Hydrology and
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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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We thank the Editor for the supportive comments on the manuscript. The comments listed below contributed to improve our manuscript and we have followed the suggestions when corresponding:

p. 706, L. 22: Based on what data do you conclude that internal production exceeds consumption? What is about input from the catchment area? The main terrestrial inputs from the catchment area to the river are coming from activities in agriculture,

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Interactive Discussion

Discussion Paper

silviculture, pulp mill plants, and urban discharges (Table 1). The nitrate load of the river is dominated by the large flow present all year long

p. 707 – 709 (Introduction): Although you use modelling in your work there is no summary of the state-of-the-art on water quality modelling in rivers with regard to nitrate. This is a must. Please state what the consequences are for and what is novel about your work in this context. Response: We have added information regarding the state of art on water modelling in rivers and nitrate. Water quality models are key tools to predict the changes in surface water quality for environmental management in the world, and hundreds of surface water quality models have been developed since (Chen et al., 2004; Ocampo et al., 2006; Bohle et al., 2009; Wexler et al., 2011; Wang et al., 2013). In recent years, river water quality modelling has risen sharply because of the increasing governmental concern for river and stream water quality (Tetzlaff et al., 2007). Different river basin models have be used upon the scale of model (e.g. SWAT, QUAL2, INCA) application (Arnold et al., 1998). However, in recent years reactive transport modelling have emerged as an essential diagnostic tool for the assessment of the fate of contaminant and the interpretation of the distribution of reactive chemical species (Soetaert et al., 1996; Soetaert and Meysman, 2012).

p. 707, L. 9: Why do you cite EEA (2010)? This report deals with Europe. I cannot see the relevance for the situation in Chile. We included (EEA 2010) to give a general scope of what has been done and the situation worldwide however, to provide more relevant information to our research and the community we have decided to rephrase the information given before and include a more appropriate reference (see below) to our study the area. (Oyarzun e al., 2007; Ribbe et al., 2008).

p. 709, L. 8: I would not consider nitrification as a source for DIN because it just transforms N into nitrate. Please comment on the N sources that actually deliver N into the stream (from outside the stream!). Response: Urban, industrial and agricultural land uses are considered sources of nitrogen because to wastewater discharge, intensive use of fertilizer and accelerated chemical weathering due to leaching of agriculture.

Silviculture is also other important source since in the catchment large volumes of sediment product of erosion have been observed (Parra et al., 2009). This information has also been added to Table 1 to show in a more precise way the sources of nutrients, especially nitrate, to the river.

p. 711, L. 5: Are there just 72 samples for the entire study or per site or year? Please Specify and discuss the consequences of the sampling scheme for the results. We collect 72 samples per year and a total of 576 samples during the study period (2004-2012) To robust our results we have included information of two more years of sampling (144 samples) until December 2014.

p. 712, L. 12: Show the river stretch included in the modeling on the map (Fig. 1 and Fig. 4). Explain why you only have considered a rather short stretch for the modelling part. We have added the 40km stretch modelled to Fig. 1. Also, we would like to clarify that we decided to analyze the estuary river and a part of the river, given the vastness of the river (180 km in length) and because inconsistency in information, this was not added to the model. Although the shortages in information, we have included in our analysis to identify trends in all and figure out what has happened in the river during our study period.

p. 712, Eq. 1: I miss the N input from the catchment into the stream as a (spatially explicit) source term in the model. Please comment on that. We consider nitrate and ammonium (concentration and flow) as inputs in the model and also include both as lateral flow.

p. 712, L. 24 – p. 713, L: 1: The in-stream measurements do not provide information on the boundary conditions but the internal state. Boundary conditions would be water fluxes and related concentrations of different N forms. Please explain how you have taken them into consideration. The first attempt in the model is to consider the boundary conditions of the system for every parameter. Our boundaries were the river (km 0) and the estuary (km 40). These conditions were incorporate in every prediction and

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for both periods, dry and wet.

p. 714, L. 5: Fig. 2a does not depict daily flow data but just annual values. Please correct. We have fix this error, a new figure with the correct information was made (daily flow). p. 714, L. 7: The extreme value distribution needs parameters. How do you obtained them and what are they? We estimate value distribution through statistics. We used percentiles and the 25th percentile of the extreme-value distribution. However, we considered to plot again precipitation data in order to show daily data

p. 714, L. 25: Fig. 4 does not display the relationship between land use and water quality. Providing such a figure would be useful. We have added a new table (Table 3) that shows the relation between land use and water quality and a statistical analysis (Spearman correlation) is included.

p. 714, L. 27 – 28: What about the input of sewage water (treated or untreated)? Please provide such data because wastewater may contribute a substantial fraction of riverine N. The river has the influence of sewage treated discharge, however, mainly as an input from Concepcion city, the biggest city in the region that discharges into the river.

p. 719, L. 15: Fig. 2b does not show single events. We have changed this figure to a new one to show the relationship between precipitation and discharge.

p. 720, L. 23: Fig. 6 does not show oxygen consumption. Figure 6 does show a decrease in oxygen, the reason why is barely appreciate is the river has a very high discharge. If we look closely in the last 10 km oxygen consumption occurs, and coincides that major urban sources are present at this portion of the river.

p. 721, L. 8 – 9: Nitrate concentrations will also be strongly influenced by N input from the catchment and from tributaries. Comment on that. Indeed, the existing 7 tributaries along the entire river influence the total N load in the river. However, for the purpose of this analysis we did not consider any tributaries in our model since in the 40 km

extension there are not tributaries to have significant discharge contributions. The rest of the contributions correspond to diffuse influence from different land uses like urban, industrial and agricultural mainly.

p. 722, L. 21: The influence of land use is not really shown anywhere in the manuscript. To illustrate this comment, we have added a Spearman correlation analysis to demonstrate the relation between nitrate and land uses (Table 3). This information also demonstrates how population and cattle have had a relative contribution to the sewage effluent and nutrient loads; see Table 1 for more information.

p. 732, Fig. 1: What about the upstream part of the watershed? Why is that area not shown? The upper part of the river itself was analyzed both temporally and spatially; see Fig. 2 and 3 and Table 1. However, given the vastness of the river (180 km in length) and because inconsistency in information, this was not added to the model. Although the shortages in information, we have included in our analysis to identify trends in all and figure out what has happened in the river during our study period.

p. 733, Fig. 2: Because the data represent annual values points are not an adequate representation. Please use step function (lines where the value remains constant across a year). This is what you actually show. We have included this suggestion in in Fig. 2

p. 737, Fig. 6: No labels of the x-axes are provided. Distinguish the points for the two seasons. We have fix this error, information on x axes are now included

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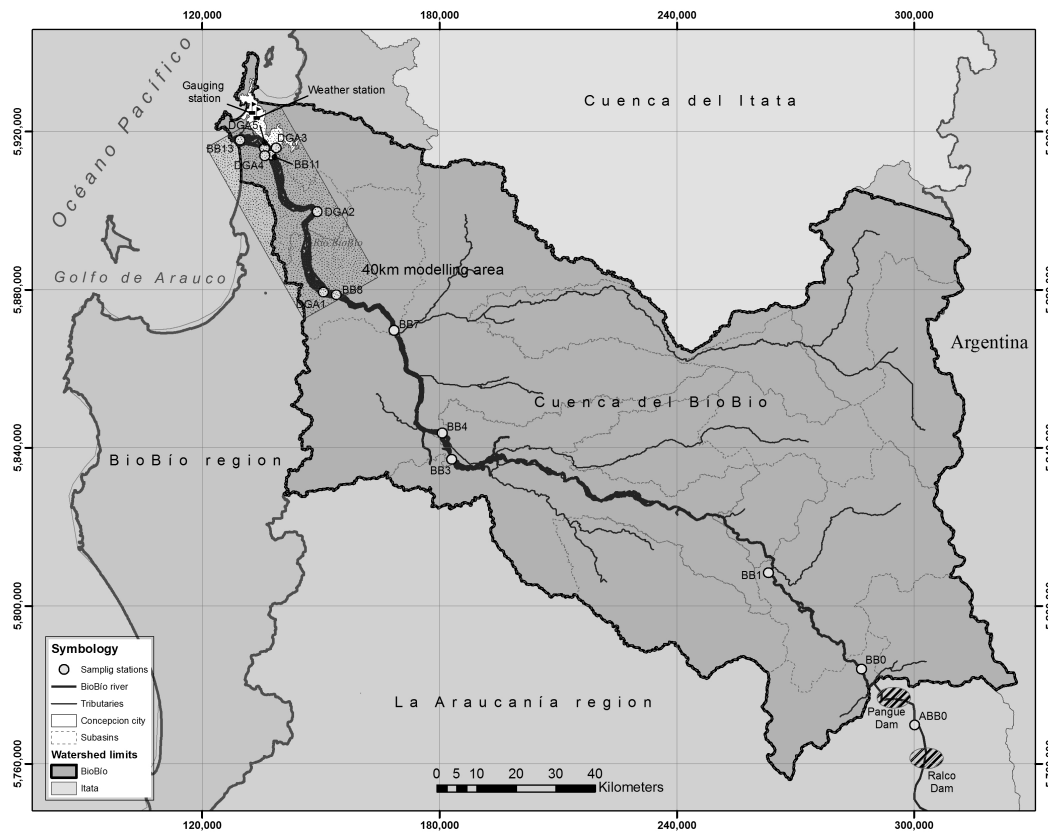
Table 1: Monitoring stations on the Biobío River. Coordinates are WGS84 values.

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-Patagua 1	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. 2.

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
Silviculture	%	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. 3.