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Discussions

Interactive comment on "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" *by* M. Yévenes et al.

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The authors would like to thank the reviewers for the valuable comments. Based on these many constructive comments of all reviewers and editor, we substantially can improve our manuscript. We tried to address the comments in the same order as the reviewer.

1. My main issues are as follows: As it is, the paper is relatively parochial – I don't think that there is enough of a generic "take-home message" for publication in an interna-

tional peer-reviewed journal at this stage. Whilst there may be a case for publishing the results on the basis of a paucity of data in Chile, this is in itself a relatively weak justification. It is good that the monitoring data have been integrated with modelling to give mechanistically plausible interpretations. However, the model employed (off-the-shelf code in 'R') is relatively simplistic and only considers nitrification and denitrification. Insufficient details are given to understand whether reactions are assumed to be temperature dependent and to account for other processes such as uptake by plants and ammonification. The manuscript lacks polish. Response: In our manuscript "Inter-annual variability of dissolved inorganic nitrogen in the Biobío River, Central Chile: an analysis base on a decadal study along with 1-D reactive transport modeling" we showed a synthesis of the basic biogeochemical processes that act in this ecosystem. To analyze the state of the dissolved nitrogen in the river system, our goal was to develop a model that in a simple way still reproduces correctly the key features of the system in the last 40 km of the river. Our thinking implies a restricted set of modelled processes. Our results, rather simple model to field data from the years 2004 to 2012 gave us the confidence that we have included processes which are important drivers in the rather complex Biobío river. However, we also agree on the feedback offered by our Referees, #1, and #2 and from the Editor in chief, critics that inspired us to improve our study.

Similarly statements made about annual average dissolved oxygen concentrations are unclear – Are the authors talking about a decrease from headwaters to mouth? Response: The dissolved oxygen concentrations present a decreasing trend towards the mouth area (Fig. 3). Dissolved oxygen levels are influenced by temperature and salinity. The solubility of oxygen, or its ability to dissolve in water, decreases as the water's temperature and salinity increase. Dissolved oxygen levels in the estuary also vary seasonally, with the lowest levels occurring during at the end of summer months when temperatures are highest.

What is the relationship with water temperature? Response: water temperature varies in relation to the season. We recorded lowest temperatures for winter (range: 10-14°C) and summer (19-23°C). The solubility of oxygen, or its ability to dissolve in water, decreases as the water temperature and salinity increase.

Abstract – What do the authors mean by production and consumption. What does internal production mean? In-stream or in catchment? Clarity required. Response: Production refers to the addition of either nitrate or other nitrification process. Consumption: refers to the loss or attenuation of nitrate through denitrification (Lansdown et al, 2014). When referring to production, we have referred to the production that is in the river, whether by everything is dragged.

P707 L8 are we talking about Chile here or for the world in general. I am not sure that there is conclusive evidence that rainfall intensity and duration have decreased globally. With global warming we should expect the opposite. Response: At the introduction section, in the first paragraph we stated global issues; we agreed there is a need to give more emphasis to Chilean issues, since this phenomenon has occurred in some areas of the world. We have explained better this paragraph as follows:

However, globally, 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 change the intensity and duration of rainfall, and land uses changes due to deforestation, industrial settlement, coastal development, forestry and agriculture activities, water abstraction and dam construction (Oyarzun et al., 2007; Sabater and Tockner, 2010; Lara et al., 2012).

L16 If riverine denitrification and plant uptake are low then river could also simply act as passive conduits for nitrate from land to sea. Response: We agree with this statement, we add this sentence to the manuscript.

L17 nutrient regeneration – not clear what this means. Response: we use the term regeneration in relation to nutrient recycling offered by Ricklefs, 2009.

P708 L2 Re 50% “retention” in estuaries: Is this a general statement for all climatic zones and all estuary types? Response: It is a general statement for coastal marine system as estuaries, clearly showed in Seitzinger et al. (1998), here the scholars identified estuaries from different latitudes around the globe.

What is meant by retained? If denitrification is the major process this is a loss rather than a retention. Response: We used retained meaning stored. In general, in rivers and estuaries, about 50% of the nitrogen load is stored in the river mouth (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., 2009).

P709 I agree that long term studies are important but there are only 8 years of quality date which is marginal in terms of identifying general trends and relationships. See Howden et al. (2011) and Burt et al. (2010): Burt T.P., Howden, N.J.K., Worrall F. and Whelan M.J. (2010) Long-term monitoring of river water nitrate: how much data do we need? Journal of Environmental Monitoring 12, 71 - 79 Howden N.J.K., Burt T.P. Worrall F. and Whelan M.J. (2011) Monitoring fluvial water chemistry for trend detection: hydrological variability masks trends in datasets covering fewer than 12 years Journal of Environmental Monitoring 13 (3), 514 - 521 Response: We agree at some extend with this comment, is always better to have more data for analysis. We decided to add two more years for this analysis until December 2014, due the continue monitoring that we do in the river, to have a total of ten years of analysis. However, according to this papers Howden et al. (2011) and Burt et al. (2010) still is not enough to talk about long term, we consider this comment and we decided to change it by “analysis of database”.

P709 Statement that land use activities have “increased” is awkward. Response: We would use the term intensified and add the references.

P709 L26 Presumably the catchment not the river covers 3% of Chile? Response: Indeed, we have corrected this mistake; we meant to say “the river basin covers 3% of Chilean territory”.

P710 L4 I guess precipitation is spatially variable. This is a large catchment. No information is given about where this average rainfall was measured or what the raingauge distributions is, or the fraction of precipitation falling as snow. What is the influence of snow melt or glacier melt on the hydrology of the catchment? Response: The river basin is large, and there are several rain gauges (10). However, we did an analysis of the last 40 km downstream of the river and estuary (Fig.1) where we consider 1 raingauge station for our modelling. Average precipitation for the whole basin is: winter is 1600mm $\pm$ 300 and for summer is 200 mm $\pm$ 250. However, the area that we studied the average precipitation is 1000 mm $\pm$ 300 for winter and 200 mm $\pm$ 250 for summer.

P710 Ralco and Pangue dams. No information is given about the location of these features. They are not shown in Figure 1. Response: We have added these features in fig 1.

P711 L1 Sampling was "carried out seasonally". This is far too vague. How many samples were collected at each station and when? It is not easy to see the sub-basins marked on the map. Response: We conducted four sampling dates, one for each season during the year. A total of 13 water samples were collected every sampling (March, June, August, December), during 10 years from 2004 to 2014. A total of XX samples were collected every year; and triplicates by station were collected. For our modelling purposes we only modelled the last 40 kilometers and that included only 9 sample sites. To robust our data, we have added two extra more years of information (available in datasets) until 2014.

P711 L10 "molecular spectrophotometer". Vague. Specific details needed of methods employed. Presumably these were standard colorimetric methods. Please give references. Response: In nutrient analysis, samples were collected in HDPE bottles and frozen until chemical analysis. Nutrient analysis was conducted by colorimetric Grasshoff et al. (1983) method.

P712 Equation 1 will yield units of mol d-1 not tonnes d-1. This is sloppy. Are the calculations of load correct? Response: We have standardized the units in the load equation, the equation should express as follows: Riverine nutrient fluxes (ton day-1) were determined using nutrient concentrations (mg L-1) in conjunction with the monthly average river flow (m3 s-1).

P712 L12 not clear what NO3-NO3-NO3- means. Equation 2. Several terms not defined. Model used appears to be off the shelf so novelty is limited. Response: We have standardized our symbols; in this case correspond only to NO3.

The model is quite simplistic (some processes omitted) and the effects of tributaries neglected (p713 L4). The effects of DO concentrations on nitrification appear to have been taken into account but not on denitrification (p713 equation2 R1 and R2) – why not? In our model we have incorporated the Reactran function as a numeric base (Soetaert and Meysman, 2012) The effects of tributaries are not neglected, we assumed a mistake on that; we have considered this information within the 40 km as lateral flow in the modelling, considering the flow and concentration of the studied parameters. A tributary was added as lateral flow. Both processes nitrification and denitrification were taken into account in DO.

P712 Regeneration – not clear what is meant here. We removed this word, because we consider was not necessary in the text.

P713 L1-2 More details needed. Nitrification and denitrification rates are mentioned but presumably these will be concentration dependent? No details are given of the type of kinetics employed. First order kinetics? In that case do the authors refer to rate constants here? Kinetic formulations for each of the processes were considered in the model. We have used First order kinetics and we referred to rate constant.

P713 L11 40 km reach. This is confusing as it is stated earlier that the study considers 80km. Which is it? Response: The study area that was modeled was the last 40 km. we would like to clarify it in The influence of the estuary and last part of the river.

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P715 It is stated (L1) that the dominant form of DIN is nitrate but this is not always the case at all stations and in all seasons. Response: In our river system, nitrate was the main solute most of the seasons, mainly during winter period. However, ammonium also was present in high concentrations in some periods and stations (Table 2).

P715 L 23. It is stated that concentrations vary with land use but these data are not shown. Ideally some sort of statistical analysis should be performed to formally test this hypothesis. Otherwise it is rather speculative. It is interesting and disappointing that the authors do not give any idea of the population of the catchment (people and animals) and the relative contribution of sewage effluent to flows and nutrient loads. Response: We have added a spearman correlation analysis to demonstrate the relation between nitrate and land uses (Table 3). Moreover, we have information on how about population and cattle have a relative contribution to sewage effluent and nutrient loads, this is showed in Table 1.

P715 Expressing concentrations in umol/L is fine most of the time but is unhelpful when you talk about DO and BOD which are more commonly expressed in mg/L To convert you nean to make an assumption of the molar mass – However, are we considering the molar mas of O or O2? Response: We have decided to show in the manuscript all concentrations in mg/L to standardize the information. We consider molar mass of oxygen is 32 1 mol of O2 = 32 grams.

P716 It is remarkable that BOD is higher in winter than in summer which suggests that it is not coming from sewage. Response: In fact, we stated that BOD is higher in winter than in summer, but we meant to say BOD values are highest during early autumn, at the end of the summer, and contrary lowest in winter, thus sewage was still an important source in summer. We have clarified this issue, in the methodology part; we have included what we consider summer (dec-march), autumn (march-June), winter (june-sept), and spring (sept-dec).

P716 L21 water volumes – Do the authors mean discharge here? Response: The

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authors mean discharge

We add the correct sentence: Seasonal variations in water discharges influenced nitrate concentration towards the mouth.

Solid lines in Fig 6 show summer concentrations of all determinants, not just nitrate. Response: We clarified this figure adding the name of all determinants in the plot as follow:

P717 L12-L15 Unclear paragraph which does not convey any insight into process dynamics. Response: We decided to remove the paragraph

P717 L21 three times higher. Compared to what? Again, too vague. There is a large body of literature which shows that leaching occurs predominantly during wet periods. Refs required. Response: Three times higher with respect to the beginning of 2004, especially during wet periods.

The present study found that DIN concentrations has spatially and temporally increased in the Biobío River during wet periods between 2011 to 2014 than 2004 (i.e. three times higher), especially during wet events. This suggests that wet periods may increase nitrate leaching and runoff to the river especially in areas with more leaching and runoff potential (Pizarro et al., 2006; Bonilla and Vidal, 2011; Andreoli et al., 2012; Kaushal et al., 2014).

P718 L4. How is chemical wethering related to nitrate leaching or even NH4+ fluxes? This suggests a poor overall understanding of the N cycle. Response: It has been reported that intense or prolonged rainfall can lead to high rates of erosion in water saturated soils that favor chemical weathering (quote) which raise levels of organic matter and leaching of minerals. This is one of the main features of the study area. The main problems in this region are erosion, followed by deforestation and reduction in soil fertility (chemical degradation) (Parra et al., 2009). As secondary issues we can include biological degradation, soil compaction, poor water quality, pesticide pollution and forest monoculture (Arumi et al., 2012). Residual soils from weathering of igneous and metamorphic rocks are located in the Cordillera de la Costa, coexisting with tiled origin of volcanic ash. Soils from glacial, glaciofluvial and alluvial deposits are located primarily in the central intermediate depression of Chile, where our study area lies and on it the largest forestry and agricultural uses are found.

P718 L28 during high precipitation. . .. Hydrological connectivity will be related to soil moisture content combined with precipitation. The reason why dry soils are buffered hydrologically from surface waters is because unsaturated hydraulic conductivity is low and the air-filled pore space is high. Again, lacks detail. Response: we redefined this idea and complemented with the information presented below: Mobility of the nutrients within the soil is closely related to the chemical properties of the soil distributions surrounded, as well as the soil moisture. In some areas, there is sufficient moisture in the soil or leaching occurs. In this case nitrate could easily leach due to be less strongly held by soil particles. Apparently, soil moisture levels had decrease in the last year periods (INIA, 2010).

P719 L 14 extreme values of what? Nitrate? Response: Extreme values of nitrate

P719 ONI index needs definition. Response: We have included an ONI index definition to the manuscript the methodology section to make it easier the discussion regarding this index. ONI index has become the de-facto standard of NOAA and use it to identify El Niño (warm) and La Niña (cool) events. ONI is the running 3-month mean SST anomaly for the Niño 3.4 region (i.e., 5oN-5oS, 120o-170oW). Events are defined as 5 consecutive overlapping 3-month periods at or above the +0.5 anomaly for warm (El Niño) events and at or below the -0.5 anomaly for cold (La Niña) events.

P720 The discussion about correlations between the fluxes of DIN and ENSO are interesting but can the authors be sure that these correlations are generally applicable? Is there enough data? Can the data be supplemented with data from other Chilean catchments? Response: Nowadays, diverse studies have explored the chance that

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nitrate concentration in rivers is influenced by ENSO events (Sigro et al., 2010). Even in Chile has been considered the association with ENSO and the water demands in Maule river, Central Chile (Meza, 2005). Nitrate concentrations had been significantly correlated on a seasonal basis in rivers, and during drought the nitrate concentrations increases during positive ENSO phases (Llanillo et al., 2013). In our case, our data represent quarterly data during a period of ten years, sufficient enough to allow us to observe a first approach to this tendency. Regarding the question if our method could be used in other Chilean catchments, the answer is yes. It is only necessary to have the precipitation data and the ONI index.

P720 The "flushing effect" discussed is all quite superficial and vague. This needs to be given more attention in terms of the relationships which exist with precipitation and soil moisture deficits and in terms of process dynamics (sources and sinks of N in the soil). Response: The export of DIN from catchments is influenced by a number of physical chemical and biological factors. Nitrate, as a main form of DIN in soils, is highly mobile and is easily leached from the soil matrix (Carpenter et al., 1998). Consequently, the main export of DIN typically coincides with high flow events. In n winter 2008 the soil moisture and precipitation were extremely high (values), respectively. We observed that increased NO3 discharge (mass flux) occurred during wet periods (such as 2008) when the soil moisture areas were rapidly increasing. During the wet year (2008), occurred an early NO3 discharge.

P720 L21 + The discussion of in-stream process dynamics is rather speculative, given that the model does not consider uptake by plants and algae and ammonification of organic N. I am not convinced that the model is capable of representing process dynamics in this river because the measured data are fairly sparse.

Response: Discharge and precipitation data are daily values, chemical data is quarterly in time, lo que la hace suficientemente sólida en términos de cantidad de datos. In the case of rivers, several studies justify (Soeatert 2007) the study at least two processes, like nitrification and denitrification. However, in our model we consider nitrification, denitrification and oxygen mineralization. Oxic mineralisation and denitrification are included as the two pathways of organic matter degradation that are energetically most favorable (Canfield et al., 2005). Nitrification is included in the model since it is one of the most important O2 consuming processes (Hoffmann et al., 2008). Uptake for plants is important in the river, however, it has been widely used in N soil models in agriculture (Roose,âĂŐ 2004).

In the conclusions it is suggested that land use is an important control over water chemistry of the river but I am not sure that the evidence has been presented in the paper to support this conclusion robustly. Response: We have added a Spearman correlation analysis that we did not include before, demonstrating the relation between nitrate and land uses, mainly urban, agriculture and silviculture (Table 3). Moreover, we have information on how about population and cattle have a relative contribution to sewage effluent and nutrient loads, this is showed in Table 1. We have worked out the information in table for better comprehension.

The authors also state that the study supports the case for continuing with high frequency data collection on water quality. However, I am still unclear as to what sampling frequency was actually employed in this study. Have I missed something? Response: Sample collection was carried every two months (in March, June, August and October, December) during every studied year. In each campaign superficial water samples were taken at each sample station along the river. High frequency sampling was not employed in this study; however the authors are interested to continue in the near future this type of monitoring in this important river.

Figures and Tables Table 1 Several aspects unclear. Affluent? Urban (No.)? Kraft pulp mills? Response: we change and organized the name of several industrial and urban inputs in the table to clarify the information. Afluent meant tributary, Urban population (N° inhabitants) and Kraft mill meant pulp mill plants, we change it already in the Table 1.

Table 2. Looks like ranges for water quality variables are give but this is not clearly stated in the caption. What do the errors represent? SD, SEM, CIs? This is sloppy. Response: We have included the captions in the table, the table can be seen below.

Fig 1. It is not clear where the catchment boundary is here. Are the provincial borders relevant to the study? Response: we completed the Fig. 1 including the catchment boundaries used in this study.

Fig. 2. This is very unclear. Why show scales in b and c up to 3000? We have plot the graph again for a better appreciation.

Why not express Q as runoff (mm/y)? Does the top graph show daily rainfall? Monthly? What are the units? Where were these data measured? Response: We expressed Q in terms of streamflow, but we also have data in terms of runoff. Our data shown days with higher precipitation and units are expressed in mm/day and the top graph is show daily rainfall. All precipitation data were measured in a rainfall station located in the city of Concepcion, see Fig. 1.

Where is the gauging station? Response: is at the River mouth, or River Mouth station (36° 50' 19" S, 73° 03' 43" W) in this study, location Concepcion city. We add this gauging station to Fig. 1.

If the average flow is approx. 1000 m3/s this works out at a mean annual runoff of 1300 mm/y which is approx. the same magnitude as the precipitation figures given. What is going on here? Response: We have clarified this misunderstanding. We gave a mean annual runoff of 1300 mm/y which correspond only to our 40 km in the analysis. The overall precipitation in the region is about 2500 mm/y (Sterhn 2008). Orographic effects in the Andes Mountains influence the amount of rainfall in the region.

Fig. 5 Caption Id DBO BOD? Response: we have standardized biochemical oxygen demand for BOD in every section of the manuscript.

Fig 6 What is the x axis here? Km? From where? Not clear which measured data refer to the summer and which refer to the winter. Response: we have fixed the axis issue. The X axis corresponds to distance expressed in Km; Km 0 represent the estuary and km 40 represents the Hualqui village.

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

Station Id	Station name	River (Km)	Coordinates	Tributary	Urban Population (N° inhabitants)	Related Industries	
ABB0	Ralco	90	38°31’59’’S 72°21’28’’W	Lonquimay		Hydroelectrical Dam	
BB0	Pangue	140	38°07' 62"S 78°30' 44"W	Pangue		Hydroelectrical Dam	
BB1	Callaqui	180	37°50' 29"S 71°41' 27"W	Huequecura			
BB3	Puente Coigue	220	37°33' 33"S 72°35' 15"W	Duqueco, Bureo	Los Angeles: 165655 Laja:22450	pine kraft pulp mill Sugar production Water treatment plant (treated)	(3.60 kt y^{-1}) 600 ton sugar/day
BB4	Nascimiento	250	37°29' 53"S 72°36' 38"W	Vergara	Angol: 48966	Eucalyptus kraft pulp mill effluent Water treatment plant (treated)	(>1 Mt y^{-1}),
BB7	San Rosendo	285	37°15' 36"S 72°44' 13"W	Laja		Eucalyptus kraft pulp mill effluent	(>1 Mt y^{-1})
BB8	Santa Juana	320	37°10' 25"S 72°53' 48"W			Eucalyptus kraft pulp mill effluent	(>1 Mt y^{-1})
DGA1	Sta. Juana-Patagual	328	37°10' 00"S 72°56' 00"W		Santa Juana: 12713		
DGA2	Hualqui	360	36°58' 57"S 72° 56' 29'W		Hualqui: 18768		(130 kt y^{-1})
BB11	Concepción	365	36°50' 58"S 73°03' 52"W		Concepción: 972741	Water treatment plant (treated)	
DGA3	La Mochita	365	36°50' 00"S 73°03' 00"W		San Pedro: 67892	Water treatment plant (treated)	
DGA4	South river mouth	370	36°51' 00"S 73°05' 00"W			Oil refineries metallurgic kraft pulp mills	
DGA5	North river mouth	370	36°50' 00"S 73°05' 00"W				

Fig. 1.

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Table 3. Spearman Correlation analysis between land use activities and climate versus water quality variables in Biobio river.

	Units	Nitrate	Ammonium	DO	BOD
Land uses					
Native Forest	%	-0.26	0.44	0.68	-0.34
Silvicuture	%	0.28	0.38	0.45	0.05
Agriculture	%	0.58	0.64	0.31	0.13
Urban	%	0.59	0.61	0.29	0.43
Grassland	%	0.18	0.23	0.33	-0.22
Climate					
Precipitation	mm	-0.60	-0.52	0.48	-0.34
Discharge (Q)	$m^3 s^{-1}$	-0.55	-0.68	0.41	0.3

Fig. 2.

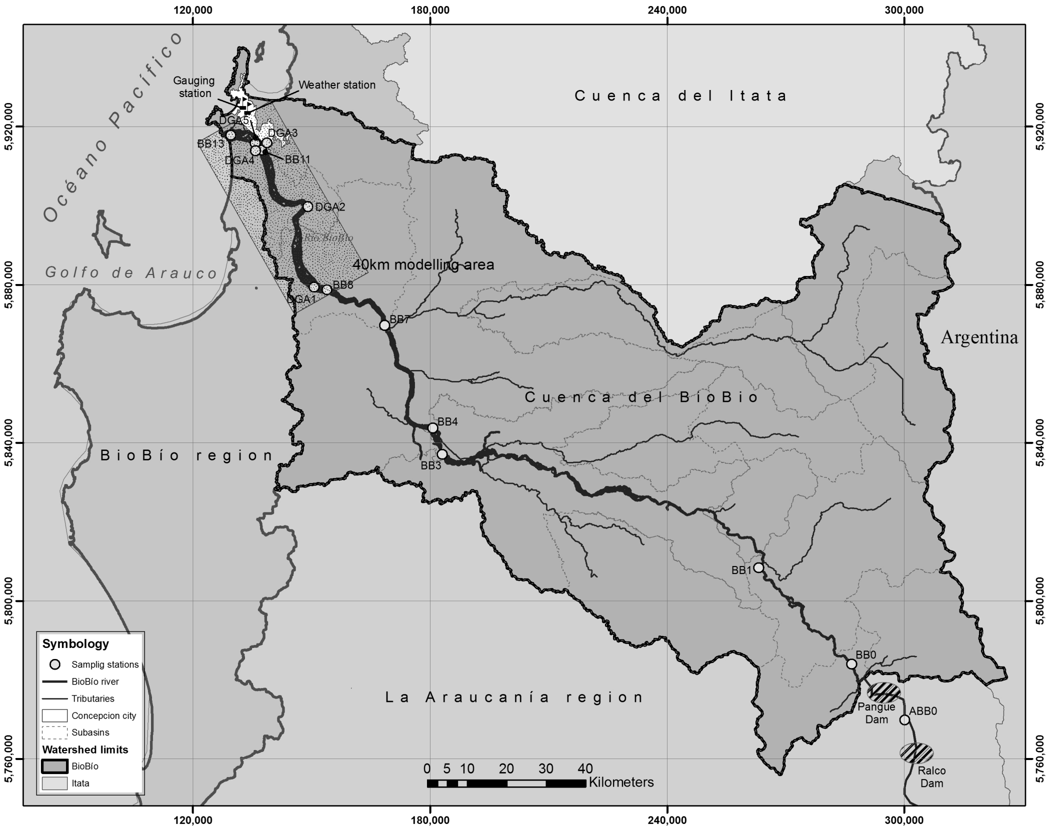

Fig. 3.

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