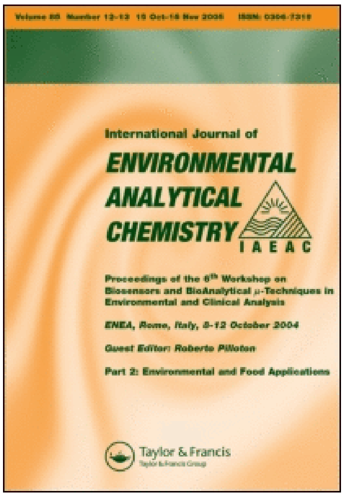

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USE OF ACCELERATED SOLVENT EXTRACTION FOR DETERMINATION OF ECOLOGICAL IMPORTANT PHOSPHORUS IN LAKE SEDIMENTS

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Phosphorus has been identified as one of the most important elements in eutrophication of lakes, and the bulk of phosphorus compounds stored in lake sediment contribute to a large extent to this process. It is therefore of great interest to get an adequate estimate of the amount of potentially mobile phosphorus for future release from lake sediment. The traditional analytical technique, which is both labour and time consuming, consists of different steps of liquid/solid extractions. The total extraction time for the procedure used today is as long as three days. The recently developed accelerated solvent extraction technique has in this study been applied to effectively extract the mobile forms of phosphorus in sediments. By using a buffered dithionite solution at 25 °C followed by water at 100 °C as solvents in sequential extractions, the total extraction process was completed within 90 minutes. The feasibility of using aqueous solutions and water as solvents with this technique is demonstrated here for the first time. The results obtained have been comparable to extractions resulted from the traditional techniques used to define and quantify the different amounts and forms of phosphorus in sediment.

Keywords: Accelerated solvent extraction; aqueous solutions; phosphorous fractionation; sediment

INTRODUCTION

Phosphorus has for a long time been identified as a key element in the eutrophication of lakes. The bulk of phosphorus in lakes is generally stored in sediments, while part of this phosphorus is mobile and contributes to the trophic status of the lake. Release of phosphorus from sediment is often referred to as internal loading of phosphorus, which has delayed the recovery of eutrophicated lakes when

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external load of phosphorus has been reduced[1]. The phosphorus release from sediment is also often a significant component of the phosphorus budget of lakes[2] and it has been reported that this release may contribute to as much as 60-80 % of the total load[3]. Predictions of future phosphorus release from sediment are, however, often hard to obtain. One reason for this is that the identification of the amount and forms of sedimental phosphorus that will contribute to the trophic status of a lake is limited with only a few exceptions. It is well known that iron is one of the most important inorganic compounds regulating the phosphorus cycle between sediment and water. When oxygen depletion occurs in the surface sediment, Fe(III) will be reduced to Fe(II) and phosphate that previously was adsorbed to Fe(III) will thereby be released[4].

Looking at organic phosphorus compounds, a large portion of the organic material that ends up on the sediment surface will be mineralised by bacterial activity. Overall, the degradation of organic phosphorus compounds is a complicated process, and the release of phosphorus from this source is hard to estimate.

When looking over a wider time perspective, the different forms of phosphorus that remain unchanged for decades can be considered permanently bound, while on the other hand the forms of phosphorus for which concentrations decrease with time are mobile. In order to make such a classification, a relatively nutrient rich lake, which is and has been in a steady state situation concerning input of nutrients, could be used as a model. The series of extraction steps used today to perform the fractionation of phosphorus, which defines and quantifies the different forms of phosphorus in the sediment[5,12], are both extensively time and labour consuming.

Procedures for sample extraction are in general regarded as bottlenecks in the analytical methods, and various attempts have been made to replace classical liquid/solid extraction techniques over the last few years. Techniques such as automated Soxhlet extraction[6], microwave-assisted extraction[7], sonication extraction[8], supercritical fluid extraction[9] and accelerated solvent extraction[10] have thus been developed. Each one of these techniques reduces the required volume of extraction solvent, provides a milder extraction environment, and shortens the sample preparation time compared to conventional sample preparation procedures.

The recently developed accelerated solvent extraction technique has quickly become an additional attractive alternative due to short extraction time, simple method development and small amount of organic solvent that is required, in comparison with the traditional methods. The technique was initially developed mainly for rapid and high yield extractions of solid samples using organic solvents at elevated temperatures[11]. The solvent is thus maintained in the liquid state by applying high pressure in the extraction cell. The use of higher temperature will increase the capacity of solvents to solubilize analytes, break associations with matrices, and give faster diffusion rates and mass transfer, which accelerates the extraction[10].

The aim of this study was to develop an extraction method using the accelerated solvent extraction technique that only extracts the forms of phosphorus lost by phosphorus-diagenesis, i.e. that no forms of phosphorus should be extracted from deeper historical sedimental layers. By comparing the results with the total phosphorus content of the sediment and the different forms of phosphorus defined by phosphorus-fractionation in a sediment profile from Lake Erken, Sweden, the mobile, i.e. the ecological important phosphorus, was extracted and determined.

EXPERIMENTAL

Chemicals

Sodium hydrogen carbonate and Sodium dithionite quality p.a. were purchased from Merck AG Darmstadt, Germany. MilliQ-water was obtained from a purification system and Nitrogen, 99.996 % (by volume), was from Aga, Stockholm, Sweden.

Sample

The sediment core used in these experiments was obtained on May 28 1997 at Lake Erken, Sweden. The core was sliced at intervals of 0–1 cm, 4–5 cm, 9–10 cm, 19–20 cm and 29–30 cm and stored in a refrigerator at 4–6 °C.

Instrumentation

A schematic illustration of the accelerated solvent extractor employed, ASE™ 200, Dionex Corp. (Sunnyvale, CA, USA) is shown in Figure 1. The extraction cells (Dionex) were of stainless steel with a volume of 11 ml and capped with PEEK seals and stainless steel frits.

Procedure

Accelerated solvent extraction

The extracting process consisted of five steps: *i)* Filling and pressurising the cell with solvent at selected temperature. *ii)* Heating the cell at selected temperature for equilibration at constant pressure for five minutes. *iii)* Static extraction at

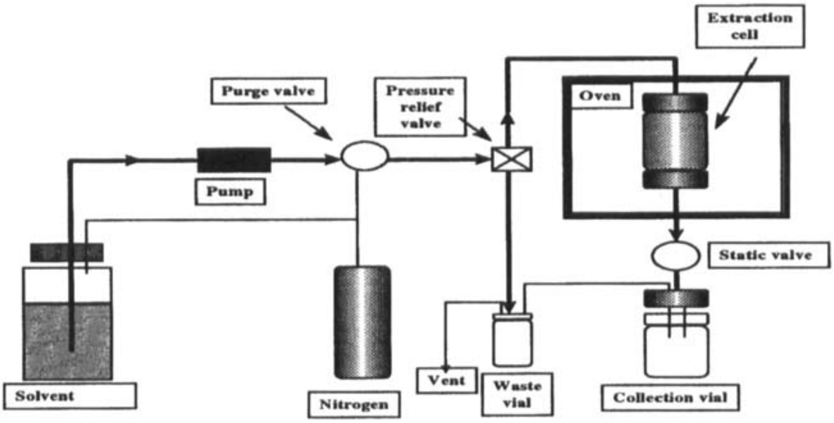

FIGURE 1 Schematic illustration of the accelerated solvent extraction system

constant pressure and temperature over a selected period of time. *iv)* Flushing the cell with fresh solvent with a selected volume expressed as a percentage of the cell volume. These steps *iii)* and *iv)* are called a cycle, and can be repeated several times. *v)* Purging of the cell with nitrogen.

The cell was filled with a cellulose filter (Dionex, 1.91 cm) at the bottom and with aliquots of wet sediment, between 0.5-1 g, placed on the cellulose filter. The water content was between 93.7 % (surface sediment) to 80.4 % (at a depth of 30 cm). No drying of the sediment was needed. Two sequential extraction methods, A and B, were performed using two different solvents. The following conditions were used for the extractions A and B:

Extraction method A: Heating for 5 minutes at 10 MPa pressure and a temperature of 25 °C. Static extractions for 10 minutes and flush 100 % followed by 40 seconds nitrogen purge. Each extraction was performed three times. As a solvent, a buffered dithionite, BD, (0.11 M $NaHCO_3$ and 0.11 M $Na_2S_2O_4$) was used. A fresh solvent mixture had to be prepared each day.

Extraction method B: Heating for 6 minutes at 10 MPa pressure and a temperature of 100 °C. Static extractions for 10 minutes and flush 100% followed by 40 seconds nitrogen purge. Each extraction was performed three times as in extraction method A. As solvent, Milli Q-water was used.

Traditional fractionation procedure of phosphorus

All slices of the sediment were also extracted according to a traditional fractionation procedure proposed by Psenner et al.[12]. This scheme consisted of a number of solvents, including a buffered dithionite, BD, (0.11 M $NaHCO_3$ and 0.11 M $Na_2S_2O_4$ shaking for 2 hours) and a sodiumhydroxide, (1 M NaOH, shaking for 19 hours).

Analysis

The total phosphorus (P_{tot}) content in each vial of each extraction from both the accelerated solvent extractions and the traditional fractionation were analysed as phosphate according to Menzel et al.[13] using visible spectrometry.

The total phosphorus content of the sediment (PTOT) was analysed as phosphate after acid hydrolysis at a high temperature, 340 °C, according to Murphy et al.[14].

RESULTS AND DISCUSSION

In evaluating the usefulness of the accelerated solvent extraction technique for selective extraction of ecological important phosphorus, sediment cores from a well-examined lake were chosen. Lake Erken is a mesotrophic lake in Sweden that is kept in a steady state, i.e. non polluted by municipal waste water or by any industry. By measuring the forms of phosphorus lost by phosphorus diagenesis in this system, an expression for the ecological phosphorus would be obtained.

The accelerated solvent extraction procedure was performed using two different solvents in sequential extractions. The first one with BD-solvent aiming to extract redox sensitive iron adsorbed phosphorus was followed by the second extraction aiming at the amount of phosphorus compounds that are released by oxidative hydrolysis using hot water as a solvent. Triplicate sub-samples of each slice were extracted in this way by the accelerated solvent extraction technique.

The results from the two sequential accelerated solvent extraction methods, A and B, are shown in Figure 2, where P_{tot} (A) is the amount of phosphorus extracted using BD-solvent at 25 °C, and P_{tot} (B) is the total amount of phosphorus extracted using water at 100 °C as solvent. The curve P_{tot}(A+B) refers to the total amount of phosphorus extracted by the sequential extraction methods A and B, while PTOT refers to the total amount of phosphorus adsorbed in the sediment.

These results can be compared with the results of the traditional fractionation procedure shown in Figure 3, where mainly two forms of phosphorus decline strongly with sediment depth/age. These two extracts are BD and NaOH-nrP respectively, where the BD extracted phosphorus mainly consists of iron adsorbed phosphorus in the sediment. The phosphorus forms extracted in the NaOH-step on the other hand consist of an inorganic part, NaOH-rP, which rep-

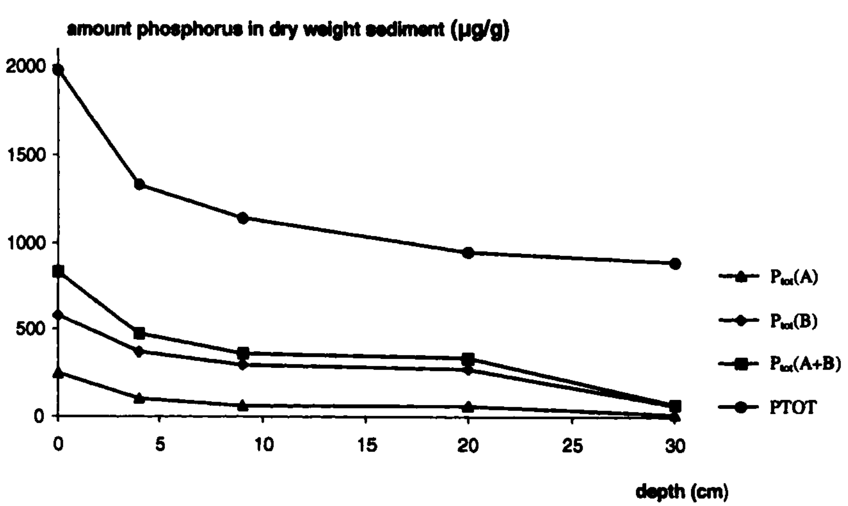

FIGURE 2 Accelerated solvent extraction of ecologically important phosphorus P_{tot}(A+B) compared to the total amount of phosphorus in the sediment PTOT

resents forms of phosphorus adsorbed to metal oxides and other surfaces as well as phosphorus compounds soluble in bases. The difference between total phosphate released by NaOH and NaOH-rP represents the major part of organic and humic phosphorus forms and is referred to as NaOH-nrP[12].

It can be seen in Figure 3 that the BD extractable part is more or less exhausted 30 cm down in the sediment profile, while the decrease of NaOH-nrP extractable part is not total. Thus, the NaOH-nrP fraction over estimated organic phosphorus that will be mobilised and recycled. The additional extractions by the traditional fractionation procedure shown in Figure 3 will not be discussed in this work, since they are of less or none importance looking at mobile phosphorus in sediment.

As Lake Erken is considered to be in a "steady state" the difference of phosphorus content between surface sediment and the deeper one, the hundred years old sediment at 30 cm, is the amount of phosphorus that could be regarded as mobile. In order to compare the two methods, the amount of phosphorus extracted from all sediment layers, see Tables I-IV, were summed up. When BD was used as a solvent in the accelerated solvent extraction technique only 45 % of the amount of phosphorus was extracted compared to the traditional BD extraction step. This was, however, compensated for in the following sequential step where water of 100 °C was used, and 118 % of the traditional NaOH-nrP step was extracted. In total, comparing all phosphorus extracted from the BD and

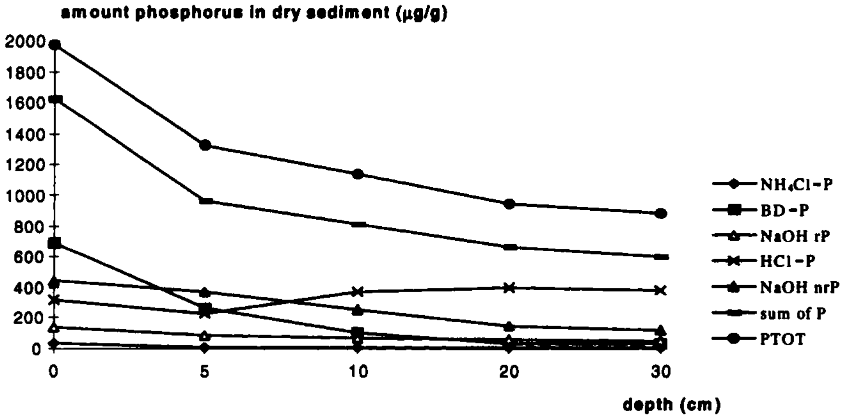

FIGURE 3 Traditional fractionation procedure of the phosphorus content

NaOH-nrP in the traditional fractionation with the BD and 100 °C water steps in the accelerated solvent extraction 83 % was recovered. This results is in line with the concept of mobile phosphorus, because the NaOH-nrP extracts more phosphorus than will be released through sediment phosphorus diagenesis, which is seen in Figure 3. The discrepancy in this case could probably be due to the fact that the release of organic bonded phosphorus is favoured by oxidative hydrolysis at the "autoclave conditions" in this second accelerated solvent extraction step.

By comparing the results from Figure 2, Figure 3 it can be concluded that the sum P_{tot}(A+B) of released phosphorus from the sequential accelerated solvent extractions could more or less be referred to as the sum of BD and NaOH-nrP in the traditional fractionation procedure. It is here suggested that the phosphorous extracted by accelerated solvent extraction with the above given parameters could be used as a model of the mobile phosphorus in lake sediment, i.e. the ecological important amount of phosphorous. This is the amount of phosphorus that could be released over the time of some years and during different aerobic or anaerobic conditions. In other words, most of the surface sediment phosphorus was extracted, while, very little from the 30 cm slice was released under the relatively mild conditions used during these experiments. It should also be emphasized that the extraction time of 90 minutes used for the accelerated solvent extraction method should be compared to several days extraction by the traditional fractionation method.

In addition, when change of solvent is needed using the accelerated solvent extraction technique, the exchange is achieved in a nitrogen atmosphere. This will not influence the sediment chemically, which is something that could occur when performing the traditional fractionation procedure[12]. The range of the standard deviation of triplicate sub-samples using accelerated solvent extraction with both solvents is shown in Table I and II. It should be noted that these values are in the same range as the RSD values achieved by traditional fractional procedure, where the RSD values from the traditional BD-P and NaOH-nrP steps are seen in Table III and IV. Some of the extracts collected after the accelerated solvent extractions turned out to be cloudy and therefore caused extended uncertainty in the spectrometric detection. It was later found that filtering of extracts could be improved by using two cellulose filters at the bottom of the cell. This would also lead to improved RSD-values, although the greater variation in the top sediment layer mainly is expected due to larger variation of organic remains.

Finally, it was interesting to note that there was a difference in extraction behaviour between the surface sediment and the deeper sediments from 10 to 30 cm, when performing the accelerated solvent extractions with the described conditions. Each sample was extracted three times with the two solvents. When extracting the surface sediment from 0-1 cm, the amount of phosphorus released at each extraction was reduced about 30 % from one extraction to the next for both solvents. The same amount i.e. 30 % of phosphorus was released at each extraction when extracting the deeper sediment, using BD as solvent. On the other hand when water of 100 °C was used as the extraction solvent at 10 MPa the amount of phosphorus released at each extraction raised, probably due to some "autoclave effect" that raised the effect of the oxidative hydrolysis. Further studies would be needed to fully understand this phenomena.

TABLE I Amount of Phosphorus[a] Extracted by Accelerated Solvent Extraction[b] and using BD-Solvent

Depth/cm	*I*	*II*	*III*	*Average*	*RSD[c] (%)*
0-1	343	261	245	283	18.5
4-5	96	118	109	107.7	10.3
9-10	60	51	91	67.3	31.1
19-20	68	66	72	68.7	4.4
29-30	12.7	12	15.9	13.5	14.8

[a] µg/g dry weight
[b] at 25°C
[c] n=3

TABLE II Amount of Phosphorus[a] Extracted by Accelerated Solvent Extraction[b] using Water as Solvent

Depth/cm	*I*	*II*	*III*	*Average*	*RSD[c] (%)*
0-1	545	643	680	622.7	11.2
4-5	409	328	373	370.0	11.0
9-10	284	272	289	282	2.5
19-20	235	271	248	252	7.2
29-30	(79.9)	56.4	53.7	63.3	22.7(3.4)

[a] µg/g dry weight
[b] at 100°C
[c] n = 3

TABLE III Amount of Phosphorus[a] Extracted by the Traditional Fractionation Procedure using BD-solvent

Depth	*I*	*II*	*Average*	*sd*	*RSD[b] (%)*
0-1	612	767	689.5	109.60	15.9
4-5	326	208	267	83.44	31.2
9-10	161	56	108.5	74.25	68.4
19-20	41	37	39	2.83	7.2
29-30	36	36	36	0	0

[a] µg/g dry weight
[b] n = 2

TABLE IV Amount of Phosphorus[a] Extracted by Traditional Fractionation Procedure in the NaOH-nrP step

Depth	*I*	*II*	*Average*	*sd*	*RSD[b] (%)*
0-1	424	464	444	28.28	6.4
4-5	359	384	371.5	17.68	4.8
9-10	255	257	256	1.41	0.5
19-20	149	159	154	7.07	4.6
29-30	124	122	123	1.41	1.1

[a] µg/g dry weight
[b] n = 2

CONCLUSIONS

The results show that the accelerated solvent technique can be used to extract inorganic compounds using water and aqueous solutions as solvents. In this case a suggested model to extract mobile forms of phosphorus i.e. the ecological important phosphorus, in a lake sediment has been developed by only using two different solvents a buffered dithionite solution at 25 °C and pure water at 100 °C, i.e. in neutral solvents. The extraction time was reduced to 90 minutes compared to several days with conventional phosphorus fractionation methods. The nitrogen atmosphere used between the different flushes and changes of solvent in the accelerated solvent extraction technique is another great advantage compared to the conventional phosphorus fractionation methods, where oxygen can react and change the speciation of phosphorus in the sediment during the extraction procedure.

In addition, the automation capability of the ASE™ used in this study can give increased sample throughput, by loading up to 24 samples at the time.

The positive results in this study using water and aqueous solutions as solvents in accelerated solvent extraction also suggest that the above described method, with some modification, could be applicable for future studies on extraction of for example ecological important metal ions in soil or sediments.

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