

# Unravel biophysical factors on river water quality response in Chilean Central-Southern watersheds

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Received: 18 June 2015 / Accepted: 14 March 2016 / Published online: 2 April 2016  
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**Abstract** Identifying the key anthropogenic (land uses) and natural (topography and climate) biophysical drivers affecting river water quality is essential for efficient management of water resources. We tested the hypothesis that water quality can be predicted by different biophysical factors. Multivariate statistics based on a geographical information system (GIS) were used to explore the influence of factors (i.e., precipitation, topography, and land uses) on water quality (i.e., nitrate ( $\text{NO}_3^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), silicate ( $\text{Si}(\text{OH})_4$ ), dissolved oxygen (DO), suspended solids (TSS), biological oxygen demand (BOD), temperature (T), conductivity (EC), and pH) for two consecutive years in the Itata and Biobío river watersheds, Central Chile ( $36^\circ 00'$  and  $38^\circ 30'$ ). The results showed that ( $\text{NO}_3^-$ ), ( $\text{PO}_4^{3-}$ ),  $\text{Si}(\text{OH})_4$ , TSS, EC, and DO were higher during rainy season (austral fall, winter, and spring), whereas BOD and temperature were higher during dry season. The

spatial variation of these parameters in both watersheds was related to land use, topography (e.g., soil moisture, soil hydrological group, and erodability), and precipitation. Soil hydrological group and soil moisture were the strongest explanatory predictors for  $\text{PO}_4^{3-}$ ,  $\text{Si}(\text{OH})_4$  and EC in the river, followed by land use such as agriculture for  $\text{NO}_3^-$  and DO and silviculture for TSS and  $\text{Si}(\text{OH})_4$ . High-resolution water leaching and runoff maps allowed us to identify agriculture areas with major probability of water leaching and higher probability of runoff in silviculture areas. Moreover, redundancy analysis (RDA) revealed that land uses (agriculture and silviculture) explained in 60 % the river water quality variation. Our finding highlights the vulnerability of Chilean river waters to different biophysical drivers, rather than climate conditions alone, which is amplified by human-induced degradation.

**Keywords** Biophysical drivers · Water quality · Leaching · Runoff · Land use

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## Introduction

Nowadays, there is a fast decreasing availability of usable freshwater due to intensive land use practices and climate conditions that moreover deteriorate the water quality (Ahearn et al. 2005; Li et al. 2008). River water quality is controlled by complex anthropogenic and natural factors at both the river and watershed scales. Therefore, understanding the spatial and temporal variations of different solutes and predicting the key

biophysical factors such as land use, topography, and climate, which affect the river water quality, can help researchers and stakeholders to establish priorities for water resource management (Chen and Lu 2014).

The interaction among biophysical factors influences the transport of solutes and is crucial to predict water quality changes in rivers (Gascuel-Odoux et al. 2009). Several studies have shown that changes in environmental pattern induced by human activities had major impacts on river water chemistry (Allan 2004; Bhat et al. 2006). Crop removal, cellulose industries, hydropower, and wildfires at the basin scale can increase the solute load of rivers through increasing runoff erosion and water leaching (Zhang et al. 2011; Kavian et al. 2011; Pizarro et al. 2014). A number of studies have shown the relationships between water quality parameters and land use, population density, and point source discharge (Ahearn et al. 2005; Broussard and Turner 2009). Concomitantly, topography and climate are considered important drivers that influence watershed river water quality (Baker 2003; Ye et al. 2009).

Chile, in particular, has large mountain ranges with specific lithogenic characteristics that help to accelerate weathering and runoff (Pizarro et al. 2010). These characteristics, combined with a wide range of land uses and hydromorphology of watersheds, increase the concern about environmental policies and point out evidence of the lack of strict useable water management strategies (Andreoli et al. 2012). In Central-Southern Chile, there is a serious concern about the biogeochemical status of freshwaters due to the replacement of native forest by high water-demanding forest plantations and the intensification of agricultural activities (Echeverría et al. 2007; Pizarro et al. 2014). While intensive land use can evidently raise solute load in rivers, natural drivers such as rainfall patterns can also contribute to modify the runoff in river basins (Vergara et al. 2013). For instance, the Itata and Biobío river watersheds, located in the Biobío region, are two important areas with high levels of precipitation subjected to an increase of human activity in the last 10 years, mainly associated with agricultural, industrial, and urban supplies (Karrasch et al. 2006; Valdovinos and Parra 2006; Parra et al. 2009). Nevertheless, the impact of the extensive silviculture activity present in the coastal mountain range on the river water quality is a growing concern (Pizarro et al. 2014). Various approaches for analyzing the

impacts of biophysical factors on water quality have been achieved (Keeler et al. 2012). Statistical tools have been successfully used in river chemistry source identification and in determining the relationships between environmental variables and water quality. However, multivariate analysis in particular provides quantitative information because it is effective in reducing data dimensionality and grouping variables according to their features (Chang 2008).

We hypothesize that the river water quality (nitrate ( $\text{NO}_3^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), silicate ( $\text{Si}(\text{OH})_4$ ), dissolved oxygen (DO), total suspended solids (TSS), water temperature ( $^{\circ}\text{C}$ ), electrical conductivity (EC), and pH) in two Central Chile basin rivers (Itata and Biobío) can be predicted from a suite of biophysical factors: topography (e.g., erodability, slope, soil moisture, and soil hydrological group), land use (e.g., silviculture, agriculture, and urbanization), and climate (e.g., precipitation). Emphasis is placed on the combination of different biophysical factors to identify areas for water leaching and runoff and to examine how the contributions of different biophysical factors influence the water quality at mesoscale or regional scale.

## Materials and methods

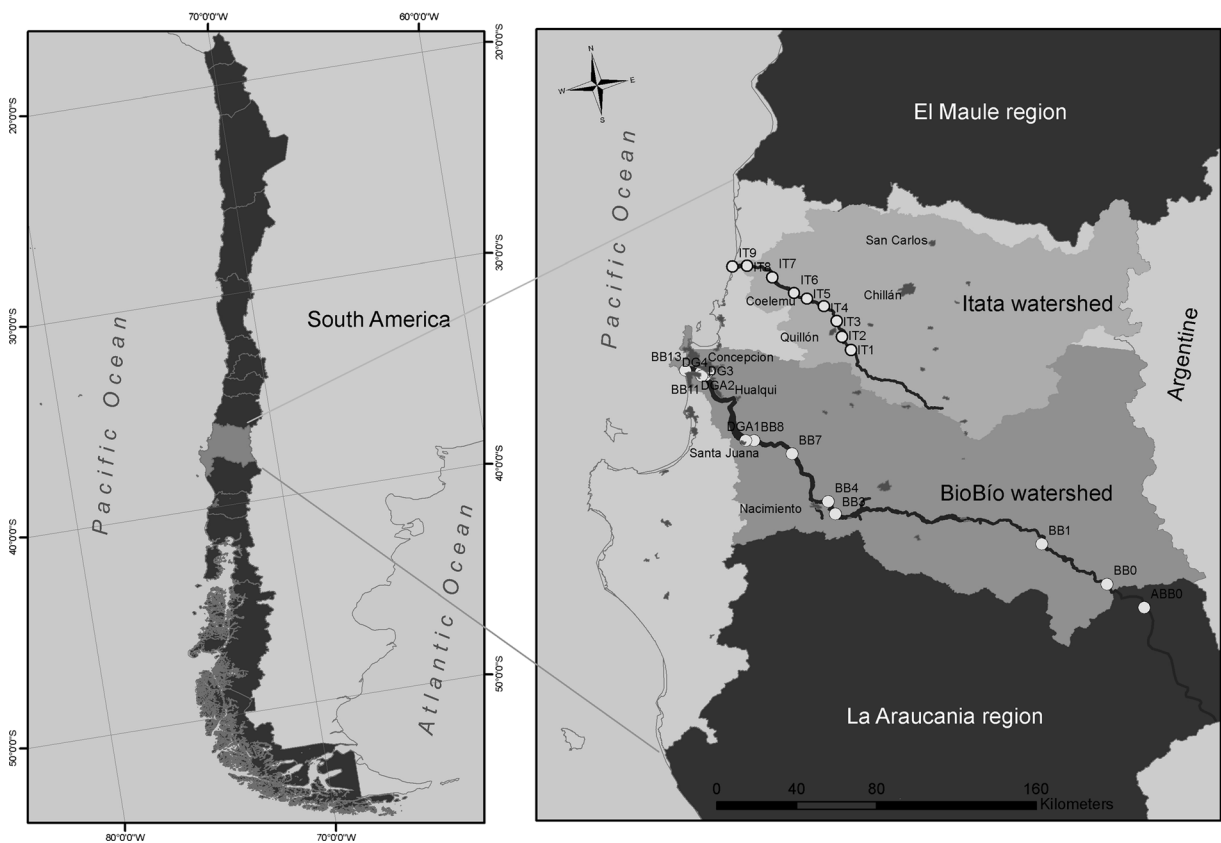
### Study area

The Itata and Biobío river basins are located in the central part of Chile (Fig. 1) and were selected mainly because of their intensive land use activities (Fig. 1). Both river basins are influenced by the temperate climates of the South as well as the Mediterranean climate of Central Chile with an average annual temperature and rainfall of 14.1  $^{\circ}\text{C}$  and 1550 mm, respectively. Soil types according to the FAO-UNESCO system include alfisols (heavy clay), inceptisol, and andisols (derived from volcanic sands; Luzio et al. 2003). The Itata River basin (36° 23' 24" S; 72° 51' 44.6" W) is approximately 11,600  $\text{km}^2$ . It has a pluvio-nival regime with a monthly mean streamflow between 760  $\text{m}^3 \text{s}^{-1}$  during winter and 22  $\text{m}^3 \text{s}^{-1}$  during summer (DGA 2004). Different land uses are present, such as agriculture, livestock, and recent industrial developments and high forestry (Salamanca and Pantoja 2009). More than 30 % of the national consumption of nitrogen fertilizers is concentrated in the Central

Valley in the Biobío region. Annual crops and fruit tree orchards are the biggest consumers of these products, followed by horticultural crops (Arumí et al. 2005). The Biobío River (36° 48' 53"S; 73° 09' 41"W), on the other hand, is located in the third largest Chilean basin, with 24,260 km<sup>2</sup> with a length of 380 km, flowing from the Andes to the Pacific Ocean. The Biobío River has a monthly mean streamflow between 1950 m<sup>3</sup> s<sup>-1</sup> during winter and 260 m<sup>3</sup> s<sup>-1</sup> in summer (DGA 2004). The river covers approximately 3 % of the total country area (Stehr et al. 2008). The Biobío River provides water for multiple purposes including hydropower generation, pulp mill industries, petrochemical discharges, and land uses like urban and agriculture. In addition, important anthropogenic stressors on the riverbed have been reported, such as the alteration of natural water flow pattern through the Pangué, Ralco, and Angostura dams (Karrasch et al. 2006).

### Water quality data sources

The stream water was sampled seasonally, during the dry (December–January) and wet seasons (April–September), from April 2013 to September 2014 at 13 sampling sites throughout the Biobío River and 9 sampling sites along the Itata River (Fig. 1). In total, seven sampling times (April, July, September, December, March, July, September) for every river were obtained, and the sampling took place at the middle of the river at different land uses (Table 1). Discrete sampling was completed following the next condition: water samples collected in the estuary were always sampled at low tide. Water samples were collected at approximately 0.3 m depth, filtered through a 0.7-μm pore size filter, and placed into HDPE bottles and frozen for subsequent chemical analysis. Moreover, DO, T, pH, TSS, and EC were measured in the field with a hand-held multi-parameter instrument (Multi 340i SETs, Merck Co. Ltd., Germany). Anions such as NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>,



**Fig. 1** Map of the study area in the Biobío region, Central Chile. **a** Itata River watershed, **b** Biobío River basin. Sampling locations are included in the map

**Table 1** Parameter/variable information of watershed characteristics in both rivers (Itata and Biobío)

	Parameters	Unit	Code	Itata			Biobío		
				Station	Range	Mean ± SD	Station	Range	Mean ± SD
Climate	Annual precipitation	mm	APP	–	329–2580	1170 ± 301	–	352–1422	1074 ± 314
	Winter precipitation	mm	WPP	–	423–2029	705 ± 112	–	590–994	846 ± 262
	Air temperature	°C	T	–	8.9–29.3	17.6 ± 6.1	–	8.4–25.2	17.1 ± 4.8
Topography	Soil moisture	mm	SM	–	01–23	3.76 ± 6.02	–	01–25	4.73 ± 7.08
	Mean elevation	m	ME	–	01–1250	150 ± 675	–	01–2300	250 ± 780
	Mean catchment slope	%	S	–	0.75–3.1	2.1 ± 1.2	–	0.75–3.6	2.2 ± 1.5
	Erodability		ERO	–	0.02–0.2	0.08 ± 0.02	–	0.02–0.3	0.10 ± 0.1
	Soil type hydrological group		SHG	–	A–D	–	–	A–D	–
Land use	Agriculture	%	AGRL	IT1 IT3 IT6	0.7–6.9	3.1 ± 2.3	BB3 BB4 DGA2	<0.1–13	1.9 ± 3.6
	Forest	%	FRSD		<0.1–2.6	1.2 ± 0.86	ABBO BBO BB1	<0.1–3.9	0.5 ± 1.1
	Silviculture	%	SILV	IT4 IT8 IT9	<0.1–4.8	1.4 ± 1.7	BB7 BB8 DGA1	<0.1–19	4.1 ± 7.8
	Grassland	%	GRASS	IT5	<0.1–0.34	0.2 ± 0.11	DGA3	<0.1–3.2	0.82 ± 1.1
	Urban	%	URB	IT2 IT7	<0.1–0.2	0.1 ± 0.04	BB11 BB13 DGA4	<0.1–0.74	0.13 ± 0.27

and  $\text{Si}(\text{OH})_4$  concentration were analyzed by colorimetric techniques by Grasshoff et al. (1983).

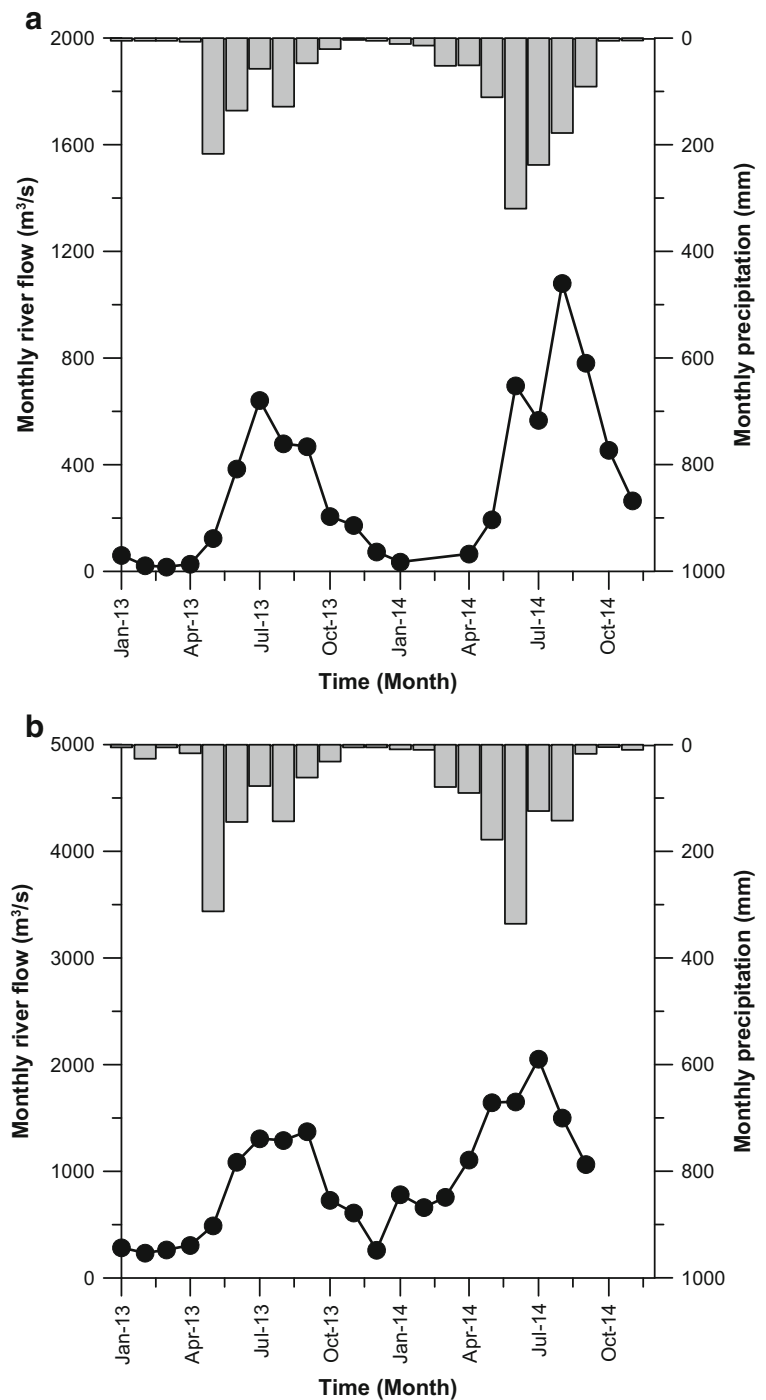
#### Selection of data, processing, and transformation

The boundaries of the watersheds were delineated using 30-m digital elevation models (DEMs) through a geographical information system (GIS) spatial analysis tool (ESRI 2006). The DEM was downloaded from the Land Processes Distributed Active Archive Center by the US Geological Survey website ([https://lpdaac.usgs.gov/products/aster\\_products\\_table/astgtm](https://lpdaac.usgs.gov/products/aster_products_table/astgtm)). Boundaries were used to calculate sub-watershed areas and to summarize land use, soil type, and topography for each watershed. The numbers of sub-watersheds in the Biobío and Itata rivers were 13 and 11, respectively (Fig. 1). Environmental factors employed in the GIS evaluation of soil and water functions are based on public databases elaborated by different government offices and public institutions (Water National Direction (DGA), Institute for Agricultural Research (INIA), University of Concepcion (UDECE), Center for Information of Natural Resources (CIREN)). The hydrological soil

groups are based on estimates of runoff potential. Soils are assigned to one or four groups (A, B, C, and D) according to the rate of water infiltration. Group A means that the soil has a high infiltration rate (low runoff potential). Groups B and C correspond to moderate to slow infiltration rate, respectively, and finally, Group D indicated a very slow infiltration rate, regarding high runoff potential (Haan et al. 1994).

Rainfall and river flow were obtained from DGA (Fig. 2a, b), whereas the slope, topography, and erodability were derived from our DEM to determine the slope gradient (S). Land use coverage was interpreted from satellite imagery Landsat Thematic Mapper (TM). Landsat TM images from 2011 of the Biobío and Itata watersheds were downloaded from the Global Visualization Viewer site by the US Geological Survey website (<http://glovis.usgs.gov/>) and processed in the ENVI software. Land uses in each sub-watershed were extracted through the extract analysis tools in ArcGIS and, once defined, verified in terrain during the surveys. Eleven land uses (Table 1) were defined: (1) forest, (2) water bodies, (3) steppe (4) shrubland (5) snow (7) silviculture, (8) dunes and beach, (9) bare soil,

**Fig. 2** a. Monthly average precipitation and monthly river flow in the Itata River watershed during the studied period. b. Monthly average precipitation and monthly river flow in the Biobío River watershed during the studied period



(10) agriculture, and (11) urban (CONAF and CONAMA 1999). However, we used and analyzed only the most intensive land uses such as forest (FRSD), grassland (GRASS), silviculture (SILV), agriculture (AGRL), and urban (URB).

Biophysical drivers in the Itata and Biobío sub-watersheds

All environmental variables, including land use, topography, and climate factors, were utilized to evaluate the

**Table 2** Seasonal ranges of water quality parameters

Itata River				
Water quality parameters	Unit	Wet season range	Dry season range	
NO <sub>3</sub> <sup>-</sup>	mg/L	0.8–1.9	0.2–1.35	
PO <sub>4</sub> <sup>3-</sup>	mg/L	0.05–0.5	0.03–0.08	
Si(OH) <sub>4</sub>	mg/L	5–12	4–9.6	
pH		7.4–8.43	7.59–8.48	
EC	μS/cm	80–189	71–193	
T°C	°C	10.2–20	19–24	
DO	mg/L	8.9–11.8	7.8–10.4	
TSS	mg/L	0.23–289	2.18–71	
Biobío River				
Water quality parameters	Unit	Wet season range	Dry season range	
NO <sub>3</sub> <sup>-</sup>	mg/L	7.7–36.4	5.1–36.4	
PO <sub>4</sub> <sup>3-</sup>	mg/L	0.5–1.98	0.3–1.38	
Si(OH) <sub>4</sub>	mg/L	3–10.5	2.8–9	
pH		7.01–8.77	7.24–7.78	
EC	μS/cm	98–474	165–1380	
T°C	°C	8.4–20.4	17.8–25.1	
DO	mg/L	7.52–10.1	6.1–9.8	
TSS	mg/L	11–3531	7.2–143	

response of river water quality to environmental gradients. Mann-Whitney statistical analysis was used to compare the relationship between river water quality variations and different seasons (rainy and dry). To analyze the importance of different factors in the water quality, a Spearman correlation analysis was done (Hooper 2003). Spearman correlation was used to identify inter-correlations between biophysical drivers and water quality. Principal component analysis (PCA) was used to extract the main factors controlling material transport and water quality. Redundancy analysis (RDA) was employed to define specific variability in sub-watersheds with river water (Chen and Lu 2014; Fu et al. 2016). The difference between these two methods is that PCA is unconstrained (search for any variable that best explains nitrate concentration and different parameters in the river), whereas RDA is constrained (search for the best explanatory variable into the PCA cloud).

#### Estimation of leaching and runoff indexes

The amount of water that leaches from soil was quantified by a model developed by Williams and Kissel (1991), which is considered the most suitable method (Braun et al. 2003; Elrashidi et al. 2005; Hamza et al.

2007; Li and Merchant 2013). This method takes into account the amount of precipitation and the hydrologic soil groups. The soil groups are defined according to the soil infiltration rates. The equations used to calculate leaching are as follows:

$$LI = \text{Percolation Index (PI)} * \text{Seasonal Index (SI)}$$

where

$$PI = (PA - 10.28)^2 / (P + 15.43) \text{ for hydrologic soil group A}$$

$$PI = (PA - 15.05)^2 / (P + 22.57) \text{ for hydrologic soil group B}$$

$$PI = (PA - 19.53)^2 / (P + 29.29) \text{ for hydrologic soil group C}$$

$$PI = (PA - 22.67)^2 / (P + 34.00) \text{ for hydrologic soil group D}$$

$$SI = (2PW/PA)^{1/3}$$

where PA is the annual precipitation and Pw is the winter precipitation.

The runoff curve number equation is widely used to transform rainfall data into direct runoff, after “losses”—evaporation, absorption, transpiration, and

**Table 3** Spearman correlation for watershed biophysical parameters and water quality river parameters in Itata River

Variables	NO <sub>3</sub> -	pH	EC	DO	PO <sub>4</sub> <sup>3-</sup>	Si(OH) <sub>4</sub>	TSS	T°C <sub>Water</sub>	AGRL	FRSD	SILV	GRASS	URB	Sub-watershed area	Soil HG	APP	WPP	ERO	Slope	
pH	-0.18																			
EC	-0.35	0.340																		
DO	-0.77	-0.16	0.185																	
PO <sub>4</sub> <sup>3-</sup>	0.78	-0.06	-0.41	-0.83																
Si(OH) <sub>4</sub>	0.23	-0.10	-0.76	-0.51	0.52															
TSS	-0.55	0.38	-0.25	0.09	-0.11	0.58														
T°C <sub>Water</sub>	0.11	-0.51	-0.51	-0.31	0.54	0.74	0.34													
AGRL	0.71	0.02	0.27	-0.58	0.32	-0.23	-0.60	-0.32												
FRSD	0.29	0.24	-0.04	-0.75	0.39	0.52	0.15	0.29	0.18											
SILV	-0.02	0.58	0.27	-0.57	0.53	0.31	0.34	0.036	0.11	0.89										
GRASS	0.36	-0.43	-0.27	-0.24	-0.07	0.22	-0.36	0.000	0.32	0.43	0.14									
URB	0.55	0.34	0.34	-0.66	0.50	-0.09	-0.21	-0.14	0.82	0.21	0.29	-0.19								
Sub-watershed area	0.53	0.15	0.27	-0.83	0.61	0.14	-0.28	0.21	0.50	0.79	0.68	0.18	0.57							
Soil HG	0.59	-0.10	0.15	-0.31	0.49	-0.073	-0.454	-0.289	0.59	0.58	0.43	0.87	0.00	0.43						
APP	0.291	-0.24	-0.432	-0.257	0.65	-0.306	-0.617	-0.250	0.64	0.39	0.77	0.71	0.25	0.50	0.87					
WPP	0.330	-0.47	0.082	-0.278	0.72	0.009	-0.491	0.018	0.84	0.45	0.78	0.90	0.040	0.41	0.87	0.84				
ERO	-0.236	0.53	0.934	0.119	-0.424	0.778	-0.303	-0.733	-0.35	0.04	0.75	-0.15	0.35	0.30	0.31	0.46	0.10			
Slope (elevation)	0.081	-0.08	-0.080	-0.406	0.474	0.499	0.083	0.632	-0.32	0.63	0.47	0.00	-0.16	0.63	0.09	0.00	0.10	-0.17		
Soil moisture	0.463	-0.31	-0.257	-0.393	0.036	0.266	-0.333	-0.018	0.75	0.53	0.26	0.98	-0.12	0.30	0.88	0.75	0.90	-0.12	0.2	

**Table 4** Spearman correlation for watershed biophysical parameters and water quality river parameters in Biobío River

	NO <sub>3</sub> <sup>-</sup>	pH	EC	DO	PO <sub>4</sub> <sup>3-</sup>	Si(OH) <sub>4</sub>	TSS	T <sup>o</sup> C <sub>Water</sub>	AGRL	FRSD	SILV	GRASS	URB	Sub-watershed area	Soil HG	APP	WPP	ERO	Slope
pH	-0.16																		
EC	0.04	-0.52																	
DO	0.09	0.40	0.49																
PO <sub>4</sub> <sup>3-</sup>	-0.14	0.52	0.00	0.61															
Si(OH) <sub>4</sub>	0.13	-0.13	0.88	0.79	0.13														
TSS	0.70	0.00	0.29	0.25	0.16	0.33													
T <sup>o</sup> C <sub>Water</sub>	-0.96	0.10	0.04	-0.07	0.20	-0.2	-0.7												
AGRL	0.58	0.36	-0.18	0.31	0.43	0.10	0.75	-0.85											
FRSD	-0.14	0.68	-0.12	0.56	0.79	0.16	0.16	0.036	0.18										
SILV	-0.07	0.54	0.00	0.68	0.75	0.25	-0.1	0.054	0.11	0.89									
GRASS	-0.07	0.39	-0.32	0.00	0.68	-0.6	0.40	0.072	0.32	0.43	0.14								
URB	0.75	0.42	-0.14	0.42	0.30	0.23	0.44	-0.83	0.82	0.22	0.29	-0.18							
Sub-watershed area	0.25	0.52	0.30	0.78	0.54	0.60	0.56	-0.38	0.50	0.79	0.68	0.18	0.57						
Soil HG	0.14	0.29	0.00	0.36	0.87	0.00	0.51	-0.08	0.63	0.58	0.43	0.19	0.00	0.43					
APP	0.29	0.38	0.10	0.58	0.75	0.23	0.62	-0.07	0.64	0.40	0.29	0.90	0.25	0.50	0.87				
WPP	0.018	0.51	-0.11	0.37	0.76	-0.02	0.51	-0.23	0.59	0.45	-0.21	0.72	0.40	0.40	0.87	0.92			
ERO	0.50	-0.24	0.50	0.64	0.35	0.56	0.22	-0.47	0.35	0.68	0.35	0.9	0.40	0.27	0.32	0.46	0.10		
Slope (elevation)	-0.47	0.24	0.48	0.48	0.32	0.56	0.18	0.32	-0.32	0.63	0.48	-0.15	-0.16	0.63	0.1	0.00	0.10	-0.17	
Soil moisture	0.45	0.51	-0.40	0.10	0.77	0.35	0.46	0.10	0.45	0.61	0.35	0.00	-0.1	0.32	0.89	0.70	0.87	-0.12	0.10



surface storage. Hence, the higher the curve number (CN) value, the higher the runoff potential will be. As the CN may be related with soil type, slopes, and land cover, the use of this index introduces the characteristic heterogeneity of Central Chile watersheds to this analysis. Therefore, this methodology requires the knowledge of type and use of soil and precipitation records, through the following equation:

$$Q = \frac{(P - \frac{5080}{CN} + 50.8)^2}{(P + \frac{20320}{CN} + 203.2)}$$

where Q=runoff (mm), P=precipitation (mm), and CN=curve number from table (Lyon et al. 2004).

Water leaching and runoff indexes were given in relative rather than absolute terms, since absolute figures could bring the impression of accuracy elsewhere; this could be supported by the biophysical data.

### Results

#### Physicochemical water quality in Itata and Biobío rivers

Table 2 shows a comparison of physicochemical parameters such as DO, pH, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, T, and BOD between different seasons (autumn-winter and spring-summer). Significant spatial variations (*p*<0.05) of TSS, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> were generally higher during the winter season (July to September). Furthermore, TSS and EC were higher in the lower part of the watershed where the river is often influenced by tides and diffuse source pollution. TSS, PO<sub>4</sub><sup>3-</sup>, and pH were higher in silviculture areas than in pasture and agriculture areas, whereas NO<sub>3</sub><sup>-</sup> and EC were higher in agricultural areas.

#### Relationship between Itata and Biobío river biophysical factors and river water

Tables 3 and 4 show correlation coefficients estimated for the river water quality and their corresponding sub-watershed land use, rainfall, and topography factors through the Spearman correlations for both rivers. In the Itata River, the correlation analysis showed that AGRL was significantly positively correlated with the soil hydrological group (*r*=0.59, *p*<0.014), precipitation (*r*=0.84, *p*<0.01), and soil moisture (*r*=0.75, *p*<0.01). Nitrate (*r*=0.71, *p*<0.02) was negatively

correlated with erodability (*r*=-0.29, *p*<0.01). Silviculture (SILV) showed a positive correlation with phosphate (*r*=0.53, *p*<0.01), rainfall (*r*=0.77, *p*<0.01), erodability (*r*=0.77, *p*<0.001), and slope (*r*=0.50, *p*<0.01). Forest (FRSD) had a positive correlation with slope (*r*=0.63, *p*<0.013), erodability, and precipitation. Negative correlations were found between OD and agriculture, FRSD, SILV, and URB.

In the case of the Biobío River, similar correlations were also found. Significant and positive correlations were found between agriculture and nitrate (*r*=0.58, *p*<0.018) and soil moisture (*r*=0.45, *p*<0.01). Likewise, SILV had a positive correlation with pH (*r*=0.54, *p*<0.1) and erodability (*r*=0.54, *p*<0.02). FRSD was significantly positively correlated with erodability (*r*=0.68, *p*<0.04). SILV was positively correlated with Precipitation (*r*=0.5, *p*<0.15) and slope (*r*=0.48, *p*<0.03). Negative correlations were found between slope and agriculture (*r*=-0.32, *p*<0.013), GRASS (*r*=-0.15, *p*<0.01), and URBN (*r*=-0.16, *p*<0.01).

**Table 5** Itata River water quality parameters and biophysical factors through principal component (PC) analysis during wet and dry season for 2013–2014

Itata River	Wet season			Dry season		
	PC1	PC2	PC3	PC1	PC2	PC3
Water quality parameters						
NO <sub>3</sub> <sup>-</sup> (mg/L)	0.322	0.07	-0.376	0.17	-0.21	0.372
EC (μS/cm)	0.232	0.32	-0.22	0.04	-0.436	-0.312
PO <sub>4</sub> <sup>3-</sup> (mg/L)	0.095	-0.48	-0.079	0.34	0.106	-0.142
TSS (mg/L)	0.052	-0.46	-0.015	0.30	-0.116	0.165
Si(OH) <sub>4</sub> (mg/L)	0.090	-0.41	-0.385	0.35	-0.21	0.10
AGRL	0.315	0.11	-0.241	0.31	-0.194	0.196
FRSD	0.247	-0.44	-0.041	0.21	0.173	-0.331
SILV	0.275	-0.05	-0.245	0.37	-0.065	-0.227
GRASS	0.291	-0.03	0.413	0.28	0.333	-0.018
URB	0.255	0.22	-0.363	0.26	-0.209	0.196
Soil HG	0.368	0.07	0.195	0.37	0.121	-0.029
APP	0.377	0.13	0.128	0.20	0.01	0.025
WPP	0.365	0.06	0.226	-	-	-
ERO	0.159	0.38	-0.294	0.20	-0.419	0.105
Elevation	0.055	-0.42	-0.038	0.04	-0.007	-0.593
Soil moisture	0.330	-0.08	0.297	0.30	0.375	0.003
Eigenvalues	6.06	3.25	2.67	6.24	3.14	2.55
Variance (%)	43	23	19	42	21	17
Cumulative Variance (%)	43	66	86	42	63	80

Regarding the PCA, the main patterns for the rivers between the wet and dry periods were identified (Table 5). In the Itata River during the wet season, the PCA indicated three significant factors (i.e., PCs with an eigenvalue >1) which explained 85 % of the total variance (Table 5). The first factor accounted for 43 % of the total variance and showed a positive correlation with AGRL, soil moisture, rainfall, soil type, TSS, EC, Si(OH)<sub>4</sub>, and NO<sub>3</sub><sup>-</sup>. The PCA made for the dry season showed that the eigenvalues accounted for 63 % of the total variance. Factor 1 accounted for 42 % of the total variance and was positively correlated with, SILV, soil type, TSS, PO<sub>4</sub><sup>3-</sup>, and Si(OH)<sub>4</sub>. The variables of major weight from each principal component (PC) were selected as precipitation, soil hydrological group, erodability, and land use (SILV, GRASS, AGRL). Based on the PCA result, biophysical key factors for the water quality of the river can be identified as follows: soil hydrological group, precipitation, SILV, AGRL, and soil moisture (Table 5). On the other hand, for the Biobío River, PCA made during the dry season showed three main factors that

explained 67 % of the total variance. The PCA for the wet season indicated four significant factors that explained 81 % of the total variance (Table 6).

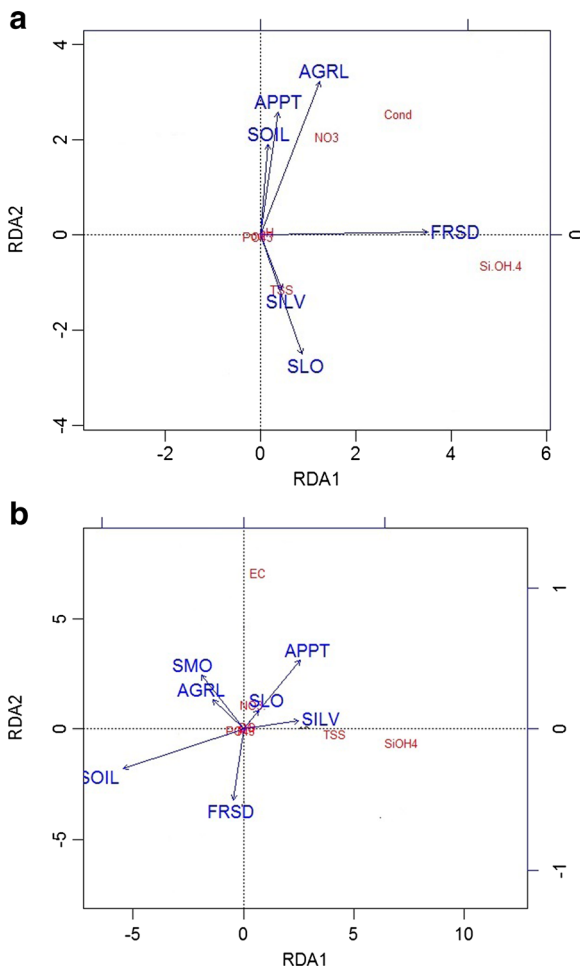
The RDA for the hydrochemistry of the Itata River showed that SILV, slope, precipitation, and soil type explained 30 % of the spatial variation. A combination of land uses (agriculture, silviculture, and urban), topography, and rainfall conditions explained 79 % of the water quality (TSS, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, EC, Si(OH)<sub>4</sub>). The RDA of the hydrochemistry of the Biobío River showed that precipitation, forest, and silviculture explained 40 % of the spatial variation of TSS, EC, Si(OH)<sub>4</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> in the river. The ordination plot indicated that the main vector was the *x*-axis showing a gradient where nutrient levels were positively correlated with slope, silviculture, and rainfall and the soil hydrological group with 54 % of the total variance (Fig. 3a, b).

#### Leaching and runoff index mapping

Figures 4 and 5 show the water leaching index mapping for both rivers. In the Itata watershed,

**Table 6** Biobío River water quality parameters and biophysical factors through principal component (PC) analysis during wet and dry season for 2013–2014

Biobío River	Wet season				Dry season			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
Water quality parameters								
NO <sub>3</sub> <sup>-</sup> (mg/L)	0.13	-0.40	-0.25	-0.31	0.41	0.24	-0.012	0.17
EC (μS/cm)	0.27	0.27	0.06	0.10	0.31	-0.12	-0.09	0.14
PO <sub>4</sub> <sup>3-</sup> (mg/L)	0.44	-0.32	-0.06	-0.21	0.38	-0.1	-0.09	0.26
TSS (mg/L)	0.35	0.25	0.014	0.52	0.41	-0.2	0.23	-0.11
Si(OH) <sub>4</sub> (mg/L)	0.37	0.23	-0.031	-0.29	0.40	0.23	0.21	0.24
AGRL	0.20	-0.22	0.286	0.17	-0.07	0.14	0.16	0.64
FRSD	-0.05	0.128	-0.435	0.16	0.25	0.11	-0.58	-0.07
SILV	0.35	0.432	-0.155	-0.05	-0.07	0.50	0.26	-0.22
GRASS	0.14	-0.014	0.263	0.58	0.17	0.31	0.10	-0.09
URB	0.13	0.1	0.153	0.439	0.35	-0.33	0.15	-0.04
Soil HG	0.38	-0.122	0.275	0.14	0.11	-0.28	-0.44	-0.06
WPP	0.20	-0.252	-0.063	-0.21	-	-	-	-
ERO	0.32	0.413	-0.231	-0.05	0.14	-0.28	-0.54	-0.06
Elevation	0.29	0.30	0.20	-0.31	-0.005	0.469	-0.423	-0.09
Soil moisture	0.42	-0.24	-0.095	-0.050	0.083	0.183	-0.459	-0.11
<i>Eigenvalues</i>	4.05	2.88	2.03	1.54	3.75	2.50	2.03	1.65
Variance (%)	31	22	16	12	29	19	16	13
Cumulative Variance (%)	31	53	69	81	29	49	67	79



**Fig. 3** a. Biplot of the river water quality parameters and watershed characteristics in the Itata River according to the redundancy analysis (RDA). b. Biplot of the river water quality parameters and watershed characteristics in the Biobío River according to the RDA

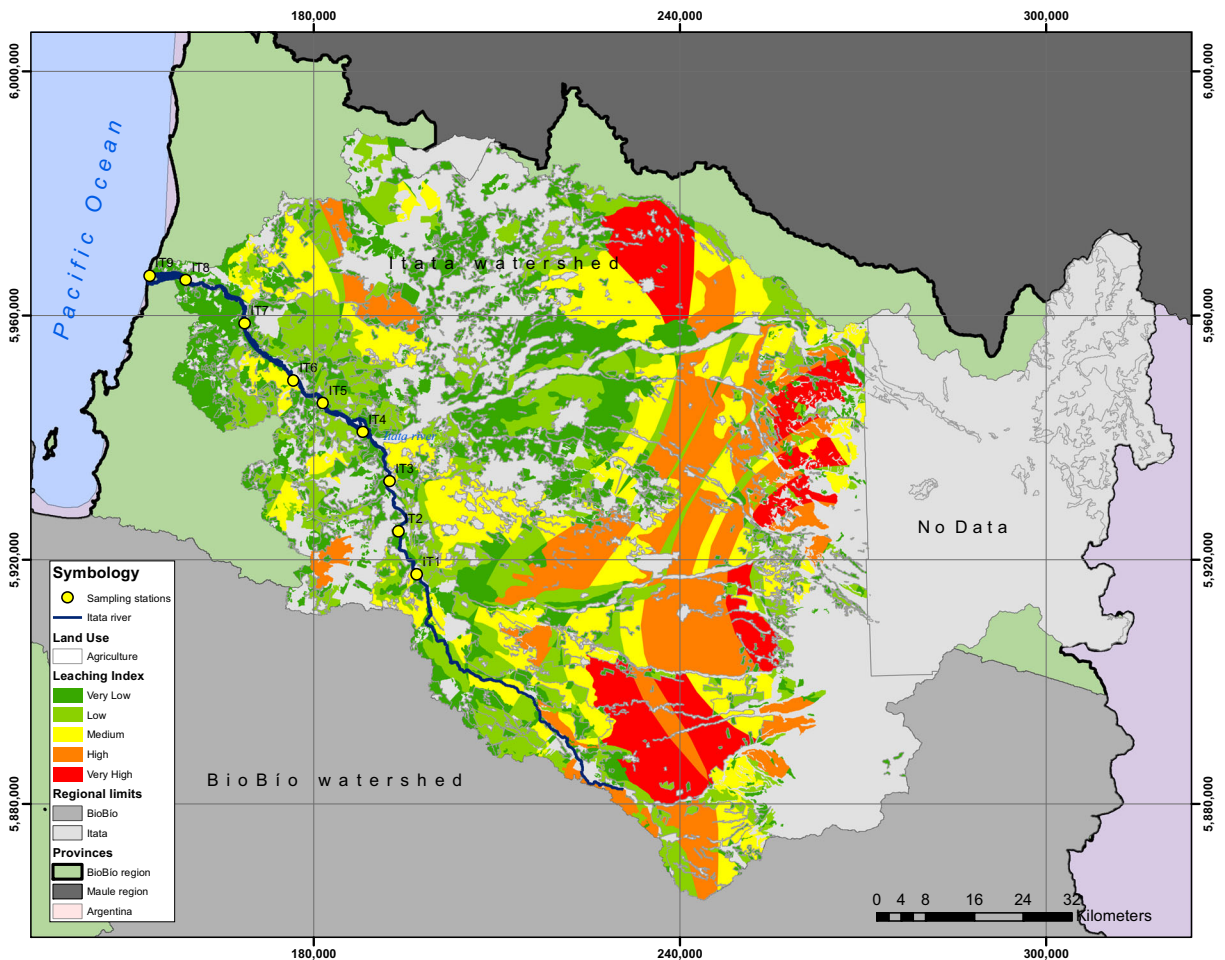
agriculture and some rural villages had a higher water leaching index than did areas in the western part of the watershed, where silviculture and deforestation cover the zone. In this area, inceptisol and alfisol soils are dominant, while in the west clayey soils prevail. In the case of the Biobío watershed, a similar trend is seen in Fig. 5. Major water leaching index is present in cities (i.e., Concepcion and San Pedro), and forested and deforested areas show the presence of andisol as the dominant soil type. On the contrary, for both river watersheds, water runoff index (NLI) showed an opposite trend; eastern areas closer to the coast, and areas with major deforestation, showed higher NLI (Figs. 6 and 7).

### Discussion

Due to the mountainous geography of Chile, several studies have shown that watersheds rapidly release their solutes through the rivers (Tolorza et al. 2014; Pizarro et al. 2014), and most biophysical drivers such as land use, climate, and topography may exert a strong influence on river water quality. In our study, we identified that water quality in both rivers (Itata and Biobío) is significantly related to soil topography (hydrological group and soil moisture), climate (precipitation), and land use. We have found that silviculture was an important predictor of TSS,  $PO_4^{3-}$ ,  $Si(OH)_4$ , and EC during the winter period (wet season) for both rivers, whereas during the dry period, agriculture and urbanization were related to  $NO_3^-$ , DO, and pH.

#### Topographic biophysical factors

Topographic factors have a significant role in explaining spatial variation in river waters, mainly in mountain areas (Tong and Chen 2002). In fact, topography factors such as soil hydrological group and slope (elevation) essentially dominated the river water quality parameters in both measured rivers. It has been described that the soil is one of the main drivers able to mobilize nutrients in a river basin (Chen and Lu 2014). Several studies have shown that high slopes have a negative relationship with  $NO_3^-$ ,  $PO_4^{3-}$ , and  $Si(OH)_4$  and that the slope effects would depend on the land use. Basically, this relationship can be explained due to the fact that areas with steeper and higher elevations are occupied with native forest, where trees are relatively stable in the forest with a slow soil turnover, so there is less probability of releasing nutrients from the soils. However, in our results, slope (elevation) was positively correlated with  $NO_3^-$ ,  $PO_4^{3-}$ , and  $Si(OH)_4$  (Tables 3 and 4). This is mainly because the areas with higher elevations (as Cordillera de la Costa, Fig. 1) do have a positive correlation with  $NO_3^-$ ,  $PO_4^{3-}$ , and  $Si(OH)_4$ , because these are areas mainly covering silviculture, where plantations are replacing more frequently than in a native forest. Thereby, areas with greater elevation lead to higher erosion rates, which in turn increased the rate of organic matter entering to the river (Ye et al. 2009). In contrast, in flat areas which have less elevation and lower slope and which are dominated by land uses



**Fig. 4** Spatial variation of water leaching in the Itata River basin

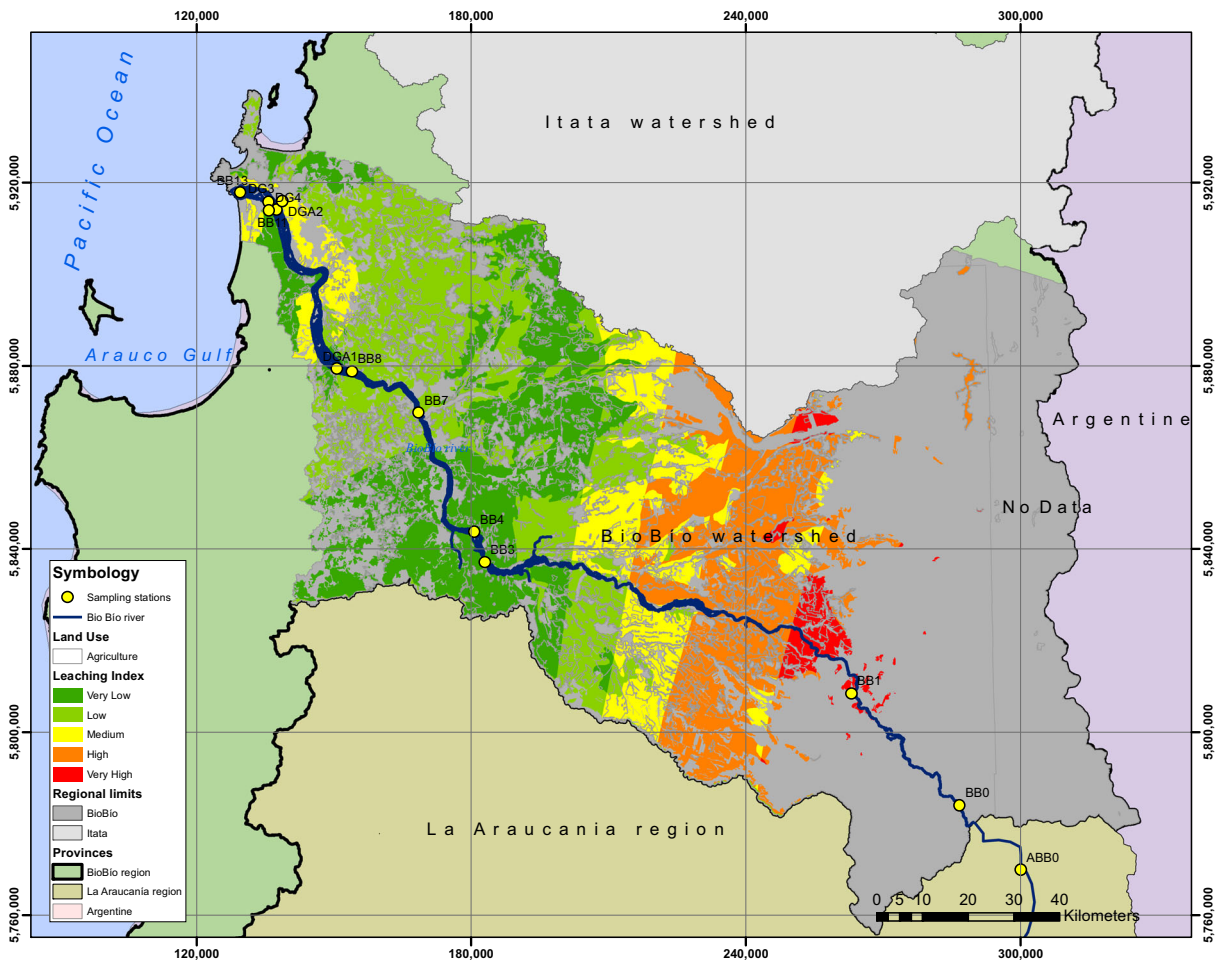
such as grassland and pasture, apparently less nutrient may be exported. Similarly results were found in the Piracicaba River basin in Brazil regarding nitrogen variation where high elevations are occupied by silviculture and flat areas are covered mainly with agriculture activities, which both showed a positive correlation with nitrate. Therefore, silviculture and agriculture areas in the coastal mountain could export more available nutrients and particulate matter.

#### Climate and land use biophysical factors

In response to the water quality of both rivers, our results have found strong similarities between both rivers in the relationship with the interference of precipitation and land uses. In our study, we have found that precipitation and discharge, mainly during the winter period, can partially explain the temporal variations in

river water quality (Chen and Lu 2014). The values of EC and higher values of TSS, DO,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{Si}(\text{OH})_4$ , in the rainy season, are related to environmental factors such as high flow rate, high soil moisture, and low nitrogen biological demand during winter. Conversely, during summer time, less precipitation combined with the soil hydrological group negatively altered soil moisture dynamics and consequently regulated soil N responses to precipitation changes (Gu and Riley 2010). Several studies have found that a modification in rainfall distribution in the region can negatively increase the demand of water supply in the watersheds associated with silviculture, which reduced soil water reserve and decreased the quality (Little et al. 2009).

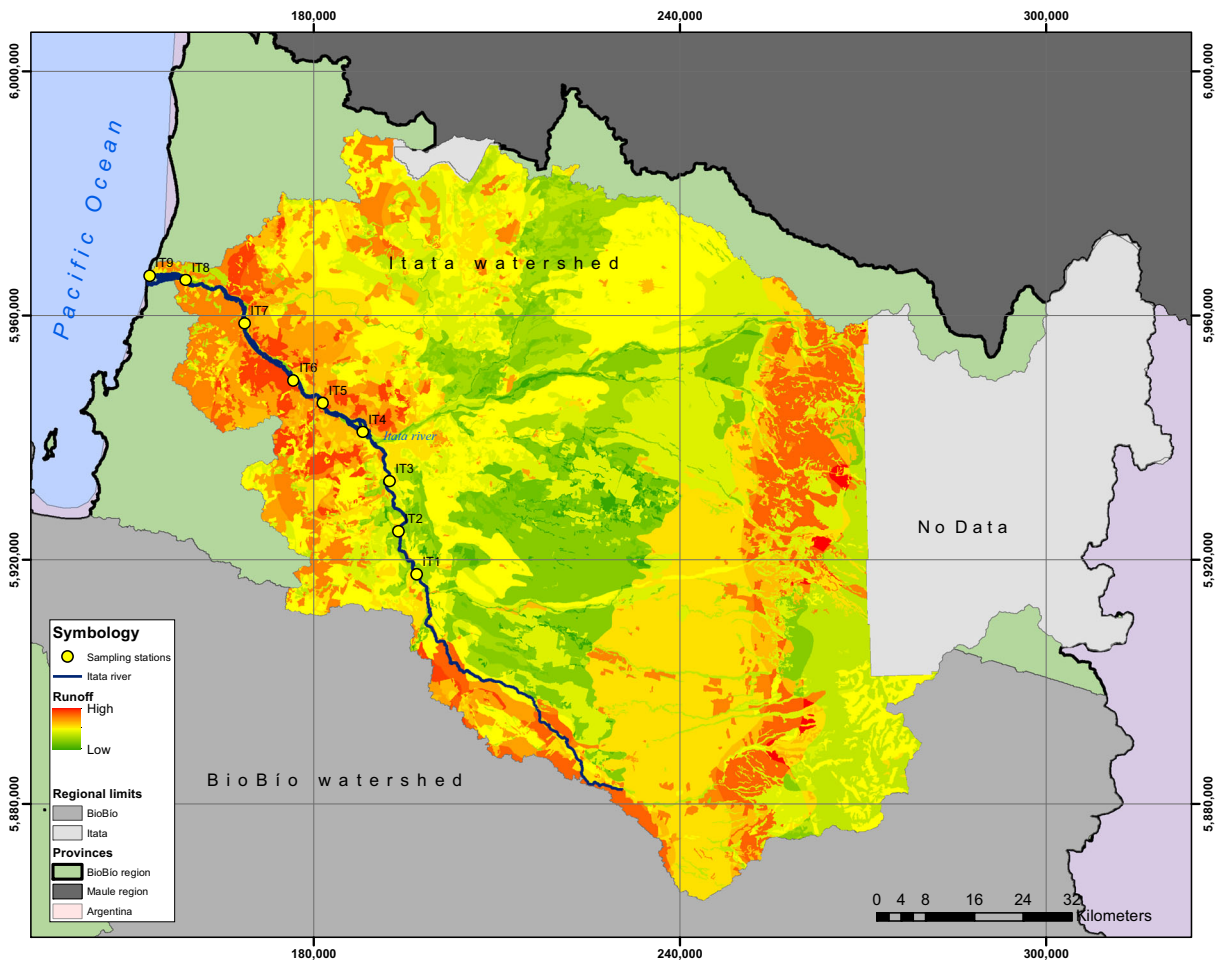
Land use variability in the two watersheds and between sub-watersheds exerts a strong control over water quality. This was shown with the major concentrations



**Fig. 5** Spatial variation of water leaching in the Biobío River basin

raised in areas with higher agricultural and silvicultural activities. Historically, land use in this area comprises practices that increase erosion by overland flow, such as the cultivation of sloping land and clear cutting (Iroumé et al. 2006; Tolorza et al. 2014). Hence, silvicultural and agricultural land uses had a significant impact on the river’s physicochemical parameters (Pizarro et al. 2010). In our study, agricultural and silvicultural land showed the largest EC and TSS values, mainly in the Biobío River, two times higher than what was recorded in the Itata River. These results agree with Mohr et al. (2014) who suggested that most of the erosional work in rivers is done in silvicultural areas by moderate precipitation events. Perez et al. (2015) compared different Chilean rivers and have found that Biobío River received the highest contributions of nutrients mainly from agricultural and urban areas.

Hence, anthropogenic impacts are important inputs of nutrients to rivers and are the cause of variation in stream nutrient concentrations (Zhang et al. 2009). The interaction of hydrology and soil chemical processes that control the mobilization of nutrients makes it difficult to establish a direct relation between different biophysical factors and water quality parameters. However, in our study,  $PO_4^{3-}$  and silicate were associated with forested and deforested areas, corresponding mainly to silviculture land, with minimal areas of native forest. The reason for this may be that a loss of plant matter in deforested sites loosens soils, reduces number of N-fixing plants, and lessens the amount of organic matter in soils. As a result, deforested areas have higher  $PO_4^{3-}$  and  $Si(OH)_4$  concentrations in some areas (Bieger et al. 2015). Little et al. (2009) showed how forest



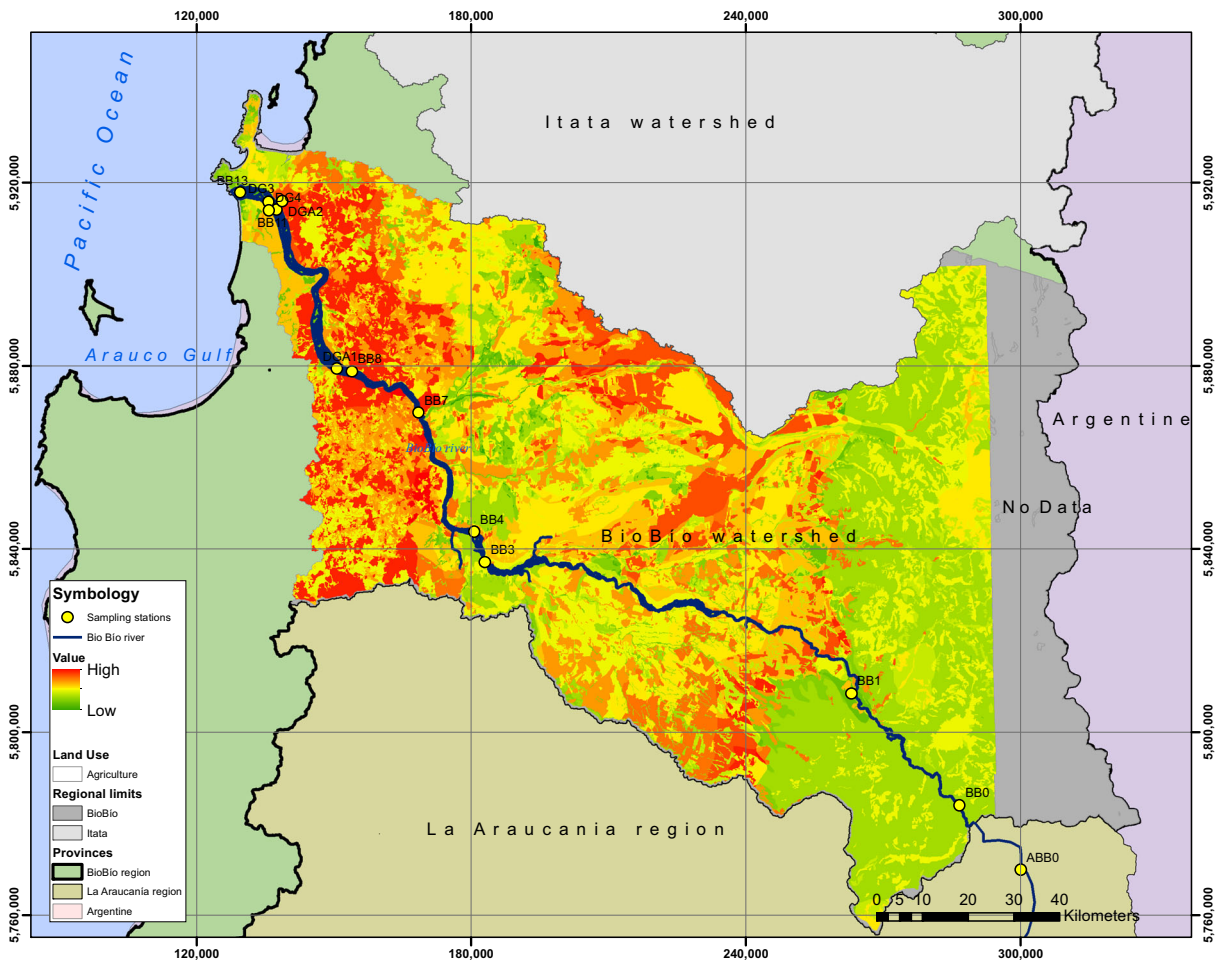
**Fig. 6** Spatial variation of runoff in the Itata River basin

could alter the hydrological regime of Mediterranean-climate basins of South-Central Chile and recorded decreasing water yield during summer runoff in a land where native forest has been occupied by silviculture. Mancilla et al. (2009) reported on the effects of the native riparian vegetation removal on the structure and composition of the aquatic community in the Biobío region. Hence, the assessment of the impacts of land use on water quantity and quality is fundamental to the development of sustainable land use alternatives in these areas.

#### Runoff and leaching indexes

Vrielijs (2006) indicated that water erosion is controlled by climatic characteristics, topography, soil

properties, vegetation, and land management. Moreover, detachment of soil particles is caused by the raindrop effect and drag force of running water. Hence, detached material is conveyed by overland flow and concentrated flow and deposited when flow velocity decreases, which is carried away and eventually deposited in aquatic systems (Lal 2001). Caruso (2002) suggested that river water physico-chemical parameters such as conductivity and TSS increased with an intensification of watershed load material attributed to erosion from the soil. In our study, the spatial distribution of the runoff map in the Biobío area can be explained mainly by the land use practices, the relief, and the characteristics of the soil type. It is important to note that the major values of runoff were found in the coastal areas close to the mountain (Cordillera de la Costa). This



**Fig. 7** Spatial variation of runoff in the Biobío River basin

spatial distribution of the runoff index is similar to those investigated by other authors for the same latitudes in Chile (Bonilla and Vidal 2011).

Although nutrients and solutes released in soils mainly come from agricultural practices, the relative influence of silviculture and forest as the main land uses had been tested. The use of a water leaching equation made it possible to achieve a prediction of water loss related to the main driving forces. According to this risk index, water leaching was found to be closely linked to crop areas. Most of the studies involving water leaching in agricultural areas have shown that leaching rate depends on crop type and especially on the land use vegetation distributions. In the Biobío region, most of the land has concentrated in silviculture activities. Lower leaching rates in hilly areas have been related to

grassland areas probably due to reduced mineralization. Our results demonstrate that water leaching responses to increasing precipitation variability depending on the precipitation amount and soil texture, and additionally, the physical properties of the soil can be affected.

**Conclusions**

Our primary findings of this study suggest that nitrate, pH, EC, and suspended solids were higher in the wet season in both rivers, and the variations in the river water were associated mainly with natural factors such as soil type, soil moisture, and precipitation. Silviculture and agriculture were identified as the most anthropogenic explanatory factors for

water quality parameters. Therefore, these findings, at the regional scale, underlie our understanding of the biophysical drivers that are affecting the river water quality, mainly in specific areas of the Itata and Biobío river watersheds.

**Acknowledgments** The authors would like to thank the Center for Climate and Resilience Research of the University of Concepción (CR2), which is supported by the CONICYT/FONDAP program 15110009 and CONICYT/FONDECYT N° 3150162; Dr. Ricardo Figueroa from Centro EULA-University of Concepción and the Water Research Center for Agriculture and Mining of the University of Concepción, supported by the CONICYT/FONDAP program 15130015; and the Dirección de Obras Hidráulicas and Dirección General de Aguas for supplying rainfall databases.

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