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# Contents of selected macronutrients in bottom sediments of two water reservoirs and assessment of their suitability for natural use

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## Abstract

The purpose of the present study was to analyse the contents of calcium, magnesium, potassium, and sodium in bottom sediments of two water reservoirs. The chemical composition of the bottom sediments and the ratios between the studied macronutrients were assessed, taking into account the nutritional requirements of plants, to determine whether the sediments were suitable for use in natural/agricultural settings.

The study was conducted at two water reservoirs: the Brody Hżeckie reservoir built on the Kamienna River in the Świętokrzyskie Province, and Zalew Zemborzycki, lake on the Bystrzyca River in the Lublin Province. Both bodies of water serve as flood water diversion and leisure facilities, and are also used, to a small extent, by the industry. They have a similar age and surface area. Bottom sediments were collected from the reservoirs a single time: 14 samples from Zalew Zemborzycki and 17 from Brody Hżeckie. Samples were tested for total contents of Ca, Mg, K, and Na. The bottom sediments from Zalew Zemborzycki contained higher amounts of calcium, magnesium, and potassium than the material from Brody Hżeckie. The values of ratios between K:Mg and K:(Ca + Mg) were similar for both reservoirs, and Ca:Mg and Ca:K were slightly more favourable for the sediments taken from Brody Hżeckie.

**Key words:** *bottom sediments, Ca, Mg, K, Na, natural use, water reservoirs*

## INTRODUCTION

Water reservoirs silt up with a varying intensity. After some time, however, most of them need to be desludged and restored [MADEYSKI, TARNAWSKI 2007; TROJANOWSKI, ANTONOWICZ 2005]. Sludge extracted from reservoir should be utilized, and the way it is used depends on its fertility and pollution. The chemical composition of bottom deposits of a water reservoir is influenced by the type of rocks that form the catchment, human activity [GAŁKA, WIATKOWSKI 2010], the way the catchment area is

used, pollutants that enter surface waters [BOJAKOWSKA *et al.* 2006], the flow patterns, and the rate of water exchange [CHOIŃSKI *et al.* 2010].

Bottom sediments, if they meet the relevant requirements, can be used to fertilize light soils as well as to remediate degraded areas. Whether bottom sediments can be recycled in the natural environment/agriculture is determined by their content of macronutrients, in particular available forms of phosphorus, potassium, and magnesium [GAŁKA, WIATKOWSKI 2010] as well as calcium.

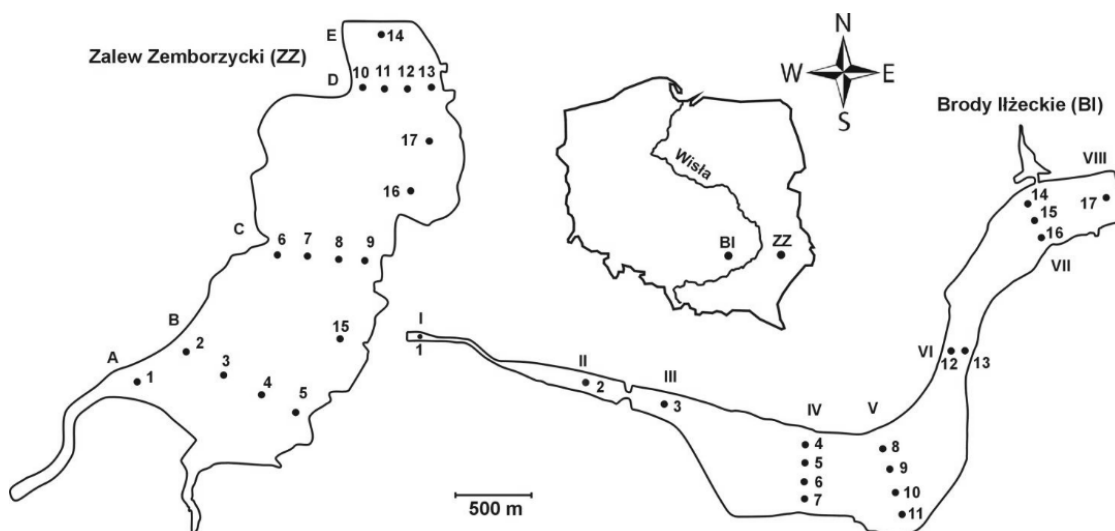


Fig. 1. Sediment sampling sites; source: SMAL *et al.* [2012], modified

The purpose of the present study was to analyse the contents of calcium, magnesium, potassium, and sodium in bottom sediments of two water reservoirs. The chemical composition of the bottom sediments and the ratios between the studied macronutrients were assessed, taking into account the nutritional requirements of plants, to determine whether the sediments were suitable for use in natural/agricultural purposes.

## MATERIAL AND METHODS

The study was conducted in two water reservoirs: Zalew Zemborzycki (the Zemborzyce artificial reservoir) built in 1974 on the river Bystrzyca in the Lublin Province, and Brody Iłżeckie, a reservoir in the Świętokrzyskie Province, built on the Kamienna River in the years 1961–1965, and rebuilt in 1986. Both bodies of water serve as flood water diversion and leisure facilities, and are also used to a small extent by the industry. Zalew Zemborzycki covers an area of 278 ha, and Brody Iłżeckie, 203 ha.

Bottom sediments were collected once in the summer season: 14 samples from Zalew Zemborzycki and 17 from Brody Iłżeckie (Fig. 1). Samples were collected at designated transects and sites using Kajak's core sampler. 5 dm<sup>3</sup> of liquid sediment was collected into polyethylene containers. The sediment samples were air-dried, homogenized, and passed through a 2 mm sieve.

The total contents of calcium, magnesium, potassium, and sodium were determined by ICP-AES using the Leeman PS 950 apparatus, following extraction of the sediment with a mixture of HNO<sub>3</sub> and HClO<sub>4</sub> (5:4; v/v).

The results were analysed statistically using Statistica Statsoft 10 to obtain means, variation range – maximum and minimum values, standard deviation, and correlation coefficients. The ratios of the analysed macronutrients were also calculated.

## RESULTS AND DISCUSSION

The pH values of the bottom sediments collected from the examined water reservoirs were varied. In the Brody Iłżeckie reservoir, the pH values of the sediments, determined in water, ranged from 5.49 to 6.80, whereas in Zalew Zemborzycki, they range from 6.85 to 7.33 [SMAL *et al.* 2012]. Sediment samples collected from the two reservoirs also had different contents of organic carbon. In Brody Iłżeckie, the content of C<sub>org</sub> in the sediments was in the range of 0.78–49.80 g·kg<sup>-1</sup> with a mean of 20.44 g·kg<sup>-1</sup>. Samples collected from Zalew Zemborzycki had much higher C<sub>org</sub> contents, ranging from 16.50 to 87.00 g·kg<sup>-1</sup>, with a mean of 41.38 g C<sub>org</sub>·kg<sup>-1</sup> [SMAL *et al.* 2015].

The sediments from Brody Iłżeckie had low calcium content, in the range of 0.84–5.64 g·kg<sup>-1</sup>, mean 2.76 g Ca·kg<sup>-1</sup> (Tab. 1). Sediments collected at the outflow zone of the reservoir (transects VI and VII) were characterized by a higher content of this element than those sampled at sites located at the inflow of the Kamienna River (transects I–IV). The sediments from Zalew Zemborzycki contained over 15 times more calcium (a mean calcium content of 70.03 g Ca·kg<sup>-1</sup>) than those from Brody Iłżeckie (Tab. 2). Calcium content in these sediments had a wide range of values (35.49 to 117.6 g Ca·kg<sup>-1</sup>). The high calcium content in Zalew Zemborzycki sediments can be explained by the presence of loess soils in the catchment area, which are rich in carbonates [TURSki *et al.* 1985]. The spatial distribution of calcium was similar in both reservoirs: lower Ca contents were recorded in the water inflow zone and higher contents were observed at the dam. The calcium content in bottom sediments from both reservoirs corresponded with the pH of these sediments [SMAL *et al.* 2012].

Calcium contents similar to those found in the sediments of Brody Iłżeckie were reported in a study by TROJANOWSKI and ANTONOWICZ [2005], who analysed the bottom sediments of Lake Dołgie Wielkie.

**Table 1.** Contents of macronutrients in bottom sediments of the Brody Hżeczek reservoir

Number of sample	Ca	Mg	K	Na	Ca:Mg	Ca:K	K:Mg	K:(Ca+Mg)
	g·kg <sup>-1</sup>							
I1	2.30	0.26	0.43	0.088	8.85	5.35	1.65	0.17
II2	1.10	0.17	0.50	0.081	6.47	2.20	2.94	0.39
III3	2.36	0.84	1.21	0.142	2.81	1.95	1.44	0.38
Mean	1.92	0.39	0.71	0.105	4.92	2.70	1.82	0.31
IV4	2.60	0.99	1.15	0.154	2.62	2.26	1.16	0.32
IV5	2.13	0.73	1.12	0.136	2.92	1.90	1.53	0.39
IV6	0.92	0.14	0.40	0.092	6.57	2.30	2.86	0.38
IV7	2.21	1.16	1.75	0.161	1.91	1.26	1.51	0.52
Mean	1.96	0.75	1.10	0.136	2.61	1.78	1.47	0.41
V8	0.84	0.13	0.38	0.091	6.46	2.21	2.92	0.39
V9	2.55	1.56	2.23	0.180	1.63	1.14	1.43	0.54
V10	2.97	1.91	2.94	0.206	1.55	1.01	1.54	0.60
V11	1.97	0.68	1.04	0.118	2.90	1.89	1.53	0.39
Mean	2.08	1.07	1.65	0.149	1.94	1.26	1.54	0.52
VII12	4.19	4.67	6.24	0.415	0.90	0.67	1.34	0.70
VII13	4.89	3.73	5.35	0.357	1.31	0.91	1.43	0.62
Mean	4.54	4.20	5.80	0.386	1.08	0.78	1.38	0.66
VIII14	5.22	3.60	5.63	0.338	1.45	0.93	0.56	0.64
VIII15	5.69	3.35	4.51	0.330	1.70	1.26	1.35	0.50
VIII16	2.06	1.56	2.14	0.195	1.32	0.96	1.37	0.59
Mean	4.32	2.84	4.09	0.288	1.52	1.06	1.44	0.57
VIII17	3.00	2.10	2.78	0.214	1.43	1.08	1.32	0.54
Overall mean	2.76	1.66	2.34	0.194	3.11	1.71	1.41	0.53
Minimum	0.84	0.13	0.38	0.081	0.90	0.67	1.16	0.17
Maximum	5.69	4.67	6.24	0.415	8.85	5.35	2.94	0.70
SD	1.54	1.44	1.96	0.100	3.41	1.08	0.65	0.13
RSD (%)	55.80	86.75	83.76	51.55	109.65	63.16	12,76	24.53

Explanations: *SD* = standard deviation; *RSD* = relative standard deviation.

Source: own study.

**Table 2.** Content of macronutrients in bottom sediments of Zalew Zemborzycki

Number of sample	Ca	Mg	K	Na	Ca:Mg	Ca:K	K:Mg	K:(Ca+Mg)
	g·kg <sup>-1</sup>							
A1	43.19	1.54	1.95	0.181	28.05	22.15	1.27	0.04
B2	51.66	1.54	1.90	0.178	33.54	27.19	1.23	0.04
B3	66.85	1.82	2.19	0.199	36.73	30.52	1.20	0.03
B4	61.81	1.82	1.78	0.184	33.96	34.72	0.98	0.03
B5	74.20	1.70	1.60	0.181	43.65	46.37	0.94	0.02
Mean	63.63	1.72	1.87	0.186	36.99	34.03	1.09	0.03
C6	35.49	1.26	1.50	0.145	28.17	23.66	1.19	0.03
C7	73.50	1.86	1.93	0.193	39.52	38.08	1.04	0.03
C8	54.46	1.02	1.09	0.142	53.39	49.96	1.07	0.02
C9	75.60	2.07	2.13	0.206	36.52	35.49	1.03	0.03
Mean	59.76	1.55	1.66	0.172	38.55	36.00	1.07	0.03
D10	117.6	2.05	2.06	0.198	57.36	57.09	1.00	0.02
D11	78.40	1.97	1.95	0.193	39.80	40.20	0.99	0.02
D12	77.00	1.99	2.08	0.200	38.69	37.02	1.04	0.03
D13	75.60	2.00	2.10	0.204	37.80	36.00	1.05	0.03
Mean	87.15	2.00	2.05	0.199	43.57	42.51	1.02	0.02
E14	74.20	2.22	2.24	0.208	33.42	33.12	1.01	0.03
Overall mean	68.54	1.77	1.89	0.187	38.72	36.26	1.07	0.03
Minimum	35.49	1.02	1.09	0.142	28.05	22.15	0.94	0.02
Maximum	117.6	2.22	2.24	0.206	57.36	57.09	1.27	0.04
SD	19.67	0.33	0.31	0.02	8.0	10.1	0.12	0.007
RSD (%)	28.70	18.64	16.40	10.70	20.66	27.85	11.21	23.33

Explanations: *SD* = standard deviation; *RSD* = relative standard deviation.

Source: own study.

Those authors claimed that the content was low compared to the contents of calcium in the sediments of other lakes of Western Pomerania. Also SKWIERSKI [2003], who studied bottom sediments of 10 water reservoirs in the Olsztyn Lake District, found that the deposits had varied contents of calcium, ranging from 0.2 to 192.8 g Ca·kg<sup>-1</sup>.

In contrast to calcium, the mean content of magnesium was similar for the sediments of both reservoirs investigated in the present study. More varied magnesium content values were found in the sediments collected from Brody Iłżeckie, in which the minimum Mg content was 0.13 g·kg<sup>-1</sup> and the maximum content was 4.67 g·kg<sup>-1</sup> (*SD* = 1.44 g Mg·kg<sup>-1</sup>). By comparison, sediments from Zalew Zemborzycycki contained from 1.02 to 2.22 g Mg·kg<sup>-1</sup> of this metal (*SD* = 0.33 g Mg·kg<sup>-1</sup>). Similar magnesium contents were recorded by TROJANOWSKI and ANTONOWICZ [2005] in the bottom sediments of Lake Dołgie Wielkie. NIEDŹWIECKI *et al.* [2007] found considerably higher magnesium contents in the sediments of Lake Rusałka, and contents similar to those reported in this present study – in Lake Słoneczne.

Differences in the spatial distribution of magnesium content were observed only for the sediments of the Brody Iłżeckie reservoir. The highest contents of this metal were found in sediments collected in the central part of the narrowest section of this water body, while sediments in the water inflow zone contained the lowest quantities of this element. NIEDŹWIECKI *et al.* [2007] found similar relationships for sediments of two lakes located in Szczecin. The accumulation of magnesium was much larger in their central part than at the outflow. Such spatial distribution of magnesium can be explained by its accumulation in the sediments of the water bodies [GAŁKA, WIATKOWSKI 2010].

No such dependencies were found for sediments collected from different zones of Zalew Zemborzycycki. Only a tendency for magnesium content to be higher in the outflow zone was noted. A similarly small variation in magnesium content has been observed by RAFAŁOWSKA and SOBCZYŃSKA-WÓJCIK [2014], who analysed bottom sediments from Pilwa Bay of Lake Dobskie. However, the content of this element in the sediments of Pilwa Bay was much higher than in Zalew Zemborzycycki (8.11–9.46 g Mg·kg<sup>-1</sup> DM).

The potassium content in the bottom sediments of the Brody Iłżeckie dam reservoir was in the range 0.38–6.24 g K·kg<sup>-1</sup> (Tab. 1). Sediments abounding in potassium were found in sectors VI and VII (near the dam); the average potassium content in those sampling areas was 5.80 and 4.09 g K·kg<sup>-1</sup>, respectively. At the water inflow, the content of this element in the sediments was several times smaller.

Compared to the reservoir in Brody Iłżeckie, the sediments in Zalew Zemborzycycki were characterized by a lower potassium content, ranging between 1.09 and 2.24 g K·kg<sup>-1</sup>. The scatter of values was also much smaller, as evidenced by the standard deviation

(0.31 g K·kg<sup>-1</sup>). There were no differences in the spatial distribution of potassium in the sediments of Zalew Zemborzycycki. In their study NIEDŹWIECKI *et al.* [2007] found that sediments in two Szczecin lakes were characterized by a much higher content of this element than found in the present study. SKWIERSKI [2003], in turn, found large variation in the potassium content (0.3–12.1 g K·kg<sup>-1</sup>) in the bottom sediments of small lake reservoirs in the Olsztyn Lake District.

The sodium content in the bottom sediments of the reservoirs investigated in the present study varied across samples. In Brody Iłżeckie, its content ranged from 0.081 to 0.415 g Na·kg<sup>-1</sup> and in Zalew Zemborzycycki – from 0.142 to 0.206 g Na·kg<sup>-1</sup>. As in the case of the other elements, spatial differences in the content of sodium in the sediments were observed only for Brody Iłżeckie, in which most of the sodium was accumulated in the sediments of the sectors located near the dam (Tab. 1, 2).

The concentrations (by overall mean) of the investigated micronutrients in bottom sediments of Brody Iłżeckie and Zalew Zemborzycycki can be arranged in the following decreasing order: Ca > K > Mg > Na. In both reservoirs, calcium was the dominant element, and the content of potassium was either higher than (Brody Iłżeckie) or similar to (Zalew Zemborzycycki) the content of magnesium. To compare, in RAFAŁOWSKA and SOBCZYŃSKA-WÓJCIK'S study [2014], these elements found in bottom sediments of Pilwa Bay formed the following order of concentrations Ca > Mg > Na > K. Similar results have been obtained by TARNAWSKI *et al.* [2012] for bottom sediments of Lake Chańcza, in which the concentrations of macronutrients were in the following order: Ca > Mg > K.

Statistical analysis showed high correlation coefficients between Mg, K and Na contents in the bottom sediments of both reservoirs (Tab. 3).

**Table 3.** Values of Pearson's correlation coefficients between macronutrients found in bottom sediments of Brody Iłżeckie and Zalew Zemborzycycki reservoirs

Macronutrient	Mg	K	Na
<b>Brody Iłżeckie reservoir <i>n</i> = 17</b>			
Ca	0.9023*	0.9033*	0.9057*
Mg		0.9941*	0.9973*
K			0.9910*
<b>Zalew Zemborzycycki reservoir <i>n</i> = 14</b>			
Ca	0.7078*	0.4612	0.6444*
Mg		0.8761*	0.9593*
K			0.9276*

Explanations: *n* = number of sediment samples, \* significant at  $\alpha_{0.05}$ . Source: own study.

In the bottom sediments of Brody Iłżeckie, in which the calcium content was small, a close correlation significant at  $\alpha = 0.05$  was found between the elements. In the case of Zalew Zemborzycycki, no significant correlation was found between Ca and K, and

the correlations between Ca – Na and Ca – Mg were significant but weaker. High correlation coefficients between Ca and Mg as well as Ca and K in bottom sediments were also found by TARNAWSKI *et al.* [2012].

Water reservoirs silt up and become shallower with time, which means they have to be cleaned and restored. Silting leads to the formation of large quantities of bottom sediments, which should be properly utilized. How such sediments are used depends on their contents of nutrients and pollutants [BARAN *et al.* 2009; GAŁKA, WIATKOWSKI 2010; SAMMEL 2015]. The most viable and environmentally friendly method of recycling bottom deposits is to use them for reclamation or fertilization of light and acidic soils [BARAN *et al.* 2009; NIEDZWIECKI *et al.* 2007; SAMMEL 2015; WIŚNIEWSKA-KIELIAN *et al.* 2012]. Ca:Mg, Ca:K, K:Mg, and K:(Ca + Mg) mass ratios are important indicators of the ability of soils to supply plants with these elements, and so they may be used to indicate how bottom sediments should be used.

The Ca:Mg ratio in the sediments of the discussed reservoirs varied considerably across sampling points. The ratio was the highest (8.85) in the sediments collected from the water inflow zone of Brody Iłżeckie, and in the remaining sampling points, it ranged from 0.90 to 6.57 (Tab. 1). In Zalew Zemborzycki, the ratio was in a wide range between 28.05 and 57.09; the widest ratio was found in the sediments from sector D (Tab. 2). For optimal plant nutrition, the Ca:Mg ratio in soil should not be higher than 5.0–7.5:1 [MERCİK 2004]. In the sediments from Brody Iłżeckie, this ratio was slightly more favourable compared to the sediments from Zalew Zemborzycki. In Polish soils, the Ca:Mg ratio is on average 6.7 and ranges from 2 to 26 [FOTYMA *et al.* 1987]. The wide ratio of calcium to magnesium observed in the sediments from Zalew Zemborzycki results from the high Ca content in that material

In the bottom sediments of Brody Iłżeckie, the Ca:K ratio ranged from 0.67 to 5.35, and in those collected from Zalew Zemborzycki, it ranged from 22.15 to 57.09. In Brody Iłżeckie, the widest Ca:K ratio was observed in samples of bottom sediments from the water inflow zone, whereas in Zalew Zemborzycki, in sediments from sector D (outflow). The optimal Ca:K ratio in soil is (10–15):1 [KIEPUL 2003]. In the sediments of Brody Iłżeckie, the discussed ratio was lower than optimal, but slightly more favourable than the very high ratio found in the sediments from Zalew Zemborzycki.

The best yield-increasing effect is obtained at a low K:Mg ratio in soil. If the ratio is higher than 3:1, fertilization with potassium does not increase crop yields [FOTYMA *et al.* 1987]. In the bottom sediments collected from the two investigated reservoirs, the K:Mg ratio was close to optimal. In Brody Iłżeckie, the K:Mg is in the range 1.16–2.94, and in Zalew Zemborzycki, it ranged from 0.94 to 1.27.

In the sediments from Brody Iłżeckie, the ratio of potassium to the sum of calcium and magnesium ranged from 0.17 to 0.70. A slightly wider ratio was observed in the sediments of sector VI. In the sediments from Zalew Zemborzycki, the discussed ratio was very low, not exceeding 0.1. In both reservoirs, the ratio of potassium to the sum of calcium and magnesium was similar and did not indicate an increase in the potassium content in relation to calcium and magnesium.

In the bottom sediments of both water reservoirs only the K:Mg ratio was optimal. The mass ratios of Ca:Mg; Ca:K and K:(Ca + Mg) in the bottom sediments of Zalew Zemborzycki diverged considerably from the optimum ratios, due to the high Ca content.

When used in the natural environment/agriculture, the sediments studied should be supplemented with potassium and magnesium fertilizers. This, however, cannot be the only one criterion for classifying bottom sediments as useful for natural, including agricultural use. In addition, it is particularly important to pay attention to the content of xenobiotics, in this organic compounds, which was not the subject of the presented studies.

## CONCLUSIONS

1. Bottom sediments collected from the investigated reservoirs differed in terms of the content and spatial distribution of the individual elements:

- the bottom sediments from Zalew Zemborzycki contained higher amounts of calcium, magnesium, and potassium compared to those from Brody Iłżeckie;
- the concentrations of the investigated macronutrients in bottom sediments of Brody Iłżeckie and Zalew Zemborzycki can be arranged in the following decreasing order: Ca > K > Mg > Na;
- sediments sampled from different sampling points of the Brody Iłżeckie reservoir had different contents of calcium, magnesium, potassium, and sodium; sediments from sectors VI and VII (near the dam) had higher contents of all of those elements; in the case of Zalew Zemborzycki, the contents of Ca, Mg, K and Na tended to be higher in bottom sediments found in the lower part of the reservoir (sector D).

2. The ratios of the K:Mg and K:(Ca + Mg) were similar in the sediments of both reservoirs, and Ca:Mg and Ca:K slightly more favourable in the sediments of Brody Iłżeckie. When the sediments in the natural environment/agriculture are used, it is advisable to supplement them with potassium and magnesium fertilizers, but this is not the only one criterion for classifying bottom sediments for natural/agricultural use.

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**Zawartość niektórych makroelementów w osadach dennych dwóch zbiorników wodnych i ocena ich przydatności do przyrodniczego wykorzystania**

**STRESZCZENIE**

Celem pracy była analiza zawartości wapnia, magnezu, potasu i sodu w osadach dennych dwóch zbiorników wodnych. Ocena składu chemicznego oraz stosunków pomiędzy badanymi makroelementami, uwzględniającymi wymagania żywieniowe roślin, były podstawą do określenia przydatności do przyrodniczego/rolniczego wykorzystania osadów dennych. Zadania prowadzono na dwóch obiektach – zbiorniku Brody Iłżeckie, w województwie świętokrzyskim, zbudowanym na rzece Kamienna, oraz Zalewie Zemborzyckim na rzece Bystrzycy, w województwie lubelskim. Oba zbiorniki pełnią funkcje przeciwpowodziowe i rekreacyjne, są też w niewielkim stopniu wykorzystywane przez przemysł. Są podobne pod względem wieku i powierzchni. Osady denne pobrano jednorazowo – 14 próbek z Zalewu Zemborzyckiego i 17 ze zbiornika Brody Iłżeckie. Analizowano w nich całkowitą zawartość Ca, Mg, K, Na. Osady denne z Zalewu Zemborzyckiego zawierały znacznie więcej wapnia, magnezu i potasu niż ze zbiornika Brody Iłżeckie. Stosunki analizowanych makroelementów były podobne (K:Mg; K:(Ca+Mg) w osadach obu zbiorników lub nieco korzystniejsze (Ca:Mg; Ca:K) w osadach zbiornika Brody Iłżeckie niż Zalewu Zemborzyckiego.

**Słowa kluczowe:** *Ca, Mg, K, Na, osady denne, przyrodnicze wykorzystanie, zbiorniki wodne*