Phosphorus fractionation in lake sediments – Lakes Volvi and Koronia, N. Greece

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Abstract

Sediments from two lakes, the meso-to-eutrophic Volvi and the hypertrophic Koronia, located in N. Greece were examined on the basis of P-fractionation. In both lakes, the rank order of P-fractions was $HCl–P > NaOH–P > BD–P > NH_4Cl–P$. The loosely sorbed phosphorus ($NH_4Cl–P$) represented $< 1\%$ of the sedimentary inorganic phosphorus, while the reductant phosphorus (BD–P) ranged 5–6%. The calcium bound phosphorus (HCl–P) showed considerable contribution (59–74%) to the sedimentary inorganic P-loads. The metal oxide bound phosphorus (NaOH–P) was higher in the hypertrophic (30–35%) than in the meso-to-eutrophic system (19–28%). Fine-sized sediments exhibited significantly higher concentrations of HCl–P in Volvi and $NH_4Cl–P$ in Koronia. Sampling month had significant effect in variance of most P-fractions and other sediment features in both lakes. Use was also made of multivariate statistics to identify the factors which influence the sedimentary phosphorus. NaOH–P was the most reactive fraction in Lake Volvi. Iron compounds and organic matter seem to play a significant role in regulating this labile P-budget. $NH_4Cl–P$ was the more reactive fraction in Lake Koronia which was influenced by sedimentation of P-absorbed on clay/silt fine particles. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Grain size; Lakes; PCA; Phosphorus; P-fractions; Sediment; Trophic status

1. Introduction

Phosphorus has been recognized as the most critical nutrient limiting lake productivity. The main sources of phosphorus in lakes are external point and non-point sources such as rainfall, runoff, soil leaching, industrial and municipal effluents. Moreover, there are also internal sources from the system itself such as aquatic plants, algal and sediments.

The trophic status of the lakes is usually dependent on the P-concentration in the water. In addition, the trophic status and the trophic development of the system is also influenced by the phosphorus content in lake sediments. Usually lake sediments act as a sink of phosphorus. However, under certain environmental conditions, the sediments may become a possible phosphorus source that will support the trophic status of the lake even after a reduction of external loading (Ramm and Scheps, 1997; Zhou et al., 2001). This internal P-loading may delay the recovery of the lakes, once the external P-sources are reduced, and must be evaluated in lake restoration programmes. The phosphorus content in sediments depends on the sediment composition, the sedimentation rate, the physicochemical conditions and the extent of diagenetic processes (Gonsiorczyk et al., 1998). Total concentrations of phosphorus in sediments cannot predict the potential ecological danger. The fraction of available phosphorus is an important parameter for predicting future internal P-loading. The factors governing P release from sediments comprise redox reactions, adsorption, mineral phase solubility

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and mineralization of organic matter. Dissolved oxygen, nitrates, sulfates, pH, temperature and salinity are the major controlling parameters (Kleeberg and Dudel, 1997; House and Denison, 2000; Thirunavukkarasu et al., 2000).

The long-term behavior of sediment bound P in promoting eutrophication of freshwater can be more efficiently evaluated on the basis of different P-fractions, instead of total phosphorus content. These fractions are P-forms binding to metals and to organic matter, measured by different sequential extraction schemes, so-called P-fractionations. P-fractionations partition sedimentary-P into different fractions such as labile P, reductant P, metal bound P, occluded P and organic P by using various chemical extractants (Chang and Jackson, 1957; Williams et al., 1976; Psenner, 1988). Moreover, in view of the potential P-bioavailability, the extracted fractions may be characterized as water-soluble P, readily desorbable P, algal available P or ecologically important P (Pettersson et al., 1988; Zhou et al., 2001).

The aim of this study was to investigate the different P-forms present in the sediments of two lakes, located in N. Greece: the meso-to-eutrophic Volvi and the hypertrophic Koronia, and to evaluate their possible contribution to the P-loadings of the two systems. For this purpose, a sequential extraction scheme was employed providing four P-fractions: the loosely sorbed P, the reductant soluble P, the metal oxide bound P and the calcium bound P. Phosphorus fractions were evaluated in relation to the concentrations of the most important P-binding elements Ca, Mg, Fe, Mn and Al, as well as to other sediment features.

2. Materials and methods

2.1. Study area

The studied lakes, Volvi and Koronia, are located in N. Greece, about 11.5 km NE of Thessaloniki (Fig. 1). The whole area is protected by the Ramsar Convention as a site of international importance for the value of the wetland habitat. The wetland includes important natural complex habitat types such as fresh water marsh, lacustrine and riverine forests, scrublands, as well as agricultural landscapes. The area provides an ideal habitat for a variety of flora and fauna species. It is a significant habitat of structural and species diversity (fishes, invertebrates, reptiles, herptiles, birds, mammals), also providing an important nesting and roosting site for many endangered bird species. Both lakes are mainly recharged by rainfall, surface and ground water as well as by thermal springs. The major sources that affect the water quality and the trophic status 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.

The morphometric data and selected chemical characteristics of the studied lakes are shown in Table 1. Volvi is an elliptic-shaped lake with surface area 69 km^2 and mean depth 13.5 m. The maximum depth ($\sim$ 24 m) is observed in the east part. Small rivers and streams transport significant quantities of particulate matter in the E-SE part of the lake resulting in a reduction of the surface area. During water stratification, starting at the
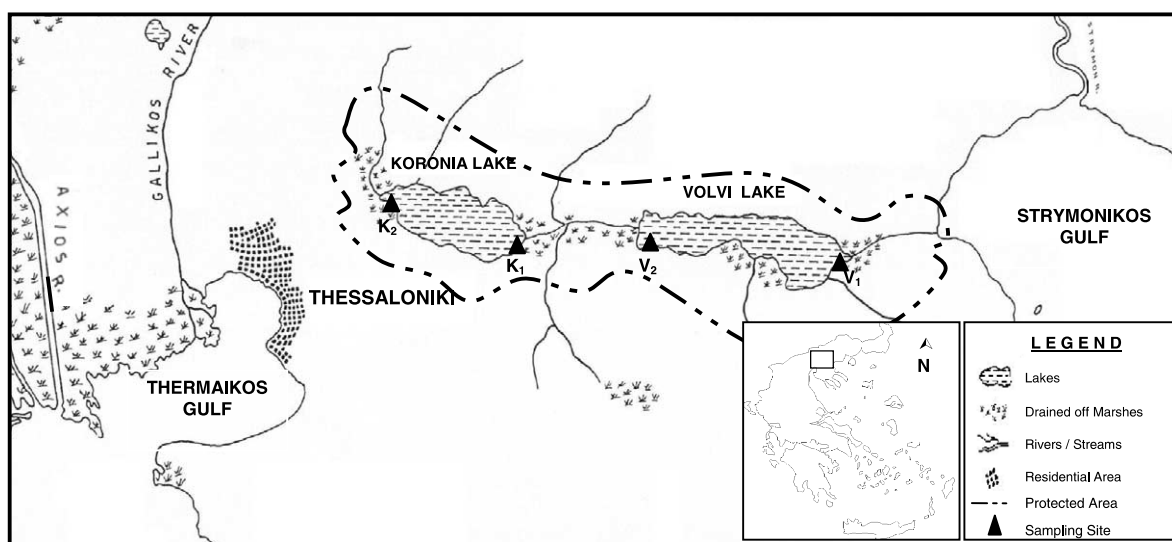

Fig. 1. Map of the studied area with sampling sites.

Table 1
Main characteristics of the studied lakes

	Lake Volvi		Lake Koronia	
Surface area (km^2)	69		42	
Mean depth (range) (m)	13.5 (10–24)		2 (1–4)	
Altitude (m)	37		75	
Natural trophic status[a]	Lower mesotrophic level		Mesotrophic level	
Nutrient/trophic parameters				
SRP[b] (µg P/l)	60		200	
TP[b] (µg P/l)	145		1040	
NO_3[b] (µg N/l)	90		135	
NO_2[b] (µg N/l)	29		26	
Chlorophyll-*a*[a] (mg/m^3)	7.6		64	
Secchi disc transparency[a] (m)	1.7		0.4	
Trophic classification[a]	Meso-to-eutrophic		Hypertrophic	
Other water quality parameters[b] *mean (range)*				
pH	9.0	(8.2–9.6)	9.7	(9.0–10.5)
Conductivity (µS/cm)	1085	(930–1140)	5789	(4000–8800)
DO (mg/l)	8.2	(6.4–10.5)	11.3	(7.8–18.6)
BOD_5 (mg/l)	6	(2–48)	62	(18–159)
COD (mg/l)	54	(16–232)	1511	(736–3200)
Fe (µg/l)	119	(20–582)	138	(39–529)
Mn (µg/l)	46	(12–90)	42	(13–116)
As (µg/l)	22	(7–35)	60	(45–68)

SRP: Soluble reactive phosphorus; TP: acid hydrolysable phosphorus.

[a] Koussouris et al. (1992).

[b] Kouimtzis (1999).

beginning of summer, anoxic conditions are observed in the bottom, mainly in the deep east part of the lake. The lake has been classified on the basis of chemical and biological water parameters, as meso-to-eutrophic lake (Koussouris et al., 1992).

Koronia is an elliptic-shaped shallow lake with a mean depth ~ 2 m and a surface area 42 km^2. The surface area has been significantly shrunk during last 20 years (by about 0.6% per year) due to over-exploitation of water for agricultural and industrial purposes and the transportation of particulate matter from small stream inflows, mainly in the west part of the lake. Moreover, the water quality has deteriorated and the lake has been classified as hypertrophic. The nutrient enrichment of the lake has seriously degraded the aquatic ecosystem and led to diverse problems such as toxic algal blooms, low transparency, severe depletion of dissolved oxygen, fish kills, loss of biodiversity, etc. Because it is shallow, winds disturb the sediment on occasions.

2.2. Sediment sampling and analysis

Surficial sediment samples were collected once a month, from May to August 1998, from two sampling sites of the Lake Volvi (V_1, V_2) and Koronia (K_1, K_2). Sediment samples were collected using an Eckman sampling device. The samples were put in air-sealed plastic bags and kept cool in the field (4 °C). After transportation to the laboratory they were kept frozen until the analysis. Before the analysis, the samples were freeze-dried, homogenized and size fractionated using stainless steel sieves in a mechanical sieving apparatus. Two grain size fractions were separated: the sand fraction (63–2000 µm) and silt/clay fraction (< 63 µm).

Water content, loss on ignition and carbonate content measurements were based on weight losses after drying and combustion of the sediments at 105, 550 and 900 °C, respectively. TOC represents the oxidizable matter after treatment of the sample with chromic acid/H_2SO_4 according to the Walkey–Black method (Tan, 1995). Total concentrations of Ca, Mg, Fe, Mn and Al were determined in sand and silt/clay sediment fractions after wet digestion with aqua regia for 2 h (APHA, 1985). The exchangeable fraction of Ca, Mg, Fe, Mn and Al was determined after extraction with CH_3COONH_4, 1M (Tan, 1995). The determination of these elements was performed by using FAAS or GFAAS techniques.

2.2.1. Phosphorus fractionation

The sequential extraction scheme of Psenner et al. (1984) with slightly modifications by Hupfer et al. (1995) was used for P-fractionation of lake sediments. Sand and silt/clay sediment fractions were subjected

to sequential chemical extraction with 1 M NH_4Cl, 0.11 M $NaHCO_3/Na_2S_2O_4$, 1 M $NaOH$ and 0.5 M HCl. The extracts were centrifuged and the supernatants were filtered through a 0.45 μm phosphorus-free membrane or a polyamid filter for the NaOH extracts. The soluble reactive phosphorus (SRP) in each fraction was determined by the molybdenum blue/ascorbic acid method (APHA, 1985). This extraction procedure fractionates sedimentary phosphorus into loosely sorbed P (NH₄Cl–P), reductant soluble P (BD–P), metal oxide bound P (NaOH–P) and calcium bound P (HCl–P).

3. Results and discussion

3.1. Sediment characteristics and elemental content

The general features and the chemical component concentrations measured in lake sediments are presented in Table 2. The sand fraction (2000–63 μm) dominated all sediment samples (52–72%) except sediments from Koronia lake during May, where a lower coarse fraction was found (38–41%). Organic matter, expressed as loss on ignition (LOI), exhibited concentrations ranging from 2.1% dw to 9.7% dw in Volvi, and from 1.8% dw to 11.2% dw in Koronia. The calcium carbonate content comprised 5.5% dw (5.1–6.9% dw) of sediments in Koronia and 4.2% dw (2.2–8.5% dw) of sediments in Volvi. Higher values of $CaCO_3$ ($\sim 50\%$) have been reported for other calcareous lakes such as Onondaga lake (USA), Lake Kinneret (Israel) and Lake Balaton (Hungary) (Penn et al., 1995).

Total calcium concentrations were higher in sediments from lake Koronia (55 and 46 mg/g in the sand and the silt/clay fraction, respectively) than in sediments from Volvi (20 in sand and 34 mg/g in silt/clay). On the other hand, the exchangeable Ca was similar in the sediments of both lakes. The concentrations of total Mg were similar in the sediments of the two lakes with the exchangeable fraction higher in Koronia. The concentrations of total and exchangeable Mn, Fe and Al were similar in both lakes.

3.2. Fractional composition of sedimentary phosphorus

The mean concentrations of the different P-fractions determined in the coarse (sand) and fine (silt/clay) sediment from the two lake systems are presented in Fig. 2(a). The relative contribution of each fraction to the sedimentary inorganic P (i.e. the sum of the four extracted P fractions) is shown in Fig. 2(b).

Sedimentary inorganic P in both, the sand and the silt/clay sediment fractions, was higher in Volvi (395 and 518 μgP/g) than in Koronia (299 and 306 μgP/g, respectively). The redox sensitive P (BD–P) and the calcium bound P (HCl–P) also exhibited higher con-

Table 2
General features and chemical components of lake sediments (mean, min, max values)

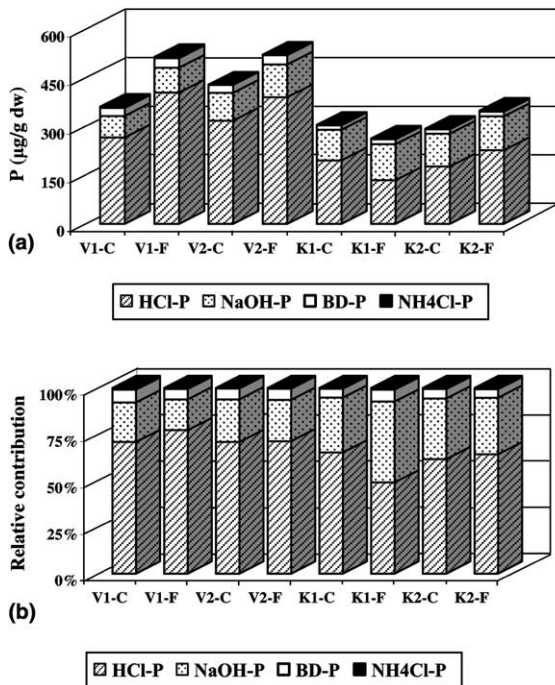|	Lake Volvi				Lake Koronia			
Sampling site:	V_1		V_2		K_1		K_2	
Water content (%):	32.0 (27.0–35.0)		33.3 (33.0–34.0)		26.0 (21.0–31.0)		24.5 (18.0–31.0)	
Sand fraction (%):	63.8 (58.0–68.9)		60.2 (51.6–70.0)		57.0 (38.1–72.0)		59.4 (41.4–69.0)	
Silt/clay fraction (%):	36.2 (31.9–42.0)		39.8 (30.0–48.1)		43.0 (28.0–62.0)		40.6 (31.0–58.6)	
	Sand	Silt/clay	Sand	Silt/clay	Sand	Silt/clay	Sand	Silt/clay
LOI (% dw)	3.1 (2.1–4.4)	3.1 (2.5–3.9)	4.3 (2.2–9.6)	5.1 (3.3–9.7)	6.6 (1.8–11)	7.1 (5.6–9.4)	5.8 (2.5–8.3)	6.4 (5.6–7.0)
TOC (% dw)	1.6 (1.4–1.9)	1.8 (1.4–2.5)	2.2 (1.4–3.5)	2.2 (1.4–3.6)	2.2 (0.9–3.8)	3.0 (1.3–5.4)	2.1 (0.8–3.2)	2.1 (1.5–3.2)
$CaCO_3$ (% dw)	5.2 (2.8–8.5)	2.9 (2.3–4.0)	3.3 (2.2–6.4)	3.0 (2.1–5.3)	5.6 (5.1–6.6)	5.6 (4.9–6.9)	5.5 (5.1–5.9)	5.1 (5.0–5.6)
Ca_t (mg/g dw)	26 (7.3–76)	34 (11–25)	15 (5.2–25)	34 (13–58)	56 (50–61)	44 (33–59)	55 (47–70)	48 (46–50)
Ca_{exc} (% of total)	26 (8.2–53)	17 (7.6–28)	34 (25–41)	20 (9.9–42)	9.5 (8.4–10)	11 (8–14)	8.0 (6.7–10)	9.5 (9.0–10)
Mg_t (mg/g dw)	7.5 (3.8–10)	8.1 (6.7–11)	7.5 (4.7–10)	8.5 (6.8–9.6)	7.0 (4.7–10)	9.6 (8.3–11)	8.5 (7.2–12)	10 (6.4–12)
Mg_{exc} (% of total)	3.7 (2.0–6.6)	5.2 (4.0–7.1)	7.1 (2.4–24)	7.5 (2.9–20)	14 (11.2–18)	10 (10–11)	9.4 (9.3–9.6)	9.4 (7.3–13)
Fe_t (mg/g dw)	24 (15–32)	27 (21–34)	28 (14–46)	30 (21–44)	28 (18–47)	28 (18–45)	26 (18–39)	31 (22–42)
Fe_{exc} (% of total)	0.005 (0.001–0.013)	0.007 (0.001–0.015)	0.006 (0.001–0.009)	0.008 (0.002–0.015)	0.003 (0.001–0.007)	0.004 (0.001–0.009)	0.004 (0.002–0.015)	0.006 (0.002–0.009)
Mn_t (mg/g dw)	0.52 (0.31–1.00)	0.63 (0.43–0.83)	0.55 (0.35–1.02)	0.69 (0.42–1.01)	0.75 (0.69–0.88)	0.74 (0.64–0.87)	0.73 (0.68–0.80)	0.71 (0.68–0.77)
Mn_{exc} (% of total)	3.8 (1.6–6.1)	4.9 (2.1–7.8)	4.3 (1.5–6.9)	5.8 (1.9–7.8)	3.2 (0.8–3.6)	2.0 (0.7–3.9)	3.2 (0.6–5.0)	2.3 (1.4–4.1)
Al_t (mg/g dw)	0.40 (0.08–0.61)	0.42 (0.18–0.59)	0.52 (0.08–1.41)	0.64 (0.20–1.36)	0.54 (0.01–1.58)	0.72 (0.09–1.68)	0.43 (0.01–1.25)	0.57 (0.08–1.27)
Al_{exc} (% of total)	0.18 (0.02–0.44)	0.30 (0.02–0.50)	0.23 (0.03–0.44)	0.37 (0.02–0.57)	1.07 (0.20–2.00)	0.14 (0.11–0.18)	0.83 (0.17–1.33)	0.30 (0.13–0.64)

Fig. 2. Phosphorus fractionation in coarse (sand) and fine (silt/clay) sized lake sediments: (a) mean concentrations of P-fractions, (b) relative contribution of each P-fractions to the sedimentary inorganic phosphorus. (V_1, V_2: sampling sites in Lake Volvi, K_1, K_2: sampling sites in Lake Koronia, C, F: coarse (63–2000 μm), fine (<63 μm sediment fraction).

centrations in Lake Volvi. Although the concentrations of P-fractions are relatively higher in the fine-sized sediment in both lakes, the observed differences were only significant (at 95% significance level) for the fractions HCl–P in Volvi and NH_4Cl–P in Koronia.

Concentrations of P-fractions for the whole sediment were calculated from concentrations in the two grain size fractions and the granulometric sediment composition. Mean values are presented in Fig. 3(a). The rank order of P-fractions in both lakes was HCl–P > NaOH–P > BD–P > NH_4Cl–P. This distribution is similar to the rank observed in Mexico estuaries and differs totally from those found in most river sediments (Huanxin et al., 1994). HCl–P has been reported to be the abundant fraction in sediments of some lakes (e.g. Lake Onondaga, USA), while in many cases the BD–P fraction predominates sedimentary P (e.g. Lake Stechlin, Germany) (Table 3). A separate discussion of each P-fraction is given below.

3.2.1. Loosely sorbed phosphorus (NH_4Cl–P)

NH_4Cl–P represents the loosely sorbed P. This fraction may contain porewater P, P released from $CaCO_3$-associated phosphorus or leached P from decaying cells

of bacterial biomass in deposited phytodetrital aggregates (Gonsiorczyk et al., 1998; Pettersson, 2001). The NH_4Cl–P is a seasonally variable pool of phosphorus compounds dissolved in the interstitial water (Rydin, 2000).

In both lakes the mean NH_4Cl–P concentrations in whole sediment were low: 3.11 μgP/g in V_1, 1.17 μgP/g in V_2, 1.64 μgP/g in K_1 and 1.92 μgP/g in K_2 (Fig. 3(a)). The highest NH_4Cl–P concentration was observed in sediments collected from V_1 in June (7.6 μgP/g) where the highest sedimentary inorganic P concentration was also found. The loosely sorbed P represents < 1% of the sedimentary inorganic P in both lake systems (Fig. 3(b)). Values ranging from 1% to 25% have been reported for calcareous lakes with the upper values being attributed to high degree of oversaturation (Penn et al., 1995).

3.2.2. Reductant soluble phosphorus (BD–P)

BD–P represents the redox-sensitive P forms, mainly bound to Fe-hydroxides and Mn compounds (Kozerski and Kleeberg, 1998). This fraction is considered as potentially mobile pool of P and is algal available. It may be released from anaerobic sediments and becomes an internal P source to water bodies, which suffer from occasional DO depletion (Kleeberg and Dudel, 1997).

The BD–P concentrations in both lakes exhibited high variability. BD–P concentrations were almost two times higher in sediments from Lake Volvi (26.3 μgP/g in V_1 and 21.0 μgP/g in V_2) than from Koronia (13.6 μgP/g in K_1 and 12.6 μgP/g in K_2). This difference might be related to the trophic status of the two lakes, since in oligotrophic systems higher BD–P concentrations are observed probably due to the oxic sediment surface that acts as boundary layer for upwards diffusing P, Fe and Mn (Gonsiorczyk et al., 1998). However, the relative contribution of BD–P to the sedimentary inorganic P was similar, 5.6% in Volvi and 4.8% in Koronia (Fig. 3(b)). These values are relatively low in comparison to the values reported for other lakes, such as Muggelsee (23–31%), Saidenbach (28%), Stechlin (54%) (Table 3). Low content of reductant P in sediments has been associated to DO depletion occurring in sediments of hypertrophic lakes during summer, and/or to high pH values or bacterial activity that might enhance P-release from this fraction (Maine et al., 1992; Ting and Appan, 1996; Perkins and Underwood, 2001). In addition, high organic content in sediments may inhibit binding of P by Fe, possibly by competition from binding sites (Kleeberg and Kozerski, 1997).

3.2.3. Metal oxide bound phosphorus (NaOH–P)

The NaOH–P represents P bound to metal oxides, mainly of Al and Fe, which is exchangeable again with OH^- and inorganic P compounds soluble in bases (Kozerski and Kleeberg, 1998). NaOH extractable phosphorus can be used for the estimation of both short-term

Table 3
Literature data concerning P-fractionation in lake sediments

	Lake Stechlin[a], Germany	Lake Haussee[a], Germany	Lake Onondaga[b], USA	Lake Saidenbach[c], Germany	Lake Neunzehnhaim[c], Germany	Lake Erken[d], Sweden	Lake Muggelsee[e], Germany	Lake Kinneret[f], Israel	Lake El Timbo[g], Argentina
Trophic status	Oligotrophic	Eutrophic	Hypertrophic calcareous	Meso-eutrophic	Oligotrophic	Moderately eutrophic	Eutrophic	Monomistic calcareous	
NH_4Cl–P (µgP/g or TP%)	1–3%	4–8%	25%	140[h]	< 10	27 (1.5%)		7%	0.06%
BD–P (µgP/g or TP%)	1290 (54%)	320		1200[h] (28%)	150[h]	345 (19%)	23–31%		
NaOH–P (µgP/g or TP%)	250[h]	400[h]	10–20%	1300[h]	1000[h]	85 (4.7%)		22%	42%
HCl–P (µgP/g or TP%)	200[h] (14%)	450[h] (32%)	30–60%	300[h]	300[h]	287 (16%)		40%	30%
P_{sum}[i]	1768[h]	1254[h]	–	2940[h]	1460[h]	744[h]			
TP(µgP/g)	2389[h]	1406		3000[h]	1600[h]	1814	2700	1110	677
OM (%)	38[h]	38[h]		20[h]	40[h]		25	12–30	
$CaCO_3$(%)	30[h]	40[h]	49					51	

[a] Gonsiorczyk et al. (1998).
[b] Penn et al. (1995).
[c] Uhlmann et al. (1997).
[d] Rydin (2000).
[e] Kleeberg and Dudel (1997).
[f] Eckert et al. (1997).
[g] Maine et al. (1996).
[h] Values roughly estimated from figure data.
[i] $P_{sum} = NH_4Cl - P + BD - P + NaOH - P + HCl - P$.
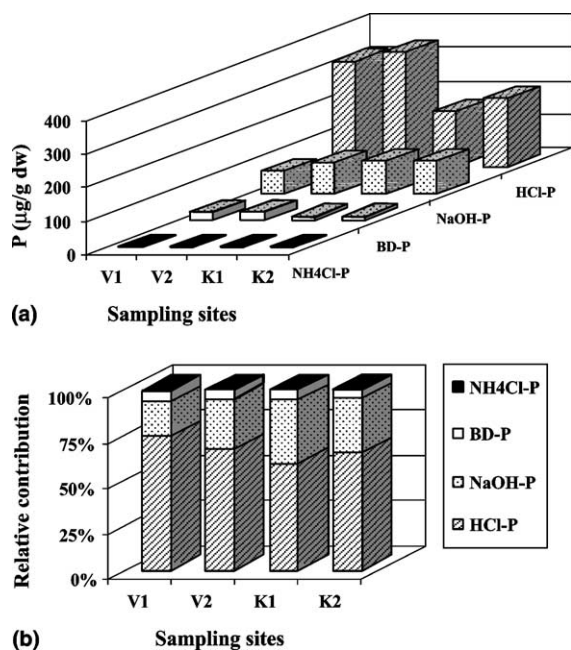
Fig. 3. Mean concentrations of P-fractions (a) and their relative contribution to sedimentary inorganic phosphorus (b) in whole sediments.

and long-term available P in sediments and is a measure of algal available P (Zhou et al., 2001). This fraction could be released for the growth of phytoplankton when anoxic conditions prevail at the sediment–water interface (Ting and Appan, 1996).

The mean NaOH–P concentrations in the whole sediment were: 70.1 μgP/g in V_1, 111 μgP/g in V_2, 99.3 μgP/g in K_1 and 98.9 μgP/g in K_2 (Fig. 3(a)). The relative contribution of NaOH–P to sedimentary inorganic P was rather similar in both lakes (35% in K_1, 30% in K_2, 19% in V_1 and 28% in V_2) (Fig. 3(b)). This Fe and Al–P fraction contributed 10–20% of the sediment TP in Onondaga lake (USA), while reports from 27 lakes suggest wide variation in this fraction (5–70%) with higher values found in eutrophic non-calcareous environments (Penn et al., 1995).

3.2.4. Calcium bound phosphorus (HCl–P)

The HCl–P represents P forms sensitive to low pH, assumed to consist mainly of apatite P, which is natural and detrital, P bound to carbonates and traces of hydrolysable organic P. Calcium bound P is a relatively stable fraction of sedimentary P and contributes to a permanent burial of P in sediments (Gonsiorczyk et al., 1998; Kozerski and Kleeberg, 1998).

Most of sedimentary inorganic P in the two lakes was in HCl-soluble forms (316 μgP/g in V_1, 313 μgP/g in V_2, 165 μgP/g in K_1 and 205 μgP/g in K_2). This fraction

dominated the sedimentary P-load in both lakes ranging from 59% to 74% (Fig. 3(b)). The high HCl–P could be attributed to the calcareous terrain of the recharge area. High portions of calcium mineral-P were also observed in lakes having varying trophic status. In these lakes Ca–P and residual-P fractions were dominant, together comprising 35–90% of the TP, with calcareous sediments close to the upper end of the range (Penn et al., 1995).

3.3. Statistical analysis

3.3.1. Analysis of variance

Sediment quality data from each lake were statistically analysed to examine whether factors such as sampling month, sampling site or sediment granulometry had a significant effect on the observed variance of P-fractions and other sediment features. 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. The statistical method was run in SPSS 8.0S software package (SPSS, 1998). The effect of sampling month was significant for the most parameters in both lakes. In Lake Volvi sampling month had a significant effect on redox sensitive-P and calcium bound-P, LOI, $CaCO_3$, total Ca and Mn and exchangeable fractions of Mg, Al and Fe. In Lake Koronia the effect of sampling month was significant for labile P-fractions (NH_4Cl–P, BD–P, NaOH–P), TOC, LOI, $CaCO_3$, total and exchangeable Mg, Al, Fe and Mn. On the contrary, neither sampling site nor sediment granulometry showed significant effect on variance of P-fractions or other sediment characteristics.

3.3.2. Principal component analysis (PCA)

Principal component analysis (PCA) has been used to identify the factors influencing the variance of P-fractions in lake sediments. PCA is a powerful pattern recognition technique that attempts to explain the variance of a large set of intercorrelated variables with a smaller set of independent variables. The initial set of factors generated by PCA is not readily interpretable therefore it is usually transformed by Varimax rotation. The elimination of factors with eigenvalues less than 1 can lead to the exclusion of meaningless factors (Hopke, 1985). Once the rotated factors are determined, their identity can be assigned based on their correlations with the original variables.

PCA was performed on normalized data using the SPSS 8.0S software package (SPSS, 1998). It was performed on the sediment data set of each lake. The Varimax rotated factor matrix for both lakes is presented in Table 4.

Four factors accounted for 88.9% of the variance of data in Lake Volvi. The *first factor* accounting for 47.2% of the total variance, was correlated primarily with NaOH–P, Fe_{total} and LOI. This factor shows the

Table 4
Varimax rotated factor matrix[a] for sediment data set

Variable	Lake Volvi				Lake Koronia		
	F_1	F_2	F_3	F_4	F_1	F_2	F_3
NH$_4$Cl–P		0.511	0.765		0.723	−0.581	
BD–P			0.934			−0.635	−0.559
NaOH–P	0.931					0.971	
HCl–P				0.862			0.959
Sand (%)	−0.472			0.703	−0.973		
LOI (%)	0.859				0.928		
CaCO$_3$ (%)		0.831			0.817		
Ca$_t$		0.991			−0.753		
Mg$_t$			0.725		0.849		
Al$_t$	0.526			−0.701	0.978		
Fe$_t$	0.968				0.971		
Mn$_t$	0.658	0.718			0.923		
Variance (%)	47.2	18.4	13.6	9.7	57.5	17.0	10.2

[a] Loadings higher than 0.400 are only given.

important role of iron compounds (more important than aluminum) and organic matter in regulating this mobile P-budget of the lake (Maine et al., 1996). It is also indicates that this P-form can be considered the most reactive one in this system. The *second factor* accounting for 18.4% of the variance was correlated with Ca$_{total}$, CaCO$_3$, Mn$_{total}$ and NH$_4$Cl–P. This factor suggests that carbonates or manganese may control the presence of loosely bound P and probably represents the autochthonous precipitation of P (Sallade and Sims, 1997; Gonsiorczyk et al., 1998). The *third factor* which is strongly correlated with BD–P, NH$_4$Cl–P and Mg$_{total}$, shows that redox conditions and the presence of Mg, both depended on algal productivity, could influence the mobile pool of the lake (Gonsiorczyk et al., 1998). Lastly, *the fourth factor* was positively correlated with HCl–P and sand content of the sediment whereas negatively with Al$_{total}$. This factor could represent the allogenic origin of the sedimentary phosphorus, probably due to erosion processes.

Three factors accounting for 84.7% of total variance were identified in lake Koronia (Table 4). The *first factor*, accounting for 57.5% of the variance, was positively correlated with NH$_4$Cl–P, LOI, CaCO$_3$ and total concentrations of Mg, Al, Fe, Mn while negatively correlated with sand content and Ca$_{total}$. This factor could be interpreted as representing the processes influencing the loosely bound P that seems to be the most reactive fraction in this system. These processes might include settlement of planktonic diatoms and deposition of fine-sized particles where P is associated with carbonates, organic matter, ferromanganese oxides (Pizarro et al., 1992; Sohrin et al., 1996; Johnson, 1997; Gibson et al., 2001; Pettersson, 2001). The *second factor*, accounting for 17% of the variance, was positively correlated with NaOH–P and negatively with BD–P and NH$_4$Cl–P thus representing the interrelationships among the algal available phosphorus fractions. Mineralization of organic matter could be one possible route of mobilized P from NaOH–P to the other P-fractions (Gonsiorczyk et al., 1998). The *third factor*, accounting for 10.2% of the variance, was primarily correlated with HCl–P and negatively with BD–P showing that the terrigenous forms P extracted by strong acids might contain P forms that could be possible source of reductant P, probably due to bacterial activity that could solubilize P-compounds (Maine et al., 1992; Sallade and Sims, 1997).

References

APHA, AWWA, WPCF, 1985. Standard methods for the examination of water and wastewater, 16th edition.

Chang, S.C., Jackson, M.L., 1957. Fractionation of soil phosphorus. Soil Sci. 84, 133–144.

Eckert, W., Nishri, A., Parparova, R., 1997. Factors regulating the flux of phosphate at the sediment–water interface of a subtropical calcareous lake: a simulation study with intact sediment cores. Water, Air, Soil Pollut. 99, 401–409.

Gibson, C.E., Wang, G., Foy, R.H., Lennox, S.D., 2001. The importance of catchment and lake processes in the phosphorus budget of a large lake. Chemosphere 42, 215–220.

Gonsiorczyk, T., Casper, P., Koschel, R., 1998. Phosphorus binding forms in the sediment of an oligotrophic and an eutrophic hardwater lake of the Baltic district (Germany). Water Sci. Technol. 37 (3), 51–58.

Hopke, P.K., 1985. Receptor Modeling in Environmental Chemistry. Wiley, USA.

House, W.A., Denison, F.H., 2000. Factors in fluencing the measurement of equilibrium phosphate concentrations in river sediments. Water Res. 34 (4), 1187–1200.

Huanxin, W., Presley, B.J., Armstrong, D., 1994. Distribution of sedimentary phosphorus in gulf of Mexico estuaries. Mar. Environ. Res. 37, 375–392.

Hupfer, M., Gachter, R., Giovanoli, R., 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. Aquat. Sci. 57, 305–324.

Johnson, A., 1997. Fe and Al sedimentation and their importance as carriers for P, N and C in a large humic lake in Northern Sweden. Water, Air, Soil Pollut. 99, 283–295.

Kleeberg, A., Dudel, G.E., 1997. Changes in extent of phosphorus release in a shallow lake (Lake Großer Muggelsee; Germany, Berlin) due to climatic factors and load. Mar. Geol. 139, 61–75.

Kleeberg, A., Kozerski, H.P., 1997. Phosphorus release in lake Großer Muggelsee and its implications for lake restoration. Hydrobiologia 342/343, 9–26.

Kouimtzis, Th., 1999. Annual report. Monitoring of surface water quality in the area of Macedonia, N. Greece. Chemistry Department, University of Thessaloniki (in Greek).

Koussouris, T.S., Bertakos, T.I., Diapoulis, A.C., 1992. Background trophic state of Greek lakes. Fresenius Environ. Bull. 1, 96–101.

Kozerski, H.P., Kleeberg, A., 1998. The sediments and the benthic pelagic exchange in the shallow lake Muggelsee. Int. Rev. Hydrobiol. 83, 77–112.

Maine, M.A., Hammerly, J.A., Leguizamon, M.S., Pizarro, M.J., 1992. Influence of the pH and redox potential on phosphate activity in the Parana Medio system. Hydrobiologia 228, 83–90.

Maine, M.A., Panigatti, M.C., Sune, N.L., Pizarro, M.J., 1996. Phosphorus forms in lotic and lentic environments of the middle Parana flood valley (Argentina). Pol. Arch. Hydrobiol. 43 (4), 391–400.

Penn, M.R., Auer, M.T., Van Orman, E.L., Korienek, J.J., 1995. Phosphorus diagenesis in lake sediments: investigation using fractionation techniques. Mar. Freshwater Res. 46, 89–99.

Perkins, R.G., Underwood, G.J.C., 2001. The potential for phosphorus release across the sediment–water interface in an eutrophic reservoir dosed with ferric sulphate. Water Res. 35 (6), 1399–1406.

Pettersson, K., 2001. Phosphorus characteristics of settling and suspended particles in Lake Erken. Sci. Total Environ. 266, 79–86.

Pizarro, M.J., Hammerly, J., Maine, M.A., Sune, N., 1992. Phosphate adsorption on bottom sediments of the Rio de la Plata. Hydrobiologia 228, 43–54.

Psenner, R., 1988. Fractionation of phosphorus in suspended matter and sediment. Ergeb. Limnol. 30, 98–113.

Psenner, R., Pucska, R., Sager, M., 1984. Die fractionierung organischer und anorganischer phosphorverbindungen von sedimenten versuch einer Definition okologisch wichtiger tractionen. Arch. Hydrobiol. (Suppl. 10), 115–155.

Ramm, K., Scheps, V., 1997. Phosphorus balance of a polytrophic shallow lake with consideration of phosphorus release. Hydrobiologia 342/343, 43–53.

Rydin, E., 2000. Potentially mobile phosphorus in lake Erken sediment. Water Res. 34 (7), 2037–2042.

Sallade, Y.E., Sims, J.T., 1997. Phosphorus transformations in the sediments of Delaware's agricultural drainageways: II. Effect of reducing condition on phosphorus release. J. Environ. Anal. 26, 1579–1588.

Sohrin, Y., Tateishi, T., Mito, S., Matsui, M., Maeda, H., Hattori, A., Kawashima, M., Hasegawa, H., 1996. Nutrients of Lake Biwa in the unusually cool and hot summers of 1993 and 1994. Lakes Reservoirs: Res. Manage. 2, 77–87.

SPSS Base 8.0S for Windows, 1998. SPSS Inc.

Tan, K.H., 1995. Soil Sampling, Preparation and Analysis. Marcel Dekker, New York.

Thirunavukkarasu, O.S., Viraraghavan, T., Selvapathy, P., 2000. A comparative account of phosphorus release from sediments of a lake and a reservoir: laboratory experiments. Fresenius Environ. Bull. 9, 461–467.

Ting, D.S., Appan, A., 1996. General characteristics and fractions of phosphorus in aquatic sediments of two tropical reservoirs. Water Sci. Technol. 34 (7–8), 53–59.

Uhlmann, D., Hupfer, M., Appelt, C., 1997. Composition of sediments in drinking water reservoirs as a basis for the assessment of potential changes in water quality. J. Water SRT-Aqua 46 (2), 84–94.

Williams, J.D.H., Jaquet, J.M., Thomas, R.L., 1976. Forms of phosphorus in surficial sediments of Lake Erie. J. Fish. Res. Board Can. 33, 413–429.

Zhou, Q., Gibson, C.E., Zhu, Y., 2001. Evaluation of phosphorus bioavailability in sediments of three contrasting lakes in China and the UK. Chemosphere 42, 221–225.