Nitrogen–phosphorus relationship in high mountain lakes: effects of the size of catchment basins

Rafael Morales-Baquero, Presentación Carrillo, Isabel Reche, and Pedro Sánchez-Castillo

Abstract: We analyzed the changes in epilimnetic total nitrogen (TN), total phosphorus (TP), dissolved inorganic nitrogen (DIN), and soluble reactive phosphorus (SRP) in 31 small high-mountain lakes in the Sierra Nevada (Spain) during an annual cycle, just after the spring thaw, and in the middle of the growing season. Chlorophyll *a*, TN, and TP increased, whereas the TN:TP ratio fell substantially between the two periods, reaching values generally between 25 and 10 (by weight). On the contrary, DIN, SRP, and DIN:SRP ratios were similar for both periods in each lake. DIN:SRP ratios generally ranged from 5 to 20 (by weight). This ratio was low in the lakes with small catchment areas and increased progressively with catchment basin size. A regression analysis for the smallest catchments showed that chlorophyll *a* concentrations were not accounted for by variability in TP concentration. The results obtained are discussed in relation to the influence of episodes of Saharan dust, rich in P, reaching the Southern Mediterranean area.

Résumé : Nous avons analysé les variations de l'azote total (NT), du phosphore total (PT), de l'azote inorganique dissous (NID) et du phosphore soluble réactif (PSR) de l'épilimnion de 31 petits lacs de haute montagne de la Sierra Nevada (Espagne) pendant un cycle annuel, tout juste après le dégel du printemps et au milieu de la saison de croissance. Les concentrations de chlorophylle-*a*, de NT et de PT ont augmenté tandis que le rapport NT:PT a diminué de façon appréciable entre les deux périodes pour atteindre des valeurs se situant généralement entre 25 et 10 (en poids). Au contraire, les concentrations de NID et de PSR de même que le rapport NID:PSR étaient semblables au cours des deux périodes et dans chaque lac. Le rapport NID:PSR se situait généralement entre 5 et 20 (en poids). Le rapport était faible dans les lacs à bassin versant peu étendu et augmentait progressivement avec la superficie du bassin. Une analyse de régression portant sur les bassins les plus petits a montré que les concentrations de chlorophylle-*a* ne se reflétaient pas dans la variabilité de la concentration de PT. Les résultats obtenus sont traités dans le contexte de l'influence de vents en provenance du Sahara qui transportaient de la poussière, riche en P, et atteignait le sud de la Méditerranée.

[Traduit par la Rédaction]

Introduction

The nitogen to phosphorus (N:P) ratio in lake water can influence phytoplankton structure and biomass (McCauley et al. 1989; Molot and Dillon 1991). This ratio is dependent on external sources of N and P (runoff, atmospheric precipitation, groundwater, etc.) and on internal processes (phytoplankton uptake, sediment release, recycling by heterotrophs, etc.). Among external sources, atmospheric inputs have been recognized as a major supply of nutrients, mainly P, for many lakes located in undeveloped lands with small catchments (Peters 1977; Rigler and Peters 1995). The importance of N inputs from the atmosphere, however, has progressively increased as a result of industrial development (Henriksen and Brakke 1988).

Received November 2, 1998. Accepted July 6, 1999.
J14872

R. Morales-Baquero[1] and P. Carrillo. Instituto del Agua, Universidad de Granada, 18071 Granada, Spain.
I. Reche. Departamento de Biología Animal y Ecología, Universidad de Granada, 18071 Granada, Spain.
P. Sánchez-Castillo. Departamento de Biología Vegetal, Universidad de Granada, 18071 Granada, Spain.

[1]Author to whom all correspondence should be addressed. e-mail: rmorales@goliat.ugr.es

Downing and McCauley (1992) established a close correlation between total N to total P (TN:TP ratios) in lake water and ratios in inputs for a wide gradient of trophic conditions throughout the world and hypothesized that "...oligotrophic lakes in undeveloped areas that have small catchment basins relative to their area should have lower TN:TP ratios because precipitation has lower N:P than export from undeveloped lands." The N:P ratios of atmospheric precipitation are not always lower than those of export from undeveloped areas (Dillon et al. 1991); the hypothesis was meant to refer to average conditions globally. In general, the N:P ratios of runoff from unfertilized land are higher than those in precipitation for a homogeneous geographical area. Consequently, as lake catchment area increases, a progressive increase in the N:P ratios of external inputs is expected. Moreover, if the N:P ratio of the precipitation is low enough, P limitation of phytoplankton should become less likely as lake catchment area decreases. Since the dissolved inorganic N to soluble reactive P (DIN:SRP) ratio has proved to be a sensitive index for phytoplankton nutrient supply in lakes (Morris and Lewis 1988), a negative relationship between this ratio and catchment area could be expected.

High mountain lakes seem to be ideal places to test and contrast the above-mentioned hypothesis and related arguments. They are normally located in remote areas, hardly affected by human activity, and have small catchment basins and severe nutrient limitation. However, some authors (Kopácek et al. 1995) found much higher TN:TP ratios than the world average calculated by Downing and McCauley (1992) in lakes of central European mountains subject to strong and regular atmospheric N deposition linked to industrial activity. They concluded that an increase in the TN:TP ratio in geographically diverse high mountain lakes of the Northern Hemisphere is expected due to the increasing N inputs of industrial activity (i.e., increased nitric acid in rainfall).

The aim of this study was to examine lake TN:TP and DIN:SRP ratios in relation to catchment size in a group of small high mountain lakes in the Sierra Nevada (Spain). Low atmospheric N:P ratios are expected in this geographical region because it is far from areas of heavy industry. Moreover, every year, the region is exposed to long massive airborne plumes of desert dust from the Sahara Desert (Moulin et al. 1997). The dust has a substantial P content in comparison with N (Talbot et al. 1986). Sampling took place just after ice thaw and later, in the middle of the growing season, when plankton communities were well developed.

Materials and methods

Site description

Around 50 small glacially formed lakes are present in the Sierra Nevada (Spain) (36°55′–37°15′ N, 2°31′–3°40′ W; maximum altitude 3482 m above sea level) at elevations of roughly 2800–3100 m above sea level. The predominant substrate in the catchment basins is siliceous rocks, mainly mica–schist with graphite and mica–schist with feldspar. The soils are very poorly developed and do not support agriculture or forestry use. The vegetation is restricted to some sparse meadows. Lake size and depth vary with annual rainfall. In this study, surface areas ranged from 0.01 to 2.1 ha and maximum depths from 0.3 to 8 m (Table 1). Lakes normally remain ice covered from October to June. Some of them have outlets that may disappear as the ice-free period advances. Lake waters are relatively soft: conductivity ranged from 5 to 77 $\mu S \cdot cm^{-1}$, total alkalinity from 50 to 400 $\mu equiv. \cdot L^{-1}$, and pH from 6.5 to 9.5 (mean values at the time of this study).

The assumption of low N:P ratios in atmospheric inputs in this area is consistent with the preliminary information on the TN:TP ratios of snow samples, which varied from 4.3 to 15.9 (average 8.8) during the winter of 1996 (M. Villar-Argaiz, Depatamento de Biología Animal y Ecología, Universidad de Granada, 18071 Granada, Spain, personal communication).

Phytoplankton is dominated by nanoplanktonic species (Sánchez-Castillo et al. 1989), and the dominant zooplankton species are *Mixodiaptomus laciniatus* and *Diaptomus cyaneus* among copepods, *Daphnia pulicaria* among cladocerans, and *Hexarthra bulgarica* among rotifers (Cruz-Pizarro 1983; Morales-Baquero et al. 1989). The lakes are fishless.

Sampling and analysis

A total of 31 lakes were studied; samples were taken at the beginning and in the middle of the ice-free period. We tried to collect the samples from all the lakes in the shortest time period possible. The first sampling took place over a 12-day period between 15 and 27 July 1991, and the second was realized over a 13-day period between 21 August and 3 September in the same year. Hereafter, these periods will be referred to as "July" and "August," respectively. Because some of the lakes dried up during the summer, and some samples were lost, the number of lakes that we could compare between the two periods varied between 20 and 24. Watershed and lake surface sizes were calculated by image analysis from maps (1 : 25 000 scale) and aerial photographs (1:2500 scale), respectively.

Samples were taken at the deepest point of each lake. An equal volume of water was extracted (using a centrifugal electric pump) from four evenly spaced levels of the vertical profile, prefiltered through a 40-µm nytal net to remove zooplankton, and then mixed together. Aliquots for analysis were taken from this mixed sample. Those for chemical analysis were stored in the dark at 4°C and analyzed within 24 h of sampling. Chlorophyll *a* (Chl *a*) was determined by filtering 1 L of water through a GF/C filter immediately after collection. The filter was placed in a glass vial, 10 mL of 95% methanol was added, and the vial was stored in the dark at 4°C during transport. The vial was then frozen at –10°C for 24 h and the extract was measured and corrected for pheopigments using an Hewlett-Packard scanning spectrophotometer. For the determination of SRP, filtered aliquots of the water samples (0.45-µm pore size Sartorius filter) were analyzed by the ascorbic acid method of Murphy and Riley (1962) using a 10-cm path length cuvette (detection limit 0.03 $\mu mol \cdot L^{-1}$ (~1 $\mu g \cdot L^{-1}$)). TP was determined as SRP after the digestion of unfiltered aliquots using a mixture of potassium persulphate and boric acid at 120ºC for 30 min. NH_4^+-N was determined in 0.45-µm filtrate using the blue indophenol method (Rodier 1990). NO_2^--N and NO_3^--N were determined following the method of Strickland and Parsons (1968) and of sodium salicylate (Rodier 1990), respectively. DIN is the sum of the three former N compounds. TN was determined using the ultraviolet method (APHA 1989) after the digestion of unfiltered aliquots using the same procedure described for TP. Concentrations and elemental ratios are reported by weight. The DIN:SRP ratio has been used as a ratio of nutrient supply to indicate N or P limitation (Morris and Lewis 1988). We used the value 10 (by weight) as a reference to indicate a lower limit of P limitation.

Data were $\log_{10}$ transformed prior to statistical analyses in order to achieve normality and homoscedasticity and to linearise their relationships. Statistical analyses were done using STATISTICA v. 4.0 except for the ANCOVA, which was performed using BMDP-PC90. In multiple regression, the ridge method (Hoerl 1962) for estimating regression coefficients was used when multicollinearity among the independent variables was found.

Results

The Chl *a* content in the lakes increased more than twice, from a mean value of 0.8 $\mu g \cdot L^{-1}$ in July to 1.9 $\mu g \cdot L^{-1}$ in August (Fig. 1). Moreover, the average TN for the lakes increased from 234.4 to 465.5 $\mu g\ N \cdot L^{-1}$, and the average TP increased more than fivefold, from 5.8 $\mu g\ P \cdot L^{-1}$ in July to 30.9 $\mu g\ P \cdot L^{-1}$ in August (Fig. 1). TN and TP concentrations in the lakes increased between July and August as described by the linear equation

$$\Delta TN = 4.388 + 9.078 \cdot \Delta TP \quad (r^2 = 0.71,\ p < 0.0001,\ n = 20).$$

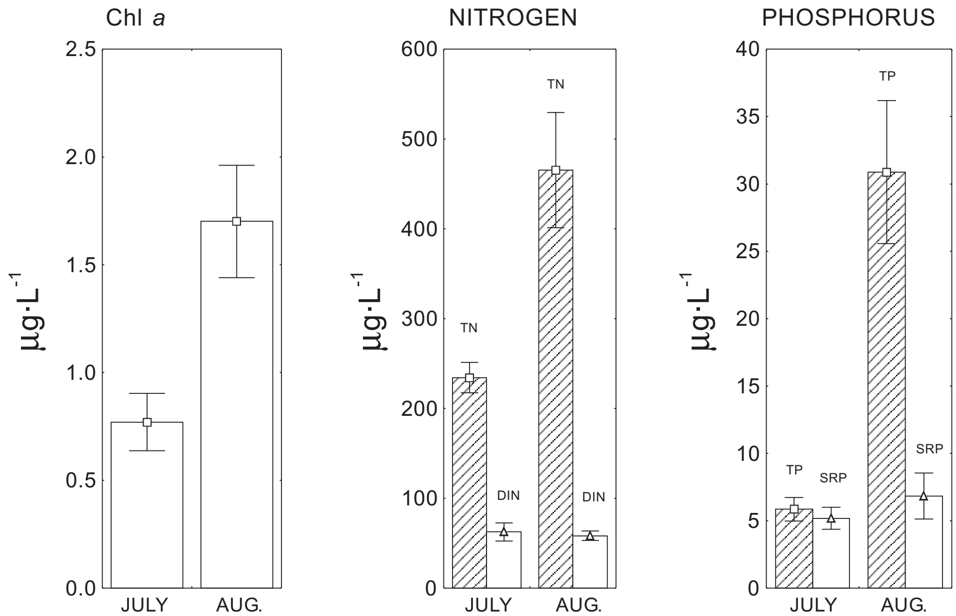
TN:TP ratios clearly differed between periods (Fig. 2). In July, TN:TP ratios were relatively high (80% of the lakes had ratios higher than 39 by weight), whereas they suffered a notable reduction in August (ratios ranged from 10 to 25) (Fig. 2). During the first period, no significant correlation existed between TN and TP, whereas during the second pe-

Table 1. Some characteristics of the Sierra Nevada study lakes.

Lake	Location UTM (30S)	Altitude (m above sea level)	Lake surface area (ha)	Catchment area (ha)	Maximum depth (m)	Outflow	DIN (μg N·L^{-1})	TN (μg N·L^{-1})	SRP (μg P·L^{-1})	TP (μg P·L^{-1})	Chl *a* (μg·L^{-1})
Virgen 1	VG665008	2950	0.08	25.1	1.3	1	108*	257	5	7	0.4*
Virgen 2	VG664009	2940	0.01	31.2	0.8	1	53	518	4	31	2.2
Dilar 1	VG659007	2870	0.01	71.3	1.0	0	—	117*	1*	2*	0.6*
Dilar 2	VG658006	2860	0.02	71.3	0.8	1	65*	177	16	18	0.3*
Yeguas	VG662013	2880	0.33	50.0	2.5	1	155	594	3	20	2.2
Lanjarón 1	VF646993	2980	0.29	35.8	2.5	1–0	23*	218*	10*	28*	1.1*
Lanjarón 2	VF641991	2940	0.05	7.0	1.0	1	28	276	8	25	1.1
Lanjarón 3	VF636985	2900	0.11	5.8	1.5	0	11	234	9	16	1.9
Mosca	VG723017	2920	0.44	39.7	2.8	1	149	308	4	11	2.1
Majano	VG712003	2900	0.27	72.2	0.8	1–0	62	809	4	33	1.9
Gemela	VG714004	2900	0.07	72.2	0.3	1	39	447	3	21	1.4
Caldera	VG708012	3050	2.10	23.5	7.0	0	101	315*	3	7	0.2
Aguas Verdes	VG674006	3050	0.19	12.8	2.8	1	45	216	8	12	0.6
Larga	VG704017	2790	1.77	29.4	7.0	0	83*	163	2	5	0.3
Rio Seco Superior	VG692008	3040	0.07	4.7	1.5	0	50	435	5	17	0.9
Rio Seco	VG694009	3020	0.42	9.9	2.0	1–0	22	292	3	8	0.5
Rio Seco Inferior	VG697008	3010	0.12	5.8	0.5	1–0	45	930	27	75	2.6
Siete Lagunas 1	VG731016	3060	0.57	10.1	2.5	0	129*	283*	8*	9*	0.9*
Siete Lagunas 2	VG735014	3020	0.34	27.4	3.5	1	68	251	4	13	0.5
Siete Lagunas 4	VG737012	2970	0.19	57.1	0.5	1	93	313	3	10	0.7
Siete Lagunas 5	VG734009	2980	0.18	50.9	2.0	1	65	380	3	16	1.7
Siete Lagunas 7	VG739004	2890	0.53	154.6	0.8	1	106	318	5	15	0.8
Caldereta 1	VG743033	2920	0.23	50.4	3.0	1	99*	255*	7*	7*	0.2*
Caldereta 2	VG745032	2900	0.59	50.4	2.0	0	17*	107*	8*	9*	0.3*
Caldereta 3	VG747033	2890	0.40	50.4	2.5	1	11*	172*	3*	4*	0.8*
Vacares	VG747046	2890	1.10	9.9	8.0	0	61*	112*	2*	3*	0.5*
Juntillas	VG766074	2940	0.11	6.3	1.5	1	42*	200*	2*	3*	0.5*
Mirador	VG691002	2870	0.07	18.2	0.4	1	13*	251*	5*	6*	1.8*
Peñón Negro	VF738983	2820	0.67	28.2	2.0	1	33	479	4	31	4.1
Caballo	VF612968	2840	0.48	10.5	4.0	0	15	161	3	10	0.3
Cuadrada	VF618975	2840	0.24	4.0	5.0	0	21	126*	6	8	0.5

Note: The first three numbers of the UTM coordinates indicate the position to the east and the last three the position to the north. Outflow: 1, lakes with outflow during both sampling periods; 0, lakes without outflow; 1–0, lakes with outflow in the first sampling but not in the second sampling. DIN, TN, SRP, TP, and Chl *a* values are averages for the two sampling periods (those marked with an asterisk are single values).

Fig. 1. Average (±SE) Chl *a*, TN, DIN, TP, and SRP in the Sierra Nevada study lakes during each period studied. Chl *a*, TN, and TP averages are significantly different (respective dependent *t* test: Chl *a* = –3.74 ($p < 0.002$, $n = 20$); TN = –3.23 ($p < 0.005$, $n = 20$); TP = –3.699 ($p < 0.002$, $n = 22$)).



riod, we found a highly significant relationship between the two $\log_{10}$-transformed variables ($r^2 = 0.70$, $p < 0.0001$, $n = 23$).

DIN and SRP concentrations and DIN:SRP ratios did not change between July and August as markedly as TN, TP, and TN:TP ratios (Figs. 1, 2, and 3). Each lake had similar DIN:SRP ratios in July and August. Only two lakes (marked with arrowheads on Fig. 3) had ratios that changed so greatly that they exceeded a value of 10 (our reference threshold for P limitation). Lakes with DIN:SRP ratios lower than 10 showed the highest values of SRP in August, whereas lakes with ratios higher than 10 had SRP values during this period below 3 $\mu g \cdot L^{-1}$ and the highest DIN values.

According to the regression analyses carried out ($\log_{10}$-transformed variables), the TN:TP ratio did not show a significant relationship to catchment area in July ($r^2 = 0.00$, $p = 0.763$, $n = 28$) or August ($r^2 = 0.02$, $p = 0.231$, $n = 23$) or when considering the average of the two periods ($r^2 = 0.00$, $p = 0.309$, $n = 20$). On the contrary, we found significant relationships between catchment basin area and the DIN:SRP ratio for both July ($r^2 = 0.24$, $p = 0.011$, $n = 26$) and August ($r^2 = 0.38$, $p = 0.0015$, $n = 22$), although the explained variance as well as the significance of the analysis increased in August. Since the relationship between catchment basin area and the DIN:SRP ratio may be affected by other factors such as outlets and depth of the lakes, we carried out an ANCOVA on the effect of the presence or absence of outflows on the DIN:SRP ratio, taking catchment basin size and depth as covariables. The result (Table 2) confirmed that catchment size had a significant effect on the DIN:SRP ratio in lakes, with and without outflows and regardless of depth.

In July, only DIN had a significant and positive correlation with catchment area (Fig. 4). In August, both DIN and SRP significantly depended on catchment area: positive for DIN and negative for SRP. Therefore, the improvement of the correlation between the DIN:SRP ratio and catchment size in August respective to July (see results above) depended mostly on the dynamics of SRP; the DIN:SRP ratio increased with catchment area, indicating a higher probability of P limitation in the lakes with larger catchments (Fig. 4).

The ratio of lake surface area (*S*) to catchment area (*A*) and lake volume (*V*) can be used in an index (*S*/*AV*) of the relative importance of atmospheric inputs in relation to runoff inputs. High *S*/*AV* values suggest a higher relative importance of atmospheric inputs. Otherwise, low *S*/*AV* values suggest a higher relative importance of runoff inputs. In Fig. 5, we show that the SRP increases were particularly evident in the lakes having a higher *S*/*AV* value.

The results obtained suggest that lakes in the Sierra Nevada with larger catchment areas are more likely to be P limited because of greater runoff inputs. The Chl *a* dependence on TP and (or) TN was assessed with a ridge regression (see Materials and methods), which considered TP and TN collinearity. For λ values between 0 and 0.1, β coefficients for log(TN) were not significant, whereas β coefficients for log(TP) were always significant ($p < 0.05$, at least). This result indicates that only TP had a significant effect on Chl *a* for the whole set of lakes. Nevertheless, catchment size determined the strength of correlation between Chl *a* and TP. Figure 6 shows the regression analysis between Chl *a* and TP for the lakes (Fig. 6A) and the changes in the explained variance of Chl *a* when the analysis was repeated sequentially in two ways. In the first analysis group (Figs. 6B and 6C, solid circles), we began calculating the regression for the four lakes with the smallest catchment areas. Then, we repeated the calculations including the lake with the next smallest catchment area, and so on. In the second analysis group (Figs. 6B and 6C, squares), the procedure was similar but starting with the four lakes with the largest catchment areas and adding sequentially the lake with the next largest

Fig. 2. Relationship between epilimnetic TN and TP concentrations in the Sierra Nevada study lakes during the two periods studied. The solid lines show examples of selected N:P mass ratios (by weight). The broken line shows the average TN:TP trend in world lakes found by Downing and McCauley (1992).

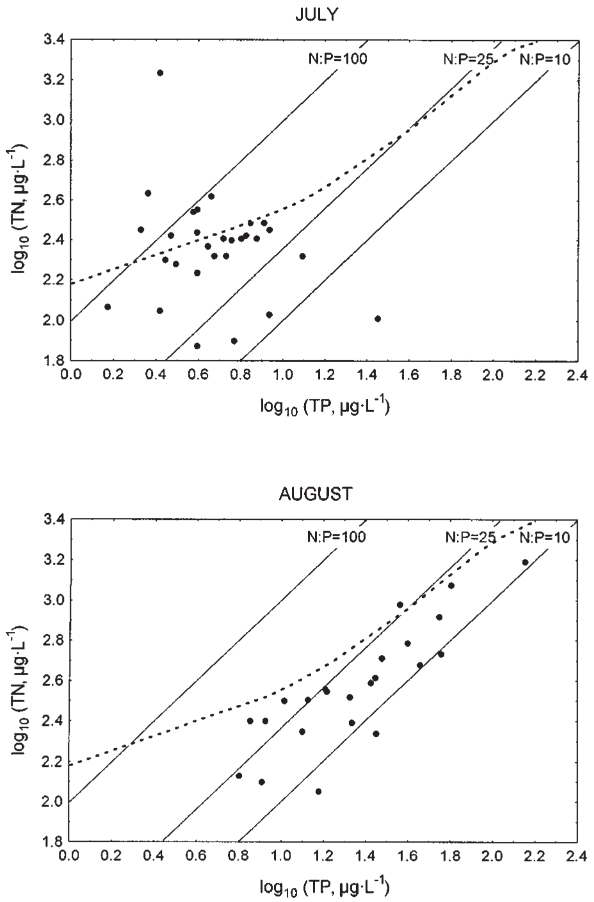
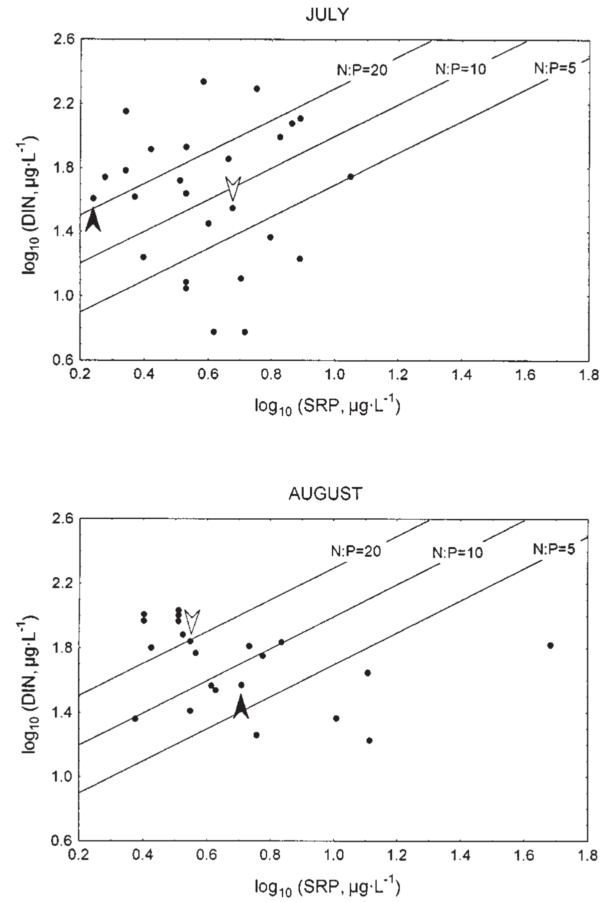


Fig. 3. Relationship between the epilimnetic DIN and SRP concentrations in the Sierra Nevada study lakes during the two periods studied. The solid lines show examples of selected N:P mass ratios (by weight). The lakes marked with arrowheads are the only ones that changed their ratios so greatly that they exceeded a value of 10 from July to August.



catchment area. Regressions were not significant when only the lakes with the smallest catchment areas were considered. With the inclusion of the ninth lake, the regressions started to be significant and the variance in Chl *a* explained by TP rose as lakes with successively larger catchments were included in the analysis. On the contrary, variance was best explained when only the lakes with larger catchment areas were included. Both regression sets suggest that lakes with small catchment areas are not P limited and this limitation is more likely as catchment area increases.

Discussion

The observed TN:TP reduction between July and August can be attributed to the increase in TP in lake waters. In July, TP was mostly in the form of SRP; however, DIN represented only a minor fraction of the TN. Levine and Schindler (1989) found that dissolved organic N has greater persistence than dissolved organic P in the water. They later used this to account for the fact that TN:TP ratios in fertilized enclosures were consistently higher than dissolved nutrient input ratios (Levine and Schindler 1992). According to our data, a higher persistence of dissolved organic N may explain the relatively high TN values in relation to TP in Sierra Nevada lakes in July. The small differences between SRP and TP suggest that P was not a limiting nutrient during this period.

The observed fall in TN:TP ratios from July to August can be understood as an accumulation of N and P in the plankton. Two pieces of evidence support this argument: first, Chl *a* increased between periods and second, TN and TP values increased in a proportion of 9:1 (by weight), which corresponds to plankton stoichiometry (Downing and McCauley 1992). Since TN increased in August, processes such as desnitrification or losses of N to the sediments are difficult to argue as alternative explanations.

In August, TN:TP ratios in the lakes were below world averages obtained by Downing and McCauley (1992). Low TN:TP ratios in Sierra Nevada fit the prediction of Downing and McCauley (1992) for lakes with small catchments in nonfertilized lands, suggesting that N:P ratios in precipitation were lower than in runoff in this area.

The importance and bioavailability of atmospheric P inputs for lakes with small catchments was demonstrated by Peters (1977). Recent research has shown that in those lakes, atmospheric precipitation can be a greater source of P than

Table 2. Results of ANCOVA indicating the effect of Sierra Nevada study lake outlets on $\log_{10}$(DIN:SRP) in August.

Source of variation	df	SS	*F*	*p*
Output	1	0.533	5.897	0.026
Both covariates	2	1.026	5.670	0.012
$\log_{10}$(area) covariate	1	0.735	8.131	0.011
$\log_{10}$(depth) covariate	1	0.495	5.471	0.031
Error	18	1.628		
Interaction				0.674

Note: Lakes were divided in two groups according to the presence or absence of outlets. Differences in mean $\log_{10}$(DIN:SRP) between groups (output) were tested including catchment area ($\log_{10}$(area)) and maximum depth ($\log_{10}$(depth)) as covariates. We show the effect of both covariates together and the single effect of each one. Nonsignificant differences between the slopes of the regression lines of covariate variables are given by the interaction probability value.

Fig. 4. Relationship between DIN (circles) and SRP (diamonds) concentrations and catchment area in the Sierra Nevada study lakes during the two periods studied. The broken vertical lines in August show reference DIN:SRP ratios for different catchment areas according to the regression obtained between DIN:SRP and catchment area in August (see text). July regression lines: $\log_{10}(\mathrm{DIN}) = 1.100 + 0.384 \log_{10}(\mathrm{area})$ ($r^2 = 0.14$, $p < 0.05$); $\log_{10}(\mathrm{SRP}) = 0.628 - 0.005 \log_{10}(\mathrm{area})$ (not significant). August regression lines: $\log_{10}(\mathrm{DIN}) = 1.271 + 0.311 \log_{10}(\mathrm{area})$ ($r^2 = 0.28$, $p < 0.01$); $\log_{10}(\mathrm{SRP}) = 1.101 - 0.305 \log_{10}(\mathrm{area})$ ($r^2 = 0.14$, $p < 0.05$).

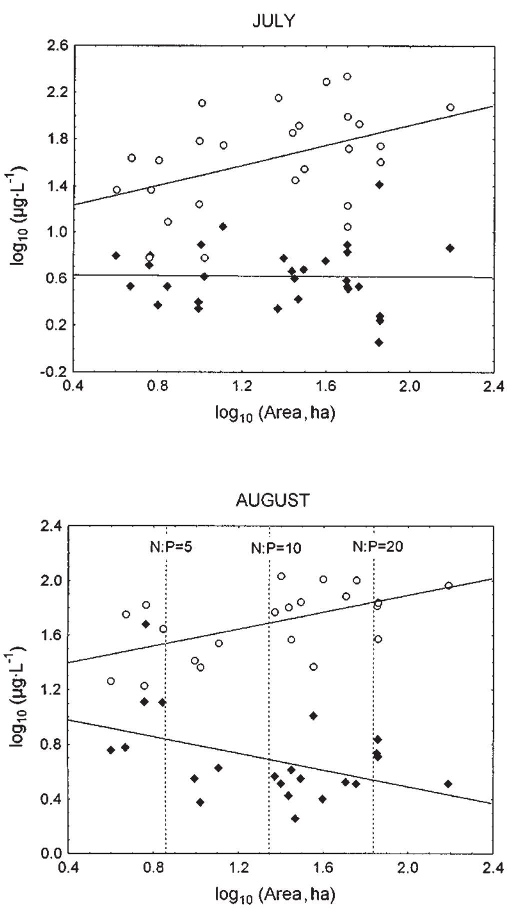
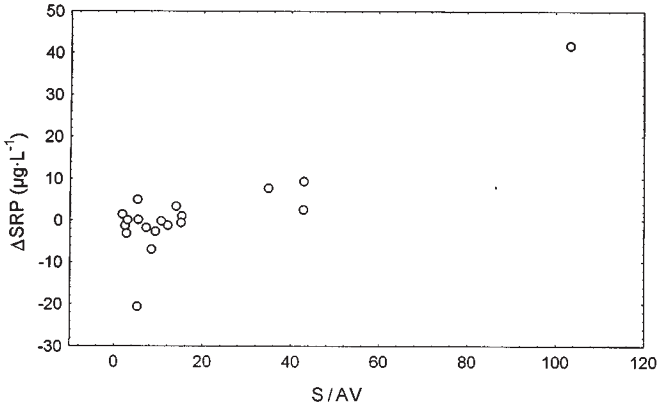


Fig. 5. Relationship between the increase in SRP (ΔSRP) from July to August in the Sierra Nevada study lakes and *S*/*AV*, where *S* is lake surface area (hectares), A is catchment area (hectares), and *V* is lake volume (cubic hectometres).



land runoff (Campbell 1994; Fee et al. 1994; Gibson et al. 1995). Especially low N:P ratios in the atmospheric precipitation of the Sierra Nevada may be expected as a consequence of the aforementioned Saharan dust. Talbot et al. (1986) measured in situ the chemical characteristics of the aerosol in an extensive Saharan dust plume. The main stream of the dust transport appeared at about 2500 m above sea level, showing a PO_4 concentration in the air of 265 ng·m^{-3} versus an NO_3 plus NH_4 concentration of 877 ng·m^{-3}, yielding an N:P ratio of 2.8 (by weight) for these compounds.

Low N:P ratios in the atmospheric inputs to the Sierra Nevada are also suggested by the positive correlation found between catchment area and the DIN:SRP ratio. This correlation indicates that lakes with smaller catchments could have more relative availability of P. Although both DIN and SRP may not reflect the exact availabilities of N or P for phytoplankton (Rigler 1966; Peters 1977), the DIN:SRP ratio, as a ratio of nutrient supply, has been used as an indicator of N or P limitation (Morris and Lewis 1988). The fact that most of the lakes studied here maintained DIN:SRP ratios during the two periods without exceeding the threshold value of 10 suggests that the observed increase in the planktonic biomass occurred under the same conditions of nutrient limitation for each lake. It has been argued that algal populations in small lakes are especially nutrient deficient because such lakes are well lit and have low turbulence (Fee et al. 1992). This argument can be applied to the Sierra Nevada lakes. Their maintenace of DIN:SRP ratios during phytoplankton growth may indicate the greater ability of dissolved inorganic compounds, compared with total compounds, to reflect external inputs. Therefore, the catchment size was related to the DIN:SRP ratio but not to the TN:TP ratio. Given the evidence, stoichiometrically supported, that nutrient recycling by herbivorous zooplankton accentuates the existing limiting conditions (Sterner 1990; Elser et al. 1995; Urabe et al. 1995), the more developed planktonic community in August could explain the improved relationship between catchment size and the DIN:SRP ratio observed in this month (Fig. 4). At this time, the failure of TP to explain Chl *a* variability when lakes with small catchments are considered agrees with a lack of P limitation in

Fig. 6. (A) Relationship between Chl *a* and TP in August in all the Sierra Nevada study lakes, (B) changes in the explained variance in Chl *a* by TP as lakes with increasing (solid circles) or decreasing (squares) catchment area are sequentially included in the regression (see text), and (C) the same as Fig. 6B but excluding the lake marked with an arrowhead in Fig. 6A. ns, regression not significant; *regression significant with $p < 0.05$; points not marked significant with $p < 0.01$ or higher significance.

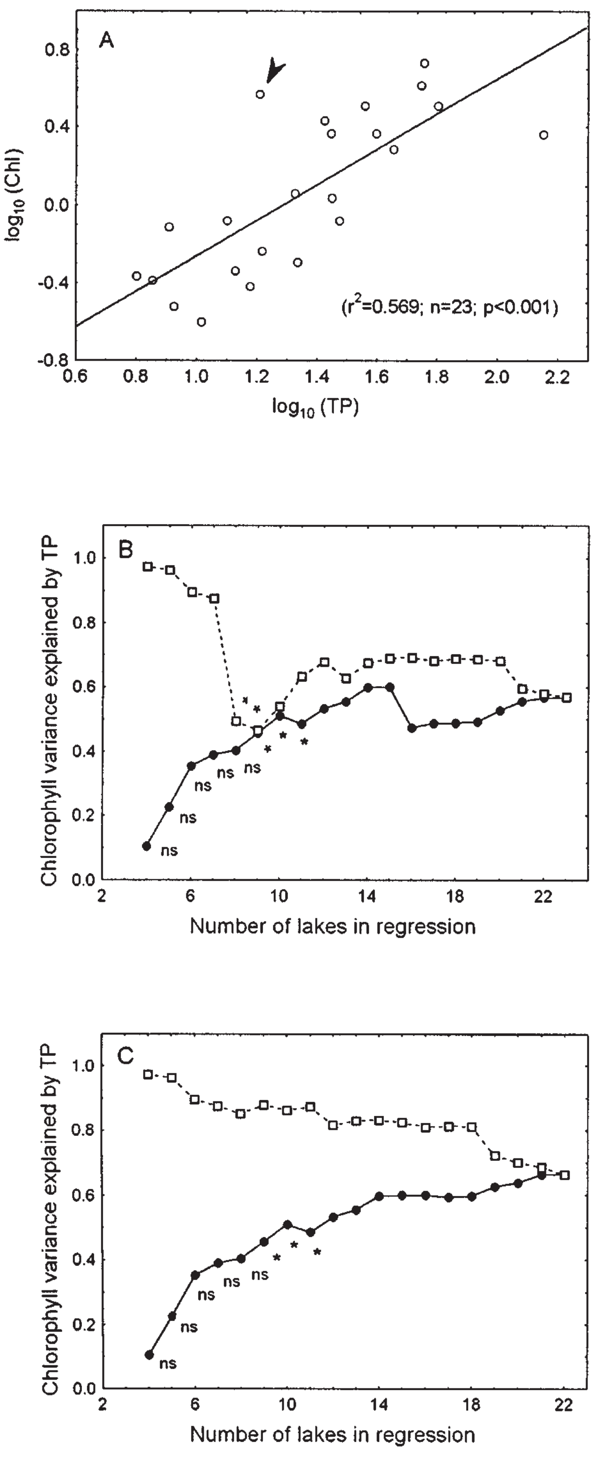
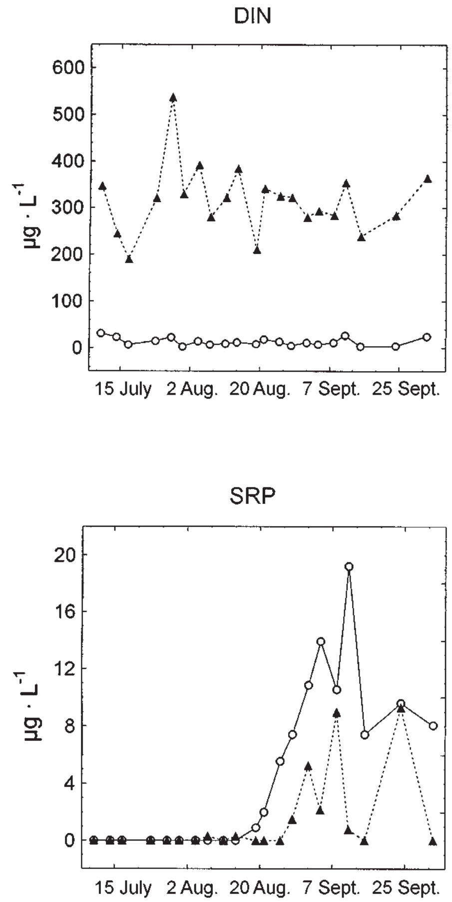


Fig. 7. Simultaneous dynamics of DIN and SRP during the entire ice-free period of 1986 in two Sierra Nevada lakes with different catchment areas, La Caldera (triangles) and Rio Seco (circles) (see Table 1) (data from Carrillo 1989).



these lakes, as the TP – Chl *a* relationship is especially well established in P-limited lakes (Dillon et al. 1988). Furthermore, in agreement with a predominant atmospheric origin of external P supplies to Sierra Nevada lakes, we found the highest SRP accumulation in the lake with the highest surface area relative to its catchment area and lake volume (Fig. 5).

A previous study describing detailed dynamics of nutrients in two lakes with different catchment areas (Carrillo 1989) (Fig. 7) also supports the abovementioned effect of catchment size on DIN:SRP ratios. The lake with higher catchment area (La Caldera) always showed higher DIN concentrations than the lake with smaller catchment area (Rio Seco) during the whole ice-free period. In both lakes, SRP increased during the second half of the season, but more conspicuously in the lake with the smallest catchment area (Rio Seco). Moreover, an increase in Chl *a* of about 100% was detected in La Caldera 5 days after one rain episode carrying Saharan dust (Carrillo et al. 1990).

On the other hand, this study provides evidence that TN:TP ratios of high mountain lakes within one geographical area change markedly at different times of the growing period. This result highlights the importance of performing comparative studies among lakes at the same seasonal stage. It also draws attention to the possibility of not finding the expected relationships concerning TN:TP ratios when the stages for each lake are not comparable. On the other hand, the validity of the results obtained in this study should be tested for larger lakes.

Finally, our results show that the high TN:TP ratios found in high mountain lakes in central Europe (Kopácek et al. 1995) do not constitute a general pattern for the entire Northern Hemisphere. Although there is evidence of dramatic increases in N precipitation in eastern North America and western Europe during this century (Brimblecombe and Stedman 1982), there is also evidence that N precipitation is not uniform in all parts of the Northern Hemisphere (Lohr et al. 1989). Moreover, local factors, such as we have discussed for the Sierra Nevada, may substantially alter N:P ratios in atmospheric precipitation. With Saharan dust flux values in the western Mediterranean of about 14 tonnes$\cdot$km$^{-2}\cdot$year^{-1} (Loÿe-Pilot et al. 1986), this possibility is worthy exploring in the future.

Aknowledgements

We thank M. Villar-Argaiz and I. Moreno-Garrido for field and laboratory help. The manuscript was improved by reviewer comments and criticisms. This research was supported by CICYT projects NAT89/1111 and AMB94/0021.

References

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. (APHA). 1989. Standard methods for the examination of water and wastewater. 17th ed. APHA, New York.

Brimblecombe, P., and Stedman, D.H. 1982. Historical evidence for a dramatic increase in the nitrate component of acid rain. Nature (Lond.), **298**: 460–462.

Campbell, P. 1994. Phosphorus budgets and stoichiometry during the open-water season in two unmanipulated lakes in the Experimental Lakes Area, northwestern Ontario. Can. J. Fish. Aquat. Sci. **51**: 2739–2755.

Carrillo, P. 1989. Análisis de las interacciones tróficas en el plancton de un sistema oligotrófico. Ph.D. thesis, Universidad de Granada, Granada, Spain.

Carrillo, P., Cruz-Pizarro, L., and Morales-Baquero, R. 1990. Effects of unpredictable atmospheric allochthonous input on the light climate of an oligotrophic lake. Verh. Int. Ver. Limnol. **24**: 97–101.

Cruz-Pizarro, L. 1983. Reproductive activity of *Mixodiaptomus laciniatus* (Copepoda, Calanoida) in the high mountain Lake La Caldera (Spain). Hydrobiologia, **107**: 97–105.

Dillon, P.J., Nicholls, K.H., Locke, B.A., de Grosbois, E., and Yan, N.D. 1988. Posphorus–phytoplankton relationships in nutrient-poor soft-water lakes in Canada. Verh. Int. Ver. Limnol. **23**: 258–264.

Dillon, P.J., Molot, L.A., and Scheider, W.A. 1991. Phosphorus and nitrogen export from forested stream catchments in central Ontario. J. Environ. Qual. 1991. **20**: 857–864.

Downing, J.A., and McCauley, E. 1992. The nitrogen:phosphorus relationship in lakes. Limnol. Oceanogr. **37**: 936–945.

Elser, J.J., Lubnow, F.S., Marzolf, E.R., Bret, M.T., Dion, G., and Goldman, C.R. 1995. Factors associated with interannual and intrannual variation in nutrient limitation of phytoplankton growth in Castle Lake, California. Can. J. Fish. Aquat. Sci. **52**: 93–104.

Fee, E.J., Shearer, J.A., DeRuyn, E.R., and Schindler, E.U. 1992. Effects of lake size on phytoplankton photosynthesis. Can. J. Fish. Aquat. Sci. **49**: 2445–2459.

Fee, E.J., Hecky, R.E., Regehr, G.W., Hendzel, L.L., and Wilkinson, P. 1994. Effects of lake size on nutrient availability in the mixed layer during summer stratification. Can. J. Fish. Aquat. Sci. **51**: 2756–2768.

Gibson, C.E., Wu, Y., and Pinkerton, D. 1995. Substance budgets of an upland catchment. The significance of atmospheric phosphorus inputs. Freshwater Biol. **33**: 385–392.

Henriksen, A., and Brakke, D.F. 1988. Increasing contributions of nitrogen to the acidity of surface waters in Norway. Water Air Soil Pollut. **42**: 183–201.

Hoerl, A.E. 1962. Application of ridge analysis to regression problems. Chem. Eng. Prog. **58**: 54–59.

Kopácek, J., Procházková, L., Stuchlík, E., and Blazka, P. 1995. The nitrogen–phosphorus relationship in mountain lakes: influence of atmospheric input, watershed, and pH. Limnol. Oceanogr. **40**: 930–937.

Levine, S.N., and Schindler, D.W. 1989. Phosphorus, nitrogen, and carbon dynamics during the recovery of a lake from eutrophication. Can. J. Fish. Aquat. Sci. **46**: 2–9.

Levine, S.N., and Schindler, D.W. 1992. Modification of the N:P ratio in lakes by in situ processes. Limnol. Oceanogr. **37**: 917–935.

Lohr, R.C., Ryding, S.O., and Sonzogni, W.C. 1989. Nutrient loading estimation in a water body. *In* The control of eutrophication of lakes and reservoirs. *Edited by* S.O. Ryding and W. Rast. UNESCO, Paris.

Loÿe-Pilot, M.D., Martin, J.M., and Morelli, J. 1986. Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean. Nature (Lond.), **321**: 427–428.

McCauley, E., Downing, J.A., and Watson, S. 1989. Sigmoid relationships between nutrients and chlorophyll among lakes. Can. J. Fish. Aquat. Sci. **46**: 1171–1175.

Molot, L.A., and Dillon, P.J. 1991. Nitrogen/phosphorus ratios and the prediction of chlorophyll in phosphorus-limited lakes in central Ontario. Can. J. Fish. Aquat. Sci. **48**: 140–145.

Morales-Baquero, R., Cruz-Pizarro, L., and Carrillo, P. 1989. Patterns in the composition of the rotifers communities from high mountain lakes and ponds in Sierra Nevada (Spain). Hydrobiologia, **186/187**: 215–221.

Morris, D.P., and Lewis, W.M. 1988. Phytoplankton nutrient limitation in Colorado mountain lakes. Freshwater Biol. **20**: 315–327.

Moulin, C., Lambert, C.E., Dulac, F., and Dayan, U. 1997. Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation. Nature (Lond.), **387**: 691–694.

Murphy, J., and Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. Ann. Chim. Acta, **27**: 31–36.

Peters, R.H. 1977. The availability of atmospheric orthophosphate. J. Fish. Res. Board Can. **34**: 918–924.

Rigler, F.H. 1966. Radiobiological analysis of inorganic phosphorus in lake water. Verh. Int. Ver. Limnol. **16**: 465–470.

Rigler, F.H., and Peters, R.H. 1995. Science and limnology. *In* Excellence in ecology. Vol. 6. *Edited by* O. Kinne. Ecology Institute, Oldendorf/Luhe, Germany.

Rodier, J. 1990. Análisis de las aguas. Omega, Barcelona, Spain.

Sánchez-Castillo, P., Cruz-Pizarro, L., and Carrillo, P. 1989. Caracterización del fitoplancton de las lagunas de alta montaña de Sierra Nevada (Granada, España) en relación con las características fisico-químicas del medio. Limnetica, **5**: 37–50.

Sterner, R.W. 1990. The ratio of nitrogen to phosphorus resupplied by herbivores: zooplankton and the algal competitive arena. Am. Nat. **136**: 209–229.

Strickland, J.D.H., and Parsons, T.R. 1968. A practical handbook of seawater analysis. Bull. Fish. Res. Board Can. No. 167.

Talbot, R.W., Harris, R.C., Browell, E.V., Gregory, G.L., Sebacher, D.I., and Beck, S.M. 1986. Distribution and geochemistry of aerosols in the tropical North Atlantic troposphere: relationships to Saharan dust. J. Geophys. Res. **91**(D4): 5173–5182.

Urabe, J., Nakanishi, M., and Kawabata, K. 1995. Contribution of metazoan plankton to the cycling of nitrogen and phosphorus in Lake Biwa. Limnol. Oceanogr. **40**: 232–241.