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QUANTITATIVE AND QUALITATIVE CHARACTERISTICS OF DISSOLVED ORGANIC MATTER IN URBAN SMALL WATER RESERVOIRS

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CHARAKTERYSTYKA ILOŚCIOWA I JAKOŚCIOWA ROZPUSZCZONEJ MATERII ORGANICZNEJ MAŁYCH ZBIORNIKÓW WODNYCH AGLOMERACJI MIEJSKIEJ

Scharakteryzowano rozpuszczoną materię organiczną w małych zbiornikach wodnych zlokalizowanych w trzech dzielnicach (Jaroty, Skanda i Wschód), południowo-wschodniej części miasta Olsztyna. Wyniki badań wykazały ilościowe (mierzona jako DOC) i jakościowe (mierzona jako parametr $SUVA_{260}$) zróżnicowanie rozpuszczonej materii organicznej w układzie sezonowym, przestrzennym oraz w zależności od intensywności użytkowania zlewni. Zbiorniki akumulują znaczne ilości materii organicznej, co potwierdziły wysokie wartości DOC. Średnie stężenie DOC w całym cyklu badawczym wynosiło 19,1 mg C•dm^{-3}, a maksymalne 42,7 mg C•dm^{-3}. O odmiennym charakterze i źródle pochodzenia materii organicznej świadczą silnie zróżnicowane wartości wskaźnika $SUVA_{260}$ (od 10,9 do 42,6). Głównym źródłem jest materia pochodzenia allochtonicznego. Znaczny udział ekosystemów łąkowych w badanej dzielnicy zwiększa zawartość związków aromatycznych w zbiornikach wodnych, czego przykładem jest dzielnica Skanda. Materia pochodzenia antropogenicznego (niska wartość $SUVA_{260}$) jest charakterystyczna dla zbiorników najsilniej zagospodarowanej dzielnicy Wschód.

Summary

Dissolved organic matter in twenty-one small water reservoirs located in three south-eastern districts (Jaroty, Skanda and Wschód) of the Olsztyn city was characterized. The study revealed the quantitative (measured as DOC) and qualitative (measured as $SUVA_{260}$) diversity of the dissolved organic matter in seasonal and spatial distribution, but also with regard to the watershed's utilization intensity. Due to their small volume, the reservoirs collect considerably much organic matter, which was confirmed by the high or very high values of DOC (over 40.0 mg C·dm^{-3}) determined in two of the examined reservoirs. The organic matter was mainly of allochthonous origin. As shown by the Skanda district example, meadows – if dominant in the watershed – increase the aromatic properties of organic matter. The significant contribution of the organic matter of anthropogenic origin was well illustrated by the example of the most developed Wschód district.

INTRODUCTION

Small water reservoirs constitute an element of the hydrographical network and occur permanently, periodically or episodically. They are created when cubes of dead ice melt or as remains of the mining activity of man [3]. Numerous reservoirs have disappeared in the past years. Ponds placed in cities and villages were filled with earth and transformed into construction sites; many ponds were dried up to get new land for farming.

Small water reservoirs make also a basic element of the so-called small surface storage. They enhance the hydrologic balance of an area, are used for economic purposes and have a grand importance for living and survival of many plant and animal species. The water-land interface is characteristic of the utmost diversity of biological life. Therefore, disappearance of small reservoirs leading to clearance of the ecotones, causes substantial impoverishment of the nature's valor and diminishes the biological diversity [10, 11, 16].

Special protection is needed for small reservoirs as they are highly vulnerable to degradation accelerated usually by development in the watersheds [9, 12].

One of many indicators used to assess the degree of biological degradation in surface water is the content of dissolved organic carbon (DOC). Such analyses are indispensable to recognize the rate and direction of matter circulation [4].

The goal of this study was to characterize the dissolved organic matter in the waters of small reservoirs located in urbanized area.

MATERIAL AND METHODS

Twenty-one small water reservoirs were examined, situated within the administrative borders of the Olsztyn city, in three south-eastern districts, namely Jaroty (four reservoirs), Skanda (eight reservoirs) and Wschód (nine reservoirs).

Jaroty is a residential district with four-floor blocks of flats built of prefabricated units. The surface of the district is mostly concrete-paved with scarce belts of green. The streets are very busy. Four reservoirs were examined in Jaroty, as described below:

J_1 – surrounded by wasteland grown with high green, man-made hummocks and dense tree stands.

J_2 – placed in a small valley with the slopes grown by a mixed forest. Shores are free of vegetation but the mud obstructs access to the water.

J_3 – borders a construction site and a park with ordered walking paths; a playground and a school are sited farther on. The shores are sporadically grown with reed mace.

J_4 – located near the terminal bus stop, surrounded by blocks of flats.

The Skanda residential district consists of densely located detached houses (one- or two-floor). Most of the reservoirs in this district are located outside the built-up zone, however close to the houses, on the north-east side. The south-western part is dominated by the forest and Lake Skanda. Eight reservoirs were examined. Their short description is the following:

S_1 – large elongated reservoir, with gently sloping, grass-grown surroundings. Farther on industrial property appears. Part of the reservoir is grown with reed mace.

S_2, S_3, S_4, S_5, and S_6 – situated one close to another in a hilly area grown with green and cut by numerous walking paths. The reservoirs are small, oval in shape, with shores poorly or moderately grown with aquatic plants.

S_7 – situated in a vast waterlogged area near a soil-surfaced road. Dense willow bushes and reeds obstruct access to the reservoir; in the distance low peat bog appears.

S_8 – surrounded by bushes and tree stands. The reservoir is intensively overgrown by vegetation; the close vicinity is heavily littered.

Wschód is an industrial district, differing by the degree of the development. The reservoirs can be found on wasteland and among ruins of buildings. Nine reservoirs were studied, as numbered and described below:

W_1 – large reservoir with shores grown with reeds. On the north adjacent to a steep slope with loose slipping down soil material. Dense bushes hinder access to water from the other sides. Farther away two-floor buildings can be found.

W_2 – in the direct vicinity of the reservoir farm buildings and a vegetable garden are located. Reeds and water plants cover the whole reservoir.

W_3, W_4, W_5, and W_6 – surrounded by wasteland, serving the motocross rallies.

W_7 – located on the farmed land. Part of the shores is grown with reeds. A melioration ditch drains to the reservoir.

W_8 – the reservoir is surrounded by heavily littered bushes and tree stands. The reservoir is intensively grown with aquatic vegetation.

W_9 – reservoir partly located in the forest; the shores are clean and free of vegetation.

The study was carried out in the spring (twenty-one reservoirs) and autumn (eighteen reservoirs) of 2003. In the autumn, the number diminished as three reservoirs dried up. Water samples were taken from the surface with a Ruttner apparatus or directly to polyethylene flasks.

In the water samples, quantity (measured as dissolved organic carbon, DOC) and quality (measured as specific UV radiation at 260 nm, $SUVA_{260}$ = Abs 260 * 1000/DOC) of the dissolved organic matter were determined. DOC content was marked in filtered on 0.45 μm Millipore filter samples. Determinations were done on organic carbon analyzer Schimadzu TOC-5000, after prior acidification of the samples with 2 M HCl to about 2 pH in order to remove CO_2. The selected fragments of absorption spectrum were obtained with the help of a double-channel Shimadzu UV-1601PC spectrophotometer and 10-mm quartz cells, and with dematerialized water as reference. The examinations were done in filtered samples (0.45-mm Millipore filters). In parallel, hydro-chemical examinations were carried out [15].

To give an overall characteristic of all data and to analyze the data with regard to the individual sampling stations, districts, and year seasons, the following statistical measures were used: arithmetic mean, range, standard deviation, minimal and maximal value. Significance of the correlation between two variables was assessed with the Person's linear correlation coefficient. The whole data set served to verify the hypothesis that there were no differences between the means for districts. The verification was done with the t-test (assessing statistical difference between two groups of means) and the Mann-Whitney U-test. The districts were compared by the analysis of variance (ANOVA) and the non-parametric alternative to ANOVA (i.e. Kołomogorow – Smirnow test). The statistically significant results of the ANOVA were further analyzed with the Tukey Test (NIR test).

RESULTS AND DISCUSSION

The study results revealed the qualitative and quantitative diversity of the dissolved organic matter. The mean DOC concentration throughout the study equaled 19.1 mg C·dm^{-3}. The largest DOC stock was determined in the reservoirs of the Wschód district and the smallest in the Skanda reservoirs; the mean values equaled 23.5 and 14.0 mg C·dm^{-3}, respectively (Fig. 1). Variability of the DOC concentrations in the examined area was displayed by the parametric analysis of variance (ANOVA). Statistically significant

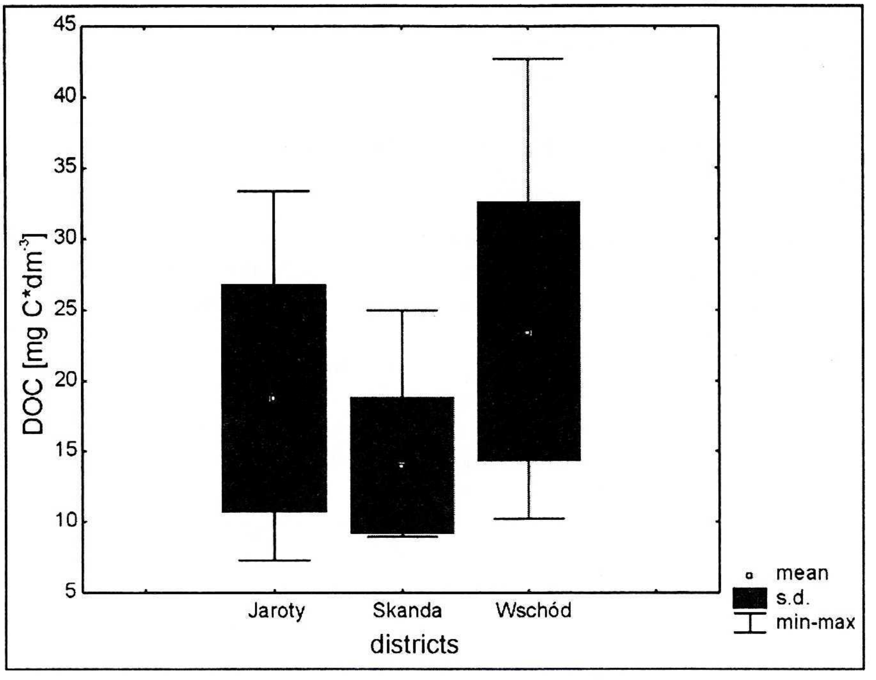

Fig. 1. DOC concentrations in the reservoirs of the individual districts

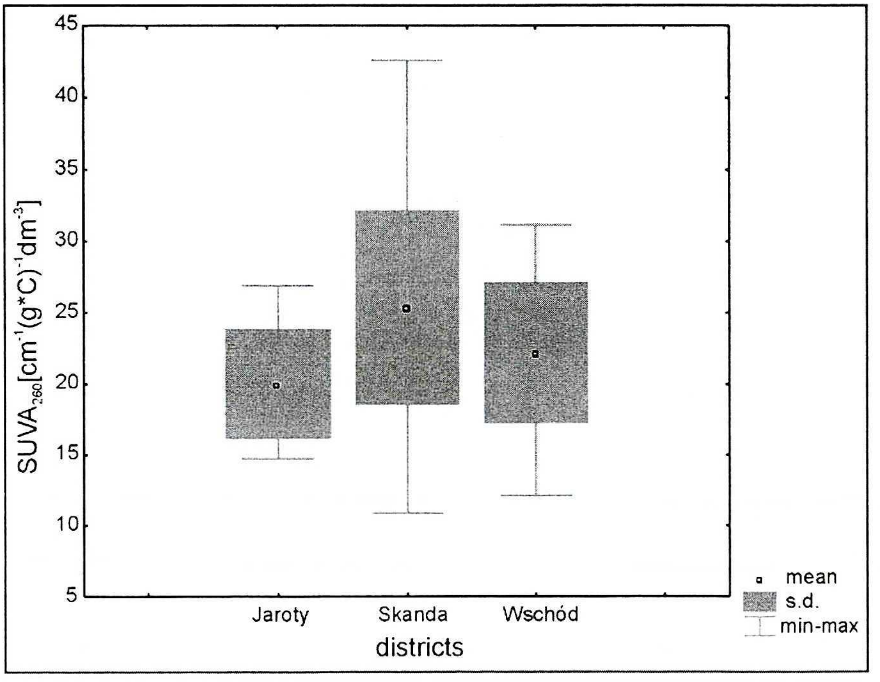

Fig. 2. Values of the $SUVA_{260}$ parameter in the reservoirs of the individual districts

differences were found between the mean DOC concentrations for the individual districts; decisive were the results obtained in the Wschód district.

The mean $SUVA_{260}$ value in the whole study amounted to 22.9. The Skanda reservoirs contained organic matter with the highest aromatic properties while the opposite occurred in the Jaroty reservoirs; the values equaled 25.3 and 20, respectively (Fig. 2). Statistical analysis confirmed the high variability of the $SUVA_{260}$ values; significant fluctuations were noted between the mean $SUVA_{260}$ values for Jaroty and Skanda, and for Jaroty and Wschód. The statistical significance regarded also the seasonal changes of this parameter in the whole data set.

The quantitative and qualitative variability of organic matter was determined also between the reservoirs in each district.

In J_2 (Jaroty), the DOC concentration in the autumn was the lowest in the whole study and equaled 7.2 mg C•dm^{-3}. It was by 26.1 mg C•dm^{-3} lower than the DOC concentration measured in J_4. Regarding the seasonal variability, in J_1 and J_2 the DOC concentration in the autumn was lower than in the spring. In J_3, the DOC concentrations remained practically unchanged throughout the study. In J_4, the quantity of DOC rapidly increased (Fig. 3).

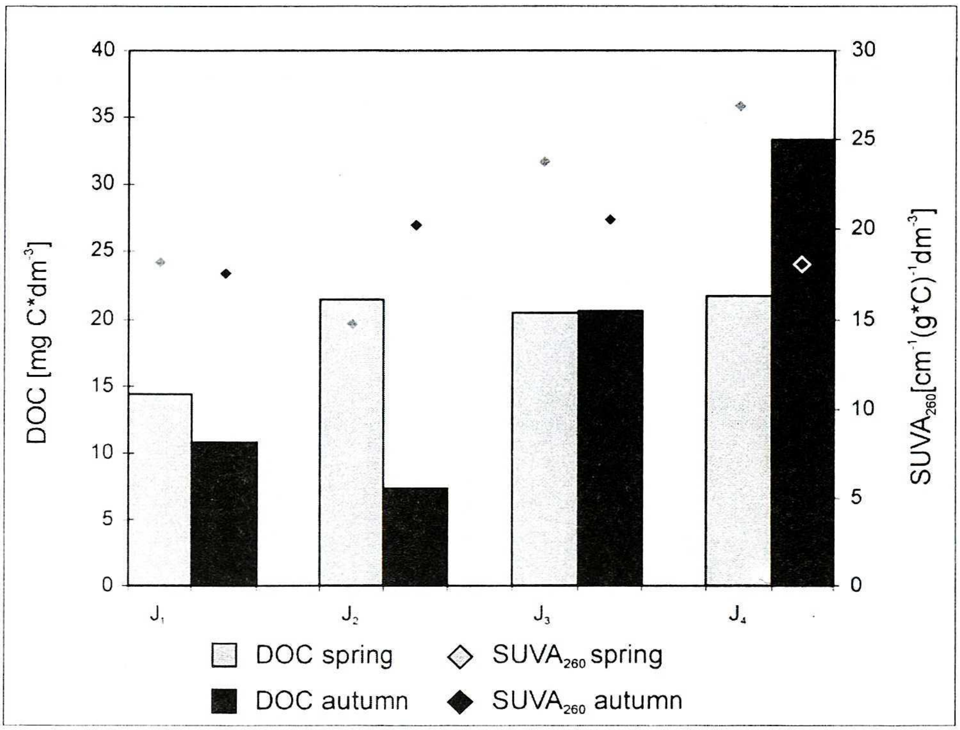

Fig. 3. DOC concentrations and $SUVA_{260}$ values in the Jaroty District reservoirs

Additionally, variable $SUVA_{260}$ is the evidence of a different character and source of organic matter. Value of the $SUVA_{260}$ parameter determines the number of polar functional groups in a molecule of organic matter and therefore its aromatic properties [5, 7, 8].

An obvious increase of the DOC concentration observed in J_4 in the autumn and the simultaneous considerable decline of the $SUVA_{260}$ value indicate high accumulation of this from of organic carbon in the reservoir. Its source may be an intensive primary production in the reservoir, as well as an import from the watershed. The autumn stock of dissolved organic matter is considerably enhanced by the decomposition of large-molecule organic matter produced in spring. Moreover, J_4 is sited in such way (near the terminal bus stop and close to the apartment blocks) that the anthropogenic pressure it undergoes is the highest of all reservoirs examined in Jaroty. It is exposed to an input of easily degradable organic matter of the anthropogenic origin.

The Skanda district was characterized by little spatial and seasonal diversity of the organic matter (Fig. 4). The highest DOC concentration (25 mg C•dm^{-3}) was determined in S_7 situated near the high peat bog. The studies by Dillon & Molot [2] confirmed the significant correlation between DOC export from the watershed and the percentage of peat bogs in the watershed (r = 0.88). The high value of $SUVA_{260}$ (the highest of all obtained results) and the very high water color (320 mg Pt•dm^{-3}) are a sign of the allochthonous origin of the organic matter in this reservoir.

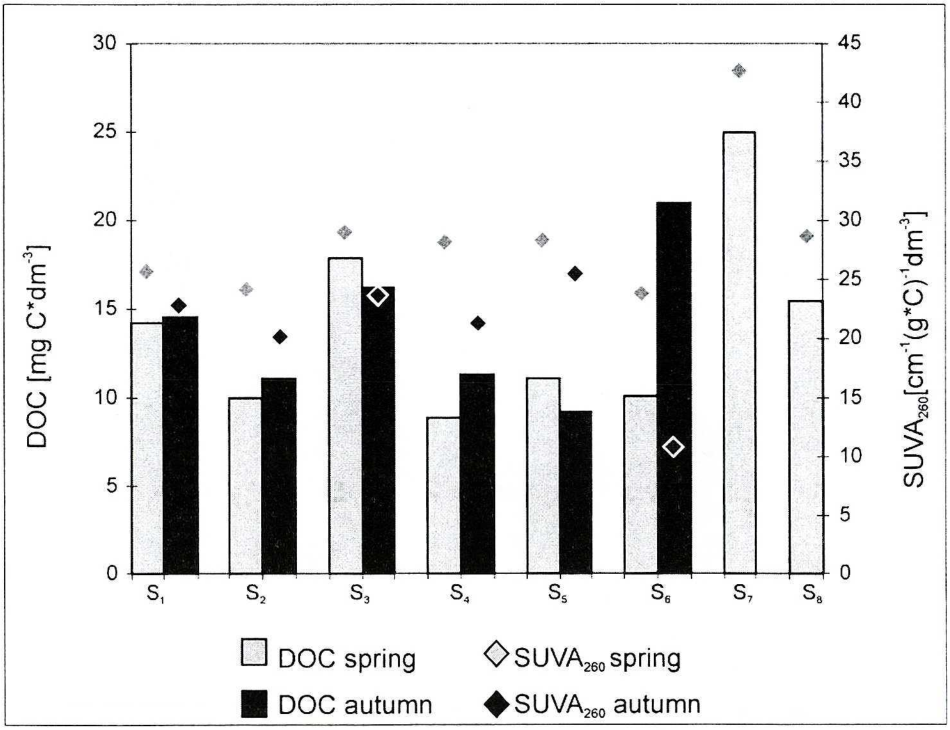

Fig. 4. DOC concentrations and $SUVA_{260}$ values in the Skanda District reservoirs

In reservoirs S_2–S_6, located on the same wasteland complex, the clear seasonal variability was observed only in S_6 where DOC concentration increased in the autumn. Such increase may result from decomposition of dead vegetative biomass accumulated after the growing season and from the input of easily degradable matter of anthropogenic origin (S_6 is placed at the bottom of the densely built-up slope). Every autumn-rain washes off organic matter from the watershed and by surface run-off puts it to the reservoir [14].

The relatively high values of DOC obtained in the Skanda district are related to the way the watershed is developed, as the chemical composition of water depends on the type of development in the watershed [1, 6]. The reservoirs in the Skanda district were characterized by the highest values of $SUVA_{260}$ (Fig. 2). Statistical tests have confirmed the seasonal variability of the $SUVA_{260}$ parameter in the Skanda reservoirs. The reason may be that most of the reservoirs are located on wasteland. Quinby [13] points at the positive correlation between the percentage of meadows in the watershed and the DOC concentration. High dominance of meadow ecosystems in the examined watershed determined the amount of the imported organic matter of terrestrial origin that in turn influenced the high values of $SUVA_{260}$.

In the Wschód district, the mean DOC value in all reservoirs equaled 23.5 mg C•dm^{-3}. The DOC concentrations determined here were the highest of all measured in this study; in W_8 in the autumn it was 42.7 mg C•dm^{-3} and in W_2 in the spring it was 41.4 mg C•dm^{-3} (Fig. 5). Wschód is an industrial district. Manufacturers, service shops and warehouses are sited here, with a nearby railway and a busy road. The area is intensively developed and the anthropogenic pressure is considerable which explains the elevated DOC values in the Wschód reservoirs.

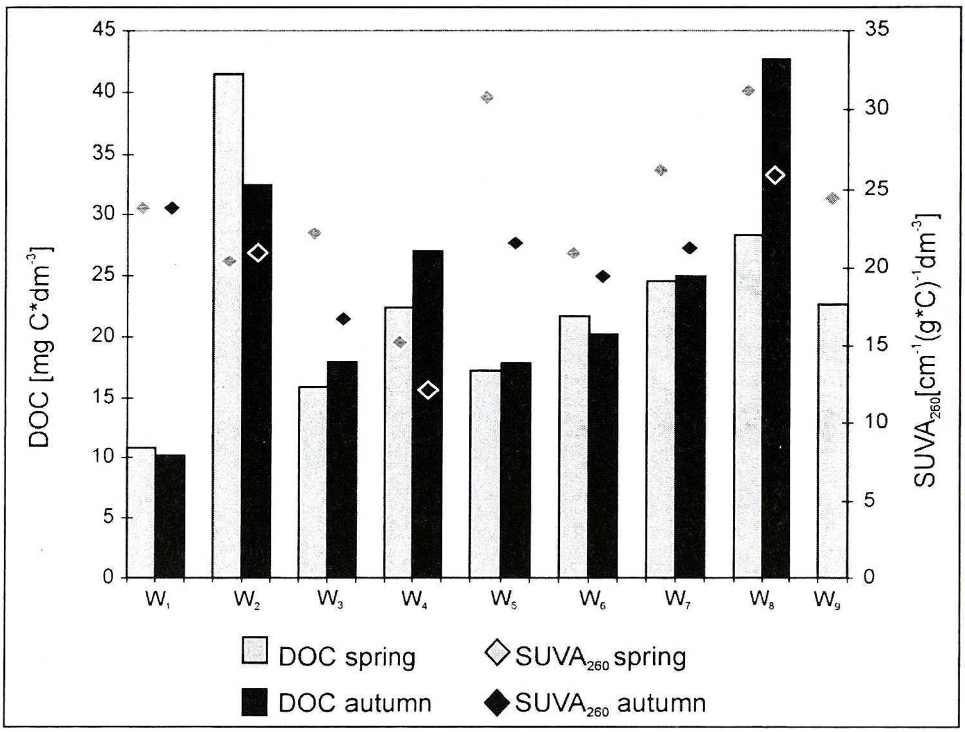

Fig. 5. DOC concentrations and $SUVA_{260}$ values in the Wschód District reservoirs

In W_2, the high input of the terrestrial-origin organic matter was displayed by high values of $SUVA_{260}$ in the spring and autumn, and by elevated – in comparison to other reservoirs – values of the electric conductivity (1165 $\mu S \cdot cm^{-1}$), calcium ions (121.4 mg $Ca^{2+} \cdot dm^{-3}$), total hardness (7.3 $mval \cdot dm^{-3}$), and alkalinity (6.8 $mval \cdot dm^{-3}$).

In W_8, the increase of DOC from spring until autumn amounted to almost 15 mg $C \cdot dm^{-3}$ (with simultaneous very high $SUVA_{260}$) that may have been caused by autolysis and microbiological decomposition of the organisms dying out after the growing season. The input of pollutants generated by man was also significant, as reflected by the high value of electric conductivity, i.e. 912 μS in the autumn, while the mean value for the whole district equaled 505 μS.

The quantity and quality of the organic matter in the examined reservoirs depended on the type of development in the direct watershed. The reservoirs were situated in heavily urbanized area, on land with ruined buildings, surrounded by wasteland, peat bogs or forest. The reservoirs' surroundings were quite diverse; different types of watersheds interpenetrated and the closeness of the urban development influenced the reservoirs with variable intensity. Small volume of the reservoirs favored accumulation of organic matter, displayed by high or very high concentrations of DOC in two of the examined reservoirs.

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