

Atmospheric inputs of phosphorus and nitrogen to the southwest Mediterranean region: Biogeochemical responses of high mountain lakes

*Rafael Morales-Baquero*¹

Instituto del Agua and Departamento de Ecología, Universidad de Granada, 18071 Granada, Spain

Elvira Pulido-Villena

Departamento de Ecología, Universidad de Granada, 18071 Granada, Spain

Isabel Reche

Instituto del Agua and Departamento de Ecología, Universidad de Granada, 18071 Granada, Spain

Abstract

We quantified dry and wet deposition of dust, nitrogen, and phosphorus over the southwest Mediterranean region (Sierra Nevada, Spain) and assessed its effects on the nutrient status and the chlorophyll *a* (Chl *a*) concentration in two high mountain lakes. Atmospheric deposition of particulate matter (PM) and total phosphorus (TP) were mainly associated with dryfall and showed a seasonal pattern similar to that reported for Saharan dust export toward the Mediterranean region, with maxima during spring and summer. In contrast, total nitrogen (TN) deposition was related to rainfall and did not follow the pattern observed for PM and TP. The molar TN:TP ratio was significantly lower (i.e., phosphorus-enriched) in dry deposition (TN vs. TP slope = 11.2) than in wet deposition (TN vs. TP slope = 95.5). In the study lakes, the molar TN:TP ratios and the Chl *a* concentrations were significantly influenced by the molar TN:TP ratio and the TP content of atmospheric deposition, respectively. Lake responses were more pronounced in the more phosphorus-limited system. These results establish a direct connection between atmospheric deposition and lake nutrient status and Chl *a*, making evident that in the Mediterranean region these inputs are an important source of phosphorus affecting biogeochemistry of oligotrophic systems.

Atmospheric deposition is a significant input of gaseous (e.g., nitrogen) and lithosphere-derived (e.g., phosphorus) elements to aquatic and terrestrial ecosystems (Chadwick et al. 1999; Guerzoni et al. 1999). Nitrogen deposition in the Northern hemisphere has increased as the result of anthropogenic activity, and its effects on lake chemistry have been intensely studied (Sullivan et al. 1990; Stoddard et al. 1999). In contrast, atmospheric inputs of phosphorus derived from Saharan dust deposition and their effects on ecosystems have received attention only recently (Ridame and Guieu 2002; Okin et al. 2004). Every year, massive airborne plumes of dust from the Sahara Desert are exported to the Atlantic Ocean by the predominant westerly winds. In the Mediterranean region, maximum loads occur during spring and sum-

mer under particular meteorological conditions (Moulin et al. 1997). Currently, there is a considerable interest in the effects of this dust deposition on the biogeochemistry of the Mediterranean Sea (Guerzoni et al. 1999; Herut et al. 1999, 2002) and, in particular, on the availability of dust-derived P to primary producers (Migon and Sandroni 1999; Ridame and Guieu 2002; Markaki et al. 2003). The effect of such atmospheric inputs appears to be particularly significant in oligotrophic waters (Bergametti et al. 1992).

Dust deposition was first recognized as a major source of nutrients to low-productivity lakes in the 1970s (Peters 1977). However, in comparison to marine ecosystems, the effects of dust deposition on lake biogeochemistry have been rarely studied (Gibson et al. 1995). In particular, high mountain lakes are expected to be particularly sensitive to dust deposition because of their extreme oligotrophy and low nutrient levels.

Sierra Nevada (Spain) is located in a region where atmospheric deposition has been poorly explored compared with rest of the Mediterranean basin. This area is an ideal site to assess the biogeochemical response of lakes to dust deposition because (1) it is close to the Sahara Desert (70% of dust export is deposited within the first 2000 km; Jaenicke and Schütz 1978); (2) it has altitudes above 3000 m above sea level (asl; the mainstream of Saharan dust transport is between 1500 and 4000 m asl; Talbot et al. 1986); and (3) there are around 50 oligotrophic and dilute lakes between 2800 and 3100 m asl that are potentially sensitive to dust deposition. In this study, we quantified dry and wet atmospheric deposition of particulate matter (PM), nitrogen (N),

¹ Corresponding author (rmorales@ugr.es).

Acknowledgments

We thank J. A. Delgado, D. Fernandez-Moreno, E. Ortega-Retuerta, J. M. Pérez, and O. Romera for their help in the field and laboratory. The NASA–Goddard Space Flight Center Total Ozone Mapping Spectrometer group provided daily data on the TOMS aerosol index. The Sierra Nevada National Park Office allowed us to carry out this study in a protected area. We are grateful to J. R. Francia (CIFA, Granada, Spain) and to the director and technical staff of the Observatorio de Sierra Nevada (Instituto de Astrofísica de Andalucía, CSIC, Granada, Spain) for allowing us to install atmospheric deposition samplers. We also thank two anonymous reviewers and the associate editor, Raymond Henry Hesslein, for suggestions to improve a previous version. This research was supported by the projects CICYT AMB99-0541 and CICYT REN03-03038 and an FPI grant from the Spanish government to E.P.-V.

Table 1. Morphometric; chemical (ANC, acid neutralizing capacity; Ca, calcium; NO_3^- , nitrate; SRP, soluble reactive phosphorus; TN, total nitrogen; TP, total phosphorus; DOC, dissolved organic carbon); and biological characteristics (Chl *a*) of the study lakes for the ice-free periods of 2000, 2001, and 2002.

	La Caldera Lake		Río Seco Lake	
	Mean	Range	Mean	Range
Lake area* (ha)	2.10		0.42	
Catchment area* (ha)	23.5		9.9	
Maximum depth* (m)	10		3	
ANC† (meq L ⁻¹)	0.31	0.23–0.43	0.12	0.05–0.20
Ca† (μmol L ⁻¹)	110	91–118	37	25–51
NO_3^- † (μmol L ⁻¹)	10.1	0.9–20.6	1.4	0.1–4.1
SRP† (μmol L ⁻¹)	0.02	0–0.13	0.07	0–0.31
TN (μmol L ⁻¹)	23.6	7.2–41.0	27.6	3.4–52.3
TP (μmol L ⁻¹)	0.15	0.04–0.35	0.53	0.17–2.78
DOC† (μmol L ⁻¹)	60.5	23.3–145.7	145.0	62.1–283.5
Chl <i>a</i> ‡ (μg L ⁻¹)	0.75	0.23–1.57	1.44	0.62–3.00

* From Morales-Baquero et al. (1999).

† Data from Pulido-Villena (2004).

‡ Only data from 2001 and 2002.

and phosphorus (P) in Sierra Nevada and we assessed the effects of N and P atmospheric inputs on the nutrient status and the chlorophyll *a* (Chl *a*) concentration in two high mountain lakes differing in trophic and watershed characteristics.

Materials and methods

Atmospheric deposition sampling—Separate samples of dry and wet atmospheric deposition were collected using MTX ARS 1010 automatic deposition samplers located in two sites of Sierra Nevada. One sampler was installed in a high-altitude site at 2900 m asl (37°03'N, 3°23'W) and collected weekly during the ice-free periods of 2000, 2001, and 2002. Due to technical difficulties, only bulk deposition was collected during 2000. The other sampler was installed at 1000 m asl (36°34'N, 3°17'W) and collected weekly from November 2000 to December 2002. Rainfall volume was supplied by meteorological stations located at 1000 m asl (Lanjarón, CIFA, J.R. Francia pers. comm.) and at 2900 m asl (CETURSA, Sierra Nevada). During the study period, the annual mean rainfall at 1000 m asl was 450 mm and at 2900 m asl was 969 mm. At this last altitude, the rainfall for the ice-free period (June–September) was 87.0 mm during 2001 and 35.1 mm during 2002. On every sampling date, dry and wet deposition buckets from both collectors were replaced and taken to the laboratory. Dry deposition was collected by rinsing the bucket with 1000 mL of Milli-Q ultrapure water, and this solution was used for chemical analyses. The volume of rain in the wet deposition bucket was recorded, and a 1000-mL aliquot was used for analysis. If the rain volume was <1000 mL, it was brought up to that volume with Milli-Q ultrapure water.

Study lakes and sampling—To explore biogeochemical responses to atmospheric inputs of the high-mountain lakes from Sierra Nevada, we selected two systems (La Caldera and Río Seco) that represent contrasting nutrient and trophic conditions (Table 1). Both lakes are located above 3000 m

asl and ice-covered for 8–9 months. They do not stratify and have very simple food webs (no fish). La Caldera is a seepage lake in rocky watershed with no terrestrial vegetation. In contrast, Río Seco is located in a catchment partially covered (~15%) by alpine meadows and has temporal inlets that drain water from the catchment. Therefore, the selected study lakes represent contrasting nitrogen and phosphorus availabilities with a higher terrestrial N export, and a higher P deficiency in La Caldera than in Río Seco (Morales-Baquero et al. 1999).

The study lakes were sampled weekly for total phosphorus (TP), total nitrogen (TN), and Chl *a* during the ice-free periods of 2000 (only TP and TN), 2001, and 2002, coinciding with the sampling of the atmospheric collector located at 2900 m asl. Samples from La Caldera (maximum depth ~10 m) were collected by pumping water from depths of 9, 7, 5, 3, and 1 m and mixing them in equal parts to produce a single integrated sample. Since Río Seco (maximum depth ~3 m) is shallower than La Caldera, samples from this lake were collected using a column sampler (10 cm in diameter and 1 m in length) from 0 to 1 m depth.

Chemical and biological analyses—Concentration of particulate matter (PM) in dry and wet deposition was determined as dry weight (60°C, 24 h) using glass-fiber filters (Whatman GF/F). Prior to filtration, 50-mL aliquots from dry and wet deposition samples were taken to analyze TP and TN concentration. TP from atmospheric deposition and lake water was analyzed as soluble reactive phosphorus (Murphy and Riley 1962) after digestion with a mixture of potassium persulphate and boric acid at 120°C for 30 min. TN was analyzed as NO_3^- following the ultraviolet method (APHA 1992) after digestion with the same procedure used for TP. Chl *a* concentration was determined spectrophotometrically after pigment extraction with methanol (APHA 1992).

Calculation of deposition rates—Concentrations of PM (mg L⁻¹) and TP and TN (μmol L⁻¹) in dry and wet depo-

sition samples collected during each week were converted to units of daily deposition using the following equation:

$$\text{Deposition (mg or } \mu\text{mol m}^{-2} \text{ d}^{-1}\text{)} \\ = \frac{\text{concentration (mg or } \mu\text{mol L}^{-1}\text{)}}{A \text{ (m}^2\text{)} \cdot 7 \text{ (d)}} \cdot F$$

where A is the bucket area and F is a correction factor for the rain volume; F is equal to 1 for dry deposition samples and when the rain volume is <1 L, but equal to volume of rain when volume ≥ 1 L.

Remote sensing—To assess whether dry deposition of PM in the study area was related to aerosol content in the troposphere, we used the aerosol index developed by the Ozone Processing Team (NASA/GSFC) from measured radiances by the Total Ozone Mapping Spectrometer (TOMS) on board the NASA Earth Probe satellite, which has been successfully applied to the study of Saharan dust (Chiapello et al. 1999). We used weekly averages of daily TOMS data (NASA Goddard Space Flight Center; Torres et al. 1998, 2002) given for 36.5°N, 4.375°W.

Statistical analysis—To assess whether the atmospheric inputs of TP, TN, and the ratio of TN:TP were dependent on the rainfall and/or dryfall, we performed multiple regression analyses with dry + wet deposition (hereafter, total deposition) of TP, TN, and TN:TP ratio as dependent variables and the rainfall volume and dry PM deposition as independent variables.

Since synchronous dynamics of variables among neighbor lakes is considered as a sign of climatic control at regional scale (Baines et al. 2000), we first performed correlation analyses between the dynamics of TN:TP ratios and Chl a concentrations of the study lakes to evaluate if there was any lake-external control. To corroborate the respective influence of atmospheric deposition on lake nutrient and trophic status, we performed linear regression analyses using the atmospheric TN:TP ratio and TP of total deposition at 2900 m asl as independent variables and the lake TN:TP ratio and Chl a concentration as dependent variables.

Results

Atmospheric deposition of particulate matter (PM)—The respective dry and wet deposition of PM was 0.3–105.8 and 0–95.8 mg m⁻² d⁻¹ at 1000 m asl (Fig. 1), with the mean annual fluxes of 8.8 and 2.4 g m⁻² yr⁻¹ (Table 2). The relative contribution of dry to the total deposition of PM was 79% in both study years (Table 2). Dry PM deposition varied seasonally, with maxima in spring and summer and minima in winter (Fig. 1), and was significantly correlated with the TOMS index ($n = 107$, $r = 0.40$, $p < 0.001$). In contrast, wet PM deposition did not show any seasonal trend (Fig. 1). Dry and wet depositions of PM were higher at 2900 m than at 1000 m in both years (Fig. 1), with higher values in 2001 (Table 2).

Atmospheric deposition of total phosphorous (TP)—The respective dry and wet deposition of TP was 0.1–3.1 and 0–

2.4 $\mu\text{mol m}^{-2} \text{ d}^{-1}$ at 1000 m asl (Fig. 1), with the mean annual fluxes of 369 and 144.4 $\mu\text{mol m}^{-2} \text{ yr}^{-1}$ (Table 2). The average contribution of dry to the total deposition of TP was 72%. Dry TP deposition showed seasonal dynamics similar to dry PM deposition (Fig. 1), and both variables were significantly and positively correlated ($n = 107$, $r = 0.45$, $p < 0.001$). In contrast, wet TP deposition did not show any seasonal trend (Fig. 1). In general, dry and wet depositions of TP were higher at 2900 m than at 1000 m (Fig. 1), with higher values in 2001 (Table 2). Both the rainfall and the dry PM deposition contributed significantly to total TP deposition, although the significance level of this last variable was higher than that of rainfall (Table 3).

Atmospheric deposition of total nitrogen (TN)—The respective dry and wet deposition of TN was 6.6–304.4 and 0–517.2 $\mu\text{mol m}^{-2} \text{ d}^{-1}$ at 1000 m asl (Fig. 1), with the mean annual fluxes of 17.7 and 21.9 mmol m⁻² yr⁻¹ (Table 2). Contrary to PM and TP, the relative contribution of dry to total deposition of TN was slightly lower (44%) than the contribution of wet deposition. No seasonal trends in dry deposition were observed, and hence it did not show any significant relationship with dry PM deposition ($n = 104$, $r = 0.03$, $p > 0.05$). Except for wet deposition in 2001, TN deposition was higher at 2900 m than at 1000 m (Fig. 1). Unlike total TP deposition, only rainfall contributed significantly to total input of TN (Table 3).

TN:TP ratio of atmospheric deposition—The molar TN:TP ratio of total deposition ranged from 13.6 to 432.1 at 1000 m asl and from 10.5 to 156.1 at 2900 m asl and showed a clear seasonal pattern with minima during spring and summer and maxima during winter (Fig. 2). At 1000 m, TN and TP of atmospheric deposition were significantly related in dry (TN = 27.5 + 11.2 TP; $n = 96$, $r^2 = 0.28$, $p < 0.001$) and wet deposition (TN = 50.5 + 95.5 TP; $n = 52$, $r^2 = 0.21$, $p < 0.001$), although these regression lines were markedly different. The slope of the relationship for the dry deposition was significantly lower than that for the wet deposition ($F_{1,144} = 16.9$; $p < 0.001$). The TN:TP ratio of atmospheric deposition was affected negatively by dry PM deposition and positively by rainfall (Table 3).

Lake biogeochemical responses to atmospheric deposition—In La Caldera, the TN:TP ratios were always higher than in Río Seco, indicative of its stronger P deficiency, although the molar TN:TP ratios of both lakes were synchronous for 2000, 2001, and 2002 (Fig. 3; $n = 33$, $r = 0.57$, $p < 0.01$). In fact, the lake TN:TP ratios showed a significant and positive relationship with the molar TN:TP ratio of atmospheric deposition in La Caldera (TN:TP_{lake} = 108.4 + 1.3 TN:TP_{atm}; $n = 29$, $r^2 = 0.40$, $p < 0.001$) and in Río Seco (TN:TP_{lake} = 45.3 + 0.2 TN:TP_{atm}; $n = 30$, $r^2 = 0.20$, $p < 0.05$). The slope of this relationship was significantly greater in La Caldera than in Río Seco ($F_{1,55} = 8.07$; $p < 0.01$).

The concentration of Chl a in La Caldera and in Río Seco showed synchronous dynamics during the ice-free period of 2001 ($n = 10$, $r = 0.78$, $p < 0.01$), although not during 2002 ($n = 12$, $r = -0.36$, $p > 0.05$). The Chl a concentra-

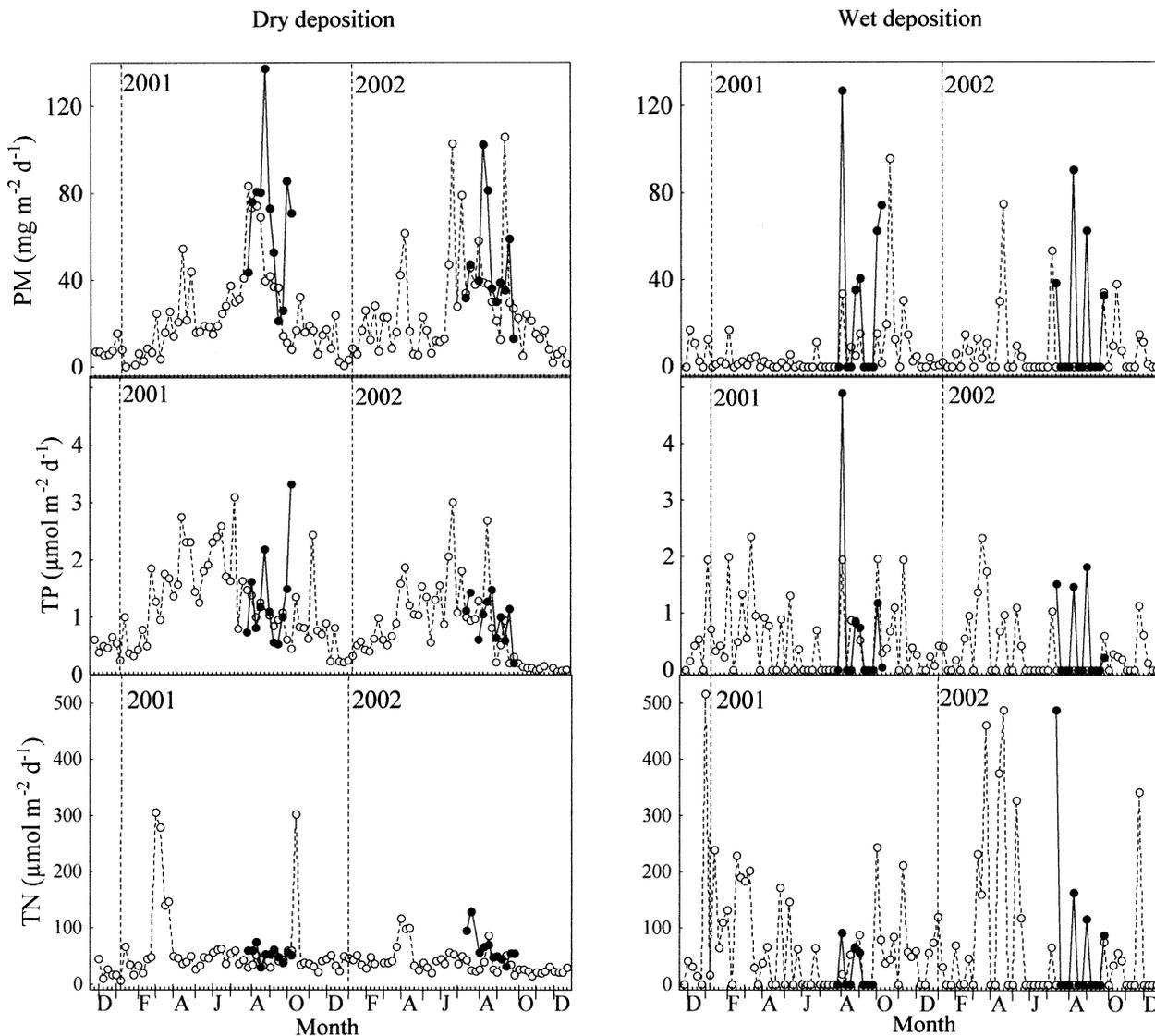


Fig. 1. Seasonal dynamics of dry and wet atmospheric deposition of particulate matter (PM; $\text{mg m}^{-2} \text{d}^{-1}$); total phosphorus (TP; $\mu\text{mol m}^{-2} \text{d}^{-1}$); and total nitrogen (TN; $\mu\text{mol m}^{-2} \text{d}^{-1}$) at 1000 m asl (empty circles) and at 2900 m asl (filled circles).

tion showed a significant and positive relationship with the total TP deposition in La Caldera ($\text{Chl } a = 0.46 + 0.13 \text{ TP}_{\text{atm}}$; $n = 19$, $r^2 = 0.66$, $p < 0.001$), but not in Río Seco ($n = 20$, $r^2 = 0.00$, $p = 0.918$). Considering exclusively the ice-free period of 2001, significant and positive relationships between TP atmospheric inputs and the Chl *a* concentration were found in La Caldera ($n = 9$, $r^2 = 0.88$, $p < 0.001$) and in Río Seco ($n = 9$, $r^2 = 0.49$, $p < 0.05$; Fig. 4). During 2002, Chl *a* concentrations were not related to TP deposition either in La Caldera Lake ($n = 10$, $r^2 = 0.15$, $p = 0.265$) or in Río Seco Lake ($n = 11$, $r^2 = 0.03$, $p = 0.612$).

Discussion

Dust deposition in the Mediterranean region conforms to a regional pattern, with values declining with distances from the north of Africa and toward the west (Goudie and Mid-

dleton 2001). For instance, maximum reported values range from 36 to $72 \text{ g m}^{-2} \text{ yr}^{-1}$ for the east Mediterranean Sea and minimum values from 0.2 to $0.4 \text{ g m}^{-2} \text{ yr}^{-1}$ in the Alps (Wagenbach and Geis 1989; De Angelis and Gaudichet 1991; Herut and Krom 1996). Our PM total deposition data (10.9 and $11.3 \text{ g m}^{-2} \text{ yr}^{-1}$ in 2001 and 2002, respectively) fit this regional trend, being similar to other sites in the west Mediterranean such as Corsica ($12\text{--}12.5 \text{ g m}^{-2} \text{ yr}^{-1}$; Löye-Pilot et al. 1986; Bergametti et al. 1989).

In the study area, Saharan dust dominated the PM deposition especially during spring and summer. Dry PM deposition exhibited a similar seasonal pattern to Saharan dust export to the Mediterranean basin, which is characterized by maximum values during spring and summer (Moulin et al. 1997). There was also a positive relationship between dry PM deposition and the TOMS aerosol index, which estimates Saharan dust content in the atmosphere (Chiapello et

Table 2. Annual and ice-free period cumulative deposition (dry, wet) of particulate matter (PM), total phosphorus (TP), and total nitrogen (TN) at the study sites located at 1000 and 2900 m asl.

	Altitude (m asl)	2000		2001		2002	
		Bulk	Dry	Wet	Dry	Wet	
PM (g m ⁻²)							
Annual	1000		8.6	2.3	8.9	2.4	
Ice-free period	2900	3.2	5.2	2.4	3.6	1.6	
	1000		3.4	0.6	3.3	0.2	
TP (μmol m ⁻²)							
Annual	1000		451.5	184.1	285.5	104.7	
Ice-free period	2900	145.2	101.9	54.1	73.9	35.2	
	1000		71.0	45.2	76.8	4.2	
TN (mmol m ⁻²)							
Annual	1000		22.1	23.1	13.3	20.6	
Ice-free period	2900	6.1	4.1	1.5	4.9	6.0	
	1000		3.2	3.8	2.8	0.5	

al. 1999). Finally, the higher PM deposition registered at 2900 m than at 1000 m is concordant with the dynamics of Saharan dust transport, with maximum loads occurring between 1500 and 4000 m (Talbot et al. 1986).

The relative contribution of dry or wet deposition to total PM atmospheric inputs is determined by the rainfall regimes, which are highly variable in the Mediterranean region. For instance, in the Turkish coast of the eastern Mediterranean, the relative contribution of dry deposition to PM inputs can reach up to 93% during the summer (Kubilay et al. 2000), whereas in the northwest Mediterranean it is considered negligible (Bergametti et al. 1992). In our study area, dry contribution to total deposition of PM (69% in 2001 and 79% in 2002) was higher than the wet contribution, which is expected for an arid area.

Phosphorus and nitrogen deposition—In the Mediterranean basin, major sources of P to atmosphere are Saharan dust (Migon and Sandroni 1999; Guieu et al. 2002) and anthropogenic activities such as biomass burning (Bergametti et al. 1992; Migon and Sandroni 1999). In this study, TP and PM deposition showed similar seasonal dynamics, suggesting an important contribution of Saharan dust to TP deposition. Establishing a regional pattern of TP deposition is difficult because of the scarcity of reported data. TP deposition registered in this study was lower than in the Israeli

coast (1300 μmol m⁻² yr⁻¹), which receives the highest Saharan dust flux in the Mediterranean region (Herut et al. 1999). Although Saharan dust deposition is lower in Corsica, a similar TP deposition was reported (1295 μmol m⁻² yr⁻¹) by Bergametti et al. (1992). However, these last authors estimated that P from Saharan dust was about 500 μmol m⁻² yr⁻¹ (40% of the total), similar to our values.

N deposition is mostly linked to anthropogenic activity (Driscoll et al. 2003). Most studies on N deposition over the Mediterranean region have focused only on inorganic fractions (Guerzoni et al. 1999), making regional comparisons of TN deposition difficult. TN deposition that we measured was lower than N (only inorganic fractions) deposition in the northwest Mediterranean (55 mmol m⁻² yr⁻¹; Guerzoni et al. 1999) and in the east Mediterranean (about 50 mmol m⁻² yr⁻¹; Herut et al. 2002; Markaki et al. 2003). The comparatively low TN deposition in our study likely reflects the scarce industrial and agricultural activity of this area.

Most P inputs over our study area were linked to dry deposition, which is similar to previous studies in the East Mediterranean (Herut et al. 1999; Markaki et al. 2003). In contrast, wet deposition contributed more than 50% to N inputs, which is similar to the northwest Mediterranean (Guerzoni et al. 1999).

Rainfall significantly affected both TN and TP inputs (Table 2), and it is an effective mechanism of dust deposition,

Table 3. Results of the multiple regression analyses performed to assess the influence of dryfall (sedimentation) and rainfall (washout) on total atmospheric inputs of total phosphorus (TP) and total nitrogen (TN) and on TN:TP molar ratio in atmospheric deposition. Dry PM deposition and rainfall (surrogates of sedimentation and washout, respectively) were selected as independent variables.

	TP (μmol m ⁻² d ⁻¹)			TN (μmol m ⁻² d ⁻¹)			TN:TP molar ratio		
	β	b	p-level	β	b	p-level	β	b	p-level
PM (mg m ⁻² d ⁻¹)	0.32	0.01	<0.001	-0.07	-0.44	n.s.	-0.36	-1.49	<0.001
Rainfall (L m ⁻² d ⁻¹)	0.24	0.08	<0.05	0.52	21.96	<0.001	0.19	5.54	<0.05
Intercept		0.97	<0.001		92.30	<0.001		0.97	<0.001
	R ² = 0.12; p < 0.001			R ² = 0.29; p < 0.001			R ² = 0.20; p < 0.001		

β, Standardized regression coefficient; b, nonstandardized regression coefficient.

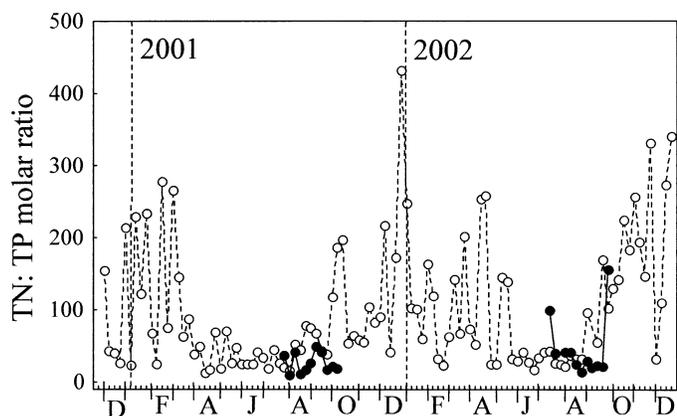


Fig. 2. Seasonal dynamics of the molar TN:TP ratio in (dry + wet) atmospheric deposition at 1000 m asl (empty circles) and at 2900 m asl (filled circles).

especially in Mediterranean areas (Guerzoni et al. 1999) where even a few drops of rainwater lead to significant TP deposition (Ridame and Guieu 2002). On the other hand, since dryfall affected significantly only TP deposition, an increase of dry PM deposition would lead to higher TP but not TN deposition.

The scarce human influence in our study area (low N deposition) along with the dry summers (relatively high P deposition) explains the marked seasonality of atmospheric TN:TP ratios (Fig. 2). This seasonal pattern contrasts with the results reported by Markaki et al. (2003) for the eastern Mediterranean, where TN:TP ratios were relatively constant over the year. In addition, in this study the slope of the TN:TP relationship in dry deposition was lower than 16, indicating that dust is relatively P-enriched compared with the Redfield ratio. In contrast, the slope of the TN:TP relationship in wet deposition was above 16, underlining the relevance of rainfall as a vehicle of N deposition.

Lake biogeochemical responses to atmospheric inputs—

The lake TN:TP ratio is influenced by external factors such as atmospheric inputs and watershed characteristics (Kopáček et al. 1995). Most studies regarding the atmospheric influence on lake nutrient status have focused on anthropogenic N-enriched deposition (Kopáček et al. 1998; Stoddard et al. 1999). However, our study attempts to establish a direct connection between P-enriched dust deposition and lake nutrient status.

The synchronous dynamics of TN:TP ratios of both study lakes suggest a climatic control in this area (Fig. 3). Indeed, the TN:TP ratio of the atmospheric deposition significantly influenced the lake TN:TP ratios in both study systems, although the magnitude of its effect (slopes of regression lines) was significantly different for each lake. This implies that a decrease in the TN:TP ratio of atmospheric deposition linked to Saharan dust deposition would lead to a more pronounced decrease in the TN:TP ratio in La Caldera than in Río Seco. This lake-specific response is likely related to the higher P-limitation in La Caldera than in Río Seco, which depends on their respective watersheds and morphometries.

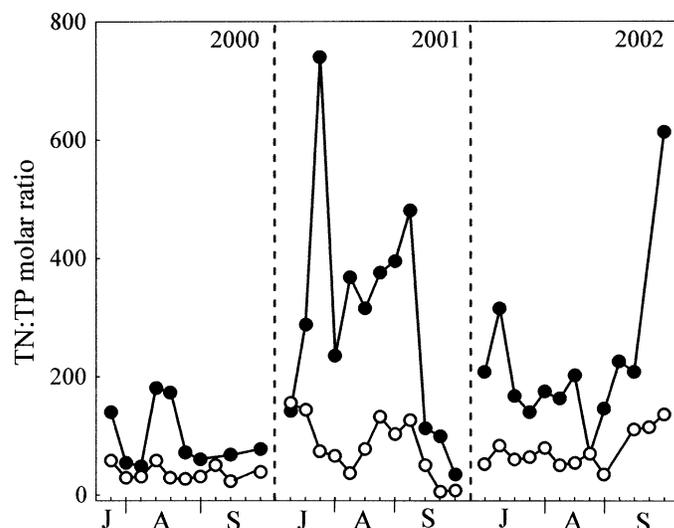


Fig. 3. Ice-free period dynamics of the molar TN:TP ratio in La Caldera (filled circles) and Río Seco (empty circles) during 2000, 2001, and 2002.

The absence of vegetation in the catchment of La Caldera probably leads to relatively low N retention (Gibson et al. 1995; Kopáček et al. 2000), accentuating P deficiency in this lake. These results underline the relevance of dust deposition in determining nutrient status, particularly in P-limited aquatic ecosystems.

Previous indirect evidences have suggested that P contained in dust stimulates primary producers, especially in the Mediterranean Sea (Herut et al. 1999; Ridame and Guieu 2002; Markaki et al. 2003). In this study, we directly related TP deposition to Chl *a*. The frequency of Saharan dust intrusions (Querol et al. 2003) and rainfall over the study area was higher in 2001 than in 2002, resulting in a higher variability of TP deposition at 2900 m (Fig. 1, filled symbols). This might explain the response of Chl *a* to TP deposition

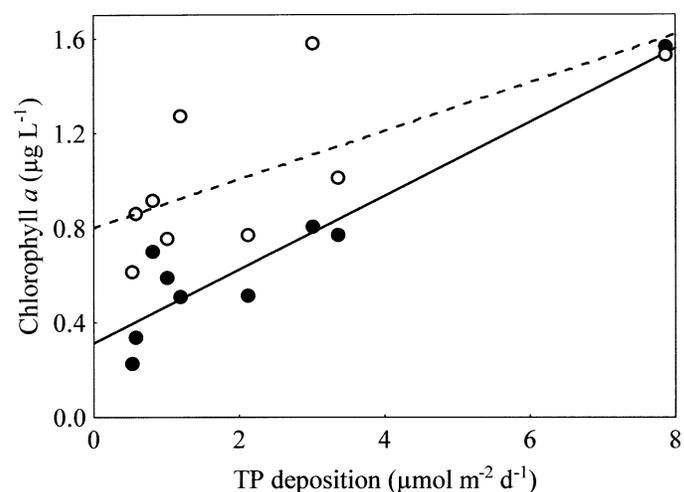


Fig. 4. Relationship between (dry + wet) atmospheric deposition of TP and Chl *a* concentration in La Caldera (filled circles) and Río Seco (empty circles) during the ice-free period of 2001.

exclusively in 2001 (Fig. 4). Nevertheless, the low variability of TP deposition in 2002 at 2900 m (Fig. 1, filled symbols) likely induced a weaker Chl *a* response and, presumably, other factors controlling phytoplankton growth could have masked the effect of atmospheric P, explaining the lack of a significant response in 2002. In conclusion, the significant relationship between TP deposition and lake Chl *a* that we found in both lakes in 2001 shows that there is a direct connection between these variables and confirms the fertilizing effect of Saharan dust deposition.

References

- AMERICAN PUBLIC HEALTH ASSOCIATION (APHA). 1992. Standard methods for the examination of water and wastewater, 18th ed. American Public Health Association.
- BAINES, S. B., K. E. WEBSTER, T. K. KRATZ, S. R. CARPENTER, AND J. J. MAGNUSON. 2000. Synchronous behaviour of temperature, calcium and chlorophyll in lakes of northern Wisconsin. *Ecology* **81**: 815–825.
- BERGAMETTI, G., L. GOMES, E. REMOUDAKI, M. DESBOIS, D. MARTIN, AND P. BUAT-MÉNARD. 1989. Present transport and deposition patterns of African dusts to the north-western Mediterranean, p. 227–252. In M. Leinen and M. Sarnthein [eds.], *Paleoclimatology and paleometeorology: Modern and past patterns of global atmospheric transport*. NATO ASI Series no. 282. Kluwer, Dordrecht.
- , E. REMOUDAKI, R. LOSNO, E. STEINER, B. CHATENET, AND P. BUAT-MÉNARD. 1992. Source, transport and deposition of atmospheric phosphorus over the northwestern Mediterranean. *J. Atmos. Chem.* **14**: 501–513.
- CHADWICK, O. A., L. A. DERRY, P. M. VITOUSEK, B. J. HUEBERT, AND L. O. HEDIN. 1999. Changing sources of nutrients during four million years of ecosystem development. *Nature* **397**: 491–497.
- CHIAPELLO, I., J. M. PROSPERO, J. R. HERMAN, AND N. C. HSU. 1999. Detection of mineral dust over the north Atlantic Ocean and Africa with the Nimbus 7 TOMS. *J. Geophys. Res.* **104**: 9277–9291.
- DE ANGELIS, M., AND A. GAUDICHET. 1991. Saharan dust deposition over Mont Blanc (French Alps) during the last 30 years. *Tellus* **43B**: 61–67.
- DRISCOLL, C. T., AND OTHERS. 2003. Nitrogen pollution in the northeastern United States: Sources, effects, and management options. *Bioscience* **53**: 357–374.
- GIBSON, C. E., Y. WU, AND D. PINKERTON. 1995. Substance budget of an upland catchment: The significance of atmospheric phosphorus inputs. *Freshwater Biol.* **33**: 385–392.
- GOUDIE, A. S., AND N. J. MIDDLETON. 2001. Saharan dust storms: Nature and consequences. *Earth-Science Rev.* **56**: 179–204.
- GUERZONI, S., AND OTHERS. 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. *Prog. Oceanogr.* **44**: 147–190.
- GUIEU, C., M. D. LÖYE-PILOT, C. RIDAME, AND C. THOMAS. 2002. Chemical characterization of the Saharan dust end-member: Some biogeochemical implications for the Western Mediterranean Sea. *J. Geophys. Res.* 107 (D15) [doi: 10.1029/2001JD000582].
- HERUT, B., R. COLLIER, AND M. D. KROM. 2002. The role of dust in supplying nitrogen and phosphorus to the Southeast Mediterranean. *Limnol. Oceanogr.* **47**: 870–878.
- , AND M. D. KROM. 1996. Atmospheric inputs of nutrients and dust to the SE Mediterranean. p. 349–359. In S. Guerzoni, and R. Chester [eds.], *The impact of desert dust across the Mediterranean*. Kluwer.
- , ———, G. PAN, AND R. MORTIMER. 1999. Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes and possible impact. *Limnol. Oceanogr.* **44**: 1683–1692.
- JAENICKE, R., AND L. SCHÜTZ. 1978. Comprehensive study of physical and chemical properties of the surface aerosols in the Cape Verde Islands region. *J. Geophys. Res.* **83**: 3585–3589.
- KOPÁČEK, J., J. HEJZLAR, E. STUHLÍK, J. FOTT, AND J. VESELÝ. 1998. Reversibility of acidification of mountain lakes after reduction in nitrogen and sulphur emissions in central Europe. *Limnol. Oceanogr.* **43**: 357–361.
- , L. PROCHÁZKOVÁ, E. STUHLÍK, AND P. BLAZKA. 1995. The nitrogen : phosphorus relationship in mountain lakes: Influence of atmospheric input, watershed, and pH. *Limnol. Oceanogr.* **40**: 930–937.
- , E. STUHLÍK, V. STRAŠKRABOVÁ, AND P. PŠENÁKOVÁ. 2000. Factors governing nutrient status of mountain lakes in the Tatra Mountains. *Freshwater Biol.* **43**: 369–383.
- KUBILAY, N., S. NICKOVIC, C. MOULIN, AND F. DULAC. 2000. An illustration of the transport and deposition of mineral dust onto the Eastern Mediterranean. *Atmos. Environ.* **34**: 1293–1303.
- LÖYE-PILOT, M. D., J. M. MARTIN, AND J. MORELLI. 1986. Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean. *Nature* **321**: 427–428.
- MARKAKI, Z., K. OIKONOMOU, M. KOCAK, G. KOUVARAKIS, A. CHANIOTAKI, N. KUBILAY, AND N. MIHALOPOULOS. 2003. Atmospheric deposition of inorganic phosphorus in the Levantine Basin, eastern Mediterranean: Spatial and temporal variability and its role in seawater productivity. *Limnol. Oceanogr.* **48**: 1557–1568.
- MIGON, C., AND V. SANDRONI. 1999. Phosphorus in rainwater: Partitioning inputs and impact on the surface coastal ocean. *Limnol. Oceanogr.* **44**: 1160–1165.
- MORALES-BAQUERO, R., P. CARRILLO, I. RECHE, AND P. SÁNCHEZ-CASTILLO. 1999. The nitrogen : phosphorus relationship in high mountain lakes: Effects of the size of catchment basins. *Can. J. Fish. Aquat. Sci.* **56**: 1809–1817.
- MOULIN, C., C. E. LAMBERT, F. DULAC, AND U. DAYAN. 1997. Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation. *Nature* **387**: 691–694.
- MURPHY, J., AND J. P. RILEY. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* **27**: 31–36.
- OKIN, G. S., N. MAHOWALD, O. A. CHADWICK, AND P. ARTAXO. 2004. Impact of desert dust on the biogeochemistry of phosphorus in terrestrial ecosystems. *Glob. Biogeochem. Cycles* **18**: Art. No. GB2005. [doi: 10.1029/2003GB002145].
- PETERS, R. H. 1977. The availability of atmospheric orthophosphate. *J. Fish. Res. Bd. Can.* **34**: 918–924.
- PULIDO-VILLENA, E. 2004. El papel de la deposición atmosférica en la biogeoquímica de lagunas de alta montaña (Sierra Nevada, España). Ph.D. thesis. Universidad de Granada.
- QUEROL, X., AND OTHERS. 2003. Estudio y evaluación de la contaminación atmosférica por material particulado en España. Informes finales. IJA-CSIC, ISCIII, CIEMAT, Universidad de Huelva, Universidad del País Vasco. Ministerio de Medio Ambiente.
- RIDAME, C., AND C. GUIEU. 2002. Saharan input of phosphate to the oligotrophic water of the open western Mediterranean Sea. *Limnol. Oceanogr.* **47**: 856–869.
- STODDARD, J. L., AND OTHERS. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* **401**: 575–578.
- SULLIVAN, T. J., AND OTHERS. 1990. Quantification of changes in lakewater chemistry in response to acidic deposition. *Nature* **345**: 54–58.

- TALBOT, R. W., R. C. HARRISS, E. V. BROWELL, G. L. GREGORY, D. I. SEBACHER, AND S. M. BECK. 1986. Distribution and geochemistry of aerosols in the tropical north Atlantic troposphere: Relationship to Saharan dust. *J. Geophys. Res.* **91**: 5173–5182.
- TORRES, O., P. K. BHARTIA, J. R. HERMAN, AND Z. AHMAD. 1998. Derivation of aerosol properties from satellite measurements of backscattered ultraviolet radiation. Theoretical Basis. *J. Geophys. Res.* **103**: 17099–17110.
- , ———, ———, A. SINYUK, AND B. HOLBEN. 2002. A long-term record of aerosol optical thickness from TOMS observations and comparison to AERONET measurements. *J. Atm. Sci.* **59**: 398–413.
- WAGENBACH, D., AND K. GEIS. 1989. The mineral dust record in a high alpine glacier (Colle Gniffet, Swiss Alps), p. 543–564. *In* M. Leinen and M. Sarnthein [eds.], *Paleoclimatology and paleometeorology: Modern and past patterns of global atmospheric transport*. Kluwer Academic.

Received: 15 December 2004

Accepted: 7 August 2005

Amended: 3 October 2005