Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2018.22500

117 (2018) 272–281
June

Accumulation of selected chemical elements in sediments of kettle hole lakes on rural areas

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Received 25 February 2018; Accepted 12 May 2018

ABSTRACT

Kettle hole lakes are a characteristic element of the post-glacial landscape. The paper analyzes the influence of morphometry of kettle holes and the characteristics of their catchments on the accumulation of total nitrogen, total phosphorus, Mg, K, Ni, Fe, Cu, Zn, and Mn. Significantly higher concentrations of nutrients were found in sediment of the lakes located on arable lands than grasslands. Heavy metals contents in the sediments generally did not diverge from natural background. The exception was Cu, for which the geoaccumulation index indicated significant contamination (class IV and V) of the sediments with this metal. All the studied metals created the following decreasing order: Fe > K > Mg > Cu > Mn > Zn > Ni. Results of PCA showed that the enrichment of sediments in metals was strongly influenced by the depth of water body and the lake catchment area. From two groups of kettle lakes distinguished by hierarchical cluster analysis, the group with significantly higher ($p < 0.05$) levels of K, Mg, Mn, and Fe in the sediments consisted of the deepest reservoirs with biggest capacities and larger catchment areas. Our results showed that the kettles lakes can be considered as reference sites for the need of existing or planned monitoring systems.

Keywords: Bottom sediments; Nutrients; Heavy metals; Kettle hole lakes; Morphometric parameters

1. Introduction

Isolated, small, water-filled depressions scattered amid fields in low-lying wetlands, which in Europe are called "kettle holes" [1], are an ubiquitous feature in many parts of the post-glacial areas of the Northern Hemisphere, in northern Eurasia, Canada and in northern states of the USA, where their density may be as high as 100 water bodies per 1 km^2 [2]. Kettle lakes belong to the most common aquatic elements in the post-glacial landscape of northern Poland, which covers 30% of the country's area. Their average density reaches 5 per 1 km^2; however, locally it can peak to 30 ponds per 1 km^2 [3]. They are usually small in area (<1 ha), isolated, polymictic water bodies, with the maximum depth rarely exceeding 2.5 m [4].

Kettle hole lakes play vital hydrological and ecological roles. They function as small natural sinks for water and organic and mineral matter from their catchments [5] as well as biodiversity hot-spots unevenly dispersed in farmlands [6]. Simultaneously, they are distinguished by a relatively, from a geological point of view, short life-time, resulting from the unbalanced input and output of mineral and organic matter. In spite of high variability of site-specific factors such as catchment area, relief, and land use, kettle lake pollution with nutrients and trace elements [7–11] made them all

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Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

particularly susceptible to degradation, silting up and finally disappearing [4,12–14]. The intensity of degradation of kettle holes depends on two factors: the character of a given catchment, seen as a supplier of matter, that is the geological structure of the catchment and the type of land use, and on the other hand, the resistance of the kettle hole lake itself, which is affected by numerous traits related to the morphometry and hydrology of this water body [15,16].

By covering land depressions, kettle holes naturally accumulate nutrients which cause eutrophication of these water bodies [17]. Bennion et al. [15] emphasize that the water in field kettle ponds is threatened by the inflow of impurities of anthropogenic character and additionally, in some cases, such lake waters undergo acidification (pH = 3.2) and eutrophication (TP > 0.4 mg dm^{-3}). However, the threat is not equal as every lake is under the influence of various factors, which affect it in slightly different ways. In nature, these processes are very slow, and can take as long as hundreds of thousands of years, but can be significantly accelerated due to the anthropogenically driven supply of contaminants.

Despite their importance in supporting ecosystem processes, biodiversity and water quality improvement, there is still little knowledge about the role of kettle holes as sinks for sediment and trace elements. There is a need to recognize mutual influences between external factors and processes that favor the accumulation of pollutants inside such small water bodies [18].

The concerns about possible contamination of kettle holes caused by heavy metals in recent decades have led to an increased interest in the role of sediment in the storage and transportation of metals in aquatic environments. A particular threat to natural biogeochemical processes is posed by heavy metals, which appear in aquatic ecosystems due to anthropogenic factors, such as a supply of toxic organic compounds from intensively used reclaimed croplands, the use of biocides on surrounding farms, input of sewage from surrounding villages, as well as traffic, tourism, etc. [19–23]. Increased concentrations of nutrients (N, P, K, Mg, and Ca) and heavy metals (Cu, Cd, Zn, Fe, Pb, Mn, and As) occur in the sediments of kettle lakes located within intensively used agricultural catchments [24,25]. The main reasons for the accumulation of heavy metals are the use of manure slurries (Cu and Zn), preservatives for seeds (As and Hg), fungicides (Cu) and certain P-fertilizers (Cd and Pb). The highest accumulations were reported for water bodies with large catchments, large elevation difference, distinct runoff pathways, and a lack of vegetation buffer zones [26].

Lake sediments are especially susceptible to heavy metal accumulation and typically have metal concentrations several orders of magnitude higher than those in overlying waters [26]. Because of the toxicity and availability of the metals, they can pose serious problems to the ecosystem and can be remobilized by changes in environmental conditions such as pH, redox, potential salinity, etc. [27–29].

Some of these compounds, by adsorption and sedimentation, are deposited more or less permanently in bottom sediments [30–33]. Noteworthy among these substances are metals, especially heavy ones, as they undergo biotransformation rather than biodegradation [34]. Metals can be immobilized in bottom sediments for a very long time [35]. By being accumulated in sediments, compounds can become a secondary source of pollutants, which – despite the removal of primary sources – can create a risk of water contamination lasting for many years [36]. For instance, metals bound by physical adsorption or chemisorption can be released to water when salinity changes (ion exchangeable form), whereas metals bound to carbonates are released when the environment becomes excessively acidic. Metals bound by co-titration with hydrated iron and manganese oxides are released to water less readily, same as metals bound to organic matter, which can appear in water due to its decomposition [37–39].

The concentrations of heavy metals in the lake sediment–water system depend on the transportation and transformation processes in which they participate. Among factors affecting their transformation might be a type of ecosystem surrounding water bodies: meadows, afforestation, farmlands or urban areas. Type and intensity of the land use determines the rate of lake transformation [18,40,41]. Nevertheless, the morphometric parameters of a single pond and their relation to the catchment area as well as position of the water body in the hydrographic network are considered as important natural factors responsible for the susceptibility of the water body to degradation [42]. The process is accelerated when the input of mineral and organic substance is higher than natural ability of the water body to eliminate them from the ecosystem. The process of degradation of kettle holes has becomes a major concern for both nature conservation groups and landowners, who acknowledge the ecological values of these water bodies. In spite of evident benefits for the environment and a serious threat to their persistence, kettle lakes are surprisingly still neglected in national natural resource management activities [19]. Awareness of the direct export of heavy metals from reclaimed farmlands into kettle lakes justifies efforts to protect them against pollution from farmlands.

This paper describes an approach to studying the accumulation and toxic levels of selected heavy metals (Mn, Cu, Zn, Ni, and Fe) in kettle lake sediments in relation to two groups of factors: (i) hydromorphological (internal) factors as well as (ii) external ones such as catchment area, its land use and reclamation system. The results of the research presented in the paper are aimed at verifying the hypothesis that the heterogeneity of morphometrical features of field ponds as well as their catchment parameters contribute to the accumulation rate of metals in sediments. The question of a toxicity level of the studied elements is highlighted against the background of kettle hole lakes either included into or outside drainage systems.

2. Materials and methods

2.1. Study area

The field kettle hole lakes included in the research are located in the south-western part of the mesoregion called Sępopolska Plain, in the Province of Warmia and Mazury (54°08′ N, 20°36′ E) [20]. The lakes are located in the North Masurian climatic region, which is characterized by high changeability of the weather, caused by the clashing maritime and continental climates. The average annual precipitation is 624 mm, and the average annual temperature is 7.1°C [43]. The relief is undulating with some slope angles reaching 15%, while most range between 2% and 4% [44]. Local soils are brown ones developed from heavy clays and loams, and black earths formed from medium and heavy clays. In lower parts of the plain and in local terrain depression lacking draining watercourses, kettle hole lakes had formed, now surrounded by fields (Fig. 1). When drainage systems were developed in this area, the lakes were made deeper, to an average depth of 1 m. The catchments of the field kettle hole lakes number 1 to 6 served as grasslands, while those of lakes number 7–9 were used as arable fields.

2.2. Sampling regime and analytical procedure

Sediment samples were taken in July 2014 in triplicates from three representative sites located in a transect in each water body: one sample from the central part, and two samples from interior parts of each wetland, roughly halfway between the perimeter and the center. Sediment samples were collected using an Ekman corer from the depth of 0–10 cm. The samples were sealed off in polyethylene flasks and stored at –20°C until analysis. In the laboratory, the samples were oven dried at 65°C prior to geochemical analyses. Dried material was ground in a mortar and passed through a 1 mm mesh sieve. pH_{KCl} was determined in the sediments.

Samples of sediments were wet mineralized in a closed system, in a mixture of 65% HNO_3 and 30% H_2O_2 [45]. The solution thus obtained underwent determinations of the content of selected metals (Mg, K, Ni, Fe, Cu, Zn, and Mn) by the atomic absorption spectrometry method (AAnalyst 300, PerkinElmer, USA) according to Ostrowska et al. [46]. The equipment was calibrated with the use of original reference solutions (Merck KGaA, 1 g/1,000 mL). In addition, total nitrogen (TN) was determined with the Kjeldahl's method (Buchi K-350), while total phosphorus (TP) was measured with the molybdenum method (UV-Vis spectrophotometer, U-5100, Hitachi, High-Technologies Corporation Tokyo, Japan).

2.3. Indicators of degradability of the kettle hole lakes

In the interpretation of the results, the Schindler's and Ohle's degradability indices were used. They were calculated on the basis of the morphometric parameters of both kettle hole lakes and their catchment:

Schindler's index:

$$W_{Schindler} = \frac{P_{catchment} + P_{lake}}{V_{lake}} \ (\mathrm{m}^{-1})$$

Ohle's index:

$$W_{Ohle} = \frac{P_{catchment} + P_{lake}}{P_{lake}} \left[- \right];$$

where P – surface area (m^2), V – capacity (m^3).

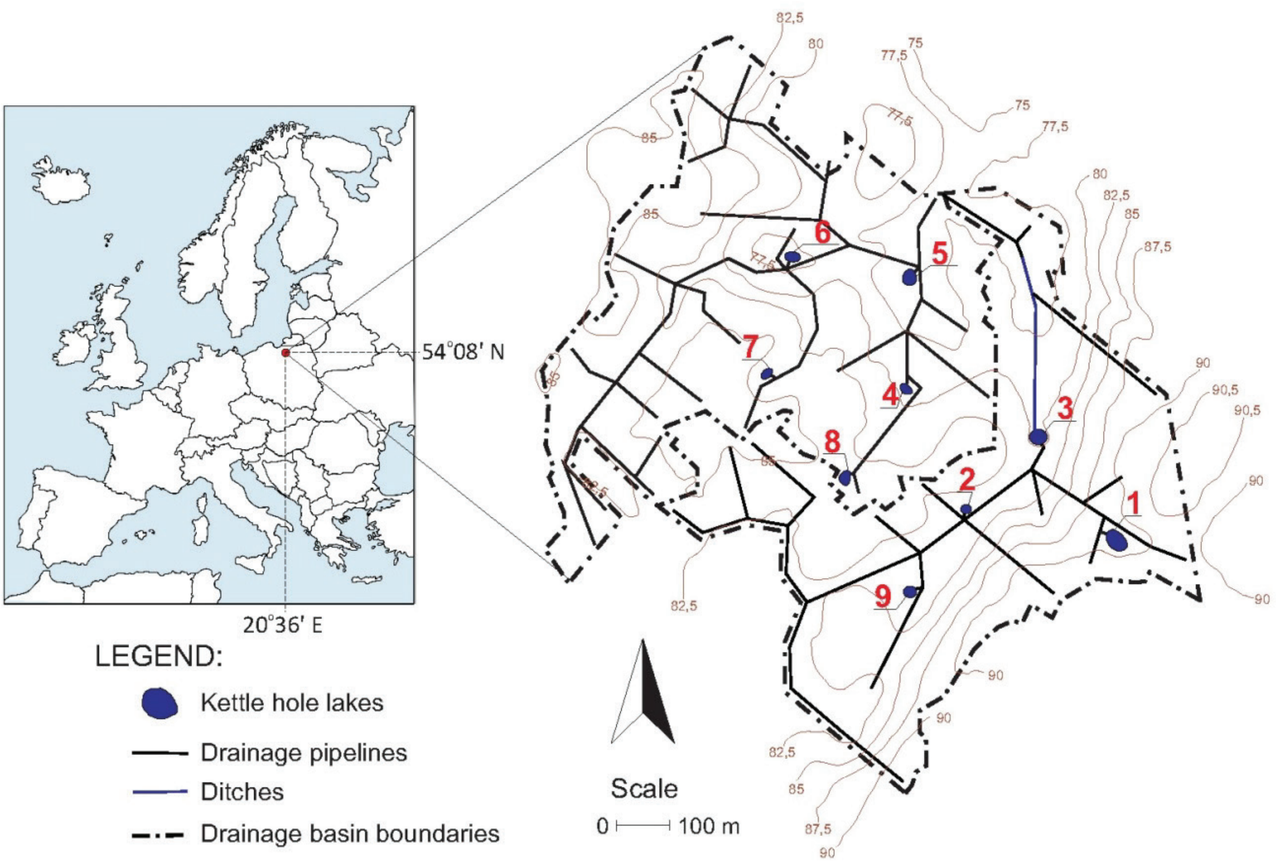

Fig. 1. Location of study site as well as kettle hole lakes on the background of reclamation ditch network.

2.4. Geoaccumulation index

The contamination level of heavy metals in the bottom sediments in the kettle hole lakes was assessed with the geoaccumulation index (I_{geo}) according to the method proposed by Müller [47], using the formula:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \cdot B_n}\right)$$

where C_n – concentration of an element in sediment, B_n – geochemical background value for the element, 1.5 – the factor which accounts for possible lithological variations in catchments under weak anthropogenic impact.

After Czarnowska [48], the evaluation of the geochemical background included the type of soil occurring in the catchment of each field kettle hole lake (Table 1).

The results were used to divide sediment samples into the following I_{geo} classes: $I_{geo} < 0$, class 0 (uncontaminated sediments); $0 < I_{geo} < 1$: class I (uncontaminated to moderately contaminated sediments); $1 < I_{geo} < 2$: class II (moderately contaminated sediments); $2 < I_{geo} < 3$:class III (moderately to highly contaminated sediments); $3 < I_{geo} < 4$: class IV (highly contaminated sediments); $4 < I_{geo} < 5$: class V (highly to extremely contaminated sediments); $I_{geo} > 5$: class VI (extremely contaminated sediments).

Table 1
Geochemical background of the content of heavy metals in kettle hole lakes

Kettle lake number	Soil	Geochemical background (mg kg^{-1})				
		Zn	Cu	Ni	Mn	Fe
1	Medium clay	41.0	10.0	13.7	344.0	20,300
2	Light clay	33.0	8.3	11.1	300.0	14,700
3	Medium clay	41.0	10.0	13.7	344.0	20,300
4	Medium clay	41.0	10.0	13.7	344.0	20,300
5	Heavy clay	46.0	14.0	17.0	527.0	22,400
6	Medium clay	41.0	10.0	13.7	344.0	20,300
7	Medium clay	41.0	10.0	13.7	344.0	20,300
8	Medium clay	41.0	10.0	13.7	344.0	20,300
9	Medium clay	41.0	10.0	13.7	344.0	20,300

2.5. Statistical analyses

Homogeneous groups and the significance of their differences for the content of the selected substances in bottom sediment samples taken from the kettles were determined using one-way analysis of variance (ANOVA) and the Duncan test as post-hoc procedure, at $p \le 0.05$.

The linear model is found when the share of dependent variables (nutrients and heavy metals) in sediment samples decreases or increases in proportion to the size of explanatory variables (environmental factors). The relationship between the morphometric parameters (explanatory variables), the catchment parameters and degradability indices and nutrient and heavy metal contents in sediments (active variables) of the kettles lakes was performed using the principal component analysis (PCA) method. To show site-specific tendency to accumulation of heavy metals, the kettle holes were grouped by hierarchical cluster analysis (HCA). The multivariate analyses were performed with the use of the XLSTAT software.

3. Results and discussion

3.1. Morphometrical characteristics of kettle lakes

The water table surface of most of the analyzed kettle holes was over 0.05 ha, and only lake 6 was larger: 586 m^2. The smallest lake (lake 2) occupied an area of 152 m^2 (Table 2). According to the geomorphological classification proposed by Kalettka and Rudat [1], these are called very small and

Table 2
Selected morphometric parameters of kettle hole lakes, their catchment basins, and indicators of vulnerability to degradation

Parameter, symbol (unit)	Kettle lake number								
	1	2	3	4	5	6	7	8	9
Morphometric parameters									
Water table area, Aw (m^2)	346	152	330	221	440	586	178	289	244
Maximum depth, D_{max} (m)	1.29	1.55	1.46	1.88	2.43	1.95	2.41	1.49	2.66
Mean depth, D_{mean} (m)	0.79	0.88	0.91	0.86	1.06	0.67	0.91	0.72	1.14
Depth index, Di = D_{mean}/D_{max}	0.61	0.57	0.62	0.62	0.46	0.44	0.34	0.38	0.48
Maximum length, L_{max} (m)	24.0	15.1	21.0	16.5	23.5	39.0	16.0	21.8	17.0
Maximum width, W_{max} (m)	19.2	10.7	19.5	14.7	23.0	22.0	15.5	18.0	16.2
Elongation index Li = L_{max}/W_{max}	1.25	1.41	1.07	1.12	1.02	1.77	1.03	1.21	1.04
Volume, V (m^3)	274	134	300	191	466	393	162	208	278
Catchment parameters									
Catchment area, Ac (ha)	2.03	0.61	3.70	2.38	8.36	8.41	1.15	0.73	4.05
Mean catchment slope, Ic (%)	4.00	4.25	5.47	3.60	3.50	5.31	4.37	2.68	2.81
Indicators of vulnerability to degradation									
Schindler's index (m^{-1})	75.4	46.7	124.4	125.8	180.3	215.5	72.1	36.5	146.6
Ohle's index	59.7	41.1	113.1	108.7	191.0	144.5	65.6	26.3	167.0

small. The depth of the analyzed kettle lakes did not vary much. The configuration of the bowls of these lakes typically had a single deepest point, around which isobates, shaped correspondingly to the lake's shores, could be plotted (Fig. 2). The maximum depth of the lakes was from 1.29 m (lake 1) to 2.66 m (lake 9). The maximum depth was over 2.0 m in just two other lakes: 5 (2.43 m) and 7 (2.41 m).

The average depth of the analyzed kettle hole lakes ranged from 0.67 to 1.14 m, which unquestionably puts them into the category of shallow water bodies. With their relatively uncomplicated bathymetry, the bowls of these lakes can be compared with regular geometric solids. Values of the depth index achieved for the analyzed lakes ranged from 0.34 to 0.62, thus indicating a certain similarity of the lake bowls to the shape

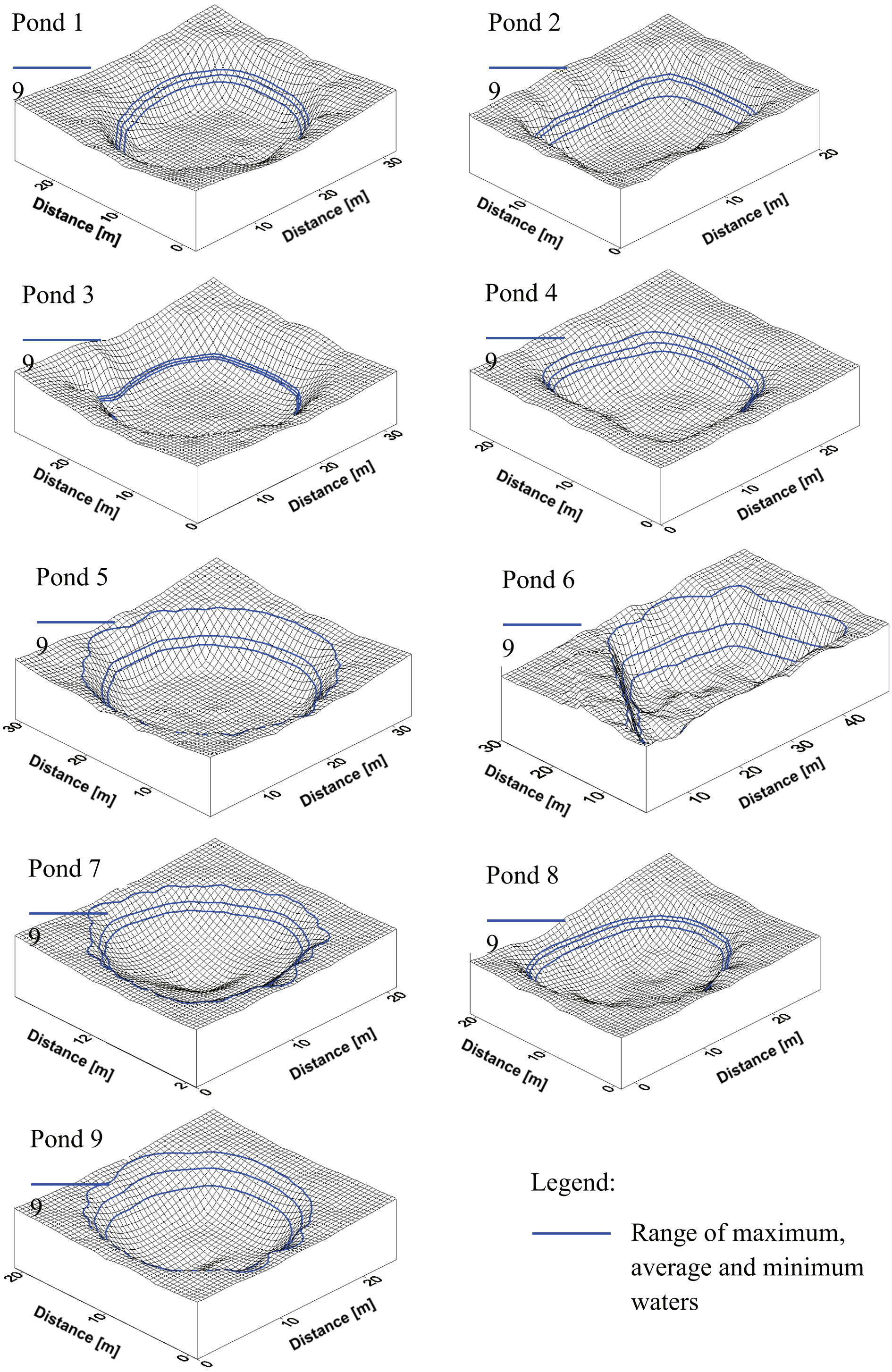

Fig. 2. Shapes of the bowls of the studied kettle hole lakes.

of a paraboloid. The elongation index (λ), which identifies the shape, was slightly over 1 for most of the lakes, typical of lakes nearly round or oval in shape. The water holding capacity of the lakes and their water resources ranged from 134 to 466 m^3.

The ponds did not vary in terms of their permanent water table assessed on the basis of observations since 1998. One of the lakes is included into a reclamation system with a ditch (lake 3), supplying it with water from adjacent grasslands. All the other ponds are endorheic.

Based on the hydrogeomorphological classification (HGM) by Kalettka and Rudat [1], the lakes were identified as typical kettle-like water bodies characterized by a relatively small area and situated in deep terrain depressions, with high banks above the water table. According to the HGM, they represent "open-water" type and the "storage" subtype.

The applied indicators of lake degradability are measures of the environmental impact on a given water body. According to the values of the Schindler's and Ohle's indices, the analyzed lakes belong to bodies of water susceptible or very susceptible to degradation. The less vulnerable are lakes 2 and 8, while the most vulnerable ones are 5 and 6.

The range of water level changes in the individual lakes varied significantly (Fig. 2). The smallest fluctuations were noted in lake 3. This is the only lake among the analyzed water bodies which is a flow-through one. It receives water from a surface run-off and from drainage pipes, and discharges water through a ditch. Among the other lakes, which are supplied water only from surface run-offs and groundwater while having no water outflow, the smallest range of changes occurred in the largest kettle hole lakes (5 and 6) which were also characterized by the largest catchments. These observations do not support the findings reported by Pietruszynski et al. [12] who analyzed 10 small young glacial water bodies in the Kaszuby Lake District and concluded that the largest fluctuations in water levels appeared in smallest lakes.

3.2. Physico-chemical characteristics of sediments in kettle lakes

The reaction (pH) of the analyzed bottom sediments varied: in kettle lake no. 4 it was slightly acidic, in lakes 2, 5 and 8 – neutral, and in lakes 1, 3, 6 and 9 – alkaline (Table 3). The highest quantities of TN appeared in the two kettle lakes with the largest catchments mostly used as grasslands, and in the two kettle lakes with the largest catchments used as arable lands.

Much lower amounts of nitrogen occurred in bottom sediments of the lakes supplied with water through run-offs from smaller catchments. The type of land use had a large influence on the TP content in sediments. In this regard, the kettle lakes located in agriculturally used catchments stood out as having much more phosphorus. The bottom sediments of the analyzed lakes were characterized by much higher amounts of iron, potassium, and magnesium. The use of the lake catchment area also affects the quality of their waters [12,42]. The existence of buffer zones would limit the outflow of substances from the catchment to the water bodies [24,49].

The analyzed metals, with respect to their concentrations in the bottom sediments, can be ordered as follows: Fe > K > Mg > Cu > Mn > Zn > Ni. Only the sediments from lakes 4 and 8 contained more manganese than copper while in sediments of lakes 7 and 8 magnesium content prevailed over potassium. However, the stated differences were not significant.

The size of heavy metals accumulation in sediments, in relation to the geochemical background, is expressed by the geoaccumulation index. Its values suggest considerable pollution of the analyzed field kettle lakes with copper (Table 4). For example, sediments in kettle lake 1 belong to class III, identified as moderately to highly contaminated sediments. Sediments in the other lakes were even more severely polluted, as they were categorized as class IV and even class V, meaning that they were highly to extremely contaminated sediments. A number of researchers underline significant correlation between the Cu content and the content of organic matter in individual sediment layers [20,22,50]. According to Paszko [51], the increased content of Cu, which is considered as a metal of low mobility, can be explained by its ability to displace other metals bonded in individual fractions of sediment.

With respect to the other metals, the sediments were classified as uncontaminated to moderately contaminated.

Table 3
Content of nutrients and heavy metals (mg kg^{-1}) as well as pH of the bottom sediments in the studied kettle hole lakes

Parameter	Kettle hole lake number								
	1	2	3	4	5	6	7	8	9
pH_{KCl}	7.28	7.17	7.44	6.48	7.16	7.22	7.52	6.93	7.35
TN*	0.448	0.700	0.602	0.980	0.896	0.952	0.504	1.064	0.532
TP	2,721.9	2,627.1	1,220.6	1,594.2	1,479.6	2,990.8	3,718.3	2,975.0	1,313.5
Mg	4,564^a	5,875^a	11,280^b	5,753^a	13,575^b	12,208^b	16,018^b	8,933^a	10,422^b
K	5,415^a	7,802^a	12,354^b	10,342^a	14,735^b	12,115^b	15,230^b	10,925^a	12,815^b
Zn	34.2	58.9	54.2	51.3	69.3	71.0	57.1	58.6	106.4
Cu	113.5	226.0	218.4	265.8	279.2	207.7	304.5	170.0	297.5
Ni	15.4	51.6	25.7	34.5	38.5	46.2	41.8	44.5	33.1
Mn	104.8^a	148.2^a	185.7^b	83.1^a	265.4^b	160.9^b	321.5^b	107.4^a	176.3^b
Fe	20,860^a	29,565^a	42,165^b	33,267^a	46,650^b	41,825^b	45,538^b	33,892^a	43,045^b

^{a,b}Groups of means significantly different in the Duncan test (One-way ANOVA, post-hoc [$p \leq 0.05$]).
*%.

3.3. Results of the principal component analysis

The relationships between the analyzed morphometric parameters determined with the PCA are associated with three PC components (PC axes with eigenvalues > 1) which represent as much as 86.3% of total variation. However, most important were the first two components (PC1 and PC2), which accounted for 51.70% and 19.46% of total variance, respectively (Fig. 3).

For the PC1, high positive scores are indicative of high Fe, K, Mg, Mn, and Cu concentrations and, to a lesser degree, high Zn concentrations. The correlations between the variables with PCA1 are of statistical significance at $p < 0.05$ (except of Zn; Table 5). Moreover, among explanatory variables enhancing accumulation of heavy metals in sediments are maximal and mean depths characterized by significant positive scores to PC1. The PC2 is characterized by a highly positive correlation with TN. Negative correlations with PC2 showed pH and Mn; however, no statistical significance has been found. In addition, among explanatory variables, no statistically significant correlation was exhibited. Interestingly, high positive scores of TP and negative scores of mean depth and Ohle's index ascribed to PC3 (Table 3; not shown in figures) indicate rather high potential to secondary pollution of the water column above the sediment with the nutrient. The scores of PC2 and PC3 indicate approximately the favorable conditions to nutrient loading leading to the eutrophication development. It is worth noticing that the multivariate analysis results showed no clear relationship between heavy metal contents and morphometric parameters (except of depth) of the kettle lakes such as water table area, length and width as well as catchment slope.

The spatial variability of heavy metals in sediments displayed the site-specific distribution of nine observed kettles holes: along negative (1, 2, 4, and 8) and positive (3, 5, 6, 7, and 9) gradient of PC1 (Fig. 3(C)). To detect the (dis)similarity groups between the sampled water bodies based on heavy metal contents in the sediments, HCA was performed. It yielded a dendrogram (Fig. 4), grouping all nine sampling

Table 4
Geoaccumulation index (I_{geo}) of heavy metals in bottom sediments of the kettle hole lakes

Kettle lake	Values of I_{geo}					Sediment I_{geo} classes				
	Zn	Cu	Ni	Mn	Fe	Zn	Cu	Ni	Mn	Fe
1	–0.8	2.9	–0.4	–2.3	–0.5	0	III	0	0	0
2	0.2	4.2	1.6	–1.6	0.4	I	V	II	0	I
3	–0.2	3.8	0.3	–1.5	0.4	0	IV	I	0	I
4	–0.3	4.1	0.7	–2.6	0.1	0	V	I	0	I
5	0.0	3.7	0.6	–1.6	0.5	I	IV	I	0	I
6	0.2	3.8	1.2	–1.7	0.5	I	IV	II	0	I
7	–0.1	4.3	1.0	–0.7	0.6	0	V	II	0	I
8	–0.1	3.5	1.1	–2.3	0.2	0	IV	II	0	I
9	0.8	4.3	0.7	–1.5	0.5	I	V	I	0	I

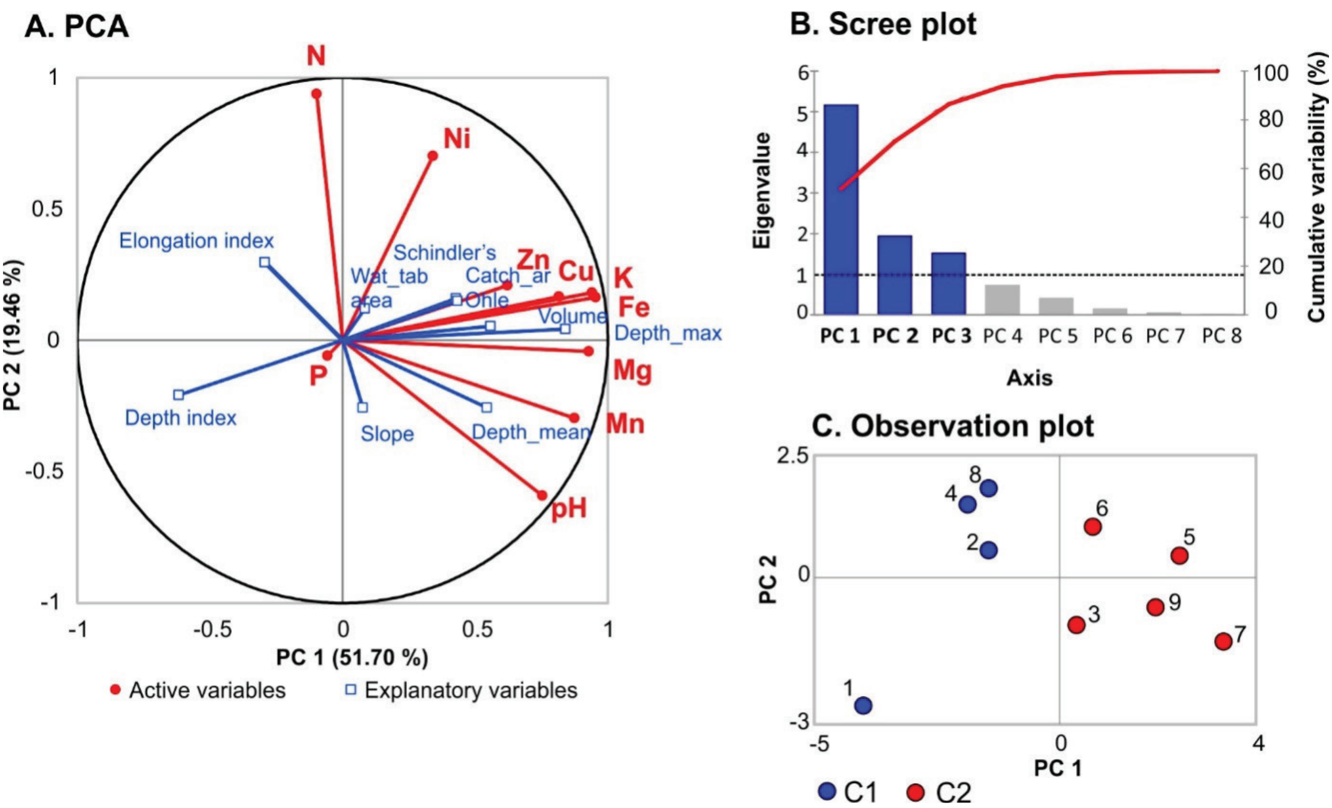

Fig. 3. (A) Plot of PCA between chemical elements in sediments (active variables) vs. morphometric and catchment parameters (explanatory variables) characterizing kettle hole lakes. (B) Scree plot for eigenvalues and cumulative variability % of explained variation. (C) Observation plot indicating division of kettle lakes between negative area (C1 – blue circles) and positive area (C2 – red circles) of PC1.

Table 5
Correlations between active and explanatory variables (factors) and the first three PCA components (PC1–PC3)

Variables	PC1	PC2	PC3
Active variables	Correlations between variables		
Fe	0.954	0.163	–0.119
K	0.941	0.181	–0.032
Mg	0.929	–0.042	0.227
Mn	0.874	–0.296	0.269
Cu	0.816	0.166	–0.243
pH	0.754	–0.591	0.104
Zn	0.621	0.209	–0.440
Ni	0.341	0.702	0.446
TN	–0.097	0.938	0.055
TP	–0.057	–0.059	0.958
Explanatory variables	Correlations between factors		
Morphometric parameters			
Water table area	0.084	0.121	0.012
Maximum depth	0.841	0.043	–0.210
Mean depth	0.544	–0.256	–0.618
Maximum length	–0.019	0.149	0.215
Maximum width	0.212	–0.060	–0.077
Elongation index	–0.292	0.296	0.408
Depth index	–0.617	–0.208	–0.552
Volume	0.311	0.010	–0.287
Catchment parameters			
Catchment area	0.528	0.160	–0.253
Mean catchment slope	0.076	–0.256	0.246
Indicators of vulnerability to degradation			
Schindler's index	0.433	0.151	–0.391
Ohle's index	0.557	0.054	–0.604
Eigenvalue	5.170	1.946	1.521
Variability (%)	51.701	19.461	15.214
Cumulative %	51.701	71.162	86.376

Note: Correlation indices marked in bold are at $p < 0.05$. Eigenvalues and percent variance explained by the first three principal components.

sites into two statistically significant clusters C1 and C2. The comparison of clusters showed that the cluster C1includes water bodies with significantly lower levels of K, Mg, Mn, and Fe (ANOVA, at $p < 0.05$) in bottom sediments when compared with the cluster C2. The contents of Zn, Ni, and Cu did not differ between the clusters. Water bodies creating cluster C1 are relatively small and shallow (the average depth does not exceed 0.88 m). However, they are distinguished by large elongation, small volume of retained water (202 m^3 on average for the lakes classified into C1) and the area of the direct catchment not exceeding 2.38 ha (Table 1). The cluster C2 consists of significantly deeper (ANOVA, t-test at $p < 0.05$) kettle hole lakes comparing with C1 as well as significantly higher Ohle's index. The lakes included in C2 are characterized by the water volume exceeding 278 m^3, average maximum

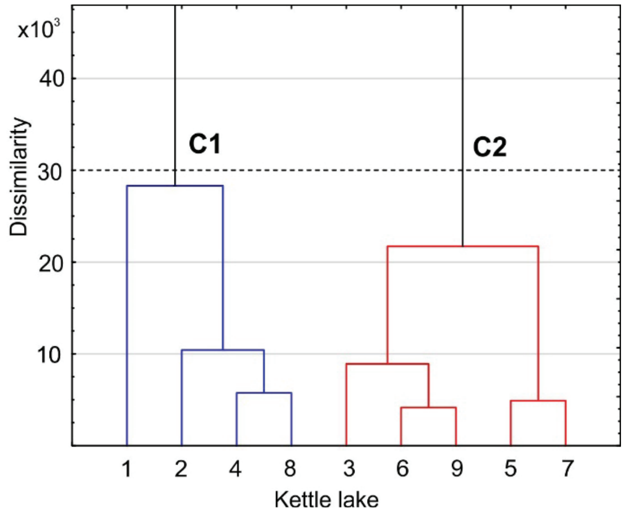

Fig. 4. Dendrogram showing HCA of kettle lakes according to the heavy metals contents in sediments. HCA was performed by using the Ward's method as linkage rule and Euclidean distances as metric for distance calculation.

depth of 2.18 m, supplied with water from a catchment area >3.70 ha (5.13 ha on average for this cluster). Gołdyn et al. [13,50] agree that the most important parameters among the factors characteristic for the morphology of lakes and their catchments that determine the content of heavy metals in sediments are the depth of a water body and the size of its catchment.

4. Conclusions

The contemporary problem of proper land management in the agricultural catchments of kettle hole lakes results from significant over loading with nutrients and heavy metals. It concerns also the areas of a lack of significant emission sources as in the Masurian Lake District – a region where elevated levels of metals in lake sediments are often not observed [52]. Our results showed that more TN accumulates in sediments of kettle lakes located on grasslands, while higher amounts of TP and the metals (except iron) were determined in sediments of lakes situated on arable lands. With respect to their content in the examined lake sediments, the analyzed metals can be arranged as follows: Fe > K > Mg > Cu > Mn > Zn > Ni. The calculated values of the geoaccumulation index indicate significant copper contamination of the bottom sediments in the lakes (I_{geo} classes IV and V were prevalent). As for the other metals, the sediments were uncontaminated to moderately contaminated.

Among the factors related to the morphology of kettle holes and their catchments, the depth of a lake and the area of its catchment are the most important ones for the content of heavy metals in sediments. Smaller amounts of metals were found in the bed sediments of lakes distinguished by small depths and small volumes of retained water, which was supplied from smaller catchments. For magnesium, potassium, manganese and iron, the determined concentrations were statistically significantly lower.

The results of our study indicate that the contents of heavy metals in bottom sediments of small water bodies dispersed in agricultural landscape are the important source of information on the long-term pressure of anthropogenic activity in their catchments. In light of this, a toxicity level of the studied elements in sediments of kettle hole lakes either included into or outside drainage systems showed no significant differences. Our findings lead to the conclusion that in the sediments of the investigated kettle lakes of northeastern Poland, the heavy metal content (apart from Cu) generally does not diverge from natural background. Thus, the kettles lakes in the region seem to be promising for further investigation of the range of natural changes in sediment geochemistry. The lakes not affected by recent pollution should be used as reference sites in the frame of existing or planned monitoring systems.

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