

FORMS AND DISTRIBUTION OF PHOSPHORUS IN SEDIMENT OF THE SHKODRA LAKE

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Abstract

Phosphorus (P) is often the limiting nutrient for algal growth in lakes and may limit its productivity. P reactivity and bioavailability in lake sediments may be determined by different forms of P and their distribution. The purpose of the research was to determine the various P forms in sediments of Shkodra lake. Also it was to estimate the use of the reagent concentration and duration of extraction in the measurement of P fraction concentrations in lake sediments. Phosphorus bound to metal oxides, mainly those of Fe and Al, is represented by NaOH-P. The P fraction that is assumed to consist mainly of apatite P is represented by HCl-P. The phosphorus forms in the sediment of Shkodra lake were determined by four chemical extraction procedures using 1M NH₄Cl (pH 7.0), 0.1 M NaOH, and 0.5 M HCl, reportedly representing loosely-bound P, Fe- and Al-bound P, and Ca-bound P respectively. The NaOH-P concentration and extraction duration were studied. Attempts were made to minimise hydrolysis by dilution of NaOH. The P in surface sediment mainly consisted of HCl-P and P-org, while NH₄Cl-P and NaOH-P only constituted a minor part. The rank order of the different P extracts was HCl-P > P-org > NaOH-P > NH₄Cl-P. The results indicated that the HCl-P fraction constituted 58%, the P-org fraction contributed 27%, the NaOH-P fraction contributed 14% and the NH₄Cl-P fraction constituted 1%, of the P-total concentration. Sediments had high concentrations of readily available P (14% of TP), hence these sediments may play an important role in internal P cycling.

Keywords: lake sediment, phosphorus fractions, chemical extraction, eutrophication.

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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). P is often the limiting nutrient for algal growth in lakes, hence it has received more attention than many other nutrients in limnology.

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 chemisorptions ability of the sediments, and biological uptake (Andersen, 1975; Søndergaard *et al.*, 1992; Koski-Vähälä & Hartikainen, 2001; Koski-Vähälä *et al.*, 2001).

P in sediments occur in different forms: inorganic P (P-inor), organic P (P-org), extractable P (P-HCl and P-NaOH) and total P (P-tot). Phosphorus bound to metal oxides, mainly those of Fe and Al, is represented by NaOH-P. 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). Phosphorus fractions sediments are characterized by their differential solubilities in various chemical extractant.

This research was focused on quantifying various P forms in sediment of Shkodra Lake. Analysis of the fraction $<71 \mu\text{m}$ 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 (K. Fytianos & A. Kotzkioti *et al.*, 2005).

The purpose of the research was to determine the various P forms in sediments of Shkodra lake. Also it was to estimate the use of the reagent concentration and duration of extraction in the measurement of P fraction concentrations in lake sediments.

Materials and Methods

Object of study was Shkodra Lake, the biggest in Balkans. The surface of lake (as a many years mean) is 452 km^2 , from which 183 km^2 lies in Albania and 269 km^2 in Montenegro. It is a typical field lake with mean depth that goes from 7 to 10 m, maximum depth is 44 m. The overall mean volume of water in Shkodra lake go to about 2.6 km^3 . The surface of the lake varies from 354 km^2 when the water level is 4.71 meters of altitude, to 505.8 km^2 when the waters reach 10m. At the highest level, lake depth is over 12 meters, while at the lowest, 8 meters

The shore of the West side of Shkodra Lake is mostly rocky, so our study is concentrated more on East shore of the lake which is muddy. Sediment samples were collected five different points in the Albanian part of the lake using Ponar Gab. Sampling points were: near Sterbeq (point 1 in figure); near Grizhw (point 2 in the figure); center of the lake (point 3 in the figure); near Bishtiqini (point 4 in the figure) and near Zogaj (point 5 in the figure). Samples were taken and immediately were carried to the laboratory. 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 $71 \mu\text{m}$ sieve (silt/clay fraction) . Silt/clay fraction ($<71 \mu\text{m}$) was stored in glass bottles.

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Figure 1 Sampling point

The content of total phosphorus (P-total) and P fractions (NH_4Cl), NaOH-P, and HCl-P in sediments is determined using the method describe in literature according to schema. Figure 2 shows schema which is used for determination of total phosphorus according to Kapanan, 2008. Figure 3 shows schema which is used for determination of NaOH-P according to Kapanan 2008. Figure 4 shows schema which is used for determination of HCl-P according to Kapanan 2008. Figure 5 shows schema which is used for determination of NH_4Cl -P. 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 (Galina Kapanan et al., 2008). We also used more dilute NaOH to diminish hydrolysis of easily hydrolysable OP compounds (Hupfer & al. 1995), which would overestimate the $\text{PO}_4\text{-P}$ in NaOH.

The fraction HCl-P constitutes the major part of the studied sediments, while NaOH-P and NH_4Cl -P only contributed a minor part.

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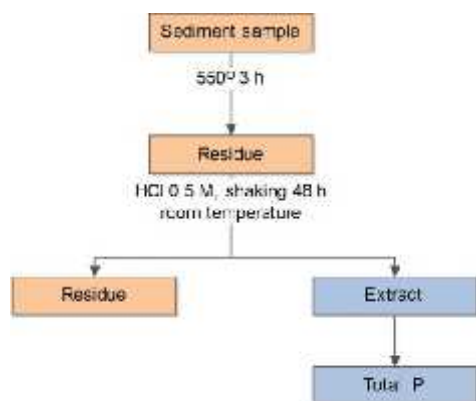


Figure 2

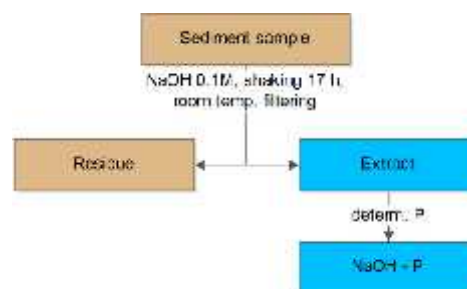


Figure 3

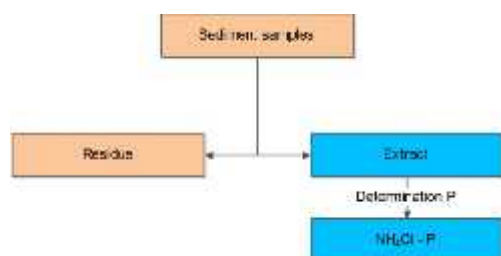


Figure 4

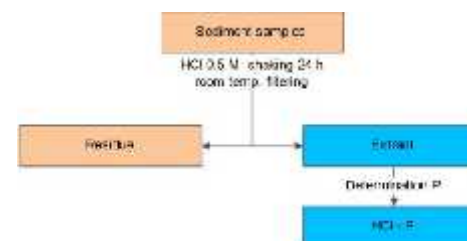


Figure 5

Phosphorus in extracts was determined in the form of phosphate using colorimetric method. Ammonium molybdate and antimony potassium tartrate reaction in an acid medium with dilute solutions of orthophosphate-phosphorus to form an intensely colored antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by SnCl_2 .

Results and discussion

The mean concentrations of phosphorus found in the sediment of Shkodra Lake with the standard deviation are presented in the table 1. The concentrations of phosphorus in all forms are presented in mg phosphor per kg sediment.

Table 2. Concentrations of P fractions (mean \pm standard error)

| Sample No. | Concentration, mg/kg, | | | | |
|------------|-----------------------|--------------------------|-------------------|--------------------|--------------------|
| | P-tot | $\text{NH}_4\text{Cl-P}$ | NaOH-P | HCl-P | P-org |
| 1 | 1078.92 \pm 72.32 | 16.077 \pm 1.20 | 230.31 \pm 6.32 | 539.92 \pm 11.26 | 292.59 \pm 83.28 |
| 2 | 1091.91 \pm 96.83 | 8.51 \pm 1.01 | 132.65 \pm 1.94 | 566.87 \pm 20.80 | 383.87 \pm 91.36 |
| 3 | 1217.84 \pm 29.59 | 11.56 \pm 0.57 | 177.27 \pm 9.48 | 601.15 \pm 1.55 | 427.85 \pm 28.16 |
| 4 | 970.52 \pm 23.49 | 7.64 \pm 0.54 | 151.89 \pm 3.59 | 91.18 \pm 15.06 | 210.59 \pm 24.61 |
| 5 | 933.8 \pm 80.67 | 13.19 \pm 1.74 | 77.07 \pm 8.36 | 724.63 \pm 35.52 | 158.50 \pm 78.30 |
| Mean | 1058.6 \pm 60.6 | 11.4 \pm 1.01 | 153.8 \pm 7.6 | 504.75 \pm 16.8 | 294.7 \pm 61.14 |

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The total phosphorus in Shkodra Lake was found to be in 1058.6 mg P / kg sediment. HCl-P fraction was found to be 504.75 mg / kg more than other forms of phosphorus in sediment. Organic phosphorus was found to be 294.7 mg/kg sediment. The concentration of NaOH-P and NH₄Cl-P was lower than other form. The rank order of the Phosphorus extract forms in sediments was found to be in order HCl-P > P-org < NaOH-P > NH₄Cl-P.

The figure 6 shows the contribution of all forms of P in the total phosphorus found in the sediment.

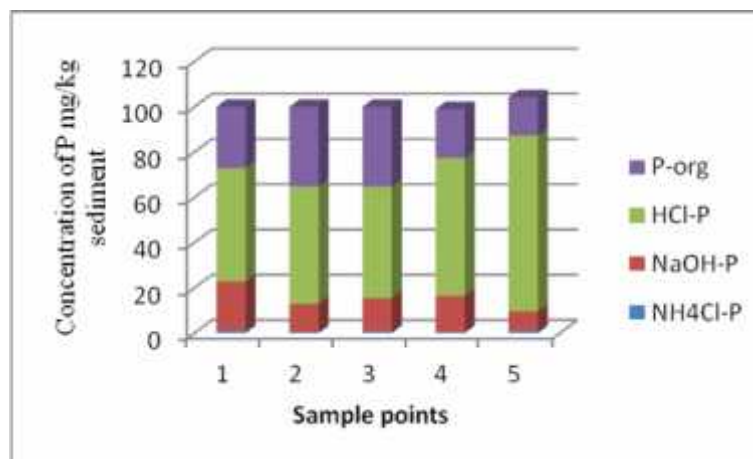


Figure 6. Contribution of all forms of phosphorus in total phosphorus.

The HCl-P fraction ranged from 49% to 77% of total phosphorus. Organic phosphorus from 21 to 35% of total phosphorus. The NH₄Cl-P fraction contributed 1%, the NaOH-P fraction contributed 14%.

The results of analyses suggest that the main form of phosphorus in sediment of Shkodra Lake is HCl-P form and Org-P form. The high concentration of HCl-P is a result of the high Ca sediment.

Conclusion

Shkodra lake sediments are rich with phosphorus, mean concentration of total phosphorus in lake sediments was found to be 1058.6 mg per kg sediment. The most spread form of phosphorus in lake Shkodra sediments was HCl-P and the least was NH₄Cl – P.

The total phosphorus found in Shkodra lake was constituted from HCl-P fraction that contributed 58%, P-org fraction contributed 27%, NaOH-P fraction contributed 14% and the NH₄Cl-P fraction constituted 1%. Sediments contain high concentrations of readily available P (14% of TP); hence sediments in Shkodra Lake play an important role in internal P cycling.

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