

Research Articles

Nutrient Dynamics in Shallow Lakes of Northern Greece

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Abstract

Goal, Scope, Background. Shallow lakes display a number of features that set them apart from the more frequently studied deeper systems. The majority of lakes in Northern Greece are small to moderate in size with a relatively low depth and are considered as sites of high value of the wetland habitat. However, the water quality of these lakes has only been evaluated segmentally and occasionally.

Objective. The objectives of this study were to thoroughly investigate nitrogen and phosphorus speciation in lakes of a high ecological significance located in N. Greece, in order to evaluate their eutrophication status and possible nutrient limitation factors, and to investigate the main factors/sources that affect the water quality of these systems.

Methods. An extensive survey was carried out during the period from 1998–1999. Water samples were collected on a monthly basis from lakes Koronia, Volvi, Doirani, Mikri Prespa and Megali Prespa located in N. Greece. Water quality parameters (temperature, dissolved oxygen, pH and conductivity), organic indices (COD, BOD₅), and N- and P-species (NO₃⁻, NO₂⁻, NH₄⁺ and PO₄³⁻, Kjeldahl nitrogen and acid-hydrolysable phosphorus) were determined according to standard methods for surface water. Statistical treatment of the data was employed.

Results and Conclusions. The physicochemical parameters determined in the lakes studied revealed a high temporal variation. The trophic state of the lakes ranged from meso- to hypertrophic. The nutrient limiting factor varied among lakes suggesting either P-limitation conditions or mixed conditions changing from P- to N-limitation throughout the year. Urban/industrial activities and agricultural runoff are the major factors affecting all lakes, although with a varying contribution.

Recommendation and Outlook. This lake-specific research offers valuable information about water quality and nutrient dynamics in lakes of significant ecological value located in N. Greece that can be useful for an effective pollution control/management of these systems. Due to the large intra-annual variability of certain physicochemical parameters, a properly designed monitoring program of lake water is recommended.

Keywords: Greece; lakes; N/P ratios; nitrogen; nutrients; PCA; phosphorus; physicochemical parameters; shallow lakes

Introduction

Changes in the ecological conditions of the lakes due to natural (changes in hydroperiods and in total precipitation inputs) and anthropogenic processes (increasing consumption of water resources, agricultural and industrial activities) became a very sensitive issue. The undesirable consequences result in an alteration of the trophic state of the lakes. The allocation of a lake to a trophic category is based on several indices such as chlorophyll levels, transparency, biomass, nitrogen and phosphorus levels, phytoplankton species as well as physical characteristics of the lake and chemical composition of the water (OECD 1982, Huszar et al. 1998).

Among physical characteristics, the depth of water is an important parameter which characterizes the lake environment (European Environment Agency 1998). Shallow lakes display a number of features that set them apart from the more frequently studied deeper systems. These lakes are characterized by a high variability of physical and chemical parameters, a lack of stable long-term thermal stratification, frequent mixing and aeration of the entire water column, resuspension of sediments and a substantial internal loading of nutrients from sediments to the water column. Water quality conditions (total P concentrations, turbidity, chlorophyll a and algal blooms) in these lakes may have complex relationships with external nutrient loads and in-lake processes (Havens et al. 2001, Sas 1989, Welch and Cooke 1995, Hansen et al. 1997, Kufel and Kufel 1997). Due to the large intra-annual variability in water chemistry, average nutrient concentrations of limited data did not provide a representative and reliable estimate of lake state. Thus, a sampling protocol, which minimizes variance as associated with the mean, and the bias associated with spatial and temporal variation, is necessary (Bennion and Smith 2000, Peterson and Urquhart 2000).

The majority of lakes in Northern Greece are small to moderate in size with a relatively low depth. Many of them have been considered as sites of high value of the wetland habitat which are protected by the Ramsar Convention (1996). However, the water quality of these lakes has been evaluated only segmentally and occasionally (Ministry of Macedonia-Thrace 1992–1998, Temponeras et al. 2000, Loffler et al. 1998, Tryfon and Moustaka-Gouni 1997, Moustaka-

Gouni et al. 1994, Moustaka-Gouni 1993, Moustaka-Gouni and Tsekos 1989, Mourkides 1986, Mourkides et al. 1978).

The particular objectives of this paper were to thoroughly investigate the speciation of N and P in five small to moderately sized lakes of high ecological significance, and also to evaluate their eutrophication status. The concentrations of nitrogen (NO_3^- , NO_2^- , NH_4^+ and Kjeldahl nitrogen) and phosphorus species (soluble reactive phosphorus and acid-hydrolysable phosphorus) in the examined lakes are presented. Physicochemical parameters such as field pH, conductivity, Total Suspended Solids (TSS) and Dissolved Oxygen (DO), Biological Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) are also given. Use of multivariate statistical analysis is made to identify the major factors influencing the chemistry of the water.

1 Materials and Methods

1.1 Lakes studied

Five lakes, Volvi, Koronia, Doirani, Mikri Prespa and Megali Prespa, all located in the area of Macedonia, N. Greece, were examined in this study. The lakes Volvi and Koronia are located 11.5 km NE of Thessaloniki. Doirani is traversed by the border between Greece and FYROM, while Mikri Prespa and Megali Prespa are two lakes in a mountainous drain basin located in northwestern Greece at the intersection of the frontiers of Greece, Albania and FYROM. The morphometric data and the general features of the lakes are shown in Table 1.

The major area of lakes Volvi and Koronia is protected by the Ramsar Convention as a site of international importance for the value of the wetland habitat, ideal for a variety of flora and fauna species (Ramsar Convention Bureau 1996). The Greek portion of the Prespa region including Mikri Prespa and part of Megali Prespa was declared as a national park in 1974 because it is one of the last refuges in Europe for more than 260 different bird species, rare and/or endangered. This area is also protected by the Ramsar Convention (1996).

The major sources that affect the water quality of the lakes are agricultural runoff, animal husbandry effluents, untreated or semi-treated domestic effluents and industrial wastewaters mainly from food, dairy and dyer industries. Other important sources are resuspended stream sediments and eroded bank materials.

1.2 Sampling and analysis

Water samples were collected monthly to monitor changes in the hydrologic cycle and possible seasonal variation. Samples from lakes Doirani, Volvi and Koronia were collected for a 24-month period (1998–1999), whereas samples from lakes Mikri Prespa and Megali Prespa were collected only for a seven-month period (June–December 1999). Two sampling sites were chosen in lakes Volvi (V_1 , V_2) and Koronia (K_1 , K_2), on the east and west sides of the lakes, and one sampling site in the other transboundary lakes. Water samples were collected just below the surface of the water. Sampling and analytical protocols were conducted according to standard methods for surface water (APHA 1985).

Temperature, dissolved oxygen, pH and conductivity were measured in the field. Water samples were kept cool in the field and were transported to the laboratory in a small refrigerator (4°C), normally within one day. They were filtered through $0.45\ \mu\text{m}$ membranes for TSS determination. NO_3^- , NO_2^- , NH_4^+ and PO_4^{3-} were determined in filtrates, while COD, BOD_5 , Kjeldahl nitrogen (N_K) and acid-hydrolysable phosphorus were determined in unfiltered samples. The N-species determined will be reported here as nitrogen and will be referred to as N-NO_3^- , N-NO_2^- , N-NH_4^+ , Dissolved Inorganic Nitrogen, DIN ($\text{N-NO}_3^- + \text{N-NO}_2^- + \text{N-NH}_4^+$) and Total Organic Nitrogen, TON ($N_K - \text{N-NH}_4^+$). The P-forms discussed here are Soluble Reactive Phosphorus (SRP) and acid hydrolysable phosphorus, expressed as total P (TP). TP minus SRP would then represent the sum of particulate P and dissolved hydrolysable polymeric inorganic and organic P.

2 Results and Discussion

2.1 Physicochemical parameters

Mean values and the range of variation for physicochemical parameters and nutrient species are summarised by box-plots in Fig. 1. A similar distribution pattern is apparent for most parameters.

The waters of the examined lakes showed a slightly to fairly alkaline character with lowest pH values measured in Mikri Prespa, Megali Prespa and Doirani. Slightly increased pH values were found in lake Volvi (9.0), especially during warm periods and probably coincided with photosynthetic activity of the autotrophic microorganisms (Goldman and Horne 1983). The extremely high pH values observed in Koronia should be attributed to pollution from industrial wastes.

Table 1: Main characteristics of the studied lakes

Lake area		Volvi	Koronia	Doirani	Mikri Prespa	Megali Prespa
Latitude (N)		40° 40'	40° 40'	41° 13'	40° 46'	40° 50'
Longitude (E)		23° 30'	23° 09'	22° 44'	21° 06'	21° 00'
Lake area	km ²	69	42 ^a	28 (15) ^b	47.4 (40) ^b	253.6 (40) ^b
Catchment area	km ²	1247	350	420	260	
Altitude	m	37	75	142	853	853
Depth (mean, max)	m	13.5 (24)	2.8 (4) ^a	5.0 (10.4)	6.7 (7.8)	20 (55)

^a The lake area has been significantly shrunk and the depth has been tremendously reduced during the last ten years

^b Area within the Greek territory

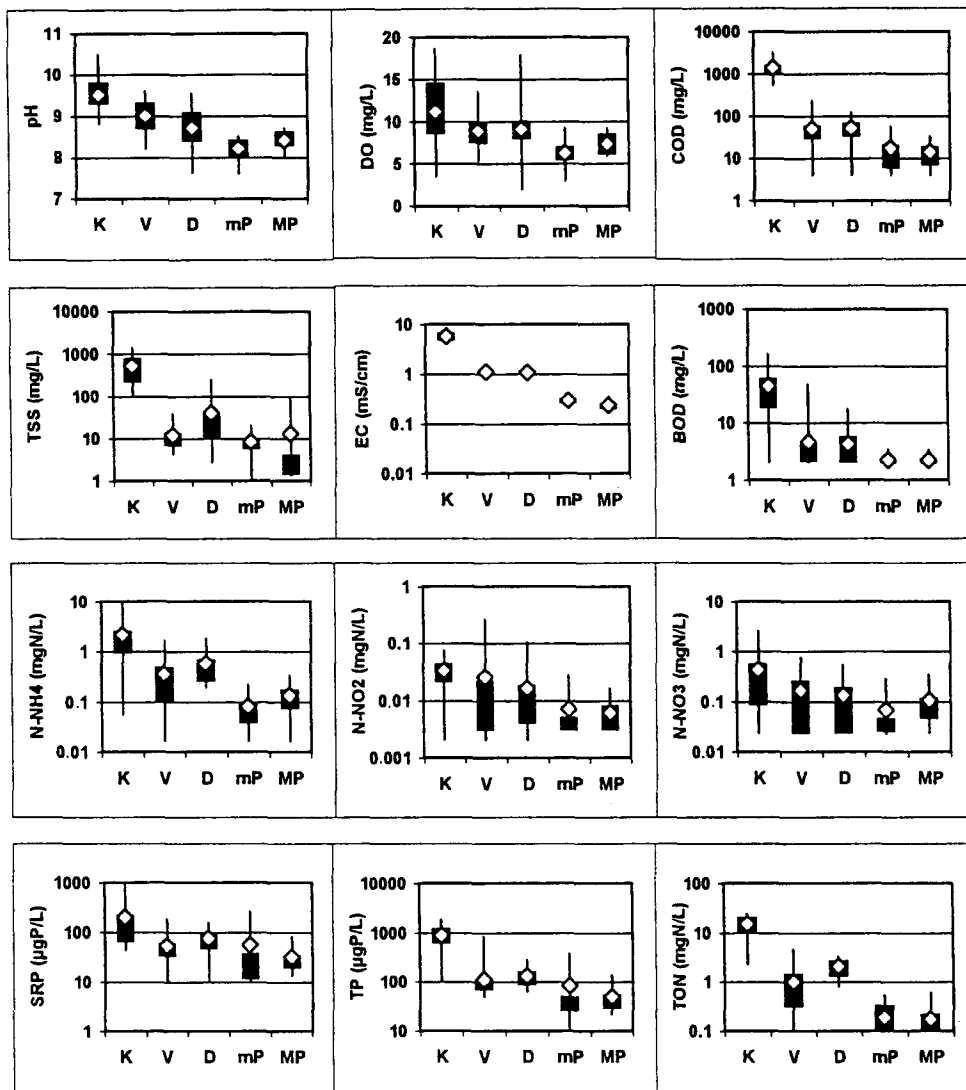


Fig. 1: Physicochemical parameters and nutrient speciation of the studied lakes. Box plots display min and max values, 25th and 75th percentiles and mean values (K: Koronia, V: Volvi, D: Doirani, mP: Mikri Prespa, MP: Megali Prespa)

The concentrations of DO showed large variability, particularly in Koronia, Volvi and Doirani, ranging from hyper-saturation to anoxic conditions. The hypersaturated conditions occasionally found might be attributed to water mixing and turbulence, as well as to significant primary production and biogenic aeration. DO concentrations were usually above 5 mg/L, the criterion proposed for the protection of aquatic life (British Columbia Ministry of Environment 1997).

Lowest conductivity values were measured in Mikri Prespa and Megali Prespa (295 $\mu\text{S}/\text{cm}$ and 234 $\mu\text{S}/\text{cm}$, respectively). Higher values were recorded in Doirani (1064 $\mu\text{S}/\text{cm}$) and Volvi (1027 $\mu\text{S}/\text{cm}$), while lake Koronia exhibited extremely high values ranging from 4000–8000 $\mu\text{S}/\text{cm}$.

The concentrations of Total Suspended Solids were also low in Mikri Prespa, Megali Prespa, Volvi and Doirani. The highest concentrations of TSS were found in lake Koronia, ranging from 100–1340 mg/L, and could be attributed to the

resuspended sediment as well as to the presence of algal biomass. Relatively low values of BOD₅ and COD were determined in lakes Mikri Prespa, Megali Prespa, Doirani and Volvi whereas high values were found in Koronia.

2.2 Speciation of nitrogen and phosphorus

The rank order of soluble nitrogen forms on the basis of median values was $\text{N-NH}_4 > \text{N-NO}_3 > \text{N-NO}_2$ in all the examined lakes. The N-NH_4 was the dominant nitrogen form, especially in lakes Koronia, Volvi and Doirani. Generally, the lake Koronia exhibited the highest concentrations of all nitrogen species, while the lowest concentrations were measured in Mikri Prespa and Megali Prespa.

The N-NO_2 concentrations in all five lakes were lower than the guide value of 0.03 mg $\text{N-NO}_2/\text{L}$ for drinking water, although they did not meet the guide values for protection of salmonid and cyprinid fish (0.003 mg N/L and 0.009 mg

N/L, for 95th percentile, respectively) (Council of European Communities 1978). Increased concentrations of N-NO₃ were determined in cold months (November–April). This is probably due to the influence of runoff from the neighboring agricultural area, where fertilizers are used in the cold period and there are more frequent events of rain. Generally, the concentrations of nitrates were lower than the guide value of 5.65 mg N/L for surface water intended for the abstraction of drinking water (Council of European Communities 1975). The concentrations of ammonium (N-NH₄) varied over a relatively extensive range. The ammonium concentrations in lakes Mikri Prespa, Megali Prespa, Volvi and Doirani met the mandatory water quality standard for protection of salmonid and cyprinid (0.78 mg N/L), whereas N-NH₄ levels in Koronia did not allow the maintenance of aquatic life. Ammonium concentrations showed significant temporal variation in lakes Volvi and Doirani with higher values from April–June that could be attributed to low algal assimilation and high ammonification processes.

Total nitrogen (TN) exhibited the highest concentrations in lake Koronia (6.5–21.6 mg N/L), consisting primarily of TON (76–95%). The TN concentrations in lake Doirani ranged from 1.25 mg N/L to 3.08 mg N/L. The contribution of TON to TN was also significant (54–86%) in nearly all months. Lower TN concentrations were determined in lake Volvi, ranging from 0.61 mg N/L to 1.51 mg N/L. The contribution of TON to TN was also significant in most cases (45–86%). Very low TN concentrations, <0.5 mg N/L in most cases, were determined in Mikri Prespa and Megali Prespa.

The rank order of lakes on the basis of median values of SRP was Koronia>Doirani>Volvi>Mikri Prespa>Megali Prespa. Highest TP concentrations were also determined in Koronia (120–1795 µg P/L). Particulate phosphorus contributed strongly (usually >86%) to TP, although SRP showed a significant contribution to TP in January, December and November (50–76%). SRP in Doirani represented a considerable fraction of TP (50–75% in most cases). The contribution of SRP to TP in lake Volvi showed a higher variability (19–81%) with values >50% from September to March. The lowest TP concentrations were determined in lakes Mikri and Megali Prespa, with peak values in November.

2.3 Trophic state classification

The development of guidelines for the classification of the trophic state of lakes is difficult (EPA 2000). The criteria given in literature introduce problems of interpretation when interregional comparisons are made. Usually, the existence of a trophic gradient is observed, but the determination of each level is not always clear. Furthermore, extreme situations are more easily defined than intermediate levels (Huszar et al. 1998). The EPA recommended the development of guidance for specific water bodies and ecological regions across the country and the use of reference conditions (conditions that reflect pristine or minimally impacted water) as a basis for developing criteria (EPA 2000). OECD (1982) proposed critical annual values for five parameters (mean values of TP, TN, chlorophyll a, secchi depth and peak values of chlorophyll a) as criteria for assessing the trophic status of a lake.

In the present study, the trophic state of each lake was evaluated using the simple input-output model of Vollenweider (1975). According to this model, $[P]=L_p/(10+q_s)$, where L_p is the areal P loading rate (g/m² y), q_s is the hydraulic loading rate (m/y) and $[P]$ is the total concentration in water (µg/L). $q_s = z/r_w$, where z is the mean depth of the lake (m) and r_w is the water residence time (y). By substituting a concentration goal for $[P]$ into the Vollenweider model, one can obtain a loading target for the watershed that can be used to guide management efforts. For $[P]$ goals equal to 10, 30 and 60 µg/L, the isolines separating regions of oligotrophic, mesotrophic, eutrophic and hypertrophic states are presented in the loading diagram of Fig. 2a. The trophic state of the studied lakes, as estimated by this model, is also shown in Fig. 2a. According to this estimation Mikri Prespa and Megali Prespa lie at the mesotrophic-eutrophic boundary, Volvi and Doirani at the eutrophic-hypertrophic boundary, whereas Koronia is classified as hypertrophic.

Vollenweider (1975) indicated that critical areal loading rates for N also could be derived by multiplying the in-lake P goals, by a 15:1 total N/P ratio, and then substituting the resulting total N values into the loading model. Using this approach, the nitrogen loading diagram is shown in Fig. 2b. According to this diagram, the areal N loading rates for Mikri Prespa and Megali Prespa were below the boundary of the mesotrophic state. Lakes Doirani and Volvi were located at the mesotrophic-eutrophic boundary, whereas Koronia had an excessive areal N loading.

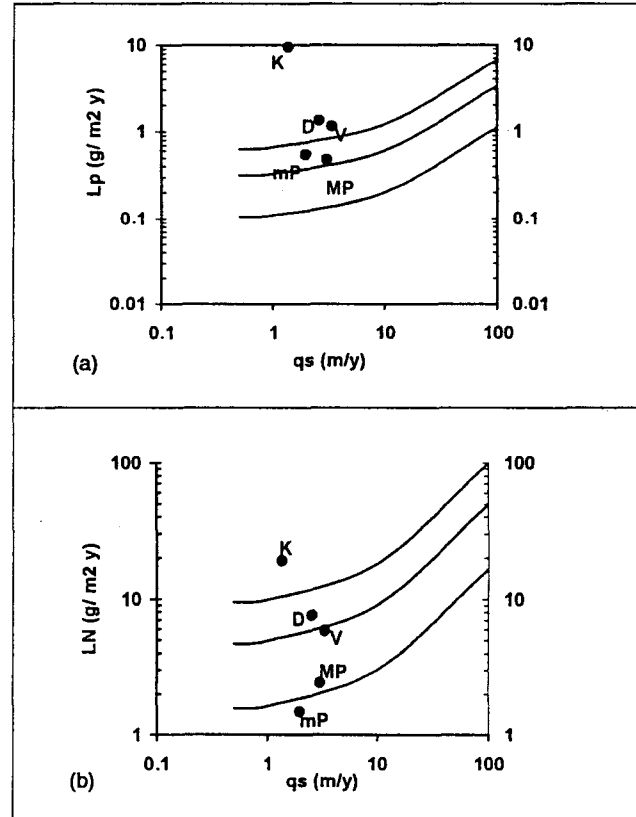


Fig. 2: Trophic classification of the examined lakes according to Vollenweider's model; (a) phosphorus loading diagram (b) nitrogen loading diagram

2.4 Nitrogen – Phosphorus ratios

N/P mass ratios were calculated, using the measured data as the ratio DIN/SRP, to determine which nutrient may be the limiting factor. Ratio data were further classified into four classes <8, 8–15, 16–23 and >24 (Jarvie et al. 1998, Voutsas et al. 2001). The 'Redfield ratio' for N/P of 16 for phosphorus limitation based on atomic values corresponds to an N/P mass ratio of 7.3 (Redfield 1958). As a consequence, the more values in the vicinity of the first class, the greater the likelihood that organisms may show N-limitation; the more values in the vicinity of the last class, the greater the likelihood that organisms may show P-limitation. The distribution of samples in four N/P classes is illustrated in Fig. 3a. The majority of samples from the lakes Volvi and Doirani exhibited N/P ratios lower than 15:1. However, N/P ratios revealed significant seasonal variation with lower values during autumn and winter showing an increased likelihood of N-limitation and higher values during spring and summer, and thus showing the likelihood of P-limitation (Fig. 3b). The high mean N/P ratio found in Doirani in summer is due to the extreme ratio values observed in June, when very low SRP was measured. Our findings can explain the controversial evaluations of other investigators concerning the limiting nutrient in this lake, reported either as N (Temponeras et al. 2000) or P (Andreidakis and Katsara 1995).

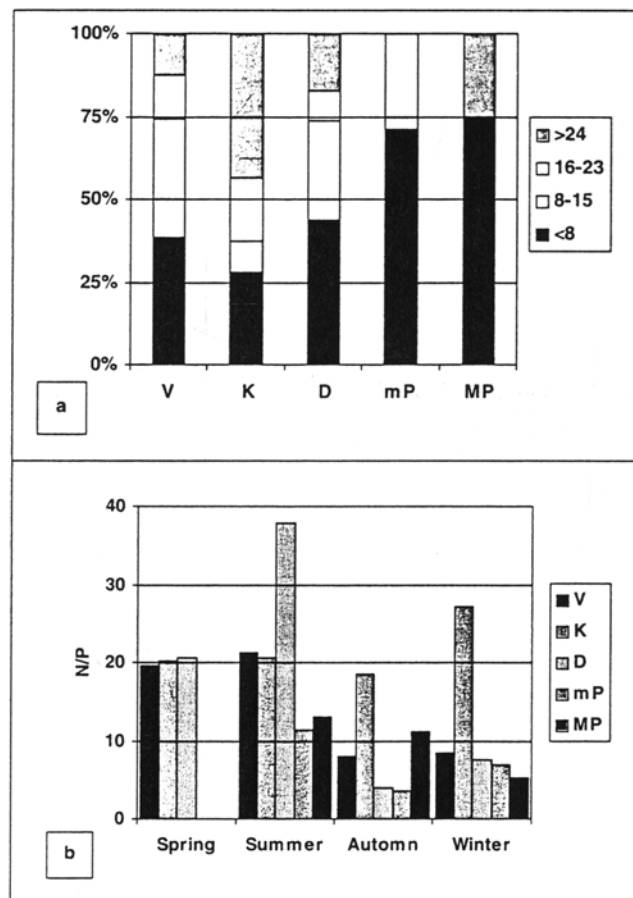


Fig. 3: Nitrogen to phosphorus ratios: (a) Distribution to different classes (b) Seasonal distribution

A different situation was observed in Koronia. The majority of samples were in the upper N/P classes, showing the highest likelihood of P-limitation during the whole year with no significant seasonal variations (Fig.3). N-limitation, in contrast, was reported for this lake ten years ago (Andreidakis and Katsara 1995). It is likely that a shift in the limiting nutrient of the lake has occurred during the last years.

Low mean N/P ratios were found in lakes Mikri Prespa and Megali Prespa for the study period (June–December), showing that nitrogen rather than phosphorus is the main nutrient limiting phytoplankton growth. However, peak N/P ratios were found in Megali Prespa in June (25) and September (24). Largely variable ratio values (4–1664) have been reported for this lake by other investigators (Tryfon and Moustaka-Gouni 1997).

2.5 Statistical analysis

Water quality data from each lake were statistically analyzed to examine whether factors such as sampling season or sampling site had a significant effect on the observed variance of the physicochemical parameters and nutrient species. A non-parametric ANOVA procedure, the Kruskal-Wallis one-way analysis by ranks, was performed since environmental data usually do not follow a normal distribution (SPSS 8.0, 1998). The results showed that the sampling period had a significant effect on the observed variance for most parameters. In contrast, the different sampling sites in lakes Koronia and Volvi did not show any significant effect.

PCA was used to compare the compositional patterns between the examined lake systems and to identify the factors influencing each one. PCA has been frequently employed on large and complex water quality data sets obtained from monitoring studies and allows a better evaluation and assessment of the situation of the systems (Reisenhofer et al. 1998, Voutsas et al. 2001, Bennion and Smith 2000, Moser et al. 1998, Wunderlin et al. 2001, Lim et al. 2001). PCA was performed on the whole data set (119 samples x 12 parameters) (SPSS 8.0 1998). The water quality data were log-transformed to reduce skew distribution. Two factors accounted for 64.4% of the variance (Table 2). The first PC accounting for 52.8% of the total variance was highly cor-

Table 2: Varimax rotated factor matrix for the whole data set (n = 1428)

Variable	PC ₁	PC ₂
pH	0.783	
DO	0.612	
EC	0.874	0.411
TSS	0.754	0.461
TON	0.902	
BOD ₅	0.883	
COD	0.895	
SRP	0.483	
TP	0.890	
NO ₂		0.546
NO ₃		0.773
NH ₄		0.668
Variance (%)	52.8	11.6

^a Variable loadings >0.400 are only given

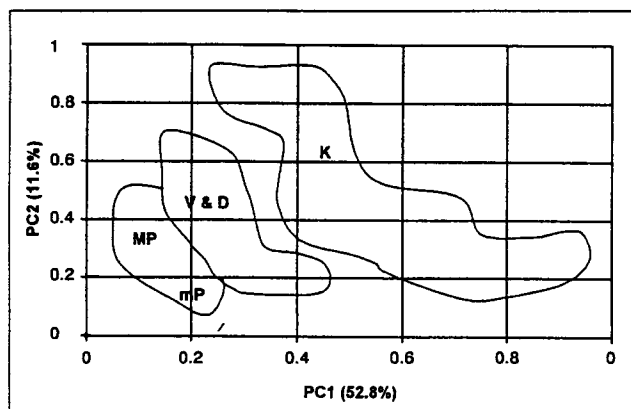


Fig. 4: First vs second principal component for the physicochemical characteristics of the lakes

related with organic pollution parameters (COD, BOD₅, TP, TON). This component represents the organic dynamics of the lake systems. It was interpreted as representing influences from urban and industrial activities (domestic and industrial effluents). The second PC, accounting for 11.6% of the variance of the whole data set, was correlated with NO₃, NO₂ and NH₄. This factor represents the dissolved nutrient dynamics of the systems and was interpreted as representing influences from agricultural activities. The PCA plot of PC₁ against PC₂ is illustrated in Fig 4. It is apparent that the lakes can be discriminated due to their organic content (PC₁) rather than their nitrogen content (PC₂). The factor PC₁ has a stronger influence on lake Koronia, suggesting that this lake is affected more by urban/industrial activities.

3 Conclusions

Physicochemical parameters and nutrient species were determined in five small to moderately sized lakes located in N. Greece. The trophic state of the lakes ranged from meso- to hypertrophic. The nutrient limiting factor varied among lakes suggesting either P-limitation conditions or mixed conditions changing from P- to N-limitation throughout the year. PCA analysis indicated that urban/industrial activities and agricultural runoff are the major factors affecting all lakes, although with varying contributions.

4 Recommendation and Outlook

This lake-specific research offers valuable information about water quality and nutrient dynamics in lakes of significant ecological value located in N. Greece that can be useful for an effective pollution control/management of these systems. Due to the large intra-annual variability of certain physicochemical parameters, a properly designed monitoring program of lake water is recommended.

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