

Baltic Coastal Zone No. 2	
(15-24) 1998	Institute of Biology and Environmental Protection University of Education of Słupsk

## SORPTION OF CATIONS BY BOTTOM SEDIMENTS OF LAKE WICKO

JAN TROJANOWSKI, CZESŁAWA TROJANOWSKA,  
ANTONINA MOCZULSKA

*Department of Chemistry, Institute of Biology, University of Education of Słupsk  
Arciszewskiego St. 22b, 76-200 Słupsk, Poland*

**Key words:** lakes, bottom sediments, sorption complex, cations.

### Abstract

In the bottom sediments of Lake Wicko sorption capacity and the sum of exchangeable bases was defined as well as total content of ions  $H^+$ ,  $Al^{3+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $CO^{2+}$ ,  $NH_4^+$ ,  $Rb^+$  and  $Li^+$ . The concentration of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$  cations has been measured. The ratio of exchangeable ions bound in the sorption complex and ions adsorbed on the surface of sediments was defined as a function of respective kinds of cations and composition of the bottom sediments. The content of the organic matter was decisive for an increase of the exchangeable sorption capacity.

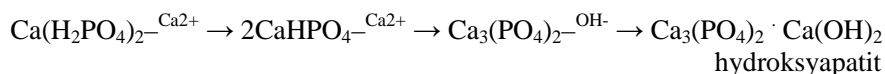
### INTRODUCTION

Exchangeable sorption phenomenons are among the only commonly occurring phenomena of interactions between liquid phase and constant phase. The mechanism of the ionexchangeable reactions consists in absorption by the sediments of some quantity of ions from the water solution. At the same time there is a releasing from the sediment to the water solution of an equivalent quantity of other ions in this way, so that electronegativity of the liquid phase and the solid phase was not violated (Striegel 1987). The existence of nonequivalented positive and negative electric charges is the reason for ionexchangeable reactions occurring in the sorption complexes. Charged particles aim at attraction of such a number of center-ions, that they can balance its surface-active charge (Ościk 1979, Grabowska-Olszewska 1981).

Ionexchangeable reactions depend on some other agents such as temperature, concentration of solution, concentration of ions in sediment, valency, energy of ion entry into the sorption complex, and degree of the sediment dispersion (Dobrzański, Zawadzki 1981).

From the liquid phase of the water solution ions can pass to the solid phase (bottom sediment) as a result of the precipitation in the shape of insoluble salts. This phenomenon is called chemisorption or chemical sorption and can have considerable effect on the quality composition of ions occurring in solution as well as on the level of ions concentration.

As for phosphate anions chemical sorption causes precipitation of insoluble calcium phosphates, magnesium, aluminium and iron (Gonsiorczyk et al. 1997). In the neutral and light basic environment phosphate ions react with compounds of calcium and magnesium precipitating in a shape of light soluble phosphates of calcium and magnesium.



Light acid reaction close to neutral favours formation of di- and tricalcium phosphates, which next under the influence of water undergoes hydrolysis till it becomes hard - solubled hydroxyapatites (Dobrzański, Zawadzki 1981, Lityński, Jurkowska 1982).

In low pH sediments (1-5,5) phosphate ions react above all with  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions, making insoluble aluminium phosphates and iron phosphates. In acid reaction sediments there are not any magnesium and calcium phosphates, because of the low number  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions (Kleeberg, Kozerski 1997). In acid sediments aluminium and iron phosphates are dominant. According to the increasing of the pH indicator of the sediments aluminium and iron phosphates undergo solution and became calcium and magnesium phosphates, which can be easier assimilated by autotrophic organisms (Lityński, Jurkowska 1982).

The exchangeable sorption problem and the problem of the creation of sorption complexes haven't been precisely studied yet. The goal of this presentation is to investigate how the concentration of calcium and magnesium ions and content of the organic matter influence exchangeable sorption in the bottom sediments of Lake Wicko and to study intensity of adsorption of exchangeable cations on the surface of sediments and in the sorption complex.

## MATERIALS AND METHODS

Research has been carried out based on the bottom sediments of Lake Wicko. The lake is situated in Słupsk voivodship near Jarosławiec. The western part is connected by a reclamation channel with Lake Kopań. Lake Wicko is connected with

the Baltic Sea by a channel as well. It's a coastal lake. Its morphometric data are listed in Table I.

Table I

Morphometry of Lake Wicko (latitude 54°32'2''N; longitude 16°37'1''E)

Property of lake	Units	Value
Surface area (P)	ha	10.6
Volume (V)	km <sup>3</sup>	0.0285
Depth (G)		
maximal	m	6.1
mean (V * P <sup>-1</sup> )	m	2.7
Dimensions		
maximal length (D)	km	5.1
maximal width (S)	km	3.7
Shoreline (L)	km	21.4

Lake Wicko is in the shape of a triangle with an area of 1059 hectares. There is a peninsula on the south bank of the lake. Localization of sampling stations is shown on Fig. 1. Samples of bottom sediments were picked up in some stations situated in the most characteristic points of the lake. Station 1 was situated near the affluents: Świdnik and Klasztorna. Station 2 was situated on the isthmus between two peninsulas, station 3 - in an area of outflow of lake water to the sea: stations 4 and 6 in the points of the greatest depth of the lake: station 5 on the most southern - situated part of the lake. Samples were taken once a quarter in 1992. Outside the stratum of the sediments samples were collected by Ekman's sampler. Bottom sediments for the stratum research were collected by Kajak's sampler.

Physical and chemical analysis of the bottom sediments were carried out by the methods suggested by Januszkiewicz (1978) and Piper (1957). Carbonates were determined by the volumetric method in Thilman's apparatus.

Organic substance was defined as losses at incineration of weighed portions, dried sediment in the temperature of 550°C; calcium, magnesium and aluminium - complexometric; manganese - colorimetric.

The general number of all, bounded with the sorption complex of sediment, exchangeable cations, which is absorbed by the 100g of sediment was named total sorption capacity (T). This capacity and joint content H<sup>+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Rb<sup>+</sup>, Li<sup>+</sup>(H) ions was determined by Mehlich's method, modified by Hoffman. S value, which meansthesum of exchangeable bases was calculated from the difference T-H. The basic ions adsorbed on the surface of the sediment were washed out with the distilled water till the disappearance of the reaction of chloride ions. Exchangeable cations from the sorption complex by ammonium chloride buffered till pH=8.2. The content of Ca<sup>2+</sup> and Mg<sup>2+</sup> cations in extracts was determined complexometrically. K<sup>+</sup> and Na<sup>+</sup> cations were determined by the flame photometry

method.

To assess the suitability of Mehlich's method by examination of the lake bottom sediments all ions were defined separately and then added up ( $\Sigma S$ ), comparing this value with (S).

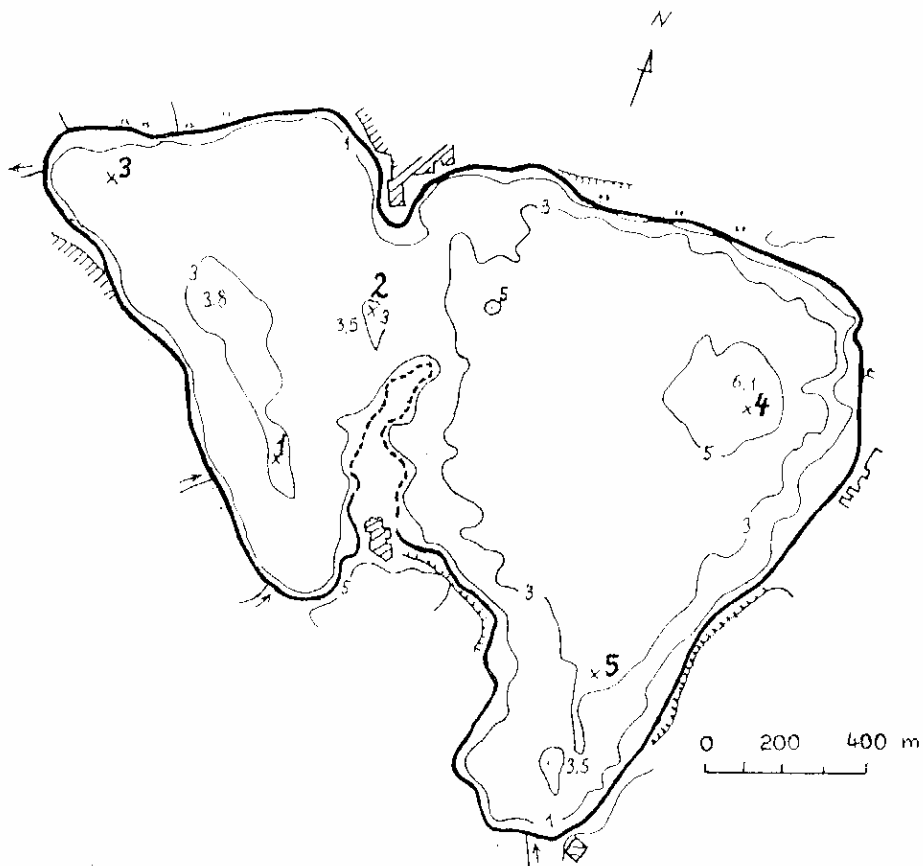


Fig. 1. Location of sampling stations in Lake Wicko

## RESULTS AND DISCUSSION

Results of the analytical research of the bottom sediments of Lake Wicko were completed in Table II. Mean components of the bottom sediments of Lake Wicko are silicates (58.8 - 93.2%) and organic matter (6.7 - 36.8%).

The content of organic carbon (C - org.) in the surface layers varied from 3.2% (st. 3) to 21.6% (st. 4). In the deeper layers of the sediment the quality of or-

ganic carbon decreases (30%) on average. The smallest quantity of this component was observed in the surface layer (st. 3) (aver. 3.5%).

Table II

Chemical composition of bottom sediments of Lake Wicko

Sampling stations	1	2	3	4	5	6
Mat. org. %	24.20	12.80	6.30	33.90	14.90	31.10
Tot-N %	1.28	0.66	0.31	1.79	0.72	1.65
Tot-P %	0.118	0.051	0.027	0.149	0.053	0.142
CO <sub>2</sub> %	0.62	0.78	0.59	0.58	1.24	0.60
CaO %	0.43	0.52	0.41	0.38	0.89	0.37
MgO %	0.11	0.11	0.10	0.11	0.18	0.11
MnO %	0.07	0.08	0.07	0.08	0.09	0.05
Fe <sub>2</sub> O <sub>3</sub> %	0.78	0.58	0.27	0.85	0.40	0.72
Al <sub>2</sub> O <sub>3</sub> %	1.20	1.42	0.82	0.68	0.95	0.72
Na <sub>2</sub> O %	0.74	0.85	1.05	0.96	1.02	0.89
K <sub>2</sub> O %	0.02	0.04	0.08	0.06	0.09	0.06
SiO <sub>2</sub> +z %	69.8	86.4	90.2	62.3	81.4	64.7
C org. %	13.9	7.3	3.5	18.8	8.3	17.3
C : N	10.9	11.1	11.3	10.5	11.5	10.5

z – insoluble components in aqua regia

Seasonal changes also have their influence on the content of organic carbon. It's lowest quality were observed in the summer, in the deeper parts of the sediments (st. 4 - 16.4%). The some dependence was observed by the content of total phosphorus (T - P) whose quality was the greatest in station 4 (0.146 mg% P), and the lowest in station 3 (aver. 0.27 mg% P) as for total nitrogen (T - N) on the average 1.79 mg% N in the station 4 and 0.31 mg% N in the station 3. Like in the case of org. - C, it was stated that in the deeper layers of sediments the content had a considerably smaller quantity of phosphorus and nitrogen compounds. In the case of sediments from the deep water (st. 4) their content decreased till value of 0.116 mg% P and 1.48 mg% N.

The bottom sediments of Lake Wicko are poor in the quality of carbonates. The greatest concentration of carbonates was observed in station 5 (mid. 1.23%), the lowest - in st. 4 (mid. 0.58%). There wasn't any distinct differences in the contents of this component in dependence on the period of collecting samples and on the depth of the layer that samples were collected from. Contents of carbonates are closely correlated with the content of calcium and magnesium. Their concentration on every sampling station wasn't high: from 0.87% CaO and 0.18% MgO (st. 1) to 0.37% CaO and 0.11% MgO (st. 6). Correlation coefficients between the amount of carbonates and the capacity of calcium and magnesium in the investigated sediments were high and amounted  $r = 0.90$  and  $r = 0.78$  respectively (on significance level 0.05 and by sine  $n = 20$ ).

As for metal: there was the smallest amount of sodium (on the average 0.92%) and potassium (0.05%). Any essential differences in the contents of those components in dependence on the researching period weren't observed. On account

of small differences in the contents of inorganic components on every layer of the sediment, its sorption properties were explored on the surface layer of the bottom sediments. Results are shown in Table III.

Table III

Mean values of: total sorption capacity of sediment (T) ; sum of trace ions  $H^+$ ,  $Al^{3+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $NH_4^+$ ,  $Li^+$ ,  $Rb^+$ ,  $Cs^+$  (H); sum of exchangeable bases (S); sum of exchangeable bases band in the sorption complex and adsorbed on the surface of sediment ( $\Sigma S$ ); the degree of saturation with bases (V) - at sampling station 1-6 of Wicko Lake

Sampling st.	T	H	S	$\Sigma S$	V
	meq · 100g <sup>-1</sup>				
1	22.33	1.60	20.73	34.53	92.83
2	21.16	1.65	19.51	35.26	92.20
3	40.75	2.51	38.24	32.45	93.84
4	53.53	2.43	51.10	46.69	95.46
5	35.98	0.88	35.10	49.21	97.55
6	30.52	2.40	28.12	40.36	92.14

Total sorption capacity (T) of bottom sediments on separate stations of Lake Wicko varied from 21.16 to 53.53 meq 100g<sup>-1</sup> of sediment. The smallest T value had indicated silicate sediments in the littoral zone (st. 2), the biggest value – in organic sediments picked up from the greatest depth (st. 4). At every stations there was observed a small content of  $H^+$  and  $Al^{3+}$  ions, as well as trace cations  $Zn^{2+}$ ,  $CO^{2+}$ ,  $Ni^{2+}$ ,  $Mg^{2+}$ ,  $Li^+$ ,  $Rb^+$ ,  $Cs^+$ . It varies in the range of 0.88 - 2.51 meq · 100g<sup>-1</sup> of sediment. The high degree of saturation with base (V) is correlated with that. It's value is 92.2 - 97.5%.

Figures 2-5 show disposition of the contents of exchangeable calcium, magnesium, sodium and potassium cations composed in the sorption complex and adsorbed on the surface of the bottom sediments on each station of Lake Wicko. The majority of sediments of Lake Wicko contain calcium and magnesium ions. They are adsorbed on the surface of sediments. Only in stations 4 and 5 calcium and magnesium ions prevailed bounded with the sorption complex. As for sodium and potassium ions, the advantage of adsorbed ions on the surface is even bigger and was observed in the whole area of Lake Wicko.

An average ratio of exchangeable ions in the bottom sediments of Lake Wicko was as follows:  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $H^+$ ,  $K^+$  = 27.0 : 6.5 : 1.3 : 1.7 : 1.0. A particularly great percent of exchangeable cations in relation to chemically bounded cations compose those sediments, where the total capacity of calcium and magnesium is small (st. 4 and 6), which is illustrated in Table IV. In conclusion, magnesium cations desorb easier from the sediments than calcium cations. Bendell-Young and Pick (1997) observed similar phenomena during their study. The ratio of exchangeable magnesium contents to contents of total magnesium (Ex-Mg : T-Mg) is on average 7.5 times more than the ratio of exchangeable calcium contents to the contents of total calcium (Ex-Ca : T-Ca, Table V).

Table IV  
 Mean contents of basic cations adsorbed on the surface of sediment (a) and bound in the sorption complex (b) in meq 100<sup>-1</sup> g sediment

Sampling station	Ca <sup>2+</sup>		Mg <sup>2+</sup>		Na <sup>2+</sup>		K <sup>2+</sup>	
	a	b	a	b	a	b	a	b
1	21.07	4.62	5.88	0.98	1.08	0.19	0.66	0.05
2	16.06	11.16	3.42	2.62	1.11	0.13	0.50	0.26
3	15.52	8.65	2.95	2.46	1.18	0.39	0.85	0.45
4	13.94	22.08	2.82	4.86	1.30	0.40	0.78	0.51
5	13.20	24.64	3.60	5.36	0.83	0.49	0.54	0.55
6	16.48	13.65	3.92	3.05	1.21	0.43	0.94	0.68

Table V  
 Values of chemical indices determining sorption of cations by bottom sediments of Lake Wicko (T-Ca and T-Mg – total content calcium and magnesium in sediment, Ex-Ca and Ex-Mg – contents of exchangeable ions, ΣS – calculated sum of exchangeable ions in meq 100g<sup>-1</sup> sediment)

Sampling station	T-Ca (meq · 100 <sup>-1</sup> g)	Ex - Ca		T-Mg (meq · 100 <sup>-1</sup> g)	Ex - Mg		T - Ca T - Mg (%)	Ex - Ca ΣS (%)	Ex - Mg ΣS (%)	T - Ca T - Mg (%)	Ex - Ca Ex - Mg (%)
		T - Ca	(%)		T - Mg	(%)					
1	505	5.09	74.46	10.8	63.5	74.46	63.5	74.46	19.88	46.75	3.74
2	735	3.70	77.11	24.2	24.9	77.11	24.9	77.11	17.11	30.37	4.51
3	390	6.19	74.59	9.8	55.2	74.59	55.2	74.59	16.69	39.79	4.46
4	400	9.01	77.14	12.2	62.9	77.14	62.9	77.14	16.45	32.78	4.69
5	620	6.10	76.91	16.7	53.6	76.91	53.6	76.91	18.21	37.12	4.22
6	340	8.86	74.65	10.7	65.1	74.65	65.1	74.65	17.27	31.77	4.32

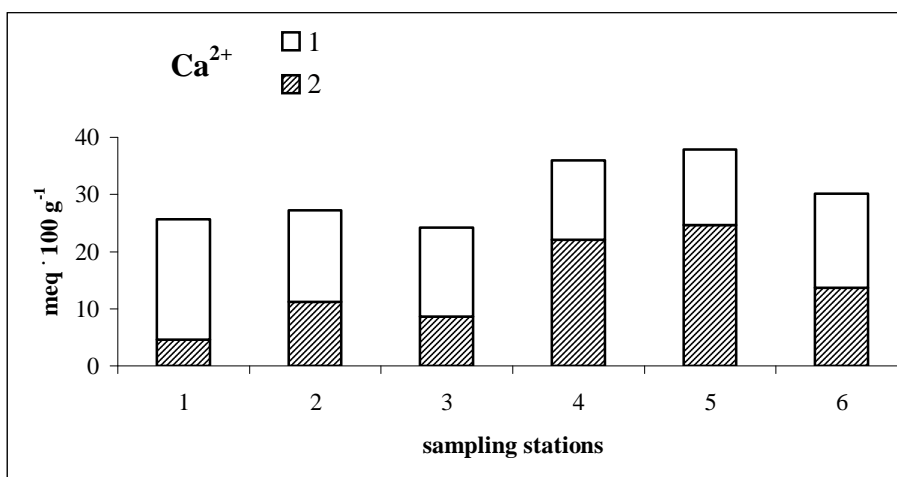


Fig. 2. Contents of calcium ions adsorbed on the surface of sediment (1) and bound in the sorption complex (2)

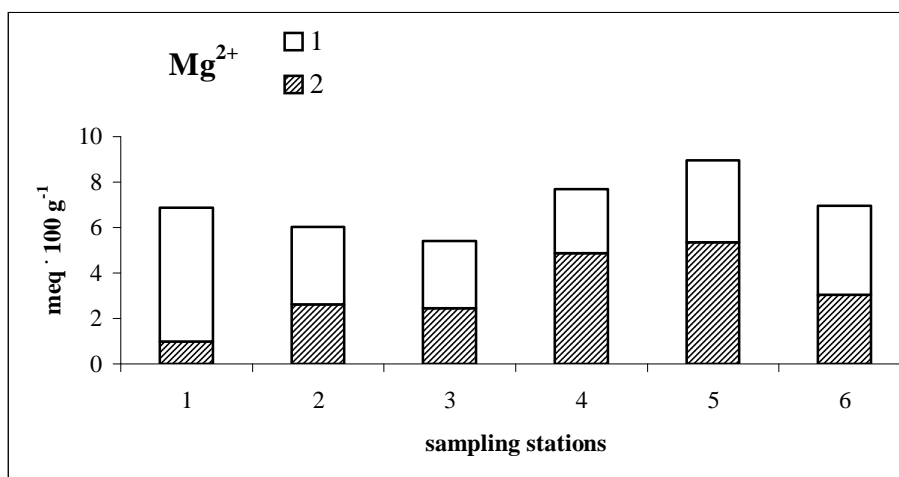


Fig. 3. Contents of magnesium ions adsorbed on the surface of sediment (1) and bound in the sorption complex (2)



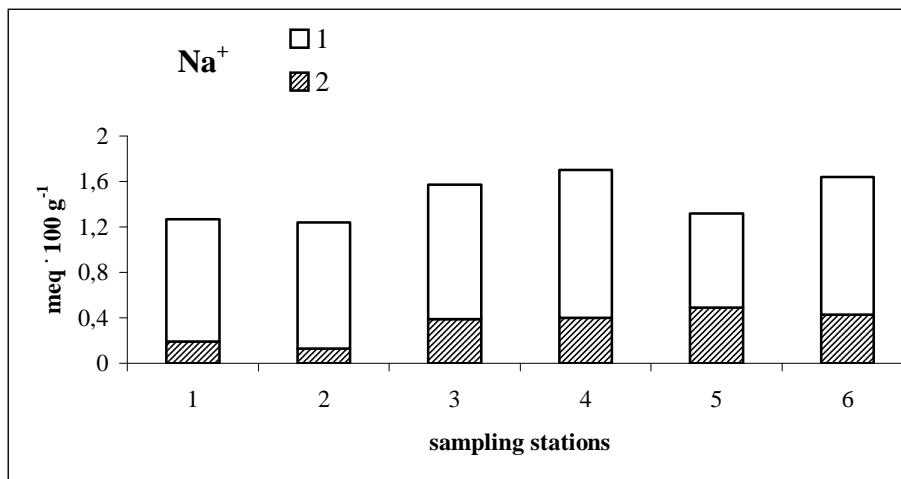


Fig. 4. Contents of sodium ions adsorbed on the surface of sediment (1) and bound in the sorption complex (2)

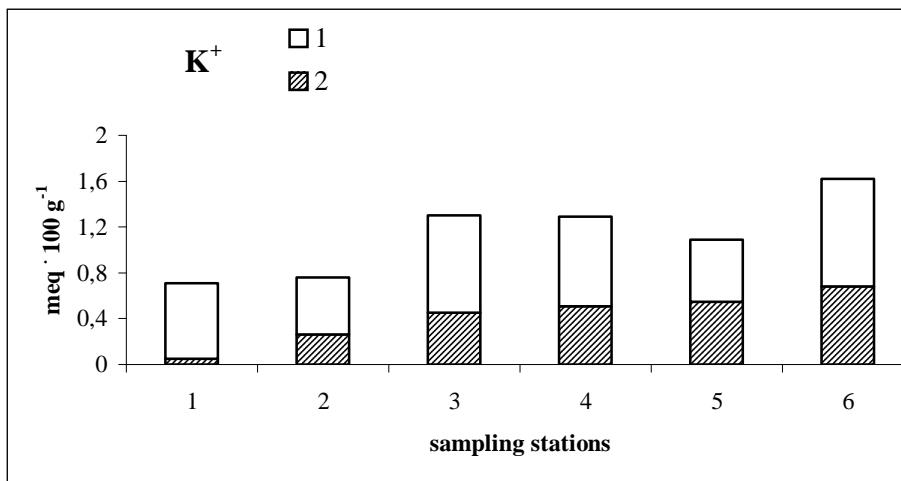


Fig. 5. Contents of potassium ions adsorbed on the surface of sediment (1) and bound in the sorption complex (2)

Exchangeable calcium (Ex - Ca) makes 74.4 - 77.1 %; exchangeable magnesium (Ex- Mg) - 16.5 - 19% of the sum of the exchangeable bases (E S). From the percentage fraction Ex - Ca and Ex - Mg in ratio to the sum of exchangeable bases we can come to the conclusion that the more Ex - Ca in the sediments the less Ex - Mg. The higher ratio T - Ca : T - Mg, the lower ratio Ex - Ca to Ex - Mg.

The ratio of exchangeable calcium and magnesium ions bounded in the sorption complex to adsorbed on the surface of the sediment was from 1.8 to 0.2. There were mostly ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the sediments of the deeper places. Those ions were permutable bounded with the sorption complex. As for the ions  $\text{Na}^+$  and  $\text{K}^+$  in all sediments were adsorbed move on the surface of sediments than bounded with the sorption complex. It may be caused by a small entry of energy ions into the sediment sorption complex and their easy desorption.

## LITERATURE

- Bendell-Young, L., Pick, F.R. 1997. Base cation compositions of pure water, peat and pool water of fifteen Ontario peat lands: Implications for peat land acidification. *Water Air Soil Pollut.*, 96, 155 - 173.
- Dobrzański, B., Zawadzki, S. 1981. *Gleboznawstwo [Soil science]*. PWRiL Warszawa.
- Gonsiorczyk, T., Casper, P., Koschel, R. 1997. Variation of phosphorus release from sediments in stratified lakes. *Water Air Soil Pollut.*, 99, 427 - 434.
- Grabowska-Olszewska, B. 1981. *Metody badań gruntów spoistych [Methods of investigation of the coherent soils]*. Wyd. Geolog., Warszawa.
- Januszkiewicz, T. 1978. Chemizm współczesnych osadów dennych jeziora Wodąg koło Olsztyna [Chemism of the present bottom sediments of Lake Wodąg near Olsztyn]. *Zesz. nauk. ART Olsztyn*, 8, 31-53. [Engl. summ.].
- Kleeberg, A., Kozerski, H.P. 1997. Phosphorus release in Lake Grosser Muggelsee and its implication for lake restoration. *Hydrobiologia*, 342/343, 9-26.
- Lityński, T., Jurkowska, H. 1982. *Żyzność gleby i odżywianie się roślin [Fertility of the soil and nourishing of the plants]*. PWN, Warszawa.
- Ościk, J. 1979. *Adsorpcja [Adsorption]*. PWN, Warszawa.
- Piper, C.S. 1957. *Analiza gleby i roślin [Analysis of the soil and plants]*. PWN, Warszawa.
- Striegel, R., 1987. Suspended sediment and metals removal from urban runoff by a small lake. *Water Resour. Bull.*, 23, 985-992.