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Use of different adsorption models for characterizing P adsorption by the bottom sediment of four degraded urban lakes (Kashubian Lakeland, northern Poland)

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ABSTRACT

The laboratory experiments on P adsorption were conducted on sediments of four degraded urban lakes, located in Kartuzy, Poland. Five isotherm models (Freundlich, Langmuir, double Langmuir, Brunauer–Emmett–Teller, Dubinin–Radushkevich) were tested to obtain the best fit to experimental data. The sediment of the studied lakes differed in sediment P adsorption abilities. The research revealed that simple determination coefficient (R^2) analysis is not sufficient when different models show similar R^2 values. In this case, the analysis of $\log K_d$ vs. $\log S$ plots could be recommended as a good tool for adsorption model identification. The sediments of three lakes (Mielenko, Karczemne, and Klasztorne Duże) showed convex sorption isotherms, while Klasztorne Małe Lake, which was restored by Phoslock® showed concave adsorption isotherms. Using Phoslock® for lake restoration significantly modified sediment P adsorption properties (higher P retention ability, higher EPC_0 value, a concave shape of adsorption isotherm) compared to natural, non-modified sediment. The results of the conducted experiments on the sediment of a lake polluted by road salt effluent (Mielenko Lake) showed that higher water EC probably can improve sediment P sorption abilities and P retention, which could potentially reduce the P pool available for primary production.

Keywords: Lake sediment; Phosphorus; Adsorption models; P inactivation; Phoslock®; Lake restoration; Road salt

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1. Introduction

Lakes located close to human settlements are particularly vulnerable to anthropogenic influences [1]. The functioning of lake ecosystems is increasingly subjected to various disorders, caused by multi-aspect human activities. These activities significantly modify the natural biogeochemical circulation of nutrients (N and P) by introducing an excess of easily bioavailable forms of these elements into surface waters [2]. In the case of nitrogen the main source of N excess is agriculture [3], while in the case of phosphorus – municipal or industrial wastewater input [1,4,5]. In recent years increasing attention has been paid to another type of freshwater pollution, which is connected to mass road salt use in the direct catchment of lakes for ice prevention [6,7]. Furthermore, climate changes are influencing the time and intensity of water mixing, and it can shape thermal and oxygen conditions, which can indirectly affect the direction and intensity of the nitrogen and phosphorus cycling [8–12].

Phosphorus in the water bodies works according to Liebig's minimum law – it is the element necessary in the lowest amounts for bacterioplankton and phytoplankton growing (primary production). The threshold P level in the water for primary production limitation is very low – 0.01 mg P dm^{-3}. Bottom sediment takes very important part

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of biogeochemical P cycling because of fact, that the upper 10 cm sediment layer sediment stores more than 90% of the total P amount in the whole lake ecosystem. Other parts of the lake ecosystem (water, plant, and animal organisms living in lake) contains a few percent of the ecosystem P pool only [8,9]. Then bottom sediment ability for P adsorption and desorption can have strong influence on water quality.

Because P is key element controlling eutrophication processes in water bodies, many lake restoration methods are targeted at phosphorus cycling modification. One of these methods is P inactivation, which essentially enhances sediment sorption properties toward P. Solid-phase phosphorus adsorbents, such as La-modified benthonite [13–18], calcite [19], alum [20], or liquid preparations (e.g., solutions of polyaluminum chloride (PAX) or ferrous chloride or sulfate) [1,21,22] were used in numerous lakes [18,23].

The processes of mass exchange in the water-sediment interface are of key importance for the functioning of lakes. Due to the slow rate of growth of the profundal layers of bottom sediments (usually estimated in mm y^{-1}) [11], a contamination of a lake in the past may affect the deterioration of water quality in that lake for many years. The range of active substance exchange reaches over a dozen cm deep into the sediment [8,9]. For this reason knowledge about P exchange processes between sediment and water in particular lakes is very important to predict changes in water quality. The research on P adsorption and desorption processes onto sediment can give important information for lake management, especially for planning future restoration measures [24,25]. P adsorption experiments enable a particularly important parameter – EPC_0 (zero equilibrium phosphate concentration) – to be assessed. EPC_0 is one of the critical parameters, which can be used to recognize the role of bottom sediment as a source or sink of P [26–29]. The shape of adsorption isotherm analysis can give crucial information regarding the adsorption mechanism. Testing different P isotherm models gives the possibility of a better understanding of experimental adsorption results and answers to the questions: whether the process creates a monolayer or multilayer of adsorbate on adsorbent; or whether the adsorption process has a physical or chemical nature [30].

The most popular mathematical P isotherm models used in the research of bottom sediment and soil are Freundlich and Langmuir models [25,27,31,32]. But other adsorption models were successfully used in the research on the removal of various compounds from wastewater [30,33]. The assumption of Langmuir and double Langmuir models is adsorbate monolayer creation, whilst Freundlich model gives the possibility of monolayer or multilayer creation. The Brunauer–Emmet–Teller (BET) sorption model describes multilayer adsorption (it is a special form of Langmuir isotherm extended to derive multilayer adsorption systems) [34]. Another kind of adsorption mechanism (expressed by Gaussian energy distribution on a heterogeneous surface) is represented by the Dubinin–Radushkevich model. This model was successfully used for modeling adsorption in porous media for a liquid–solid interface [30,34].

The river-lake system, located in Kartuzy (Kashubian Lakeland, Poland) can be seen as an example of urban lakes, subjected to various anthropopressure [35–39]. One of these lakes (Klasztorne Małe Lake) was also subjected to technical restoration by two methods: artificial aeration and P inactivation using Phoslock® [35]. For this reason, this lake complex is a good example for studying the role of bottom sediment in selected aspects of biogeochemical cycling of phosphorus and its modification by geoengineering. Moreover, La-modified bentonite is used for lake restoration in a relatively short period compared to other types of preparations, and there is a great need to analyze the long-term effects of treatments.

Given the above, the main aims of this research were:

- To investigate P adsorption and desorption processes by profundal sediment (taken at the deepest point) of four polluted urban lakes;
- To analyze which mathematical model of P isotherm best fits the experimental data;
- To determine whether the past restoration using La-modified bentonite (Phoslock®) still influences P sediment sorption properties in the restored lake.

2. Materials and methods

2.1. Description of lakes

The research was carried out on four lakes, located in the Kartuzy city (Kashubian Lakeland, north-eastern Poland): Lakes Mielenko, Karczemne, Klasztorne Małe, and Klasztorne Duże. These water bodies are hydrologically connected by a small stream – Klasztorna Struga, creating a specific lake-river system, with the short distances between its consecutive parts (Fig. 1). Hence their water quality is strongly dependent on each other – the lakes located higher in the system can be a source of nutrient loads for those, which are located lower in the catchment. The Kartuzy lakes are of glacial origin (the last phase of Baltic glaciation) [40]. The relevant morphometry and catchment properties of these water bodies are given in Table 1.

Since the beginning of the 20th century the investigated lakes have been subjected to strong anthropopressure because of the growth of Kartuzy City. All lakes received wastewater, but with different intensity [38,39,41]. Lakes

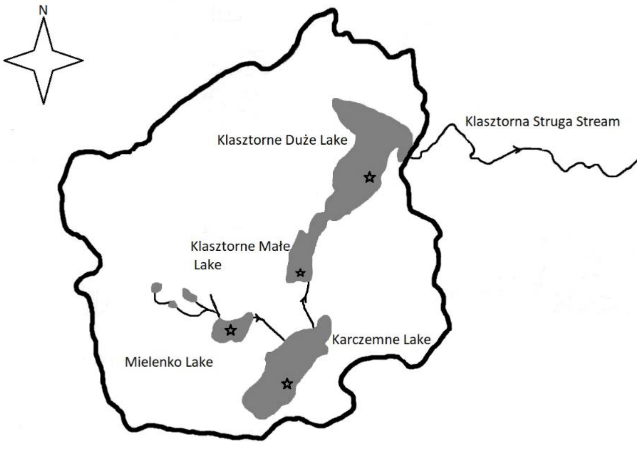

Fig. 1. Sketch of drainage basin area with location of studied lakes and the research stations.

Table 1
Morphometric characteristic and total catchment area of four lakes located in Kartuzy [38]

Parameter	Mielenko Lake	Karczemne Lake	Klasztorne Małe Lake	Klasztorne Duże Lake
Area, km^2	0.078	0.404	0.137	0.575
Maximum depth, m	1.9	3.2	20.0	8.5
Maximum length, m	460	1,282	720	1,320
Maximum width, m	252	445	250	570
Volume, 10^3 m^3	102.9	798.3	1,106.0	2,780
Relative depth index (Halbfass formula)	0.0068	0.0050	0.054	0.0112
Depth index	0.68	0.62	0.40	0.59
Shoreline development index	1.3	1.4	1.4	1.5
Shoreline length, km	1.314	3.163	1.850	4.100
Total catchment area, km^2	3.82	5.15	7.45	12.25

Karczemne and Klasztorne, located in the middle part of the system, in close proximity to the city, were the most polluted [35,36,41,42]. This situation resulted in their extreme degradation. Mielenko Lake was much less polluted in comparison with Lakes Karczemne and Klasztorne Małe. Klasztorne Duże Lake also had a lower pollution level.

Among all four lakes of Kartuzy, Klasztorne Małe Lake was recognized as the most polluted by [41]. As a result, it was subjected to different restoration attempts. The first attempt was hypolimnetic aeration (in the middle of the 1980 s) [35]. Unfortunately, the procedure failed because of technical problems with the equipment used. The second attempt was conducted in 2006 and consisted of phosphorus inactivation using Phoslock® adsorbent (Phoslock® amount – 37.5 t) [35,36]. This method also did not cause long-term water quality improvement. The main reason of the failure was a lack of raw sewage inflow reversal.

2.2. Sampling

Undisturbed bottom sediment cores were taken using a Kajak sediment sampler at the deepest point of every lake, in the summer of 2019. At each station, three cores were taken. Sediment cores (length – 10 cm) were immediately divided into two layers (0–5 and 5–10 cm). Lake water for laboratory experiments was taken at each station into 5 L tanks. Dissolved oxygen content in the near-bottom water was measured *in situ* using a ProOdo Multiline, YSI probe.

P forms (SRP, TP) analyses were performed in the near-bottom water (after decantation of 10 cm water layer directly from the sediment cores taken above) and interstitial water (separated via centrifugation from sediment at 3,000 rpm min^{-1}, t = 20 min). The results of these analyses are shown in Table 2.

Lake water used for the experiments was filtered through a 0.45 µm pore filter, and determination of consecutive parameters was performed: soluble reactive phosphorus (SRP) by the molybdenum blue method (Nanocolor spectrophotometer by Macherey–Nagel); pH, electric conductivity – by HQ 40 d multi-probe by HACH Inc., (Loveland, CO, USA); alkalinity – by the titration method, according to Hermanowicz et al. [43].

The physical and chemical characteristics of lake water used for the experiments are given in Table 3.

2.3. P adsorption experiments

Sediment samples represented two sediment layers (0–5 and 5–10 cm) from each lake. Before use, every sample was fully mixed. The experiment was performed in two stages.

The first stage was made according to a study by Augustyniak et al. [23]. 2.0 g of fresh sediment aliquots (in triplicates) were placed in 50 cm^3 Falcon-type centrifuge tubes (previously weighed) and phosphate solutions (25 cm^3) were added (P concentrations of 0.00, 0.165, 0.33, 0.66, 1.32, 2.64, 5.28, and 10.56 mg P dm^{-3}). Two drops

Table 2
P concentration in the water medium of water-sediment interface of four Kartuzy lakes

P form	Water layer	Mielenko	Karczemne	Klasztorne Małe	Klasztorne Duże
SRP, mg P dm^{-3}	Near-bottom	0.110 ± 0.009	0.300 ± 0.010	2.520 ± 0.011	0.260 ± 0.010
	Interstitial 0–5 cm	0.620 ± 0.015	5.950 ± 0.025	5.200 ± 0.015	2.430 ± 0.035
	Interstitial 5–10 cm	0.890 ± 0.018	4.050 ± 0.028	6.550 ± 0.023	3.930 ± 0.038
TP, mg P dm^{-3}	Near-bottom	1.250 ± 0.011	0.400 ± 0.009	3.380 ± 0.019	1.940 ± 0.028
	Interstitial 0–5 cm	3.530 ± 0.015	8.450 ± 0.034	17.300 ± 0.065	5.470 ± 0.035
	Interstitial 5–10 cm	3.940 ± 0.019	6.470 ± 0.031	18.350 ± 0.055	5.530 ± 0.027

Table 3
Characteristic of key chemical properties of water used for experiments

Chemical properties	Mielenko	Karczemne	Klasztorne Małe	Klasztorne Duże
SRP, mg P dm^{-3}	0.100 ± 0.002	0.179 ± 0.006	0.141 ± 0.005	0.140 ± 0.005
Alkalinity, mval dm^{-3}	2.30 ± 0.1	2.80 ± 0.2	1.90 ± 0.1	1.90 ± 0.1
Electric conductivity (EC), µS cm^{-1}	809.0	489.9	462.3	351.7
pH	7.50	7.70	7.75	7.80
DO (*in situ*), mg O_2 dm^{-3}	7.2	0.1	0.0	0.0

of chloroform were added to inhibit bacteria activity. The centrifuge tubes were shaken in an orbital shaker with 250 rpm (Innova 40 incubator by New Brunswick Scientific, Enfield, CT, USA) at a constant temperature of 20°C. After 24 h of equilibration, the solutions were centrifuged at 4,000 rpm for 10 min (Rotina 420, Hettich Zentrifugen) and the supernatants were decanted and filtered through a 0.45 µm pore filter into clean and dried glass beakers and analyzed for phosphate P. The P adsorbed on sediment samples was calculated using the difference between the initial and equilibrium concentration. Before the next stage of the experiment tubes with sediment were weighed, according to the recommendation of Huang et al. [25].

The second stage was performed according to Huang et al. [25] and Pant and Reddy [32] schemes. 25 cm^3 of lake water (without P additions) was poured into tubes with remain sediment samples (after the first stage of experiment) and equilibrated over the next 24 h in the same conditions as set during the previous equilibration. After 24 h, the amount of desorbed P was analyzed from supernatants after centrifugation and filtration, according to Huang et al. [25] and Pant and Reddy [32]. Hysteretic *P* (P_{ret} – *P* retained in sediment) was assessed based on P adsorption and desorption results.

2.4. Estimation of adsorption parameters

The results obtained from the experiment were fitted to five mathematical isotherm models: Freundlich, Langmuir, double Langmuir, BET, and Dubinin–Radushkevich models (Table 4). The analysis of isotherm shape was made according to Hintz [44] and Giles et al. [45] assumptions.

Table 4
Adsorption models used for experimental data analysis

Adsorption model	Equation
Freundlich	$S = K_f \times C_e^{\frac{1}{n}}$ (1)
Langmuir	$S = \frac{S_{\max} \times k \times C_e}{1 + kC_e}$ (2)
Double Langmuir	$S = \frac{S_1 \times k_1 \times C_e}{1 + k_1 \times C_e} + \frac{S_2 \times k_2 \times C_e}{1 + k_2 \times C_e}$ (3)
BET	$S = \frac{S_{\text{BET}} \times k_{\text{BET}} \times C_e}{\left(C_s - C_e\right) \times \left[1 + \left(k_{\text{BET}} - 1\right) \times \frac{C_e}{C_s}\right]}$ (4)
Dubinin–Radushkevich	$S = S_{\text{DR}} \times \exp\left(-B \times \varepsilon^2\right)$ (5)

Since the bottom sediment has a certain amount of previously adsorbed P, described by Froelich [26] as "native sorbed P", P adsorption isotherm origin lays below the *X*-axis [26,28], and then amount of adsorbed P by sediment can be expressed as:

$$S = S_0 + S' \quad (6)$$

EPC_0 (P equilibrium concentration) parameter represents the P concentration, which is the equilibrium between adsorption and desorption processes. If the P concentration in water is below EPC_0 value, P is desorbed from sediment, while above this concentration P is adsorbed by sediment [26]. EPC_0 was assessed from the Freundlich equation with correction for desorbed phosphorus ($-S_0$) at the initial experimental concentration (0 mg P dm^{-3}) – EPC_0 expresses zero of that function [23,28]:

$$S = \left(K_f \times C_e^{\frac{1}{n}}\right) - S_0 \quad (7)$$

The Gibbs free energy change ΔG_{ads} (kJ mol^{-1}) was also calculated using the formula [17,23]:

$$-\Delta G_{\text{ads}} = RT\ln K_d \quad (8)$$

All adsorption parameters were estimated with non-linear estimation method [23,33] using Statistica software package 13.0 [46].

The coefficient of determination (R^2), non-linear χ^2 test, and root mean square error (RMSE) were assumed to be the measure of the curve fitting at the determined parameters to the experimental data [30,33,34]. Non-linear Chi-square error function (χ^2) was assessed using the formula [34]:

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(S_{\exp,i} - S_{\text{mod},i}\right)^2}{S_{\text{mod},i}} \quad (9)$$

where $S_{\exp}$ is the adsorbed phosphorus (experimental data) (mg g^{-1} d.w.), S_{mod} is the adsorbed phosphorus (model data) (mg g^{-1} d.w.).

Residual RMSE was calculated using the formula [34]:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} \left(S_{\exp} - S_{\text{mod}}\right)_i^2}{n-1}} \quad (10)$$

2.5. Sediment analysis

Sediment chemical analysis was performed according to the scheme described by Augustyniak et al. [23]. The gravimetrical analysis included: water content and solid matter content in sediment (after drying at 105°C), organic matter (as ignition loss at 550°C with carbonate regeneration), inorganic carbon (as weight loss at 1,000°C), silicon (after ignition at 900°C) (Barnstead Thermolyne 62700 Furnace). Fe, Al, Mn, and Ca were analyzed spectrophotometrically (Spectroquant Prove 100 by Merck, Darmstadt, Germany) after preliminary mineralization in the mixture of concentrated acids (H_2SO_4, $HClO_4$, and HNO_3). Total nitrogen (TN) was analyzed by the Kjeldahl method (using BÜCHI K-425 unit, B-24 distillation unit).

Sediment phosphorus fractions were analyzed according to the scheme proposed by van Hullebush et al. [47]. SRP content in the extracts was measured using the molybdenum blue method (Nanocolor spectrophotometer by Macherey–Nagel).

Lanthanum content in sediment was measured using Perkin Elmer, (Waltham, MS, USA) NexION® 2000 inductively coupled plasma mass spectrometry (ICP-MS) system. The samples for that analysis were prepared using Perkin Elmer's Titan MPS microwave sample preparation system.

3. Results

3.1. Adsorption characteristics

The P sorption isotherms for all investigated lakes are shown in Fig. 2.

The amount of adsorbed phosphorus (S) rose with an increase in the final concentration of P (C_e). The surface sediment layer (0–5 cm) was usually more effective in P adsorption, showing higher adsorption capacity, compared with deeper sediment layer 5–10 cm (Fig. 2).

The only exception was Karczemne Lake sediment, where sediment layer 5–10 cm revealed slightly higher maximum S value than sediment layer 0–5 cm. The highest P adsorption ability was noted for restored Klasztorne Małe Lake sediment (1,724.69 mg P kg^{-1} d.w. for the sediment layer 0–5 cm), whilst the sediment of Klasztorne Duże Lake had the lowest S value (315.57 mg P kg^{-1} d.w., sediment layer 5–10 cm). It is worth noting that the shape of isotherms for both analyzed sediment layers of Klasztorne Małe Lake differed from isotherms for other Kartuzy lakes (Fig. 2).

The obtained P adsorption results fit all tested isotherm models very well (Table 5). The R^2 values ranged from 0.787 (Klasztorne Małe Lake, double Langmuir model, and sediment layer 0–5 cm) to 0.996 (Klasztorne Duże Lake, BET model, and sediment layer 0–5 cm). The R^2 coefficient analysis revealed, that sediment P adsorption type was different for every lake sediment. It is worth noting that both Langmuir models showed a weaker fit to real data of P adsorption for Klasztorne Małe Lake sediment. In that case, Freundlich, BET, and Dubinin–Radushkevich models reflected much better obtained experimental data (Table 5). R^2 values for Mielenko Lake sediment were the highest in the case of double Langmuir model. Experimental data of P adsorption by Klasztorne Duże Lake sediment were the most suitable to the BET adsorption model (R^2 amounted to 0.996 and 0.941 for sediment layer 0–5 and 5–10 cm, respectively). Phosphorus adsorption by Karczemne Lake sediment corresponded to the Dubinin–Radushkevich model (the highest R^2 value – 0.963 – for sediment layer 0–5 cm), but for layer 5–10 cm the highest R^2 value (0.937) was calculated for three isotherm models (both Langmuir and BET models) (Table 5). Analysis of χ^2 values, as well as RMSE values (Table 5) revealed, that obtained error calculation results mainly were in accordance with R^2 assessment. The similarity of results of analyzed error measures in the case of Karczemne Lake and Klasztorne Małe Lake rather didn't allow clearly to identify the most suitable isotherm model by using selected error measures.

Further analysis of isotherms' shape was made according to [44,45] (plotting logK_d vs. log S) (Fig. 3). It showed that Klasztorne Małe Lake P adsorption isotherms correspond to S1-class isotherm type, which characterizes concave Freundlich isotherm for ($1/n > 1$). Estimated $1/n$ values for this lake exceeded 2 (maximum 2.2910 for sediment layer 0–5 cm) (Table 5), while the assessed values of this coefficient were below 1 for the three analyzed lakes (Table 5). The minimum $1/n$ value (0.3517) was calculated for the Mielenko Lake sediment (layer 0–5 cm) (Table 5).

The shape of logK_d vs. log S curves only partly allowed to classify the obtained isotherms. That analysis seems to confirm the supposition that the best suitable P adsorption model for Mielenko Lake is the double Langmuir model, and for Klasztorne Duże Lake – the BET model, and the Dubinin–Radushkevich and Langmuir model – for Karczemne Lake sediment. But it is worth noting that the shape of obtained curves is rather characteristic for a higher P concentration range in the water. All logK_d vs. log S curves showed an increasing tendency (drawn as dashed lines) at low P concentration in the water, which suggests the concave shape of isotherms at that P concentration range (Fig. 3).

The values of K_f partition coefficient from Freundlich model ranged from 92.19 dm^3 kg^{-1} (Klasztorne Duże Lake, sediment layer 5–10 cm) to 1,309.88 dm^3 kg^{-1} (Klasztorne Małe Lake, sediment layer 0–5 cm; Table 5).

"Native sorbed phosphorus amounts" (S_0) observed during the experiment ranged from 7.66 mg P kg^{-1} d.w. (Mielenko Lake, sediment layer 0–5 cm) to 52.72 mg P kg^{-1} d.w. (Karczemne Lake, sediment layer 5–10 cm) (Table 5).

The calculated EPC$_0$ concentration also differed among the investigated lakes. The highest P equilibrium concentration was noted for Klasztorne Małe Lake sediment (0.232 mg P dm^{-3}), and the lowest (1.09×10^{-6} mg P dm^{-3}) was for the surficial sediment layer of Mielenko Lake (0–5 cm) (Table 4).

The assessed Gibbs free energy change (ΔG_{ads}) was negative for all studied sediments. The lowest values were noted for Mielenko Lake sediment (–18.89 kJ mol^{-1}), while the highest values were observed for the sediment of Klasztorne Duże Lake (–10.32 kJ mol^{-1}) and it allows to classify observed P adsorption processes as physisorption (Table 5).

In analyzing the data for both Langmuir and BET adsorption models (Table 5), several discrepancies were observed concerning the assessed maximum sorption capacities of Klasztorne Małe Lake sediment depending on adsorption models. Calculated S_{max} in the Langmuir model (214,986.5 and 126,982.0 mg P kg^{-1} d.w.; sediment layer 0–5 and

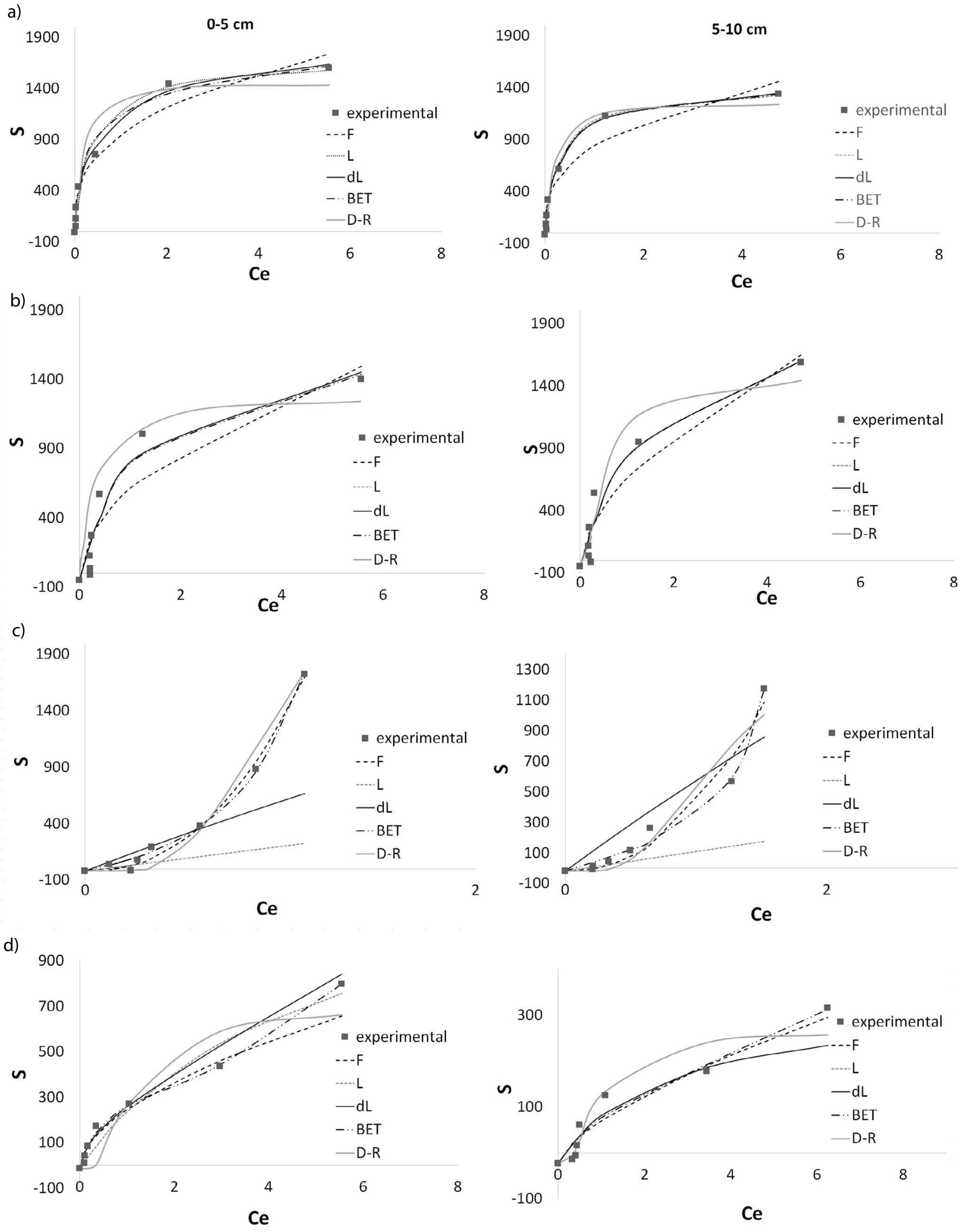

Fig. 2. P adsorption isotherms by bottom sediments of four lakes in Kartuzy: (a) Mielenko Lake, (b) Karczemne Lake, (c) Klasztorne Małe Lake, (d) Klasztorne Duże Lake; S – in mg P kg^{-1} d.w., C_e – in mg P dm^{-3}.

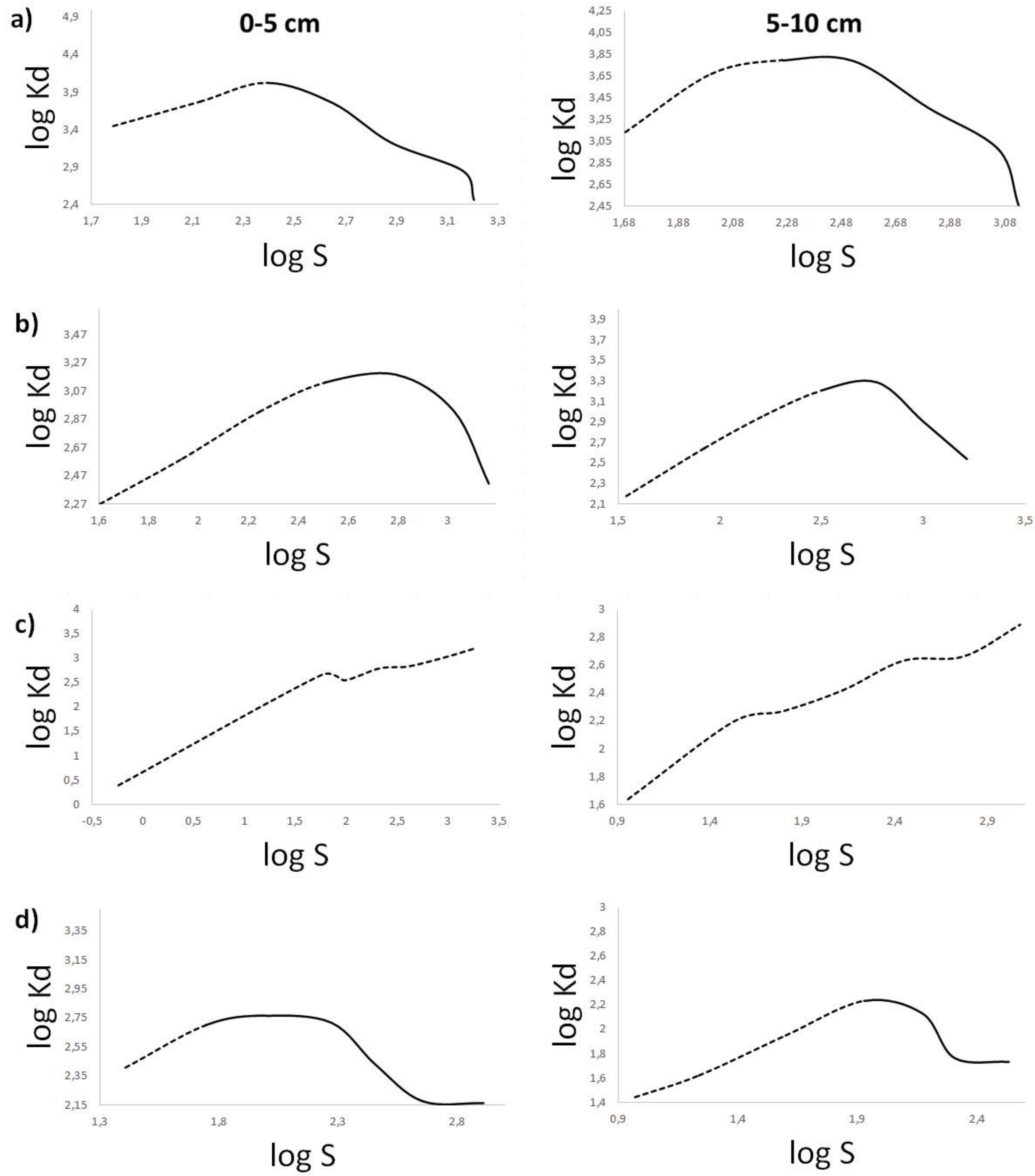

Fig. 3. Dependence between log$S$ and logK_d for bottom sediments of four lakes in Kartuzy: (a) Mielenko Lake, (b) Karczemne Lake, (c) Klasztorne Małe Lake, and (d) Klasztorne Duże Lake.

5–10 cm, respectively) was two orders of magnitude higher, compared to values assessed to other lakes sediments of the Kartuzy complex (within the range from 361.0 mg P kg^{-1} d.w. in Klasztorne Duże Lake sediment to 2,216.0 mg P kg^{-1} d.w. in Karczemne Lake sediment, respectively). But maximum monolayer capacity in BET model (S_{BET}) was at a similar level to S_{BET} values calculated for deposits of the other Kartuzy lakes analyzed (Table 5). The assessed adsorbate monolayer saturation concentration from the BET adsorption model (C_s) was the lowest for sediment taken from Klasztorne

Table 5
P adsorption parameters for bottom sediment of four lakes in Kartuzy

Model	Sorption parameter	Sediment layer	Mielenko Lake	Karczemne Lake	Klasztorne Małe Lake	Klasztorne Duże Lake
Freundlich	1/*n*	0–5 cm	0.3517	0.5032	2.2910	0.5567
		5–10 cm	0.3554	0.5731	2.1785	0.6764
	K_f (dm^3 kg^{-1})	0–5 cm	956.57	652.12	1,309.88	258.45
		5–10 cm	846.87	697.00	440.2	92.19
	R^2	0–5 cm	0.955	0.924	0.992	0.979
		5–10 cm	0.962	0.906	0.961	0.836
	χ^2	0–5 cm	0.267	0.810	**0.069**	0.091
		5–10 cm	0.352	0.734	**0.029**	0.162
	RMSE	0–5 cm	0.124	0.190	0.050	0.056
		5–10 cm	0.131	0.165	0.076	0.028
Langmuir	$S_{\max}$ (mg kg^{-1})	0–5 cm	1,701.0	1,847.8	214,986.5	1,433.5
		5–10 cm	1,429.8	2,216.0	126,982.0	361.0
	k (dm^3 mg^{-1})	0–5 cm	2.54	0.79	0.001	0.21
		5–10 cm	3.24	0.62	0.001	0.40
	R^2	0–5 cm	0.972	0.926	0.812	0.956
		5–10 cm	0.983	**0.937**	0.841	0.872
	χ^2	0–5 cm	0.424	542.4	14.387	0.219
		5–10 cm	0.183	**0.616**	7.724	0.167
	RMSE	0–5 cm	0.098	0.136	0.598	0.054
		5–10 cm	0.062	**0.136**	0.390	0.037
Double Langmuir	S_1 (mg kg^{-1})	0–5 cm	419.06	923.92	6,598.61	1,309.19
		5–10 cm	1,196.48	1,108.97	5,196.52	179.55
	k_1 (dm^3 mg^{-1})	0–5 cm	21.506	0.792	0.090	0.010
		5–10 cm	2.087	0.616	0.063	0.400
	S_2 (mg kg^{-1})	0–5 cm	1,448.79	923.92	6,958.54	175.53
		5–10 cm	279.89	1,106.96	5,196.70	181.46
	k_2 (dm^3 mg^{-1})	0–5 cm	1.001	0.791	0.010	4.270
		5–10 cm	12.771	0.617	0.058	0.400
	R^2	0–5 cm	**0.987**	0.926	0.787	0.987
		5–10 cm	**0.993**	0.937	0.825	0.872
	χ^2	0–5 cm	**0.139**	0.542	2.158	62.8
		5–10 cm	**0.152**	0.617	0.614	167.0
	RMSE	0–5 cm	**0.066**	0.136	0.400	0.041
		5–10 cm	**0.058**	0.136	0.162	0.037

BET	S_{BET} (mg kg^{-1})	0–5 cm	1,443.082	1,830.0	2,890.89	346.98
		5–10 cm	1,357.272	2,215.9	226.39	219.55
	k_{BET} (dm^3 mg^{-1})	0–5 cm	139.42	1.037×10^6	0.238	20.499
		5–10 cm	332.34	0.276×10^6	2.253	9.88
	C_s (mg dm^{-3})	0–5 cm	37.32	1.313×10^6	1.923	9.46
		5–10 cm	92.71	0.448×10^6	1.847	14.688
	R^2	0–5 cm	0.973	0.926	**0.994**	**0.996**
		5–10 cm	0.992	0.937	**0.989**	**0.941**
	χ^2	0–5 cm	0.270	0.543	0.149	**0.037**
		5–10 cm	0.171	0.618	0.133	0.146
	RMSE	0–5 cm	0.093	0.136	**0.042**	**0.017**
		5–10 cm	0.061	0.136	**0.039**	**0.025**
Dubinin–Radushkevich	S_{DR} (mg kg^{-1})	0–5 cm	1,449.4	1,528.6	5,337.4	346.98
		5–10 cm	1,262.8	1,528.7	2,027.7	219.55
	B (mol^2 kJ^{-2})	0–5 cm	3.5×10^{-8}	1.2×10^{-7}	4.8×10^{-7}	3.4×10^{-7}
		5–10 cm	3.5×10^{-8}	1.1×10^{-7}	4.6×10^{-7}	2.5×10^{-7}
	R^2	0–5 cm	0.922	**0.963**	0.971	0.820
		5–10 cm	0.960	0.913	0.912	0.896
	χ^2	0–5 cm	0.660	**0.337**	1.866	5.909
		5–10 cm	0.321	0.637	0.231	**0.094**
	RMSE	0–5 cm	0.151	**0.089**	0.100	0.102
		5–10 cm	0.091	0.150	0.139	0.033
Other parameters	EPC$_0$ (mg dm^{-3})	0–5 cm	1.09×10^{-6}	0.006	0.157	0.006
		5–10 cm	9.05×10^{-6}	0.010	0.232	0.131
	S_0 (mg kg^{-1})	0–5 cm	7.66	52.72	18.79	14.77
		5–10 cm	13.66	49.38	18.22	23.30
	ΔG_{ads} (J mol^{-1}K^{-1})	0–5 cm	–18.89	–15.59	–15.18	–13.93
		5–10 cm	–18.59	–15.81	–13.39	–10.32
	P_{ret} (% S)	0–5 cm	87.24	88.71	98.2	83.63
		5–10 cm	91.63	89.78	98.8	74.60

Małe Lake (1.847 and 1.923 mg dm^{-3}), while the highest – for Karczemne Lake deposits (1.313 × 10^{6} and 0.448 × 10^{6} mg dm^{-3}; Table 5). The S_{DR} constant from the Dubinin–Radushkevich equation (maximum P amount adsorbed within the sediment micropores) ranged from 219.55 mg kg^{-1} (Klasztorne Duże Lake, sediment layer 5–10 cm) to 5,337.4 mg kg^{-1} (Klasztorne Małe Lake, sediment layer 0–5 cm).

The constants related to bonding energy from both Langmuir and BET adsorption models (k, k_1, k_2, and k_{BET}) showed the lowest values for Klasztorne Małe Lake sediment (0.001 dm^{3} mg^{-1} for Langmuir model; from 0.010 to 0.090 dm^{3} mg^{-1} for double Langmuir model and 0.238 and 2.253 dm^{3} mg^{-1} for BET model; Table 5). The highest k, k_1, and k_2 constants were calculated for sediment taken from Mielenko Lake (3.24 dm^{3} mg^{-1}, layer 5–10 cm, 21.506 dm^{3} mg^{-1}, layer 0–5 cm, and 12.771 dm^{3} mg^{-1}, layer 5–10 cm; respectively). The highest values of k_{BET} were assessed for deposits of Karczemne Lake (1.037 × 10^{6} and 0.276 × 10^{6} dm^{3} mg^{-1}, sediment layers 0–5 and 5–10 cm, respectively; Table 5). B constant from the Dubinin–Radushkevich model is also connected to adsorption energy and its assessed values ranged from 3.5 × 10^{-8} mol^{2} kJ^{-2} (Mielenko Lake sediment) to 4.8 × 10^{-7} mol^{2} kJ^{-2} (Klasztorne Małe Lake sediment) (Table 5).

3.2. Phosphorus retention by sediment (hysteretic P)

The amount of phosphorus permanently adsorbed by sediments of analyzed lakes (hysteretic $P - P_{ret}$) was the highest for Klasztorne Małe Lake deposits (more than 98% of adsorbed P), while the lowest hysteretic P values were assessed for sediment taken from Klasztorne Duże Lake (74.63% P_{ads}, sediment layer 5–10 cm) (Table 5). The amount of desorbed P was dependent on the initial P concentration for sediment taken from three lakes (Mielenko, Karczemne, and Klasztorne Duże). That dependence was almost not seen for the deposits of restored Klasztorne Małe Lake (Fig. 4).

3.3. Sediment chemical composition

Since the main components of the bottom sediment of the investigated lakes were silica and organic matter, they can be classified as a mixed, silica-organic type, with rather low level of carbonates. Sediment taken from Klasztorne Małe Lake had a higher share of calcium and inorganic carbon (ca. 58–68 mg Ca g^{-1} d.w. and ca. 17–20 mg IC g^{-1} d.w.) (Table 6). Deposits of Karczemne Lake were the most abundant in organic matter (above 460 mg g^{-1} d.w. for both analyzed sediment layers). Klasztorne Duże Lake sediment contained the lowest amount of that component (ca. 329 mg g^{-1} d.w.) (Table 6). The amounts of Fe and Al were not very high (between 15 and 20 mg Fe g^{-1} d.w. and 9–11 mg Al g^{-1} d.w.). The Mn level was low and did not exceed 1.5 mg Mn g^{-1} d.w. (Table 6).

Because of using Phoslock® preparation for phosphorus inactivation in Klasztorne Małe Lake, the lanthanum amounts were measured in the sediment of all investigated lakes. The deposits of the restored lake had much higher lanthanum level (0.797 ± 0.020 and 1.330 ± 0.020 mg La g^{-1} d.w.) comparing to very low amounts in other Kartuzy lakes sediments (between 0.016 and 0.024 mg La g^{-1} d.w.; Table 6).

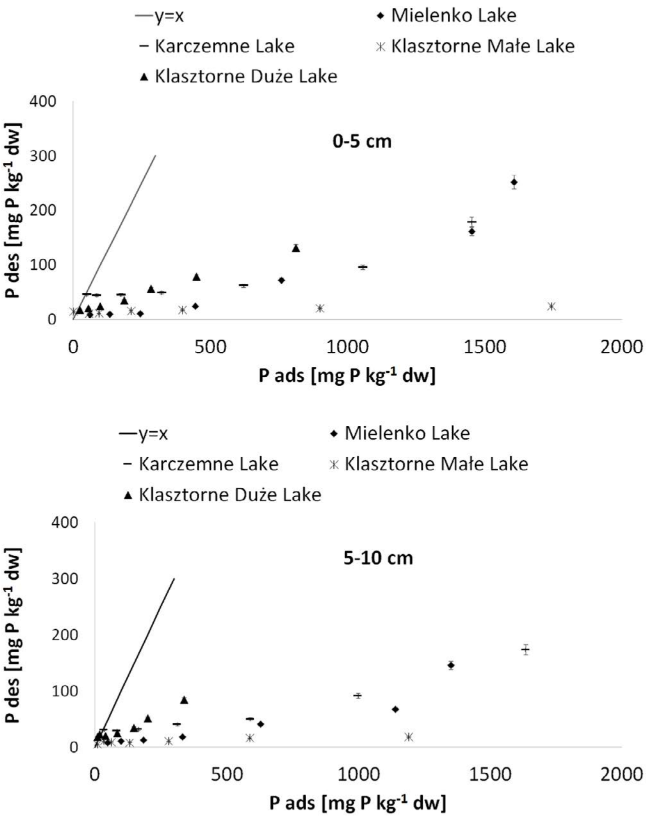

Fig. 4. Relationship between P adsorption and P desorption by bottom sediments of four lakes in Kartuzy.

The nitrogen and phosphorus contents in the bottom sediments of four lakes in Kartuzy were very high and reach up to 35.1 ± 2.9 mg N g^{-1} d.w. and 12.424 ± 0.110 mg P g^{-1} d.w. (Karczemne Lake, sediment layer 5–10 cm) (Table 6). Other Kartuzy lakes sediments had slightly lower total nitrogen (TN) levels, but total phosphorus (TP) amounts were almost half as low as in Klasztorne Małe Lake (ca. 6.6 mg P g^{-1} d.w.), and in the sediment of Mielenko and Klasztorne Duże lakes the TP level was ca. 3 mg P g^{-1} d.w. Sediment P fractions analysis showed that the quantitatively dominant fraction in Karczemne Lake deposits was the hardly bioavailable HCl-P fraction (46.8%TP and 36.9%TP in the 0–5 and 5–10 cm layers, respectively). Medium bioavailable NaOH-nrP and NaOH-rP fractions dominated in the sediment of Klasztorne Małe Lake (sum of both NaOH-P fractions occupied ca. 60% TP in both sediment layers), while NaOH-nrP was the dominant fraction in the Mielenko and Klasztorne Duże lakes (ca. 47% TP and 31% TP, respectively). Most mobile fractions (NH_4Cl-P and BD-P) occurred in the small quantities, and their share in TP was from ca. 6% TP (Karczemne Lake) to ca. 15% TP (Klasztorne Duże Lake) (Table 7).

4. Discussion

It is a very frequent situation in the lakelands, that a lake is an active part of a river-lake system. The activation of the nutrient internal loading phenomenon may cause that a lake will become a source of nutrient pollution for water

Table 6
Mean (±SD) amount of selected components of bottom sediment of four lakes in Kartuzy (in mg g^{-1} d.w.)

Sediment component	Sediment layer	Mielenko Lake	Karczemne Lake	Klasztorne Małe Lake	Klasztorne Duże Lake
Organic matter	0–5 cm	418.6 ± 20.3	462.1 ± 21.2	374.2 ± 10.7	329.6 ± 12.2
	5–10 cm	409.9 ± 19.9	466.7 ± 20.5	348.5 ± 11.1	327.9 ± 11.8
Si	0–5 cm	191.4 ± 9.9	171.3 ± 8.2	165.2 ± 7.2	226.8 ± 11.3
	5–10 cm	208.6 ± 9.9	168.5 ± 8.2	187.6 ± 9.8	233.3 ± 10.1
Al	0–5 cm	10.2 ± 0.9	9.3 ± 0.8	10.7 ± 1.1	9.3 ± 1.0
	5–10 cm	9.6 ± 0.7	9.5 ± 0.8	10.2 ± 1.2	11.2 ± 1.3
Fe	0–5 cm	18.5 ± 1.8	18.7 ± 2.0	17.1 ± 1.9	17.4 ± 1.3
	5–10 cm	19.1 ± 1.9	20.6 ± 2.2	20.7 ± 2.0	15.6 ± 1.4
Ca	0–5 cm	11.7 ± 1.3	21.0 ± 2.1	69.9 ± 2.9	25.9 ± 2.1
	5–10 cm	12.0 ± 1.1	17.9 ± 1.9	57.5 ± 3.1	17.3 ± 1.8
Mn	0–5 cm	0.7 ± 0.03	1.0 ± 0.05	1.1 ± 0.09	1.2 ± 0.08
	5–10 cm	0.4 ± 0.05	1.1 ± 0.08	1.4 ± 0.09	0.8 ± 0.07
TKN	0–5 cm	25.9 ± 2.0	28.1 ± 2.3	22.3 ± 1.9	21.3 ± 2.6
	5–10 cm	25.4 ± 2.4	35.1 ± 2.9	22.3 ± 2.5	16.3 ± 1.9
TP	0–5 cm	3.011 ± 0.070	11.197 ± 0.160	6.740 ± 0.090	3.393 ± 0.065
	5–10 cm	3.137 ± 0.080	12.424 ± 0.110	6.603 ± 0.098	2.995 ± 0.088
IC	0–5 cm	10.3 ± 0.6	9.6 ± 0.8	20.9 ± 1.2	13.5 ± 0.9
	5–10 cm	10.5 ± 0.6	9.6 ± 0.8	16.9 ± 0.9	13.1 ± 1.1
La	0–5 cm	0.022 ± 0.001	0.020 ± 0.001	0.797 ± 0.020	0.016 ± 0.001
	5–10 cm	0.018 ± 0.001	0.022 ± 0.001	1.330 ± 0.020	0.024 ± 0.001

bodies located below in the cascade system [48]. In the case of lakes in Kartuzy, the particular threat is bottom sediment of Karczemne Lake, which is extremely rich in phosphorus. Analyzing the directly mobile phosphorus pool (a sum of NH_4Cl-P and BD-P fractions) in this lake, these amounts (mean values 0.619 and 0.750 mg P g^{-1} d.w.) compared to TP (11.197 and 12.424 mg P g^{-1} d.w.) (Table 7), could be seen as rather low. But in absolute terms, the potential bioavailability of sediment P is high, and it certainly influences the primary production processes and water quality of Karczemne Lake.

The influence of bottom sediment P on the water quality in lakes depends strongly on the lake water mixing regime [25,49]. Shallow lakes show better oxic conditions in the near-bottom water layer, which favors rapid organic matter mineralization in sediment, and intensive water mixing can cause resuspension and enhance the mineralization effect. At the first sight, these conditions seems to be responsible for the very often observed lower TP amount in the shallow water bodies sediment (or e.g., littoral parts of bottom deposit), compared to the sediment of deeper, stratified lakes [8,24]. But the current study shows, that massive pollution by municipal sewage can lead to extremely high TP levels, even in a shallow, polymictic lake, which was also confirmed by Grochowska et al. [39].

The maximum P adsorption was observed for restored Klasztorne Małe Lake sediment (1,724.69 mg P kg^{-1} d.w. for the sediment layer 0–5 cm), while the sediment of Klasztorne Duże Lake showed the lowest S value (315.57 mg P kg^{-1} d.w., sediment layer 5–10 cm) (Fig. 2). These results were within the range reported by other researchers [8,23–25]. The order of magnitude of Gibbs free energy change (ΔG_{ads}) confirmed the physical character of observed adsorption processes. The assessed (ΔG_{ads}) value was negative for all investigated sediments (Table 5), which revealed that P adsorption was a spontaneous reaction [25].

An analysis of the value of the determination coefficient (R^2), which represents the level of matching experimental data to specific isotherm models, is a commonly used tool for choosing the best mathematical adsorption model [33]. The possibility, that adsorption occurs according to the selected model rises with rising R^2 value. But this criterion was insufficient for the examined lakes. When we have models with the same R^2 value (as in the case of Karczemne Lake sediment), it is difficult to choose, which adsorption model is the most suitable. An analysis of the adsorption type based on the relationship curves between log$S$ and logK_d, in accordance with the guidelines provided by Hintz [44], can help to determine, which type of adsorption model reflects the experimental data P adsorption for the analyzed lake sediments. Another measures of fitting isotherm to experimental adsorption data, as RMSE or χ^2, also can be helpful in identification of the best-fitted model [30,34].

It is noteworthy that logK_d vs. log$S$ charts based on experimental data for three lakes have one thing in common – the growing nature of the curve for low log$S$ values. Only at higher log$S$ values do the curves take the characteristic course for the given adsorption models. This may indicate that at low P concentrations in the water P adsorption isotherms by the sediments of lakes Mielenko, Karczemne, and Klasztorne Duże are concave. Concave sections of adsorption curves in the low concentration of adsorbate suggest weaker adsorption power – more efficient adsorption occurs with a convex shape of an isotherm – in this case in the range of higher concentrations of P in water. Hintz [44] suggests, that the concave shape of an isotherm in a low adsorbate concentration can be explained by the presence of adsorbate molecules, which had earlier been bound by sediment. In that situation, the standard isotherm equation can be mathematically transformed (e.g., a constant should be added to the formula or an additional power function should be introduced) to obtain better fit of the curve to experimental data [44].

The conducted P adsorption experiments showed the differences between P adsorption phenomena by the sediment of the analyzed lakes. Mielenko Lake sediment showed the lowest S_0 and EPC_0 values, and the double Langmuir model had the best fit to the experimental data (R^2 values 0.987 and 0.993 for sediment layer 0–5 and 5–10 cm, respectively; Table 5). It could be possible that the sediment of Mielenko Lake has different active adsorption sites, with different affinity to phosphates as it is characterized by different values of maximum sorption capacities (S_1 and S_2) and various values of k_1, k_2 constants (related to bonding energy) in a double Langmuir equation (Table 5). A similar situation was observed by Augustyniak et al. [23] for the sediment of restored Długie Lake as well as by Limousin et al. [31] for soils. It is worth noting that the k, k_1, and k_2 constants values from Langmuir and double Langmuir models were the highest among the analyzed sediment of four lakes in Kartuzy (Table 5), which means higher P affinity to active adsorption sites. According to Koski-Vähälä and Hartikainen [50] water EC can influence EPC_0. These authors maintain that EPC_0 decreases with even a slight increasing in EC. This phenomenon could be the reason for the very low EPC_0 values observed for the sediment of Mielenko Lake (Table 4). The water of Mielenko Lake had almost twice higher EC, compared to other lakes in the system (Table 3). A possible explanation of that fact is the presence of a relatively large area in the direct catchment, in which anti-ice material (sand and road salt) has been stored for many years. The effluent from this place is drained by a stormwater collector and directed into that lake. Hence, the lowest values of EPC_0 and S_0, which were noted for Mielenko Lake sediment, suggest that an increase in water EC can improve sediment P sorption abilities and P retention (Table 5). According to research conducted by Jones et al. [7], road salt pollution can influence freshwater biota, reducing zooplankton abundance, and increasing phytoplankton abundance. Dugan et al. [6] also share that point of view. But improving sediment P adsorption abilities could potentially reduce the sediment P pool available for primary production. The results of P fraction analysis revealed that the most mobile P pool in sediment (a sum of NH_4Cl-P and BD-P fractions) is the lowest for the sediment of Mielenko Lake, among the investigated lakes in Kartuzy (Table 7). Furthermore, the TP values in that lake sediment are relatively high (Table 7), despite the low maximum depth of that lake and this fact seems to confirm that supposition.

Karczemne Lake P adsorption characteristics showed that the Dubinin–Radushkevich model best fit the experimental data for surficial sediment layer (0–5 cm) ($R^2 = 0.963$ – Table 5). Hintz [44] maintains, that the modified version of the Dubinin–Radushkevich equation has similar properties to a Tóth isotherm, which gives a $\log K_d$ vs. $\log S$ plot corresponding to L2-class curve. A Langmuir or double Langmuir isotherm can also show L2-class curve. R^2 values were little lower for these models (0.926 and 0.937 for sediment layer 0–5 and 5–10 cm, respectively), and the same R^2 was assessed for BET model (Table 5). A double Langmuir model did not show differences between the estimated maximum sorption capacity values (S_1 and S_2), or between k_1 and k_2 constants, which means that both types of active sorption sites are similar. However, the BET model estimation revealed very high values of k_{BET} and C_s (Table 5), which could help to explain observed the highest amount of TP in this sediment. Because a large pool of sediment P in this lake is bound to Ca compounds (as HCl-P fraction) (Table 7), probably freshly adsorbed P with time under favorable environmental conditions (high water pH, higher temperature in the bottom zone of shallow lake) is later chemisorbed with Ca compounds [9]. Millero et al. [51] maintain that P sorption on carbonate minerals is multi-step process. Bańkowska-Sobczak et al. [19] research on the use of calcite materials for P inactivation suggested that the HCl-P fraction is better formed under anoxia. Although Karczemne Lake is shallow, polymictic water body, anoxia can occur during windless periods, as it was during sampling (Table 3). The water of Karczemne Lake as well as other lakes in Kartuzy is not very abundant in Ca, but particularly in that lake it can be a result of high water temperature during the summer season and intensive photosynthetic processes (leading to CO_2 depletion), which favors the precipitation of calcium compounds (Table 6).

The third analyzed water body – Klasztorne Małe Lake – was recognized by Januszkiewicz and Jakubowska [41] as the most polluted lake in the complex. No data on previous sediment analysis is available from this period. The first complex top-layer sediment chemical analysis, including P fractionation studies, was reported in Tylmann et al. [36] and Grochowska et al. [37]. Both reports revealed a very high pollution level of Klasztorne Małe Lake deposits. The sediment chemical analysis in the current study did not show significant changes in phosphorus or other components contents compared to previous studies. The concentrations of phosphates and TP in the near-bottom and interstitial water were the highest in this lake (Table 2). The reason for that situation was the developed meromixis, which caused that the near-bottom water of Klasztorne Małe Lake is permanently anoxic [38].

For lakes treated with the P inactivation method, a very important issue for lake water quality prediction is how the "active layer" works. Numerous studies were performed on the efficiency of Phoslock® in P adsorption from the water in laboratory conditions (e.g., [52–54]). In addition, some research was conducted on the effects of the full scale use of Phoslock® for lake restoration (e.g., [14,16,18]). The presented analyses were made 13 y after implementing of a Phoslock® preparation for P inactivation in Klasztorne Małe Lake.

The results of experiments revealed, that the shape of estimated isotherms for both analyzed sediment layers of Klasztorne Małe Lake differed from isotherms for other Kartuzy lakes (Fig. 2). In analyzing the data concerned both Langmuir and BET adsorption models (Table 5), some discrepancies were observed with regard to the assessed maximum sorption capacities of Klasztorne Małe Lake

Table 7
Mean (±SD) amount of phosphorus fractions in bottom sediment of four lakes in Kartuzy (in mg g^{-1} d.w.)

P fraction	Sediment layer	Mielenko Lake	Karczemne Lake	Klasztorne Małe Lake	Klasztorne Duże Lake
NH_4Cl-P	0–5 cm	0.033 ± 0.005	0.188 ± 0.011	0.052 ± 0.008	0.128 ± 0.009
	5–10 cm	0.043 ± 0.006	0.181 ± 0.012	0.059 ± 0.009	0.105 ± 0.008
BD-P	0–5 cm	0.206 ± 0.015	0.431 ± 0.021	0.539 ± 0.025	0.235 ± 0.018
	5–10 cm	0.226 ± 0.018	0.569 ± 0.025	0.663 ± 0.028	0.353 ± 0.014
NaOH-rP	0–5 cm	0.440 ± 0.017	2.142 ± 0.032	1.757 ± 0.052	0.280 ± 0.014
	5–10 cm	0.364 ± 0.012	2.983 ± 0.040	2.077 ± 0.048	0.452 ± 0.012
NaOH-nrP	0–5 cm	1.422 ± 0.028	1.983 ± 0.031	2.125 ± 0.024	1.081 ± 0.015
	5–10 cm	1.498 ± 0.022	3.057 ± 0.042	1.900 ± 0.021	0.905 ± 0.012
HCl-P	0–5 cm	0.341 ± 0.008	5.236 ± 0.044	1.524 ± 0.025	1.041 ± 0.025
	5–10 cm	0.368 ± 0.010	4.581 ± 0.044	1.149 ± 0.033	0.699 ± 0.011
res-P	0–5 cm	0.570 ± 0.017	1.236 ± 0.023	0.743 ± 0.011	0.630 ± 0.012
	5–10 cm	0.637 ± 0.019	1.053 ± 0.025	0.755 ± 0.010	0.480 ± 0.010

sediment depending on adsorption models. But the determination coefficient (R^2) was clearly lower for both Langmuir models (Table 5), and higher R^2 values were assessed for Freundlich, BET, and Dubinin–Radushkevich models, confirming that Langmuir and double Langmuir models are rather not suitable for the description of P adsorption by this sediment. Further data analysis made according to Hintz [44] (plotting logK_d vs. log$S$) (Fig. 3), confirmed the concave shape of P adsorption isotherm (S1-class) for Klasztorne Małe Lake sediment and pointed at Freundlich adsorption model as being possibly suitable. The Freundlich isotherm model can be applied to describe multilayer adsorption [34]. Undoubtedly that difference between sorption characteristics among Klasztorne Lake sediment and other lakes in Kartuzy was the effect of sediment modification by applied La-modified bentonite. The Dubinin–Radushkevich adsorption model also revealed high agreement with experimental data (R^2 exceeding 0.9), which can confirm the usability of that isotherm model for characterising the adsorption process in sediment treated with modified bentonite. Augustyniak et al. [23] reported, that using of PAX addition modified and enhanced the sorption abilities of Długie Lake sediment, and the double Langmuir model fitted the best to experimental P sorption data, confirming that P adsorption occurred on two kinds of active sorption places. But the present study showed, that using La-modified bentonite modifies the P adsorption abilities of sediment in a completely different way and "active layer" shows another adsorption behavior, which can be described in two possible ways: as multilayer adsorption (defined by Freundlich or BET models) or as adsorption in porous media (Dubinin–Radushkevich model). The exponent from the Freundlich equation is an indicator of the diversity of free enthalpies associated with adsorption from a solution by various components of a heterogeneous sorbent [34]. For $1/n < 1$ the isotherm is convex – adsorbate is binding to the centers with lower and lower values of free enthalpies. This kind of isotherm is described as favorable adsorption isotherm. When the $1/n$ value is closer to 0, the adsorption process is more heterogeneous [34]. This situation was observed for the sediment of three analyzed lakes in Kartuzy (Mielenko, Karczemne, and Klasztorne Duże) (Table 5). But for Klasztorne Małe Lake the $1/n$ value was higher than 1 (exceeding 2 – Table 5), which confirms the concave shape of the P adsorption isotherm. A possible explanation of this situation is that the previously adsorbed particles enhances further adsorption processes by offering the next adsorption sites [31]. Giles et al. [45] maintain, that in the case of the S-class isotherm the solute–solute forces are as strong as forces between solute-solid. According to Saadi et al. [34], Rao et al. [55], and Haghseresht and Lu [56], the $1/n$ value higher than 1 is indicative for unfavorable adsorption isotherms. $1/n$ values close to 1 for P sorption on modified bentonites were reported by Chen et al. [57] and El Bouraie and Masoud [58]. But those experiments were conducted with much more higher initial P concentrations, ranged 10–150 mg P dm^{-3} [55] and 0.05–25 mg P dm^{-3} [56]. The results of experiments revealed that sediment of Klasztorne Małe Lake had the highest P sorption abilities (Fig. 2) which were confirmed by the lowest phosphate final concentration among all tested sediments. Moreover, hysteretic P amounts for the sediment of this lake exceeded 98% of P_{ads}, and they were the highest among studied sediments, which confirms very high P adsorption abilities at the higher P concentration in water (Table 5, Fig. 4). However, the assessed EPC_0 values were the highest among all studied sediment of Kartuzy lakes (Table 5), which means that sediment could act as a source of P in the case of a radical lowering of the phosphate concentration in ambient water and, theoretically, it could be effective as P sink in a much higher level of P in water.

Considering P exchange between sediment and water, a very important issue is P mobility caused by redox potential changes [13]. According to opinion of Meis et al. [15], Phoslock® can be effective in managing P release from sediment under aerobic conditions. During a longer period of anaerobic conditions Phoslock® can be less effective in blocking internal P loading, and the higher dose of preparation is needed for this purpose. In such a scenario, an insufficient dose of Phoslock® used for Klasztorne Małe Lake restoration could have caused the high P level observed in the Klasztorne Małe monimolimnion zone (Table 2). The study of Łopata et al. [59] found a lower ability of Phoslock® to keep P in sediment during anoxia, compared to PAX. Although many authors [e.g., 13,52] maintain that Phoslock is effective in limiting P loading during anoxia, the P adsorption experiments in this study were conducted in the oxic conditions and it could be a possible explanation for the higher efficiency in the P sorption (and the highest P retention) among investigated sediments of four lakes in Kartuzy (Table 5). However, this hypothesis needs further research.

The last among the investigated lakes was Klasztorne Duże Lake. Sediment of this water body showed the lowest P adsorption abilities. Assessed S_{max}, S_1, and S_2 for both Langmuir adsorption models were the lowest (Table 5). Among the tested models the BET model showed the best fit to the obtained experimental data (the highest R^2 values) (Table 5). Comparing the obtained results according to Hintz [44] confirmed, that the BET isotherm model is the most suitable for experimental data at a higher P concentration in water. This means that P adsorption by the sediment of Klasztorne Duże Lake could occur through multilayer creation. The BET model is rather unpopular for bottom sediment studies – the Freundlich and Langmuir models are the most used among many P adsorption studies of sediments and soils [e.g., 25,31,32,57,60]. The sediment of Klasztorne Duże Lake had the highest content of silicon among analyzed sediments. Si in sediment may have a negative influence on the P binding. Si compounds in the similar environmental conditions show similar behavior to P compounds, and the competition between Si and P in the active sorption sites can occur [61]. It then seems to be possible that the different character of P adsorption by Klasztorne Duże Lake sediment (the lowest level of P adsorption and retention (Figs. 2–4, Table 5) is connected to a higher Si level in this deposit, compared to other studied sediments.

In view of the current study, it seems to be possible, that long-term phosphorus contamination of Kartuzy lakes system had led to the formation of sediments that are able to bind a higher amounts of P more effectively at a higher concentration in the water above the sediment. Bottom sediment can be treated as highly heterogeneous, multi-component system, and adsorption processes in that kind of medium can occur in various ways. P adsorption processes mechanism is very complex and can occur on the way of ligand exchange or competition with, for example, humic substances [62] or silicates [61]. The fact, that Dubinin–Radushkevich isotherm model also can characterize well the P adsorption process on bottom sediments supports the hypothesis, that adsorption mechanism is based on the pore filling, and process has multilayer character [30]. The obtained results show as well, that multilayer creation on heterogenous surface (Freundlich, BET, and Dubinin–Radushkevich models), or monolayer creation on different kinds of adsorption active sites (double Langmuir model) is more probable, than simple monolayer creation, as it is assumed in Langmuir model.

The previously adsorbed phosphorus pool influences on the shape of logK_d vs. log$S$ showing a rising character at low P concentration in the water, which could confirm the hypothesis about weaker sediment P adsorption abilities at these conditions. Then adsorption equations should then be mathematically modified for better correspondence with experimental data. Testing different isotherm models is good practice for analyzing P adsorption processes by lake bottom sediment and it could be useful for the further prognosis of sediment influence on water quality in a lake.

5. Conclusions

The performed research revealed:

- The sediment of investigated lakes differed in phosphorus adsorption abilities, and it was expressed by various adsorption models, which showed the best fit to experimental data (mainly according to determination coefficient R^2 values). Rational functions (Langmuir, double Langmuir, and BET equations), power functions (Freundlich equation), and transcendental functions (Dubinin–Radushkevich equation) can be used for P adsorption characteristic by lake bottom sediment.
- When we have similar R^2, χ^2, or RMSE values for several adsorption models the analysis of logK_d vs. log$S$ curves can help with choosing suitable adsorption models.
- The sediments of three lakes (Mielenko, Karczemne, and Klasztorne Duże) showed convex sorption isotherms shape (L4, L2, and L3 classes – respectively) at P higher concentration, and Klasztorne Małe Lake – concave adsorption isotherms (S1-class). But at low P concentration in the water all tested sediment showed concave character of adsorption isotherms, which could suggest weaker P adsorption abilities. This could be the effect of the presence of the earlier adsorbed P in sediment.
- Using Phoslock® on Klasztorne Małe Lake significantly modified sediment P adsorption properties (higher P retention ability, higher EPC_0 value, a concave shape of adsorption isotherms), which confirms different P adsorption behavior of the sediment "active layer" compared to natural, non-modified sediment. However, a high P concentration observed in the water medium of water-sediment interface under permanent anoxia in lake suggests, that redox conditions could have influence "the active layer" effectiveness in P adsorption.
- The results of the conducted experiments on the sediment of a lake polluted by road salt effluent (Mielenko Lake) showed that higher water EC probably improves sediment P sorption abilities and P retention, and it could potentially reduce the P pool available for primary production.

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Symbols

$1/n$ — Constant, which characterizes heterogeneity of the adsorption process

B — Dubinin–Radushkevich isotherm constant related to adsorption energy, mol^2 kJ^{-2}

C_e — Phosphorus concentration after 24 h equilibration procedure, mg dm^{-3}

C_s — Adsorbate monolayer saturation concentration, mg dm^{-3}

EPC_0 — P equilibrium concentration, mg dm^{-3}

k — Constant related to bonding energy in Langmuir equation, dm^3 mg^{-1}

k_1 — Constant related to bonding energy in Langmuir equation (type I active sites), dm^3 mg^{-1}

k_2 — Constant related to bonding energy in Langmuir equation (type II active sites), dm^3 mg^{-1}

k_{BET} — BET constant (connected to surface bonding energy), dm^3 mg^{-1}

K_d — Division coefficient, dm^3 kg^{-1}

K_f — Freundlich sorption constant, dm^3 kg^{-1}

R — Ideal gas constant, J mol^{-1} K^{-1}

R^2 — Determination coefficient

RMSE — Root mean square error

S — Total phosphorus adsorbed by sediment (solid phase), mg kg^{-1} d.w.

S' — Phosphorus amount adsorbed during experiment, mg kg^{-1} d.w.

S_0 — Preliminary adsorbed phosphorus in the sediment-so-called "native sorbed phosphorus", mg kg^{-1} d.w.

S_1 — Maximum sorption capacity of sediment in double Langmuir equation (type I active sites), mg kg^{-1} d.w.

S_2 — Maximum sorption capacity of sediment in double Langmuir equation (type II active sites), mg kg^{-1} d.w.

S_{BET} — Maximum adsorption capacity of adsorbent corresponding to monolayer, mg kg^{-1} d.w.

S_{DR} — Dubinin–Radushkevich theoretical isotherm saturation capacity (the amount of adsorbate adsorbed in micropores), mg kg^{-1} d.w.

S_{exp} — Adsorbed phosphorus (experimental data), mg g^{-1} d.w.

S_{max} — Maximum sorption capacity of sediment in Langmuir equation, mg kg^{-1} d.w.

S_{mod} — Adsorbed phosphorus (model data), mg g^{-1} d.w.

T — Temperature, K

χ^2 — Non-linear χ^2 test

ε — Polanyi potential constant, J mol^{-1}

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