Phosphorus fractionation in lake sediments

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Abstract. The influence of reagent concentration, extraction time, and lithological composition of sediment samples on the concentration and composition of the extracted phosphorus fractions was examined. Good reproducibility was achieved for dry samples. The proportions of P fractions were found to depend on the texture of lake sediments, which speaks about an essential role of cohesivity of sediments and sorption of phosphorus in the sediment flocs. The NaOH–P concentration was higher in the samples with a high silt content. Extraction duration did not influence the concentration of metal oxide bound P extraction with a low (0.1 M) NaOH concentration. The total P concentration showed a significant positive correlation with silt ($r = 0.897$), organic matter ($r = 0.564$), and carbonate content ($r = 0.546$). Sedimentary inorganic P in the studied sediments consisted mainly of HCl–P, while NaOH–P and NH_4Cl–P constituted only a minor part.

Key words: lake sediments, phosphorus fractions, lithological composition.

INTRODUCTION

Sediment phosphorus has been the subject of a number of studies because of its role in the state and development of lake ecosystems (Dillon & Rigler, 1974; Boström et al., 1982; Golterman, 2004). Concentrations of P in lake sediments depend on its concentrations in the lake water, the transport of soluble phosphate between solid components, adsorption–desorption mechanisms, the chemisorption ability of the sediments, and biological uptake (Andersen, 1975; Søndergaard et al., 1992; Koski-Vähälä & Hartikainen, 2001; Koski-Vähälä et al., 2001). Due to the differences in the origin and genesis of the studied water bodies, as well as a large number of external and internal factors, the biogeochemical cycling of P fractions and, thus, their concentrations in sediments can vary greatly. Therefore, it is necessary to analyse different ecosystem components separately and then identify the general rules governing their dynamics (Punning et al., 2007). A prerequisite for sound environmental field studies on phosphorus is application of reliable analytical methodologies. The lack of uniformity between the different extraction methods does not allow comparison of results or validation of procedures. Indeed, the results do not depend only on the extraction method used. For accurate analyses and especially data interpretation, knowledge of P fractions is required, as environmental behaviour is often critically dependent on the physical and chemical form of P. Nevertheless, extraction methods often yield reproducible

results that allow a description of the sediment's P fractions and an estimation of the dominant binding compounds in a given sediment (Pettersson et al., 1988). For the study of the biogeochemical cycling of phosphorus, chemical fractionation methods have been predominantly used. These methods involve a successive addition of different extraction media to sediment samples, each of which is expected to extract a particular fraction of phosphorus. Phosphorus bound to metal oxides, mainly those of Fe and Al, is represented by NaOH–P. The concentration of the NaOH–P fraction can be used for the estimation of both short-term and long-term available P in sediments and it is a measure of available algal P (Zhou et al., 2001). The P fraction that is assumed to consist mainly of apatite P is represented by HCl–P. The most important inorganic P pools seem to be NaOH–P and HCl–P (Golterman, 2004). Most methods of phosphorus determination are based on the reaction of P with an acidified molybdate reagent to yield a phosphomolybdate heteropolyacid, which is then reduced to an intensely-coloured blue compound and determined spectrophotometrically (Murphy & Riley, 1962; McKelvie et al., 1995). There is still debate on the methodological question about the duration of reactions and the concentration of reagents in relation to the concentrations of P extracted. Extractions of NaOH were invalidated by Hieltjes & Lijklema (1980), Golterman (1996), Golterman et al. (1998), and Romero-González et al. (2001). All these authors demonstrated that the duration of the extraction and the reagent concentration always influence the quantities of P extracted and they stressed that more investigations are needed.

Due to the effects of the physical–chemical and environmental conditions on the interface of water and sediments, the proportion of P compounds could be modified and P compounds that have already accumulated within sediments could be partly released. As permanent P exchange takes place within this interface, over time the lake sediment can act as an internal source of phosphorus for the overlying water (Lijklema, 1986; Ramm & Scheps, 1997; Zhou et al., 2001). The existence of different P fractions in association with fractions of different particle size is affected by the sedimentation environment.

The objective of this research was to estimate the use of the following factors in the measurement of phosphorus fraction concentrations in lake sediments as a tool for understanding the potential mobility of P from sediments to the over-laying water: (1) reagent concentration, (2) duration of extraction, (3) stability and reproducibility of the concentrations of extracted P, and (4) lithological composition of the sediment.

METHODS

Samples

For analysis sediment samples were taken from eutrophic and mesotrophic lakes in which the amount of organic matter and authigenic carbonates, as well as the texture of the sediment, vary extensively. The first step was lithological analysis

Table 1. Lithological description; share of sand, silt and clay fractions in the sediment samples (%); organic matter (OM, %) and carbonate content (Carb., %) in the dried samples

Sample No.	Lithology	Sand	Silt	Clay	OM	Carb.
1–5	Homogeneous greenish-grey gyttja	*	*	*	24.20–26.90	3.45–4.93
6	Carbonaceous dark-grey gyttja	*	*	*	5.68	26.50
7–10	Sand (128.5 to193 μm)	100	0	0	0.22–0.56	0.16–0.51
11–18	Silt (14.8 to 22.2 μm)	0–5	88–93	3–9	3.55–24.02	2.54–5.47
19–24	Silty sands (21.9 to 100.4 μm)	14–54	38–66	6–21	1.63–14.68	1.94–8.11

* Not determined.

of the sediment, because sediment lithology significantly influences the kinetics of P fractions. The sediment samples were analysed for the concentrations of organic and mineral matter. Organic matter was estimated by loss-on-ignition (LOI) after heating at 550 °C for 210 min. The content of $CaCO_3$ was calculated as the loss of weight after ignition of the LOI residue at 950 °C for 150 min (Heiri et al., 2001). Altogether, 24 lake sediment samples of different genesis, composition, and texture (samples 7–24) were examined (Table 1). For the determination of the grain size of the mineral particles, it was necessary to remove organic matter. Samples 7–24 were treated with hydrogen peroxide and measured using a Fritsch Laser Particle Sizer 'Analysette 22'. Within those samples the median diameter variability of particles ranged from approximately 128.5 to 193 μm for sand, 21.9 to 100.4 μm for silty sands, and 14.8 to 22.2 μm for silt.

Generally, dry samples were used for the evaluation of the extraction scheme of the P fraction, although some tests were also performed on wet samples. In the current paper, the analyses of dry samples are presented. The data were statistically analysed using the XLSTAT (2007.2) program.

Analyses

The modified Hieltjes & Lijklema (1980) methodology was used to analyse the concentrations of total phosphorus (P-tot) and P fractions (NH_4Cl–P, NaOH–P, and HCl–P) in lake sediments. A detailed scheme for the extraction of different P fractions is presented in Fig. 1. In this scheme four single-step leaching procedures applied to the sub-samples are shown. After the burning of a sample (180 min, 550 °C), sediments were subjected to separate chemical extraction with 1 M NH_4Cl (2 h + 2 h) to remove loosely sorbed P (NH_4Cl–P), 0.1 M NaOH (17 h) to remove metal oxide bound P (NaOH–P), 0.5 M HCl (24 h) to extract apatite P or calcium bound P (HCl–P), and 0.5 M HCl (48 h) to extract P-tot. After centrifugation at 3500 rpm for 10 min, the concentration of soluble reactive P was measured from the supernatant according to Murphy & Riley (1962).
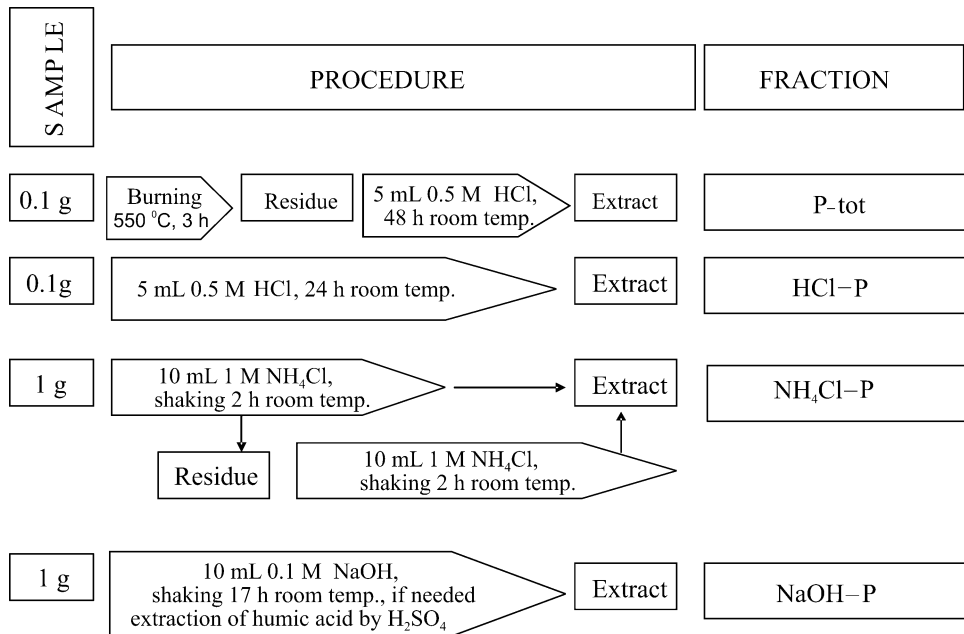
Fig. 1. A scheme of phosphorus fractionation: four leaching procedures for separate sub-samples for total P (P-tot), apatite P (HCl–P), loosely bound P (NH$_4$Cl–P), and metal oxide bound P (NaOH–P) (modified from Hieltjes & Lijklema, 1980).

Before any measurements, the spectrophotometer was calibrated using suprapure KH$_2$PO$_4$. To minimize matrix and temperature related differences between standards and samples, calibration standards were always treated in the same way as the samples. Calibration curves had good linearity over a wide concentration range (1–1000 µg L^{-1}; $n = 12$; $r = 0.998$–0.999). The phosphorus absorbance spectra obtained using a Helios Beta Thermo Fisher Scientific indicated a higher peak at 892 nm and a lower peak at 885 nm. The most commonly encountered intensity of the blue peak in our study was at 890 nm.

The concentration of inorganic phosphorus (P-inorg) was calculated as the sum of NH$_4$Cl–P, NaOH–P, and HCl–P fractions. Organic phosphorus (P-org) was calculated according to Williams et al. (1976) and Hieltjes & Lijklema (1980) as the difference between P-tot and P-inorg. Sometimes all extractable P does not go into the solution at extraction. It may remain in insoluble particles and so the extractant cannot dissolve it. On ignition, however, the particulate organic carbon is transformed into carbon dioxide and all phosphorus becomes available to the extractor. Therefore, overestimation of P-org and underestimation of P-inorg is possible (Kruusement & Punning, 2000).

For each phosphorus fraction five independent replicates were made to examine the extraction time and stability of the concentrations of the extracted P fraction. Duplicate sub-samples of the HCl–P fraction extraction were withdrawn at the

following time intervals: 5, 12, 24, 28, 36, and 48 h. Duplicate sub-samples of the NH_4Cl–P fraction of 2 + 2, 4, and 6 h extraction were examined. The influence of the NaOH concentration on the concentrations of the extractable NaOH–P fraction was also tested. For extraction, NaOH solutions of different concentration (0.1 M and 1 M) were used at room temperature 20±1 °C, and NaOH–P fraction concentrations were measured after extraction during 5, 15, 17, 24, 36, and 48 h.

The uniformity of phosphate concentration throughout a sample was verified by calculating the relative standard deviation (RSD) of replicate samples. Two separate verifications were performed: (1) replicate determination by five replicate determinations on the well-mixed content of one sample; (2) parallel analyses by the application of the extraction procedure on five sub-samples taken from the same sample. The influence of the storage time of the sediment at +4 °C was also investigated. The stability of the P fraction concentrations was tested during a period of three months and P fraction concentrations were determined after 1, 2 and 3 months; each time the wet samples were dried immediately before analysis (a sub-sample was always taken from the same sample).

RESULTS

The results obtained for the HCl–P fraction (5–48 h) showed that its concentrations reached constant values after 24 h. Pettersson & Istvanovics (1988) found an increase in the concentrations of the NH_4Cl–P fraction with increasing extraction time. Examination of the duration of the extraction of the NH_4Cl–P fraction (2 + 2 h, 4 h, 6 h) did not support this conclusion: the yield of NH_4Cl–P was constant. Data on the reproducibility of different P fractions from dry samples did not reveal significant differences either 'within' samples or 'between' sub-samples for the different P fractions (less than 5%, except two samples of NH_4Cl–P) (Table 2). Replicate determinations of one sample ranged from 0.07% to 0.66% of NH_4Cl–P; from 0.01% to 1.99% of NaOH–P; from 0.01% to 0.06% of HCl–P, and from 0.01% to 0.04% of P-tot. The RSD distribution from

Table 2. Relative standard deviations (RSD, %) obtained in the reproducibility study

Sample	Replicate determinations of one sample ('within sample')				Parallel determination of sub-samples ('between sub-samples of sample')			
	NH_4Cl–P	NaOH–P	HCl–P	P-tot	NH_4Cl–P	NaOH–P	HCl–P	P-tot
1	0.32	0.24	0.01	0.01	3.22	1.98	0.36	0.27
2	0.25	0.10	0.01	0.01	3.48	2.29	2.18	0.52
3	0.66	0.19	0.01	0.04	4.75	1.14	0.41	0.28
4	0.07	0.20	0.02	0.02	4.77	2.09	0.11	0.11
5	0.35	1.99	0.02	0.01	6.97	0.38	0.28	0.14
6	0.47	0.01	0.06	0.04	9.23	0.43	0.29	0.26

parallel determinations of the sample showed highest values of up to 2.29% for NaOH–P, except the NH$_4$Cl–P fraction for which RSD was up to 9.23% (1 µg g^{-1}, approximately the detection limit for NH$_4$Cl–P analysis).

The results of the study of the influence of the duration of extraction and the concentration of NaOH are shown in Fig. 2. For studying the efficiency of NaOH extraction, concentrations of 0.1 M and 1 M were used. From Fig. 2a it is evident that the NaOH–P concentration depends greatly on the NaOH concentration. When 0.1 M NaOH was used the concentration of the extracted P fraction stabilized after 15 h for samples 3 and 6, but for samples 1 and 4 the NaOH–P concentrations increased with RSD = 2% and RSD = 7%, respectively (Fig. 2b).

Analyses of samples 7–24 after storage at +4 °C for one, two, and three months (Fig. 3) for the concentrations of P fractions and P-tot showed that all P fraction concentrations varied significantly with the grain size of the samples and the concentrations of the different P fractions. So, the highest concentrations of all P fractions were found in fine-grained silt (P-tot ranged from 359 to 1330 µg g^{-1}, NaOH–P from 5 to 105 µg g^{-1}, and HCl–P from 90 to 431 µg g^{-1}) and the lowest in coarse-grained sand. The dominant P-inorg constituent was HCl–P, which contributed 92% of the P-tot concentration for sand, 75% for silty sand as well as for sample 6 containing the highest proportion of calcium carbonate, and 34% for silt (Table 3). In samples 1 to 5 the maximum NH$_4$Cl–P percentage of the P-tot concentration was 1.5%, that of NaOH–P was 2.5%, and HCl–P ranged from 65% to 81% (Tables 1, 3). The HCl–P fraction contributed 75% of the P-tot concentration.
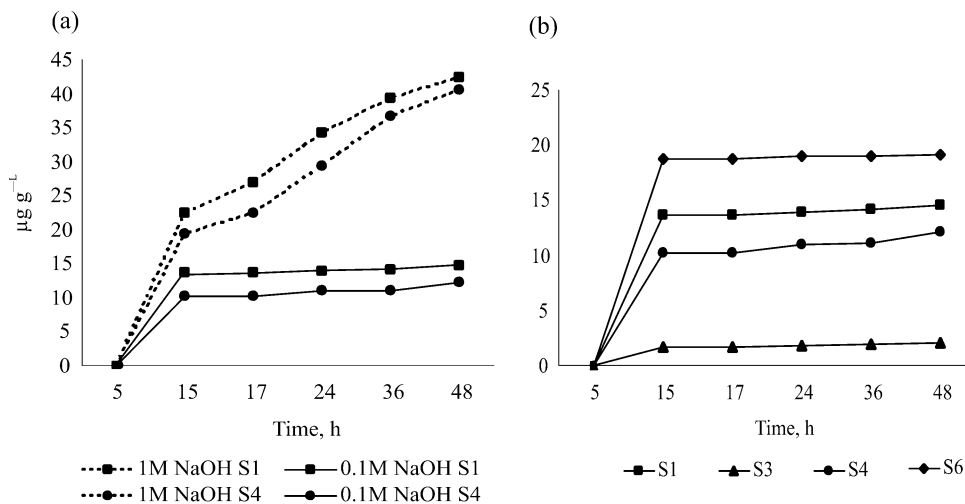

Fig. 2. The influence of the duration of extractions and the reagent concentration on the concentration of NaOH–P fraction (sample 1 (S1), sample 2 (S2), sample 3 (S3), sample 4 (S4), sample 6 (S6)): (a) two samples (S1, S4) treated with NaOH of different concentration (1 M and 0.1 M); (b) four samples (S1, S3, S4, S6) treated with 0.1 M NaOH during different time.
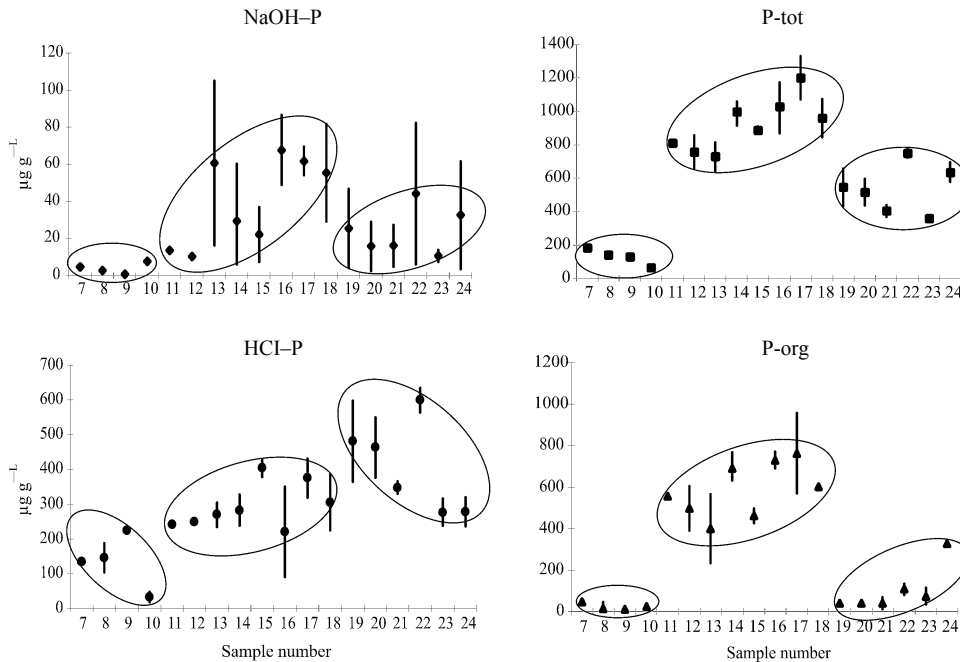
Fig. 3. Variation of the concentrations of P fractions (mean) in samples 7–24 stored at +4 °C during three months. Fractions include: P bound to metal oxides (NaOH–P), apatite P or calcium bound P (HCl–P), organic P (P-org), and total P (P-tot). Lines represent the minimum and maximum concentrations taken from analysis of three replicated sub-samples measured three times during three months (each time the wet sample stored at +4 °C was dried immediately before analyses). The ovals mark different types of sediments (Table 1: samples 7–10, sand; samples 11–18, silt; samples 19–24, silty sand).

DISCUSSION

Data obtained showed that the most important correlation of P fraction concentrations was with the texture of the analysed samples. Evidently sediments with smaller grain size (higher portion of clay and silt) have a greater capacity to adsorb P. This was demonstrated previously by other researchers (Moore & Reddy, 1994; Jin et al., 2006). As seen from the correlation matrix (Pearson's, Table 4), the concentrations of P-tot and P-org fractions have a positive significant correlation ($P < 0.01$) with the fine-grained material (silt) ($r = 0.897$, $r = 0.821$, respectively). Also, the concentration of P-tot was significantly positively dependent on carbonate and organic matter content ($r = 0.564$, $r = 0.546$, respectively).

Sand has typically a very low P sorption potential because of its low amorphous Fe and Al concentrations (Bridgham et al., 2001). In our research sand sediments had a significant negative correlation ($P < 0.01$) with P-tot ($r = -0.879$), P-inorg ($r = -0.567$), and P-org ($r = -0.764$) fractions, and organic matter ($r = -0.663$) and carbonate contents ($r = -0.589$). Being dependant on in-lake processes, the

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Table 3. Concentrations of P fractions (mean ± standard error) and relative contribution of different P fractions to P-tot in the sediments (for the lithological composition of samples see Table 1)

Sample No.	Concentration, µg g⁻¹, dw					Relative contribution to P-tot, %			
	P-tot	NH$_4$Cl-P	NaOH-P	HCl-P	P-org	NH$_4$Cl-P	NaOH-P	HCl-P	P-org
1–6	840.59±8.23	7.31±2.14	11.95±83.67	570.90±19.71	251.17±24.70	1	2	67	30
7–10	170.60±24.17	0	12.65±8.79	154.23±26.60	3.71±23.49	0	2	95	3
11–18	890.22±45.74	0	39.43±6.29	328.09±27.86	367.55±30.48	0	3	34	63
19–24	567.11±41.28	0	24.92±8.36	441.19±40.46	101.00±35.39	0	2	75	23

Table 4. Pearson's correlation coefficients between the carbonate (Carb., %) and organic matter content (OM, %), sand (%), silt (%), and clay (%) fractions in sediments, and the concentrations of P fractions (µg g⁻¹). Bold values denote significant correlation ($P < 0.01$), italic coefficients denote moderately strong relationships ($P < 0.05$), and coefficients in regular font denote weak relationships ($P =$ not significant), $n = 19$

Variable	Sand	Silt	Clay	NaOH-P	HCl-P	P-tot	P-inorg	P-org	OM	Carb.
Sand	1									
Silt	**−0.992**	1								
Clay	**−0.598**	*0.490*	1							
NaOH-P	−0.426	0.439	0.147	1						
HCl-P	*−0.525*	*0.445*	**0.789**	0.232	1					
P-tot	**−0.879**	**0.897**	0.371	*0.640*	*0.474*	1				
P-inorg	**−0.567**	*0.493*	**0.773**	0.379	**0.988**	**0.552**	1			
P-org	**−0.764**	**0.821**	0.061	**0.571**	0.080	**0.914**	0.167	1		
OM	**−0.663**	**0.704**	0.101	0.291	−0.004	**0.564**	0.042	*0.648*	1	
Carb.	**−0.589**	**0.573**	0.400	0.463	*0.660*	**0.546**	**0.701**	0.305	*0.456*	1

particulate organic matter, as well as different micro- and macro-components, is closely associated with suspended mineral particles (i.e. adsorbed in iron oxide) on the surface of particles and is deposited or transported in this form throughout the lake. The large specific surface area, surface energy, and electrostatic charge of small and colloidal particles are mainly driven by coagulation. During adsorption strongly binding organic compounds displace those that are weakly bound (Gu et al., 1994). The NaOH–P concentration range was larger for the samples with a high silt content, but the relationship between NaOH–P and silt was weak ($r = 0.439$, P = not significant).

The duration of the extraction and the reagent concentration always influence the concentration of extracted P (Golterman, 2004). Extraction duration does not influence the concentration of NaOH–P with a low (0.1 M) NaOH concentration, but has a strong effect when 1.0 M NaOH is used. This could be due, not only, to the extraction of the metal oxide bound P but also to the hydrolysis of the P-org (Golterman, 2004). Evidently, the sharp increase in the NaOH–P fraction at treatment with concentrated NaOH was caused by the humification of organic matter within the sample. The evident darkening of the extract over time and the formation of deposits after adding sulphuric acid also support this assumption. This is clear evidence of the presence of humic acid in the extract.

The HCl–P fraction was dominant within P-tot in most samples in our study (Table 3). Similarly to other P fractions, the HCl–P concentrations also varied greatly during the storage experiment (Fig. 3). The percentage of HCl–P decreased in some samples but increased in others during the storage experiment. This phenomenon may be attributed to different biological activities and physico-chemical conditions in the samples stored at $+4\,°C$. According to Jiang et al. (2006), in both anoxic and aerobic conditions, HCl–P can be mobile and exchanged in the presence of biological activities in the sediments. The mechanisms by which sediment storage could affect the solubility of inorganic and organic P are poorly understood, but probably include both physical and chemical changes (Worsfold et al., 2005). Sediment texture can control the fractionation and stability of P, especially in fine-grained sediments. Good repro-ducibility required homogeneity of the sediment, which could not always be controlled. In general, on the basis of these results, it can be concluded that no instability was demonstrated, and we achieved good reproducibility for dry samples. Wet samples did not conserve the single P-fraction concentrations over time.

CONCLUSIONS

The lake sediment samples exhibit a high degree of heterogeneity in composition and texture, which determines their different role in matter transformation within a lake. Although most protocols draw upon the 'standard' Hieltjes & Lijklema (1980) and Murphy & Riley (1962) techniques, small variations in analytical

procedure can produce large errors in measurement under certain circumstances. Therefore, no truly standardized methodology can be offered. Protocols of sampling, storage, and analysis must be based on thorough site-specific methods and stability testing to ensure desirable accuracy and precision, within resource limitations.

In general, no instability was demonstrated, and good reproducibility was achieved. The samples should be dried as soon as possible after sampling to preserve the undamaged state of P fractions.

The single-step four extraction procedures used in this study contributed to a better understanding of the geochemical cycle of phosphorus, which can be used in future analyses of specific lakes. The duration of the extraction and the concentration of NaOH always influenced the quantities of P extracted and, therefore, it could not only be extraction of the metal oxide bound P (NaOH–P), but also the hydrolysis of P-org. The extraction time needed to remove NaOH–P is at least 17 h if 0.1 M NaOH is used.

Sediment texture can control the fractionation and stability of P, especially in fine-grain sediments. In the studied sediments sedimentary inorganic P consisted mainly of HCl–P, while NaOH–P and NH_4Cl–P only contributed a minor part.

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Fosfori fraktsioneerimine järvesetetes

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Järve ökosüsteemi seisundi kirjeldamiseks on oluline taimetoitainete, eriti fosfori (P) biogeokeemilise ringe analüüs. Tingituna P esinemisvormide mitmekesisusest on standardsete metoodikate rakendamine sageli komplitseeritud. On teada, et sette tüüp, selle koostis ja füüsikalis-keemilised omadused võivad analüüsi tulemusi oluliselt mõjutada. Et fosfori potentsiaalsest mobiilsusest järvesetete ja vee piiril paremini aru saada, oli töö eesmärgiks uurida järgmisi fosfori esinemisvormide määramismeetodit mõjutavaid faktoreid: 1) reaktiivi kontsentratsioon, 2) ekstraheerimise kestus, 3) stabiilsus ning korduvus, 4) järvesetete litoloogiline koostis. Uuringute käigus viidi läbi 24 erineva terasuurusega setteproovi (liiv, liivsavi, savi), kus orgaanilise aine sisaldus varieerus 0,22–26,9%, fosforifraktsioonide sisalduse määramine. P ekstraheeriti ja analüüsiti järgmistes fraktsioonides: NH_4Cl–P, HCl–P, NaOH–P ning P-tot (üldfosfor). Enamikus fraktsioonidest oli P kontsentratsioon heas korrelatsioonis proovi terasuuruse ja karbonaatse aine sisaldusega. Selgus, et fosfori määramisel on vajalik kohene proovi kuivatamine: märgproovis võib kohesiivsete setete korral P sisaldus aja jooksul muutuda. Suurema orgaanilise aine sisalduse korral on oluline raua ja alumiiniumiga seotud fosfori eraldamiseks vältida kõrgema kontsentratsiooniga NaOH kasutamist, kuna see võib viia orgaanilise aine hüdrolüüsimisele ning orgaanilise ainega seotud P vabanemisele.