

Article

Sorption Properties of the Bottom Sediment of a Lake Restored by Phosphorus Inactivation Method 15 Years after the Termination of Lake Restoration Procedures

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Abstract: Artificial mixing and phosphorus inactivation methods using aluminum compounds are among the most popular lake restoration methods. Długie Lake (Olsztyńskie Lakeland, Poland) was restored using these two methods. Primarily, P precipitation and inactivation methods significantly increased the sorption properties of Długie Lake bottom sediment. Fifteen years after the termination of the restoration procedure, the alum-modified “active” sediment layer still has higher P adsorption abilities, which can limit P internal loading. Relatively low amounts of phosphates in the near-bottom water of Długie Lake, even in anoxia, as well as the fact that the assessed maximum sediment P sorption capacity is still higher than $\text{NH}_4\text{Cl-P}$ (labile P) and BD-P (Fe-bound P) sum (“native exchangeable P”), confirm that hypothesis. Among the tested P adsorption models for the sediment, the double Langmuir model showed the best fit to the experimental data (the highest R^2 values). This may indicate that phosphorus adsorption by the tested sediments most likely occurs through phosphate binding at two types of active sorption sites. P adsorption by the studied lake sediment during experiments was significantly connected to aluminum content in sediment. The research into the adsorption properties of sediment can be used as a tool for the evaluation of lake restoration effects.

Keywords: lake; sediment; phosphorus sorption; lake restoration; phosphorus inactivation; artificial mixing

1. Introduction

Currently, one of the biggest environmental problems is the constantly deteriorating surface water quality, resulting from the industrial revolution and a qualitative leap in improving the hygienic conditions of households and the growing human population [1,2]. Water bodies located in the direct vicinity of human settlements have very often been the victims of avalanche degradation resulting from the discharge of untreated municipal or industrial sewage. There have been many cases in the world of urban lakes transforming into hypertrophic and even saprotrophic water bodies [3–7].

In the case of the observed continuous deterioration of water quality in water bodies, the first absolutely necessary actions are to cut off the point sources of nutrients, the treatment of stormwater entering into lake, and the implementation of proper practices in land use (e.g., changes in cropland management practices and the promotion of particular crop types). Particularly, agriculture is a serious nutrient source for lakes and rivers, and in the case of water bodies with huge, agricultural catchments,

it is very difficult to maintain good water quality. However, if these actions will be carried out, it is possible to observe a positive influence on lake water quality [8–11].

It should be emphasized that protective measures in the catchment should be performed before any other technical action directly in the lake bowl. Results should be monitored, and in the case, that such protective measures are not sufficient in the fight against negative eutrophication symptoms, technical solutions should be taken into consideration. This allows us to decrease the costs of the whole technical action [8,9,11]. In many cases, the only chance to stop or to reverse the eutrophication process in degraded lakes is to apply appropriate technical methods in the lake bowl [5–7,12,13]. These techniques are defined by Pan et al. [14] and Mackay et al. [15] as geoengineering. The main goal of geoengineering is to manipulate biogeochemical processes in order to obtain the improvement of a lake's ecological structure and function.

The phenomenon of internal nutrient loading in lakes is a serious barrier that can have a negative impact on the effects of restoration measures [16]. One of the popular methods used for the limitation of internal phosphorus loading is phosphorus inactivation [5,6,12,17].

The principle of this method is the addition of the factor eliminating phosphorus from the lake water and increasing the sediment P sorption capacity. Salts of iron, aluminum, calcium, zirconium or lanthanum are the coagulants used for this purpose. Also, a wide spectrum of solid materials (e.g., naturally occurring minerals or soils, synthetically produced materials, modified clays and soils or industrial by-products) can be used as P adsorbents [18,19]. These compounds can be dosed into lake water, or directly to the water-sediment interface [5,6,12,20–26]. In the case of degraded lakes in which there is thermal stratification, the anoxia occurring in hypolimnetic water promotes the intensification of the internal loading phenomenon. In such cases, aluminum salts are the most economically attractive option for lake treatment. Aluminum-phosphate complexes are insensitive to changes in redox potential in the anoxic bottom zone, while the main factor destroying aluminum-phosphate complexes is pH change [12,17]. Because of the fact that a phenomenon of sedimentation and the creation of a new layer of bottom sediment continuously occurs, the “active” sediment layer (a product of treatment) is covered with new sediment. Cooke et al. [17], Lewandowski et al. [23] and Rydin [24] maintain that phosphorus bound during inactivation remains permanently buried in the sediment. However, Reitzel et al. [27] and van Hullebush et al. [28] pay attention to the fact that, in shallow lakes, the sediment resuspension together with an increase in pH can dissolve aluminum-phosphate complexes and destroy the “active” layer. However, in stratified lakes the “active” layer should theoretically bind phosphorus under stable pH conditions until the sorption active sites are exhausted.

One of the most important questions in every lake restoration case are: how long its positive effects will persist and what factors can steer that persistence.

Thus, the aims of this study were as follows:

1. To determine the sorption characteristics of Długie Lake sediment;
2. To determine whether implemented lake restoration methods influenced P adsorption by sediment;
3. To determine whether the “active” layer of sediment (enriched with aluminum) produced during restoration (completed in 2003 year) still has a higher sorption capacity in relation to phosphorus.

2. Material and Methods

2.1. Lake Description

The object of the study was Długie Lake (area 0.268 km², max. depth 17.3 m), located in the western part of Olsztyn city (Olsztyńskie Lakeland, Poland). It is a seepage type of lake, without natural inflows and outflows. Długie Lake has been massively polluted by raw sewage input, which occurred in the second half of 20th century for twenty years (1956–1976). As the result of that pollution, the lake was transformed into a saprotrophic lake type [5,6,29]. The sewage inflow cut off (in 1976) did not result in the improvement of lake water quality, because of the internal loading phenomenon taking place in the lake. Then, it was obvious that the implementation of restoration techniques was the only way to

obtain better water quality. Two technical restoration methods were successfully applied on Długie Lake: an artificial mixing method with the complete destratification of lake water (1987–1989 and 1991–2000 periods) and phosphorus inactivation method using an aluminum coagulant–polyaluminum chloride PAX 18 (2001–2003 period). The total pure aluminum dose per m^2 was equal 20.25 g m^{-2} [6]. The second restoration technique was supported with biomanipulation (the introduction of predatory fish species such as pike-perch (*Sander lucioperca* L.) and pike (*Esox lucius* L.)), which was implemented in cooperation with fishing users of the lake (Polish Angling Association).

2.2. Sampling

Dissolved oxygen content in the near-bottom water was measured using the probe ProOdo YSI Inc. (Yellow Springs, OH, USA).

The undisturbed bottom sediment cores were taken using Kajak's bottom sampler at November 2018 at three stations, localized at the deepest points of three separated lake parts (St. 1: the shallowest southern basin of the lake; St. 2: the deepest middle part of the lake; and St. 3: the northern basin of the lake) (Figure 1). At every station three cores were taken. Sediment cores (20 cm long) were immediately divided into four layers (0–5 cm, 5–10 cm, 10–15 cm and 15–20 cm). Lake water for further laboratory experiments was taken into 5 dm^3 tanks.

2.3. Water Analyses

After transportation to the laboratory sediment samples were subjected to centrifugation (3000 rpm, $t = 20 \text{ min.}$, MPW-351 centrifuge, MPW Med Instruments, Warsaw, Poland) for interstitial water separation. Water phosphorus forms (mineral, total and organic), nitrogen forms (ammonia, total and organic), iron and manganese were measured (Nanocolor spectrophotometer by Macherey-Nagel (GmbH&Co. KG, Düren, Germany), Spectroquant Prove 100 by Merck (KGaA, Darmstadt, Germany), and IL 550 TOC-TN analyzer by HACH Inc. (Loveland, CO, USA)). Lake water used for experiments was also analyzed (mineral P and total phosphorus (TP) by molybdenum blue method using Nanocolor spectrophotometer by Macherey-Nagel (GmbH&Co. KG, Düren, Germany); pH and conductivity by HQ 40 d multi probe by HACH Inc. (Loveland, CO, USA)).

2.4. Sorption Laboratory Experiment

Two grams of fresh sediment aliquots (in triplicates) were placed in the 50 cm^3 Falcon type centrifuge tubes and phosphate solutions (25 cm^3) were added (P concentrations of 0.00; 0.15; 0.30; 0.60; 1.20; 2.40 mg dm^{-3}). Two drops of chloroform were added to inhibit bacteria activity [30–32]. The centrifuge tubes were shaken in an orbital shaker at 250 rpm (Innova 40 incubator by New Brunswick Scientific Co. Inc., Edison, NJ, USA) at the constant temperature of $20 \text{ }^\circ\text{C}$. After 24 h of equilibration, the solutions were centrifuged at 4000 rpm for 10 min (Rotina 420, Andreas Hettich GmbH&Co. KG, Tuttlingen, Germany) and the supernatants were decanted and filtered through a $0.45 \text{ }\mu\text{m}$ 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.

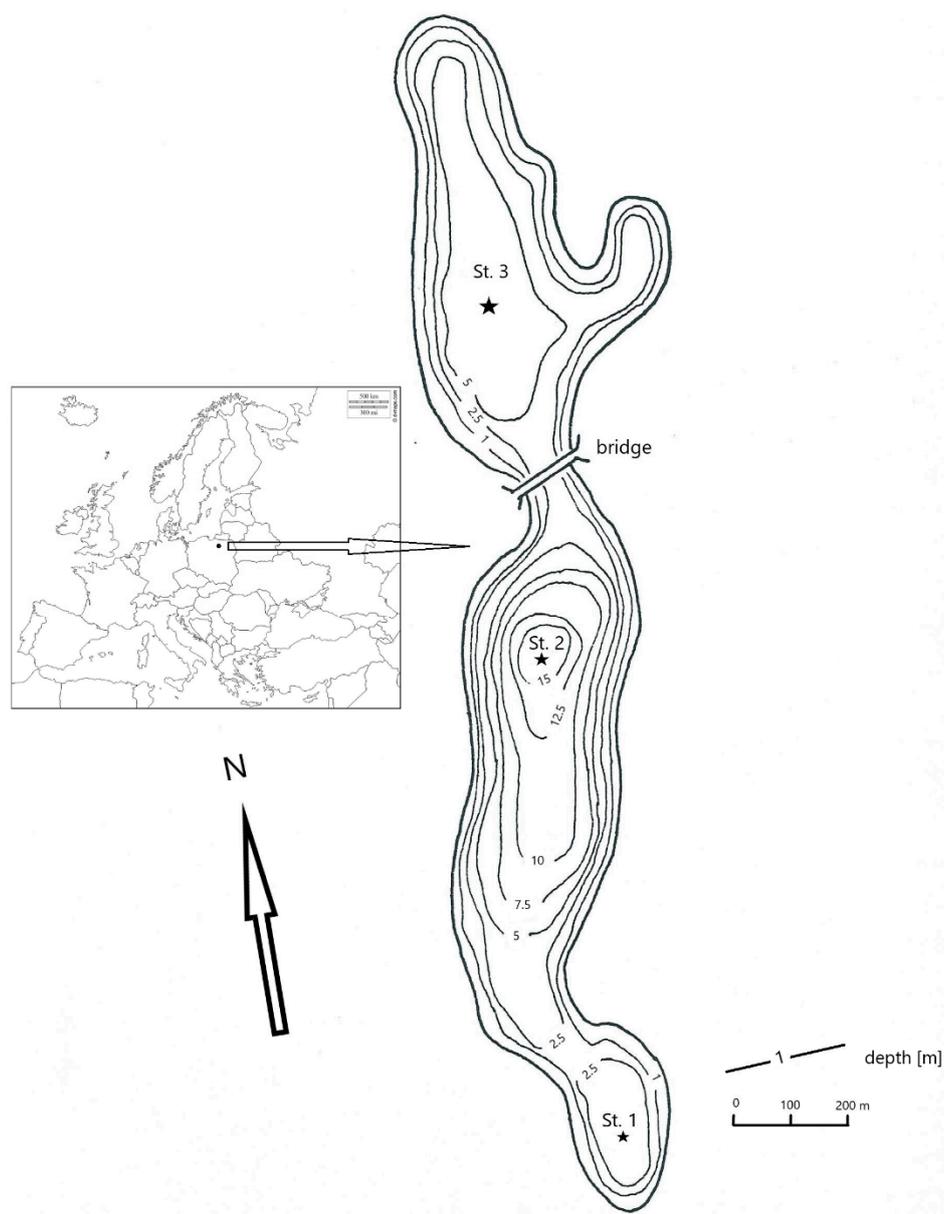


Figure 1. Location of research stations on Długie Lake (source: Inland Fisheries Institute in Olsztyn, d-maps.com).

2.5. Estimation of Sorption Parameters

Obtained results were fitted to the Langmuir sorption model,

$$S = \frac{S_{max} \times k \times C}{1 + k C} \quad (1)$$

and double Langmuir model,

$$S = \frac{S_1 \times k_1 \times C}{1 + k_1 \times C} + \frac{S_2 \times k_2 \times C}{1 + k_2 \times C} \quad (2)$$

where:

C—phosphorus concentration after the 24-h equilibration procedure (mg dm^{-3});

S—total phosphorus adsorbed by sediment (solid phase), ($\text{mg kg}^{-1} \text{ dw}$);

$$S = S_0 + S' \quad (3)$$

S_0 —native sorbed phosphorus

the phosphorus pool, which was desorbed at an initial concentration of 0 mg P dm^{-3} ($\text{mg kg}^{-1} \text{ dw}$);

S' —phosphorus amount adsorbed during experiment, ($\text{mg kg}^{-1} \text{ dw}$);

S_{max} —maximum sorption capacity of sediment in the Langmuir equation ($\text{mg kg}^{-1} \text{ dw}$);

k —constant related to bonding energy in the Langmuir equation ($\text{dm}^3 \text{ mg}^{-1}$).

S_1 —maximum sorption capacity of sediment in the double Langmuir equation (type I active sites) ($\text{mg kg}^{-1} \text{ dw}$);

S_2 —maximum sorption capacity of sediment in the double Langmuir equation (type II active sites) ($\text{mg kg}^{-1} \text{ dw}$);

S_{max2} —the total sorption capacity of sediment in the double Langmuir equation (the sum of S_1 and S_2 maximum sorption capacities) ($\text{mg kg}^{-1} \text{ dw}$)

$$S_{max2} = S_1 + S_2 \quad (4)$$

k_1, k_2 —constants related to the bonding energy in the double Langmuir equation ($\text{dm}^3 \text{ mg}^{-1}$).

These equations coefficients ($k, S_{max}, S_1, k_1, S_2, k_2, S_{max2}$) were estimated using a non-linear estimation method [33–36] via the Statistica software package 13.0 (Tibco Software Inc., Palo Alto, CA, USA) [37].

The coefficient of determination R^2 was assumed to be the measure of the curve fitting at the determined parameters to the experimental data.

The Freundlich model coefficients also were assessed using the non-linear estimation method [33–37]:

$$S = K_f \times C^{\frac{1}{n}} \quad (5)$$

where:

S, C —as in the Equation (1);

K_f —Freundlich sorption constant ($\text{dm}^3 \text{ kg}^{-1}$);

$1/n$ —a constant which characterizes the heterogeneity of the adsorption process.

EPC_0 parameter was assessed using the Freundlich equation with correction for desorbed phosphorus ($-S_0$) at the initial experimental concentration (0 mg P dm^{-3}) [38]:

$$S = \left(K_f \times C^{\frac{1}{n}} \right) - S_0 \quad (6)$$

The Gibbs free energy change was calculated using formula [39]:

$$-\Delta G_{ads} = RT \ln K_d \quad (7)$$

where:

K_d —division coefficient ($\text{dm}^3 \text{ kg}^{-1}$);

R —gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$);

T —temperature (K).

2.6. Sediment Analyses

In non-centrifuged sediment samples the water content and solid matter were measured after drying at $105 \text{ }^\circ\text{C}$ (Barnstead Thermolyne 62700 Furnace, Barnstead International, Dubuque, IA, USA) until a constant weight was reached.

The sediment chemical composition included organic matter as a loss of ignition at $550 \text{ }^\circ\text{C}$ after carbonate regeneration (using CO_2 saturated deionized water), and carbonates (as CO_2) after ignition at $1000 \text{ }^\circ\text{C}$ (Barnstead Thermolyne 62700 Furnace, Barnstead International, Dubuque, IA,

USA). The sediment samples were mineralized with a mixture of H_2SO_4 , $HClO_4$ and HNO_3 (1 + 2 + 3). After mineralization, the sample was filtered through ash-free filter No 390. The remains on the filter were treated as silica and mineralized at 900 °C. In the filtrate the consecutive parameters were measured spectrophotometrically (Spectroquant Prove 100 by Merck KGaA, Darmstadt, Germany): iron, aluminum, manganese, calcium, magnesium. Total nitrogen (TN) was analyzed by Kjeldahl method (using a BÜCHI K-425 unit, B-24 distillation unit, BÜCHI Labortechnik AG, Flawil, Switzerland).

Sediment phosphorus fractions were analyzed according to scheme proposed by [30]. Mineral P content in the extracts was analyzed with the molybdenum blue method (Nanocolor spectrophotometer by Macherey—Nagel, GmbH&Co. KG, Düren, Germany)

3. Statistical Analysis

The results were subjected to statistical analysis using the Statistica 13.0 Software package [37]. The multiple regression analysis [40] was performed in order to identify chemical factors (independent variables—bottom sediment chemical components: Si, organic matter, Fe, Al, Mn, Ca, Mg, Mn), which are significantly connected to the estimated sorption parameters (dependent variables: S_{max} , k , S_1 , k_1 , S_2 , k_2 , S_{max2} , $1/n$, K_f , EPC_0 , S_0). That analysis allowed to obtain the linear models type:

$$Y = B_0 \pm B_1 X_1 \pm B_2 X_2 \pm \dots \pm B_i X_i + E_{ij} \quad (8)$$

where:

Y —dependent variable (in the present research, the particular sorption characteristic in the Freundlich, Langmuir or double Langmuir model);

B_0 —constant (intercept);

$B_1 \dots B_i$ —regression coefficients;

$X_1 \dots X_i$ —independent variables (bottom sediment chemical components: Si, organic matter, Fe, Al, Mn, Ca, Mg, Mn);

E_{ij} —residual component;

R —multiple correlation coefficient;

R^2 —multiple determination coefficient.

All results were subjected to log transformation in order to approximate of the data to the normal distribution.

4. Results

4.1. Sorption Parameters

The relationship between the equilibrium concentration (C_e) and the amount of adsorbed phosphates is shown in Figures 2–4. The amount of adsorbed phosphorus (S) increased with increasing concentrations of equilibrium phosphorus (C_e). The surface layer of the sediment usually showed a greater sorption capacity than the deeper layers. The largest amount of phosphates was adsorbed by sediments from the layer of 5–10 cm at Station 2—356.39 mg P kg⁻¹ dw, while the weakest sorption capacity with respect to phosphorus was shown by sediment taken at St. 1—202.47 mg P kg⁻¹ dw (sediment layer 0–5 cm).

The obtained real adsorption results fitted well to all tested adsorption models. The values of the determination coefficient R^2 were in the range from 0.93 (Freundlich model for sediment layers, 10–15 cm and 15–20 cm; and double Langmuir model for sediment layer, 10–15 cm at St. 1) to 1.00 (double Langmuir model for sediment layer, 0–5 cm, St. 1). The double Langmuir model usually showed the best fit to experimental data, in that R^2 values usually were higher for that model than for two other models (Tables 1 and 2).

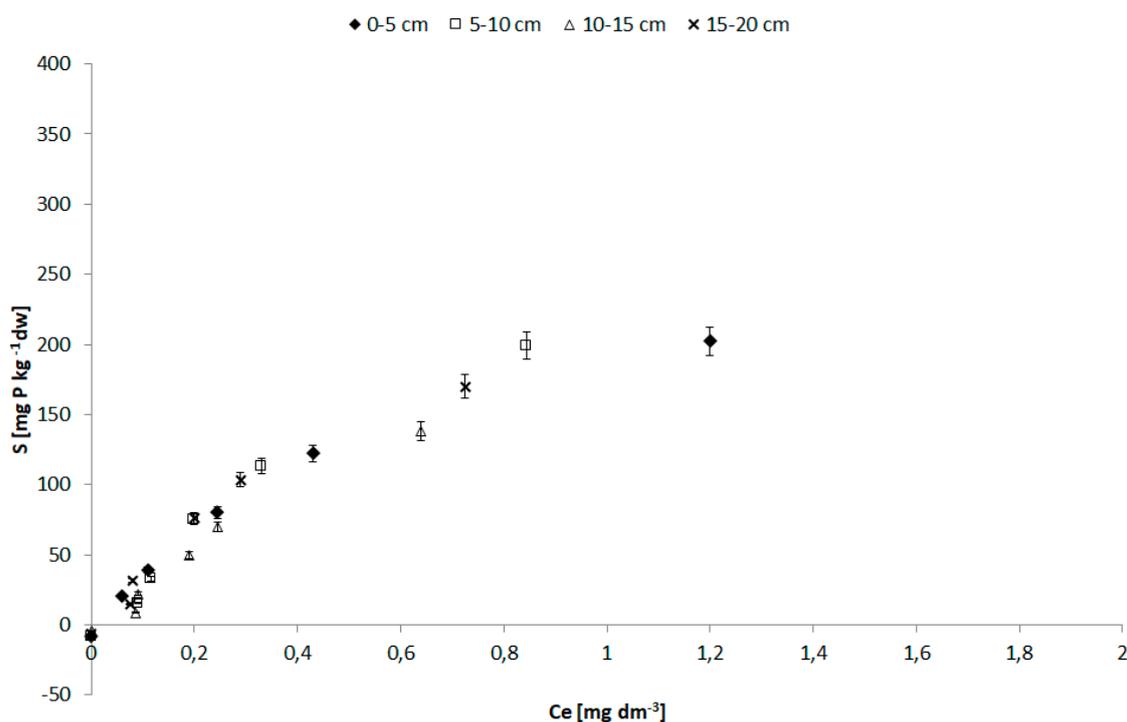


Figure 2. The P adsorption isotherms for sediment taken at St. 1.

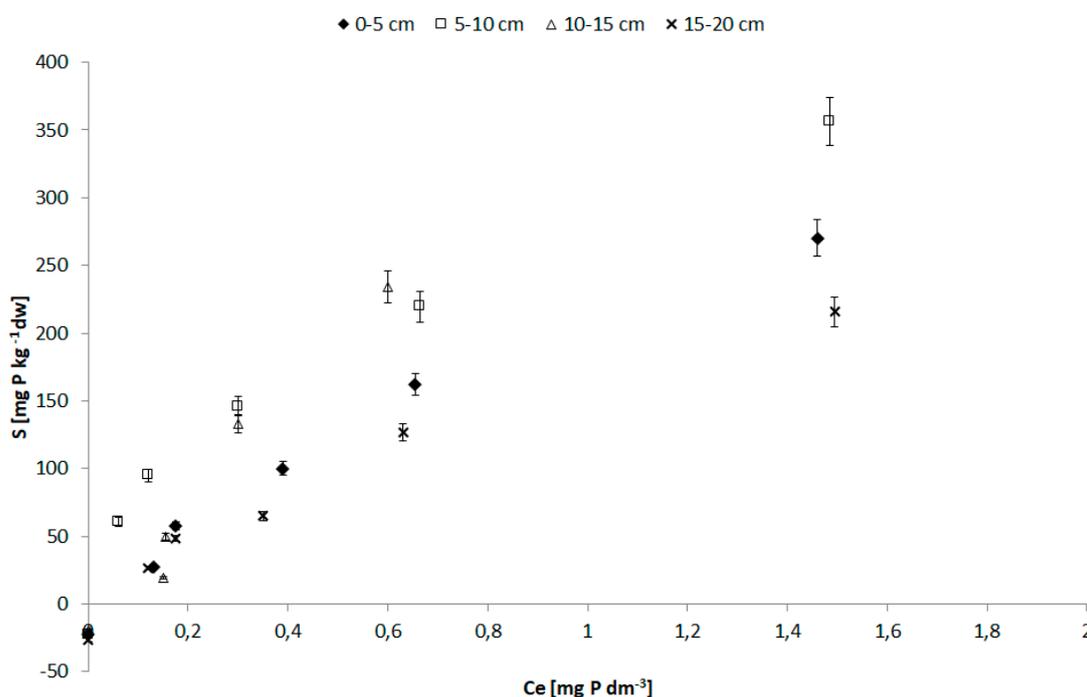


Figure 3. The P adsorption isotherms for sediment taken at St. 2.

The values of the maximum P sorption capacity (S_{max}) obtained from the Langmuir model were varied. The highest value of S_{max} ($524.2 \text{ mg P kg}^{-1} \text{ dw}$) was noted for the sediment layer 15–20 cm (St. 2) (Table 1). The sediment taken at St. 3 had the lowest S_{max} (between 241.7 and $279.0 \text{ mg P kg}^{-1} \text{ dw}$) (Table 1). Also, k coefficient values (the constant from Langmuir equation referring to the binding energy, expressed in $\text{dm}^3 \text{ mg}^{-1}$) were varied, but generally the highest values were observed for the surficial sediment layers (0–5 cm) at all three research stations. The highest k value was calculated for

sediment taken at St. 3 ($3.74 \text{ dm}^3 \text{ mg}^{-1}$ - sediment layer 0–5 cm), whilst the lowest $-0.62 \text{ dm}^3 \text{ mg}^{-1}$ —at St. 1 (sediment layer 10–15 cm) (Table 2).

The values of the correction factor from the Freundlich equation ($1/n$), which characterize the heterogeneity of the adsorption process ranged from 0.4276 (St. 3, sediment layer, 0–5 cm) to 0.8476 (St. 1, sediment layer, 10–15 cm) (Table 2). The minimum value of the partition coefficient from the Freundlich equation (K_f) was assessed for bottom sediment taken at St. 3 (sediment layer 15–20 cm) and it amounted to $116.0 \text{ dm}^3 \text{ kg}^{-1}$, whilst the maximum K_f value was calculated for the surficial sediment layer, (0–5 cm) taken at the deepest St. 2 ($309.7 \text{ dm}^3 \text{ kg}^{-1}$) (Table 2).

The assessed P equilibrium concentration (EPC_0) ranged from $0.001 \text{ mg P dm}^{-3}$ (St. 3, sediment layer, 0–5 cm) to $0.059 \text{ mg P dm}^{-3}$ (at the same station, sediment layer, 10–15 cm).

“Native sorbed phosphorus” (S_0) values were the highest for sediment layer 10–15 cm taken at St. 3— $27.36 \text{ mg kg}^{-1} \text{ dw}$ —and the lowest for sediment taken at St. 1 (sediment layer 10–15 cm)— $4.62 \text{ mg kg}^{-1} \text{ dw}$.

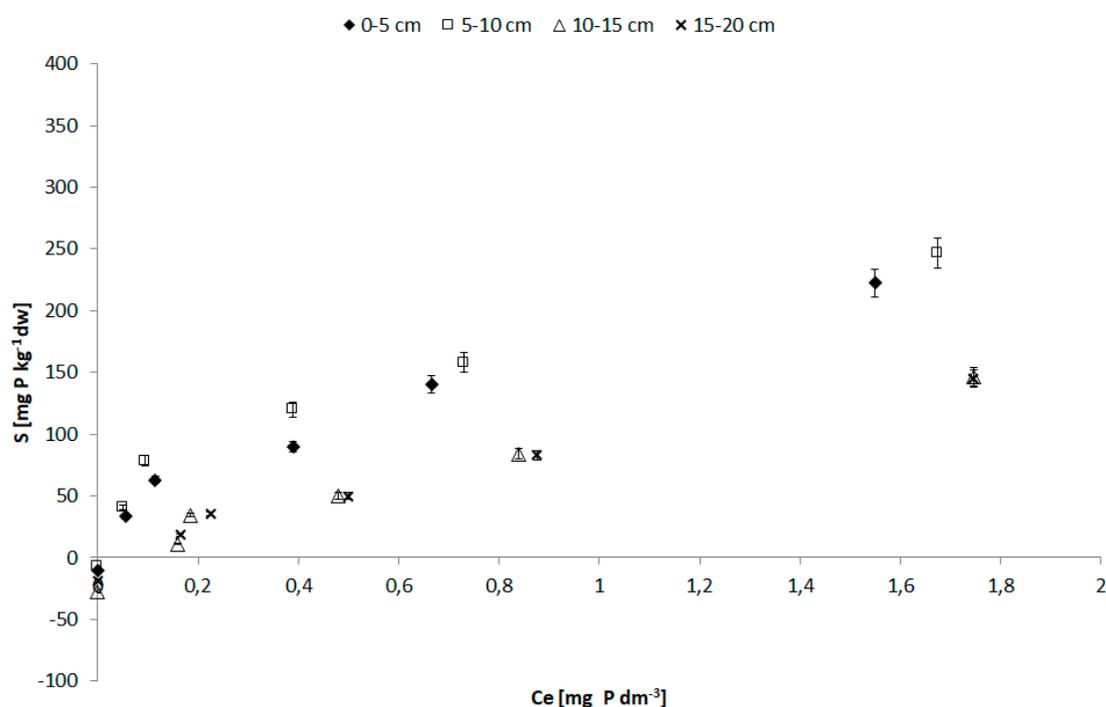


Figure 4. The P adsorption isotherms for sediment taken at St. 3.

Table 1. The assessed values of Langmuir sorption model characteristics for profundal bottom sediment of Długie Lake.

Station	Sediment Layer	Langmuir Model			Double Langmuir Model					
		S_{max} (mg kg^{-1})	k ($\text{dm}^3 \text{ mg}^{-1}$)	R^2	S_1 (mg kg^{-1})	k_1 ($\text{dm}^3 \text{ mg}^{-1}$)	S_2 (mg kg^{-1})	k_2 ($\text{dm}^3 \text{ mg}^{-1}$)	S_{max2} (mg kg^{-1})	R^2
St. 1	0–5 cm	320.0	1.60	0.99	319.91	1.53	3.11	11.32	323.0	1.00
	5–10 cm	470.5	0.94	0.96	229.35	0.93	241.11	0.94	470.5	0.96
	10–15 cm	497.7	0.62	0.93	218.30	1.02	927.69	0.10	1146.0	0.93
	15–20 cm	325.4	1.61	0.95	163.36	1.62	161.97	1.61	325.3	0.95
St. 2	0–5 cm	375.9	1.05	0.98	534.3	0.24	106.61	3.47	640.9	0.99
	5–10 cm	458.8	2.39	0.94	109.8	32.43	1178.18	0.202	1288.0	0.99
	10–15 cm	508.3	0.91	0.99	1212.89	0.08	224.1	1.92	1437.0	0.99
	15–20 cm	524.2	0.71	0.97	16.4	12.65	601.74	0.501	618.14	0.98
St. 3	0–5 cm	269.2	3.74	0.93	470.3	0.357	65.86	27.7	535.9	0.99
	5–10 cm	279.0	2.44	0.95	98.66	16.04	2066.9	0.047	2165.6	0.99
	10–15 cm	241.7	1.27	0.94	1155.6	0.067	54.7	12.206	1210.3	0.97
	15–20 cm	254.2	0.94	0.95	38.2	20.81	1303.9	0.061	1342.1	0.98

Table 2. The assessed values of the Freundlich sorption model characteristics, “native sorbed phosphorus” values and Gibbs free energy for profundal bottom sediment of Długie Lake.

Station	Sediment Layer	Freundlich Model					
		1/n	K_f ($\text{dm}^3 \text{kg}^{-1}$)	R^2	EPC_0 (mg dm^{-3})	S_0 (mg kg^{-1})	ΔG_{ads}
St. 1	0–5 cm	0.5875	192.9	0.98	0.004	8.02	−13.72
	5–10 cm	0.7545	239.4	0.95	0.012	8.32	−13.48
	10–15 cm	0.8476	210.2	0.93	0.011	4.62	−12.92
	15–20 cm	0.6840	222.2	0.93	0.006	6.36	−13.78
St. 2	0–5 cm	0.4771	309.7	0.99	0.004	22.96	−15.17
	5–10 cm	0.6429	231.9	0.98	0.027	22.63	−13.32
	10–15 cm	0.6090	183.5	0.98	0.020	16.81	−12.98
	15–20 cm	0.7045	212.0	0.97	0.033	19.31	−12.93
St. 3	0–5 cm	0.4276	199.7	0.98	0.001	7.21	−14.49
	5–10 cm	0.4712	187.8	0.98	0.002	10.53	−14.06
	10–15 cm	0.5432	126.9	0.97	0.059	27.36	−11.23
	15–20 cm	0.5898	116.0	0.97	0.046	18.92	−11.40

Assessed mean Gibbs’ free energy change values were negative and ranged from $-11.23 \text{ kJ mol}^{-1}$ (St. 3, sediment layer, 15–20 cm) to $-15.17 \text{ kJ mol}^{-1}$ (St. 2, sediment layer, 0–5 cm). They often increased with sediment depth (Table 2).

The conductivity, pH, and phosphate concentration of the lake water used for experiments were $260 \mu\text{S cm}^{-1}$, 7.71, and $0.007 \text{ mg P-PO}_4 \text{ dm}^{-3}$, respectively. These values were taken into consideration during the experiment’s final results calculation.

The multiple regression analysis [40] was performed in order to identify sediment chemical components (especially Al content, as a factor used for lake restoration), which are significantly connected to estimated sorption parameters. The results are shown in Table 3. The sorption characteristics were dependent on OM, Fe, Mn, Si and Mg. The sorption capacities from Langmuir models (S_{max} , S_2 and S_{max2}) were significantly dependent on Al content in sediment. Also, the constants $1/n$, k_2 and EPC_0 parameter were significantly connected to Al content in sediment (Table 3).

Table 3. Multiple regression analysis of P sorption parameters depending on bottom sediment chemical composition ($n = 12$, $p \leq 0.1$, raw data was log transformed).

Fitted Model Equation	R	R ²
$S_{max} = 1.969 \text{ Fe}_{\text{sed}} + 1.644 \text{ Al}_{\text{sed}} + E_{ij}$ k—non significant	0.885	0.782
$S_0 = 5.289 - 3.622 \text{ Si}_{\text{sed}} + 2.792 \text{ Fe}_{\text{sed}} - 4.471 \text{ Mn}_{\text{sed}} + E_{ij}$	0.967	0.935
$1/n = 0.389 \text{ Al}_{\text{sed}} + E_{ij}$	0.952	0.907
$K_f = 1.514 + 1.063 \text{ Fe}_{\text{sed}} - 1.145 \text{ Mg}_{\text{sed}} + E_{ij}$	0.670	0.450
$EPC_0 = -0.463 - 0.327 \text{ Mn}_{\text{sed}} + 0.166 \text{ Mg}_{\text{sed}} + 0.14 \text{ OM}_{\text{sed}} - 0.095 \text{ Al}_{\text{sed}} + E_{ij}$ S_1 —non significant k_1 —non significant	0.924	0.854
$S_2 = 13.253 \text{ Al}_{\text{sed}} + E_{ij}$	0.695	0.480
$k_2 = -14.566 \text{ Al}_{\text{sed}} + E_{ij}$	0.875	0.767
$S_{max2} = -42.279 + 7.371 \text{ Al}_{\text{sed}} + 6.985 \text{ OM}_{\text{sed}} + 8.523 \text{ Si}_{\text{sed}} + E_{ij}$	0.965	0.931

(Fe_{sed} : iron content in sediment, Al_{sed} : aluminum content in sediment, Mn_{sed} : manganese content in sediment, OM_{sed} : organic matter content in sediment, Mg_{sed} : magnesium content in sediment, Si: silica content in sediment; all in mg g^{-1} dw).

4.2. Water

During the research, dissolved oxygen was present in the near-bottom water at two shallow stations (9.5 mg O₂ dm⁻³ at St. 1 and 9.6 mg O₂ dm⁻³ at St. 3), whilst anoxia was noted at the deepest part of Długie Lake (St. 2).

The phosphorus form concentration in the water medium of the water–sediment interface was different at particular research stations. At two shallow stations (St. 1 and St. 3), the noted concentration of TP, min P and org P was lower than at the deepest St. 2. The minimum TP value was observed at St. 3 (1.02 mg P dm⁻³, surficial layer 0–5 cm) whilst the maximum TP amount (4.1 mg P dm⁻³) was noted at the deepest layer of analyzed water (15–20 cm) (Figure 2). The organic P form dominated quantitatively in the near-bottom water at all three research stations and in interstitial water at two shallow stations (St. 1 and 3). The mineral P form share was generally higher in the interstitial water at St. 2. It is worth noting that the clear decrease of P concentration (both P forms—mineral and organic) occurred in the layer of 10–15 cm at the St. 1 and 2, whilst concentration rose with the sediment depth at St. 3 (Figure 5).

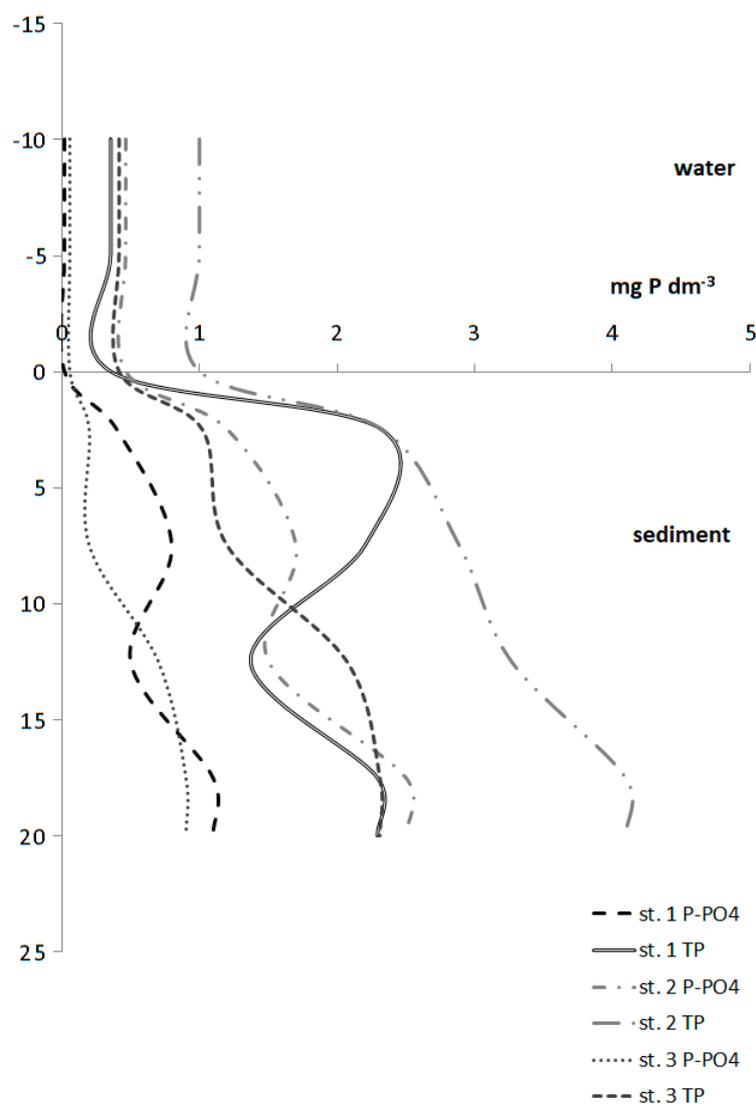


Figure 5. The total phosphorus (TP) and mineral P profiles in the water–sediment interface of Długie Lake.

Nitrogen compound concentrations were varied at the research stations. At the deepest St. 2, the nitrogen concentration in near-bottom water was the highest ($20.43 \text{ mg N dm}^{-3}$), and it was much lower at the two shallow stations ($0.68 \text{ mg N dm}^{-3}$ and $2.50 \text{ mg N dm}^{-3}$ at St. 1 and 3, respectively). In the near-bottom water, the organic form of N quantitatively dominated, whilst the share of mineral N (ammonia) rose with the sediment depth in the interstitial water at all research stations. The TN concentration observed in the interstitial water was the highest at the deepest Station 2 (max $30.3 \text{ mg N dm}^{-3}$, layer 5–10 cm), and the lowest TN amount occurred at St. 1 (min $2.06 \text{ mg N dm}^{-3}$, layer 0–5 cm) (Figure 6).

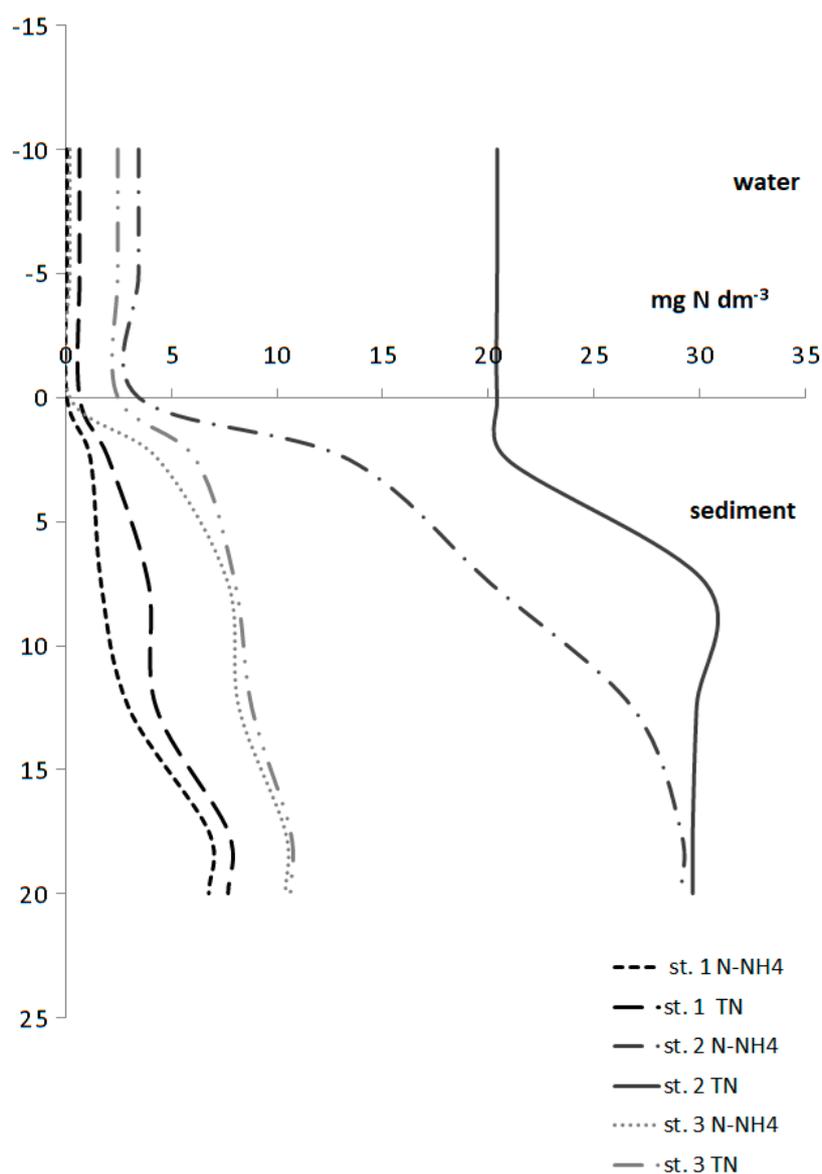


Figure 6. The total nitrogen (TN) and ammonia profiles in the water-sediment interface of Długie Lake.

Fe and Mn amounts observed in the water-sediment interface ranged from $0.02 \text{ mg Fe dm}^{-3}$ and $0.04 \text{ mg Mn dm}^{-3}$ (near-bottom water at St. 1) to $3.60 \text{ mg Fe dm}^{-3}$ and $3.50 \text{ mg Mn dm}^{-3}$ (interstitial water at St. 2, layer 15–20 cm) (Figure 7).

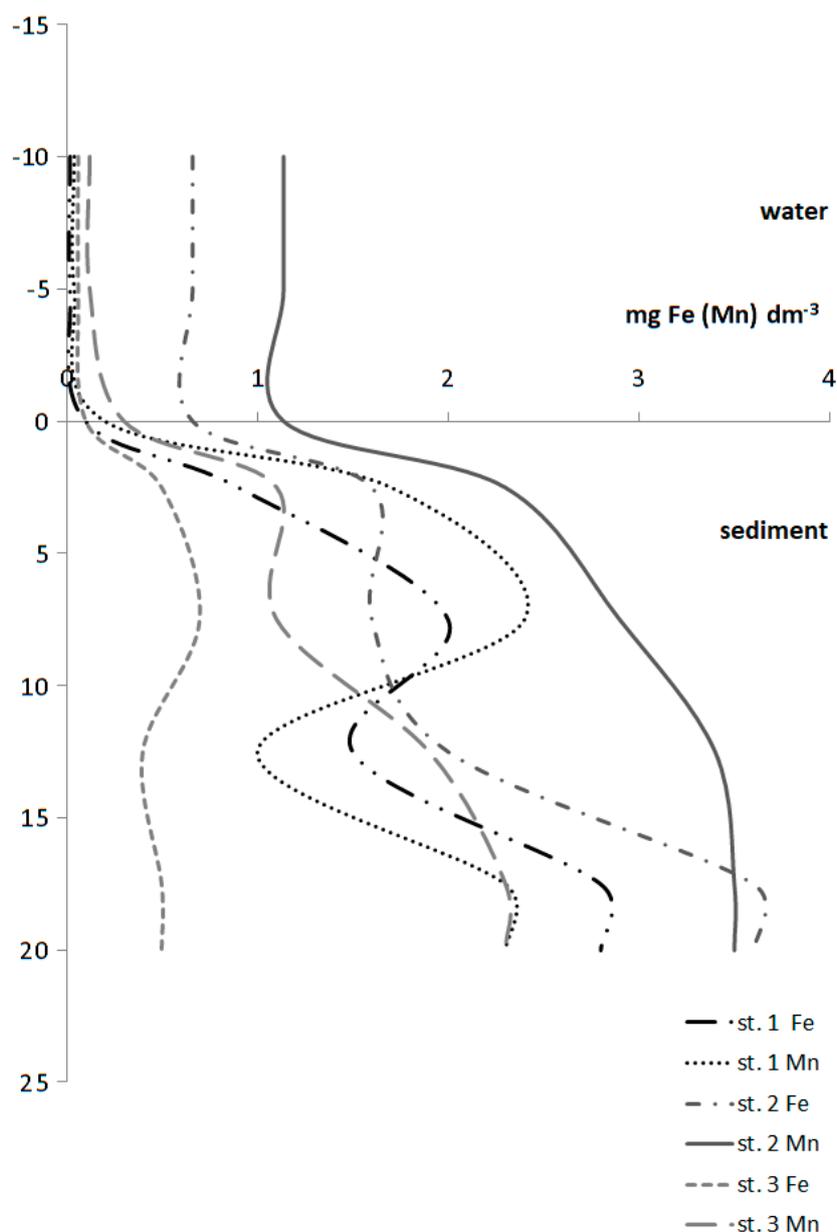


Figure 7. The Fe and Mn profiles in the water-sediment interface of Długie Lake.

4.3. Sediment Chemical Composition

The sediment of Długie Lake was highly hydrated: the percentage of dry weight was mainly below the level of 10% dw (except for the two deeper sediment layers at St. 1, at 15.59% dw and 11.24% dw) (Table 4). This can be classified as the mixed silica–organic type (St. 1) and organic–silica type (St. 2). The share of organic matter exceeded 50% dw at St. 3 only (except the deepest sediment layer 15–20 cm), and in general, the sediment can be classified as organic type. The rest of the analyzed components occurred in low amounts, not exceeding several percentage of dw (Table 4). The aluminum content, particularly considered as a factor used for phosphorus inactivation, was the highest in the deeper sediment layers (10–15 cm at St. 1 and 2 and 5–10 cm at St. 3), whilst the maximum Al content was noted in sediment taken at St. 3 (18.95 ± 1.72 mg Al g^{-1} dw in the layer 5–10 cm) and St. 2 (18.90 ± 1.33 mg Al g^{-1} dw in the layer 10–15 cm) (Table 4).

Table 4. The mean (\pm SD) values of main components of Długie Lake sediment (in mg g^{-1} d.w.).

Station	Sediment Layer	OM	Si	IC	Fe	Al	Ca	Mg	Mn	TN	% dw
St. 1	0–5 cm	326.26 \pm 12.51	220.61 \pm 3.94	9.25 \pm 0.61	22.58 \pm 2.46	12.75 \pm 0.85	18.40 \pm 2.09	5.94 \pm 0.51	0.36 \pm 0.04	16.16 \pm 0.65	7.58
	5–10 cm	311.40 \pm 12.33	227.22 \pm 3.99	10.08 \pm 0.72	26.56 \pm 2.54	13.08 \pm 0.81	21.70 \pm 2.15	5.18 \pm 0.63	0.31 \pm 0.03	15.45 \pm 0.46	9.86
	10–15 cm	305.43 \pm 12.26	228.72 \pm 4.23	10.19 \pm 0.82	21.04 \pm 2.02	14.57 \pm 0.89	18.39 \pm 2.18	6.10 \pm 0.92	0.29 \pm 0.03	15.09 \pm 0.56	15.59
	15–20 cm	296.49 \pm 12.18	229.08 \pm 4.24	10.72 \pm 0.88	21.82 \pm 2.08	12.87 \pm 0.81	22.28 \pm 2.03	5.10 \pm 0.99	0.26 \pm 0.03	14.63 \pm 0.72	11.24
St. 2	0–5 cm	498.06 \pm 23.77	137.25 \pm 10.27	9.65 \pm 0.59	18.91 \pm 1.26	15.39 \pm 1.53	17.40 \pm 1.21	4.05 \pm 1.02	0.28 \pm 0.07	27.71 \pm 0.72	3.10
	5–10 cm	463.74 \pm 22.58	145.60 \pm 10.83	9.82 \pm 0.63	19.97 \pm 1.28	17.33 \pm 1.25	16.00 \pm 1.15	5.44 \pm 0.99	0.27 \pm 0.04	26.29 \pm 0.81	4.33
	10–15 cm	455.18 \pm 23.24	146.07 \pm 11.03	10.38 \pm 0.78	20.58 \pm 1.33	18.90 \pm 1.33	16.49 \pm 1.18	6.94 \pm 0.92	0.41 \pm 0.04	26.97 \pm 0.68	5.35
	15–20 cm	442.68 \pm 22.86	161.84 \pm 11.26	8.97 \pm 0.62	21.96 \pm 1.44	16.16 \pm 1.28	14.49 \pm 1.03	8.15 \pm 1.20	0.39 \pm 0.05	25.99 \pm 0.24	6.02
St. 3	0–5 cm	511.92 \pm 13.57	135.29 \pm 7.83	8.81 \pm 0.25	15.27 \pm 1.63	15.77 \pm 1.62	16.11 \pm 1.28	5.43 \pm 0.51	0.49 \pm 0.12	29.91 \pm 1.05	3.48
	5–10 cm	511.20 \pm 13.78	133.61 \pm 7.96	8.86 \pm 0.27	14.21 \pm 1.28	18.95 \pm 1.72	19.09 \pm 1.36	4.30 \pm 0.23	0.28 \pm 0.09	29.36 \pm 0.99	4.61
	10–15 cm	502.98 \pm 12.98	135.94 \pm 8.03	9.24 \pm 0.18	16.47 \pm 1.33	16.79 \pm 1.27	17.16 \pm 1.32	5.34 \pm 0.33	0.26 \pm 0.06	29.08 \pm 0.81	5.87
	15–20 cm	482.78 \pm 12.23	150.41 \pm 8.23	9.31 \pm 0.21	17.94 \pm 1.81	15.32 \pm 1.27	16.78 \pm 1.22	5.00 \pm 0.56	0.23 \pm 0.09	27.46 \pm 0.90	6.38

4.4. Phosphorus Fractions

The total phosphorus content in the bottom sediment of Długie Lake was high and ranged from 3.786 ± 0.210 mg P g⁻¹ dw (St. 1, sediment layer 0–5 cm) to 6.505 ± 0.220 mg P g⁻¹ dw (St. 2, sediment layer 10–15 cm). The largest pool of sediment P was stored as a NaOH–nrP fraction (phosphorus bound to organic matter). The maximum amount of this P fraction was noted for sediment on St. 2 (2.338 ± 0.043 mg P g⁻¹ dw, 35.9% TP, sediment layer 10–15 cm), whilst the lowest of NaOH–nrP amount occurred at St. 1 (0.862 ± 0.012 mg P g⁻¹ dw, 22.7%TP, sediment layer 15–20 cm). The NaOH–rP fraction (P bound mainly to Al) was the second P fraction in terms of quantity. Its maximum amount was noted at St. 2 (2.298 ± 0.073 mg P g⁻¹ dw, 35.3%TP, sediment layer 10–15 cm) and the lowest was in the surficial sediment layer (0–5 cm) at the St. 3 (0.612 ± 0.007 mg P g⁻¹ dw). The HCl–P and res–P fractions included from 11.5%TP to 28.3%TP and from 10.6%TP to 26.3%TP, respectively. The most mobile P fractions (NH₄Cl–P and BD–P) occurred in the smallest amounts among the all P fractions, occupying ca. 1%TP and 2.4–3.6% TP, respectively.

5. Discussion

Artificial mixing was the first method of restoration, which was implemented on Długie Lake [5,6,29]. The direct impact of this method on the bottom zone was the improvement oxic conditions in the near-bottom water of aerated parts of Długie Lake (St. 2 and 3). Oxygen presence in that water stratum favored P binding by the sediment (the TP in water decreased and an increase of sediment TP was also observed, especially in the first period of aeration) [29]. Long-term artificial mixing caused the depletion of iron and manganese in the lake water, and this phenomenon was the limit for further P removal from Długie Lake water. In the present study, this stage of Długie Lake restoration was represented in the deepest layer of analyzed sediment cores (15–20 cm). The observed values of the sorption capacity of this sediment layer were mainly the lowest (Figures 2–4), and this was caused probably by diagenetic processes, which limit the direct P adsorption abilities [41].

The restoration of Długie Lake by the phosphorus inactivation method with the use of polyaluminum chloride PAX 18 caused an increase in the aluminum content in bottom sediment at all sites studied. Before P inactivation, Al amounts in sediment did not exceed ca. 12–14 mg Al g⁻¹ dw [42]. Maximum amounts of this element were detected in the sediment layer 10–15 cm (14.57 ± 0.89 mg Al g⁻¹ dw and 18.90 ± 1.33 mg Al g⁻¹ dw at St. 1 and 2, respectively) and 5–10 cm (18.95 ± 1.72 mg Al g⁻¹ dw at St. 3) (Table 4). This fact is in accordance with observations by other authors [17,23]. Sediments from these layers also had the highest NaOH–rP fraction contents (phosphorus bound to aluminum oxides and hydroxides: 1.028 ± 0.008 , 2.298 ± 0.073 and 0.735 ± 0.003 mg P g⁻¹ dw, at St. 1, 2 and 3, respectively (Table 5), which is undoubtedly the result of the restoration activities.

Oxic conditions in the lake in the bottom zone were varied: two shallow parts were well oxygenated, while the deepest lake part was anoxic for most of the year. In spite of that fact, the mineral phosphorus concentration noted in 2018 (15 years after the termination of the lake restoration procedure) amounted to 0.46 mg P dm⁻³ (Figure 5), and organic phosphorus was the dominant P form at all research stations. Before starting the restoration procedures on Długie Lake in 1987, the maximum phosphate concentration in the near-bottom water exceeded 2.80 mg P dm⁻³, and in 1999 (the year without artificial mixing), this was 1.2 mg P dm⁻³ [29].

The research by [43] showed that the phosphorus inactivation implemented on Długie Lake did not have a direct impact on the nitrogen compound content in the lake. Total nitrogen amounts were lower compared to the period before restoration, but this was a result of primary production limitation due to the phosphorus level decreasing. The nitrogen compound amounts observed during the present research in the near-bottom and interstitial water, as well as iron and manganese contents, were regulated by the oxygen level in the near-bottom water.

Table 5. The mean (\pm SD) values of phosphorus fractions and total phosphorus in Długie Lake sediment (in mg g^{-1} d.w.).

Station	Sediment Layer	$\text{NH}_4\text{Cl-P}$	BD-P	NaOH-rP	NaOH-nrP	HCl-P	res-P	TP
St. 1	0–5 cm	0.035 ± 0.006	0.136 ± 0.018	0.957 ± 0.006	1.263 ± 0.018	0.767 ± 0.018	0.628 ± 0.022	3.786 ± 0.210
	5–10 cm	0.025 ± 0.005	0.108 ± 0.016	0.893 ± 0.006	1.300 ± 0.012	0.879 ± 0.012	0.789 ± 0.019	4.129 ± 0.280
	10–15 cm	0.024 ± 0.005	0.104 ± 0.016	1.028 ± 0.008	1.371 ± 0.011	1.006 ± 0.014	0.788 ± 0.013	4.186 ± 0.160
	15–20 cm	0.034 ± 0.007	0.138 ± 0.018	0.924 ± 0.007	0.862 ± 0.012	1.074 ± 0.014	0.764 ± 0.015	3.796 ± 0.120
St. 2	0–5 cm	0.040 ± 0.003	0.162 ± 0.015	1.598 ± 0.062	1.948 ± 0.022	0.626 ± 0.015	0.778 ± 0.022	5.151 ± 0.340
	5–10 cm	0.045 ± 0.005	0.206 ± 0.016	2.100 ± 0.088	2.018 ± 0.025	0.882 ± 0.013	0.787 ± 0.030	6.237 ± 0.320
	10–15 cm	0.042 ± 0.004	0.215 ± 0.018	2.298 ± 0.073	2.338 ± 0.043	0.921 ± 0.020	0.692 ± 0.018	6.307 ± 0.220
	15–20 cm	0.040 ± 0.003	0.164 ± 0.013	0.839 ± 0.043	2.274 ± 0.032	0.836 ± 0.011	1.033 ± 0.015	5.187 ± 0.280
St. 3	0–5 cm	0.048 ± 0.004	0.137 ± 0.002	0.612 ± 0.007	1.860 ± 0.012	0.602 ± 0.012	1.164 ± 0.009	4.423 ± 0.130
	5–10 cm	0.051 ± 0.003	0.132 ± 0.003	0.735 ± 0.003	2.150 ± 0.014	0.552 ± 0.009	1.028 ± 0.011	4.572 ± 0.132
	10–15 cm	0.045 ± 0.003	0.130 ± 0.003	0.659 ± 0.006	2.219 ± 0.010	0.539 ± 0.008	1.099 ± 0.009	4.768 ± 0.180
	15–20 cm	0.046 ± 0.004	0.131 ± 0.002	0.650 ± 0.003	2.113 ± 0.011	0.602 ± 0.011	0.939 ± 0.008	4.481 ± 0.160

The experimentally obtained P adsorption results showed that the sediment taken at St. 2 had the highest sorption capacity. The largest amount of phosphates was adsorbed by sediments from the surface layer (5–10 cm) at Station 2, at 356.39 mg P kg⁻¹ dw, while the weakest sediment sorptive abilities with respect to phosphorus were shown by sediment taken at St. 1, at 202.47 mg P kg⁻¹ dw (Figures 2–4). These values are within the range recorded for the sediments of other Olsztyn lakes [44] or around the world [45–50]. The pH level during experiments was favorable for P adsorption processes onto sediment. The research conducted by [44] on five urban lakes, located in Olsztyn showed that alkaline pH (9.0) decreased the abilities of P adsorption in sediment, in which organic matter is a main component binding P. Assessed mean Gibbs' free energy change values were negative and ranged from −11.23 kJ mol⁻¹ (St. 3, sediment layer 15–20 cm) to −15.17 kJ mol⁻¹ (St. 2, sediment layer 0–5 cm). They often increased with sediment depth (Table 1). Assessed ΔG_{ads} values were similar in range to values observed in [46,48]. The negative ΔG_{ads} values noted during experiments confirm that P sorption was a spontaneous reaction [46] and the order of magnitude of ΔG_{ads} was typical for physical adsorption processes.

The best match of real phosphorus adsorption data to the adsorption model was obtained for the double Langmuir model, as was indicated by the highest values of the determination coefficient R^2 (Tables 1 and 2). This may indicate that phosphorus sorption by the tested sediments most likely occurs through phosphate binding at two types of active sorption sites. A similar phenomenon was also observed by [33] with regards to phosphate adsorption on chitosan and modified chitosan. Holford et al. [51] and Limousin et al. [52] claim that the double Langmuir model was the best model in characterizing phosphate adsorption on soils. Natural bottom sediment can be treated as a multi-component system, with different active sorption centers, and that fact seems to cause a better fit of observed adsorption results to the double Langmuir equation.

The phosphorus sorption characteristics were dependent on OM, Fe, Mn, Si and Mg, which is in accordance with numerous research works [38,44,45,53–55] (Table 3). The multiple regression analysis revealed that the sorption capacity from Langmuir models (S_{max} , S_2 and S_{max2}) was significantly dependent on Al content in sediment (Table 3). Thus, it seems to be possible, that the modification of sediment sorption capacity using an aluminum coagulant created additional active sorption sites, as well as the second type sites described in the double Langmuir equation. The constants $1/n$, k_2 and EPC_0 parameter were significantly connected to Al content in sediment as well (Table 3). The EPC_0 parameter informs us about the concentration at which there is an equilibrium between processes of phosphate sorption and release by bottom sediments [26,38,53,56]. Pan et al. [49,50] described the dual nature of particles (suspended solids or bottom sediment), which can be sink or source of P, depending on relationship between EPC_0 and P concentration in the water. The negative dependence between EPC_0 and aluminum content seems to confirm that the restoration technique used in Długie Lake significantly influenced the increase of P sorption properties.

Taking into consideration the fact that the theoretical sorption capacity assessed using Langmuir models is higher than real S_0 values observed during the experiment (“native sorbed phosphorus”), as well as a sum of highly mobile phosphorus fractions ($NH_4Cl-P + BD-P$), which represents sediment “native exchangeable P” [57], the sediment of Długie Lake theoretically should bind P, because the % of sediment saturation by P (%DSP) for S_{max} (Langmuir model) ranged between ca 25% DSP (St. 1, layer 10–15 cm) and 72% DSP (St. 3, layer 10–15 cm). For the double Langmuir model, the % DSP with regards to S_{max2} was much lower (between ca. 8% DSP at St. 3, sediment layer 5–10 cm, and 53% DSP at St. 1 for the deepest sediment layer).

Lewandowski et al. [23] also observed a higher sorption capacity for sediment layers modified by aluminum sulphate, which was used for the restoration of the Süsser See Lake in Germany. These authors as well as Cooke et al. [17] and Rydin [24] maintain that phosphorus bound during inactivation remains permanently buried in the sediment. Reitzel et al. [27] mention that the Al flocs created during restoration undergo an aging process, which can decrease the sorption capacity, compared to freshly formed flocs. However, present research can confirm the thesis that the “active” Al-modified sediment

layer of Długie Lake theoretically should still bind phosphorus under stable pH conditions until the sorption active sites are exhausted.

6. Conclusions

The present research revealed the following:

1. The double Langmuir model matched the P adsorption experimental data of Długie Lake sediment best (the highest R^2 values). This fact may indicate that phosphorus adsorption in the tested sediments most likely occurs through phosphate binding at two types of active sorption sites.
2. Phosphate adsorption by the investigated lake sediment during experiments was significantly connected to aluminum content in sediment, as was indicated by the multiple regression equations obtained for the following adsorption parameters: S_{max} , S_{max2} , S_2 , k_2 , $1/n$ and EPC_0 . A modification of sediment sorption capacity using aluminum coagulant probably increased the number of additional active sorption sites, as well as the second type of sites described by the double Langmuir equation.
3. The fact that the theoretical sorption capacity assessed using Langmuir models is higher than S_0 , as well as a sum of highly mobile phosphorus fractions ($NH_4Cl-P + BD-P$), confirm that the both kinds of sediment of Długie Lake (the “active” layer and layers created after ending restoration procedures) still should bind P.
4. The relatively low amounts of phosphates, noted in the near-bottom water of Długie Lake, even in anoxia, confirm that the aluminum-modified sediment layer still can control internal P loading in the lake.

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