Journal of Hazardous Materials 175 (2010) 608–613

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Nutrients dynamics in the main river basins of the centre-southern region of Chile

Jaime Pizarro[a,*], Pablo M. Vergara[a], José A. Rodríguez[a], Pedro A. Sanhueza[a], Sergio A. Castro[b]

[a] Departamento de Ingeniería Geográfica, Facultad de Ingeniería, Universidad de Santiago de Chile, Av. Lib. B. O'Higgins 3363, Santiago, Chile
[b] Departamento de Biología, Facultad de Química y Biología, Universidad de Santiago de Chile, Av. Lib. B. O'Higgins 3363, Santiago, Chile

ARTICLE INFO

Article history:
Received 19 May 2009
Received in revised form 7 October 2009
Accepted 12 October 2009
Available online 20 October 2009

Keywords:
Chilean rivers
Nitrate
Phosphate
Annual trends
Nutrients

ABSTRACT

Chilean basins have long been exposed to nutrient discharges from human activities and land use changes. A historical seasonal NO_3^-–N and PO_4^{3-}–P database of the last 23 years of the main nine rivers of central-southern region of Chile was analysed. Generalized additive models indicated that annual trends in NO_3^-–N and PO_4^{3-}–P are nonlinear. River basins such as Bío-Bío, Bueno, Imperial, Maule, Rapel and Valdivia showed a clear increase in NO_3^-–N, while PO_4^{3-}–P increased only in the Rapel and Maule basins. Although no seasonal difference in NO_3^-–N and PO_4^{3-}–P was found in the analysed basins, there was a negative relation between these nutrients and water flow. Sampling stations with high NO_3^-–N concentration were found mostly in sub-basins located in the "central valley" of central Chile, while several PO_4^{3-}–P "over-concentrated" sampling stations were located mostly upstream. If NO_3^-–N emissions into Chilean river basins continue at current rates it is probable that the concentration of this nutrient will tend to match that of the most "polluted" rivers around the world.

1. Introduction

Phosphorous and nitrogen are two essential nutrients for the aquatic biota, and limits their primary productivity [1]. However, overload of these nutrients accelerates the eutrophication process, and deteriorates river water quality [1].

In the last century, wastes from anthropogenic activities (e.g., domestic wastes, agriculture) have strongly affected most freshwater ecosystems [2–9]. As a result, the total river-load of dissolved nitrate–nitrogen (NO_3^-–N) has increased nearly six times and the total phosphate–phosphorous (PO_4^{3-}–P) nine times over pre-industrial levels in the main rivers around the world [10,11]. The latter has motivated researchers to assess the impacts of anthropogenic activities on the deterioration of water quality in local, regional and continental river systems using image processing techniques and extensive monitoring programs [9,12–15].

The central-southern section of Chile includes several latitudinal distributed river basins that originate at the top of the Andean mountains flowing into the Pacific Ocean (Fig. 1). Historically, the main productive activities in Chile's central-southern region have been agriculture, forestry and livestock (Table 1), whose intensities have been increasing over time as population growth in this region. Accordingly, we should expect a significant increase in the levels of nitrate and phosphate in Chilean rivers. Previous studies have shown that the concentration and fluxes of dissolved nitrogen in small watersheds of Chile's central-southern region is significant increased by agriculture, forestry and livestock [16–18]. Regardless of the contribution of the later findings to the understanding of the anthropogenic impact upon nutrient, it is necessary to know the long-term temporal behaviour of nutrients in the main river basins of Chile. In this study we analyzed an historical seasonal NO_3^-–N and PO_4^{3-}–P database of the nine main rivers in Chile's central-southern region over the last 23 years (Table 1). Our interest was three-fold: first we evaluated the annual and seasonal dynamics in concentration of both nitrate–nitrogen (NO_3^-–N) and phosphate–phosphorous (PO_4^{3-}–P); second we identified rivers where NO_3^-–N and PO_4^{3-}–P concentration has increased in the study period by comparing their annual and seasonal trends in these rivers; and finally, we proposed possible mechanisms that explain these trends.

2. Materials and methods

2.1. Study site

We studied the nine main basins of central-southern Chile (from 33°53′ to 39°50′ lat S., Fig. 1). The climate of these basins varies latitudinally, from a semi-desertic climate in the north to a temperate rain in the south (with mean annual precipitation ranging from 300 mm to 1800 mm). As a consequence of this climate gradient, water flows tend to be larger in the southern river basins. Furthermore, the dry season occurs in late spring and summer and the wet season in late autumn and winter. According to bio-

* Corresponding author. Tel.: +56 2 7182226.
E-mail address: jaime.pizarro@usach.cl (J. Pizarro).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.10.048

Table 1
Summary of studied basins, including their area (km^2), percentage (%) of landscape area used for agriculture, forestry or livestock, as well as the mean annual water flow ($m^3\ s^{-1}$) during the study period.

Basin	Area	Agriculture	Forestry	Livestock	Water flow
Rapel	13,695	0.22	0.01	0.05	30.8
Mataquito	6,190	0.17	0.03	0.06	46.5
Maule	20,295	0.22	0.09	0.04	78.1
Itata	11,294	0.01	0.07	0.01	67.8
Bío-Bío	24,264	0.03	0.2	0.07	154.0
Imperial	12,763	0.01	0.12	0.07	55.6
Toltén	8,398	0	0.04	0.3	114.0
Valdivia	10,275	0	0.13	0.28	145.4
Bueno	15,637	0	0.03	0.44	99.3

Table 2
Number of sampling stations, data records of NO_3^-–N and PO_4^{3-}–P and sampling years for the nine river basins analyzed in this study.

Basin	NO_3^-–N			PO_4^{3-}–P		
	Sampling stations (n)	Data records (n)	Years*	Sampling stations (n)	Data records (n)	Years*
Rapel	18	764	20	18	741	21
Mataquito	9	307	19	10	324	20
Maule	20	852	19	21	893	21
Itata	16	681	21	16	694	22
Bío-Bío	14	755	21	14	837	22
Imperial	12	779	20	12	851	22
Toltén	7	413	20	7	447	22
Valdivia	16	680	21	16	714	23
Bueno	20	822	21	20	863	22

*Number of sampling years.

climate conditions, these river basins have historically differed in their human activities, with the lands of the northern basins used mostly for agriculture and the southern basins for livestock (Table 1).

2.2. Sampling and analysis

Sampling data belongs to the National River Monitoring Network of the Dirección General de Aguas (DGA) of the Ministry of Public Works of Chile. The DGA's sampling stations are systematically distributed along the main tributaries of each basin (sub-basins), covering from the river head to the river mouth (Fig. 1, Table 2). Water samples were collected on a seasonal basis using high density polyethylene (HDPE) containers (500 mL). NO_3^-–N was measured according to the methodology described by [19], using molecular absorption spectroscopy with a detection limit of 0.002 mg L^{-1}. PO_4^{3-}–P was measured by method 4500 as suggested by SMEWW [20] using molecular absorption spectroscopy with a detection limit of 0.003 mg L^{-1}.

2.3. Statistical analysis

To assess yearly and seasonal trends in NO_3^-–N and PO_4^{3-}–P we used Generalized Additive Mixed Models (GAMM), which allowed us: (1) to analyze nonlinear temporal trends, fitting smooth curves (penalized cubic regression splines); (2) to analyze hierarchical nested data such as those in this study [21,22]; Random errors associated with sampling stations were spatially nested within sub-basins, and those associated with sub-basins within river basins. In addition, we included random intercepts for year and season to correct for non-independence of observations within the same stations [22]. Previously, we normalized NO_3^-–N and PO_4^{3-}–P data by log transforming.

In order to analyse annual trends, and considering that NO_3^-–N and PO_4^{3-}–P could be affected by other independent variables (such as water flow and station), we developed models with different variable combinations, including water flow as a continuous

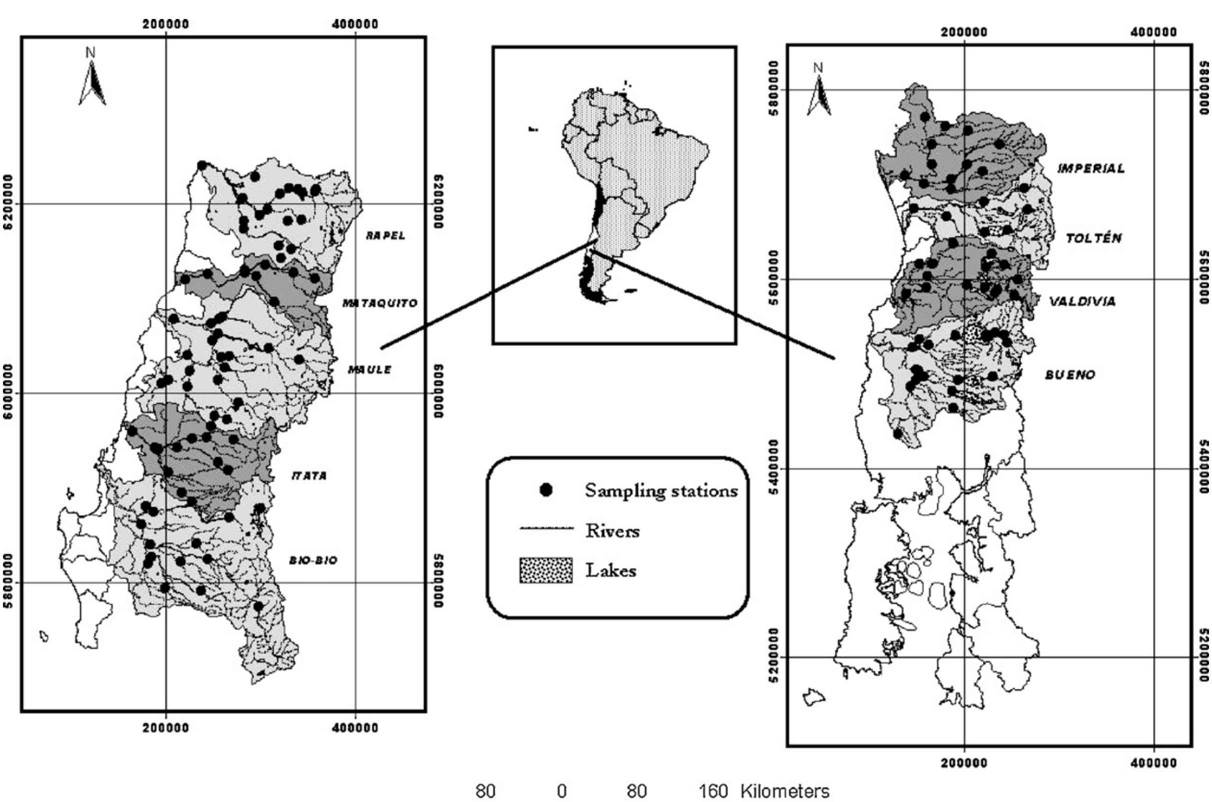

Fig. 1. Map of the nine river basins studied in the centre-southern Chilean region.

Table 3
Annual mean NO_3^-–N and PO_4^{3-}–P concentrations and their standard errors (SE) in the largest nine river basins of central-southern Chile. For each river basin the percentage of sampling stations with significant level concentration (% significant, see Section3) as well as the mean elevation (in m.a.s.l.) of all sampling stations (S elevation) and elevation of significant sampling stations (SS elevation) are shown.

Basin	Mean	SE	% significant	S elevation	SS elevation
NO_3^-–N					
Rapel	1.57	0.31	83.3	242.8	206.7
Mataquito	0.55	0.22	50.0	334.5	29.0
Maule	0.49	0.22	71.4	151.9	122.7
Itata	0.35	0.09	25.0	144.8	49.5
Bío-Bío	0.21	0.12	21.4	171.9	46.0
Imperial	0.4	0.16	58.3	155.9	107.7
Toltén	0.11	0.08	0.0	237.1	–
Valdivia	0.31	0.11	12.5	114.3	0.0
Bueno	0.18	0.11	20	175.5	11.3
PO_4^{3-}–P					
Rapel	0.23	0.16	27.8	242.8	253.6
Mataquito	0.29	0.18	44.4	338.3	36.3
Maule	0.24	0.17	50.0	158.5	129.0
Itata	0.41	0.14	81.3	144.8	174.4
Bío-Bío	0.15	0.1	21.4	171.9	26.7
Imperial	0.23	0.1	33.3	155.9	212.5
Toltén	0.23	0.11	57.1	237.1	390.0
Valdivia	0.10	0.07	12.5	114.3	0.0
Bueno	0.12	0.08	10.0	175.5	0.0

covariate and season and sampling station as factors with multiple levels (including each season and each sampling station, respectively). We used the Akaike's Information Criterion to rank and select the most parsimonious models. The Akaike Information Criterion (AIC) is a measure of the model deviance penalized by its number of parameters so that the preferred model is the one with the lowest AIC value [23]. We considered that a model is parsimonious if its ΔAIC $\leq$4. Water flow was standardized at the basin level to control the differences in water flow between basins.

Table 4
General additive mixed models for NO_3^-–N and PO_4^{3-}–P ranked according to their Akaike Information Criterion (AIC). Adjusted R^2 is also shown for each model. Best parsimonious models are indicated by bold cases.

Model variables*	AIC	ΔAIC	R^2
NO_3^-–N			
s(years) + flow + season + sampling station	1298.8	**0.0**	0.59
s(years) + season + sampling station	1302.2	**−3.4**	0.59
s(years) + flow + sampling station	1305.6	−6.8	0.59
s(years) + sampling station	1306.4	−7.6	0.59
s(years) + flow + season + river basin	1652.4	−353.6	0.22
s(years) + flow + river basin	1654.7	−355.9	0.22
s(years) + season + river basin	1655.1	−356.3	0.22
s(years) + river basin	1655.3	−356.6	0.22
s(years) + flow + season	1659.0	−360.2	0.04
s(years) + flow	1661.3	−362.5	0.04
s(years) + season	1661.8	−363.0	0.04
PO_4^{3-}–P			
s(years) + flow + season + sampling station	1028.6	**0.0**	0.28
s(years) + flow + sampling station	1036.3	−7.8	0.28
s(years) + season + sampling station	1040.9	−12.3	0.28
s(years) + sampling station	1049.1	−20.5	0.28
s(years) + flow + season + river basin	1071.9	−43.3	0.25
s(years) + flow + season	1078.6	−50.0	0.24
s(years) + flow + river basin	1080.1	−51.5	0.25
s(years) + flow	1086.3	−57.8	0.23
s(years) + season	1090.1	−61.5	0.23
s(years) + river basin	1091.7	−63.1	0.25

* s(years) represent a smooth function of time.

3. Results

NO_3^-–N and PO_4^{3-}–P concentration varied differently among basins, with a mean NO_3^-–N concentration per basin ranging from 0.11 mg L^{-1} to 1.57 mg L^{-1}, corresponding to Toltén and Rapel basins, respectively (Table 3). The mean concentration of PO_4^{3-}–P per basin ranged from 0.10 mg L^{-1} to 0.41 mg L^{-1}, corresponding to the Valdivia and Itata basins, respectively (Table 3).

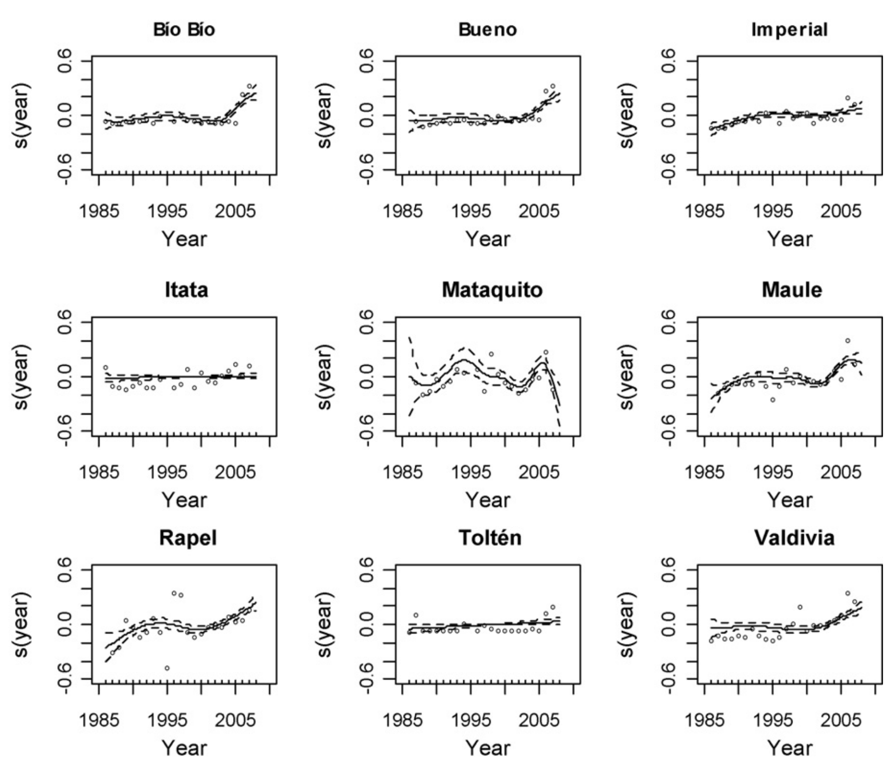

Fig. 2. Annual concentration (mg L^{-1}) trends of NO_3^-–N in the nine river basins studied in the centre-southern Chilean region. *Y*-axis represents log-transformed partial residuals, with smoothing GAMM curves [s(year)] represented by continuous lines while upper and lower confidence intervals by dashed lines. Circles represent the observed log-transformed mean in annual concentration of NO_3^-–N per basin.

Table 5
Estimated degrees of freedom (edf) and significance (*p*-value) of smooth functions of time (year) for the best models predicting NO_3^-–N and PO_4^{3-}–P concentration in river basins of central-southern Chile.

Basin	NO_3^-–N		PO_4^{3-}–P	
	edf	*p*-value	edf	*p*-value
Rapel	4.3	<0.001	6.6	<0.001
Mataquito	7.3	<0.001	8.1	<0.001
Maule	6.5	<0.001	8.0	<0.001
Itata	1.0	0.793	8.4	<0.001
Bío-Bío	5.6	<0.001	5.5	<0.001
Imperial	3.2	<0.001	7.2	<0.001
Toltén	1.0	0.136	5.1	<0.001
Valdivia	3.7	<0.001	6.5	<0.001
Bueno	4.5	<0.001	7.1	<0.001

Table 6
Regression coefficients (estimate) with their standard errors (SE), *t*-values (*t*), and *p*-values for independent variables of the best models predicting NO_3^-–N and PO_4^{3-}–P concentration in river basins of central-southern Chile (see Table 4).

Variable	Estimate	SE	*t*	*p*-value
NO_3^-–N				
Flow	−0.01	0.004	−2.3	0.021
Autumn	0.013	0.011	1.2	0.235
Spring	−0.014	0.011	−1.3	0.186
Summer	−0.024	0.013	−1.8	0.066
PO_4^{3-}–P				
Flow	−0.017	0.005	−3.8	<0.001
Autumn	−0.004	0.01	−0.4	0.671
Spring	0.016	0.01	1.6	0.114
Summer	−0.021	0.013	−1.6	0.109

$^{*}p < 0.05$, $^{***}p < 0.001$.

3.1. Nitrate trends

According to AIC values, the best two models explaining NO_3^-–N included the effects of year, water flow, season and sampling station (Table 4). These best two models accounted for 60% variance in NO_3^-–N. For all basins, annual trends in NO_3^-–N were mostly nonlinear, as shown by smooth functions fitted to the data (Fig. 2, Table 5). From these plots, Bío-Bío, Bueno, Imperial, Maule, Rapel and Valdivia showed an evident increase in NO_3^-–N during the sampling period (Fig. 2). For these basins, NO_3^-–N did not increase at a constant rate, since the increase rate was greater after 2000 (Bío-Bío, Bueno, Valdivia, Maule, Rapel and Imperial increased 9.89, 7.56, 4.32, 2.26, 1.85 1.43 times, respectively; Fig. 2). For the Itata and Tolten basins there was no clear temporal trend in NO_3^-–N, since their smooth functions were not significant (Table 5). The Mataquito basin, however, shows a clear increase between 1987 and 1995, and during 2006. During these periods the mean NO_3^-–N value was 1.25 times and 2.50 times larger, respectively, than the mean value during the total sampled period (Fig. 2).

Model results indicated that there is no seasonal difference in NO_3^-–N in the analysed basins (Table 6). We found a negative relation between NO_3^-–N and water flow (Table 6). Furthermore, in 56 sampling stations (41.0%) NO_3^-–N concentration was significantly higher than in the reference station which was that with the lowest annual mean NO_3^-–N (0.025 mg L^{-1}). The Rapel and Maule basins had the largest proportion of these "over-concentrated" sampling stations (Table 3; Fig. 3). Moreover, all the basins over-concentrated sampling stations were located mostly in the lower section of all the studied basins (Table 3; Fig. 3).

3.2. Phosphate trends

The best model accounting for PO_4^{3-}–P included the effect of year, water flow, season, and sampling station, which only explained about 30% variance in PO_4^{3-}–P (Table 4). For all basins,

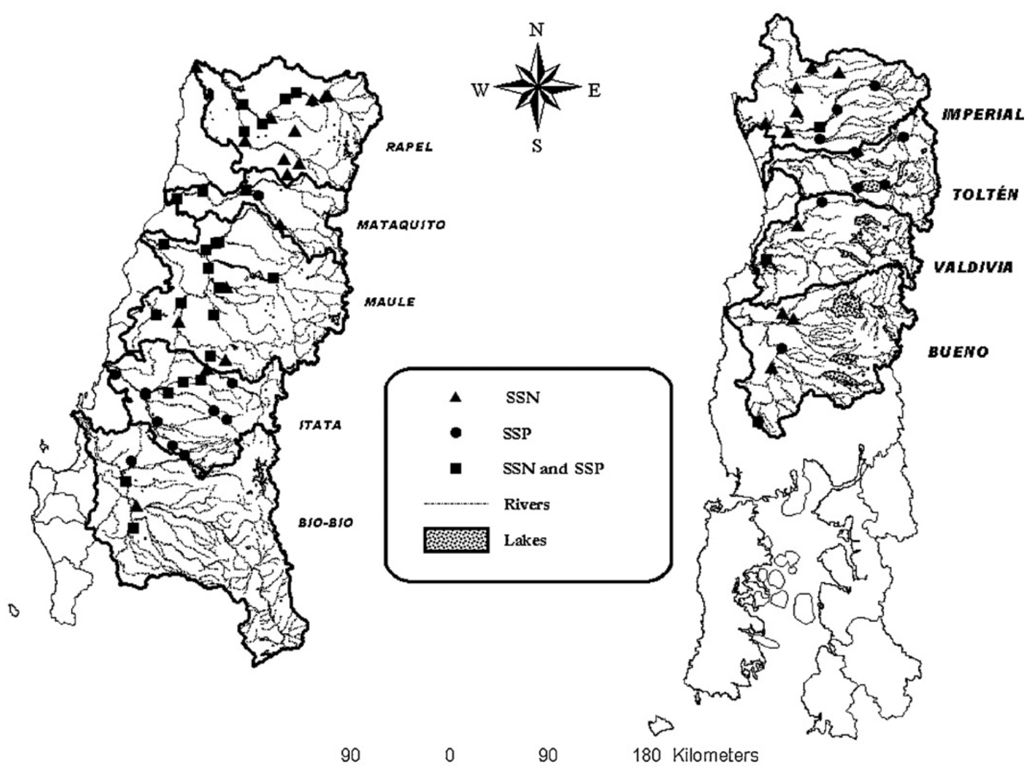

Fig. 3. Map of the nine river basins studied in the centre-southern Chilean region showing the sampling stations with significant level concentration of NO_3^-–N (SSN) and PO_4^{3-}–P (SSP).

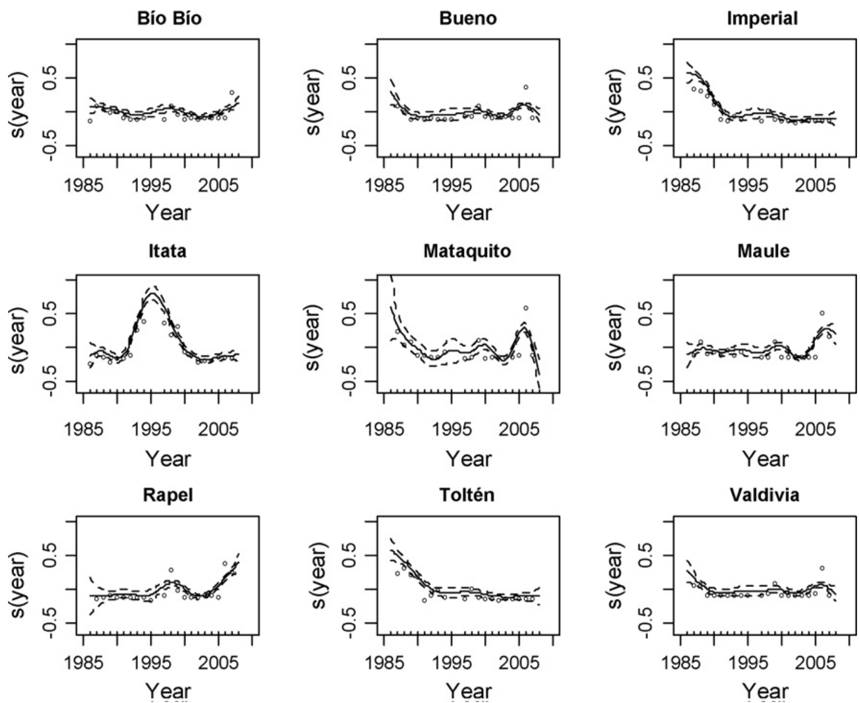

Fig. 4. Annual concentration (mg L^{-1}) trends of PO_4^{3-}–P in the nine river basins studied in the centre-southern Chilean region. *Y*-axis represents log-transformed partial residuals, with smoothing GAMM curves [s(year)] represented by continuous lines while upper and lower confidence intervals by dashed lines. Circles represent the observed log-transformed mean in annual concentration of PO_4^{3-}–P per basin.

annual trends in PO_4^{3-}–P were mostly nonlinear and significant as shown by smooth functions fitted to the data (Fig. 4, Table 5). From these plots, only Rapel and Maule showed an evident increase in PO_4^{3-}–P during the last years (after 2000) of the sampling period (Rapel and Maule increased 10.37 and 7.85 times, respectively, Fig. 4). The Itata basin, however, shows a clear increase between 1990 and 2000, a period in which the mean concentration was 1.9 times greater than the mean value during the total period (Fig. 4). Three basins, Imperial, Mataquito, and Tolten, showed a clear negative annual trend in PO_4^{3-}–P concentration during the sampling period (Fig. 4). In the Imperial and Tolten basins this decrease in PO_4^{3-}–P occurred mainly during the first 80 years of the sampling period (1986 and 1993, Fig. 4). The Bío-Bío, Bueno, and Valdivia basins did not show a clear trend even though their smooth functions were significant, (Fig. 4, Table 5).

Model results indicated that there is no seasonal difference in PO_4^{3-}–P in the analysed basins (Table 6). We found a negative relation between PO_4^{3-}–P and water flow (Table 6). Furthermore, in 47 sampling stations (35.6%) PO_4^{3-}–P concentration was significantly higher than the reference sampling station with the lowest annual mean PO_4^{3-}–P concentration (0.008 mg L^{-1}). The Itata basin had the highest proportion of these "over-concentrated" sampling stations (Table 3; Fig. 3). Moreover, in the Mataquito, Maule, Bío-Bío, Valdivia, and Bueno basins, the sampling stations with large PO_4^{3-}–P concentration were located mostly in the lower sections (Table 3; Fig. 3). In contrast, in the Itata, Rapel, Imperial, and Tolten basins the sampling stations with large PO_4^{3-}–P concentration were located mostly in the upper sections (Table 3; Fig. 3).

4. Discussion

Contamination by NO_3^-–N and PO_4^{3-}–P is a global phenomenon affecting freshwater systems resulting from intensive human activities [24]. Chilean basins in the central-southern region have been largely affected by human activities over the last centuries. Human population has increased dramatically over the last 30 years and land use changed drastically from small to large scale agriculture and forestry. Accordingly, our results indicate that PO_4^{3-}–P and NO_3^-–N inputs have increased during this time period atleast two and six basins, respectively. Although the annual average NO_3^-–N concentration was higher in Rapel, while its most pronounced increases occurred in those basins that were less "polluted" at the beginning of the sampling period (e.g., Bío-Bío, Bueno and Valdivia), suggesting that N concentration in these basins may became important in the middle term. High NO_3^-–N concentration in the Rapel basin probably results from the large population density, tourism in the Rapel reservoir, and particularly the intensive industrial–agricultural activities (Fig. 3) [25,26]. The significant increase in the last 10 years in the Bueno and Valdivia basins can be explained by the fact that both basins share similar human activities (e.g., livestock), and in the last decade human population has increased greatly. Similarly, the Bío-Bío basin has experience a large expansion in forestry and manufacturing industries in this time period.

Our results show that PO_4^{3-}–P concentration follows a nonlinear trend in most studied basins, but only Rapel and Maule showed a positive increase in the last decade. On the contrary, in several basins, such as Itata, Bío-Bío, Bueno, and Valdivia, we found variable fluctuations in PO_4^{3-}–P concentration, but we failed in finding any trend. Probably, the large increase in PO_4^{3-}–P between 1990 and 2000 in the Itata basin was due to the expansion of pine forest plantations during the 1990s decade. It should be noticed, however, that the best models for PO_4^{3-}–P concentration accounted for less than 30% of its variance as shown by the adjusted R^2 (see Table 4). This means that variables independent of time, or not associated with water flow or sampling station, could be more important in predicting PO_4^{3-}–P concentration in Chile's basins.

Models indicated that variance in NO_3^-–N was accounted for differences between sampling stations rather than by differences between basins (Table 4). On the contrary, the addition of the sampling station as a factor did not improve the fit of PO_4^{3-}–P models. This implies that source emissions of NO_3^-–N are not homogeneously distributed along the basin, and therefore the efforts for controlling water quality should be focused only on those sub-basins in which NO_3^-–N concentration has increased significantly. Moreover, we found that sampling stations with a large concentration of NO_3^-–N were located in the lowland areas within each basin. Specifically, these sampling stations were distributed over the "central valley" of central-southern Chile. The central valley is a flat area where historically human activities such as industries, livestock, and urban areas have developed more. Nevertheless, activities within the central valley are not homogeneously distributed among the basins because of the latitudinal bio-climatic gradient and the fact that the northernmost basins, such as Rapel or Maule, have been exposed to human perturbation for a longer time.

According to our results, PO_4^{3-}–P and NO_3^-–N concentrations have different temporal dynamics among and within river basins. At the basin scale, there are more river basins exhibiting increasing trends NO_3^-–N than in PO_4^{3-}–P concentration. We found an important contribution of the sampling station in accounting for variation in NO_3^-–N concentration, but the sampling station was not an important factor for the PO_4^{3-}–P models (Table 4). Moreover, NO_3^-–N "over-concentrated" sampling stations were located mostly in the lower sections or sub-basins, while several PO_4^{3-}–P "over-concentrated" sampling stations were located upstream rather than in the lower basin sections (Table 3). PO_4^{3-}–P emissions may probably decrease downstream as a result of either the precipitation in phosphate compounds or photosynthetic processes.

We did not find a seasonal variation in PO_4^{3-}–P and NO_3^-–N concentration, contrasting with other studies carried out in other important river basins [8,27,28]. Seasonal differences of these parameters may be explained by soil loss and dilution in wet or flood seasons [9]. Water flow affected PO_4^{3-}–P and NO_3^-–N concentration negatively. Therefore, since water flow in Chilean rivers studied are dominated by two processes, snow melting in spring–summer and rain in winter, our results suggest that dilution could be the most important water flow-associated mechanism explaining the concentration of PO_4^{3-}–P and NO_3^-–N. We must also admit that total nitrogen may be present as NH_4^+–N, especially in basins with a large number of people and more agricultural activities, such as basins located further north of the Bío-Bío basin (see Fig. 3). However, it is necessary to highlight that nitrate, as quantified in this study, represents the most important contributor to total dissolved nitrogen in the world's largest rivers (nearly 75%) [29].

The water quality of the river basins of central-southern Chile, in terms of their NO_3^-–N concentration, ranges between 0.1 mg L^{-1} to 1.6 mg L^{-1}, which is relatively similar to the concentration ranges of the world's largest rivers and several watershed of the USA [29]. Of these rivers, the northernmost Rapel, Mataquito, and Maule basins show the highest concentrations (>0.5 mg L^{-1}) and are comparable to European basins [10,29] or Chinese rivers [8]. Unfortunately, our results are not comparable with other studies carried out in small Chilean watersheds [16–18], which could have increased our understanding about how local anthropogenic activities (e.g., logging or fire) contribute in explaining the current nutrient levels in the main rivers of southern Chile. However, our results showed that if NO_3^-–N emissions into Chilean river basins continue to increase at current rates, it is probable that its concentration will tend to match that of the most "polluted" rivers around the world. Therefore, we propose that our results can be used as a reference source for future monitoring programs, ecosystem research, and mitigation projects in river basins of central-southern Chile.

Acknowledgements

This study was financed by FONDECYT 11080085 and DICYT 010612PK. We thank to Dirección General de Aguas (DGA) for allowing us to use a public database and an anonymous reviewer for his valuable comments on the manuscript.

References

[1] R. Pourriot, M. Meybeck, Limnologie Générale, Masson, Paris, 1995.
[2] N. Rabalais, Nitrogen in aquatic ecosystems, Ambio 31 (2) (2002) 102–112.
[3] E. Dumont, J. Harrison, C. Kroeze, E. Bakker, S. Seitzenger, Global distribution and sources of DIN export to the coastal zone: results from a spatially explicit, global model, Global Biogeochem. Cycles 19 (2005) GB4S02.
[4] E.W. Boyer, R.W. Howarth, J.N. Galloway, F.J. Dentener, P.A. Green, C.J. Vörösmarty, Riverine nitrogen export from the continents to the coasts, Global Biogeochem. Cycles 20 (2006) GB1S91.
[5] S. Carpenter, N. Caraco, D. Correell, R. Howarth, A. Sharpley, V. Smith, Non-point pollution of surface waters, Ecol. Appl. 8 (1998) 559–568.
[6] J. Galloway, F. Dentener, D. Capone, E. Boyer, R. Howarth, S. Seitzinger, G. Asner, C. Green, E. Holland, D. Karl, A. Michaels, J. Porter, A. Townsend, C. Vörösmarty, Nitrogen cycles: past, present and future, Biogeochemistry 70 (2004) 153–226.
[7] P. Green, C. Vörösmarty, M. Meybeck, J. Galloway, B. Peterson, E. Boyer, Pre-industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on topology, Biogeochemistry 68 (2004) 71–105.
[8] S. Li, W. Liu, S. Gu, X. Cheng, Z. Xu, Q. Zhang, Spatio-temporal dynamics of nutrients in the upper Han River basin, China, J. Hazard. Mater. 162 (2009) 1340–1346.
[9] J. Chen, X. Gao, D. He, X. Xia, Nitrogen contamination in the Yangtze River system, China, J. Hazard. Mater. 73 (2) (2000) 107–1131.
[10] M. Meybeck, Carbon, nitrogen and phosphorous transport by world rivers, Am. J. Sci. 282 (1982) 401–450.
[11] S.V. Smith, D.P. Swaney, L. Talaue-McManus, J.D. Bartley, P.T. Sandhei, C.J. McLaughlin, V.C. Dupra, C.J. Crossland, R.W. Buddemeier, B.A. Maxwell, F. Wulf, Humans, hydrology, and the distribution of inorganic nutrient loading to the ocean, Bioscience 53 (2003) 235–245.
[12] J.M. Omernik, Non-point source-stream nutrient level relationship: A nationwide study, (1977) EPA-600/3-77-105.
[13] M.C. Watzin, A.W. McIntosh, Aquatic ecosystems in agricultural landscapes: A review of ecological indicators and achievable ecological outcomes, J. Soil Water Conservation 54 (4) (1999) 636–644.
[14] T.F. Cuffney, M.R. Meador, S.D. Porter, M.E. Gurtz, Responses of physical, chemical and Biological indicators of water quality to a gradient of agricultural land use in the Yakima River Basin, Washington, Environ. Monit. Assess. 64 (1) (2000) 259–270.
[15] J.P.H.B. Ometo, L.A. Martinelli, M.A. Ballesteri, A. Gessner, A.V. Krusche, R.L. Victoria, M. Williams, Effects of land use on water chemistry and macroinvertebrates in two streams of the Piracicaba river basin, southeast Brazil, Freshwater Biol. 44 (2000) 327–337.
[16] C. Little, D. Soto, A. Lara, J.G. Cuevas, Nitrogen exports at multiple-scales in a southern Chilean watershed (Patagonian lakes district), Biogeochemistry 87 (2008) 297–309.
[17] C.E. Oyarzún, A. Huber, Nitrogen export from forested and agricultural watersheds of southern Chile, Gayana Bot. 60 (1) (2003) 63–68.
[18] L. Ribbe, P. Delgado, E. Salgado, W.-A. Flügel, Nitrate pollution of surface water induced by agricultural non-point pollution in the Pocochay watershed, Chile, Desalination 226 (2008) 13–20.
[19] J. Rodier, Análisis de las Aguas, Aguas Naturales, Aguas Residuales, Agua de Mar. Ediciones Omega, Barcelona, 1981.
[20] SMEWW Standard Methods for Examination of Water and Wastewater. American Public Health Association, Washington, Method 4500-E, 1995.
[21] X. Lin, D. Zhang, Inference in generalized additive mixed models by using smoothing splines, J. R. Stat. Soc. B 61 (1999) 381–400.
[22] W.N. Venables, B.D. Ripley, Modern Applied Statistics with S., fourth ed., Springer, 2002.
[23] H. Akaike, A new look at the statistical model identification, IEEE Trans. Automat. Control 19 (1974) 716–723.
[24] H.B.N. Hynes, The Ecology Of Running Waters, Liverpool University Press, Liverpool, 1970.
[25] S. Li, S. Gu, W. Liu, H. Han, Q. Zhang, Water quality in relation to the land use and land cover in the Upper Han River basin China, Catena 75 (2008) 216–222.
[26] S. Li, S. Gu, X. Tan, Q. Zhang, Water quality in the upper Han River basin, China: the impacts of land use/land cover in riparian buffer zone, J. Hazard. Mater. 165 (2009) 317–324.
[27] T. Venugopal, L. Giridharan, M. Jayaprakash, P. Periakali, Environmental impact assessment and seasonal variation study of the groundwater in the vicinity of River Adyar, Chennai, India, Environ. Monitor. Assess. 149 (1–4) (2009) 81–97.
[28] J.K. Bohlke, R.C. Antweiler, J.W. Harvey, A.E. Laursen, L.K. Smith, K. Lesley, R.L. Smith, M.A. Voytek, Multi-scale measurements and modeling of denitrification in streams with varying flow and nitrate concentration in the upper Mississippi River basin, USA, Biogeochemistry 93 (1–2) (2009) 117–141.
[29] R.E. Turner, N.N. Rabalais, D. Justic, Q. Dortch, Global patterns of dissolved N, P and Si in large rivers, Biogeochemistry 64 (2003) 297–317.