (Muscutt et al., 1990; Neal et al., 2004) which explain the high values of DIN in these periods. Subsequently, low concentrations of nitrate and ammonium were observed, which could be explained by the ongoing rain events that drain through soil horizons that have already had accumulated solutes flushed out, creating a negative relationship between discharge and solute concentration (Ahearn et al., 2004).

The response of inter-annual variability in nitrate and ammonium levels to climatic variability was relatively high compared to observations in other watersheds with similar characteristics in Chile (Pizarro et al., 2010). Although mean annual concentrations of nitrate varied inter-annually from 2004 to 2012, it is important to note that concentrations in the river strongly increased with river flow. Water flow depletion due to low rainfall was observed which may have altered river watershed functionality.

4.3 Processes controlling DIN reactivity along the river

The 1-D model results indicated that nitrification is apparently the most important process in the river mouth and a sizable quantity of oxygen is consumed during summer (Fig. 6) as a product of ammonium oxidation. Since the model reproduces the spatial patterns of yearly averaged concentrations of nitrate, ammonium, oxygen, and $\mathrm{DBO_5}$ for each of the eight years, model rates can be used to compile budgets. The model estimates an average nitrate budget of 159 megamole ($0.159\,\mathrm{Gmol\,yr^{-1}}$) in the years 2004 to 2012, which is apparently high in the context of previous estimates of nitrate (Leniz et al., 2012). Nitrate along the river transect is mainly governed by nitrate production by nitrification and nitrate consumption. It can be observed that ammonium concentration is mainly the result of the interaction between nitrification and advective-dispersive transport, with ammonium exports to the mouth. The oxygen budget is apparently dominated by oxygen consumption probably due to nitrification (Fig. 7).

In the case of oxygen concentrations, levels remained relatively constant and showed a clear seasonal trend; with higher values (around 300 µmol L^{-1}) at 0 and 40 km as a consequence of better ventilation of the water and/or influence of marine water in the river mouth. Nitrate variability is the result of the increase in the magnitude of biogeochemical transformations and in some cases from in situ production. The latter is probably a result of important productivity processes occurring at the river mouth (Leniz et al., 2012; Vargas et al., 2013). Spatial DIN distribution in summer revealed an increase of DIN from the most fluvial influence station to the adjacent ocean, suggesting that the coastal area is both a source of DIN into the river mouth and a sink of this nutrient due to internal cycling. This pattern was more pronounced in summer during coastal upwelling events, and to a lower extent in winter when these events cease, supporting the effect of nitrate rich water advection into the river (Daniel et al., 2013).

Historical nitrate loads from the Biobío River watersheds apparently responded strongly to climatic conditions. During winter, the mean nitrate load concentrations in the river, towards the coastal sea, clearly showed that nitrate and ammonium were exported into the coastal sea during 2004 to 2008 (Table 3). However after 2008, nitrate concentrations decreased towards the mouth. This suggests that during winters with drought trends nitrate concentrations were lower than during wet years, due mainly to lower river flow and low biological demand. Saldias et al. (2012) indicated that the Biobío River had a turbid river plume during winter, with a seasonal peak in discharge and plume area during July and August. Therefore, the incidence of turbid waters during wet periods (winter) can be an important driver of nutrient input towards the river mouth and the coastal sea.

Nitrate export estimations showed low nitrate loadings during summer as a result of the decrease in the volume of water. Downstream, a decrease in more than 40 %

of the water flow has been recorded from the data between 2009 and 2012. In winter (July 2004), 87 ± 31 t of nitrate were added to the river continuum per day at the station BB11, while during summer (December 2004) only 5 t were added per day. Significant water volume reduction occurred in the winters between 2009 and 2012 (Fig. 7), over the BB8 station which resulted in nitrate increases. This indicates a decrease in the nitrate load (28 t N ± 19 t) in July 2012 and decreases (11 ± 12 t nitrate) during summers of the same period (Table 3). During 2006, a drought year, higher values of nitrate loads were observed during summer (22 ± 8 t nitrate). With these results it was observed that years with lowest precipitation, also reduced the water flow and the nitrate loading in the river. Large scale decreases in water volume in the river as a result of climatic variability or anthropogenic activities could affect nitrogen distribution and primary production in the system. Best and Lowry (2014), suggested that in the near future intense water demand worldwide will require large volumes of river water to supply urban and industrial needs, which would be extracted from regions with ample fresh water resources. However, it is necessary to investigate potential feedbacks from the rivers to this impact. It would not be enough to quantify the potential effects using a typical water budget approach. Focusing on water quantity, together other lines of research concerning biogeochemistry and water quality, introduces an important perspective to this important issue.

5 Conclusion

This study suggests that climatic variability, urban and deforested areas exert a strong control on water chemistry in the Biobío River watershed. The remarkable importance of relatively long-term quantification of riverine nutrient variability is reflected in the biogeochemical variables. DIN concentrations in the river appear to be largely controlled by riverine nitrate loads. The temporal variability of precipitations and discharge is positively correlated with nitrate loads and concentrations. Nitrate and ammonium in Biobío River, mainly from the downstream section, is controlled apparently by external sources through advection of nitrate carried into the river mouth, by internal biogeochemical transformations that consume nitrate (i.e. assimilation, denitrification) in the mid-section of the river, this produce nitrate (i.e nitrification) in the river mouth. The analyses demonstrate that there is an influence of climate on riverine DIN concentrations; high DIN production occurs during wet years, while high consumption occurs during dry years. Extremely reduced river flow and drought during summer also strongly affects the annual DIN concentration, reducing the DIN production.

By using data of nitrogen, water quality parameters and 1-D reactive transport ecosystem modeling, we have detected seasonal and inter-annual variability in the Biobío River, South-Central Chile. The modelling approach developed for this study highlights the determinant role of the spatio-temporal variability, surface area, and volume in the nitrogen biogeochemical dynamics. These results indicate a need to continue conducting studies using high frequency data acquisition systems. In future research, relation of storms and nutrient uptake, sources and sinks can be quantified through isotopic composition investigation of the waters and sediment. Finally, we identify a need for further investigations of nitrate sources (natural and anthropogenic), and retention in the watershed in response to dry and wet events, and climatic variability.

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Table 1. Monitoring stations on the Biobío River. Coordinates are WGS84 values.

Station Id	Station name	River (km)	Latitude	Longitude	River affluent	Urban (No.)	Related industries	
ABB0	Ralco	90	38°31′59″	72°21′28″	–			
BB0	Pangue	140	38°07′62″	78°30′44″	–			
BB1	Callaqui	180	37°50′29″	71°41′27″	–			
BB3	Puente Coigue	220	37°33′33″	72°35′15″		Los Angeles: 165 655 Laja:22 450	Hydroelectric dams pine kraft pulp mill (3.60 kt yr^{-1}) Sugar roduction 600 t sugar day^{-1}	Seeding 31.2 4–5 leaves 92 End of tiller 92 Total 215.2 (Nitrogen fertilizer input) Producer fertilization (Farmers)*
BB4	Nascimiento	250	37°29′53″	72°36′38″	Vergara	Angol:48 966	Eucalyptus kraft pulp mill effluent (> 1 Mt yr^{-1}), WWTP effluent	
BB7	San Rosendo	285	37°15′36″	72°44′13″			Eucalyptus kraft pulp mill effluent (> 1 Mt yr^{-1})	
BB8	Santa Juana	320	37°10′25″	72°53′48″			Eucalyptus kraft pulp mill effluent (> 1 Mt yr^{-1}) Agriculture 211.800 ha	
DGA1	Sta. Juana-Patagual	328	37°10′00″	72°56′00″		Santa Juana: 12 713		
DGA2	Hualqui	360	36°58′57″	72°56′29’		Hualqui: 18 768	Oil refineries metallurgic kraft pulp mills (130 kt yr^{-1})	
BB11	Concepción	365	36°50′58″	73°03′52″		Concepción: 972 741		
DGA3	La Mochita	365	36°50′00″	73°03′00″		San Pedro: 67 892		
DGA4	South river mouth	370	36°51′00″	73°05′00″				
DGA5	North river mouth	370	36°50′00″	73°05′00″				
BB13	River mouth (Estuary)	380	36°08′49″	73°08′32″				

[*] Claret et al. (2011); Parra and Diaz (2013).

Table 2. Averaged values of chemical parameters for winter and summer for each station in the Biobío River. Units are in µmol L^{-1} for nitrate, nitrite, ammonium, dissolved oxygen and BOD. Temperature (T) in °C. Conductivity in µ SC and Total suspended solid in mg L^{-1}

	Season	T	pH	Cond	TSS	O_2	DBO_5	NO_3	NO_2	NH_4
ABB0	Winter	7.3 ± 3.6	7.2 ± 0.45	64 ± 16	24.4 ± 36.8	368 ± 22	43 ± 22	3.87 ± 2.74	0.11 ± 0.00	3.89 ± 7.78
		4-16.3	6.4–7.9	43–85	1.3–126	300–368	19–94	0.81–9.19	0.11–0.11	1.11–23.89
	Summer	18.9 ± 1.8	7.4 ± 0.29	47 ± 7.9	18.7 ± 31.7	289 ± 24	37.5 ± 9.4	0.81 ± 0.00	0.11 ± 0.00	1.61 ± 1.28
		17–21.6	7.1–7.9	36–60	1–126	259–331	31–59	0.81–0.81	0.11–0.13	1.11–4.44
BB0	Winter	6.1 ± 1.1	7.4 ± 0.45	74 ± 18	19.8 ± 62	367 ± 16	37 ± 6.25	2.26 ± 0.97	0.11 ± 0.00	1.9 ± 1.5
		4–7.5	6.6–8.3	51–99	1–265	337–386	31–44	0.81–3.39	0.00–0.11	1.1–5.5
	Summer	12.3 ± 1.8	7.6 ± 0.4	80 ± 12	14.3 ± 50.4	339 ± 10	41 ± 15	0.97 ± 0.48	0.13 ± 0.04	1.3 ± 0.72
		8.2–19.3	6.8–8.6	53–100	1–266	319–353	32–75	0.11–1.61	0.11–0.22	1.1–4.4
BB1	Winter	6.1 ± 1.1	7.3 ± 0.3	60 ± 9.7	2.8 ± 2.8	373 ± 25	37 ± 5.7	2.42 ± 0.48	0.11 ± 0.00	2.22 ± 3.12
		4–7.7	6.8–7.7	41–72	1–13.5	312–403	31–47	1.94–3.23	0.11–0.11	1.11–11
	Summer	14 ± 2.6	7.4 ± 0.3	55.4 ± 12	2.5 ± 2.4	333 ± 17	38 ± 9.4	0.81 ± 0.32	0.11 ± 0.00	1.39 ± 0.78
		8.2–20.5	6.8–7.9	40–81	1–13.5	313–356	31.25–56	1.13–1.61	0.11–0.13	1.11–3.33
BB3	Winter	8.9 ± 0.6	7.48 ± 0.26	56 ± 10	12 ± 10.5	347 ± 19	34 ± 5.3	11.61 ± 3.71	0.11 ± 0.02	1.7 ± 2.7
		7.9–9.6	7.07 ± 7.7	42–66	3.5–35	318–365	32–44	7.10–16.94	0.11–0.17	1.1–8.3
	Summer	18.4 ± 1.3	7.7 ± 0.3	70 ± 20	8.7 ± 9.5	320 ± 30	37 ± 10.	1.13 ± 2.74	0.11 ± 0.00	2.56 ± 1.72
		12.1–22	6.6–7.9	44–98	1.4 ± 35	278–350	32–56	1.61–4.19	0.11–0.11	1.11–5.56
BB4	Winter	8.2 ± 1.1	7.54 ± 0.68	61 ± 15	11.5 ± 7.8	351 ± 19	47 ± 28	14.19 ± 10.	1.50 ± 1.70	1.4 ± 0.6
		6.1–9.5	6.9–9.3	42–95	3.5–35	312–375	31–100	5.81–33.8	0.11–1.43	1.11–2.8
	Summer	17.3 ± 2.3	7.7 ± 0.6	73 ± 15	9.3 ± 7.2	310 ± 21	43. ± 19	1.61 ± 2.26	0.33 ± 0.61	1.33 ± 0.39
		13–22	6.4–8.7	50–141	2.8–30	278–335	31–81	0.05–6.45	0.11–1.96	1.11–2.22
BB7	Winter	9.2 ± 0.98	7.5 ± 0.27	87 ± 48	15.8 ± 12	329 ± 18	41 ± 12.5	7.42 ± 16.29	0.24 ± 0.13	1.2 ± 1.4
		7.5–9.9	7.1–7.8	56–171	3.7–3.7	303–353	29–65	10.65–28.71	0.11–0.39	1.11–3.3
	Summer	23.9 ± 2.7	7.7 ± 0.2	99 ± 23	11.4 ± 10.9	263 ± 15	31 ± 1.56	2.58 ± 6.45	0.13 ± 0.04	1.32 ± 0.5
		11.0–30	7.3–7.8	49–135	2.4–37	244–281	31–34	3.23–11.29	0.11–0.20	1.11–2.22
BB8	Winter	9.8 ± 1.35	7.2 ± 0.25	58 ± 12	11.5 ± 7.8	359 ± 13	45 ± 16	12.10 ± 2.74	0.13 ± 0.04	2.65 ± 2.90
		8.0–12	6.9–7.6	44–83	3.6–36	113–362	31–75	7.10–16.29	0.11–0.20	1.11–9.98
	Summer	21 ± 2.9	7.6 ± 0.47	87 ± 24	9.5 ± 7	270 ± 13	33 ± 3.4	2.10 ± 3.87	0.13 ± 0.02	1.28 ± 0.56
		11.0–26	6.4–7.9	50–126	2.9–36	253–288	31–41	0.16–8.06	0.11–0.20	1.11–2.78
BB11	Winter	10.1 ± 1.4	7.6 ± 0.75	58 ± 11	16.8 ± 12	338 ± 16	43 ± 22	12.42 ± 3.39	0.13 ± 0.02	1.48 ± 0.73
		9.0–12	6.9–9.5	45–81	6.3–51.4	315–367	31–90	5.81–16.45	0.11–0.20	1.11–3.33
	Summer	21.8 ± 1.7	7.7 ± 0.4	85 ± 23	14 ± 11	273 ± 11	35 ± 4.6	3.71 ± 4.84	0.11 ± 0.00	0.39 ± 1.22
		12.3–27	6.7–8.3	59–124	3.6–51	259–291		0.15–12.90	0.11–0.13	1.11–2.22
BB13	Winter	10.9 ± 1.4	7.3 ± 0.2	80 ± 19	15.5 ± 18.5	315 ± 30	53 ± 25	18.77 ± 6.94	0.57 ± 0.54	18.33 ± 37.8
		9–13.5	7–7.7	56–111	2.8–86	246–356	31–109	4.35–29.	0.11–1.59	1.11–118
	Summer	21.3 ± 1.7	7.6 ± 0.5	225 ± 181	13 ± 16	250 ± 43	59 ± 30.	16 ± 17	1.09 ± 1.30	11.89 ± 10.7
		13–27	6.7–8.5	12.2–3300	2.8–86	176–300	31–109	2.90–57.7	0.30–1.52	1.11–38.3

Table 3. Nitrate load during winter and summer from 2004 to 2012 at the river mouth (BB11).

	Nitrate loading ($t\,d^{-1}$)	
	Winter	Summer
2004	87 ± 40	9 ± 0.5
2005	118 ± 75	5 ± 9.1
2006	49 ± 19	22 ± 8
2007	31 ± 18	6 ± 0.6
2008	107 ± 58	25 ± 3.7
2009	73 ± 44	11 ± 2.8
2010	25 ± 13	7 ± 13
2011	87 ± 55	8 ± 0.8
2012	28 ± 19	11 ± 12

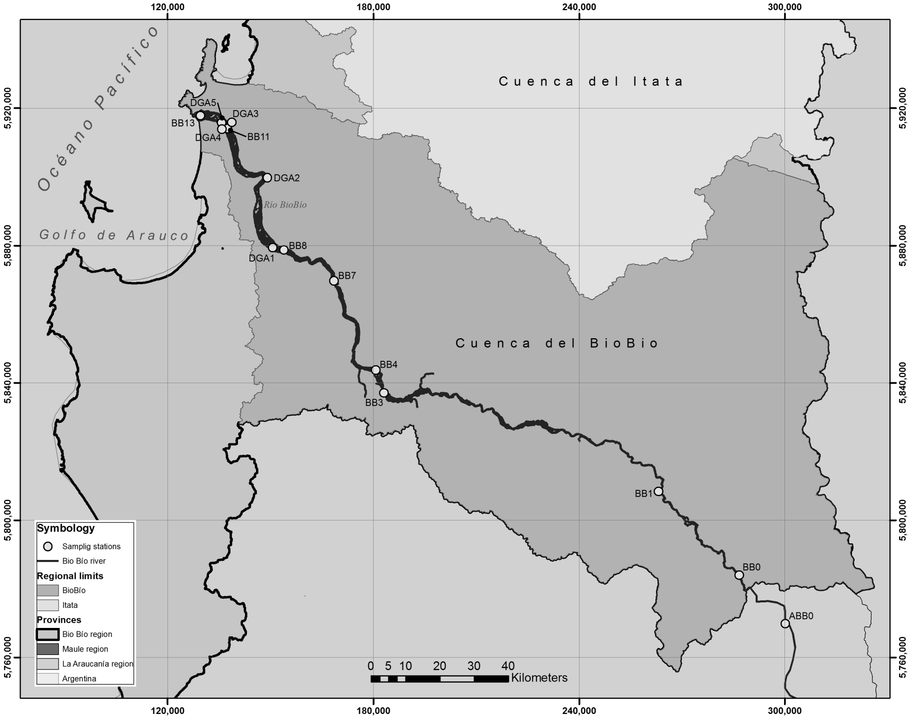

Figure 1. Study area located in the Biobío River basin in Biobío region.

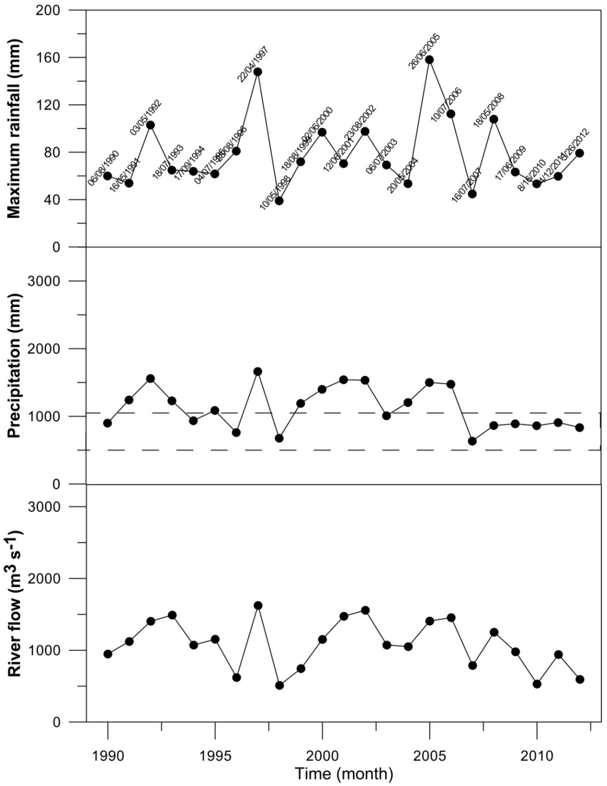

Figure 2. Maximum rainfall, precipitation and River flow conditions since 1990 to 2012. **(a)** Maximum rainfall events recorded at the Biobío River mouth station from 1990 to 2012. **(b)** Analysis of extreme precipitation events in the climatic data from Biobío River mouth station, Chile. Lower dashed line represents 25th percentile and upper line represent 75th percentile of extreme value distribution. Pointed line represents the river discharge ($m^3\,s^{-1}$) at the river mouth. **(c)** River flow at the Biobío River mouth station.

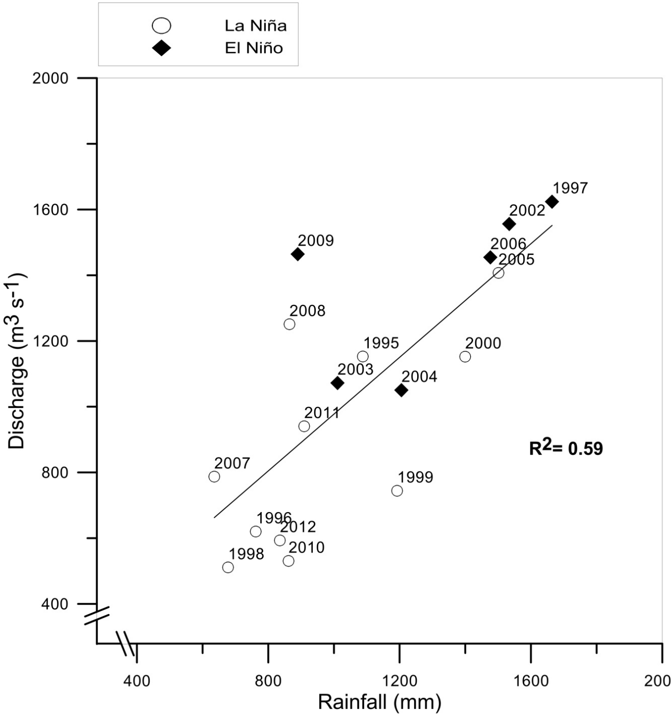

Figure 3. Relationship between rainfall and discharge, related to ENSO events during the studied period.

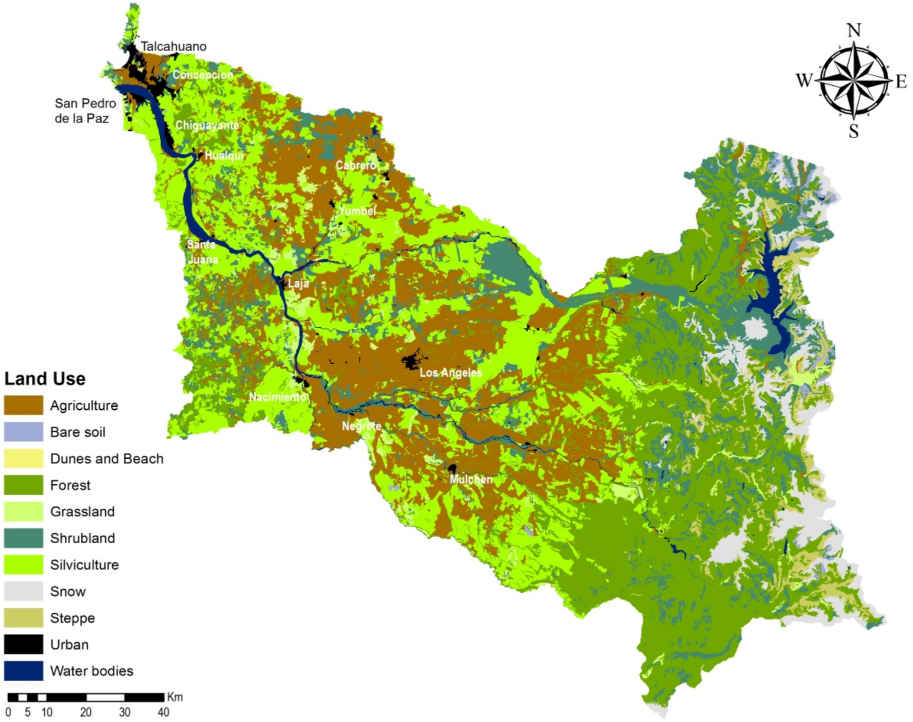

Figure 4. Land use data was interpreted from Landsat TM satellite imagery. Landsat TM images (2011) of the Biobío river watershed were downloaded from the US Geological Survey, Global Visualization Viewer site. Compared with existing data from the Department of Geography at the University of Concepcion. Ten land use classes were classified as follow: (1) forest, (2) water bodies, (3) steppe, (4) scrubland, (5) snow (6), grassland (7), silviculture (8), agriculture (9), and urban (10).

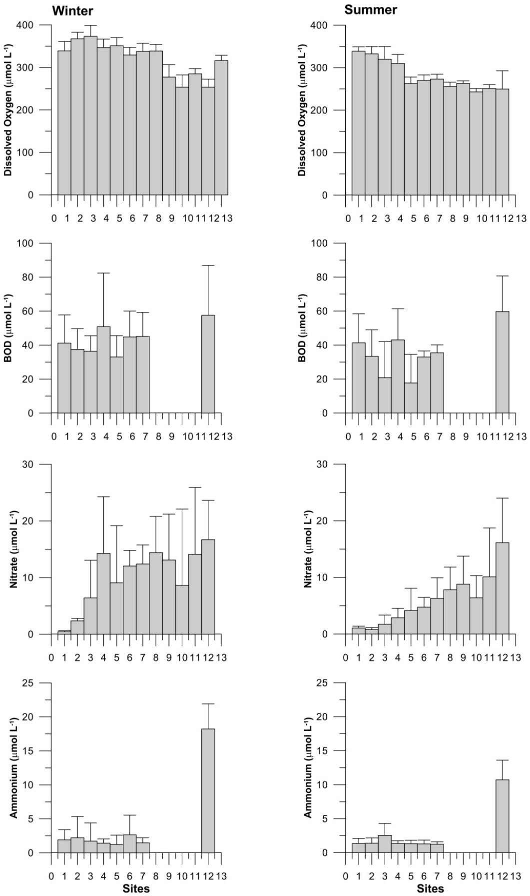

Figure 5. Spatial distribution of averaged chemical parameters (nitrate, ammonium, dissolved oxygen and DBO_5) in the river continuum from upstream (number 1 corresponding to ABB0 station) to downstream (number 13 to BB13 station in the estuary).

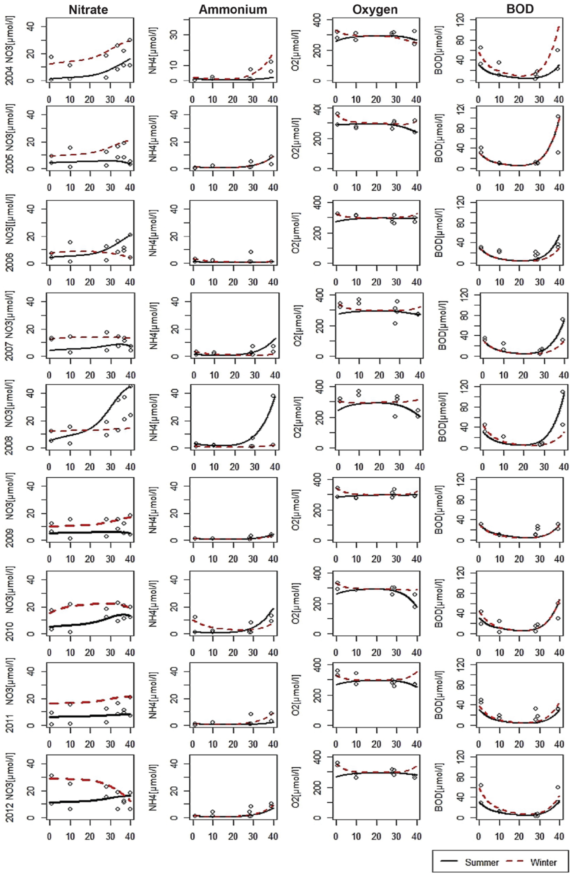

Figure 6. Fit the biogeochemical model from 2004 to 2012. Calibration was done on data for 2007 to 2012. Data from 2004 to 2006 was used to validate the model. Circle symbols (°) represent observational data.

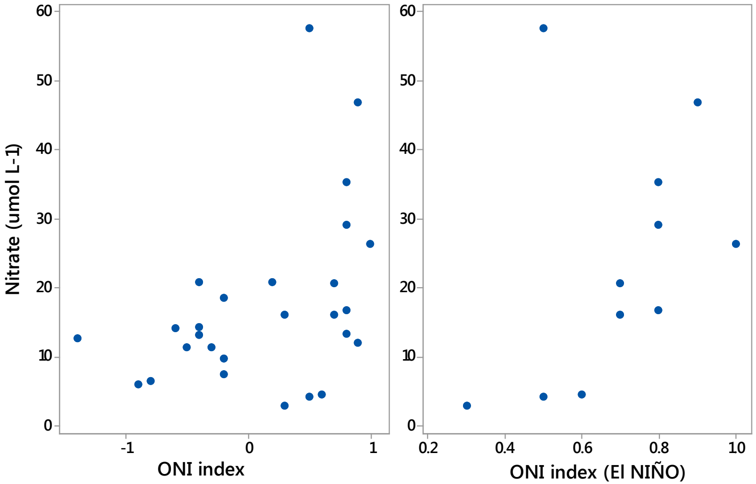

Figure 7. Relationship between ONI index and nitrate concentrations ($\mu mol\,L^{-1}$), related to **(a)** (left panel) positive and negative ONI values, **(b)** (right panel) El NIÑO events during the studied period (2004–2012).