Chemical composition and the nitrogen-regulated trophic state of Patagonian lakes

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Abstract

Chemical composition and nutrient concentrations of 39 relatively poorly known Patagonian lakes (38–50°S and from 70° to 68°W) are described and analysed using principal component analysis (PCA). The general relationships between nutrients (total phosphorus, bioavailable phosphorus and dissolved inorganic nitrogen) and plankton biomass are examined.

We seek to demonstrate that the extreme oligotrophy characterising many lakes and reservoirs of the Argentine Patagonian region of South America owes more to nitrogen deficiency than to a shortage of available phosphorus. The data show a range of trophic conditions with variable water chemistry characteristics.

The first two axes of the PCA ordination explain most of the variance (63%). The first component of the variance in the environmental data is a trophic gradient, with positive correlations with the concentrations of nutrients (TP, SRP, DIN) and electrical conductivity and a negative correlation with transparency. For all the reservoirs considered, the calculated annual, summer and winter chlorophyll-a carrying capacities of the available phosphorus were consistently and significantly ($P < 0.05$) in excess of observations but maximum chlorophyll-a values correlate with DIN availability. Indeed the chlorophyll-a carrying capacities, as an index of the resource-sustainable maximum biomass, of the available nitrogen gives a better predictive yield relationship than does P. Our findings are remarkable in so far as the general expectation that dinitrogen-fixing phytoplankton should thrive in the absence of dissolved inorganic nitrogen, at least to the supportive limits of the available phosphorus, is unfulfilled.
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Keywords: Trophic state; Nitrogen; Chemical composition; Patagonia; Lakes

Introduction

This paper addresses the assumptions that underpin one of limnology's most preciously held paradigms. This is that phytoplankton production and biomass in lakes are primarily constrained by the nutrient supply and especially by phosphorus (Schindler, 2006). The role of increasing phosphorus supplies in generating the biomass and species structures characterising eutrophication is

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not in question but the converse, that oligotrophic systems are necessarily deficient in phosphorus, is open to debate. Exceptions are explicitly accepted, in so far as limitations are known to be imposed on phytoplankton standing crop in deep water columns of large lakes through light absorption. While nutrients other than phosphorus are accepted as having a critical controlling role in the sea (Howarth & Marino, 2006), the general understanding of (say) nitrogen limitation in lakes is that it is a symptom of high phosphorus loading and of the stress this places on the supplies of the other resources. It is a long-held contention (Schindler, 1977) that, in such instances, the growth of dinitrogen-fixing micro-organisms is promoted, perhaps to the supportive capacity of the phosphorus available, so that phosphorus continues to be regarded as being the ultimate limiting factor, even in otherwise nitrogen-deficient systems.

In this article, we seek to confirm existing circumstantial evidence that the extreme oligotrophy characterising many lakes and reservoirs of the Argentine Patagonian region of South America owes more to a direct nitrogen deficiency than to a shortage of phosphorus and that it is scarcely compensated by dinitrogen fixation. Moreover, we show it to be a widespread phenomenon. However, far from suggesting that the lake biota are insensitive to nutrients other than nitrogen, we consider the likely responses of the lakes to enrichment with phosphorus.

We begin by describing the region, its lakes and reservoirs and their biological productivity. We consider observed phytoplankton biomass as a dependent on total phosphorus, total nitrogen and water depth. We also consider observed biomass levels as a function of resource-determined carrying capacity, as well as the
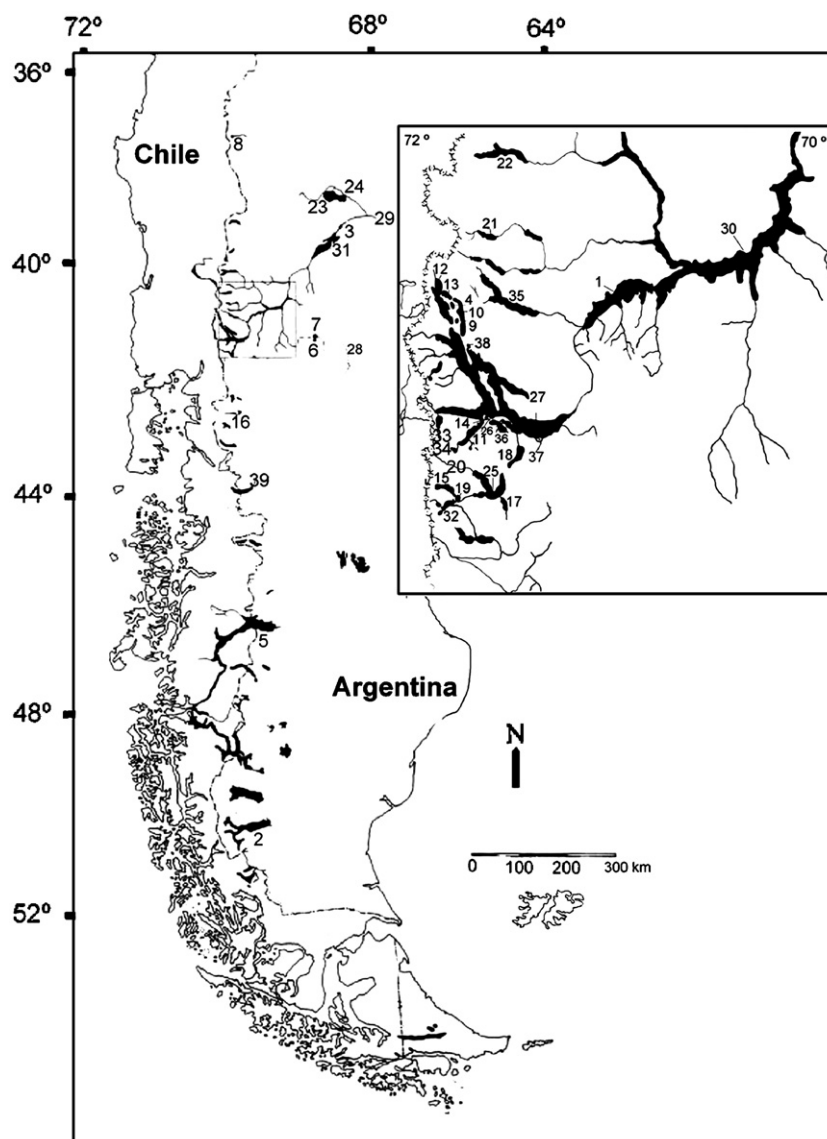

Fig. 1. Geographical location of the studied lakes (lake numbers according to Table 1).

results of some recent bioassays. In a concluding discussion, we relate our findings to the paradigm of lake trophic states. Particular attention is drawn to the apparently nitrogen-limited capacity and to the probable responses to increased nutrient loadings.

Study area

The 39 lakes we considered are located in the Andean Patagonian region (38–50°S and from 70° to 68°W) (Fig. 1). According to De Aparicio and Difrieri (1985), this region may be divided into two major sub-regions: the Andean Patagonia and the Patagonian Plateau or Steppe. The water bodies in Andean Patagonia are of glacial origin, are chemically very dilute and tend to be silica-dominated (Pedrozo, Childrud, Temporetti, & Diaz, 1993). Andean Patagonian soils, derived mainly from volcanic ash are poorly developed, though rich in allophane. In contrast, the soils of the Patagonian Steppe are typically alkaline with high salt content; the hydrological balance is negative and salinisation processes dominate.

The regional climate is continental (Speck et al., 1982), ranging from humid cold-temperate near the Andes Mountains to arid on the Patagonian Plateau. Rain falls mostly in the late winter–early spring period. Owing to the loss of moisture from the prevailing westerlies, there is a strong west-to-east gradient in the annual precipitation: 2700 mm/yr on the Argentine–Chilean border (altitude~1020 m); only 50 km to the East (800 m), it is just 500 mm/yr; on the Patagonian Plateau (800 m), annual precipitation is 150 mm/yr. The mean annual temperature ranges between 3 °C at high altitudes (above 2000 m) and 8 °C in better-protected valleys in the Andes and between 7.5 and 12.5 °C on the Steppe.

The Andean lakes have been classified as warm monomictic, being subject to a period of summer stratification (Quiros & Drago, 1985). The surface areas of the lakes range from 0.1 to 1892 km² (Table 1). Their maximum depths are between 3 and 550 m. All the lakes are circumneutral in reaction, with one exception, the naturally very acidic Lake Caviahue. The acidity of Lake Caviahue (pH 2.56, acidity: >5 mmol H^+ L^{-1}) is controlled by the high sulphate content of the Upper Agrio River (pH 1.78, acidity: >20 mmol/L) and can be attributed to sulphuric acid generated in the source water from the Copahue Volcano (altitude 2800 m a.s.l.; Pedrozo et al., 2001).

Materials and methods

This work invokes chemical analyses of the waters of 39 water bodies (see Fig. 1 and Table 1). These are varied in their limnological characteristics:

- Thirteen are very deep (>100 m), situated at altitudes between 187–936 m of altitude.

- Five have maximal depths of between 50 and 80 m, and are located at altitudes of between 725 and 780 m a.s.l.
- Four are shallow lakes on the Patagonian plateau (maximum depths in the range 5–18 m), at altitudes of between 100 and 270 m a.s.l.
- Seven are shallow Andean lakes (maximum depths between 4 and 12 m), at altitudes between 600 and 800 m a.s.l.
- Three are high-altitude shallow lakes located at 1545–1950 m a.s.l. (maximum depths between 5 and 12 m).
- One deep (95 m), naturally acidic lake at high altitude (1650 m a.s.l.).
- Six reservoirs (maximum depths, between 15 and 140 m), located at between 300 and 705 m a.s.l.

The waterbodies were sampled between 1990 and 2003: 13 have sampled just once, during the summer; for the other 26, sampling has been undertaken either at bimonthly intervals during a given year, or at monthly intervals, increasing to fortnightly in summer. Chemical analyses were carried out soon after collection. All the results used in the present data analysis have been published previously (Diaz, 1994; Diaz, Pedrozo, & Temporetti, 1998; Labollita & Pedrozo, 1998; Markert et al., 1997; Pedrozo et al. 1993, 2001; Pedrozo, Temporetti, Diaz, Wenzel, & Bonetto, 1991; Tartarotti, Baffico, Temporetti, & Zagarese, 2004; Temporetti, 1998; Temporetti et al., 2001), following methods cited therein. Some of the morphometric information cited has been derived from, variously, Rapacioli (1985), Quiros (1988) and Baigun and Marinone (1996). The present analyses use average or maximal values as indicated where ever possible (single values are invoked for the lakes Argentino, Buenos Aires, Futalaufquen and Vinter). Variables considered include: altitude, area, maximum lake depth (Z_{max}), the depth of Secchi-disc extinction (SD), pH, conductivity, chlorophyll-*a* concentration (chl*a*), together with the concentrations of nutrients in the water, total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), dissolved inorganic nitrogen (DIN = the sum of nitrate, nitrite and ammonium) and those of the major ions (Na^+, K^+, Ca^{++}, Mg^{++}, $SO_4^=$, HCO_3^-, Cl^- and SiO_2).

A feature of this analysis is the comparison of measured (observed) chl*a* concentrations with the chlorophyll-carrying capacities of the nutrients as proposed by the equations of Vollenweider and Kerekes (1980), Reynolds (1992) and Reynolds and Maberly (2002). Analysis of variance (ANOVA) was used to check the agreement between the modelled concentrations and the observed measurements of chl*a*. The ordination of data pertaining to the lakes was performed using the software Canonical Community Ordination (version 4) for Windows (CANOCO) (ter Braak and

Table 1. Physical and chemical mean variables for studied lakes and reservoirs in Andean–Patagonian region

Lakes	Location number	Altitude (msnm)	Area (km²)	Z_{max} (m)	Secchi Disk (m)	pH	Cond (µS cm⁻¹)	TP (µg L⁻¹)	SRP (µg L⁻¹)	TN (µg L⁻¹)	DIN (µg L⁻¹)	Na (mg L⁻¹)	K (mg L⁻¹)	Ca (mg L⁻¹)	Mg (mg L⁻¹)	SO_4 (mg L⁻¹)	HCO_3^{-} (mg L⁻¹)	SiO_2 (mg L⁻¹)	chl a (µg L⁻¹)
Alicura	1	705	67.5	110	6.7	6.8	31.0	7.2	3.0	56.3	3.7	1.8	1.3	3.3	1.3	1.1	16.3	10.2	0.7
Argentino	2	187	1466	500	1.0	7.3	42.7	6.5	0.9	—	1.1	0.4	0.2	4.0	0.1	6.0	15.6	1.6	0.0
Arroyito	3	300	39	15	3.5		35.0	13.6	4.8	90.8	19.0	1.8	1.3	3.3	1.3	1.1	16.3	10.2	1.9
Bayley Willis	4	750	0.5	10	3.0	6.7	68.9	46.2	0.6	223.6	0.2	2.9	0.9	3.9	1.6	0.9	27.9	24.2	1.9
Buenos Aires	5	200	1892	550	8.0	7.8	92.0	2.9	0.6	—	1.0	2.9	0.5	8.5	1.0	6.8	32.1	5.9	0.0
Carrilaufquen Chica	6	150	5	5	0.3	8.5	440.0	190.4	52.2	588.5	65.6	249.5	11.0	34.6	34.4	184.0	36.1	49.3	10.8
Carrilaufquen Grande	7	150	20	7	0.2	8.8	1751.5	195.0	99.8	1520.9	88.1	744.7	17.2	26.8	30.0	528.0	37.9	72.4	8.6
Caviahue	8	1650	9.22	95	3.0	2.4	1565.0	321.6	305.6	80.0	80.6	15.4	7.1	25.1	15.6	475.0	0.0	14.0	0.8
Ceferino	9	750	0.1	9	0.0	7.8	55.0	18.6	0.5	99.6	0.1	3.5	1.0	5.1	1.8	0.5	34.7	27.6	1.3
Correntoso	10	750	19.5	50	10.0	6.3	29.6	4.3	0.9	98.9	7.2	1.5	0.5	3.6	2.2	1.5	24.3	10.3	0.1
Escondido	11	765	0.1	10	3.3	7.1	65.0	5.0	2.8	—	37.1	2.6	0.4	6.6	1.5	1.4	25.0	17.0	0.0
Espejo	12	750	41.6	245	12.0	6.5	26.7	8.0	1.2	96.0	11.1	1.6	0.5	3.2	1.2	2.5	17.5	11.0	0.3
Espejo Chico	13	750	1.9	68	15.0	6.2	28.1	8.0	1.0	—	22.3	1.4	0.4	3.0	1.0	1.5	16.7	10.9	0.6
Ezquerra	14	760	0.6	4	0.3	7.1	62.3	9.6	4.0	—	16.2	4.2	0.6	6.2	2.7	3.1	38.4	11.7	5.1
Fonk	15	780	4.5	85	8.0	6.7	29.8	12.9	8.0	—	12.6	1.9	0.5	3.4	0.3	0.6	17.0	14.3	1.4
Futalaufquen	16	510	44.6	168	14.0	7.8	66.0	6.2	3.4	—	7.1	1.0	0.8	5.8	0.4	2.7	30.0	6.8	0.5
Guillelmo	17	826	5.4	100	11.0	7.1	64.0	8.7	4.7	—	14.7	1.5	0.3	8.1	0.4	2.5	28.2	11.0	0.6
Gutierrez	18	750	16.4	111	13.0	6.7	58.1	3.4	3.4	—	4.6	1.7	0.4	8.0	0.5	0.9	30.4	11.3	0.4
Hess	19	725	2.12	80	8.0	7.7	38.2	6.1	0.7	48.4	3.2	2.0	0.6	4.1	1.4	2.2	21.5	16.1	0.3
Ingenieros	20	600	0.1	3	0.5	6.8	40.0	18.0	7.7	—	0.6	2.4	0.7	8.8	1.8	1.3	40.6	12.0	0.2
Lacar	21	625	49	277	14.0	6.9	51.0	4.0	1.1	97.5	15.1	1.8	0.5	3.3	0.9	1.2	18.7	15.1	1.5
Lolog	22	620	35	200	15.0	7.0	36.1	3.8	3.7	36.0	12.8	1.8	0.4	4.1	1.3	0.7	16.9	15.1	0.1
Los Barreales	23	422	413	120	1.2	8.3	171.9	15.2	5.1	85.2	9.7	27.9	13.7	98.9	24.4	186.0	108.6	0.7	1.0
Mari Menuco	24	420	174	140	6.7	8.2	900.0	10.8	3.5	71.9	5.0	27.9	13.7	98.9	24.4	186.0	108.6	0.7	0.6
Mascardi	25	795	39.2	218	10.3	6.9	43.9	9.9	1.6	—	5.3	1.3	0.4	5.5	1.0	4.8	18.7	9.9	0.2
Moreno	26	765	10.6	180	7.0	6.8	37.1	8.8	6.2	50.2	13.3	1.2	0.3	4.8	1.4	1.3	22.7	10.0	0.4
Nahuel Huapi	27	765	557	464	7.0	7.5	39.3	9.0	1.9	71.0	9.8	1.8	0.5	3.3	0.9	1.2	18.7	15.1	1.4
Ñe-Luan	28	1000	0.6	6	0.5	8.4	342.0	199.5	26.2	881.5	44.4	249.5	11.0	34.6	34.4	184.0	36.1	49.3	10.1
Pellegrini	29	270	100.7	18	1.2	8.4	4100.0	24.0	9.0	—	20.0	27.9	13.7	98.9	24.4	186.0	108.6	0.7	14.1
Piedra del Aguila	30	500	305	120	4.6	7.0	50.5	8.2	2.1	73.6	3.5	1.8	1.3	3.3	1.3	1.1	16.3	10.2	1.2
Ramos Mexia	31	381	816	60	4.0	7.9	58.5	12.6	4.4	84.6	15.6	4.4	0.8	7.1	2.1	7.0	17.0	5.2	2.0
Roca	32	725	4.94	80	9.0	6.9	36.0	8.0	2.5	—	0.3	1.6	0.3	4.0	1.1	1.3	14.5	10.4	0.8
Schmoll	33	1950	0.1	5.0	5.0	7.1	30.0	5.8	1.2	—	0.3	1.5	0.3	4	0.5	0.9	9.9	10	0.1
Tonchek	34	1750	0.1	12.0	9.0	7.0	31.0	7.0	1.4	—	0.3	1.5	0.3	4	0.5	0.9	9.9	10	0.6
Traful	35	750	75.3	200	15.0	6.9	44.7	8.0	6.8	48.7	2.6	1.8	0.6	4.6	1.4	1.0	25.3	13.4	0.4
Trebol	36	800	0.3	12	4.0	7.6	67.5	6.2	4.0	151.0	2.8	4.0	0.6	6.3	2.7	2.1	37.0	13.5	0.9
Verde (Chall Huaco)	37	1545	0.05	6	2.1	7.2	29.0	15.7	3.9	40.0	8.4	1.5	0.3	5.2	0.9	2.4	9.9	10.0	9.7
Verde VLA	38	765	0.1	9	4.0	6.7	62.2	10.0	8.0	143.0	11.2	4.0	1.0	6.4	3.8	1.9	46.5	22.6	2.3
Vintter	39	936	57	300	15.0	7.2	23.9	1.8	0.9	—	1.8	0.7	0.9	2.5	0.8	3.8	7.80	3.7	0.3

Smilauer, 1998). Principal component analysis (PCA) was used to detect the major environmental variables in the data set. Standardized PCA (based on the correlation matrix thus generated) was obtained for the sample variables and their log-transformed values. The ordination diagram (biplot) was constrained to provide linear combinations of the environmental variables (canonical axes).

Results

Chemical composition and trophic state

Important characteristics of the 39 Andean Patagonia lakes are presented in Table 1. Overall, the data show a broad range of solute concentration and trophic state. Secchi-disc transparency (range: 0.2–15.0 m), pH (2.4–8.8) and conductivity (26.7–4100 µS/cm) are also conspicuously variable.

The deep, glacial Andean lakes are generally dilute with respect to most solutes (Table 2: $Ca^{++} > Mg^{++} > < Na^+ > K^+$; $HCO_3^- > SO_4^= > Cl^-$) and dominated by silica. The lakes of the steppe (# 6, 7, 28, 29) are smaller, shallower and richer in solutes ($Na^+ > Mg^{++} > Ca^{++} > K^+$; $HCO_3^- > Cl^- > > SO_4^=$). An eastward gradient of increasing salinity is well represented by the plateau reservoirs (#1, 23, 24, 30, 31) located on the two main tributaries of the Rio Negro. While the annual precipitation decreases from West to East Patagonia, the slope of the terrain is also gentler, the depths of the reservoirs diminish and their residence times increase. chl*a* contents increase accordingly. The extreme case is the Lake Caviahue (#8), with its remarkably low pH, high sulphate content, conductivity and dissolved phosphorus (60–90% of total P).

Table 2 also permits the chemical composition of Patagonian lakes to be compared with published derivations of world- and continental averages. The solute contents of Andean lakes are lower for all determinands than the world averages given by Holland (1978), with the exception of silica, which is similar to the world averages for freshwaters given by Horne and Goldman (1994) and by Holland (1978). Supplied by water flowing eastwards from the Andes, the reservoirs are also strikingly dilute, pending the increasing influence of the aridity of the plateau region.

There is also a wide range of nutrient concentration and availability: soluble reactive phosphorus represented between the 1% and 77% of the TP (1.8–321.6 µg L^{-1}) and the dissolved inorganic nitrogen between 0.6 to 18% of the TN (56–1521 µg L^{-1}). Mean chl*a* concentrations in the range (0.1–14.1 mg L^{-1}) can be aligned with those associated with categories between ultra-oligotrophic and eutrophic (OECD, 1982).
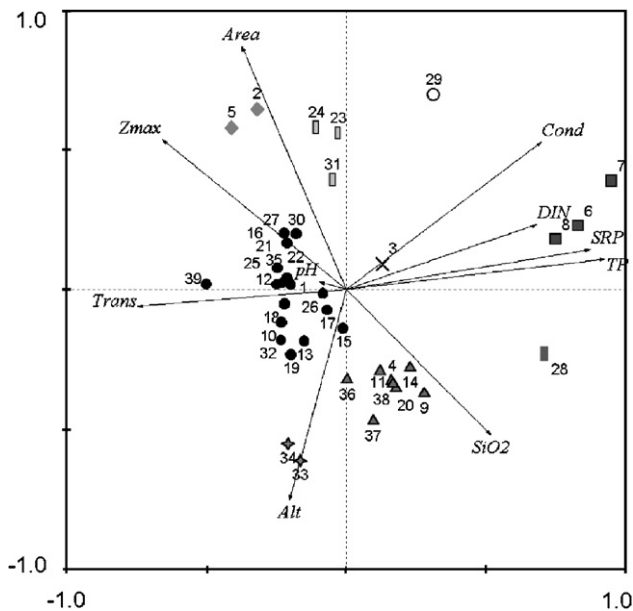
Table 2. Major ion composition of Patagonian lakes compared with freshwater world average

	Reference	SiO$_2$ (mg L^{-1})	Na (mg L^{-1})	K (mg L^{-1})	Ca (mg L^{-1})	Mg (mg L^{-1})	SO$_4$ (mg L^{-1})	Cl (mg L^{-1})	HCO$_3$ (mg L^{-1})
Freshw. world average	Horne and Goldman, 1994	**12.0**	**6.3**	**2.3**	**15.0**	**4.1**	**11.2**	**7.7**	**58.6**
America North	Holland, 1978	9.00	9.00	1.40	21.00	5.00	20.00	8.00	68.00
America South	Holland, 1978	11.90	4.00	2.00	7.20	1.50	4.80	4.90	31.00
Europe	Holland, 1978	7.50	5.40	1.70	31.10	5.60	24.00	6.90	95.00
Asia	Holland, 1978	11.70	9.30		18.40	5.60	8.40	8.70	79.00
Africa	Holland, 1978	23.20	11.00		12.50	3.80	13.50	12.10	43.00
Australia	Holland, 1978	3.90	2.90	1.40	3.90	2.70	2.60	10.00	31.60
World	Holland, 1978	**13.1**	**6.3**	**2.3**	**15**	**4.1**	**11.2**	**7.8**	**58.4**
Patagonia									
Andes lakes	This paper	12.52	1.99	0.52	5.00	1.26	2.06	1.12	24.02
Platteau reservoirs	This paper	11.70	10.94	5.33	35.78	9.15	63.73	1.52	47.17
Platteau lakes	This paper	42.93	317.91	13.23	48.72	30.81	270.52	34.87	54.63

Ordination of the waterbodies

Six variables highly autocorrelated in the correlation matrix were excluded from the 17-variables data set (Table 1) for the subsequent analyses (e.g., major ions with the conductivity). In the PCA ordination diagram (Fig. 2), lakes are represented by points and quantitative environmental variables by directional arrows. The first axis of the PCA ordination, which explains 63% of the variance, is a trophic gradient, with positive correlations with nutrients (TP, SRP, DIN) and electrical conductivity and a negative correlation with transparency (Fig. 2). The factor loadings in the second axis suggest that the next component of the variation is related positively to the areas of the lakes and negatively with their altitude.

The large number of lakes related to the trophic gradient is separable into two groups (Table 3): one corresponds to nutrient-richness (SRP, TP, DIN) and high conductivity and includes the lakes high in phosphorus: Carrilaufquen Chica (#6), Carrilaufquen Grande (#7), Caviahue (#8). Ñe Luan (#28) is particularly silica-rich and Pellegrini (#29) has the highest conductivity but is low in silica. The pH also is an important environmental variable in this group of lakes, which includes the most alkaline (steppe lakes, $pH = 8.4–8.8$) and the most acidic (Lake Caviahue, $pH = 2.4$) measured. The second, larger group of lakes on the nutrient-transparency gradient is distinguished by their circumneutrality. This group includes the largest and deepest lakes in the region, having very low SiO_2 concentrations lakes (Argentino and Buenos Aires; #2, #5), opposite a subgroup of shallow lakes (Bailey Willis, Ceferino, Escondido, Ezquerra, Ingenieros, Trebol, Verde (Chall Huaco) and Verde (VLA) having relatively high silica concentrations (#4, 9, 11, 14, 20, 36, 37, 38). Close to them are the lakes Schmoll and Tonchek (#33, 34), also small and shallow, characterized by their high-mountain locations, ultraoligotrophic states, silica-richness and low conductivity. Three reservoirs from the Patagonia Plateau make up another small group: Los Barreales, Mari Menuco and Ramos Mexia (#23, 24, 31); their common features are large surface area, relative depth and intermediate levels of nutrients, conductivity and transparency. Finally, the remaining group is the ultraoligotrophic and oligotrophic lakes located in the glacial valleys of the Andes.

Fig. 2. Lake–environment biplot PCA. The points represent the lakes and the arrows represent each environmental variable pointing in the direction of its maximum change.

Table 3. Main characteristics of the studied lakes that perform the different groups showed in Fig. 2

| Main characteristics of the lakes	Lakes	Lake number
High SRP, TP, DIN concentrations	Carrilauquen Chica, Carrilaufquen Grande	6, 7
High conductivity, extreme pH	Caviahue, Ñe Luan, Pellegrini	8, 28, 29
Largest and deepest lakes	Argentino, Buenos Aires	2, 5
Very low Silica concentrationsShallow lakes	Bailey Willis, Ceferino, Escondido, Ezquerra	4, 9, 11, 14
High Silica concentrations	Ingenieros, Trebol, Verde (CH), Verde (VLA)	20, 36, 37, 38
Small, shallow, high-montain lakes	Schmoll, Tonchek	33, 34
Reservoirs	Los Barreales, Mari Menuco, Ramos Mexia	23, 24, 31
Ultraoligo- to oligotrophic glacial lakes	Alicura, Correntoso, Espejo, Espejo Chico,	1, 10, 12, 13
Deep, high transparent lakes	Futalaufquen, Guillelmo, Gutierrez, Hess,	16, 17, 18, 19
Low conductivity, low nutrients	Lacar, Lolog, Mascardi, Moreno, Nahuel Huapi	21, 22, 25, 26, 27
	P. del Aguila, Roca, Traful, Vinter	30, 32, 35, 39

See the text for explanations.
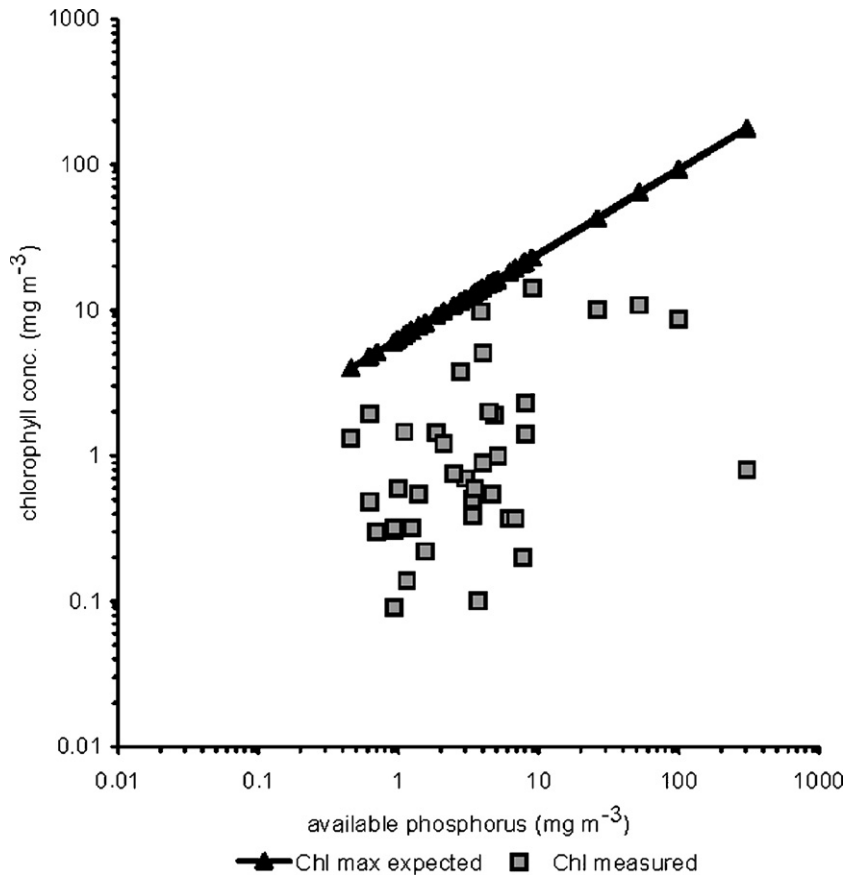
Fig. 3. Maximum chlorophyll for bioavailable phosphorus capacity (Reynolds, 1992) for Patagonian lakes.

They are also broadly similar in depth, area, transparency, altitude, silica, their low conductivities, low nitrogen and phosphorus contents.

Estimating chlorophyll carrying capacity

This last named group of lakes is also distinguished by the typically low chlorophyll populations that they support. At first sight, the low phytoplankton biomass is attributable to low nutrient availability. However, the distribution of the maximum observed chl$a$ concentrations when plotted against the maximum concentration of SRP (Fig. 3) does not suggest a tight coupling between resource availability and biomass yield. Moreover, the chlorophyll concentrations observed seemed low against phosphorus supposed to be available to phytoplankton uptake. We decided to compare the data with the capacity model of Reynolds (1992; see also Reynolds and Maberly (2002)), for downloadable web-based software, which was developed to predict the maximum biomass yield, or the biomass may be supportable on the basis of the bioavailable phosphorus fraction, the proportion:

$$\log[\text{chl}]_{max} = 0.585 \log[P]_{max} + 0.801.$$

Calculations of capacity against the phosphorus available in Andean Patagonian lakes using this equation are inserted in Fig. 3. In very few instances does the maximum observed chlorophyll come close to the supposed capacity. In several instances, the shortfall is an order of magnitude.

The corresponding exercise using DIN as the predictor was undertaken with less confidence because the equations of Reynolds (1992) and Reynolds and Maberly (2002) were not based on experimental results but upon the C:N and C:chl$a$ stoichiometry of growing cells. However, the relationship, $0.11 \, \text{g chl}_a/(\text{g N})$, was used to generate the prediction inserted into Fig. 4. It is clear that the real observations coincide much more nearly with the supposed capacity of the nitrogen. Indeed, the linear regression fitted to the present observations suggests a similar, but slightly better, yield of $0.132 \, \text{g chl}_a/(\text{g N})$. This is strongly suggestive of the possibility that nitrogen and not phosphorus regulates the supportable planktic biomass, at least in the more oligotrophic lakes of the region.

In relation to phytoplankton supportive capacities of the five reservoirs contributing to the data set, observed values of total phosphorus, bioavailable phosphorus and dissolved inorganic nitrogen were used to calculate
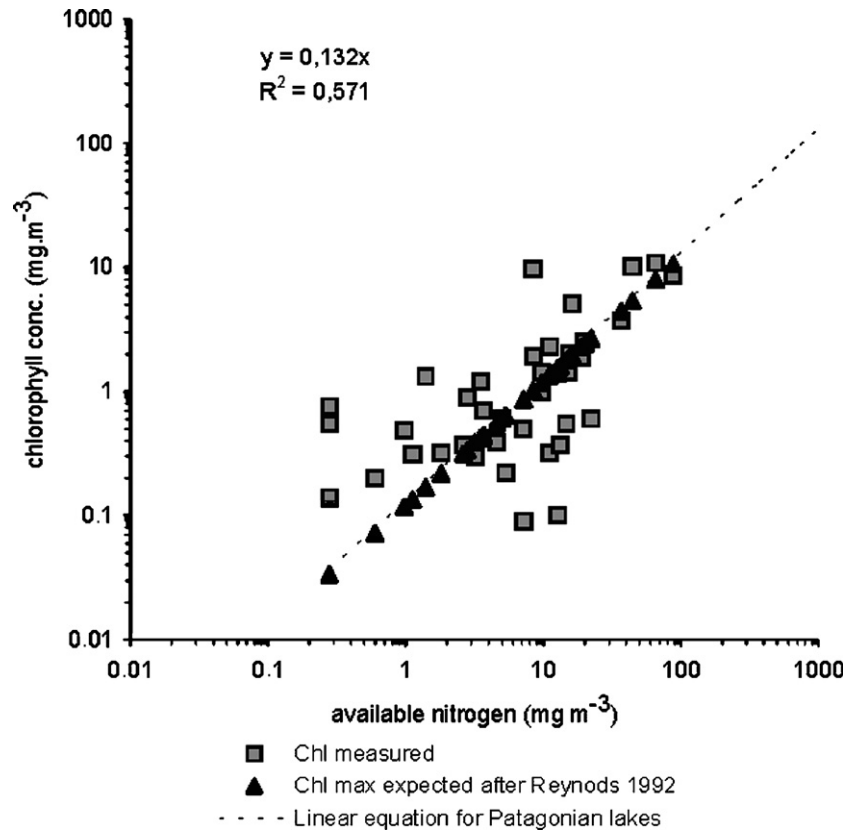
Fig. 4. Maximum chlorophyll for dissolved inorganic nitrogen (Reynolds, 1992) for Patagonian lakes.

seasonal estimates of the planktic chlorophyll that each is likely to sponsor (Table 4). The tabulation compares the appropriate observed chlorophyll concentrations with the P- and N-based capacities advocated by Reynolds and Maberly (2002), as well as the average observed chlorophyll concentrations values with the expected values generated from the Vollenweider-OECD equation (in its final form; Vollenweider & Kerekes, 1980). The prediction is that:

$$\log[\text{chl}a]_y = 0.91 \, \log \, (P_1)_y - 0.435,$$

where $(P_1)_y = [L[P]_{A/V}] \, [1 + (H/V)^{1/2}]$, $_V = 1/T$, T being equal to V/Q_{mean}, where V is maximum volume and Q_{mean} is the average outflow discharge; and where $L[P]_A$ is the areal TP load.

For all the reservoirs, the calculated averages for annual, summer and winter average of chla calculated according to the Vollenweider-OECD equation from the TP load significantly overestimated ($P < 0.05$) the average chlorophyll concentrations observed. In contrast, maximum annual, summer and winter chlorophyll are generally well predicted by one or other of the calculations of seasonal capacity. Nitrogen appears to set the most severe restriction on the capacity in winter and through the year in four of the reservoirs, although,

in summer and especially in Chocon, the supply of biologically available phosphorus arguably becomes critical to the supportive capacity.

Discussion

The new data presented in this paper are fully consistent with previous findings for Patagonian lakes (Drago & Quiros, 1996), distinguishing the Andean lakes, in which the surface water chemistry is most influenced by the watershed rock ("rock dominance", in the terminology of Gibbs, 1970), from the plateau lakes, in which evaporative crystallisation processes are dominant. The waterbodies are again shown to be aligned with a gradient of increasing salinity in the Andes-Atlantic direction (Land de Castello, 1981).

Of particular interest are the strikingly low SRP and DIN contents of the Andean lakes and of the upstream reservoirs. Bioavailable P levels are generally $<10 \, \mu g \, P \, L^{-1}$ and, in many instances, $<3 \, \mu g \, P \, L^{-1}$, which are broadly typical of oligotrophic (OECD, 1982) and unpolluted lakes of the world (Meybeck, 1982). However, it is the DIN levels in these lakes that are most remarkable, being everywhere $<30 \, \mu g \, N \, L^{-1}$, commonly $<15 \, \mu g \, N \, L^{-1}$ and, in several instances,

Table 4. The yields of chlorophyll predicted by different capacity calculations

Reservoir	Observed ($mg\,m^{-3}$)	Chl LTP ($mg\,m^{-3}$)	Chl BAP ($mg\,m^{-3}$)	Chl N ($mg\,m^{-3}$)	Observed ($mg\,m^{-3}$)	Chl LTP ($mg\,m^{-3}$)	Chl BAP ($mg\,m^{-3}$)	Chl N ($mg\,m^{-3}$)	Observed ($mg\,m^{-3}$)	Chl LTP ($mg\,m^{-3}$)	Chl BAP ($mg\,m^{-3}$)	Chl N ($mg\,m^{-3}$)
Alicura	0.66	2.87	1.52	0.52	0.43	2.87	1.52	0.52	0.91	2.87	1.52	0.52
Piedra del Aguila	1.20	3.09	1.67	0.49	1.30	3.09	1.67	0.49	1.29	3.09	1.67	0.49
Chocón	1.96	2.63	1.52	1.93	1.10	2.63	1.52	2.04	1.94	2.63	1.52	2.04
Barreales	0.98	4.17	2.03	1.24	1.05	4.17	2.03	1.10	0.96	4.17	2.03	1.10
Marí Menuco	0.64	3.58	1.66	0.66	0.23	3.58	1.66	0.43	0.97	3.58	1.66	0.43
Probability		$P = 0.00034$	$P = 0.051$	$P = 0.75$		$P = 0.00010$	$P = 0.0054$	$P = 0.81$		$P = 0.00028$	$P = 0.061$	$P = 0.43$
Significance level		***	ns	ns		***	**	ns		***	ns	ns

Chl LTP: mean chlorophyll content from annual TP load (Vollenweider & Kerekes, 1980), where $\log[chl]_y = 0.91 \log(P_l)_y - 0.435$; Chl BAP: maximum chlorophyll for bioavalable phosphorus capacity (Reynolds, 1992) and Chl N: maximum chlorophyll for nitrogen (Reynolds, 1992). Significance level: *$P<0.05$; **$P<0.01$; ***$P<0.001$; ns, not significant.

$<3\,\mu g\,N\,L^{-1}$. They are quite ten times below the average of world fresh waters. The molecular ratios of N:P are frequently <1 and far below the value of 16, said to distinguish nitrogen-limited systems from those constrained by phosphorus (Rhee & Gotham, 1980). The reason for this nitrogen poverty in the Andean lakes owes, presumably, to deficiencies in the leachates from mountainous catchments dominated by an assortment of igneous, volcanic and plutonic rocks, all highly eroded by glaciation. The extensive mature forest cover of the Andes at this latitude is effective in sequestering and retaining much of the available N, in a near-closed cycle that leaves little to overspill into the drainage. In this paper, we demonstrate a strong tendency of the low levels of phytoplankton biomass observed to be well within the supportive capacity of the bioavailable phosphorus but to be, instead, correlated with nitrogen availability, in proportions predicted from stoichiometry.

We believe that our data demonstrate that the extreme oligotrophy characterising many lakes and reservoirs of the Andean lakes of Patagonia owes directly to nitrogen deficiency rather than to a shortage of available phosphorus. This is not a commonly acknowledged possibility among limnologists, a majority of whom accepts the paradigm that phytoplankton production and biomass in lakes are constrained by phosphorus availability. Neither is our deduction a new one, as it simply verifies previous suspicions about nitrogen limitation in lakes in adjacent parts of the Andes (Soto, Campos, Steffen, Parra, & Zuñiga, 1994). The low nitrogen availability in these lakes may be contingent upon contemporary deficiencies in the leachates from soils, perhaps abbetted by efficient retention in the vegetation. It is also likely that, far from major cities and industrial areas, atmospheric sources of combined nitrogen are substantially lower than at many well-studied northern-hemisphere locations.

By way of a corollary, we note that oligotrophy in freshwater systems is not exclusively the direct consequence of phosphorus deficiency. However, the "puzzle" persists as to why the deficiency is not overcome by the activities of planktic dinitrogen-fixing Cyanobacteria, which seem unable to augment the standing biomass of phytoplankton in the Andean lakes, at least to the limits of the phosphorus capacity. Potential dinitrogen-fixing species, such as *Anabaena solitaria*, occur commonly among these lakes (Diaz, Pedrozo, & Baccala, 2000) but only rarely do they produce the dinitrogen-fixing organelles (heterocysts) that are indicative of active N-fixation. In contrast, in the plateau lakes, Carrilaufquen Grande and Carrilaufquen Chica, *Anabaena* spp. are dominant and actively fix nitrogen.

The "puzzle" is not confined to aquatic ecosystems: the ecological and environmental controls of nitrogen fixation in symbiotic and heterotrophic bacteria are also

sparsely understood (Vitousek et al., 2002). Besides a low DIN concentration (more likely, a low ammonium concentration, of $<0.5\,\mu M\,N$), nitrogen fixation in free-living, planktic Cyanobacteria demonstrably requires a low-redox, microaerophilous proximal environment to protect the nitrogenase enzyme, a high electron-transport energy and ATP-generation capacity to be able to reduce the relatively inert N_2, the biochemical availability of molybdenum and iron or vanadium at the core of the nitrogenase enzyme, and an adequate supply of phosphorus (overview of Reynolds, 2006). Light energy should not be a limiting constraint in the high-clarity Andean lakes when it plainly is not so in the more turbid Plateau lakes. We can be less confident about the bioavailability of the trace metals, although published findings on the distribution of the micronutrients (Markert et al., 1997) do not suggest that shortage of any of these elements might determine the poverty of nitrogen fixation.

On the other hand, there are good reasons to suspect the decisive intervention of low phosphorus concentrations. Stewart & Alexander (1971) showed experimentally that nitrogenase activity was steadily lost in cultures of heterocystous *Anabaena* and other Nostocalean species after transfer to P-free medium and was not restored without the addition of further phosphate to the medium to give a concentration equivalent to 5 µg P L^{-1}. Inspection of our data in Table 1 shows that the ability to support active, nitrogen fixation coincides with SRP concentrations $>8\,\mu g\ P\,L^{-1}$, and especially so with the rather higher SRP concentrations observed in the plateau lakes. Thus, although DIN levels in Patagonian lakes are characteristically low and frequently drawn down to levels that constrain the recruitment of further biomass, it is the poverty or otherwise of bioavailable phosphorus that provides the additional capacity to support dinitrogen-fixing Cyanobacteria and the means of circumventing the nitrogen limitation.

In these terms, we have to concede that because the ability to support a large biomass in Patagonian lakes is ultimately a function of the phosphorus available and that, far from contravening Schindler's (1977) contention about the its role as "the ultimate limiting factor", our findings demonstrate a probable dependence on phosphorus in distinguishing between the oligotrophic and eutrophic lakes in Patagonia. However, our further demonstration that, despite having generally very low phosphorus concentrations, Patagonian Andean lakes have a still greater deficiency in DIN, which is decisive in regulating their biomass carrying capacity. That the findings do not conform to the generally understood chlorophyll–phosphorus relationships demonstrates the error of assuming that phytoplankton biomass is exclusively contingent upon the phosphorus available (Sommer, 1992).

References

Baigun, C., & Marinone, M. C. (1996). Cold-temperate Lakes of South America: Do they Fit Northern Hemisphere Models? *Archiv für Hydrobiologie*, *135*(1), 23–51.

De Aparicio, F. O., & Difrieri, H. A. (1985). *La Argentina. Suma de Geografías*. Buenos Aires: Tomo I, Peuser.

Diaz, M. (1994). *Fitoplancton de lagos Andino-patagónicos. Su relación con factores abióticos* Tesis Doctoral, Facultad de Ciencias Exáctas y Naturales. Universidad Nacional de Buenos Aires 178pp.

Diaz, M., Pedrozo, F., & Temporetti, P. (1998). Phytoplankton of some Araucanian Lakes Differing in Trophic State (ARGENTINA). *Hydrobiologia*, *369/370*, 45–57.

Diaz, M. M., Pedrozo, F. L., & Baccala, N. (2000). Summer classification of Southern Hemisphere temperate lakes (Patagonia, Argentina). *Lakes and Reservoirs: Research and Management*, *5*, 213–229.

Drago, R., & Quiros, R. (1996). Thee hydrochemistry of the inland waters of Argentina: A review. *International Journal of Salt Lake Research*, *4*, 315–325.

Gibbs, R. (1970). Mechanisms contrrolling world water chemistry. *Science*, *170*, 1088–1090.

Holland, H. D. (1978). *The Chemistry of the Atmosphere and Oceans*. New York: Wiley-Interscience.

Horne, A. J., & Goldman, C. R. (1994). *Limnology* (2nd ed). New York: McGraw-Hill Inc. 576pp.

Howarth, R. W., & Marino, R. (2006). Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. *Limnology and Oceanography*, *51*(1, Part 2), 364–376.

Labollita, H., & Pedrozo, F. L. (1998). Factors controlling trophic state of reservoirs at the basins of Limay, Neuquen and Negro rivers (Argentina). *Newsletter, International Lake Environment Committee Foundation N*, *32*, 3.

Land De Castello, R. (1981). Alguns aspectos limnologicos abioticos de las cuencas de los rios Limay y Neuquen, con especial referencia al embalse Ramos Mexia. *Ecosur*, *8*(16), 1–27.

Markert, B., Pedrozo, F. L., Geller, W., Friese, K., Korhammer, S., Baffica, G., et al. (1997). A contribution to the study of the heavy metal and nutritional element status of some lakes in the southern Andes of Patagonia (Argentina). *The Science of the Total Environment*, *206*, 1–15.

Meybeck, M. (1982). Carbon, Nitrogen and Phosphorus transport by world rivers. *American Journal of Science*, *282*, 401–450.

OECD. (1982). *Eutrophication of waters: Monitoring, assessment and control*. Paris: Organisation for Economic Co-operation and Development.

Pedrozo, F., Temporetti, P., Diaz, M., Wenzel, T., & Bonetto, C. (1991). Estudio limnológico preliminar de la Laguna

Carrilaufquen Chica (Río Negro, Argentina). *Biología Acuática*, 15, 56–57.

Pedrozo, F., Childrud, S., Temporetti, P., & Diaz, M. (1993). Chemical composition and nutrient limitation in rivers and lakes of Northern Patagonian Andes (39.5–42°S; 71°W) (Rep. Argentina). *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, 25, 207–214.

Pedrozo, F., Kelly, L., Diaz, M., Temporetti, P., Baffico, G., Friese, K., et al. (2001). Chemistry, plankton and trophic state of natural Andean Acid Lake of volcanic origin in Patagonia. *Hydrobiologia*, 452, 129–137.

Quiros, R., & Drago, E. (1985). Relaciones entre variables, fisicas, morfometricas y climaticas en lagos patagonicos. *Revista de la Asociación de Ciencias Naturales del Litoral*, 16, 181–189.

Quiros, R. (1988). Relationships between air temperature, depth, nutrients and Chlorophyll in 103 Argentinian lakes. *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, 23, 647–658.

Rapacioli, R. A. (1985). *El Lago Caviahue y su Cuenca*. Technical Report, EPAS, Government Office, Provincia del Neuquén, Argentina.

Reynolds, C. (1992). Eutrophication and the management of planktonic algae: What Vollenweider couldn't tell us. In D. W. Sutcliffe, & J. G. Jones (Eds.), *Eutrophication: Research and application to water supply* (pp. 4–29). Ambleside: Freshwater Biological Association.

Reynolds, C. (2006). *The ecology of phytoplankton*. Cambridge: Cambridge University Press.

Reynolds, C. S., & Maberly, S. C. (2002). A simple method for approximating the supportive capacities and metabolic constraints in lakes and reservoirs. *Freshwater Biology*, 47, 1183–1188.

Rhee, G.-Y., & Gotham, I. J. (1980). Optimum N:P ratios and co-existence of planktonic algae. *Journal of Phycology*, 16, 486–489.

Schindler, D. W. (1977). Evolution of phosphorus limitation in lakes. *Science*, 196, 260–262.

Schindler, D. W. (2006). Recent advances in the understanding and management of eutrophication. *Limnology and Oceanography*, 51(1, Part 2), 351–355.

Sommer, U. (1992). The scientific basis of eutrophication management. *Reconciling basic physiology and empirical biomass models. Memorie Istituto Italiano de Idrobiologia*, 52, 89–111.

Soto, D., Campos, H., Steffen, W., Parra, O., & Zuñiga, L. (1994). The Torres del Paine lake district (Chilean Patagonia). A case of potentially N-limited lakes and ponds. *Archiv für Hydrobiologie (Supplement)*, 99(1–2), 181–197.

Speck, N. H., Sourrille, E. H., Wijnhoud, S., Minist, E., Vofkheimer, W., & Menendez, J. A. (1982). *Sistemas Fisiográficos de la zona de Ingeniero Jacobacci-Maquinchao*. Colección Científica, Tomo XIX: INTA 215pp.

Stewart, W. D. P., & Alexander, G. (1971). Phosphorus availability and nitrogenase activity in blue-green algae. *Freshwater Biology*, 1, 389–404.

Tartarotti, B., Baffico, G., Temporetti, P., & Zagarese, H. (2004). Mycrosporine-like amino acids in planktonic organisms living under different UV exposure conditions in Patagonia lakes. *Journal of Plankton Research*, 26, 453–762.

Temporetti, P. (1998). *Dinámica del Fósforo en Cuerpos de Agua con Cría Intensiva de Salmónidos* Doctoral Thesis, Centro Regional Universitario Bariloche. Argentina: Universidad Nacional del Comahue.

Temporetti, P., Alonso, M., Baffico, G., Diaz, M., Lopez, W., Pedrozo, F., et al. (2001). Trophic state, fish community and intensive production of Salmonid in Alicura Reservoir (Patagónia, Argentina). *Lakes and Reservoirs: Research and Management*, 6, 259–267.

Ter Braak, C. J. F., & Smilauer, P. (1998). CANOCO Reference manual and user's guide to Canoco for windows: Software for canonical community ordination (version 4). Ithaca, NY, USA: Microcomputer Power.

Vitousek, P. M., Cassman, K., Cleveland, C., Crews, T., Field, C. B., Grimm, N. B., et al. (2002). Towards an ecological understanding of biological nitrogen fixation. *Biogeochemistry*, 57, 1–45.

Vollenweider, R. A., & Kerekes, J. (1980). The loading concept as basis for controlling eutrophication philosophy and preliminary results of the OECD Programme on eutrophication. *Progress in Water Technology*, 12(2), 5–38.