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Chemical composition and phosphorus fractionation of sediments in the Bohemian Forest lakes

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Abstract
The upper sediment layers of seven Bohemian Forest lakes were analyzed for the chemical composition (DM, pH, content of C, P, Fe, Al) and P fractionation. Differences among sediments from all lakes were small, except Plešné Lake. Due to low pH, no inorganic carbon could be found in sediments. Sediment from Plešné Lake contained the highest amount of organic carbon (OC) (361 mg g^{-1}) and the highest concentrations of P (4.0 mg g^{-1}) in comparison to other lakes (1.8–2.4 mg g^{-1}), apparently reflecting the basin geology. The sequential phosphorus fractionation according to Psenner & Puczko (1988) was used to examine differences in phosphorus components. The largest part of P (80–90%) was extracted in $NaOH_{25}$ fraction, e.g. bound with Al oxy-hydroxides and organic matter. Contribution of other P fractions of all samples was small (1–5%). P fractionation showed, that the important portion of P in sediments is bound to stabile Al oxy-hydroxides. Relative small amount of P is bound to redox labile Fe compounds. From this proportion it is evident that release of P from sediments is independent of oxygen depletion, but it is governed by pH in water above the sediment.

Key words: sediment composition, phosphorus fractionation, Bohemian Forest, acidification

Introduction

Chemistry and biology of the Bohemian Forest lakes have been studied for more than one century. Veselý (1994), Fott & al. (1994), and Vrba & al. (1996) summarized historical, as well as recent data on the chemistry and biota of the lakes with particular emphasis on changes due to acidification. Similarly, chemical and biological analyses of the lake sediments have been performed from numerous points of view (e.g. Steinberg 1991; Veselý & al. 1993; Schmidt & al. 1993 and Hruška & al. 1999). Whereas a good deal of palaeolimnological records of Bohemian Forest lakes is currently available in the literature, there are (with the exception of Kopáček & al. (2000)) not much information concerning chemistry of sediments.

The purpose of this study is to present data on composition of the uppermost sediment layers of seven stratified Bohemian and Bavarian Forest lakes with respect to P chemistry.

Methods and materials

Sediment samples were gained from Čertovo Lake, Černé Lake, Prášilské Lake, Plešné Lake (November 1998), and Grosser Arbersee, Kleiner Arbersee, with Rachelsee (August-September 1999) in the Czech Republic and Germany. The samples were collected using a 5-cm-

Table 1. – Steps of P sequential fractionation according to PSENNER & PUCZKO (1988). (RP – reactive P, OP - organic P).

Extraction (time/temperature)	Fraction name		P-forms
1. deoxygenated distilled H_2O 2 × (10 min / 25 °C)	H_2O	RP OP	dissolved and loosely bound inorganic P dissolved and loosely bound organic P
2. 0.1M $Na_2S_2O_4$ + 0.1M $NaHCO_3$ (30 min / 40 °C)	BD	RP OP	redox-sensitive P bound to Fe (Mn) hydroxides and compounds P-bound to organic matter sorbed on Fe hydroxides
3. 1M NaOH (16 h / 25 °C)	$NaOH_{25}$	RP OP	P bound to metal (Fe and Al) oxy-hydroxides P bound in precipitates of humic compounds with metals, P in microorganisms including poly-P
4. 0.5 HCl (24 h / 25 °C)	HCl	RP OP	P bound to carbonates and apatite-P acid labile organic P
5. 1M NaOH (24 h / 85 °C)	$NaOH_{85}$	RP OP	refractory and other organic P

diameter gravity corer. The uppermost layers 5 cm sediment samples were passed through a 1-mm sieve, homogenized, and pH, dry mass (DM), loss on ignition (LOI) and sediment grain size (GS) were determined. A part of each homogenized sediment sample was freeze dried and than analyzed for total C (TC), total P (TP), Fe, and Al.

The fractionation of P in sediment samples into five fractions (Table 1) was done according to PSENNER & PUCZKO (1988): Approximately 0.25g DM of wet sediment was placed into 50-ml polypropylene centrifugation tube and stepwisely extracted with 40 ml of each extractant. The sediment samples were centrifuged (2000×g, 30 min) between the fractionation steps and the supernatant was filtrated (0.4 μm). RP, TP, Fe and Al were determined in each fraction. Dissolved organic P (OP) was calculated as a difference between TP and RP.

The particle size distribution was determined by wet sieving (fractions: > 1 mm, 1 mm–230 μm, 230–60 μm, and <60 μm). Dry mass and loss on ignition (LOI) were determined in all size fractions.

RP concentrations were determined according to MURPHY & RILEY (1962). TP, Fe, and Al concentrations in both solid and liquid samples were determined colorimetrically after mineralization with nitric and perchloric acids (KOPÁČEK & al., submitted). TC in freeze-dried samples and OC in aqueous liquid samples were analyzed with a Shimadzu TOC 5000A analyzer.

Results

Sediment characteristics

Sediments of all studied lakes revealed the same pattern of moderately low pH, low compaction, high TC content (Table 2). The pH ranged from 6.1 to 6.5; the lowest DM content (1.8%) was analyzed in Rachelsee, whereas the highest DM contents (4.4% and 4.6%) were analyzed in Prášilské Lake and Kleiner Arbesee, respectively. The highest OC (361 mg g^{-1}) and TP (4 mg g^{-1}) and the lowest Fe (10 mg g^{-1}) concentrations were analyzed in Plešné Lake. The lowest OC (255 mg g^{-1}) and TP (1.8 mg g^{-1}) concentrations contained the sediment from Čertovo Lake. The average Fe concentration of all lakes, without Plešné Lake, was 24.6 mg g^{-1}. The second smallest Fe concentration (13.7 mg g^{-1}) and also the smallest Al concen-

Table 2. – Chemical composition and grain sizes of all sediment samples. Units: % for DM, LOI, particle size classes (1-0.23mm, 230–60µm, and <60µm); mg g^{-1} for OC, P, Fe, and Al.

Abb.	Locality	pH	DM	LOI	OC	P	Fe	Al	1-0.23mm	230–60µm	<60µm
CN	Čertovo Lake	6.2	3.1	55.3	255	1.8	33.4	44.7	1.9	20.6	75.8
CT	Černé Lake	6.1	2.2	65.7	289	2.1	25.1	47.6	6.6	50.0	42.0
PR	Prášilské Lake	6.2	4.4	60.7	298	2.4	23.7	39.9	1.0	25.4	73.0
PL	Plešné Lake	6.1	2.9	74.2	361	4.0	10.0	39.8	0.8	11.1	87.5
GA	Grosser Arbersee	6.5	2.4	57.8	266	2.2	31.0	53.2	0.5	23.6	75.0
KA	Kleiner Arbersee	6.1	4.6	57.8	261	2.0	13.7	32.1	4.3	30.6	61.7
RA	Rachelsee	6.1	1.8	71.5	316	2.3	20.7	51.5	0.2	8.4	91.3

tration (32.1 mg g^{-1}) had the Kleiner Arbersee. Al concentrations of all other lakes ranged from 39.8 to 53.2 mg g^{-1}.

The size distribution of all sediments was rather similar (Table 2). The largest fraction was the <60µm size class (about 77%) except Černé Lake (42%), where the 230–60µm size class made up 50% of sediment. The latter size class made up about 20% of sediments of the other lakes. The LOI of 1-0.23mm size class was smaller that the <60µm size class in Čertovo Lake, Černé Lake and Plešné Lake. The opposite distribution was in the sediments from Prášilské Lake, Grosser Arbersee, Kleiner Arbersee and Rachelsee, where LOI of 1-0.23mm size class was higher than of the <60µm size class.

P-fractionation

The results of the sediment P-fractionation are given in Tables 3 and 4, and summarized in Fig. 1. The $NaOH_{25°C}$ comprised the largest part of P in all sediments and ranged from 79% in Čertovo Lake sediment to 89% in Kleiner Arbersee sediment. The OP part was always

Table 3. – P-fractionation results. Concentrations of P in each fraction are given in mg g^{-1} DM, percentage means partition of P in each fraction on total solubled P.

Lake	H_2O		BD		$NaOH_{25°C}$		HCl		$NaOH_{85°C}$	
	IP	OP	IP	OP	IP	OP	IP	OP	IP	OP
CT	0.00	0.02	0.15	0.07	0.33	0.87	0.03	0.00	0.03	0.03
	0%	1%	10%	5%	22%	57%	2%	0%	2%	2%
CN	0.01	0.03	0.04	0.07	0.58	1.12	0.03	0.02	0.03	0.03
	0%	2%	2%	4%	30%	57%	2%	1%	2%	2%
PR	0.01	0.02	0.05	0.07	0.78	0.89	0.04	0.00	0.03	0.01
	0%	1%	3%	4%	41%	47%	2%	0%	2%	1%
PL	0.02	0.04	0.18	0.08	1.33	1.40	0.04	0.00	0.02	0.05
	1%	1%	6%	3%	42%	44%	1%	0%	1%	2%
GA	0.00	0.01	0.05	0.04	0.64	0.99	0.07	0.01	0.01	0.06
	0%	0%	3%	2%	34%	53%	4%	0%	1%	3%
KA	0.01	0.01	0.02	0.02	0.46	0.94	0.03	0.00	0.02	0.06
	0%	1%	1%	1%	29%	60%	2%	0%	1%	4%
RA	0.04	0.08	0.04	0.06	0.53	1.19	0.02	0.00	0.00	0.06
	2%	4%	2%	3%	26%	59%	1%	0%	0%	3%

Table 4. – Fe, Al and OC concentrations in fractions from P-fractionation. Concentrations of elements in each fraction are given in mg g^{-1} DM.

Lake	H_2O			BD			$NaOH_{25°C}$			HCl			$NaOH_{85°C}$		
	Fe	Al	OC	Fe	Al	OC	Fe	Al	OC	Fe	Al	OC	Fe	Al	OC
CT	0.5	0.4	3.2	1.6	1.0	20	1.6	24	117	11.1	2.7	1.9	2.0	0.8	18
CN	0.3	0.5	3.6	7.4	0.7	18	3.2	28	156	8.2	2.4	2.1	1.2	3.4	23
PR	0.1	0.2	2.3	8.2	1.1	28	2.8	22	140	7.1	1.7	1.8	1.5	5.2	30
PL	0.3	0.6	4.7	5.5	0.8	21	2.8	27	185	1.3	0.3	2.4	0.6	0.9	22
GA	0.1	0.9	1.9	4.2	0.6	21	2.2	37	117	9.2	5.0	3.1	0.4	6.3	40
KA	0.1	0.8	0.9	7.9	5.2	20	1.0	19	114	2.3	2.6	2.4	0.3	4.9	48
RA	0.7	3.2	6.6	2.3	2.9	6	1.4	36	112	5.2	3.3	2.5	0.8	4.4	28

prevailing over the IP part in this fraction. The second largest fraction, BD, comprised from 2% in Kleiner Arbersee to 15% in Čertovo Lake sediments. The IP_{BD} part was significantly higher than OP_{BD} in Čertovo and Plešné Lake. The other fractions contributed to only a small part (2–4% each) of TP.

The distributions of Fe and Al within the fractions revealed a similar pattern for all sediments. Fe was extracted mostly in BD and HCl fractions in all sediments but in different proportions. The HCl fraction usually contained more Fe than the BD fraction, except for Prášilské Lake, Plešné Lake and Kleiner Arbersee, which shows higher Fe_{BD} values. The most of extractable Al was found in the $NaOH_{25°C}$ fraction (up to 91% in Plešné Lake, 76% on average). The second largest Al fraction was the $NaOH_{85°C}$ fraction comprising about 10% of extractable Al. The largest fraction of OC was extracted by $NaOH_{25°C}$ (71% on average). The second largest OC fraction was the $NaOH_{85°C}$, containing about 16% of extractable C, except Grosser and Kleiner Arbersee, where this fraction made up 22% and 26%, respectively.

Discussion

The glacial lakes of Bohemian Forest have steep, but mostly undisturbed forest basins with minimum output of erosion particles in the surface runoff. An important mechanism of sediment formation in these lakes is the precipitation of humic substances with Al, both originat-

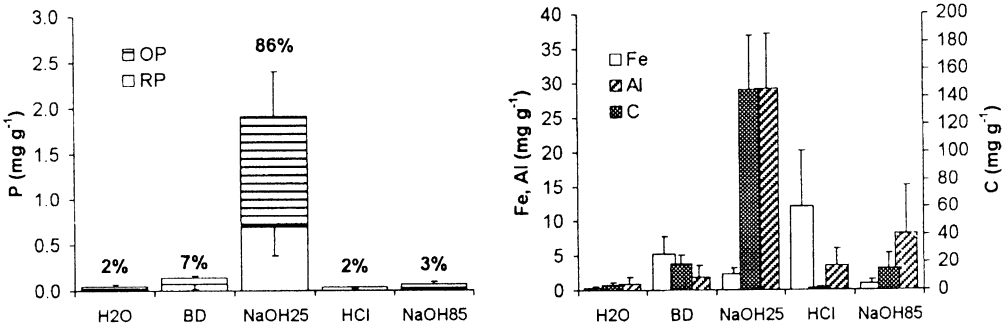

Fig. 1. – Distribution of RP, OP, Fe, Al and OC in fractions obtained from sediments using the P-fractionation procedure of Psenner & Puczko (1988). The participation of fractions on total extractable P is given in percentage over the columns. The solid lines show standard deviations of each parameter within all sediments.

ing from soils of the basins (Kopáček & al. 2000). The sediments are composed largely of these precipitates together with autochthonous organic detritus and a minority of mineral allochthonous particles. These specific conditions well explain the low sediment compaction and high OC. Some inner-group variability can be explained. The highest P and the lowest Fe concentrations were found in Plešné Lake sediment, which differs in the basin geology from the other lakes. The bedrock of Plešné Lake is formed by granites containing more P and less Fe than gneiss and mica-schist in the all other lake basins.

The P distribution within the fractions of the acidic sediment groups showed a similar pattern like Piburger See sediments by Psenner & Puczko (1988). The main part of P was extracted to $NaOH_{25°C}$ fraction, while the P in all other fractions was relatively unimportant. The most of P extracted in both NaOH fractions was mostly combined with organic matter and aluminium, but inorganic P prevailed in both BD and HCl fractions, combined with Fe. A small P portion in HCl and $NaOH_{85°C}$ fractions (2–3% of TP) indicates very low portion of allochthonous particles (Psenner & Puczko 1988).

Fresh precipitates with high sorption capacity can easily sorb a significant amount of P. The result of this process is that the most of P is combined with Al-humic precipitates, which solubility depends on pH, but not on redox conditions. The very low portion of loosely bound P and P in pore water (H_2O fraction) supports the hypothesis that sediments of the Bohemian Forest lakes do not release a significant amount of P but act as an effective trap for P entering the lakes.

Conclusions

The chemical analysis of sediments from all seven studied lakes showed that the chemical composition reflects the bedrock composition, mainly in TP concentration. The sediments were very soft and rich of organic matter and can be classified as a *dy* category. Due to relatively small forest watersheds with undisturbed vegetation cover, minimum portion of inorganic particles were found in the sediments. The precipitation of allochthonous humic compounds with Al is the most important process responsible for the formation of organic matter in sediments and their properties.

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