

THE BEHAVIOUR OF PHOSPHORUS IN AN OLD PARALLEL CHANNEL SLAŇÁKY IN THE POODŘÍ (CZECH REPUBLIC)

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Abstract: Within the Poodří nature reserve and the Odra River old parallel channel, Slaňáky, various forms of phosphorus were investigated due to increased high concentrations of total phosphorus (P_{tot}) in the surface water. Surface water samples were subjected to chemical analyses using absorption spectrophotometry (P_{tot} and P-PO₄³⁻) and accompanying parameters (t, O₂, pH, Cond, TSS) were measured. Next, grain size analysis of the sediment and sediment analyses using X-ray fluorescence were carried out (P, Fe, Al, Ca, Si, K, Mn, S, etc.). The seasonality of P_{tot} concentrations in the water was not confirmed, the reservoir behaved as a pool. The concentrations of the dissolved inorganic form P- PO₄³⁻ were low when compared to P_{tot}, thus suspended phosphorus prevailed. This may be related to the low depth of the given water body, where stratification does not occur in contrast to deep water bodies. However, sediment resuspension is frequent, and phosphorus largely accumulates. The concentrations of P_{tot} in the sediment ranged around 4900 mg/kg, where the inorganic form prevailed (87.24 – 93.73 %) over the organic (6.27 – 12.76 %). At the same time, the sediment samples were abundant for sand fractions (2 – 0.03 mm), 47.86 – 60.89 %, and finest silt and clay (< 0.063 mm), 33.07 – 44.60 %.

Keywords: phosphorus, old parallel channel, shallow reservoir, sediment, resuspension

1. INTRODUCTION

Various forms of phosphorus bound onto the sediment and their mutual interactions with water and sediment have lately been studied in connection with eutrophication and its possible solutions. The issue has been reported in many studies as phosphorus, due to its mobility, stored in the sediment is considered a prominent source of phosphorus in the surface water. The behaviour of phosphorus in the sediment is thus the key factor that helps to understand the dynamics of phosphorus in the flowing and stagnant surface water (Wang et al., 2013; Pettersson et al., 1988; Dodds, 2003).

Phosphorus can be present in surface waters in organic or inorganic form. Inorganic phosphorus is in the form of phosphates and polyphosphates, which are called orthophosphates. Orthophosphates (P - PO₄³⁻) are the most abundant form of inorganic phosphorus and the most available to water bodies (Frínču & Iulian, 2021).

The release of phosphorus from the sediment and its potential bioavailability shall always depend on several factors difficult to quantify, such as the character of the water body, or the duration of phosphorus release from the sediment. The release of phosphorus from the sediment may be short-term or long-term as it is controlled by a combination of factors related to the source of phosphorus, conditions inside the sediment, and conditions on the interface of water and sediment. At the same time, it is controlled by various mechanisms of physical, chemical, and biological character (Boström et al., 1988; North et al., 2015).

One of the mechanisms that facilitates the release of phosphorus from the sediment into the water column is resuspension. In shallow surface water, resuspension may be induced by the wind, which leads to an increase in the concentration of suspended solids in water. Solids onto which phosphorus is bound may resuspend several times before permanent sedimentation. Resuspension increases turbidity but

need not lead to a rise in the phosphorus release. The whole process depends on specific equilibrium conditions between sediments and water, and on the capacity of phytoplankton to absorb phosphorus. Phosphorus in the upper sediment layer (c. 10 cm) is most often assumed to participate in the overall water body metabolism. However, phosphorus mobility has been observed deeper, i.e., 20 – 25 cm of the upper layer (Søndergaard et al., 2003; Da-Peng & Yong, 2010; Hu et al., 2006).

Among the factors that in the short term directly influence the release of phosphorus via different mechanisms there are: adsorption and desorption onto iron oxides and oxyhydroxides, the concentration of dissolved oxygen that affects the redox conditions on the interface of water and sediment, and thus the reduction dissolution of phosphorus bound onto the iron oxides and subsequent release from the anoxic surface of sediments, temperature, pH or concentration of nitrates, release by means of mineralization organic matter and enzymatic processes, bioturbation related to the action of invertebrates, etc. (North et al., 2015; Boers et al., 1998).

Under the given conditions of pH, redox potential and ion forces, the solubility of phosphorus in the interstitial water in the sediment is controlled by the chemical composition of phosphates and their interactions with other minerals or amorphous materials. Apart from iron (Fe), phosphates often combine with aluminium (Al), calcium (Ca) or the bond to carbonates or clay fractions within adsorption (Fytianos & Kotzakioti, 2005).

Phosphorus manifests a high affinity to iron, and thus their biogeochemical cycle is closely related. It is highly influenced by redox transformations between rather well soluble Fe (II) and low soluble Fe (III). Oxidation of Fe (II) in aerated water solutions initially leads to the formation of amorphous to slightly crystalline Fe (III) nanoparticles - precipitates. About their high specific surface and sorption capacity, these Fe (III) compounds are highly reactive and may act as mobile colloid carriers or immobilizing solids for other elements (e.g., arsenic) or other nutrients, such as phosphate. On the contrary, phosphate also affects the oxidation of Fe (II) and precipitation of Fe (III) via many inter-dependent manners. Amorphous Fe (III) phosphates arising under natural oxidation-reduction conditions and neutral pH also tend to contain Ca (Voegelin et al., 2013; Senn et al., 2015; Kaegi et al., 2010; Mao et al., 2011).

In water where the capacity to retain phosphorus depends on the content of iron, the pH value also plays its role. This capacity of the oxygenated sediment layer falls along with a rising pH due to the competition of hydroxyl ions and

phosphorus ions. It was also established that a high pH value may significantly increase the inner phosphorus load in connection with intense resuspension. In the eutrophic water sediments, the photosynthetically increased pH may produce more phosphorus which is freely adsorbed onto iron and thus the release is boosted (Jing et al., 2015; Spivakov et al., 1999; Jensen et al., 1992; North et al., 2015).

The release mechanisms are also connected with temperature and biological activity. This is to talk of stimulation of organic matter mineralization, release of inorganic dissolved phosphorus along with a rise in temperature, and of the increased sedimentation of organic material in relation to the seasonal variability in phytoplankton efficiency. As the organic load increases during the spring and the mineralization processes get also strengthened, the depth of oxygen and nitrate penetration into the sediment falls (North et al., 2015; Spivakov et al., 1999; Carlton & Wetzel, 1988; Jensen & Andersen, 1992).

Next, bioturbation of benthic invertebrates or the production of gas bubbles in the deeper sediment layers during the microbial decay of organic matter may significantly improve the release process. There is evidence that bioturbation of benthic invertebrates may accelerate the release of phosphorus, particularly in the sediments with a low total iron content. On the contrary, their action may inhibit it via the supply of aerobic water into the sediment, which leads to an increase in the oxygenation of the sediment top layer (Woodruff et al., 1999; North et al., 2015). In the shallow surface water, submerged macrophytes are likely to grow. These macrophytes may have a both positive and negative impact on the phosphorus cycle (North et al., 2015; Barko & James 1998; Granéli & Solander, 1988).

Considering the prominent influence of the above-mentioned processes and factors on the retention or release of phosphorus, the knowledge of the interactions on the interface of water and sediment is decisive to understand the function of shallow stagnant water bodies. Several mechanisms may be involved in the release or retention of phosphorus in the sediments, but two are most important: release of phosphorus bound onto iron dependent on redox conditions, and microbial processes (North et al., 2015). The degree of eutrophication indicates the ratio of total mineral nitrogen and total phosphorus (Ispas et al., 2020).

2. MATERIAL AND METHODS

2.1. Study area

The studied locality is situated in the cadastral district of the Studénka, town near the Nový Jičín (N: 49° 42' 42" E: 18° 05' 31") in the Czech Republic,

within the Poodří nature reserve (further referred to as CHKO Poodří). The backbone river of CHKO Poodří is the Odra River, and it includes a system of old riverbeds, pools, alluvial forests, alluvial meadows, and an extensive pond system as fluvial landscape. It is subject to protection in line with Act 114/1992 Coll., on the Conservation of Nature and Landscape, as amended (Matějová & Nováková, 2016). The old riverbed Slaňáky makes part of a 4-r.km- parallel channel formed by a system of interconnected pools. It falls into the Odra River basin (Matějová et al., 2015). This study is exceptional due to the type of water body. The old parallel channel Slaňáky is a small (0.7 ha) shallow (0.76 – 1.94 m) pool of a seemingly stagnant character with an artificially built inlet and outlet. This locality is very complex from the hydrological point of view and hasn't been studied for water quality.

Six profiles (P1-P6) were determined in the studied locality (see Figure 1). Point samples were drawn for surface water analysis in monthly intervals from August 2015 to August 2016 in the old riverbed Slaňáky. The water temperature, (t), pH, concentration of dissolved oxygen (O₂), conductivity (Cond) and total dissolved solids (TSS) were measured directly in the field using a multiparameter YSI Pro Plus in the regular monthly intervals. The field measurements and surface water sampling were carried out using an inflatable raft KK65.

Sediment samples from the old riverbed

Slaňáky were taken in October 2016. The samples were drawn from a raft using an Ekotechnika piston sampler on a telescopic pole. Surface water was sampled using an in-depth sampler along the whole water column. The surface water and sediment samples and field measurements of selected surface water quality parameters were carried out in line with standardized procedures of valid European norms.

2.2. Laboratory analysis

The determination of forms of phosphorus and suspended solids was carried out the day following surface water sampling. Phosphorus and its forms were determined using the absorption spectrophotometric analysis (ammonium molybdate) using a spectrophotometer by HACH, type Lange DR 2800. For the total phosphorus analysis, the surface water samples were diluted in 1:1 proportion.

To determine the total suspended solids, we used 100 ml of surface water sample and filters (0.4 µm). Next, the used filters were dried in a drier at the constant temperature of 105°C.

In the sediment samples we carried out a wet grain size analysis to determine the grain size distribution of the sediment. The grain size distribution of the sediments was based on the sediment grain size classification categories: > 2 mm (gravel); 0.5 – 2 mm (coarse grained sand); 0.25 –

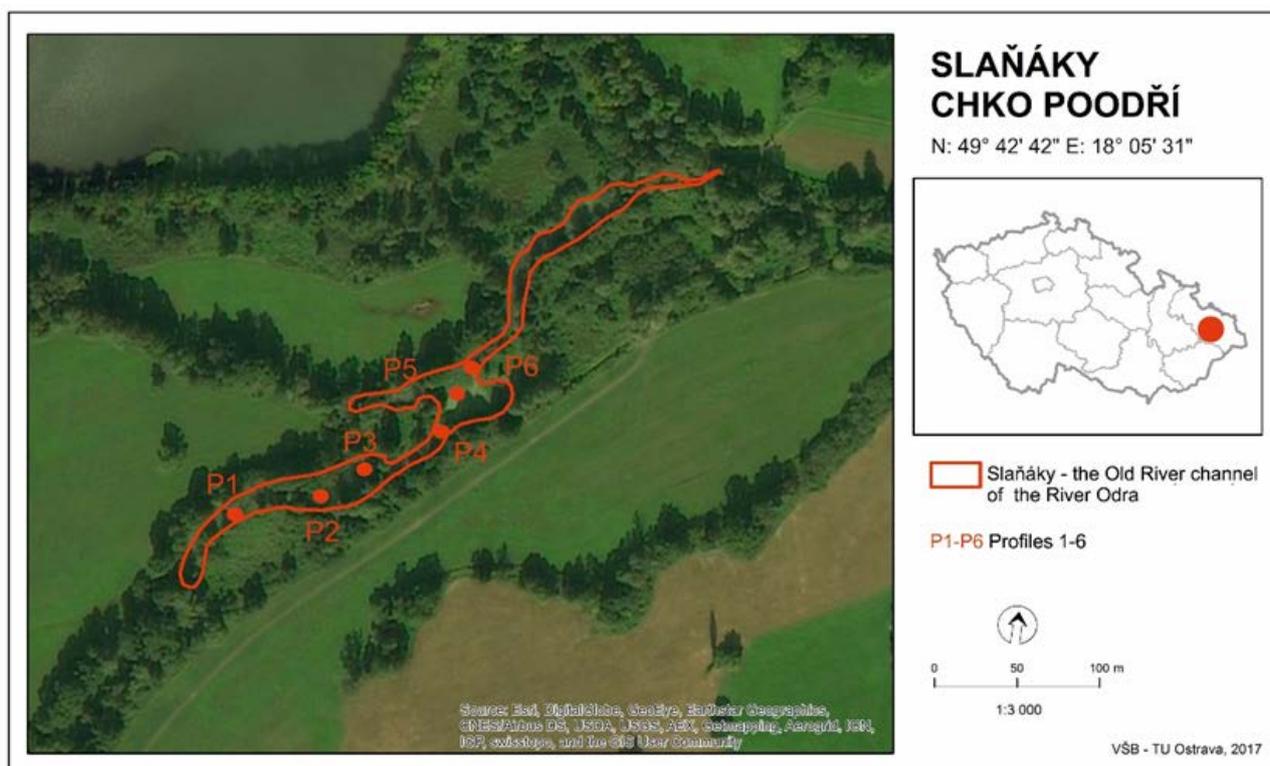


Figure 1. Map of profiles in parallel channel Slaňáky in the Poodří nature reserve

0.5 mm (medium grained sand); 0.063 – 0.25 mm (fine grained sand) and < 0.063 mm (silt and clay). The quantitative element composition of the sediment, including phosphorus determination, was determined using X-ray fluorescence.

Besides phosphorus we also determined Si, Fe, Al, K, Ca, S, and Mn. The samples were measured before and after combustion at 550°C. The loss represented the organic proportion. The results helped to characterize the proportions of inorganic and organic constituents of the given elements. The laboratory measurements of surface water and sediment was carried out in line with standardized methods and procedures stated in valid European norms.

3.RESULTS AND DISCUSSION

About the identified high concentrations of

total phosphorus (P_{tot}) in surface water of the old parallel channel Slaňáky, ranging from 0.16 to 0.82 mg/l (mean annual value of 0.31mg/l), we also analysed the sediment to determine the source of phosphorus in the Slaňáky. Apart from total phosphorus in the surface water, we also analysed the form of inorganic solved phosphorus P- PO₄³⁻, which is considered 100 % bioavailable form PO₄³⁻ Reynolds & Davies 2001; Boström et al.,1988). The values ranged from 0.01 to 0.16 mg/l (mean annual value of 0.06 mg/l). The results of the quantitative element X-ray fluorescence of phosphorus and other analysed elements in the sediment are given in Table 1. The elements are listed in the table according to the analysed quantity in the different sediment samples, where the sediment dominated in silicon (Si) and finished with manganese (Mn) out of the listed analysed elements. In all the sediment samples, the

Table 1. The results of sediment analysis

Sample P1		Portion		Sample P2		Portion		Sample P3		Portion	
Ash content at 550°C = 88.75 %		inorg.	org.	Ash content at 550°C = 88.69 %		inorg.	org.	Ash content at 550°C = 93.73 %		inorg.	org.
%											
Si	19.412	19.922	-0.512	Si	19.752	20.292	-0.541	Si	21.942	21.117	0.825
Al	4.570	4.668	-0.098	Al	4.470	4.656	-0.186	Al	4.176	3.909	0.267
Fe	3.710	3.823	-0.112	Fe	4.231	4.242	-0.010	Fe	2.653	2.820	-0.167
K	1.593	1.650	-0.057	K	31.619	1.666	-0.047	K	1.475	1.512	-0.037
mg/kg*											
Ca	8023	8157	-134	Ca	8689	8163	526	Ca	6710	6814	-104
S	7190	4996	2194	S	6805	4668	2137	P	4580	3928	652
P	5451	5372	79	P	5793	5589	204	S	2031	1989	42
Mn	419	446	-27	Mn	763	837	-74	Mn	824	783	-783
Sample P4		Portion		Sample P5		Portion		Sample P6		Portion	
Ash content at 550°C = 91.94 %		inorg.	org.	Ash content at 550°C = 93.64 %		inorg.	org.	Ash content at 550°C = 87.24 %		inorg.	org.
%											
Si	21.063	20.493	0.569	Si	20.858	21.172	-0.314	Si	19.628	19.681	-0.529
Al	4.307	4.450	-0.143	Al	4.249	4.673	-0.424	Al	4.555	4.6673	-4.667
Fe	2.587	2.820	-0.233	Fe	3.026	3.278	-0.252	Fe	3.828	3.8682	-0.04
K	1.525	1.493	0.031	K	1.511	1.609	-0.098	K	1.662	1.6663	-0.004
-	-	-	-	Ca	1.064	1.064	0.001	-	-	-	-
mg/kg											
Ca	4576	4782	-206	-	-	-	-	Ca	6628	6454	174
P	3915	3694	221	P	3988	4142	-154	P	5675	5413	262
S	2702	2295	407	S	2486	2982	-496	S	4708	3574	1134
Mn	419	446	-27	Mn	763	837	-74	Mn	824	783	-783

* < 1% to mg/kg (1%= 10000mg/kg)

Since the sediment samples before combustion also contain an organic component, the resulting values of the inorganic component are enriched with this organic matter, therefore in Table 1 the resulting values of the organic component for the individual elements are in negative numbers (Matějová, 2019).

order of elements was identical, except for sample 2. Besides the total element analysis in the sediment, the analysis also determined the proportion of inorganic and organic form of element contained in the sediment. Based on the results, inorganic forms of phosphorus and of the other analysed elements clearly prevailed, ranging from 87.24 to 93.73 %, over the organic forms, ranging from 6.27 to 12.76 % (Table 1).

The results of the grain size distribution of the sediment are given in Table 2. Considering the different grain size fractions, the sediment of the old riverbed Slaňáky contains 33.7 – 44.6 % of silt and clay. The dominant is, though, the sand fraction (fine-, medium-, and coarse-grained sand) with 60.89 to 47.86 % (Fig. 2). Due to the detected low concentrations of P- PO_4^{3-} in surface water, the sediment analysis showed that the phosphorus in the old Slaňáky channel is mainly in undissolved, suspended inorganic form. Phosphates bound easily and form simple salts and complexes with other elements contained in the sediment, particularly aluminium and calcium (Jarvie, et al., 2002). This is also implied from the proportion of inorganic and organic phosphorus in the sediment, where the inorganic dominates. The claim that phosphorus mostly combines in the finest clay fractions

(Hakanson & Jansoon, 2002; Pitter, 2009) is not confirmed in this case as the sediment in the old riverbed is of a predominantly sandy character. Thus, the chemical composition of sediment is decisive (Lagová et al., 2013).

As mentioned above, the old riverbed Slaňáky is a specific water body. It is a natural reservoir of a seemingly stagnant character, where inlet and outlet were man-made. It is a shallow reservoir with a varied depth profile (measured depths from 0.76 to 1.94 m), with no prominent stratification, (Fig. 3). Thanks to the low reservoir depth, frequent resuspension of the sediment is likely to occur, suspended particles get dispersed in the water column, onto which phosphorus is adsorbed. This way, the value of P_{tot} in the surface water increases.

Based on the classification of OECD (1982), the old riverbed Slaňáky is eutrophic surface water. However, it is free of algae and cyanobacteria. High concentrations of P_{tot} in the surface water have been confirmed in the summer. On the contrary, in winter the concentrations of P_{tot} decrease, which corresponds to the findings of other authors dealing with phosphorus in shallow eutrophic water. This development of phosphorus concentrations in the water column is caused by the frequent release of phosphorus contained in the sediments (Søndergaard

Table 2. Grain size distribution

Fraction	P1	P2	P3	P4	P5	P6
	%					
Silt and clay	34.70	39.63	34.88	33.07	37.56	44.60
Fine grained sand	20.12	17.79	33.87	28.64	27.95	15.99
Medium grained sand	27.87	11.41	11.54	12.29	17.47	6.94
Coarse grained sand	12.90	22.15	14.48	18.63	12.57	24.93
Gravel	4.41	9.02	5.23	7.37	4.45	7.54

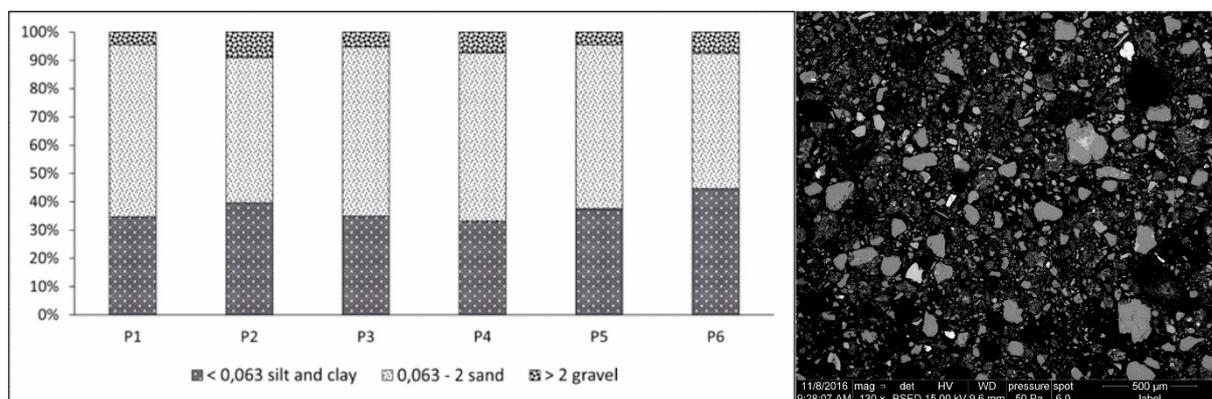


Figure 2. Grain size in sediment with sand fraction and photo from electron microscope

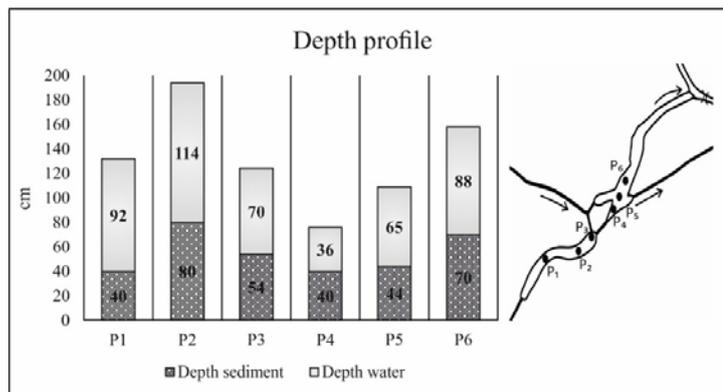


Figure 3. Depth of sediment and depth of the surface water

et al., 2002; Welch & Cooke, 2005; Søndergaard et al., 2005). The action of excess P_{tot} load in shallow surface water is prominent and may lead to a high production of macrophytes (Najib et al., 2017) as in the case of the old riverbed Slaňáky.

4. CONCLUSION

The research results showed that the old riverbed Slaňáky is a shallow natural eutrophic reservoir with abundant macrophytes, where high phosphorus load in the surface water is caused by the internal processes of phosphorus release from the sediment. Phosphorus is contained there predominantly in its inorganic form and forms compounds with iron, aluminium, calcium, or other elements contained in the sediment with dominant sand fraction. These get into the water column via different mechanisms or during changes in the conditions of the environment, i.e., when the water temperature changes along with redox conditions, pH or increased biological activity. The mechanism of phosphorus release from the sediment is increased by resuspension of the sediment, which is frequent in shallow surface water bodies.

Acknowledges

All data was processed at the Department of Environmental Engineering, Faculty of Mining and Geology, VSB - Technical University of Ostrava.

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Received at: 21. 02. 2022

Revised at: 21. 03. 2022

Accepted for publication at: 06. 04. 2022

Published online at: 29. 04. 2022