

The structure of phosphorus compounds in mid-forest humic lakes

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Abstract

This study presents the vertical distribution of phosphorus fractions in three postglacial mid-forest humic lakes: oligohumic, mesohumic, and polyhumic. Total phosphorus concentrations were similar in these humic lakes (mean 76 $\mu\text{g l}^{-1}\text{P}$). The greatest share of phosphorus was in mineral fractions, while a lesser share was in organic, especially soluble, fractions. Concentrations of mineral forms (phosphates and polyphosphates) were the lowest at the time of maximum development of phytoplankton, especially of bacterioplankton near the bottom of the oligohumic lake. An exceptionally high participation of soluble polyphosphates was found in the polyhumic lake near the surface.

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INTRODUCTION

Drawa National Park (DNP) occupies a central part of the forest complex of the Drawska Primeval Forest in the Pomeranian Lakeland in Poland. The park protects many trophic types of lakes, including a few humic lakes. Humic lakes are characterized by a strong content of dissolved humic substances (DHS) which migrate mainly in large amounts from the catchment area (Joniak and Kraska 1999). In humic lakes, considerable quantities of macro- and microelements form complexes with DHS, impeding their bioavailability (Jones 1992). The special features of these lakes include high water color, low transparency, low pH, low conductivity, and low concentration of free inorganic nutrients, especially phosphorus (Piotrowicz et al. 2002).

In aquatic environments most of phosphorus is represented by particulate organic forms in living and dead material. Small fractions are found as soluble organic or inorganic forms (Grobbelar and House 1995). It has long been known that waters of humic lakes rich in organic matter tend to exhibit higher total phosphorus concentrations than otherwise comparable clear-water lakes (Lean 1973). A limitation of many hydrochemical studies of humic lakes is that conclusions about phosphorus circulation are drawn on the basis of its two forms: total phosphorus (TP) and soluble reactive phosphorus (SRP) (Arvola et al. 1996, Keskitalo et al. 1998, Górnjak et al. 1999). Few publications are concerned with all forms of phosphorus; few also address the vertical distribution (Shaw 1994, Piotrowicz et al. 2002). The aim of this research was to define precisely the qualitative composition and vertical structure of mineral and organic phosphorus compounds in mid-forest humic lakes.

MATERIALS AND METHODS

The subject of the investigation were three postglacial mid-forest lakes: oligohumic Piaseczno Małe (PML), mesohumic Głodne IV (GL IV), and polyhumic Głodne III (GL III), which are located in the DNP in northwest Poland. The lakes have small areas and similar depths (up to about 8.5 m). The drainage area of GL III covers 91 ha, while those of GL IV and PML are much smaller (see Table 1 for details).

The investigation was carried out in 1999 – 2001. Physicochemical characteristics of the samples were also recorded at 1 m intervals throughout the water column, with Secchi disc visibility (SDV), temperature, pH, oxygen saturation, and conductivity measured. Forms of phosphorus: total soluble (TSP), total particular (TPP), soluble reactive (SRP), particular reactive (PRP), soluble unreactive (SUP), particular unreactive (PUP), soluble organic (SOP), particular organic (POP) and calcium, and color were analyzed in the laboratory

(Standard Methods 1992). Chlorophyll *a* was determined with ethanol according to Nusch (1984) and bacteriochlorophyll *d+e* according to Overmann and Tilzer (1989). The euphotic zone depth (Zeu) was calculated according to Eloranta (1999).

Table 1

Morphometric and physicochemical properties of the studied lakes.

Parameter		Lake		
		Głodne III	Głodne IV	Piaseczno Małe
Water surface area	ha	0.65	0.42	8.0
Max. depth	m ⁻¹	8.5	7.2	8.4
Basin area	ha	91	7.32	21.6
Transparency	m ⁻¹	1.3	2.3	3.6
Water color	mg t l ⁻¹ P	112	40	30
pH		4.5	4.6	7.1
Conductivity	μ cm ⁻¹ S	29	24	69
Calcium	mg l ⁻¹ Ca	2.2	1.2	7
DOC	mg l ⁻¹ C	17.6	9	15.8
Total phosphorus	μg l ⁻¹ P	75	78	77
Total soluble P	μg l ⁻¹ P	47	46	45
Soluble inorganic P	μg l ⁻¹ P	20	21	20
Total reactive P	μg l ⁻¹ P	14	17	13
Total unreactive P	μg l ⁻¹ P	24	23	28
Total organic P	μg l ⁻¹ P	37	38	36

RESULTS

The physicochemical parameters of the water suggested that the most advanced stage of the humification process was in GL III, while GL IV and PML were less transformed (Table 1). The location of the lakes in deep natural hollows mid-forest was the reason for the formation in early spring and the continuance for the greater part of the year of sharp stratification of thermal and oxygenic conditions. The bioavailability of mineral substances was at low levels in all three lakes (conductivity <100 μS cm⁻¹ and low levels of phosphorus, nitrogen, and calcium, among others). In both Głodne Lakes the pH was acidic, while in PML it was neutral or weakly alkaline. Oxygen saturation of the epilimnion waters, and sometimes the metalimnion, was very good (>80% O₂). Oxygen deficits were registered in the hypolimnion throughout most of the year. A characteristic feature of the humic lakes was a decrease in the thickness of the euphotic zone (Zeu) which paralleled the rise of the gradient of humic substances content: 3-4 m thick Zeu in PML, 2-3 m in GL IV, and 1 m in GL III.

Most of the phosphorus in the lakes was in mineral form, mainly unreactive polyphosphates (Table 1). Carlson's (1977) trophic state index (TSI) suggests that the lakes are mesotrophic. Total phosphorus, for which the TSI_{TP} index was on average 62, had the greatest impact on the value of TSI_{tot} . Despite high, similar TP content in all lakes, they were not rich in bioavailable forms of phosphorus, especially SRP. The soluble fractions of phosphorus, which accounted on average for 60%, dominated in the total pool of phosphorus. Even though the soluble inorganic forms constituted about 30% of TP, the concentration of the bioavailable SRP was very small. In GL III, it had a mean value of $8 \mu\text{g l}^{-1} \text{P}$, compared to $9 \mu\text{g l}^{-1} \text{P}$ in GL IV and $4 \mu\text{g l}^{-1} \text{P}$ in PML.

In the vertical profile of lakes, a high qualitative and quantitative variation in phosphorus distribution was observed. In both Głodne Lakes, concentrations of SRP increased along with depth, reaching a maximum in the metalimnion (Fig. 1A and 1B), while in PML the highest values were found near the surface (Fig. 1C). The examination of the vertical distribution of bacterioplankton biomass, measured as concentrations of bacteriochlorophyll *d+e*, revealed a positive relationship with TRP ($r = 0.62$, $p < 0.003$, $n = 21$) in the mesohumic lake (GL IV). An opposite distribution of concentrations was observed in the case of soluble unreactive phosphorus (polyphosphates), whose maximum values in both Głodne Lakes were recorded near the surface, while in PML it was in the metalimnion.

Mineral forms of phosphorus were characterized by a higher vertical variation than organic phosphorus. In GL III, organic forms (especially the soluble fractions) increased with depth (Fig. 1A). At the same time, a strong positive relationship between concentrations of POP and densities of chlorophyll was observed ($r = 0.74$, $p < 0.001$, $n = 17$). In GL IV, which was characterized by the highest richness of organic phosphorus among the studied lakes, the maximum of soluble and particulate forms was recorded near the bottom (Fig. 1B). A moderate relationship between the concentration of SOP and chlorophyll *a* ($r = 0.46$, $p < 0.033$, $n = 21$) as well as bacteriochlorophyll *d+e* ($r = 0.45$, $p < 0.042$, $n = 21$) indicated an equivalent role of both groups of organisms in the process of release of this form into water. A similar pattern of vertical changes in concentrations of organic forms was found in the case of PML, but the changes were smaller (Fig. 1C).

DISCUSSION

Landscape structure in the catchment area is a factor determining the potential hydrochemical state of lakes (Kajak 2001). This is particularly important in the case of small mid-forest lakes that receive large amounts of mineral and organic substances in soluble forms and suspensions, carried with

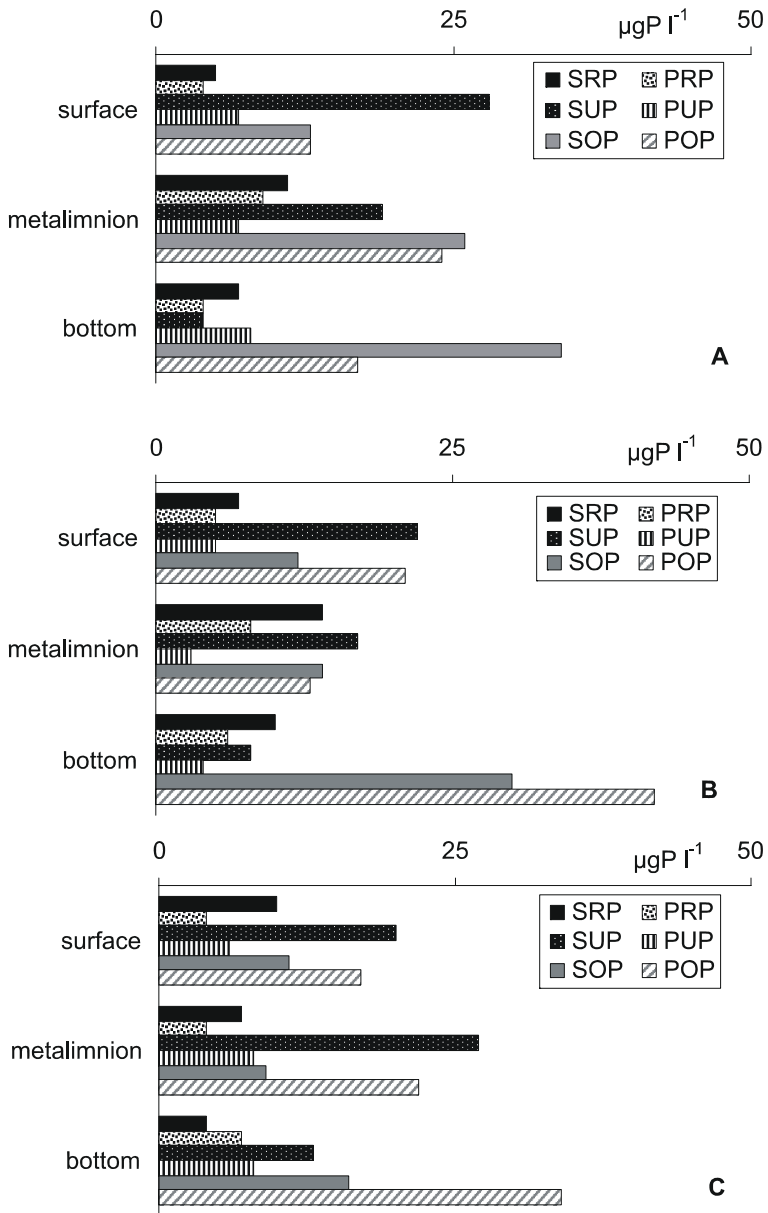


Fig. 1. Vertical structure of phosphorus fractions (mean annual values) in polyhumic Głodne Lake III (A), mesohumic Głodne Lake IV (B) and oligohumic Piaseczno Małe Lake (C).

waters of surface run-off (Klimaszyk 2006). An important abiotic factor in dystrophic humic lakes is the high content of dissolved organic matter, especially DHS. The increased concentration of humic substances in water leads to changes in abiotic factors, e.g., an increase in water color, decrease in pH, and limitation of the bioavailability of nutrients (Górniak 1999).

Phosphorus, as a key factor in the process of eutrophication of freshwater ecosystems, is subjected to biochemical and physicochemical transformations in humic lakes (Hongve 1994). As a result, its structure is dominated by organic forms and mineral unreactive polyphosphates, while the least abundant are the bioavailable mineral orthophosphates. In contrast to nitrogen, phosphorus has no way out of the aquatic ecosystem in any gaseous form, but high-molecular-weight phosphorus compounds form a colloidal fraction, which, with part of the molecular fraction, is deposited at the bottom of the lake via sedimentation (Lean 1973). Thanks to continuous subvention of phosphorus from the catchment area to the lake by way of surface run-off and groundwater (Klimaszyk 2006), the large amounts of mineral forms satisfy the needs of hydrobionts. However, the decreasing trend in annual precipitation causes a decline of TP values: in the studied lakes by more than 40% over three years.

Because of the high TP concentration, phosphorus determines the trophic state of the studied lakes. However, even though the concentrations of TP are quite high, humic lakes are poor in bioavailable nutrients, including orthophosphate ions PO_4^{3-} (e.g., Keskitalo et al. 1998). Only soluble mineral compounds, mainly SRP and SUP, are available to algae (Münster 1999). The remaining forms may constitute an additional source of available forms, after their transformation: biological (mineralization) or chemical (dissolution) (Grobelaar and House 1995). The presence of high concentrations of soluble polyphosphates in the lakes (SUP) suggests a low rate of their transformation into the reactive form (SRP). Similarly, continuously high concentrations of organic forms near the lake bottom attest to the low activity of alkaline phosphatases of the bacteria that mineralize organic phosphorus at low temperatures (Reihardt 1973).

The observed statistically significant correlations between the vertical variation in concentrations of both bacterial and algal pigments and concentrations of phosphorus forms indicates a certain capability of this ecosystem to create stable of biotope conditions. In the trophogenic layers (corresponding to Zeu depth) with abundant phytoplankton, polyphosphates (a form hardly available to algae) prevailed among mineral forms of phosphorus. However, polyphosphates were depleted in zones of the highest density of metabolically active bacterioplankton. The range of chemical processes, decreasing the stock of reactive phosphorus in the trophogenic layer, including sedimentation on the colloidal particle into the hypolimnion, should also be

taken into consideration (Lean 1973). Physiological processes of organisms, cell autolysis, and the decomposition of bacterial humic-mineral complexes, are often mentioned among the sources of PO_4^{3-} ions (Kajak 2001). Furthermore, in situations where great amounts of particulate organic phosphorus are stored near the bottom of a lake, enzymatic activity of microorganisms should also be considered (Kufel 1996). Reserves of energy chemically bound with DHS can be made partially available to autotrophic algae by the organisms of the microbial loop: bacterioplankton and flagellated algae. This plays a key role in the functioning of humic lake ecosystems (Jones 1992).

This research showed that the depletion of the stocks of mineral phosphorus is progressing, especially of reactive forms in the zones of lakes where the largest densities of phyto- and bacterioplankton are found. Therefore, considerable amounts of this element were present as particulate organic forms related to the biomass of organisms in the trophogenic zone (in mesohumic and oligohumic lakes), or as dissolved forms in deeper water layers (in the polyhumic lake).

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