Differences in the Properties of the Bottom Sediments in the System of Wdzydze Lakes (Northern Poland)

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Abstract: The influence was determined of the anthropo-pressure on the changes in the properties of the bottom sediments, with particular consideration given to the properties of humic acids formed in the sediments. The system of the Wdzydze Lakes consists of four separate basins, the northern basins being under the anthropo-pressure related to the impact of the local tourism. This study tested the bottom sediments of the Wdzydze Lake system, especially properties of humic acids extracted from the bottom sediments. The analysis of the properties of the bottom sediments showed small differences in the parameters determined. This proves the impact of local tourism on the ecosystem to be rather small so far. The results of this research suggest that a complex of positive environmental factors in a lake ecosystem can usefully outweigh the negative results of the anthropo-pressure.

Keywords: humic acids; lake; bottom sediments

Growing trophy in an aquatic basin is a slow and natural process, which occurs when the supply of nutrients in the catchment increases. Nevertheless, an enormous increase in the fertility of the lake water has occurred in recent decades causing accelerated eutrophication. This constitutes the most significant and frequently occurring anthropogenic interference in the functioning of aquatic ecosystems. An increasing supply of nutrients, particularly phosphorus, is the most common cause of eutrophication. Anthropogenic increases in the inflow of biogenic elements are predominantly the result of the introduction of raw sewerage, an increasing use of agricultural fertilisers, and increasing erosion within the catchment. The dumping of communal sewerage leads to phosphorus increases, while the fertilisation of fields causes mainly nitrogen increases (Lampert & Sommer 1997). Water basins, to some degree, can neutralize the negative consequences arising from the introduction of increasing biogenic element loads. The values of nitrogen and phosphorus loads, considered acceptable or dangerous, are available in literature (Wetzel 1983). The differences between those values are not great. Small, as well as big basins, such as Lakes Erie and Ontario, are equally at risk of eutrophication.

The consequence of the biogenic increases is the massive development of blue-green algae, while in the littoral zone the light conditions for aquatic macrophytes deteriorate (Lampert & Sommer 1997). There may be subsequent phosphorus loads released from the bottom sediments due to the changes occurring in the aquatic ecosystem.

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The anthropogenic inflow of biogenic elements in Lake Wdzydze is associated with the development of a tourist base situated mainly in its northern part. Moreover, municipal and farm sewerage inflow was discharged into the lake in the recent past. Tests in Lake Wdzydze revealed heightened levels of phosphorus, considered dangerous (Przewozniak 2001).

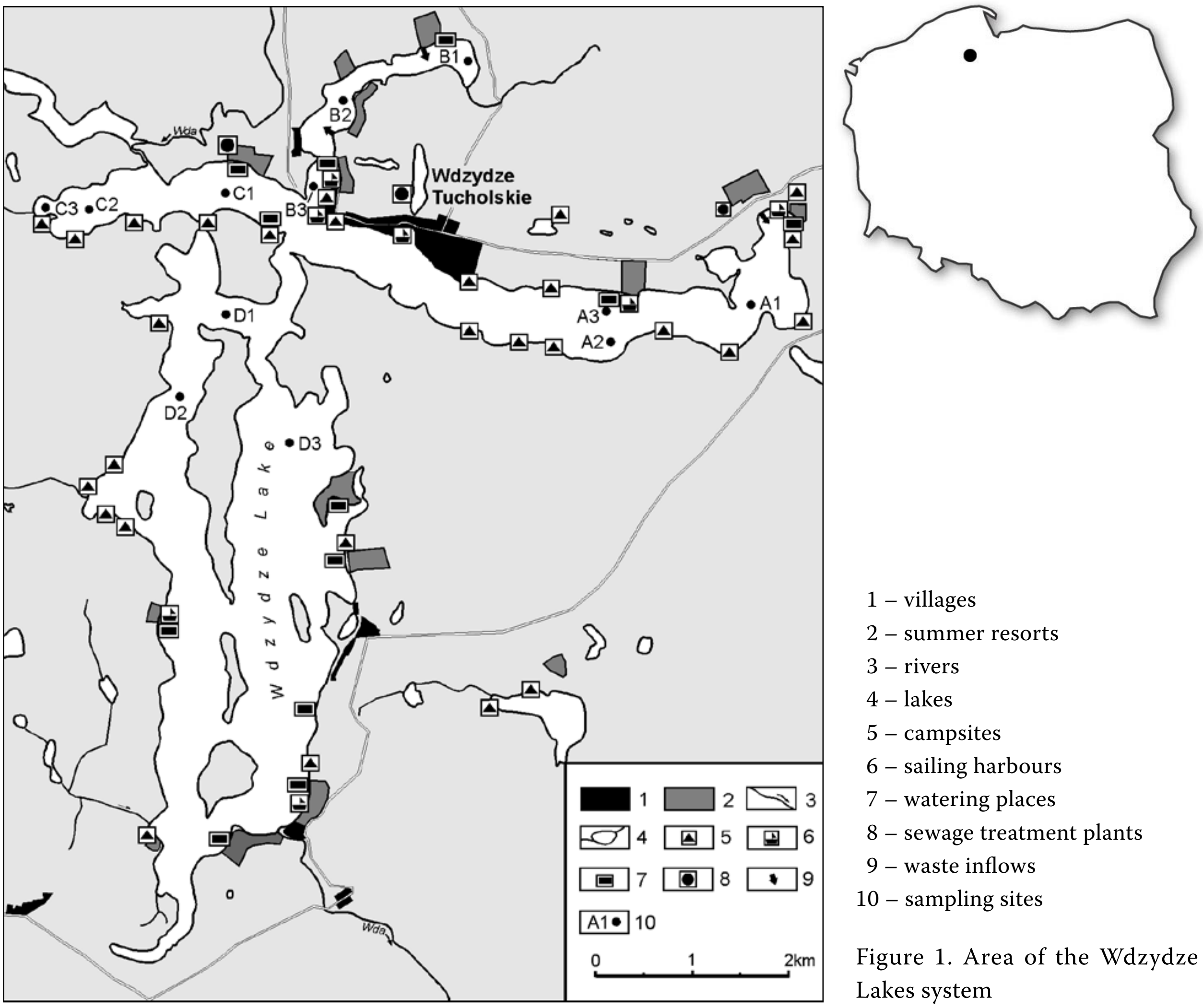
The aim of this study was to determine the influence of the anthropo-pressure on the changes in the properties of the bottom sediments, with particular consideration given to the properties of humic acids formed in the sediments.

MATERIALS AND METHODS

Study area

The system of Wdzydze Lakes is situated in the European Lowland in the Pojezierze Pomorskie area (Pomorskie Lakeland District). The vast outwash plain stretching in this particular place was formed out of post-glacial sand and gravel. The thickness of these formations varies from several centimetres to approximately 10 m. Lower levels consist of clay containing large quantities of $CaCO_3$. The ceiling of the clay is situated approximately 1 m above the lake water level.

Lake Wdzydze system consists of a number of distinguishable basins, which are separated from one another by underwater thresholds (Figure 1) which physically divide the lake within the complex. Its individual parts lay in subglacial troughs crossing at right angles. They originate from the last glaciation period (Vistula glaciation) and were formed by erosion under the Scandinavian glacier and water released by thawing ice. Trough slopes are tall (up to 15 m) and very steep, with gradients in places approaching 40°. Often are there narrow shallows along the shores. The age



1 – villages
2 – summer resorts
3 – rivers
4 – lakes
5 – campsites
6 – sailing harbours
7 – watering places
8 – sewage treatment plants
9 – waste inflows
10 – sampling sites

Figure 1. Area of the Wdzydze Lakes system

Table 1. The morphometrical data of basins

Name and symbol of basin		Length (km)	Width (km)	Area (ha)	Shore-line (km)	Maximal depth (m)	Mean depth (m)	Volume (10^6 m^3)
Golun	A	6.1	1.2	320.4	15.0	18.0	8.2	26.4
Jelenie	B	2.9	0.4	71.0	6.6	18.8	6.9	4.9
Radolne	C	3.0	0.6	134.6	6.9	13.1	6.0	8.1
Wdzydze	D	8.2	2.8	918.8	27.6	68.0	19.6	180.1

of the lake is estimated at approximately 11 thousand years.

The lake basic morphometric data is as follows: total surface 1444.8 ha, max depth 68 m, shoreline length 56.1 km, total volume 219.5 10^6 m^3. The bottom of the lake is varied with a number of deep wells. The slopes of the lake basin are steep and in many places their gradient exceeds 30°.

The lake is surrounded mainly by forests dominated by Scotch pine (*Pinus sylvestris*), mixed in places with oak (*Quercus sp.*). There are mixed forests near the shoreline of the lake consisting of beech-oak or ash-alder. The human population in the catchment area of the lake is rather small. The number of permanent inhabitants in the villages close to the lake is only 350 (population density is lower than 15 people per km^2). There are a few tourist villages near the lake housing recreation centers, as well as individual summer houses and camping grounds. In the summer months of July and August, there are on average 5800 people, 2600 in the recreation centers and 1100 in the camping grounds. Tourism seems to have a greater impact on the northern part of the lake.

Waste water and sewerage management around the lake was properly organised in the mid 1990's. Raw or partially treated sewerage was being discharged directly into the lake until 1995, when a biological treatment plant, with a capacity of 180 m^3/day in the summer season, was built. In the following years, a number of smaller treatment plants were built and the pollution inflow into the lake ceased.

Wdzydze Lake comprises the following parts: Golun (basin A), Jelenie (basin B), Radolne (basin C) and Wdzydze (basin D). The basic morphometric data for the lakes is presented in Table 1.

Sampling

The sediment samples were obtained from the lake deep water wells, 3 from each basin, with the Ekman sampler. Table 2 shows the depths from which the samples were obtained and which lakes they originated from. Basins A–C are subjected to a certain anthropo-pressure caused by the presence of a well developed tourism base, situated along the shores. The samples from basin D were used as reference material due to its large size and therefore its natural resistance to any changes caused by human activity, as well as only a small number of tourism centers located nearby.

Analysis

The contents of total carbon (TC) and inorganic carbon (IC) were determined in dried sediment samples with the Primacs^{SC} Analyser made by Skalar (Breda, The Netherlands), while total nitrogen (Nt) was determined using the Kjeldahl method. On the basis of these results, the calculations were made of the contents of organic carbon (TOC) from the difference TOC = TC – IC, as well as of the values of the TOC:Nt ratio. The contents

Table 2. Partition on the basins and depth of sampling

Basin	Sample symbol	Depth of sampling (m)
Golun	A1	17.1
	A2	9.0
	A3	16.1
Jelenie	B1	15.3
	B2	17.6
	B3	7.8
Radolne	C1	12.6
	C2	10.4
	C3	3.1
Wdzydze	D1	12.0
	D2	21.0
	D3	17.0

of inorganic carbon were recalculated for $CaCO_3$ (IC × 8.33).

Organic matter values by percentage were calculated: TOC × 1.74 (Murdoch *et al.* 1997), calcium carbonate and the mineral part without carbonates. The determination of the types of sediments followed Markowski (1980).

The contents of total phosphorus (TP) were determined using the Bleck method (1965), the absorbance was measured at the wavelength of 430 nm. TOC:TP and Nt:TP were calculated.

HA fractions from the air-dried sediment samples were extracted with 0.5M NaOH, precipitated at pH 2.0 with 5.0M HCl, and then purified with the mixture HF-HCl, according to the method by Schnitzer and Skinner (1968). The extracted HAs were analysed for elemental composition with a 2400 Perkin-Elmer Analyser (C, H, N). The oxygen content (O) was calculated by the difference: O = 100% – (C + H + N). The spectral properties were measured with a Perkin-Elmer Lambda 20 UV-VIS Spectrometer (for 0.003% HA solutions in 0.05M NaOH), and the thermal properties with a Derivatograph C, MOM, Hungary. Thermal analyses were performed with mixtures of 40mg HAs in 360mg Al_2O_3, within the range of 20–700°C and with the heating rate of 3.3°C per min. The curves recorded were: thermogravimetric (TG), differential thermogravimetric (DTG), and differential thermoanalytic (DTA). The interpretation and calculations of thermograms were done according to the method published earlier (Gonet 1989; Dziadowiec *et al.* 1994; Gonet & Cieslewicz 1998). The area under the DTG curve is proportional to the amount of the substance reacting in the specific temperature range.

On the basis of the analytical results, the following data were calculated:

- temperatures of peaks of effects registered on the DTA curve (higher temperatures, which the peaks occur at, indicate a higher thermal resistance of the humic acids analysed),
- mass losses corresponding with the energetic effects registered on the DTA curve (in weight percentages),
- ratio of surfaces under the DTA curve and the DTG curve in a low temperature range – (DTA_{exo1}:DTG_{exo1}) and in a high temperature range (DTA_{exo2}:DTG_{exo2}) – this characterises the energetic value of the material undergoing destruction in a certain temperature range.

Parameter Z (Eq. 1) – high values of parameter Z indicate high contents of aromatic structures, as these structures are believed to require temperatures above 350°C to decompose,

$$Z = DTG_{exo2}:DTG_{exo1} \tag{1}$$

Parameter Q (Eq. 2) – states the energetic value of the sample as a whole, higher values of this parameter indicate a higher energetic value of the material under the tests,

$$Q = SDTA:SDTG \tag{2}$$

where:

DTG_{exo2} – peak area under the DTG curve corresponding with the second exothermic reaction (350–700°C)

DTG_{exo1} – peak area under the DTG curve corresponding with the first exothermic reaction (100–350°C)

Table 3. Physico-chemical properties of bottom sediments

Sample	TOC	$CaCO_3$	Nt	TP	TOC:Nt	TOC:TP	Nt:TP	pH
	g/kg							
Range for A	112–166	225–468	12–17	1.6–1.7	9.3–10.4	70.0–103.7	7.5–10.0	7.3–7.4
Mean ± SD	146 ± 29.6	323 ± 128.0	15 ± 2.6	1.6 ± 0.06	9.7 ± 0.61	89.3 ± 17.36	9.2 ± 1.44	7.3 ± 0.06
Range for B	120–129	234–379	11–13	1.3–1.6	9.9–11.6	75.0–98.4	7.5–8.5	7.3–7.4
Mean ± SD	126 ± 4.9	304 ± 72.7	12 ± 1.0	1.5 ± 0.17	10.5 ± 0.95	84.7 ± 12.22	8.0 ± 0.50	7.4 ± 0.06
Range for C	130–160	328–420	13–16	1.3–1.6	10.0–10.3	90.0–100.0	8.7–10.0	7.3
Mean ± SD	145 ± 15.0	367 ± 47.4	14 ± 1.5	1.5 ± 0.17	10.1 ± 0.17	96.7 ± 5.77	9.6 ± 0.75	7.3 ± 0.00
Range for D	90–107	422–545	10–11	1.1–1.2	8.9–10.7	81.8–89.2	8.3–10.0	7.4–7.5
Mean ± SD	98 ± 8.5	492 ± 63.4	10 ± 0.6	1.1 ± 0.06	9.5 ± 1.01	86.7 ± 4.24	9.1 ± 0.85	7.5 ± 0.06

DTA_{exo2} – peak area under the DTA curve corresponding with the second exothermic reaction (350– 700°C)
DTA_{exo1} – peak area under the DTA curve corresponding with the first exothermic reaction (100–350°C)
SDTA – $DTA_{exo2} + DTA_{exo1}$
SDTG – $DTG_{exo2} + DTG_{exo1}$

On the basis of the elemental composition analyses, the calculations were made of atomic ratios and the degree of internal oxidation (ω) according to the equation (Zdanov 1965):

$$\omega = (2O + 3N - H):C \qquad (3)$$

where:

O, N, H, C – are from the elemental composition, in atomic percentages

The absorbance values were used for the calculations of the absorbance ratios $A_{2/4}$ ($A_{280}:A_{465}$), $A_{2/6}$ ($A_{280}:A_{665}$) and $A_{4/6}$ ($A_{465}:A_{665}$).

RESULTS AND DISCUSSION

Bottom sediments

Total organic carbon contents (TOC) in basin A varied from 112 to166 g/kg, while in basins B and C, they were found more evenly distributed from 120 to 129 g/kg and 130 to 160 g/kg, respectively. The sediments showed relatively low contents of organic matter, in comparison to the generally available values for the lake sediments that may reach TOC contents of up to 470 g/kg (Punning & Tõugu 2000), where the anthropo-pressure becomes evident. The analysed sediments show also high contents of carbonates with their average values ranging from 304 to 367 g/kg in basins B and C, respectively. In comparison to the samples from basins A–C, the sediments from basin D had lower contents of organic carbon and generally higher contents of carbonates – on average 492 g/kg (Table 3).

The calculations were made, on the basis of the data available, of percentages of organic matter, carbonates and mineral parts (without carbonates) and this led to the determination of the types of sediments (Table 4). All of the sediment samples analysed belong to the type of carbonate sediments. Two sediment samples from basin D showed very high contents of carbonates ($CaCO_3$ > 50%) and therefore were classified as calcareous gyttja, while the remaining sediment samples with lower carbonate contents and higher contents of organic matter were classified as argillo-calcareous gyttja.

The pH values were in a narrow range of 7.3–7.5. pH values resulted from relatively high contents of carbonates. The sediment samples had total nitrogen values similar to one another. Mean Nt concentrations ranged from 12 to 15 g/kg (basins A and B, respectively). No significant nitrogen

Table 4. Classification of sediments

Sample symbol	Organic matter	Carbonates	Mineral part	Kind of sediment
	in weight percentage			
A1	19.5	46.8	33.7	argillo-calcareous gyttja
A2	28.8	22.5	48.7	argillo-calcareous gyttja
A3	27.8	27.7	44.4	argillo-calcareous gyttja
B1	20.9	37.9	41.2	argillo-calcareous gyttja
B2	22.4	29.8	47.7	argillo-calcareous gyttja
B3	22.2	23.4	54.4	argillo-calcareous gyttja
C1	27.9	32.8	39.3	argillo-calcareous gyttja
C2	25.0	35.4	39.6	argillo-calcareous gyttja
C3	22.7	42.0	35.3	argillo-calcareous gyttja
D1	18.6	42.2	39.1	argillo-calcareous gyttja
D2	15.6	54.5	29.9	calcareous gyttja
D3	17.1	51.0	31.9	calcareous gyttja

Table 5. Elemental composition of humic acids

Sample	C	H	N	O
	in atom percentage			
Range for A	31.94–32.86	48.28–49.18	3.23–3.72	15.03–16.38
Mean ± SD	32.29 ± 0.50	48.63 ± 0.48	3.45 ± 0.25	15.63 ± 0.69
Range for B	31.88–32.58	48.17–49.82	3.31–3.42	14.99–16.17
Mean ± SD	32.27 ± 0.36	48.97 ± 0.83	3.35 ± 0.06	15.41 ± 0.66
Range for C	32.69–33.17	47.33–47.62	3.46–3.52	15.75–16.52
Mean ± SD	32.92 ± 0.24	47.43 ± 0.17	3.48 ± 0.04	16.17 ± 0.39
Range for D	32.02–32.32	48.40–49.19	3.05–3.20	15.58–16.23
Mean ± SD	32.18 ± 0.15	48.73 ± 0.41	3.12 ± 0.08	15.97 ± 0.34

excess was found in the sediment samples. The contents of this element in lakes undersignificant anthropo-pressure can reach as much as 34 g/kg (Punning & Tõugu 2000), however, the samples from basin D showed lower contents of this element. A significant positive correlation between TOC and Nt contents existed only in the samples from basin C ($r = 1.0$, $P < 0.05$) and this could indicate some changes associated with the anthropo-pressure in the sediments from basins A and B. The contents of total phosphorus showed a rather small variance ranging from 1.3 to 1.7 g/kg (basins A–C) and from 1.1 to 1.2 g/kg in the sediment samples from basin D. It is generally accepted that the bottom sediments contain on average from 0.5 to 6.0 g/kg of total phosphorus (Murphy *et al.* 2001; Horvatinčić *et al.* 2006). Nevertheless, higher contents were observed elsewhere – 7.32 g/kg (Lake Hollingsworth – Florida) (Brenner *et al.* 1999) and even higher – 8.5 g/kg (Ogorelec *et al.* 2006). Phosphorus contents, noted for lakes with a forest catchment without any presence of sewerage or waste water inflow, ranged from 0.6 to 1.2 g/kg. The concentrations noted in the sediment samples from Lake Wdzydze are relatively low in comparison to the data quoted above.

The following calculations were made: TOC:Nt, TOC:TP and Nt:TP. The values of TOC:Nt ranged from 9.3 to 11.6, while in the samples from basin D they ranged from 8.9 to 10.7. The values of this ratio reflect the origins of organic matter cumulated in the bottom sediments. Due to its chemical composition, the organic matter originating from algae always shows the C/N ratio values in the range of 5 to 10. Higher values of this ratio indicate that the organic matter originates from terrestrial plants, which are characterised by significantly higher values of this ratio (C/N ≥ 20) (Nakai & Koyama 1987; Meyers & Lallier-Vergès 1999). The calculated values of the TOC:Nt ratio suggest that the main source of organic matter in the bottom sediments analysed is algae, while organic matter of the land origin constitutes only a small fraction. The matter originating on land shows

Table 6. Values of atomic ratios and degree of internal oxidation (ω) for humic acids

Sample	H:C	N:C	O:C	O:H	ω
Range for A	1.47–1.53	0.098–0.116	0.47–0.51	0.31–0.34	−0.249 ÷ −0.167
Mean ± SD	1.50 ± 0.031	0.107 ± 0.009	0.48 ± 0.023	0.32 ± 0.015	−0.217 ± 0.044
Range for B	1.49–1.56	0.103–0.105	0.46–0.50	0.30–0.34	−0.311 ÷ −0.181
Mean ± SD	1.52 ± 0.038	0.104 ± 0.001	0.48 ± 0.021	0.32 ± 0.021	−0.251 ± 0.066
Range for C	1.44–1.45	0.104–0.017	0.47–0.51	0.33–0.35	−0.173 ÷ −0.119
Mean ± SD	1.44 ± 0.006	0.106 ± 0.002	0.49 ± 0.020	0.34 ± 0.010	−0.141 ± 0.029
Range for D	1.50–1.54	0.094–0.100	0.49–0.50	0.32–0.34	−0.263 ÷ −0.210
Mean ± SD	1.52 ± 0.021	0.097 ± 0.003	0.50 ± 0.006	0.33 ± 0.010	−0.231 ± 0.028

Table 7. Absorbance values (in nm) and absorbance ratios values for humic acids solutions

Sample	280	465	665	$A_{2/4}$	$A_{2/6}$	$A_{4/6}$
Range for A	0.331–0.362	0.066–0.072	0.020–0.021	4.90–5.01	15.90–18.37	3.17–3.68
Mean ± SD	0.345 ± 0.016	0.069 ± 0.003	0.020 ± 0.001	4.97 ± 0.059	17.13 ± 1.235	3.45 ± 0.258
Range for B	0.331–0.432	0.076–0.097	0.019–0.040	3.87–5.42	9.32–23.00	2.41–4.24
Mean ± SD	0.379 ± 0.051	0.084 ± 0.011	0.028 ± 0.011	4.55 ± 0.793	14.99 ± 7.136	3.18 ± 0.947
Range for C	0.364–0.474	0.068–0.086	0.017–0.021	5.35–5.50	21.54–22.89	4.00–4.16
Mean ± SD	0.416 ± 0.055	0.077 ± 0.009	0.019 ± 0.002	5.41 ± 0.079	22.10±0.705	4.08±0.080
Range for D	0.339–0.415	0.079–0.080	0.018–0.032	4.22–5.25	10.49–23.07	2.49–4.39
Mean ± SD	0.378 ± 0.038	0.079 ± 0.001	0.024 ± 0.007	4.76 ± 0.517	16.69 ± 6.292	3.44 ± 0.950

lower contents of phosphorus in comparison to the aquatic plants, thus the C/P ratio values for this type of material are high (Ruttenberg & Goñi 1997). The highest mean values of the TOC:TP and Nt:TP ratios, 96.7 and 9.6, respectively, were found in the sediments from basin C. The values corresponding noted in the samples from basin D were 86.7 and 9.1, respectively (Table 3).

Humic acids

Humic acid samples extracted from the bottom sediments showed similar contents of carbon and nitrogen, while greater differences were found with hydrogen and oxygen values. The samples of HA extracted from the bottom sediments in basin C had lower contents of hydrogen and higher contents of oxygen. Humic acids extracted from the sediments in basin D showed lower contents of carbon and nitrogen in comparison to the remaining samples (Table 5). The differences in the elemental composition are reflected by the values of the H:C ratios and by the values of the internal oxidation degree (ω). Humic acid samples extracted from the sediments in basin C had the lowest values of the H:C ratio and the highest values of the internal oxidation degree. The values of the H:C ratio were generally higher than those quoted for HA originating from the lake sediments – 1.30 ± 0.13 (Ishiwatari 1985). The values of the H:C ratio in HA samples from basin D were similar to those in basins A and B, the former showing lower values of the N:C ratio. A lower H:C ratio suggests higher aromaticity of organic compounds (Van Krevelen 1950). The degree of internal oxidation (ω) describes the origins and the character of humic acids. The samples showed a negative degree of internal oxidation, confirming anaerobic conditions prevailing during diagenetic transformations. Positive values are characteristic for soil HAs with

Table 8. Temperature of energetic effects and sample weight losses corresponding with energetic effects on the DTA curve for humic acids

Sample	endo	exo1	exo2	endo	exo1	exo2
		(°C)			in weight percentage	
Range for A	69–72	299–310	475–478	6.65–8.73	47.32–48.57	43.96–45.08
Mean ± SD	70 ± 1.5	304 ± 5.6	476 ± 1.5	7.53 ± 1.08	48.05 ± 0.65	44.42 ± 0.58
Range for B	71–84	304–305	467–477	6.12–7.37	45.02–49.32	43.74–48.86
Mean ± SD	78 ± 6.5	305 ± 0.6	473 ± 5.1	6.81 ± 0.64	47.26 ± 2.16	45.93 ± 2.64
Range for C	71–86	302–305	461–474	6.95–7.95	41.98–47.01	46.04–50.55
Mean ± SD	80 ± 7.9	303 ± 1.5	468 ± 6.7	7.46 ± 0.50	44.75 ± 2.55	47.80 ± 2.42
Range for D	83–85	299–301	474–481	7.35–7.47	43.00–47.40	45.16–49.53
Mean ± SD	84±1.0	300 ± 1.0	478 ± 3.5	7.42 ± 0.06	45.23 ± 2.20	47.35 ± 2.19

Table 9. Parameters of thermal decomposition of humic acids

Sample	DTA_{exo1}:DTG_{exo1}	DTA_{exo2}:DTG_{exo2}	*Q*	*Z*
Range for A	6.56–7.04	5.19–6.01	5.90–6.46	0.91–0.93
Mean ± SD	6.83 ± 0.244	5.61 ± 0.410	6.24 ± 0.301	0.92 ± 0.012
Range for B	6.05–7.13	5.43–6.54	6.18–6.37	0.89–1.09
Mean ± SD	6.68 ± 0.560	5.84 ± 0.607	6.29 ± 0.097	0.98 ± 0.103
Range for C	6.22–7.49	5.55–6.15	5.99–6.76	0.98–1.20
Mean ± SD	6.88 ± 0.636	5.82 ± 0.304	6.33 ± 0.393	1.07 ± 0.115
Range for D	5.78–7.60	5.49–6.90	6.38–6.57	0.95–1.15
Mean ± SD	6.50 ± 0.968	6.36 ± 0.763	6.46 ± 0.100	1.05 ± 0.100

aerobic conditions (Gonet 1989; Debska 1997; Cieslewicz & Gonet 2004) (Table 6).

UV-VIS spectra of alkali solutions of humic acids show a small inflection at the wavelength of 280 nm associated with the presence of lignin type compounds (Kononova & Aleksandrova 1973; Kumada 1987; Ramunni *et al.* 1994). This confirms that the main organic matter source in the sediments is algae. An additional absorption band of variable intensity was also noted at a wavelength of approximately 404 nm and this confirms the presence of structures of pigment origin (Ishiwatari 1973; Povoledo *et al.* 1975). The presence of this band is often used for distinguishing the material originating on land from that originating in water (Fooken & Liebezeit 2000). The results indicate that HA samples extracted from the bottom sediments in basin C had the highest contents of lignin origin structures (A_{280}) – on average 0.416. The highest mean values of absorbance at A_{465} and A_{665} were noted for the samples from basin B. This is extraordinary, considering that the absorbance values at 465 nm are thought to be connected with organic matter in its early decomposition stages, while at 665 nm with substances of a high humification degree (Chen *et al.* 1977). UV-VIS spectra of humic acids formed in an aqueous environment show the presence of an additional band at a wavelength of approximately 660 nm (Cieslewicz 2005). The presence of these bands makes the interpretation of both absorbance values and the calculated absorbance values difficult. The absorbance values measured with HA samples originating from the bottom sediments in basin D resemble those registered for the samples in the remaining basins (Table 7). The highest mean values of the absorbance ratios – $A_{2/4}$, $A_{2/6}$, $A_{4/6}$ – were noted for HA samples from the sediments in basin C. Higher values of the $A_{2/6}$ and $A_{4/6}$ ratios indicated that humic acids were characterised by a higher content of lignin-type compounds and a lower degree of humification, but so far this interpretation works well for soil HA only. The values of the absorbance ratios for the samples from basin D resembled those from basin A (Table 7).

Thermal decomposition of humic acids was represented on the DTA curve by a single endothermic effect and two exothermic effects. The lowest temperatures for the endothermic effect peaks were noted with humic acid samples extracted from basin A. Peak 1 of the exothermic effect occurred at similar temperature values in all of the samples, while peak 2 appeared at the highest temperature values in the samples from basin A – on average 476°C. Mass losses corresponding with the endothermic effect ranged on average from 6.81 (basin B) to 7.53% (basin A). Greater mass losses were noted for the exothermic effect 1 in the majority of HA samples from basins A and B. The peaks of thermic effects in the samples from basin D were noted at temperatures similar to those in HA samples from basins A–C, with the exception of a single sample, where greater mass losses were registered in a low temperature range (exo1) (Table 8).

Thermal decomposition parameters reflect the material energetic value and the contents of aliphatic and aromatic structures. The material undergoing destruction in the first exothermic reaction had a higher energetic value in comparison to the material destroyed in the second exothermic reaction in most sediment samples. In comparison to other samples, humic acids from basin D showed a lower energetic value of the material destroyed in exothermic reaction 1 (averaging 6.50) and a higher energetic value of the material under combustion in a high temperature range. Generally, the material in HA samples from basin D showed a higher energetic value in comparison to the remaining samples (parameter Q). Parameter Z (the ratio of the quantity of the material destroyrd in exothermic reactions 1 and 2 respectively, DTG2/DTG1) indicates that most of the analysed HA samples have more aliphatic than aromatic structures ($Z < 1$). The values of parameter Z in the samples from basin D were close to those registered for HA samples from basin C (Table 9).

CONCLUSIONS

The research of the bottom sediments from the individual basins, constituting Lake Wdzydze complex, showed small variances in the properties of the bottom sediments of these lakes and humic acids extracted from them. This proves the impact of local tourism on this ecosystem to be rather small so far. The parameters of humic acids in the bottom sediments also showed minor variances, thus indicating small differences between the intensity of anthropo-pressure on these lakes. We conclude that tourism has had no significant influence on this ecosystem. Sewerage and waste water pollution of the lakes in the past did not cause any permanent chemical changes in the lake sediments either. This was possibly due to the large size of the lakes (morphometric parameters), as well as to a good supply of high quality underground water. The results of this research suggest that a complex of positive environmental factors in a lake ecosystem can successfully outweigh the negative results of the anthropo-pressure.

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