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Magisterská diplomová práce

**Changes of phosphorus and iron concentrations in pore water
vertical profiles of hypertrophic reservoir measured by gel
minipeepers**

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Anotace:

Sedimenty odebrané v roce 2006 (duben, červen, září) z přítokové a hrázové části hypertrofí nádrže byly inkubovány a analyzovány v laboratoři za simulace in situ podmínek. Cílem bylo zjistit rychlosti uvolňování fosforu a železa a změny ve složení vertikálních profilů pórové vody v horních 6 cm. Vertikální toky měřených analytů v pórové vodě byly zjištěny pomocí gelových minipeeperů. Tato metoda se ukázala jako vhodná pro sledování koncentrací forem P, Fe a základních iontů. Byly zjištěny rozdíly mezi přítokovou a hrázovou částí.

Annotation:

Sediment cores obtained during the year 2006 (April, June, September), originated from inflow and dam sites in hypertrophic reservoir were incubated and analyzed in the laboratory under in situ conditions. The aim of this study was to find out the release rates of phosphorus and iron and to define the changes in the concentrations of dissolved compounds in pore water in the first 6 cm in the sediment. Gel minipeepers were used to measure the vertical profiles of dissolved analyts in pore water. This method was found suitable for investigation of P, Fe and basic ions concentrations. Differences between inflow and dam site were found.

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Poděkování

Děkuji svému školiteli Jakobovi Borovcovi za vedení této práce a trpělivost při vysvětlování studované problematiky. Děkuji také všem svým přátelům, kteří mě po celou dobu podporovali a pomáhali při konečných úpravách. V neposlední řadě patří dík mým rodičům.

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1. Background

Sediments play a pivotal ecological role as a source/sink of nutrients to/from freshwater ecosystems (Søndergaard et al., 2003). The phosphorus (P) pool in the sediment can be more than 100 times higher than the pool present in lake water, therefore the lake P concentrations could be dependent in some cases on the sediment–water interactions. The release of phosphorus and nitrogen (N) from lake sediments has been studied for decades (Mortimer, 1941, 1942; Nurnberg, 1987; Andersen & Jensen, 1992; Gardner et al., 2001). Phosphorus has long been recognized as a key factor responsible for eutrophication of fresh waters and for this reason knowledge of its concentration is an important parameter determining the eutrophic state of an aquatic ecosystems (Golterman & de Oude, 1991).

1.1. Processes playing role in the P cycle

Most of the P incoming into lakes is in the form of inorganic P although some organic P may arrive as well. Different situation is when P enters the sediment by far the greatest part is in the organic form and is usually rapidly taken up in the growing season (Golterman, 2004). In terms of P in the sediments, two processes are related to the P fate: settled P that will eventually be buried in the sediment, and P that will be transformed into an available form, e.g. one that may potentially contribute to eutrophication, before permanent burial (Boers, 1998).

All sediments and suspended matter are taking up P and may release it when conditions change. The environmental factors that regulate the release rates of dissolved P (mostly PO_4) are temperature, pH, redox potential and concentration of dissolved oxygen (Böstrom et al., 1988; Jensen & Andersen, 1992). There are numerous processes leading to P release from the underlying sediment to the water column, including desorption, dissolution of P bounded in precipitates and inorganic material (Mortimer, 1941; Moore & Reddy, 1994), microbial

mineralization of organic matter (OM) (Gätcher & Meyer, 1993) and the diffusion of dissolved P from sediment pore water (Böstrom et al., 1988; Moore et al., 1998). French, 1983, gave an overall range of P release rate values between -10 and $50 \text{ mg m}^{-2}\text{d}^{-1}$ for aerobic and $0-150 \text{ mg m}^{-2}\text{d}^{-1}$ for anaerobic conditions.

With improved understanding of P behavior in sediments, it came to be generally accepted that all interactions between sediments and overlying water mentioned above occur only in the top active layer of 10 cm or less (Smits et al., 1993; Di Toro, 2001). This layer is defined as the depth up to which there is influence of bioturbation and a potential P flux to the water column proceeds. The P flux from sediment upward to the overlying water is also largely influenced by the existence of the aerobic layer, in which the dissolved iron and other metals are oxidized into forms that have strong adsorbing capacities for SRP (Wang, 2003).

The pore water of the sediment, which normally contains less than 1% of the sediments total P pool is important for the P transport between the sediment and the overlying water (Böstrom, 1982). Diffusion rates in pore water are considerably less than in open water due to presence of solid particles and its tortuosity. For instance, freshly deposited sediments have high porosities (60–90%) but decreasing with depth up to 20% in the depth of a few centimeters (cm) (Ullman & Aller, 1982).

In his experimental study, Koretsky et al., (2006) demonstrated that the pore water vertical zonation results from the oxidation of OM being coupled to a succession of increasingly less energetically–favorable terminal electron acceptors, e.g. O_2 , $\text{NO}_3\text{-N}$, Mn^{4+} , Fe^{3+} and SO_4^{2-} . More rapid depletion of electron terminal acceptors occurs in late spring and summer when OM is available and temperatures become higher. Subsequently, the typical sediment profile will have oxygen penetrating a few millimeters (mm) into the sediment, followed by $\text{NO}_3\text{-N}$ and SO_4^{2-} which can be found several cm into the sediment depending on the decomposition rate and $\text{NO}_3\text{-N}$ input (Søndergaard et al., 2003).

Typically, the zones of Fe oxide and P enrichment are present just below the oxic surface layer since Fe³⁺ oxides reductively dissolve to produce much more soluble Fe²⁺. Emergent Fe²⁺ diffuses upward from deeper, more reduced sediment layers and reacts with oxygen or nitrate which are diffusing downward from oxic or pore waters. (Koretsky et al., 2006).

1.2. Comparison of pore water sampling

Concentrations of solutes in pore waters react very sensitively to changes in environmental conditions. Therefore, these concentrations are essential indicators for biochemical processes in lake sediments (Kleeberg & Kozerski, 1997).

Pore water can be sampled by various techniques, including centrifugation (Hamilton & Morris, 1985), slicing the sediment into segments and pressing the pore water out (Kleeberg & Kozerski, 1997) or dialysis cells and gel minipeepers (Hesslein, 1976; Zhang & Davison, 1994; Teasdale et al., 1995). Dialysis cells (multi chambered peepers) consist from an acrylic body with a vertical array of dialysis chambers which are separated from the environment by a dialysis membrane. This type of peeper is used for the depth profile sampling mostly carried out in the field experiments and it usually have to be deployed by divers (Lewandowski et al., 2002).

Jacobs, 2002 used peepers which were designed to provide the capability of sampling and replenishing the dialysis chambers without retrieving the peeper from the sediment and thus to permit a continuous monitoring. The disadvantage is a spatial resolution of these peepers, which is 1/5.5 cm, and thus, lower compared to other peeper types (e.g. DET or DGT techniques). Also the exposition time might be limited due to organisms and biofilms clogging either the membranes or the tubing.

Lewandowski et al., 2002 designed a novel two-dimensional sampler (2D peepers) to revealed 2D images of the SRP concentrations, diffusive fluxes and turnover rates in vertical and horizontal structures.

Gel minipeepers, which consist of thin films of polyacrylamid gel are used for small scale detection experiments on the SWI (Teasdale et al., 1995). The disadvantage of this type of peeper could be the fact that the polyacrylamid gel is continuous medium and the measured profile might be distort by lateral ion diffusion proceeding in the gel. Both type of peepers pointed above rely on a similar equilibration principle but the equilibrium in polyacrylamid gel is established in 48 hours in contrast to days or weeks in case of the dialysis chambers.

Generally, the gel minipeeper experiments are important to gain the detailed knowledge about the spatial and temporal variations in pore water chemistry which is not so well-known from the point of small scale detection. This treatment is very usable especially in polluted ecosystems, where most of the pollutants are finally sorbed in the sediments (Koretsky et al., 2006). The method of sampling the pore water by using gel minipeeper presented in this study was useful to gain the insight into profiles of pore water reliable solutions.

The core treatment in the laboratory compared to lake experiments has an advantage of easier sampling during the incubation period but the results might be distorted due to different hydrological conditions compared to the lake situation because the constant input of the sedimentation, the bioturbation and other processes are partly cut off.

1.3. General scheme of microbial processes zonation

The strong coupling between the deposition of OM and bacterial activities in the sediment has been shown for both marine and freshwater ecosystems (Wobus et al., 2003). Their study was based on sediment samples from four reservoirs of different trophic states, comparing the chemical gradients in pore water, the composition of microbial communities and extracellular

enzyme activities. The assessment of extracellular enzyme activities (esterases, phosphatases, glukosidases and aminopeptidases) in the sediment samples revealed the specific patterns of metabolic potentials in accordance with its trophic state. Sediment was sampled at the lake deepest point by the corer, followed by slicing the sediment samples in the laboratory into layers of 0.5–1 cm. The pore water was extracted by centrifugation. For the microbiological examination and the determination of enzyme activities, the sliced fresh material was diluted and homogenized by the sonication.

In the upper oxygenated part of the SWI the degradation of OM take place via aerobic respiration, which is the process generating the largest free energy, followed by suboxic zone, where nitrification/denitrification occur (Konhauser, 2007). The intensity of the nitrification is governed by $\text{NH}_4\text{-N}$ concentrations: $\text{NH}_4\text{-N}$ is oxidized to nitrate which might cause the nitrification peak very close to the SWI. The deeper O_2 penetration, the higher rate of nitrification (Blackburn, 1993). In contrast, denitrifying bacteria reduce nitrate to negligible concentrations and completely degrade OM to CO_2 . The denitrifiers might be in competition with some chemolithoautotrophic bacteria which are able to couple nitrate reduction and sulphide oxidation (Konhauser, 2007).

In the zone of the nitrate removal, the reduction of Fe^{3+} takes place, iron oxyhydroxids are the preferred sources for Fe^{3+} reducing bacteria, more crystalline Fe^{3+} oxides such as hematite, and magnetite are also microbially reducible (Geobacter metallireducens, Shewanella putrefaciens, also some sulfate, nitrate reducers and methanogens as well have ferric iron reducing capacity). The significant Fe peak in pore water may occur between the Fe and SO_4^{2-} reduction zones. Fe^{2+} diffusing upwards from reduction zone can be oxidized by MnO_2 or $\text{NO}_3\text{-N}$ causing the precipitation as ferric hydroxide adsorb on any available solids. There is evidence in suboxic sediments of diagenetic magnetit formation (Karlin et al., 1987), other minerals that have been observed are vivianite and siderite.

Two groups of SO_4^{2-} reducing bacteria are known below the suboxic layer, the first one utilizes lactate, formate, propionate, butyrate, pyruvate, and aromatic compounds which they oxidized to acetate. The second group oxidize acetate all the way to CO_2 . The rates of the dissimilatory sulphate reduction depend on the amount of OM entering the anoxic zone producing the hydrogen sulphide (Jørgensen, 1982).

We can not strictly divide the sediment into zones, even though the microbial communities aggregate into specific microniches which usually overlap each other (e.g. Fe and sulphate reduction microorganisms). The bacterial trait of switching which is used when their preferable substrate is consumed (Konhauser, 2007).

1.4. The main purposes of this study

- 1) to determine the release rates of P, Fe, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and SO_4^{2-} for better understanding of the interactions on the sediment–water interface
- 2) to evaluate the vertical profiles of dissolved P, Fe, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and SO_4^{2-} in the pore water by using gel minipeepers
- 3) to identify the possible microbial processes on the basis of measured pore water concentrations

2. Materials and methods

2.1 Site description

The samples for the purpose of this study were obtained from the Jordan reservoir which is situated in the southern part of Bohemia (49°25'17" N, 14°39'54" E). The Jordan reservoir is hypertrophic and 3 km long with the surface area of 50 ha, $z_{\max} = 12.5$ m, $z_{\text{mean}} = 5.2$ m, volume of $2.76 \cdot 10^6$ m³ and the water residence time 75 days.

2.2. Sediment sampling

Two sampling sites were selected on the basis of differences in physical and chemical characteristics. The first site called Jo–A was located in the shallow tributary area with the depth of 2.2 m, the water column was not thermally stratified and the SWI remained oxic during the sampling dates. The second site described as Jo–B was situated near the dam site with depth of 8.7 m. Thermal stratification of the water column was observed in the summer and autumn. Sediment samples were collected during 2006 (April, June and September) with a 5 cm internal diameter and 50 cm long gravity corer. Each sampling date three cores from each locality were obtained. The temperature and the dissolved oxygen (DO) water column profiles were measured at 0.5 m intervals. (Sonde4, Hydrolab, USA).

2.3. Laboratory analysis

In the laboratory the undisturbed sediment cores were incubated for 6 days in darkness and in situ (temperature, oxygen) conditions in the incubation chambers. The summer and autumn cores with anoxic sediments were treated in the N₂–filled box to inhibit the oxidation. The overlying water in the sediment cores was mixed by the peristaltic pump. The water was pulled up at 0.5 cm above the sediment and sewed just below the water surface. The water amount in the cores was approximately 0.5 litre and was changed by pumping every 40

minutes. Water samples from the cores were taken daily and filtered through glass-fiber filter (MN GF-5, pore size 0.4 μm). Filtered water samples were measured for pH, TDP (total dissolved phosphorus), SRP (soluble reactive phosphorus), ammonium ($\text{NH}_4\text{-N}$), iron (Fe), nitrate ($\text{NO}_3\text{-N}$) and sulphate (SO_4^{2-}) concentrations.

The phosphorus release rate was calculated over a time interval of 24 hours as the difference between two P contents measured in the water above the sediment. The final release rate was the average value of all rates measured during this incubation period.

After the cores incubation, gel minipeepers were inserted into the cores to find out the dissolved ion concentration profiles at the SWI and in the interstitial water.

The sediment core from each site where the gel minipeeper was not inserted was sliced at 0.5 cm segments down to 2 cm and analyzed for dry weight (DW, 105°C) and loss on ignition (LoI, 550°C, 2h). Wet sediment samples were homogenized by passing through 1 mm nylon sieve and freeze dried. Total phosphorus (TP) and total iron (TFe) concentrations were analyzed in the freeze dried samples.

2.4. Gel minipeeper preparation

Gel was prepared according to Zhang & Davison (1994) with some modification mentioned below.

The gel polymer contained 15 % acrylamid and 0.3 % crosslinker (N, N¹ methylenbisacrylamid) mixed and diluted with distilled-deionized water (DDW) to required concentration. The polymerization process was initiated with ammonium peroxodisulfate (60 μl of 10% wt/vol for 20 ml of solution) and catalyzed by TEMED (20 μl for 20 ml of solution). After the initiator and the catalyst were added, the solution was again mixed and poured between two glass plates separated by 2 mm thin dissepiment. The gel was washed by DDW for 1 month to set the zero in $\text{NH}_4\text{-N}$ concentration. Finally the gel was covered with

semipermeable polyethersulfone membrane (0.45 μm pore size) and put in the plastic probe (2 mm thin, 11 cm long) with the sharpened end for better insertion into the sediment. The water content in the gel was between 85–95%.

Gel in the plastic probe was put into the sediment and exposed for 2 days. After the probe removal from the sediment, it was quickly washed by DDW in order to prevent the ingress of sediment particles inside the probe and finally the gel was cut into 5 mm pieces. The part exposed just below the SWI was cut into 2.5 mm down to 1 cm for more exact approach. Cut pieces were extracted in weighted plastic bottles with 15 ml of DDW for two weeks to set the equilibrium. The plastic bottles were carefully washed by DDW before use to reach the conductivity of 0.5 $\mu\text{S}/\text{cm}$. The DDW where the gel was extracted was analyzed for TDP_{DDW} , SRP_{DDW} , Fe_{DDW} , $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and SO_4^{2-} dissolved organic phosphorus (DOP) was counted as the difference between TDP_{DDW} and SRP_{DDW} .

The gel itself was extracted in 5 ml of HClO_4 for two days, followed by a sample analysis for total dissolved phosphorus (P_{gel}) and total dissolved Fe (Fe_{gel}).

The sum of TDP_{DDW} in the analyzed water and total dissolved phosphorus in the gel (P_{gel}) comprised the total dissolved phosphorus in pore water.

2.5. Analytical methods

The dry weight (DW) was determined after drying at 105°C for 2 hours, the loss on ignition (LoI) by the combusting at 550°C for 2 hours. Sediment samples for total contents of P and Fe in the solid phase were freeze dried followed by colorimetric measurement after nitric–perchloric acid digestion (Kopáček et al., 2001).

TDP , SRP , Fe , $\text{NH}_4\text{-N}$, P_{gel} , Fe_{gel} were analyzed by the FIA (Flow injection analyzer Lachat, USA), DOP was calculated as the difference between TDP_{DDW} and SRP_{DDW} measured in pore water. $\text{NO}_3\text{-N}$ and SO_4^{2-} were determined by ion chromatography (Dionex, USA).

3. Results

3.1. Solid phase

The sediment characteristics from two different sites were compared (Table 1). At site Jo–A the vertical profile of both DM and LoI were similar in the spring and summer sediment cores, in contrast to autumn samples where the lowest values were observed in the uppermost part (0–0.5 cm). Comparing the inflow (Jo–A) and the dam (Jo–B) sites, DM was higher at the site Jo–A, the values ranged from 16% to 26% and increased clearly with the depth. The DM values at the site Jo–B ranged from 3% to 9%.

The samples of sediment layers were also analyzed for LoI. The LoI values unchanged at the Jo–A site (12%) and were spatially variable at the Jo–B site (18–26%) in the spring and summer cores, the decrease of LoI with depth occurred in autumn cores at both sites, it is considered that the LoI values were indirectly proportional to DM.

Concentrations of TP, TFe differed between both sites, the Jo–B values were higher compared to Jo–A. The decrease of TP and TFe concentrations with depth was observed at Jo–B in spring, TP decreased from 2.3 to 1.8 mg/l and TFe concentrations from 56 to 49 mg/l. Jo–A concentrations unchanged during spring and summer, but the TFe concentrations increased with depth in the autumn (from 30 to 34 mg/l). The TFe: TP ratio represented the sediment sorption capacity, the ratio valued from 20 to 27 and increased slightly with depth, except the unchanged values in Jo–A summer profile.

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Table 1. The summary of DM, LoI, total contents of P, Fe and TFe:TP ratio in the upper 2 cm of the sediment at sites Jo-A and Jo-B in three sampling dates.

	spring						summer					autumn				
	depth cm	DM %	LoI %	TP mg/g	TFe mg/g	TFe:TP mg/g	DM %	LoI %	TP mg/g	TFe mg/g	TFe:TP mg/g	DM %	LoI %	TP mg/g	TFe mg/g	TFe:TP mg/g
Jo-A	0-0.5	19	12	1.8	36	20	18	12	1.6	34	21	16	13	1.6	30	19
	0.5-1	20	12	1.8	37	20	20	12	1.7	36	21	21	12	1.8	33	18
	1-1.5	21	12	1.5	35	23	22	12	1.7	35	21	23	12	1.7	33	19
	1.5-2	22	12	1.6	35	23	23	12	1.6	34	21	26	8	1.7	34	20
Jo-B	0-0.5	8	21	2.3	56	24	9	18	2.5	46	18	3	31	2.4	47	20
	0.5-1	6	26	2.3	50	22	8	21	2.3	51	23	8	18	2.4	49	21
	1-1.5	8	21	2.0	46	23	7	24	2.1	46	22	8	20	2.1	47	22
	1.5-2	9	18	1.8	49	27	9	20	2.0	43	22	8	22	4.0	48	23

3.2. Phosphorus release

The thermal stratification of the water column was observed in the summer and autumn at Jo-B, in contrast to Jo-A, where no thermal stratification was measured. The P, NH₄-N, NO₃-N, SO₄²⁻ concentrations observed in the water column are noted in Table 2. together with selected physical (temperature, pH) and chemical (DO) parameters.

Average release rates of SRP, TDP, Fe, NH₄-N, NO₃-N, SO₄²⁻ obtained from sediment core incubations are described at Table 3. Release rates measured at the SWI during core incubations were mostly negative or varied around 0 mmol/m²/d, these values reflected most likely the uptake of dissolved elements into the sediment. The values which indicated high release of TDP and Fe were measured only in the summer at Jo-A, TDP with the average value 2.45 mmol/m²/d, Fe 0.18 mmol/m²/d and NH₄-N 12.2 mmol/m²/d attached to decrease of NO₃-N, SO₄²⁻ concentrations

Release rates at Jo-B were not largely different one from another, the uptake prevailed the release during the dated period, except the summer NH₄-N concentration with the value 1.09 mmol/m²/d.

Table 2. The summary of temperature, dissolved oxygen, pH values, TP (total phosphorus), RP (reactive phosphorus), SRP (soluble reactive phosphorus), NH₄-N (ammonium), NO₃-N (nitrate) and SO₄²⁻ (sulphate) concentrations measured in the reservoir 0.3 m above the bottom in the overlying water.

		Temp °C	DO mg/l	pH	TP µg/l	RP µg/l	SRP µg/l	NH ₄ -N mg/l	NO ₃ -N mg/l	SO ₄ ²⁻ mg/l
Jo-A	spring	7.5	12	7.52	52	17	7	0.25	6.7	35
	summer	16	9.5	8.73	88	18	7	0.54	0.1	34
	autumn	17.3	15.7	7.49	68	14	3	0.01	0.0	34
Jo-B	spring	2.9	2.2	7.2	156	124	138	1.15	1.5	42
	summer	3.6	0.1	6.89	359	246	246	1.59	1.6	36
	autumn	5.1	0.0	6.79	559	438	153	3.31	0.3	28

Table 3. Soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), dissolved Fe, ammonium (NH₄-N), nitrate (NO₃-N) and sulphate (SO₄²⁻) average release rates were based on sediment core incubations. The core incubation lasted for 5 days, the release rate for particulate days was calculated as the difference between two concentrations measured in 24 hours. The final release rate was the average value of all rates measured during this incubation period.

		SRP	TDP	Fe	NH ₄ -N	NO ₃ -N	SO ₄
mmol/m ² /d							
Jo-A	spring	0.01	0.0	-0.02	-0.24	-1.18	0.23
	summer	2.52	2.45	0.18	12.16	-9.56	-23.8
	autumn	0.03	0.0	-0.03	1.44	0.53	4.31
Jo-B	spring	-0.07	-0.08	0.1	-0.4	-0.84	3.17
	summer	-0.41	-0.39	0.05	1.09	-1.47	0.31
	autumn	-0.04	-0.22	-0.02	0.2	-0.03	0.47

3.3. Sediment zonation

The pore water vertical profiles were divided according to SO₄²⁻ and NO₃-N concentrations (Fig. 1, a, b, c, d) into upper (suboxic) and lower (anaerobic) part for better interpretation of results. Penetration of SO₄²⁻ and NO₃-N differed in three sampling dates at both sites, therefore we should consider that the range of the upper part varied during the year. The SO₄²⁻ and NO₃-N concentrations in the lower part at both sites were utilized and this part could be determined as the anaerobic zone.

According to SO₄²⁻ and NO₃-N penetration observed at Jo-A the upper part was considered to be down to 27.5 mm in the spring, back to 12.5 mm in the summer and back to 17.5 mm in the autumn. Jo-B penetration of SO₄²⁻ and NO₃-N in the summer and autumn was the same as

well as the range of upper part as observed at Jo-A, just the spring upper part was different from Jo-A and reached down to 22.5 mm.

From this point of view the upper part in the sediment was assumed to be the „active“ sediment layer and the lower part as the layer with most likely permanent burial of P.

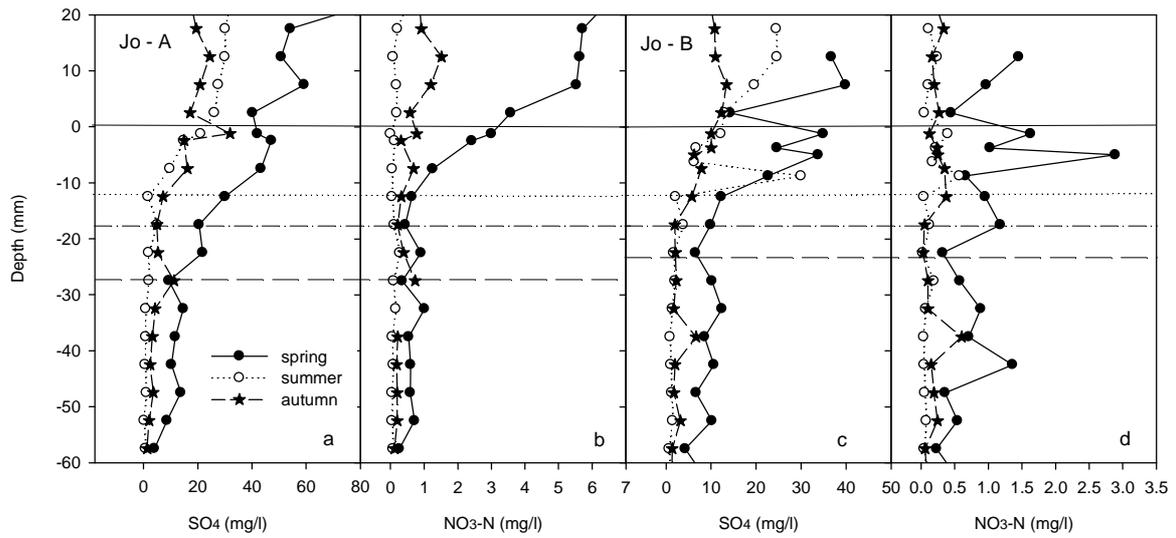


Figure 1: Sulphate and nitrate pore water concentrations measured at Jo-A and Jo-B as follows during three sampling dates. Solid line: sediment water interface, sampling dates: long dashed line (— —): spring, dotted line (....): summer and dash dotted line (-.-.-): autumn upper part. These lines constituted the approximate boundary between suboxic and anaerobic zone.

3.4. Pore water and effects of diagenetic processes

Generally, TDP is formed by SRP, DOP and P_{gel} , the ratio of these phosphorus forms varied with season. The ratios measured in the upper part were as follows: SRP:DOP: P_{gel} in the spring at Jo-A 30:20:50 and 50:10:40 at Jo-B. The amount of P_{gel} increased in the summer and autumn, the average ratio increased up to 10:10:80 at Jo-A and 20:20:60 at Jo-B in the upper part. In the lower part more than 80% was formed by P_{gel} during all sampling dates.

3.4.1. Pore water vertical profiles observed at Jo-A

Upper part

High decrease in SO_4^{2-} concentration (Fig. 1, a) with depth was found in the spring, the values decreased from 42 mg/l at 1.25 m to 9.3 mg/l at 27.5 mm below the SWI. The summer and autumn SO_4^{2-} profiles were similar to each other with the concentrations range from 32mg/l to 5.2 mg/l.

Concentrations of $\text{NO}_3\text{-N}$ (Fig. 1, b) in the spring showed the rapid decrease between the overlying water and the layer 1.25 mm below the SWI. The $\text{NO}_3\text{-N}$ values of overlying water concentrations were 5.5 mg/l and decreased up to 3 mg/l at 1.25 mm below the SWI. The summer and autumn $\text{NO}_3\text{-N}$ profiles overlapped each other and $\text{NO}_3\text{-N}$ depletion was observed at 1.25 mm below the SWI with the values 0 mg/l in the summer and 0.8 mg/l in the autumn.

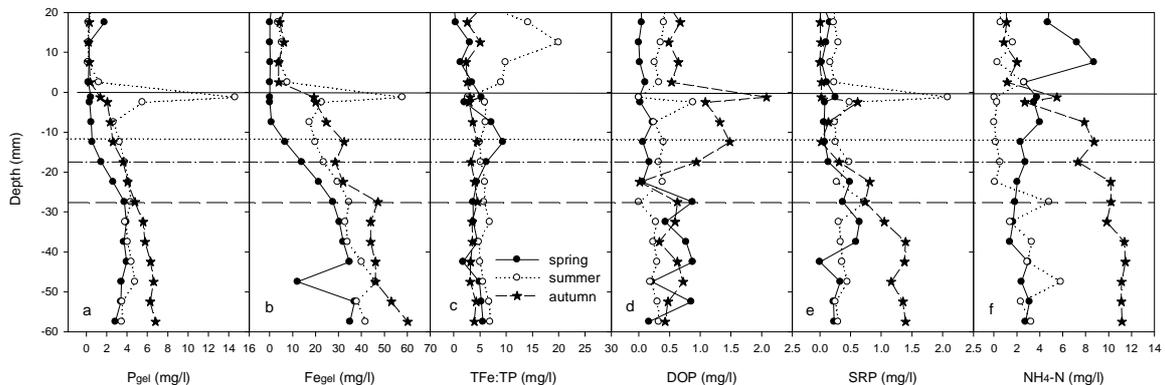


Figure 2: Inflow part (Jo-A) pore water vertical profiles of phosphorus (a), iron (b), extracted from gel by HClO_4 (P_{gel} , Fe_{gel}), the ratio of total concentrations of iron and phosphorus (c) (TFe:TP), dissolved organic phosphorus (d) (DOP), soluble reactive phosphorus (e) (SRP) and ammonium (f) ($\text{NH}_4\text{-N}$) as a function of depth. Solid line: sediment water interface, sampling dates: long dashed line (— —): spring, dotted line (....): summer and dash dotted line (-.-.): autumn upper part. These lines constituted the approximate boundary between suboxic and anaerobic zone.

The concentrations of P_{gel} (Fig. 2, a) and Fe_{gel} (Fig. 2, b) were seasonally variable and increased with depth. Spring P_{gel} concentrations at Jo-A were the lowest compared to summer and autumn, with the values increased from 0.4 mg/l to 3.7 mg/l. The distinct P_{gel} peak (14.6 mg/l) was measured in the summer at 1.25 mm below the SWI related to Fe_{gel} peak (58 mg/l)

observed in the same layer. Fe_{gel} concentrations reached the highest values in the autumn (up to 32.4 mg/l).

Molar ratios (TFe:TP) are noted in Fig. 2, c. The highest range was observed in the summer cores. The ratio value at 2.5 mm above the SWI was 9 in contrast to the ratio at 1.25 below the SWI which was significantly lower with the value 2.7.

The spring Jo-A profile of TFe:TP values showed increase from 3.5 at 2.5 mm above the SWI to 5.2 at 1.25 below the SWI. The autumn profile of TFe:TP was not as dynamic related to spring and summer ones, the ratio remain unchanged throughout the whole vertical profile.

High increase in DOP concentrations (Fig. 2, d) with season was observed. The values range in the upper part was greatest in the autumn from 2 to 0.06 mg/l. The distinct decline in DOP concentrations was observed in two layers, the first one at the depth of 2.5 mm, where the concentration decreased from 2 mg/l to 1 mg/l indicated the nitrate reduction zone. The second decline was observed at 22.5 mm and was defined as the sulphate reduction zone with the concentration decrease from 0.94 to 0.06 mg/l. Summer values of DOP profile ranged between 0.2–0.9 mg/l with the obvious declines at 7.5 mm and 27.5 mm below the SWI.

The SRP concentrations (Fig. 2, e) remained relatively constant in all three sampling dates except the highest peak measured in the summer with the value 2.1 mg/l.

Dissolved NH_4-N profiles (Fig. 2, f) were spatially and temporally variable, the concentrations in the upper part remained stable in the spring (0.03–0.08 mg/l) and did not change a lot in the summer (4–2 mg/l) in contrast to autumn concentrations which increased with depth and varied between 2.7–10 mg/l.

Lower part

Lower part was characterized as the anaerobic zone and indicated the SO_4^{2-} and NO_3-N depletion. The concentrations of all measured dissolved compounds (P_{gel} , Fe_{gel} , DOP, NH_4-N

and TFe:TP) remained stable in this part. The P accumulation in the lower part was observed just in the SRP autumn profile.

3.4.2 Pore water vertical profiles observed at Jo-B

Upper part

The obvious decrease in SO_4^{2-} concentrations (Fig. 1, c) with depth was found in the spring, Jo-B values decreased from 35 mg/l at 1.25 mm up to 6.5 mg/l at 22.5 mm below the SWI. The summer and autumn SO_4^{2-} profiles were similar to each other except the sharp summer peak measured at 8.75 mm with the value of 30 mg/l. Otherwise, the summer and autumn concentrations ranged between 12.2–1.7 mg/l.

Concentration of $\text{NO}_3\text{-N}$ (Fig. 1, d) showed the high concentrations in the spring compared to summer and autumn profiles which were characterized by $\text{NO}_3\text{-N}$ depletion at 1.25 below the SWI.

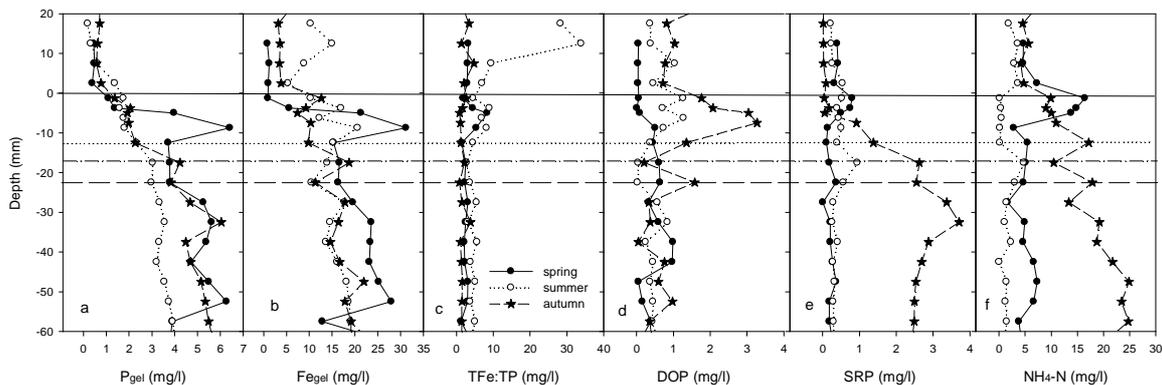


Figure 3: Dam part (Jo-B) pore water vertical profiles of phosphorus (a), iron (b), extracted from gel by HClO_4 (P_{gel} , Fe_{gel}), the ratio of total concentrations of iron and phosphorus (c) (TFe:TP), dissolved organic phosphorus (d) (DOP), soluble reactive phosphorus (e) (SRP) and ammonium (f) ($\text{NH}_4\text{-N}$) as a function of depth. Solid line: sediment water interface, sampling dates: long dashed line (— —): spring, dotted line (....): summer and dash dotted line (-.-.): autumn upper part. These lines constituted the approximate boundary between suboxic and anaerobic zone.

The P_{gel} peak (Fig. 3, a) reached the value 6.4 mg/l and was associated with Fe_{gel} peak (Fig. 3, b) with the value 31.2 mg/l, these concentrations were observed at 8.75 mm and strongly coincided with decrease in $NH_4\text{-N}$ and $NO_3\text{-N}$ concentrations. The P_{gel} summer and autumn values were similar to each other in contrast to lower part. Concentrations of Fe_{gel} increased with depth, as mentioned above the highest values were observed in the spring with sharp peak noted at 8.75 mm, the summer and autumn values varied between 20.5–7.4 mg/l.

The highest range in TFe:TDP ratio (Fig. 3, c) was noted in the summer, the ratio value at 2.5 mm above the SWI was 7 with the decrease up to 4.5 at 1.25 mm below the SWI. In contrast the spring value at 2.5 mm above the SWI was 2.9 mg/l and 1.25 below the SWI 1.8 mg/l. Autumn values just above and just below the SWI did not change.

Increase in DOP concentrations was observed mainly in the autumn (Fig. 3, d), the values at Jo-B in the upper part ranged from 3.3 to 0.2 mg/l. The distinct decline in DOP concentrations was observed at 17.5 mm and decreased from 1.4 up to 0.2 mg/l.

The SRP concentrations (Fig. 3, e) remained relatively constant in the spring and summer, the increasing values with depth were observed in the autumn with the maximal value 2.6 mg/l at 17.5 mm below the SWI.

Dissolved $NH_4\text{-N}$ profiles (Fig. 3, f) showed the most dynamic values in the spring, with the maximum peak value of 16.5 mg/l at 1.25 mm below the SWI. This peak was absent in summer and autumn profiles which remained relatively stable throughout whole profile.

Lower part

SO_4^{2-} and $NO_3\text{-N}$ concentrations in the lower part at Jo-B were near to detection limits. Concerning P_{gel} , Fe_{gel} , DOP and TFe:TP there was not observed any obvious increase in these concentrations. The lower part, however, exhibited a marked SRP and $NH_4\text{-N}$ concentration increase in the autumn.

4. Discussion

4.1. Solid phase

The contents of OM measured as LoI were lower at Jo–A along to lower values of TP and TFe in the sediment particles in contrast to Jo–B. There was not found high difference among the measured layers besides the autumn profiles at both sites which showed the lowest values in the uppermost part which indicated the freshly settled seston (Gätcher & Meyer, 1993).

Jensen et al. (1992b) demonstrated in the study of Danish lakes that lake sediments with TFe:TP ratio above 15 (by weight) decreased P release, while the lakes with the TFe:TP ratio below 10 were unable to retain P. In our study TFe:TP ratio in the sediment varied about 20, which is the value possible to control the internal P loading. As mentioned above the high release values were measured just in the summer at site Jo–A and the release most likely as the reflection of high sedimentation rate.

4.2. Release rates

We have to accept that our values based upon sediment core incubations in the laboratory presented the net release rates. The processes in isolated cores are difficult to compare to lake situation, because the influence of bentic "animals" in the cores is limited to the water column of a few cms above the sediment and might be more important in core treatments than in in-lake studies in contrast we can not simulate all the in-lake processes.

Nowlin et al. (2005) have measured the release rates in eutrophic reservoir, the SRP values at the dam site varied between 0.2–0.4 mmol/m²/d in contrast to river site where the values ranged between 0.05–0.06 mmol/m²/d. This release rates values were obtained from core sediments incubation the other method of determining the release rates was carried out in situ in hypolimnetic water. Previous studies that also compared sediment P release rates derived from sediment core incubations and in situ hypolimnetic P accumulation have found that rates

generated by both methods generally correspond with one another (Nürnberg, 1987) in contrast Nowlin investigated that P release rates determined from sediment core incubation were more than an order of magnitude greater than release rates determined from hypolimnetic accumulation.

We measured P release rates by sediment core incubation, the determined values were higher at Jo-A and ranged between 0.01-2.52 mmol/m²/d, the dam site (Jo-B) release rates valued between -0.04 up to -0.41 mmol/m²/d.

The difference in release rates between site Jo-A and Jo-B was presumably because of different physical conditions and DO concentrations in the overlying water. Compared to other studies we supposed that the release rates at Jo-B should be higher in contrast to Jo-A, because of anoxic conditions observed during the summer stratification in the hypolimnion, but the summer values demonstrated that the contrast was right. At site Jo-B negative release rates which indicated uptake were observed during the three sampling dates in spite of anoxic conditions observed in the summer. Negative release rates could be explained by DOP and SRP profiles, because there was found no gradient in both DOP and SRP which could indicate release.

Sediments from inflow site (Jo-A) in the summer cores showed the high release rates probably due to high temperatures, presence of DO and intensive turnover caused mainly by particle sedimentation entering the reservoir or produced in the water column (e.g. algae, detritus) (Sondergaard et al., 2003) these particles might be rich in easily degradable OM and created the hot spots for microbial activity. There was not found the summer increase in SRP concentrations in the water above the sediment which might be caused by high SRP release from Jo-A sediment (mean value 6 µg/l) it was supposed that the released SRP might be removed by uptake or precipitation.

Release rates at site Jo–B lower compared to Jo–A, most likely because of relatively smaller amounts of OM were deposited due to “open” water area and the low temperatures together with anoxic conditions slowed down the mineralization rate.

Our observation resembled other studies, several authors have shown that the SRP and Fe release from aerobic sediment surface in shallow polymictic lakes occurred (e.g. Marsden, 1989; Gonsiorczyk et al., 1997), followed by the formation of anoxic microlayer at the SWI due to enhanced microbial activity in the sediment during summer (Gächter et al., 1988). Another studies (Lee et al., 1977; Böstrom et al., 1982; Jensen & Andersen 1992a), demonstrated that the sediment of shallow eutrophic lakes released SRP to oxic lake water and suggested that other factors than redox conditions at the SWI are involved.

Physical stirring or bioturbation among others might caused the transport of dissolved inorganic material from deeper sediment layers up into the oxic zone of the sediment and thus be responsible for contact between sediment and overlying water by changing the conditions as sorption/desorption, mixing pore and overlying water, followed by SRP release (Lewandowski et al., 2002).

4.3. Gel minipeepers

The distribution of vertical sediment pore water profiles into upper and lower part arised from $\text{NO}_3\text{-N}$ and SO_4^{2-} concentrations. $\text{NO}_3\text{-N}$ and SO_4^{2-} are used as electron acceptors by microbes when DO is depleted. The upper sediment part was characterized as the suboxic zone which was considered as the layer with the most intensive processes comparing to lower part which was supposed to be anaerobic due to $\text{NO}_3\text{-N}$ and SO_4^{2-} utilization. Due to anaerobic conditions in the lower part most likely methanogenesis and permanent burial of P occurred (Konhauser, 2007). We did not measure the DO pore water concentrations but according to previous measurements DO penetration was assumed to be about 0.5 mm.

4.3.1. Phosphorus forms in pore water

The proportional ratios of TDP_{DDW} , P_{gel} , Fe_{DDW} and Fe_{gel} released from gel depended on saturation of dissolved compounds in pore water and their ability to precipitate. Because of high concentrations of Fe_{gel} in pore water most of the TDP seemed to be precipitated inside the gel, which is the cause of more than 80% of TDP released after $HClO_4$ extraction throughout whole profile.

4.3.2. Comparison of inflow (Jo–A) and dam (Jo–B) site

Spring upper part

Concentrations of NO_3-N and SO_4^{2-} reached high values and penetrated down to 27.5 mm at Jo–A and down to 22.5 at Jo–B, because of high DO values, low temperatures and low amount of OM which replied for slower microbial activity compared to summer and autumn.

Generally, the profiles of P_{gel} and Fe_{gel} at Jo–A in pore water did not differ too much and remained stable down to 12.5 mm, the increase was observed down from this layer.

In contrast Jo–B showed different P_{gel} profile, the sharp peak was observed at 8.75 mm and was coincident with Fe_{gel} peak found in the same layer this peak indicated the microbial activity. Concentration increase was also consistent with NO_3-N and NH_4-N decrease and it was assumed that sulphate reduction and NH_4-N oxidation took place. NH_4-N was consumed within nitrification, whereas NO_3-N originating from nitrification was probably utilized in the upper layers. Generally, gradient of NH_4-N at Jo–B indicated release, but no release was observed, the concentration of NO_3-N produced by nitrification decreased because of its utilization for sulphur oxidation (SO_4^{2-} release rate value 3.17 mmol/m²/d).

According to Holdren & Armstrong (1986) SRP can be immobilized by the oxidation of Fe^{2+} if the atomic TFe:TP ratio (mol:mol) in pore water exceed values ≥ 1.8 . At site Jo–B the ratio

below the SWI at 1.25 mm was 1.8 and 2.9 at 2.5mm above the SWI which indicated higher SRP concentrations and Fe utilization.

As pointed above it is generally known, that TFe:TP ratio governs the formation of new sorption sites for orthophosphate when Fe^{2+} is oxidized to Fe^{3+} in the oxic surface layer, such that a high ratio prevents P release as long as the oxidation capacity in the surface layer is maintained.

Concentrations of DOP and SRP did not obviously change throughout whole profile.

Spring lower part

The lower part in the spring did not show the concentration changes except the P_{gel} and Fe_{gel} concentrations which seemed to decrease with depth.

Summer upper part

The summer profiles of $\text{NO}_3\text{-N}$ and SO_4^{2-} demonstrated their use as electron acceptors when DO is depleted, that is why its utilization sharply increased in the summer in connection with OM input followed by mineralization processes. The consumption of $\text{NO}_3\text{-N}$ to the values near the detection limit at 1.25 mm below the SWI was obvious at both sites. Most likely because of high OM input especially at Jo-A which was coupled to dissimilatory nitrate reduction or nitrate respiration as the processes regarded to be important for OM mineralization (Konhauser, 2007). According to Einsele-Mortimer model the presence of $\text{NO}_3\text{-N}$ can enhance or reduce TDP release. Bostrom, (1988) demonstrated that the $\text{NO}_3\text{-N}$ concentration ≥ 0.5 mg /l is high enough to prevent the release of Fe bound P. Compared to our observations we could consider the same situation at Jo-A where $\text{NO}_3\text{-N}$ concentrations < 0.5 mg /l caused SRP release (2.52:mmol/m²/d). Values at Jo-B did not reply for this proposition, because in spite of $\text{NO}_3\text{-N}$ concentrations lower than 0.5 mg /l SRP release was not observed.

If the $\text{NO}_3\text{-N}$ concentrations are low, but the SO_4^{2-} levels and the supply of biodegradable OM high, desulphurication and sulphur cycling may become important part of sediment processes (Holmer & Stockholm, 2002). The SO_4^{2-} reduction activity was not measured, however, the vertical profiles indicated that SO_4^{2-} reduction might be important for P mobilization (Kleeberg & Kozerski, 1997). Although the SO_4^{2-} reduction processes are supposed to be strictly anaerobic, the SO_4^{2-} reduction under suboxic conditions in the upper part was likely explained by the ability of microorganisms to carry out their anaerobic reactions even in the presence of oxygen. The SO_4^{2-} consumption to detection limits was apparent in the summer cores at both sites at 12.5 mm.

High summer peaks of P_{gel} and Fe_{gel} accumulation at Jo-A at 1.25 mm below the SWI demonstrated $\text{NO}_3\text{-N}$ and SO_4^{2-} utilization (Koretsky et al., 2006). The occurrence of anaerobic conditions probably induced the dissolution of P and Fe compounds which were undissolved in the spring. Most amounts of P and Fe cumulated below the SWI because of very high OM input as the result of OM decomposition, the decomposition rate was supposed to be faster than diffusion. The TFe:TP ratio value was 2.7 at 1.25 mm below the SWI and 9 at 2.5 mm above the SWI which indicated that the Fe sorption capacity run down and P release to overlying water was observed (SRP release rate: 2.52 mmol/m²/d). It could be confirmed by sharp SRP peak at 1.25 mm below the SWI as the result of complete OM degradation. Comparing to DOP peak at 2.5 mm which was considered as the layer with partial degradation of OM.

P_{gel} and Fe_{gel} profiles at Jo-B increased slightly with depth and compared to Jo-A no obvious peak was observed. . The Jo-B Fe_{gel} values above the SWI indicated the Fe release which was consistent with core incubation (0.05 mmol/m²/d).

TDP_{DW} is formed by SRP and DOP, the ratio of these two compounds seemed to be dependent on OM input variable with season and mineralization activity. DOP formed the large part at

both sites in the upper part of the sediment and could be used as an organic substrate for NO_3^- -N and SO_4^{2-} reduction. The decrease down to 0 mg/l in DOP concentrations was observed at Jo-A at 1.25 below the SWI as the indication of sulphate respiration zone followed by increase up to 0.88 mg/l at 2.5 mm. The second depth where DOP was depleted was found at 27.5 mm. In contrast Jo-B DOP values decreased slightly with depth.

Summer lower part

The increase with depth in P_{gel} and Fe_{gel} concentrations was observed at both sites. TFe:TP ratio as well as the DOP, SRP and $\text{NH}_4\text{-N}$ concentrations remained stable.

Autumn upper part

Compared to summer profiles the depletion of $\text{NO}_3\text{-N}$ and SO_4^{2-} migrated downwards to 17.5 mm at both sites. $\text{NO}_3\text{-N}$ and SO_4^{2-} were used as terminal electron acceptors for microbial activities.

Concentrations of DOP strongly depended on the OM input that was the cause of the highest values measured in the autumn. The obvious peak of DOP depletion was noted at 2.5 mm at Jo-A, this layer was characterized as the $\text{NO}_3\text{-N}$ reduction zone. The second peak of DOP depletion was observed at 22.5 mm at Jo-A and at 17.5 mm at Jo-B indicated the SO_4^{2-} reduction zone or methanogenic microorganisms activity, which constituted the boundary between the suboxic (upper part) and anaerobic (lower part) zone of the sediment. The highest DOP values were measured in autumn cores, not only in the sediment but also in the overlying water, high DOP values indicated freshly settled, easily degradable material.

Compared to DOP the SRP profile showed the opposite trend. Autumn values were the lowest and increased with depth.

High $\text{NH}_4\text{-N}$ concentrations indicated high rates of microbial decomposition of organic nitrogen compounds

Autumn lower part

Compared to spring and summer high autumn SRP and $\text{NH}_4\text{-N}$ accumulation together with decreasing DOP concentrations was noted in the autumn most likely because of high amount of easily degradable material.

4.3.3. Estimation of microbial activity

The knowledge of the function of sediments and determination of microbial activities was gained by chemical profiles measured in pore waters.

The depletion of electron acceptors in pore water in the summer and autumn at both sites showed that the bacterial activity in the sediment was closely linked to the trophic conditions in the overlying water and partly resulted from OM sedimentation (Konhauser, 2007).

We delined the main processes which might occurred in the sediment according to presence of electron acceptors and profiles of dissolved compounds. In the upper part of the sediment with contains of electron acceptors ($\text{NO}_3\text{-N}$ and SO_4^{2-}) most likely the aerobic respiration took place at Jo-A. This oxic layer was followed by suboxic layer depending on the sediment processes. Suboxic layer at both sites penetrated just down to 12.5 mm in the summer, moved down to 17.5 mm in the autumn and migrated downward up to 22.5 at Jo-B and up to 27.5 mm at Jo-A in the spring. This upper layer was characteristic by high concentrations of $\text{NH}_4\text{-N}$, DOP and TFe:TP ratio in contrast to lower part at both sites especially in the autumn suggested as the result of mineralization activity.

The SO_4^{2-} depletion at the end of this anoxic zone was characterized by dissimilatory SO_4^{2-} reduction which was proportional to the quantity and reactivity of OM entering the anoxic zone (Berner, 1964). As mentioned above the SO_4^{2-} depletion was evident in the summer and

autumn in the upper part. Trends of SO_4^{2-} and $\text{NO}_3\text{-N}$ in the summer and autumn were identical and consumed within the first 2 cm at both sites.

The terminal step in anaerobic degradation of OM is methanogenesis, which usually occurs when 90% of dissolved sulphate was reduced, respectively (Higgins et al., 1981). Methanogenesis could be coupled to sulphate reduction. The anaerobic zone was characteristic by decrease in DOP concentrations and TFe:TP ratio, in contrast to increase in P_{gel} , Fe_{gel} , $\text{NH}_4\text{-N}$ and SRP concentrations. An anaerobic zone is also the zone where polyphosphate could be used as an energy source for the uptake of fatty acids and their storage during the absence of electron acceptors (Konhauser,2007).

5. Conclusions

In the hypertrophic Jordan reservoir the SRP release rates in the summer coincided with the organic matter input, temperature and DO. The anoxic sediment SRP release rates at Jo–B were negative compared to oxic Jo–A site where due to high organic input, temperature and DO in the summer high release rates were observed together with Fe utilization.

The processes which took place in pore water were fundamental for understanding the phosphorus cycle between the sediment and overlying water. The gel minipeeper treatment represented in this study was the way how to accurately reveal the pore water structure. This study presented mainly the vertical profiles of dissolved particular forms of phosphorus and iron in pore water which were strongly associated to microbial activity and varied with season. The range of upper part differed during the sampling dates, in the spring reached down to 27.5 mm at Jo–A and down to 22.5 mm at Jo–B, migrated upwards in the summer at both sites up to 12.5 mm and was found to be at 17.5 mm in the autumn.

Generally, the major part of TDP was formed by P_{gel} which indicated high amount of P able to precipitate and sufficient contents of dissolved Fe.

TDP_{DDW} composed from DOP and SRP, the ratio of these two P forms strongly depended on NO_3-N and SO_4^{2-} depletion.

Significant decrease in NO_3-N and SO_4^{2-} concentrations up to depletion throughout the profile was observed in the summer and autumn just below the SWI at 1.25 mm connected to high OM input.

The upper part of the sediment was characteristic by DOP accumulation due to intensive decomposition rate which was obvious in the autumn and was not observed in the spring, in contrast to lower anaerobic part with increasing SRP concentrations.

6. References

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