



## The influence of the physico-chemical composition of bottom sediments on their sorption capacity in relation to phosphates

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### ABSTRACT

This paper presents the results of a research on the impact of the composition of bottom sediments on their phosphate sorption capacity under aerobic and anoxic conditions. The research was carried out in 2013–2016 with the use of bottom sediments from two small-scale retention reservoirs (the Ożanna reservoir and the Rzeszów reservoir). A physical and chemical analysis of the bottom sediments was carried out, which led to the conclusion that the sediments deposited at the bottom of the examined water bodies differ both in terms of their physical properties and chemical composition. The isotherm best describing the course of phosphate sorption in the deposits of the examined reservoirs, as well as the theoretical maximum phosphate sorption capacity of the sediments ( $q_{max}$ ) under close-to-real conditions (i.e., on undisturbed sediment cores), were determined. The analysis of the results allowed to conclude that the phosphate sorption capacity of the sediments is influenced both by the aerobic conditions and the physical and chemical properties of the sediments, such as the granulometric composition, pH, organic matter content and the content of metals with which phosphorus forms sparingly soluble compounds.

*Keywords:* Phosphorus sorption; Bottom sediments; Small retention reservoirs

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### 1. Introduction

With the world's ever-growing population and recent climate fluctuations observed, issues related to water scarcity are becoming a priority [1]. Water is a finite resource, and its efficient and sustainable distribution is and will continue to be of great importance worldwide. One of the measures aimed at reducing water scarcity is water retention [2]. The purpose of creating retention reservoirs is to solve the problem of water deficit. These water bodies have numerous features that distinguish them from rivers and natural lakes. For this reason, they constitute a separate category of surface water reservoirs [3,4]. The term "small-scale retention" is simplistically used to refer to a

water reservoir of a small size [5], and includes all measures (technical and non-technical) applied to improve water balance in a catchment area by slowing or reducing surface and subsurface water runoff [6,7]. Small retention dam reservoirs are usually shallow, thermally unstratified for a large part of the year and characterised by rapid water change [8]. These are usually multi-purpose facilities, the main objective of which is to improve the water balance of the catchment area, including the prevention of drought and flooding, but which will also contribute to enhancing the recreational value of neighbouring areas [1,8,9]. The maintenance of artificial reservoirs can be problematic, mainly due to increased content of allochthonous or autochthonous compounds in the waters, resulting in

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changes leading to a deterioration of the chemical composition and environmental potential of the reservoir [8,10].

The functioning of water reservoirs is related to the formation of bottom sediments, which are one of the key elements of the water ecosystem [11]. Bottom sediments form a mixture of mineral and organic components resulting from the deposition of allochthonous and autochthonous substances [12,13]. The composition of sediments accumulated at the bottom of water reservoirs depends on multiple natural and anthropogenic factors. Most of the pollutants entering the waters of reservoirs are deposited in bottom sediments. Therefore, sediments are considered a good indicator for assessing the quality of aquatic ecosystems [11,14].

Biogenic compounds are considered to be one of the most significant factors affecting water quality and stimulating the process of eutrophication and degradation of reservoirs. Also, due to their capacity to accumulate and be re-released from sediments, they play an essential part in controlling primary production in reservoirs [15,16]. It is assumed that nitrogen and phosphorus are chiefly responsible for eutrophication. However, numerous studies have shown that in freshwater ecosystems, the intensity of this process depends primarily on the amount of phosphorus in the water [17]. The geochemistry of phosphorus in surface waters has been widely analysed in the literature on the subject and is still a topical issue due to the key role of this element in the eutrophication process of inland waters [18]. Phosphorus inputs to reservoir waters are subject to a series of reactions, which reduce the solubility of this element leading to its precipitation from the water and accumulation in bottom sediments [18,19]. The amount of phosphorus deposited in bottom sediments is determined by the biological, physicochemical and hydrochemical conditions prevailing in the water reservoir. The difference between the amount of phosphorus reaching the sediment and the amount of phosphorus released into the water body determines the amount of phosphorus permanently deposited in the sediment and reflects the efficiency of the lake's "defence mechanisms". Meanwhile, the difference between the amount of phosphorus delivered to the lake and the amount permanently accumulated in the sediment determines the rate at which the eutrophication process in the water body proceeds [20]. Although phosphorus can be accumulated in various elements of the aquatic ecosystem, it can be predominantly found in bottom sediments, where it is accumulated through sorption and biological assimilation processes [18,20,21]. Sorption is one of the main processes affecting the movement of organic and inorganic compounds in the aquatic environment [22,23]. For this reason, sediments are often referred to as geosorbents [22,24]. Phosphorus sorption is a two-step process in which a rapid exchange of phosphates occurs between the overlying water and the sediment particles (adsorption), followed by a slow transfer of phosphates into the solid phase (absorption). The sorption process is controlled by the phosphate concentration in the overlying water and the capacity of the sediment to replenish phosphate [25]. The sorption isotherm describes the relationship between the concentrations of adsorbed and dissolved components at a given temperature [26]. Phosphorus adsorption increases

with growing phosphorus concentration in the overlying water until all sorption sites are filled. At this point, adsorption reaches a maximum level [25]. The maximum phosphate sorption capacity of sediments is an important parameter, which provides information on the maximum amount of phosphorus that can be adsorbed by the sediments [27].

The quality of bottom sediments and their impact on the condition of the aquatic environment is becoming more and more important, as there is undoubtedly a direct relationship between the composition of bottom sediments and water pollution. Physical and chemical composition of sediments often gives a better insight into the condition of the aquatic environment compared to data on the chemical composition of the water, which tends to fluctuate more over time, and the actual environmental condition of a water body can be assessed by monitoring pollutants accumulated in bottom sediments. Effective management of small retention dam reservoirs, or undertaking any reclamation measures, should be preceded by comprehensive tests of the physical and chemical properties of bottom sediments [11,14].

## 2. Study area and methods

The examination covered two small-scale retention reservoirs located in the south-eastern part of Poland, in the Podkarpackie Province – the Ożanna reservoir and the Rzeszów reservoir (Fig. 1).

The Ożanna reservoir was put into use in 1978. It is located in the central part of Ożanna village (Kuryłówka municipality, Leżajsk district). The dam of the reservoir is located at 5 km of the Złota river [28]. The purpose of the reservoir was to even out the flow of the Złota river, prevent its further erosion, improve the humidity conditions in the adjacent area, secure water supply for domestic and flood control purposes for the surrounding villages, as well as create conditions for fish farming and recreation. In 1998, desilting of the reservoir was performed and 26,000 m<sup>3</sup> of bottom sediment was removed [28,29]. The catchment area of the reservoir are mainly forests and agricultural fields [28].

The Rzeszów barrage was created in 1974 by damming the Wisłok river valley at 63 km. The main tributaries of the reservoir are the Wisłok and Strug rivers. The reservoir performs a flood control and recreational function. It is used to raise the water level for the water intake of the city of Rzeszów, as well as being to generate energy with a small hydroelectric power station with a capacity of 660 kW [28–31]. As a result of intensive deposition of debris carried by the tributaries and its accumulation in sediments, the reservoir has become significantly shallower. The measurements of siltation carried out in 1986 showed that the reservoir had been reduced in volume by about 66% in the course of its exploitation [28,30]. For this reason, attempts were made at reservoir restoration in 1986–1987 and 1995–1997. As a result of these efforts, approximately 300,000 m<sup>3</sup> of sediment was removed from the bottom of the reservoir. However, these were only short-lived results [30,32]. The catchment area of the reservoir is mainly made up of agricultural fields [28]. A detailed summary of the examined water bodies is presented in Table 1.

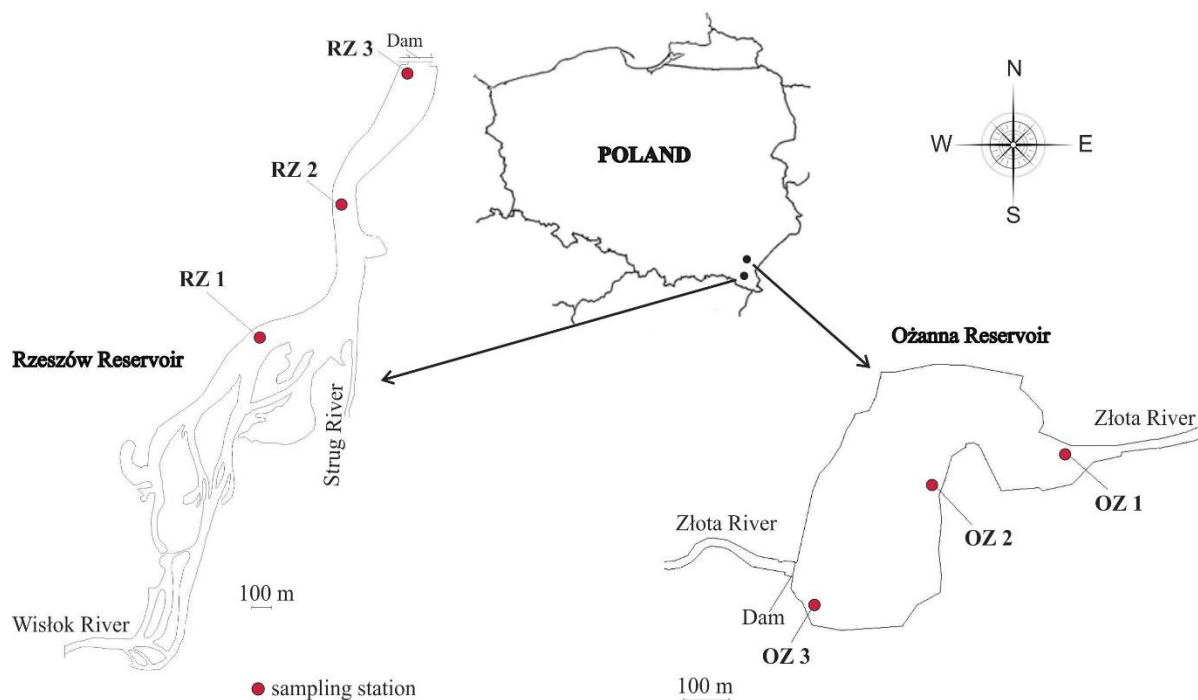


Fig. 1. Locations of the studied reservoirs and sampling stations.

Three test sites each were identified for each of the examined reservoirs: near the dams, in the central part of the reservoirs and in the area of the main tributaries. Bottom sediment samples were collected between 2013 and 2016 using a Kajak-KC gravity core sampler. The top 5 cm layer of bottom sediments was extracted for analysis. In order to determine organic matter (OM) content, the sediments were subjected to heat treatment in a muffle furnace for 4 h at 550°C. The organic matter content was calculated based on the losses after heat treatment [33]. The pH value of the sediments was determined potentiometrically in suspension with 1 mol·dm<sup>-3</sup> KCl solution (Hach HQ30D Meter, USA) [34]. The granulometric composition of the bottom sediments was determined using a wet sieving and aerometric method. Sediment grains with a diameter of less than 0.05 mm were determined using the aerometric method, which allowed to determine the content of the dust and clay fraction, while the content of the sand fraction was determined using the sieving method [35,36]. The granulometric classification of the examined sediments was made in accordance with the applicable standard [37]. In order to determine the content of metals and total phosphorus, the sediments were subject to mineralisation in concentrated HNO<sub>3</sub> acid under high pressure (2–4.5 MPa) (UniClever II Microwave Mineralizer by Plazmatronika). Subsequently, total phosphorus content was determined with the spectrophotometric method based on the reaction of ammonium molybdate [38]. In addition, manganese (Mn), iron (Fe), aluminium (Al) and calcium (Ca) contents were determined (Inductively Coupled Plasma Optical Emission Spectroscopy Method, GBC ICP-OES Spectrometer by Quantima) [39].

Table 1  
Selected parameters of the Ożanna and Rzeszów reservoirs [28–30]

Parameters	Reservoir	
	Ożanna	Rzeszów
Volume (thou. m <sup>3</sup> )	275	1,800 (670)
Average depth (max) (m)	1.4 (3.7)	0.6 (4.9)
Area (ha)	20	68.2
Mean retention time (d)	3.5	0.8
Catchment area (km <sup>2</sup> )	136.3	2,025.0

Determination of the isotherm best describing the process of phosphate sorption by bottom sediments

The test was carried out under aerobic and anoxic conditions using solutions containing P-PO<sub>4</sub><sup>3-</sup> concentrations ranging from 0.0 to 27.84 mg·P·dm<sup>-3</sup>, formed by dissolving KH<sub>2</sub>PO<sub>4</sub> in reservoir water diluted 1:10 with distilled water. To create anoxic conditions, the water was deoxygenated using anhydrous sodium(IV) sulphate. Bottom sediments (0–5 cm) collected into Plexiglas tubes were flooded with solutions of equal phosphate concentration and then the top 1 cm of sediment was resuspended for 10 min using a mechanical stirrer (approximately 150 rpm). The reactors were then left for resedimentation of the suspension. After 2 h of exposure, the P-PO<sub>4</sub><sup>3-</sup> concentration was measured in the overlying water. The tests were conducted at a constant temperature of 21°C. The results obtained were used to

Table 2  
Models of sorption isotherms used for modeling [40–42]

Isotherm name	Definition
Langmuir	$q_e = \frac{q_{mL} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$ (1)
Toth	$q_e = \frac{q_{mT} \cdot K_T \cdot C_e}{\left(1 + (K_T \cdot C_e)^{1/n_T}\right)^{1/n_T}}$ (2)
Langmuir–Freundlich	$q_e = \frac{q_{mLF} \cdot (K_{LF} \cdot C_e)^{n_{LF}}}{1 + (K_{LF} \cdot C_e)^{n_{LF}}}$ (3)
Marczewski–Jaroniec	$q_e = q_{mMJ} \left( \frac{(K_{MJ} \cdot C_e)^{n_{MJ}}}{1 + (K_{MJ} \cdot C_e)^{n_{MJ}}} \right)^{n_{MJ}/n_{MJ}}$ (4)
bi-Langmuir	$q_e = \frac{q_{mbl1} \cdot K_{bl1} \cdot C_e}{1 + K_{bl1} \cdot C_e} + \frac{q_{mbl2} \cdot K_{bl2} \cdot C_e}{1 + K_{bl2} \cdot C_e}$ (5)

where  $q_e$  – equilibrium concentration of the active ingredient in the solid-phase ( $\text{mg} \cdot \text{g}^{-1}$ ),  $C_e$  – equilibrium concentration of the active ingredient in the aqueous phase ( $\text{mg} \cdot \text{dm}^{-3}$ ),  $q_m$  – sorption capacity of the sorbent,  $K$  – sorption equilibrium constant,  $n$  – isotherm exponent,  $m$  – isotherm exponent (the subscripts used in the formulas mean: L – Langmuir, T – Toth, LF – Langmuir–Freundlich, MJ – Marczewski–Jaroniec, bL – bi-Langmuir).

mathematically model the sorption process. Five isotherm models were used for estimation (Table 2):

The values of the unknown parameters of the isotherm models were determined in such a way as to obtain the smallest possible deviation between the experimentally determined and model-calculated values, by minimising the error function (i.e., the sum of squares of the deviations) RRS:

$$\min \text{RRS} = \min \sum_{i=1}^k (q_{ei,\text{exp}} - q_{ei,\text{calc}})^2 = \min \sum_{i=1}^k (q_{ei,\text{exp}} - f(C_e, q_m, K_1, L_2, \dots))^2 \quad (6)$$

The Levenberg–Marquardt algorithm was used to determine the optimal parameters of the isotherm models. In turn, the statistical validity of the fit of the model isotherms to the experimental data was assessed by calculating the error function, adjusted determination coefficient and Fisher’s test values (Table 3).

### 3. Results and discussion

Using the determined parameters of the isotherm models, the theoretical course of sorption isotherms was plotted (Figs. 2 and 3).

Using the adjusted determination coefficient and Fisher’s test for all sorption cases, the adequacy criteria values of each model were determined (Table 4). Based on the analysis of the adequacy criteria, it can be concluded that each of the isotherm models, in each case examined,

Table 3  
Error functions [40–42]

Name	Definition
Adjusted determination coefficient Adj.- $R^2$	$\text{Adj.-}R^2 = 1 - (1 - R^2) \frac{k-1}{k-p-1}$ (7)
Fisher’s test $F$	$F = \frac{(k-p) \sum_{i=1}^k (q_{ei,\text{exp}} - \bar{q}_e)^2}{(n-1) \sum_{i=1}^k (q_{ei,\text{exp}} - q_{ei,\text{calc}})^2}$ (8)

where:  $k$  – number of measurement points,  $q_{ei,\text{exp}}$  – the measured value of the  $i$ -th equilibrium concentration of the active ingredient in the solid-phase,  $q_{ei,\text{calc}}$  – calculated value of the  $i$ -th equilibrium concentration of the active ingredient in the solid-phase,  $q_e$  – arithmetic mean of the measured equilibrium concentration values,  $R^2$  – coefficient of determination,  $p$  – number of parameters of the theoretical model,  $n$  – number of degrees of freedom.

shows a high ( $\text{Adj.-}R^2 > 0.7$ ) or very high ( $\text{Adj.-}R^2 > 0.9$ ) level of adequacy. Based on the values of both analysed adequacy criteria, it can be concluded that the theoretical models assuming surface heterogeneity (Langmuir–Freundlich, Toth, Marczewski–Jaroniec isotherms) are by far more precise. Hence the conclusion that the sorption surface of the examined sorbent (bottom sediments) is definitely heterogeneous in nature, with numerous types of active sites responsible for binding molecules from the aqueous phase. Taking into account the obtained values of  $\text{Adj.-}R^2$  and the  $F$ -test, it was established that the sorption course of phosphate–phosphorus in the bottom sediments of the examined small-scale retention reservoirs is best described by the Langmuir–Freundlich isotherm, which allows to model it with high accuracy for both reservoirs in question. For the Ożanna reservoir, the Langmuir–Freundlich isotherm proved to be most suitable in relation to sites located in the central part of the reservoir and in the tributary area under anoxic conditions. In turn, for the Rzeszów reservoir, the Langmuir–Freundlich isotherm was most suitable in relation to sites located near the dam and in the central part of the reservoir under anoxic conditions. In other cases, the selected isotherm yields the second or third best result in terms of the level of adequacy, or a result that differs only slightly from the best one.

For all isotherm models, parameter values were estimated by minimising the error function, that is, they were determined in such a way so that the errors between the measured values and those predicted by the isotherm were as small as possible. In this way, values of the parameter  $q_{\text{max}}$  were obtained for the Langmuir–Freundlich isotherm, representing the theoretical maximum phosphate sorption capacity of the sediments (Table 5).

The obtained theoretical values of the maximum phosphate sorption capacity of bottom sediments from the Ożanna reservoir ranged from 0.0563 to 0.1652  $\text{mg} \cdot \text{g}^{-1}$  under aerobic conditions, while under anoxic conditions they were lower, ranging from 0.0555 to 0.0658  $\text{mg} \cdot \text{g}^{-1}$  (Table 5). The theoretical maximum sorption capacity of sediments in relation phosphates for the Rzeszów reservoir under aerobic

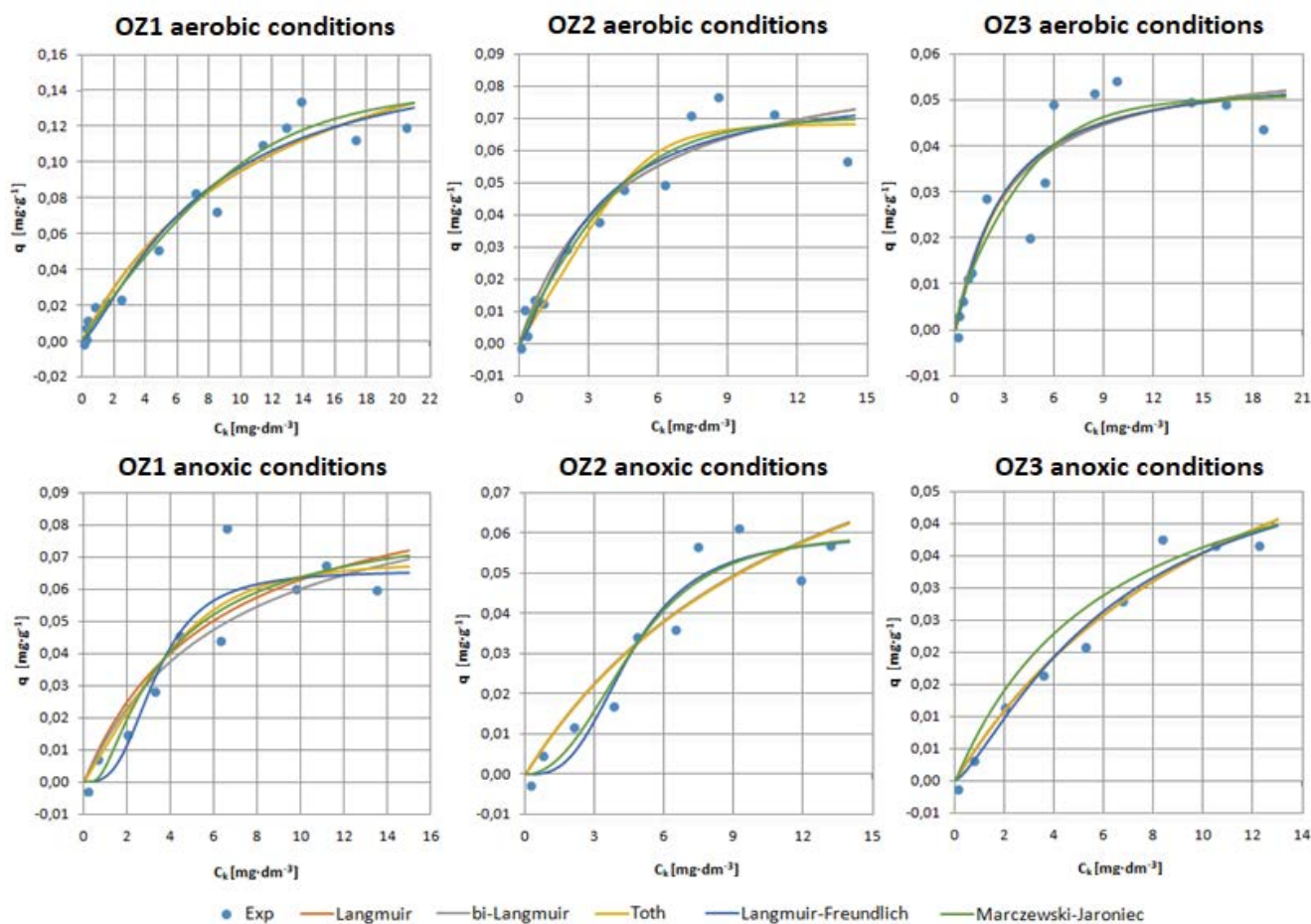


Fig. 2. Experimental phosphate–phosphorus sorption isotherms for bottom sediments of Ożanna reservoir determined under aerobic and anoxic conditions.

conditions ranged from 0.2997 to 0.6770  $\text{mg}\cdot\text{g}^{-1}$ , and from 0.1237 to 0.2289  $\text{mg}\cdot\text{g}^{-1}$  under anoxic conditions (Table 5).

For the sediments from the Rzeszów reservoir,  $q_{\text{max}}$  values were 3 to 4 times higher than for the sediments from the Ożanna reservoir, both under aerobic and anoxic conditions. This may be related to the granulometric properties of the sediments. Sediments with a high content of fine fraction are more susceptible to accumulation of pollutants [22], and the smaller the sediment particles, the higher the sorption capacity of the sediments [43]. The sediments from the Ożanna reservoir are mainly made up of sand, while those from the Rzeszów reservoir consist of a mixture of clay and dust (Table 6) with a smaller grain size and larger specific surface area, which acts as a natural geosorbent for phosphorus compounds. In addition, phosphorus sorption can also be affected by the pH of the sediments. According to Omari et al. [44], the amount of adsorbed phosphorus in sediments increases with increasing pH, which is related to the content of carbonates that bind phosphorus at alkaline pH. The sediments from the Rzeszów reservoir have a higher pH (ranging between 6.38–8.06) than the sediments from the Ożanna reservoir (ranging between 4.37–7.07) (Table 7). For both reservoirs examined, higher maximum phosphate sorption capacity of sediments was obtained

under aerobic conditions. A number of researchers have also obtained higher values of phosphate sorption capacity for sediments subjected to aerobic incubation [27,47]. Lower values of the maximum phosphate sorption capacity of sediments under anaerobic conditions are probably due to the desorption of phosphorus bound by iron, which under reducing conditions changes from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  [45]. When examining sediments from several lakes, Belmont et al. [27] obtained higher values for the maximum phosphate sorption capacity under aerobic conditions than under anaerobic conditions for the sediments from Lake Istokpoga, 0.154 and 0.123  $\text{mg}\cdot\text{g}^{-1}$  (TP = 0.449  $\text{mg}\cdot\text{g}^{-1}$ ), respectively, and for the sediments from Lake Kissimmee, 0.283 and 0.186  $\text{mg}\cdot\text{g}^{-1}$  (TP = 0.919  $\text{mg}\cdot\text{g}^{-1}$ ), respectively [27]. The maximum phosphate sorption capacity of sediments determined for sediments from Indian River Lagoon was also greater under aerobic conditions than under anaerobic conditions, 0.133 and 0.032  $\text{mg}\cdot\text{g}^{-1}$  (TP = 0.497  $\text{mg}\cdot\text{g}^{-1}$ ), respectively [45]. For the sediments from the Ożanna reservoir, it was observed that  $q_{\text{max}}$  values decreased further downstream, under both aerobic and anoxic conditions (Table 5). This is likely to be affected by the grain size of the sediments (Table 6). The further downstream, the higher the sand content and the lower the dust content in the sediments (Table 7).

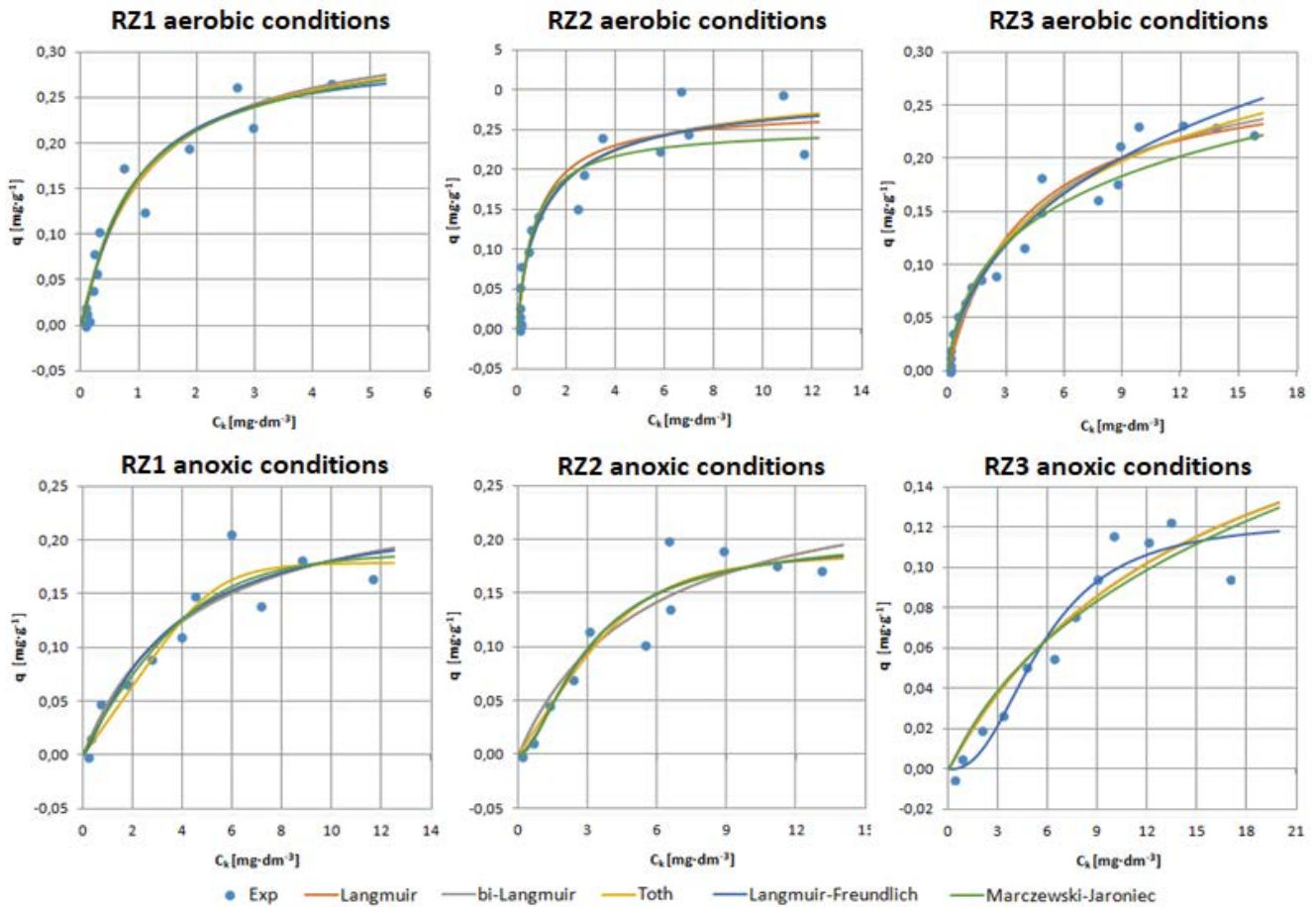


Fig. 3. Experimental phosphate–phosphorus sorption isotherms for bottom sediments of Rzeszów reservoir determined under aerobic and anoxic conditions.

This results in a smaller specific surface area of the sediments, which become less susceptible to the accumulation of phosphorus compounds. In addition, organic matter content of sediments, which decreases further downstream, may have an impact on the lower sorption capacity. Organic matter content in sediments is one of the factors that can affect their sorption capacity. Typically, as its value increases, the phosphate sorption capacity of sediments also increases [45,46]. A significantly higher  $q_{\max}$  value under aerobic conditions was determined for the sediments collected in the area close to the tributary (OZ1), which also showed the highest content of dust fractions, OM, Mn and Fe and lower pH (Tables 6 and 7). The higher OM content and lower pH may suggest a higher content of humic substances in the sediments, which may form metal-phosphorus-organic complexes with poor solubility. Under anoxic conditions, the  $q_{\max}$  values obtained were very similar for all the sites, although they tended to decrease further downstream (Table 5). Slightly higher content of such metals as Fe and Mn relative to TP means that the metal-phosphorus bonds formed are not sufficiently stable under anoxic conditions and may break down due to easy reduction of oxidised forms of iron and manganese. The  $q_{\max}$  values for the sediments from the Rzeszów reservoir under aerobic

conditions increased further downstream (Table 5). This could also be affected by the granulometric composition of the sediments. The further downstream, the higher the content of clay fraction with particle diameter below 0.002 mm, and the lower the content of dust fraction with larger particle diameter (0.002–0.05 mm) (Table 6) tended to be, which could probably have had an impact on the increasing phosphate sorption capacity of the sediments along the longitudinal axis of the reservoir towards the dam. A significantly higher  $q_{\max}$  value (the highest value) determined for the sediments in the dam area was accompanied by the highest content of the finest fraction (clay fraction) (Table 6), with only slightly lower contents of Fe, Ca, Al, Mn and OM compared to the sediments from other sites in the Rzeszów reservoir (Table 7). The finest particles agitated during resuspension have the longest setting time, which also increases the time of direct contact between adsorbent and adsorbate, both in experimental and actual conditions. In turn, under anoxic conditions, the lowest  $q_{\max}$  value was observed for the site located at the dam area, while the highest for the site at the tributary area (Table 5). The chemical composition of the sediments may be a decisive factor. Sediments from the dam area of the Rzeszów reservoir were characterised by the lowest content of Fe, Ca, Al, Mn

Table 4  
Summary of adequacy criteria values for calculated isotherm models

Isotherm model	Ożanna reservoir											
	Aerobic conditions						Anoxic conditions					
	OZ1		OZ2		OZ3		OZ1		OZ2		OZ3	
	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F
Langmuir	0.9513	54.68	0.9067	11.74	0.8654	8.03	0.8106	5.75	0.8654	7.96	0.9624	29.04
bi-Langmuir	0.9469	46.87	0.8833	9.61	0.3550	6.69	0.7299	4.10	0.8117	5.95	0.9436	20.74
Langmuir–Freundlich	0.9558	53.56	0.9038	11.38	0.8529	7.47	0.8429	7.32	0.8941	10.72	0.9573	27.94
Toth	0.9513	50.77	0.9216	13.27	0.8533	7.49	0.8282	6.52	0.8429	6.97	0.9549	24.89
Marczewski–Jaroniec	0.9583	66.68	0.9083	12.27	0.8627	7.25	0.7646	5.10	0.8740	9.50	0.9496	19.79

Isotherm model	Rzeszów reservoir											
	Aerobic conditions						Anoxic conditions					
	RZ1		RZ2		RZ3		RZ1		RZ2		RZ3	
	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F	Adj.-R <sup>2</sup>	Test F
Langmuir	0.9672	30.56	0.9167	35.31	0.9561	66.22	0.8893	41.56	0.8702	30.02	0.8863	28.29
bi-Langmuir	0.9606	25.86	0.9100	32.89	0.9578	68.88	0.8709	32.33	0.8269	23.35	0.8539	22.63
Langmuir–Freundlich	0.9642	29.40	0.9156	34.87	0.9507	87.81	0.8916	37.96	0.8656	30.67	0.9157	42.12
Toth	0.9639	28.32	0.9172	35.52	0.9613	75.98	0.9108	43.55	0.8654	30.41	0.8722	25.46
Marczewski–Jaroniec	0.9701	33.13	0.9145	56.63	0.9356	129.33	0.8920	38.92	0.8428	26.78	0.8637	20.33

and organic matter compared to sediments from the other sites (Table 7). It is commonly known that Fe, Al, Ca and Mn hydroxides are the main adsorbents of phosphorus. According to Zhou et al. [47] in the sediments from Taihu lake, the content of Fe and Al was the main factor determining the adsorption capacity of the sediments in relation to phosphorus compounds, which is related to the large specific surface area of the hydroxides of these metals. The sediments from this lake contained more Fe and Al than Mn and Ca. The chemical composition of the bottom sediments also affected the sorption capacity of the sediments from the three sites, whose maximum phosphate sorption capacities were as follows: 0.493 mg·g<sup>-1</sup> (TP = 0.793 mg·g<sup>-1</sup>) for Gonghu Bay, 0.531 mg·g<sup>-1</sup> (TP = 0.824 mg·g<sup>-1</sup>) for East Dongting Lake, and 0.562 mg·g<sup>-1</sup> (TP = 0.572 mg·g<sup>-1</sup>) for Huangda Lake [46]. According to Huang et al. [46], the phosphate sorption capacity of sediments is affected by their content of iron, calcium and organic matter. Calcium compounds had a significant impact on phosphorus sorption of the sediments in East Dongting Lake (highest Ca content in the sediments), while iron compounds-on phosphorus sorption of the sediments in Huangda Lake (highest Fe content in the sediments). Sediments from Huangda and East Dongting Lakes also had a higher organic matter content than the sediments from the third site. Due to their chemical composition, the sediments from East Dongting and Huangda Lake s had a higher phosphate sorption

Table 5  
Theoretical maximum sorption capacity ( $q_{\max}$ ) of sediment relative to phosphate

Station	$q_{\max}$ (mg·g <sup>-1</sup> )	
	Aerobic conditions	Anoxic conditions
OZ1	0.1652	0.0658
OZ2	0.0798	0.0597
OZ3	0.0563	0.0555
RZ1	0.2997	0.2289
RZ2	0.3070	0.2002
RZ3	0.6770	0.1237

capacity than the sediments from Gonghu Bay. Lower stability of bonds with Fe and Mn in the reducing environment, due to their lower content in the sediments, may have had an impact on the lower value of the maximum sorption capacity in the dam area of Rzeszów reservoir. Under anoxic conditions, phosphorus sorption is significantly lower despite relatively high content of phosphorus-binding elements and OM. One of the decisive factors affecting the  $q_{\max}$  value for the Rzeszów reservoir under anoxic conditions may also be the highest content of the dust fraction, which may contain coal dust and soot particles with high sorption properties in relation to many

Table 6  
Granulometric composition and classification of bottom sediments of reservoirs

Station	Granulometric fraction (%)				Classification
	Loam (<0.002 mm)	Dust (0.002–0.05 mm)	Sand (0.05–2.0 mm)	Rocky gravel (2.0–200 mm)	
OZ1	0.01	10.72	89.27	0.00	Fine sand
OZ2	0.01	9.75	90.24	0.00	Fine sand
OZ3	0.01	10.72	89.27	0.00	Fine sand
RZ1	13.82	75.72	10.43	0.00	Loam dust
RZ2	23.25	68.63	8.11	0.00	Dusty loam
RZ3	26.59	61.60	11.80	0.00	Dusty loam

Table 7  
pH of sediments and the content of phosphorus, organic matter and metals that may affect the sorption of phosphorus in bottom sediments

Station		TP	Fe	Ca	Al	Mn	OM	pH
		mg·g <sup>-1</sup> ·s.m.o.	mg·g <sup>-1</sup> ·s.m.o.	mg·g <sup>-1</sup> ·s.m.o.	mg·g <sup>-1</sup> ·s.m.o.	mg·g <sup>-1</sup> ·s.m.o.	%	–
OZ1	Average	0.370	6.10	1.203	4.20	0.135	3.29	–
	Min.	0.051	1.25	0.287	1.47	0.045	0.31	4.37
	Max.	1.099	14.66	2.426	8.14	0.382	8.52	6.42
	SD	0.323	4.68	0.698	2.47	0.091	3.12	0.70
OZ2	Average	0.185	6.01	1.258	4.33	0.134	2.04	–
	Min.	0.058	1.97	0.599	1.66	0.075	0.39	4.47
	Max.	0.495	12.54	2.414	9.05	0.263	5.68	6.26
	SD	0.140	3.90	0.664	2.66	0.062	1.59	0.54
OZ3	Average	0.091	2.75	0.652	2.90	0.081	1.11	–
	Min.	0.037	1.31	0.414	1.83	0.034	0.30	4.42
	Max.	0.320	8.04	1.275	7.87	0.283	4.26	7.07
	SD	0.077	1.87	0.228	1.74	0.068	1.08	0.86
RZ1	Average	0.844	21.93	26.04	27.02	0.605	6.81	–
	Min.	0.668	18.46	20.20	22.49	0.466	5.84	6.47
	Max.	1.320	29.56	34.19	33.88	0.722	9.07	8.04
	SD	0.179	3.07	3.93	3.55	0.078	1.12	0.73
RZ2	Average	0.837	22.84	26.51	28.25	0.622	7.65	–
	Min.	0.664	16.33	19.95	19.31	0.477	5.28	6.46
	Max.	1.022	26.96	40.31	33.25	0.851	10.42	8.06
	SD	0.122	3.52	6.09	4.52	0.133	1.73	0.73
RZ3	Average	0.695	19.77	25.01	24.04	0.513	6.55	–
	Min.	0.542	12.69	19.79	14.98	0.358	4.24	6.38
	Max.	0.863	23.84	27.65	27.80	0.665	8.40	7.96
	SD	0.088	3.24	2.45	3.79	0.096	1.17	0.62

organic and inorganic substances, including metals [48]. Not only the content of organic matter, but also its type may affect the sorption properties of sediments. The research conducted in 2017–2020 found that the sediments from the Rzeszów reservoir collected in the tributary area have the highest humic matter content (31.3 mg·g<sup>-1</sup>) compared to the other areas (near the dam 17.26 mg·g<sup>-1</sup>; in the central part of the reservoir 20.8 mg·g<sup>-1</sup>) [49].

#### 4. Summary

The theoretical maximum phosphate sorption capacity of sediments calculated for close-to-real conditions provides information about the natural ability of the sediments to immobilise phosphates, as well as about the resistance of the reservoir to degradation. The higher the sorption properties, the greater the capacity to slow down the eutrophication process. The natural phosphate sorption



capacity of sediments may play an important role in reducing the contribution of internal supply of the reservoir as a source of phosphorus in the eutrophication process.

For the sediments from the Rzeszów reservoir,  $q_{\max}$  values were 3–4 times higher than for the sediments from the Ożanna reservoir, both under aerobic and anoxic conditions. Analysis of obtained  $q_{\max}$  values, physical and chemical composition of the sediments examined showed that phosphate sorption of the bottom sediments of the examined water bodies is affected both by aerobic conditions at the water-sediment interface (in the case of both reservoirs in question higher maximum phosphate sorption capacity of sediments was obtained under aerobic conditions), as well as by physical and chemical properties of the sediments, in particular grain size, pH, content and type of organic matter and content of metals with which phosphorus forms sparingly soluble compounds. In the case of sediments with high content of sand and low content of organic matter and metals, the sorption capacity of the sediments under aerobic and anoxic conditions may differ only to a negligible extent.

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