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SEQUENTIAL FRACTIONATION OF PHOSPHORUS IN LAKE SEDIMENTS OF NORTHERN GREECE

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Abstract. The amounts and forms of potentially mobile P in surface sediments from two lakes, Volvi and Koronia, located in Northern Greece were evaluated using a sequential chemical extraction. Five sedimentary P reservoirs were separately quantified: loosely sorbed P (NH_4Cl-P); iron associated P (BD-P); calcium bound P (HCl-P); metal oxide bound P (NaOH-P) and residual P (organic and refractory P). Samples were taken in two seasons and the average concentration of the fractions of phosphorus were calculated. The results indicated that the TP content and chemically extractable phosphorus in the sediments of Koronia Lake were higher than those of Volvi Lake. Sediment TP was also strongly and positively correlated with sediment Fe. Fine-sized sediments exhibited significantly higher concentrations for both lakes than the sand fraction. The P in the surface sediment mainly consisted of HCl-P and Res-P, while NH_4Cl-P and BD-P only constituted a minor part. The rank order of the different P extracts was the same for the two lakes and was Residual-P > HCl-P > NaOH-P > BD-P > NH_4Cl-P.

Keywords: lake sediment, phosphorus, sequential fractionation

1. Introduction

Sediments play a fundamental role in determining concentration, distribution and the final fate of several pollutants acting as a principal transport vehicle and the site of accumulation or release (Søndergaard *et al.*, 1996; Kleeberg *et al.*, 1997).

Phosphorus is often the limiting nutrient for algal growth in lakes and may limit marine productivity (2). Phosphorus may enter an aquatic system in the particulate form or dissolved-P may become associated with particles as they settle out of the water column. Sedimentation is a major P sink for the epilimnia of lakes, transporting P to the hyoplimnion and ultimately the sediments. The long-term contribution of sediment bound P in promoting eutrophication of freshwater can be more efficiency evaluated on the basis of different P-fractions instead of total phosphorus content, since the total concentrations of phosphorus in sediments cannot predict the potential ecological danger (Psenner *et al.*, 1984).

Physical and chemical characterization of sediments is important for evaluating the phosphate exchange processes between bottom sediments and overlying waters (Gonsiorezyk *et al.*, 1978). In many lakes a significant fraction of the annual phosphate loading accumulates in the sediments. Depending upon environmental conditions, partial release of these phosphates may occur (Rydin, 2000). Solubility of phosphate in the interstitial water of a sediment under prevailing conditions of pH, redox potential and ionic strength is controlled by the chemical composition of the phosphates present and their interactions with other minerals or amorphous materials (Maine *et al.* 1992). The association of phosphate with iron, aluminum and calcium, and the adsorptive properties of carbonates and clays are of special interest (Jensen *et al.*, 1992). Since the amount of phosphorus release from sediment is called internal phosphorus loading, which can enhance lake eutrophication, the fractionation of sediment P can be conducive to understanding P cycling in the aquatic ecosystem. Phosphorus release is a function of the quantity and distribution of phosphorus fractions within the sediments, the degree of saturation of exchangeable phosphorus and of hydrological conditions (Fu *et al.*, 2000; Ruttenberg, 1992; Bulchand *et al.*, 1994).

Several extraction schemes have been developed to elucidate the chemical nature of sediment phosphates (Hupfer *et al.*, 1995; Barbanti *et al.*, 1988). Sequential extraction of P as suggested by several authors is a useful tool for characterisation of various P compounds (Zhou *et al.*, 2001; Psenner *et al.*, 1998; De Groot, 1990; Pardo, 1998).

Chemical fractionation, involving sequential extraction procedures, is based on differences in reactivity of solid phases to different extractant solutions (Hieltjes *et al.*, 1980). The objective of the present study was to estimate the bioavailability/mobility of phosphate from lake sediments in Northern Greece using a sequential extraction procedure and to evaluate their possible contributions to the P-loadings of two lakes.

2. Materials and Methods

2.1. SITE DESCRIPTION

The studied lakes, the meso-to-eutrophic Volvi and the hypertrophic Koronia, are located in N. Greece, about 11.5 km NE of the city of Thessaloniki. 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 major sources that affect water quality and 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 dyes industries. Other important sources are resuspended stream sediments and eroded bank materials.

The data and selected chemical characteristics of the studied lakes are shown in Table I. Volvi Lake with a surface area 69 km^2 and mean depth 13.5 m, has been

TABLE I

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	Lower mesotrophic level		Mesotrophic level
	V1[a]	*V2*[a]	*K*[a]
pH	8.87	8.95	8.95
Conductivity (μS cm^{-1})	1145	1134	5080
DO (mg L^{-1})	8.1	8.2	7.8
COD (mg L^{-1})	84	40	61
TOC (mg L^{-1})	16.3	18.2	17.2
TC (mg L^{-1})	94.5	94.7	213
IC (mg L^{-1})	78.3	76.50	195
TP (μg P L^{-1})	218	44	262
NO$_3$ (μg N L^{-1})	152	105	232
Fe (μg L^{-1})	126	134	147
Mn (μg L^{-1})	52	56	64

[a] V_1 and V_2: sampling sites in Lake Volvi; K: sampling site in Lake Koronia.

classified on the basis of chemical and biological water parameters as a meso- to eutrophic lake. Koronia Lake, with a surface area 42 km^2 and a mean depth 2 m, has been classified as hypertrophic (Kaiserli *et al.*, 2002). The surface area has been significantly reduced during recent years due to over-exploitation of water for agricultural and industrial purposes.

2.2. SEDIMENT SAMPLES AND PROCEDURE

Sediment samples were collected using an Eckman sampling device from the top 20 cm layer of the bottom from one sampling site of the lake Koronia (K) and two sampling sites from the lake Volvi (V_1, V_2) in two seasons. Samples taken were immediately carried to the laboratory and stones and plant fragments were removed by passing the samples through a 2 mm sieve. The samples were air dried, homogenized by grinding and finally passed through a 75 μm sieve (silt/clay fraction) and 75–150 μm (sand fraction) and stored in glass bottles.

Analysis of the fraction <75 μm is recommended in sediment studies because clay and silt particles generally contain the highest concentrations of pollutants, and are most readily transported in suspension in natural waters.

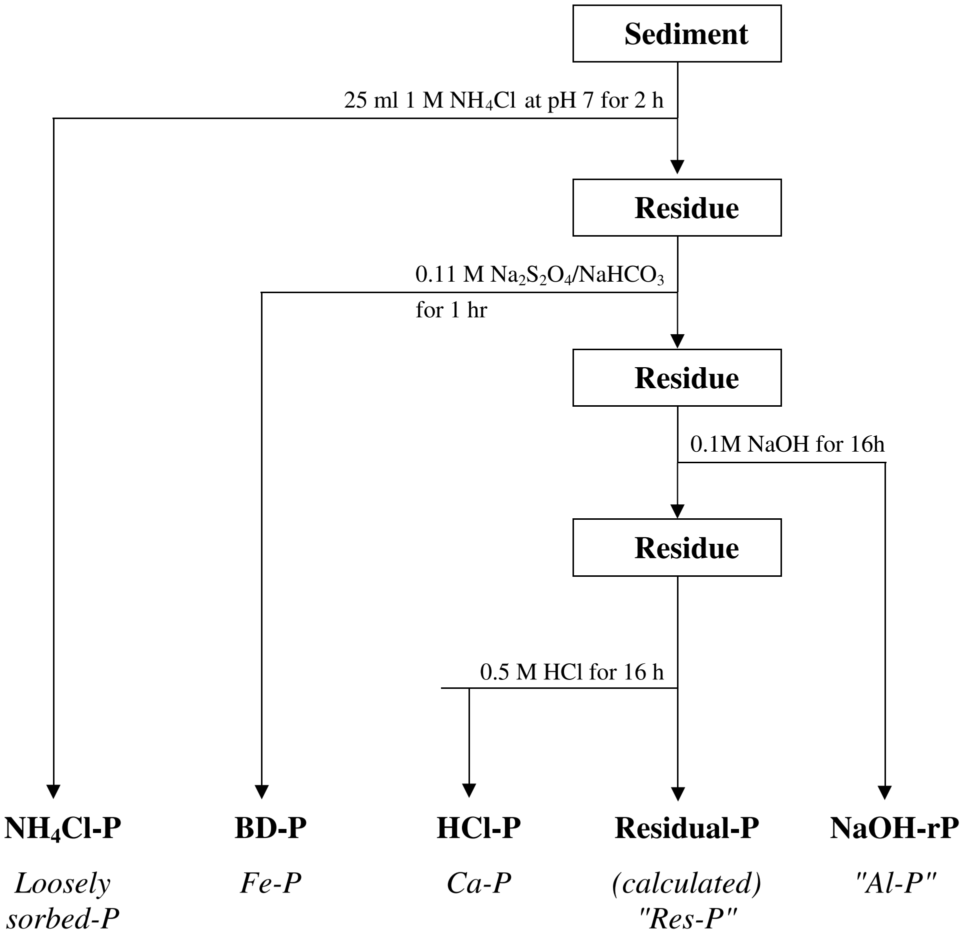

Figure 1. Sequential extraction method followed in the present study.

In order to characterize various P-species in lake sediments, a sequential extraction scheme according to Psenner *et al.* (1984) was used with some modifications by Hupfter *et al.* (1995) (Figure 1).

Fraction 1: NH_4Cl-extractable phosphorus at neutral pH
This fraction is often termed labile (desorbed, hydrolyzed) loosely bound or adsorbed phosphorus. It gives an estimate of the immediately available phosphorus.

Fraction 2: Buffered dithionite extractable phosphorus (at 25 °C)
It is assumed that reductant soluble phosphorus forms are extracted, mainly from iron hydroxide surfaces.

Fraction 3: NaOH-extractable phosphorus
Reactive NaOH-P represents phosphate adsorbed to metal oxides (Al_2O_3) and other surfaces, exchangeable against OH^- and phosphorus compounds soluble in bases.

Fraction 4: HCl-extractable phosphorus
It represents P bound to carbonates, apatite-P and P released by the dissolution of oxides (not adsorbed to the surface). It may contain traces of hydrolyzed organic phosphorus.

Fraction 5: Residual phosphorus
It is the difference between TP (total phosphorus) – determined by digestion method – and the sum of soluble reactive phosphorus (SRP) in the fractions 1–4. Organic and refractory P compounds are included in this fraction.

When considering P-franctions and their mobilization, there is a need to know how much (or what fraction) of the sediment can be available to algae and/or bacteria. According to Bostrom *et al.* (1982), a good approach would be to consider all P that can be released within the occuring ranges of temperature, pH and redox as bioavailable.

In each fraction, soluble reactive P (SRP) was determined after filtration through a pre-rinsed 0.45 μm membrane filter (Schleicher and Schuell) according to the molybdenum blue/ascorbic acid method (APHA, 1985). Total P (TP) of sediments was determined according to Vogler (1965). TOC was determined after treatment of the sample with $K_2Cr_2O_7/H_2SO_4$ according to the Walkey-Black Method (Tan, 1995). Total concentrations of Ca, Fe, Mn, Mg and Al in sediment fractions were measured after wet digestion with an atomic absorption spectrometer (Perkin-Elmer 2380) operating in the flame mode. The exchangeable fraction of these metals was determined after extraction with 1 M CH_3COONH_4 at pH 7 (Fytianos *et al.*, 2003). The determination of these metals was performed by using FAAS or GFAAS techniques. Sediment was also analyzed for dry weight (DW) by drying at 105 °C for 24 hr and for loss of ignition (LOI) by drying to constant weight at 550 °C.

3. Results and Discussion

Chemical properties of the examined lake sediments are shown in Table II.

TP ranged from 0.9 to 1.30 mg P g^{-1} DW. The water content ranged from 9 to 49.4%. Both Fe and Ca differed greatly from lake to lake, Fe ranging from 3.9 to 16.4 mg Fe g^{-1} DW and Ca from 0.7 to 4.2 mg Ca g^{-1} DW. Median NH_4Cl-P, NaOH-P, HCl-P, BD-P and Res-P were 8.2, 94.6, 219.3 and 974 μg P g^{-1} DW for Koronia lake (fraction <75 μm), respectively, and for Volvi lake (fraction <75 μm) 7.3, 10.6, 250.3, 4.1 and 771.7 μg P g^{-1} DW (site V_1) and for site V_2 8.2, 13.9, 241.4, 5.4 and 677.1, respectively (Figure 2). Mean Fe:TP ratio was approximately

TABLE II

Chemical properties of the examined lake sediments (mean values)

Parameters	Lake Koronia		Lake Volvi			
			V_1		V_2	
	F	C	F	C	F	C
Ca_t (mg g^{-1} dw^{-1})	4.2	4.2	2.6	1.0	1.5	0.7
Mg_t (mg g^{-1} dw^{-1})	17.3	16.3	5.6	4.2	8.9	5.2
Fe_t (mg g^{-1} dw)	16.4	16.4	6.4	4.4	5.9	3.9
Mn_t (mg g^{-1} dw)	0.32	0.30	0.05	0.02	0.052	0.023
Al_t (mg g^{-1} dw)	8.17	7.99	8.83	1.99	4.09	3.57
TOC (% dw)	1.745	0.965	0.678	0.308	1.170	0.103
Total-P (μg g^{-1} dw)	1305	1156	1044	809	946	776
Water content (%)	49.4		23		9	
LOI (% dw)	6.5		4.1		3.7	

F: Silt/clay fraction (<75 μm sediment faction).
C: Coarse fraction (75–150 μm sediment fraction).
V_1 and V_2: Sampling sites in Lake Volvi.

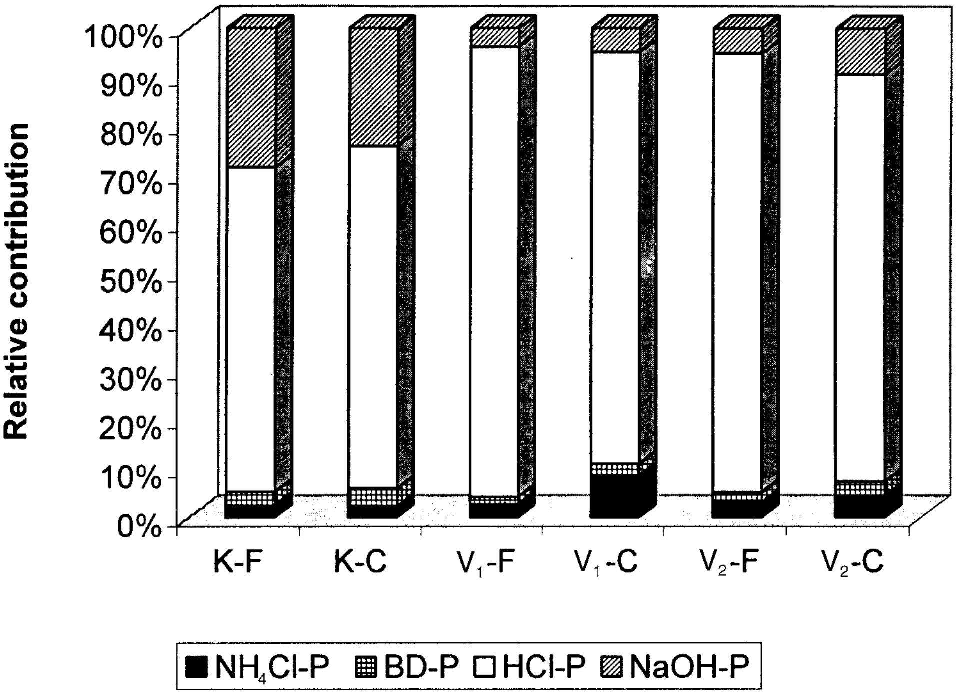

Figure 2. Relative contribution of each P-fraction to the sum of soluble reactive phosphorus (SRP) (fractions 1–4).

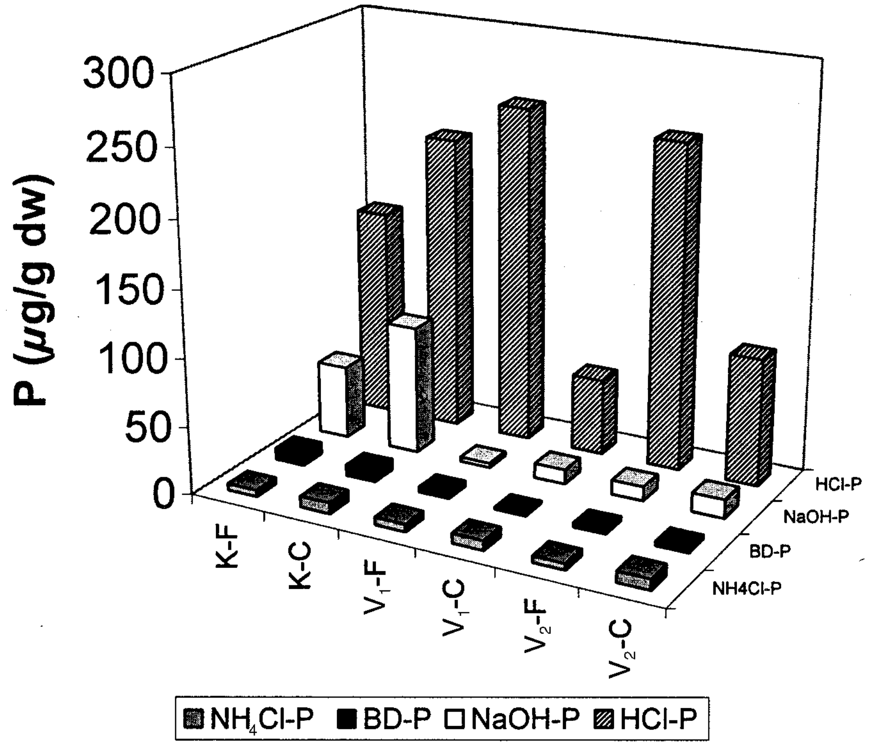

Figure 3. Mean concentrations (μg g^{-1} dw) of the P-fractions.

12 (by weight) in Koronia Lake and 4.5 in Volvi. There is an apparent relation between TP and Fe in the sediments (Moutin *et al.*, 1993; Søndergaard *et al.*, 1996).

In contrast to Fe, there was no correlation between Ca and any of the phophorus fractions. This is consistent with the findings of others (Jensen *et al.*, 1992) and confirms that the amount of Ca present in the sediment has no impact on the distribution of the various phosphorus pools (De Groot, 1991).

The molar ratio of Ca/Mg was higher at site V_1 than at other sites. Thus Ca bound P may be the dominant form of P in HCl-P extracts rather than Mg-P.

The P in the surface sediment mainly consisted of HCl-P and Res-P, which accounted for 12 and 82% of TP for Koronia, 24 and 75% of TP for V_1 and 25 and 72% of TP for V_2, respectively. The remainder was mainly NaOH-P, while NH_4Cl-P and BD-P only consistuted a minor part. The relative contribution of each P-fraction to the sum of soluble reactive phosphorus (SRP), is presented in Figure 3.

The mean values of the concentrations of the P-fractions of the two grain sizes are presented in Table III.

Fractional composition of the two examined lakes was similar except for HCl-P and NaOH-P. TP concentration in the surface sediment and water of Koronia was

TABLE III

Phosphorus fractionation in the two sized sediments of the examined lakes (μg g^{-1} dw)

Parameters	Lake Koronia		Lake Volvi			
			V_1		V_2	
	F	C	F	C	F	C
NH_4Cl-P	8.2	4.9	7.3	5.7	8.2	4.9
BD-P	9.0	8.2	4.1	1.6	5.4	3.3
HCl-P	219.0	155.0	250.0	56.3	241.0	93.8
NaOH-P	94.6	53.8	10.6	3.3	13.9	10.6
Residual-P	974.0	934.2	772.0	742.0	677.0	664.4
Total-P	1304.8	1156.1	1044	808.9	945.5	777.0

V_1 and V_2: Sampling sites in Lake Volvi.
C: Coarse sediment fraction (75–150 μm).
F: Fine sediments fraction (<75 μm).

higher than in Volvi lake. The correlation between NH_4Cl-P and LOI emphasizes that the NH_4Cl-P phosphorus fraction is very dynamic and may therefore be a useful indicator of the processes that determine sediment water interactions, despite the fact that is usually constitutes only a few percent of the TP pool (Pettersson *et al.*, 1988; Søndergaard, 1988).

4. Conclusions

Even though the data presented in this study are limited and cover a relatively small range of sediments of the examined lakes, some useful conclusions can be drawn.

TP content and chemical extractable phosphorus in the sediments of the hypertrophic Koronia lake were higher than those of Volvi lake. Sediment TP also has an apparent relation to the sediment Fe. Fine sized sediments exhibited significantly higher concentrations for both lakes than the sand fraction.

Most of sedimentary inorganic P in the surface sediment mainly consisted of HCl-P and P, while NH_4Cl-P and BD-P only constituted a minor part. The fraction HCl-P dominated the sedimentary P-load in both lakes ranging from 66 to 91%. HCl-extractable phosphorus represents P bound to calcium and magnesium and P released by the dissolution of oxides. The rank order of the different P extracts was the same for the two lakes and was Residual-P > HCl-P > NaOH-P > BD-P > NH_4Cl-P. According to Dorich *et al.* (1985) and Zhou *et al.* (2001) the NaOH extractable phosphorus can be used to estimate both short-term and long-term available phosphorus in sediments and is a measure of algae – available P. This fraction could be released for the growth of phytoplankton when anoxic conditions prevail at the sediment-water interface.

Also, several changes were not prominently seen in the examined lake sediments. Inspite of the limited examined samples and the lack of statistical analysis, the sequential extraction procedure used in this study contributed to a better understanding of the geochemical cycle of phosphorus and to a realistic evaluation of its bioavailability and mobility in the two lakes.

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