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## QUANTITY AND QUALITY OF ORGANIC CARBON IN BOTTOM SEDIMENTS OF TWO UPLAND DAM RESERVOIRS IN POLAND

The quantity and quality of organic carbon were studied in bottom sediments of two small, shallow, polymictic dam reservoirs located in SE Poland: Zalew Zemborzycki (ZZ) and Brody Iłżeckie (BI). Total content of organic carbon ( $C_{org}$ ), and its fractions have been determined. The maps of  $C_{org}$  spatial distribution have been compiled. Wide ranges of sedimentary  $C_{org}$  were noted as well as differences between two reservoirs in respect of its content and spatial distribution. The  $C_{org}$  content in the sediments showed a longitudinal zonation pattern in the ZZ and a transverse one in the BI. The composition of sedimentary  $C_{org}$  showed the highest percentage of the insoluble fraction followed by humus acid fraction and the lowest – hemicelluloses fraction. In the humus acid fraction, fulvic acids overbalanced humic acids.

### 1. INTRODUCTION

Organic matter in water ecosystems such as natural and man-made lakes, encompasses two major forms: dissolved and particulate organic matter [1]. They come from the allochthonous (input from the surrounding watershed area through the leaching from soil, surface runoff, vascular plant breakdown) and the autochthonous sources (phytoplankton, aquatic macrophytes). Dead planktonic organism cells settle to the bottom of water body where they are incorporated into sediments as integral components and thus, enrich them with organic matter.

In dam reservoirs, the presence of independent zones may affect varied content of  $C_{org}$  in sediments. Most reservoirs comprise three major zones: a riverine zone (with a high flow rate), a lake-like, lacustrine zone (stagnant waters) and a transitional zone (with a low flow rate or stagnant waters) [2]. Consequently, differentiated sediment properties are noted, in that the  $C_{org}$  content. Generally, autochthonic organic carbon

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dominates in the lacustrine zone of the reservoir, whereas allochthonous carbon transported by a watercourse prevails in the riverine region. An important source for the load of allochthonous carbon to waters and sediments may be forests and peatlands of terrestrial watersheds [3, 4]. However, considering ecology, aquatic (autochthonic) humus substances seem to be more important for reservoirs than the soil ones [5].

Humus compounds of bottom sediments play a substantial role in the aquatic ecosystem functioning. They constitute an energy source for benthic organisms. It is evidenced by increasing contribution of sedimentary carbon available for microorganisms along with a rising percentage of humus acids in organic carbon content [3]. They provide sediments with nitrogen [6] and forming the iron-phosphorus-humus complexes, immobilize biogenic compounds [7, 8].

Besides, they sorb heavy metals and organic pollutants [9–12], thereby reducing their toxicity to aquatic organisms. Humus compounds are known to regulate the environmental behavior and bioavailability of organic and inorganic contaminants in aquatic ecosystems. As a result of these characteristics, the identification and recognition of organic carbon fraction are crucial for prediction of pollutant fate and transport in sediments [9, 13].

Sediments in the water environment undergo various processes, i.e. physical, physicochemical and biochemical, that can induce transformations and affect the composition of humus substances. The function of their components during the sorption process varies. In general, the highest adsorption capacity is reported for humus acids, especially humic acids [12]. The studies on the differentiation of composition of humus substances and their potential impact on the interactions with organic and inorganic pollutants are pivotal. They provide fundamental knowledge which is very useful for the natural environment management and remediation of contaminated sediments.

A vast body of literature on the problem of organic carbon in the bottom sediments of water bodies deals with its total content, while only few scientific papers address its qualitative composition [3].

The objective of the presented research was quantitative and qualitative analysis (fractional composition) of organic carbon ( $C_{org}$ ) in the bottom sediments of the Zalew Zemborzycki and Brody Iłżeckie Reservoirs. Besides, the spatial distribution of  $C_{org}$  content in the sediments of these reservoirs was analyzed.

## 2. STUDY AREA AND METHODS

### 2.1. CHARACTERISTICS OF DAM RESERVOIRS

The Zalew Zemborzycki (ZZ) was built on the Bystrzyca River near Lublin ( $51^{\circ}10'43''N$ ,  $21^{\circ}10'01''E$ ) in 1974, while the Brody Iłżeckie (BI) Reservoir on the

Kamienna River close to Starachowice (51°00'13"N, 22°31'25"E) in 1964. The surface areas of the reservoirs are 282 and 204 ha, respectively; the maximum storage volumes are 6.3 and 7.6 million m<sup>3</sup>, respectively. The maximum depths are 4 and 6 m, respectively. Both reservoirs are polymictic with no thermal-oxygen stratification. Mean annual flow rate in ZZ is 2.81 m<sup>3</sup>/s mean time of water storage 26 days and in BI 3.05 m<sup>3</sup>/s and 29 days, respectively. The reservoirs have similar functions, they control water flow, provide recreational opportunities and are used by industry only to a small degree. The BI water basin supplies water to the industrial plants, while the ZZ feeds water to the Thermal Power Plant Wrotków in Lublin. The studied reservoirs are characterized with a different water outflow system, namely the top in the ZZ and lower in the BI. The Brody Hżecckie Reservoir was rebuilt in the second half of the 1980s when the sediments were completely removed from the great part of it. The dredging operation was performed in the area of IV and V sector (Fig. 1 right). Whereas in the Zalew Zemborzycycki, no works have been done that could disturb the sediment mass deposition since its construction.

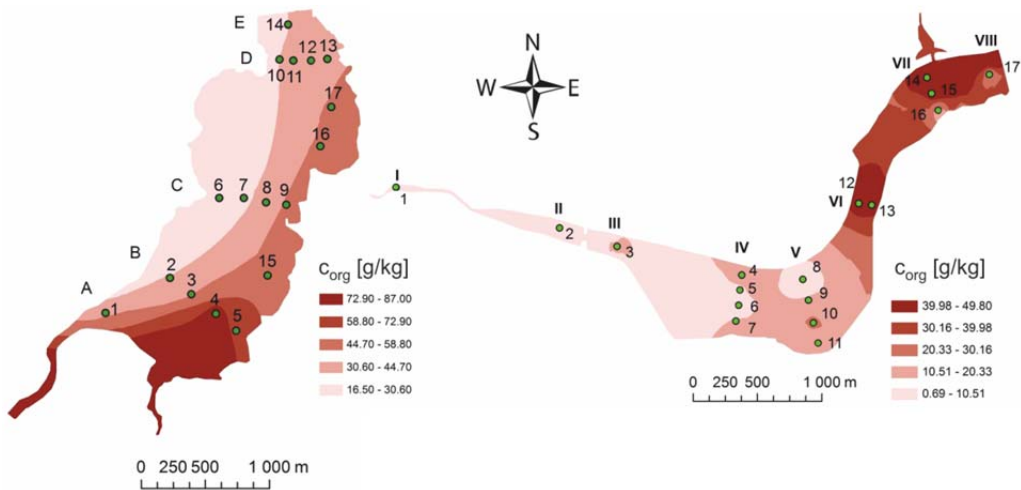


Fig. 1. Sampling sites and spatial distribution of  $C_{org}$  in bottom sediments of the reservoirs: left: the Zemborzycycki Reservoir right: the Brody Hżecckie Reservoir

The studied objects differ by the structure of geology of their catchments. The direct catchment of BI reservoir in substantial part is built with ferruginous sandstones, claystones and clays, claystones and variegated clays, water-glacial sands, loesses and loess like rocks, valley fills, river valley sands and silts [14, 15]. According to the soil-agricultural map (1:25 000) of the catchment, prepared by the Institute of Soil and Plant Cultivation in Puławy based on the original map [16], in the Brody Hżecckie direct catchment area, agriculturally used soils consist primarily of Cambisol and Podzol with Luvisol soils. In the direct catchment of the Zalew Zemborzycycki silts, loess-like

rocks on marls and gaizes prevail [15, 17]. Also, alluvial-periglacial sands with chalky gravels and eolian sands in dunes, sands, fluvial and fluvial-periglacial silts on the terrace above the floodplain occur there. Soils developed from these rocks dominate in the catchment area. In the agriculturally used soils the main soil types are Podzols with Luvisols and Cambisols [18].

## 2.2. SEDIMENT SAMPLING

The bottom sediment samples were collected using the Kajak sediment core sampler in July 2010 and in both reservoirs they were taken from 17 sites. In the ZZ, these were the following sampling locations: 4 samples in each of three transverse transects, that is in the upper (B), middle (C) and lower (D) part of the reservoir, one sediment sample at the place of the Bystrzyca inflow (A) and one at the frontal dam (E) (Fig. 1 left). Additionally, single samples were taken from the bay parts of the reservoir, between B and C transects (15), C and D (16, 17). In the BI reservoir, 13 samples were collected in four transverse transects (IV, V, VI, VII) 2–4 samples subject to the transect length and 3 samples in the part of the Kamienna River inflow (II, II2, III3) and one sample at the frontal dam (VIII17) (Fig. 1 right). At each selected sampling site, from 10 up to 15 cores of hydrated sediments were taken to form the representative sample (ca. 5 dm<sup>3</sup>). The sediments were air dried without water removal to be afterwards homogenized in an agate mortar.

## 2.3. METHODS

Organic carbon quality was determined by the modified Griffith–Schnitzer [19]. fractionation method. The following carbon fractions were established: total organic carbon, humus acids dissolved in 0.1 M NaOH (C-NaOH) including humic acids (HA) and fulvic acids (FA), fraction soluble in 0.5 M H<sub>2</sub>SO<sub>4</sub> (hydrolyzing carbon – hemicelluloses, C-H<sub>2</sub>SO<sub>4</sub>) and insoluble fraction – the residue (C-Res) from the C<sub>org</sub> – (C-NaOH + C-H<sub>2</sub>SO<sub>4</sub>) difference. In the humus acid fraction, the humic acid content was determined after the precipitation in H<sub>2</sub>SO<sub>4</sub> solution and content of fulvic acids was determined from the difference (C-NaOH – C-HA). In the sediment samples and in the extracted carbon fractions, total organic carbon content (C<sub>org</sub>) was measured using the wet oxidation procedure. The mixture of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SO<sub>4</sub> was used as oxidation solution and the excess of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> was titrated with Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Three sediment samples from the BI reservoir (II, I2, IV6) were excluded from the fractional analysis because of very low C<sub>org</sub> content.

The results were analyzed statistically to determine the minimum and maximum values, mean values, the median, kurtosis and skewed distribution. In order to evaluate the differences between the means for the transects, Tukey's test was applied with establishing the least significant difference (LSD).

The maps of  $C_{org}$  spatial distribution were made and to interpolate the distributions, the kriging technique was applied. As the investigated variables did not satisfy the stationary condition, they underwent the trend analysis. The detected trends were removed and then empirical semivariograms were calculated to be afterwards fitted to the mathematical functions and used to estimate the studied values in the space by means of the ordinary kriging procedure. The analyses were based on ArcGIS program.

### 3. RESULTS

The concentration of organic carbon in sediments of the studied reservoirs showed substantial differentiation depending on a sampling location. In the ZZ sediments, it ranged from 16.5 to 87.0 g C/kg d.w.s. (Table 1).

Table 1

Content of organic carbon ( $C_{org}$ ) and its fractions in the bottom sediments of Zalew Zemborzycycki

Transect, site/statistics	Depth [m]	Fractions of organic carbon [g C/kg d.w.s.] <sup>a</sup>						
		$C_{org}$	C-NaOH	C-HA	C-FA	C-H <sub>2</sub> SO <sub>4</sub>	C-Res	HA:FA
A1	1.2	40.80	2.88	0.85	2.03	1.62	36.30	0.42
B								
Minimum	1.8	32.07	2.52	0.82	1.70	1.14	28.41	0.41
Maximum	2.2	87.00	5.07	1.87	3.20	1.74	80.49	0.65
Mean B	2.1	55.72	3.78	1.30	2.48	1.37	50.57	0.53
C								
Minimum	2.2	16.50	1.98	0.48	1.50	0.42	13.89	0.23
Maximum	3.2	45.90	4.02	0.84	3.18	1.05	41.46	0.32
Mean C	2.9	28.73	2.73	0.59	2.14	0.71	25.37	0.28
D								
Minimum	3.5	30.60	2.94	0.43	2.27	0.39	27.18	0.12
Maximum	3.8	40.80	4.02	0.77	3.59	0.90	35.88	0.32
Mean D	3.6	36.38	3.43	0.65	2.78	0.69	32.26	0.25
E14	4.0	30.00	2.76	0.48	2.28	1.11	26.13	0.21
15	2.2	57.00	3.30	0.98	2.32	0.90	52.80	0.42
16	3.3	45.00	3.69	0.91	2.78	0.84	40.47	0.33
17	3.5	47.10	3.48	0.74	2.74	0.84	42.78	0.27
Overall minimum	1.2	16.50	1.98	0.43	1.50	0.39	13.89	0.12
Overall maximum	4.0	87.00	5.07	1.87	3.59	1.74	80.49	0.65
Overall mean	2.9	41.38	3.29	0.83	2.45	0.96	37.13	0.35
LSD <sup>b</sup> (B, C, D) <sup>c</sup> = 32.474, median <sup>c</sup> = 40.50, kurtosis <sup>c</sup> = 2.66, skewness <sup>c</sup> = 1.24								

<sup>a</sup>d.w.s. – dry weight of sediment.

<sup>b</sup>LSD – the least significant difference.

<sup>c</sup>For  $C_{org}$ .

The highest sedimentary  $C_{org}$  content (mean 55.72 g C/kg d.w.s.) was determined in transect B of this waterbody as compared to the sediments of the others where the organic carbon level averaged 28.73 g C/kg d.w.s. (transect C) and 36.38 g C/kg d.w.s. (transect D). However, the statistical analysis did not exhibit any significant differences between the compared pairs of mean values of  $C_{org}$  for the transects.

In 7 sediment samples, the  $C_{org}$  level was within the 30.60–44.70 g C/kg d.w.s. interval (Fig. 2a), where the mean value for the reservoir (41.38 g C/kg d.w.s.) and the median (40.50 g C/kg d.w.s.) were also found (Table 1). Four samples had the content below the aforementioned range and four samples above it, whereas only two samples showed the greatest  $C_{org}$  concentration range (>58.8 g C/kg d.w.s.). As a result, the organic carbon distribution in the Zalew Zemborzycycki sediments was clearly right skewed ( $A_s = 1.24$ ) (Table 1).

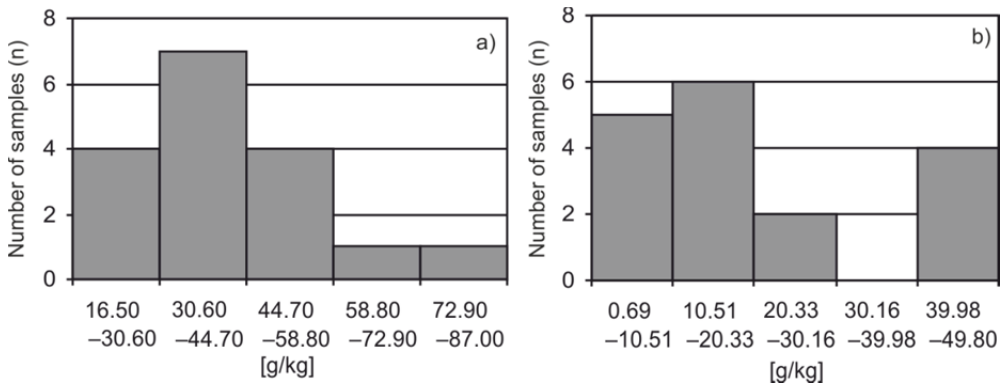


Fig. 2. Histogram of  $C_{org}$  distribution in bottom sediments of the reservoirs:  
a) Zalew Zemborzycycki, b) Brody Ilzeckie

The analysis of the  $C_{org}$  spatial distribution has demonstrated a noticeable longitudinal zonation pattern of this element content in the sediments of the Zalew Zemborzycycki (Fig. 1 left). The lowest organic carbon content had sediments in the left-bank part of the ZZ, while the highest in the right-bank area. The medium  $C_{org}$  levels were noted in the sediments along the middle part of the reservoir.

In the Brody Ilzeckie Reservoir, the  $C_{org}$  concentration in sediments was more varied than in the ZZ and ranged between 0.78 and 49.80 g C/kg d.w.s. (Table 2). It tended to increase approaching the dam and was definitely the greatest in the sediments of the lower part (average 49.05 and 38.60 g C/kg d.w.s. in transect VI and VII, respectively).

A part of the river tributary (I–III) and that, where the sediments were dredged (transect IV and V) markedly differed from the others in terms of  $C_{org}$  content in sediments. The organic carbon level in the sediments of sectors I–V oscillated from 0.78 up to 23.55 g C/kg d.w.s., the mean value 9.41 g C/kg d.w.s. Average  $C_{org}$  concentration in the sediments of transect IV and V was similar and reached 10.50 and 12.71 g

C/kg d.w.s. values, respectively. Whereas in the sediments of the other areas,  $C_{org}$  concentration was higher by ca. 3.5 times (41.03 g C/kg d.w.s.). The mean value for the entire reservoir (20.44 g C/kg d.w.s.) was higher than the median (14.40 g C/kg d.w.s.). The differences between the mean values for transect IV, V of the first part and VI, VII of the other part were statistically significant (Table 2).

Table 2

Content of organic carbon ( $C_{org}$ ) and its fractions in sediments of the Brody Itzeckie Reservoir

Transect, site/statistic	Depth [m]	Fractions of organic carbon [g C/kg d.w.s.] <sup>a</sup>						
		$C_{org}$	C-NaOH	C-HA	C-FA	C-H <sub>2</sub> SO <sub>4</sub>	C-Res	HA:FA
Minimum	1.2	0.78						
Maximum <sup>b</sup>	2.5	12.30	2.04	0.72	1.32	0.60	9.66	0.55
Mean I-III	1.7	4.73						
IV								
Minimum	2.0	1.80	1.71	0.65	0.79	0.84	7.89	0.54
Maximum	3.2	15.0	1.86	1.06	1.21	1.20	12.06	1.34
Mean IV	2.7	10.50	1.81	0.85	0.96	1.04	10.55	0.95
V								
Minimum	2.8	3.75	0.55	0.28	0.27	0.57	2.30	0.48
Maximum	3.8	23.55	2.07	1.06	1.40	0.90	20.61	1.49
Mean V	4.2	12.71	1.59	0.68	0.91	0.77	10.36	0.89
Minimum I-V	1.2	0.78	0.55	0.28	0.27	0.57	2.30	0.48
Maximum I-V	3.5	23.55	2.07	1.06	1.40	1.20	20.61	1.49
Mean I-V	2.6	9.41	1.73	0.75	0.98	0.85	10.34	0.87
VII2	4.5	49.20	2.31	0.85	1.46	0.75	46.14	0.58
VII3	4.5	48.90	2.22	0.62	1.60	0.81	45.87	0.39
Mean VI	4.5	49.05	2.27	0.74	1.53	0.78	46.01	0.48
VII								
Minimum	3.8	17.40	2.52	0.53	1.66	0.75	13.14	0.27
Maximum	4.5	49.80	3.12	1.01	2.27	1.26	45.87	0.61
Mean VII	4.2	38.60	2.77	0.80	1.97	1.05	34.78	0.42
VIII17	5.0	26.70	3.27	1.32	1.95	0.87	22.56	0.68
Minimum VI-VIII	3.8	17.40	2.22	0.53	1.46	0.75	13.14	0.27
Maximum VI-VIII	5.0	49.80	3.27	1.32	2.27	1.26	46.14	0.68
Mean VI-VIII	4.4	41.03	2.69	0.86	1.80	0.93	36.49	0.48
Overall minimum	1.2	0.78	0.55	0.28	0.27	0.57	2.30	0.27
Overall maximum	5.0	49.80	3.27	1.32	2.27	1.26	46.14	1.49
Overall mean	3.24	20.44	2.14	0.80	1.34	0.88	21.55	0.70
LSD <sup>c</sup> (B, C, D) <sup>d</sup> = 23.166, median <sup>d</sup> = 14.40, kurtosis <sup>d</sup> = -0.78, skewness <sup>d</sup> = 0.81								

<sup>a</sup>d.w.s. – dry weight of sediment.

<sup>b</sup>Point III3.

<sup>c</sup>LSD – the least significant difference.

<sup>d</sup>For  $C_{org}$ .

The histogram of distribution of  $C_{org}$  values in the BI reservoir sediments (Fig. 2b) indicates that in 5 samples organic carbon level was found within the lowest interval values (0.69–10.51 g C/kg d.w.s.), in 6 samples within the higher range (10.51–20.33 g C/kg d.w.s.) and finally, in 4 samples in the highest (39.98–49.80 g C/kg d.w.s.). Among the studied samples, no sedimentary  $C_{org}$  contents were established in the medium range of values. Consequently, it is the right skewed  $C_{org}$  distribution ( $As = 0.81$ ) (Table 2).

Unlike the ZZ, spatial distribution of  $C_{org}$  in the sediments of the Brody Ilzeckie Reservoir showed transverse zonation (parallel to the frontal dam) pattern of this element content (Fig. 1 right). The lowest organic carbon content had sediments in the area of transects I–IV, while the highest in the VII and VIII. The medium  $C_{org}$  levels were noted in the sediments in the transects V and VI of the reservoir.

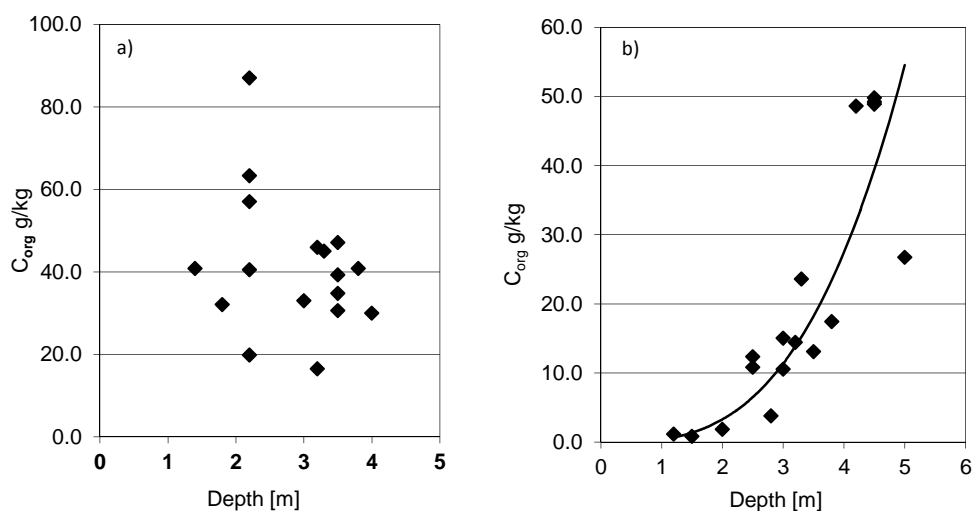


Fig. 3. Dependence of the content of  $C_{org}$  on depth: a) Zalew Zemborzycycki, b) Brody Ilzeckie

Analyses of  $C_{org}$  in dependence on the depth did not show a clear relationship. In BI, an increase of  $C_{org}$  content with increasing the depth of the sediment was observed, whereas in ZZ no relationship was noticed (Fig. 3).

### 3.1. FRACTIONAL COMPOSITION OF ORGANIC CARBON

Carbon of humus acid fraction extracted in 0.1 M NaOH contains C of humic and fulvic acids. Carbon content in this fraction in the sediments of ZZ ranged from 1.98 up to 5.07 g C/kg d.w.s. and, alike the case of  $C_{org}$ , it was highest in the sediments of transect B (mean 3.78 g C/kg d.w.s.) and lowest in the sediments of transect C (mean 2.73 g C/kg d.w.s.) (Table 1). The contents, presented as percentage in proportion to



$C_{org}$ , were the opposite of that, namely the smallest in the sediments of transect B (mean 7.08%), while in those of transect C – the greatest (mean 10.07%) (Table 3). Overall, average share of humus acid fraction in  $C_{org}$  in the sediments of the ZZ reservoir maintained at 8.48% level, oscillating between 5.79 and 12.00%.

Table 3

Percentage share of organic carbon fractions in bottom sediments of Zalew Zemborzycycki in total  $C_{org}$  content

Transect, site/statistic	Fractions of organic carbon [% $C_{org}$ ]				
	C-NaOH	C-HA	C-FA	C-H <sub>2</sub> SO <sub>4</sub>	C-Res
A1	7.06	2.08	4.98	3.97	88.97
<b>B</b>					
Minimum	5.83	2.05	3.68	1.66	88.15
Maximum	7.86	2.96	5.30	4.30	92.52
Mean B	7.08	2.43	4.65	2.83	90.10
<b>C</b>					
Minimum	7.91	1.83	6.03	0.92	84.18
Maximum	12.00	2.91	9.49	3.82	90.33
Mean C	10.07	2.20	7.89	2.89	87.04
<b>D</b>					
Minimum	7.48	1.70	5.78	1.27	87.50
Maximum	10.69	2.42	8.80	2.21	90.38
Mean D	9.48	1.85	7.64	1.86	88.66
E14	9.20	1.60	7.60	3.70	87.10
15	5.79	1.72	4.07	1.58	92.63
16	8.20	2.02	6.18	1.87	89.93
17	7.39	1.57	5.82	1.78	90.83
Overall minimum	5.79	1.05	3.68	0.92	84.18
Overall maximum	12.00	2.96	9.49	4.30	92.63
Overall mean	8.48	2.05	6.43	2.54	88.98

In the Brody Hżeczek Reservoir, likewise the  $C_{org}$  concentration, the C content of NaOH fraction was more variable and lower in the sediments of the dredged part (0.55–2.07, mean 1.73 g C/kg d.w.s.) as against the sediments of the not dredged part (2.22–3.27, mean 2.69 g C/kg d.w.s.) (Table 2).

Average total C content of humus acid fraction was 2.14 g C/kg d.w.s. This fraction concentration of  $C_{org}$  expressed in per cent seems interesting. The sediments of the not dredged part of the BI had the share comparable to that in the sediments of the ZZ and it averaged 8.33%, at the range of 4.54–17.93% (Table 4). Whereas in the dredged part characterized by far less organic carbon content, it was higher (14.15%) than in both, sediments of the BI and ZZ reservoir.

In the sediments of the Zalew Zemborzycy, fulvic acids were shown to predominate over humic ones in the humus acid fraction (Table 1). The content of humic acids ranged from 0.43 up to 1.87 g C/kg d.w.s. (average 0.83 g C/kg d.w.s.), whereas of fulvic ones between 1.50 and 3.59 g C/kg d.w.s. (average 2.45 g C/kg d.w.s.). The percentage share of the humic acids in  $C_{org}$  averaged 2.05% at the interval 1.05–2.96%, while that of the fulvic acids at 3.68–9.49% (average 6.43%) (Table 3). As a result, the HA:FA ratio in the sediments of the ZZ was equal to mean 0.35 at the 0.12–0.65 interval (Table 1). Notably, it was higher in the sediments of transect B (mean 0.53) as compared to transect C (mean 0.28) and D (mean 0.25).

Table 4

Percentage share of organic carbon fractions  
in bottom sediments of Brody Ilżeckie Reservoir in total  $C_{org}$  content

Transect, site/statistic	Fractions of organic carbon [% $C_{org}$ ]				
	C-NaOH	C-HA	C-FA	C-H <sub>2</sub> SO <sub>4</sub>	C-Res
Minimum	–	–	–	–	–
Maximum	16.59	5.85	10.73	4.88	78.54
Mean I–III	–	–	–	–	–
IV					
Minimum	12.40	4.33	5.49	5.83	73.06
Maximum	15.83	7.78	8.07	11.11	81.25
Mean IV	13.72	6.49	7.20	8.05	78.24
V					
Minimum	8.79	2.85	5.94	3.69	61.33
Maximum	16.86	10.10	9.66	24.00	87.52
Mean V	13.87	6.48	7.39	9.66	76.47
Minimum I–V	8.79	2.85	5.49	3.69	61.33
Maximum I–V	16.86	10.10	10.73	24.00	87.52
Mean I–V	14.15	6.41	7.74	8.46	77.39
VI12	4.70	1.73	2.97	1.52	93.78
VI13	4.54	1.27	3.27	1.66	93.80
Mean VI	4.62	1.50	3.12	1.59	93.79
VII					
Minimum	5.19	1.09	3.33	1.54	75.52
Maximum	17.93	4.89	13.05	6.55	93.27
Mean VII	9.49	2.67	6.82	3.54	86.97
VIII17	12.25	4.94	7.30	3.26	84.49
Minimum VI–VIII	4.54	1.09	2.97	1.52	75.52
Maximum VI–VIII	17.93	4.94	13.05	6.55	93.80
Mean VI–VIII	8.33	2.66	5.67	2.84	88.83
Overall minimum	5.54	1.09	2.97	1.52	61.33
Overall maximum	17.93	10.10	13.05	24.00	93.80
Overall mean	11.66	4.80	6.85	6.05	82.29

In the BI reservoir, in the older sediments of the not dredged part, alike the ZZ sediments, fulvic acids outweighed humic ones and average ratio of HA to FA was higher than in ZZ – 0.48 (Table 2). As for the younger sediments of the dredged part, this regularity was conformed in most cases, yet an inverse relationship was noted for three cases, i.e. higher C of humic acids than fulvic ones. Finally, the mean ratio of HA:FA was considerably higher and averaged 0.87.

A content of organic carbon dissolved in H<sub>2</sub>SO<sub>4</sub> solution (hemicelluloses) in the sediments of both reservoirs was markedly lower than that of humus acids. In the ZZ sediments, it averaged 0.96 g C/kg d.w.s. (the 0.39–1.74 g C/kg d.w.s. interval) (Table 1). A similar level was reported for the younger and older sediments of the BI, that is 0.85 and 0.93 g C/kg d.w.s., respectively (Table 2). A mean share of C of this fraction in proportion to total C<sub>org</sub> concentration also tended to be lower than that of humus acids and was equal to 2.54% (the range of 0.92–4.30%) in the ZZ sediments (Table 3) and 2.84% (1.52–6.55%) in the BI sediments (Table 4). In the younger sediments of the latter one, the share was higher and more varied; it was found within the interval 3.69–24.00% (mean 8.46%).

In the organic carbon composition of the sediments of both investigated reservoirs, the most abundant proved to be compounds that are alkali- and acid-insoluble. The content of the rest in the ZZ sediments oscillated between 13.89 and 80.49 g C/kg d.w.s. (mean 37.13 g C/kg d.w.s.) (Table 1) and accounted for 84.18–92.63% (mean 88.92%) of C<sub>org</sub> (Table 3). In the older sediments of the BI reservoir, it was found at a similar level on average, i.e. 36.49 g C/kg d.w.s. and 88.83%, whereas in the younger sediments, it was lower (10.36 g C/kg d.w.s. and 77.39%) (Tables 2, 4).

#### 4. DISCUSSION

The results showed differences between the reservoirs in terms of organic carbon content and its spatial distribution pattern. A characteristic feature of the sediments in the Zalew Zemborzycki is the C<sub>org</sub> content increasing with the distance from the western shoreline area to the eastern one. There may be some reasons that act to cause such effect and one of them is a difference in hydrodynamic features of particular parts of the reservoir. In the upper and partly in western side, it is riverine because the parent river runs closer to the western shoreline and in farther distance to the eastern one [20]. Generally, riverine zones of the reservoirs are shallow and have relatively high flow rates [21]. Organic matter is transported there by advective currents but relatively little of it is deposited. Low concentrations of sedimentary organic carbon in the western part of the ZZ may be ascribed then to the lower depth and higher water dynamics as compared to other areas. Weaker accumulation of organic matter in the shallow water zone and in the zone of higher water dynamics were confirmed by a number of authors [22–26]. Another important underlying reason for the observed relationship

can be relatively strong water waving, as this area is unscreened from the prevailing western wind. Wind-driven turbulence causes moving a suspension and resuspended sediments [27].

Unlike the western part, the eastern one and especially cove sites (4, 5, 15), is situated at the greatest distance from the river channel. This fact together with forest vegetation surrounding it and screening from the wind cause this area of the reservoir to show features of lacustrine environment which promotes sedimentation [3, 4, 22]. Besides, it should be highlighted that a high  $C_{\text{org}}$  content in sediments of this part of the reservoir is also likely to be attributed to the character of peat soils occurring there, and not removed before the construction of the reservoir [28].

The established regularity of the  $C_{\text{org}}$  longitudinal zonation pattern is consistent with that determined in the first operation years of the ZZ reservoir [29] and at the beginning of the 2000s [30]. The dependence is not typical of dam reservoirs. Generally, the sedimentary elements distribution is parallel to the frontal dam [31, 32]. Such distribution, i.e. transverse zonation for BI was stated. The lowest and most differentiated  $C_{\text{org}}$  values were noted in the sediments of the upper and in the dredged parts of this reservoir, followed by the medium and highest contents.

Taking into account the sampling locations, in ZZ, a lower  $C_{\text{org}}$  content in the sediments of transect C as compared to the others was found. This can be associated with the reservoir narrowing at this area, where the water flow is faster and consequently, lower sedimentation of fine particles is observed. It is also reflected in the grain size composition, i.e. a higher percentage of coarse fractions and a lower share of fine ones, as indicated in the earlier studies [33]. Such conditions are not conducive to organic matter accumulation in sediments of this part of the Zalew Zemborzycki [22].

The obtained  $C_{\text{org}}$  values in the ZZ sediments were comparable to those determined 30 and 10 years ago [29, 30] and that implies a relatively stabilized cycle of accumulation of the organic carbon compounds and fate in this reservoir. The  $C_{\text{org}}$  concentration in the ZZ sediments appeared to be close to that established for the Myczkowce reservoir (46.0–49.0 g/kg) [34] and Krishnagiri in India (18.0–67.0, mean 46.0 g/kg) [21] but higher than in the sediments of the Solina reservoir (21.4–30.2 g/kg), as reported by Koszelnik et al. [34], and in the sediments of the Dobczyce reservoir [22]. In turn, the organic carbon content was lower than that determined by Górnjak and Jekaterynczuk-Rudczyk [35] in the sediments of the Siemianówka reservoir. The sedimentary  $C_{\text{org}}$  concentration in the last water basin averaged 90.0 g/kg after a dozen years of its operation.

The research results demonstrate a high sediment  $C_{\text{org}}$  content in the not dredged part of the BI. It is notable that the mean  $C_{\text{org}}$  content in the sediments of this area approached this element average concentration in the sediments of the ZZ. This fact may imply similar accumulation conditions and organic matter transformations in both reservoirs. Then, great variability and low  $C_{\text{org}}$  content values in the sediments of the

dredged part of the BI reservoir, as compared to the not dredged one, provides evidence of very slow carbon accumulation process in the sediments after the treatment.

There was not stated an explicit relationship between the  $C_{org}$  content in sediment and depth. In the BI, a positive correlation was established, whereas no dependence was stated in the ZZ. On the whole, literature evidences that the  $C_{org}$  content increases with the depth of the reservoir – from the inflow to the dam [22, 26, 36]. The lack of dependence in the ZZ was due to the sediments of south-eastern part, where the depth was within the lower ranges and  $C_{org}$  contents were high. This indicates that the other factors (discussed above) were dominant for  $C_{org}$  accumulation and distribution there.

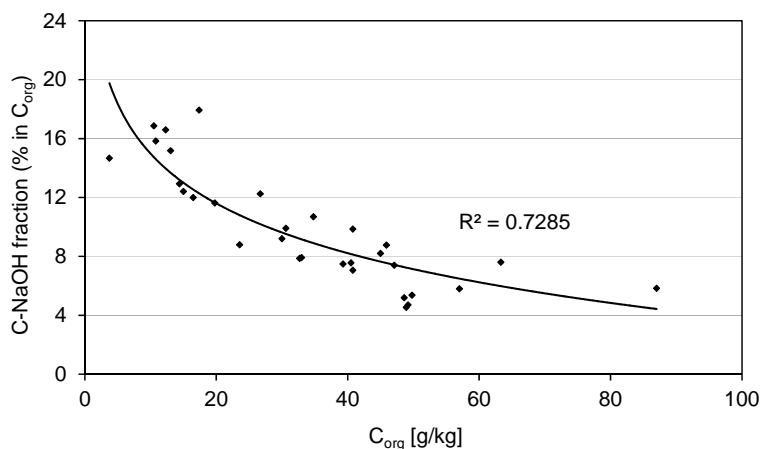


Fig. 4. Dependence of the content of humus acid fraction on the total organic carbon content in bottom sediments of the reservoirs

The sediments with a higher content of  $C_{org}$  (ZZ and not dredged part of BI) showed a lower percentage of humus acid fraction than the sediments with lower  $C_{org}$ . This regularity emerges from a relationship established between the percentage of humus acid fraction and total amount of organic carbon (Fig. 4); the dependence is inversely proportional. Such a relationship was also reported by Górnjak [3] for sediments of the Suwałki region and the Łęczyńsko-Włodawskie Lake District. The author associates it with the intensive accumulation of poorly decomposing macrophyte tissues and organic carbon-abundant string algae in sediments that relatively reduces humus substances contribution to total  $C_{org}$  concentration in sediments.

Generally, in sedimentary  $C_{org}$  fulvic acids were found to outweigh humic ones and average HA:FA ratio in the sediments of the ZZ, while in the not dredged part of BI it was 0.35 and 0.48, respectively. In the younger sediments of the dredged part, it was substantially higher (0.87). The value of the proportion less than 1.0 was also determined by Górnjak [3] in the sediments of the Siemianówka dam reservoir

(0.88–0.98) and the Zegrzyński (0.42–0.65). However, an opposite relationship concerning river sediments was reported by Devesa-Rey and Barral [37].

## 5. CONCLUSIONS

There was noted great differentiation of  $C_{org}$  content in the studied sediments subject to a sampling site. In the Zalew Zemborzycki, the transect B area (the upper part of the reservoir) showed the highest  $C_{org}$  concentration as compared to the sediments of the other areas. In the Brody Iłżeckie Reservoir sediments,  $C_{org}$  level was the lowest in the part of the river tributary and the dragged part but tended to increase while advancing towards the frontal dam. It was evidently the greatest in the sediments of the lower, not dredged part. The  $C_{org}$  content spatial distribution in the sediments exhibited the longitudinal zonation pattern in the ZZ and transverse, parallel to the frontal dam, in the BI reservoir. The results of the research indicate that in small and shallow reservoirs, spatial distribution (accumulation) of organic carbon compounds is related to such factors like, a parent river current, reservoir depth, water waving, reservoir shape (coves/bays) and also, features of soils occurring at the bed (if not removed before the reservoir construction).

The composition of sedimentary  $C_{org}$  in both waterbodies under study showed the highest percentage of the insoluble fraction followed by humus acid fraction and the lowest – hemicelluloses fraction. Generally, in the humus acid fraction, fulvic acids predominated over humic acids. Carbon content of the humus acid fraction in the sediments of the ZZ and not dredged part of the BI water basin in proportion to total  $C_{org}$  content was similar, i.e. 8.48 and 8.33%, respectively. In the dredged part of the latter one, it was more differentiated and higher (14.15%).

There was observed similarity in term of total carbon content and its fractions in the bottom sediments of the Zalew Zemborzycki and those of the not dragged part of the Brody Iłżeckie Reservoir. That may indicate the stabilized and similar conditions and fate of organic matter in these objects and point to autochthonic matter is its major source.

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