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Optical Properties of Dissolved Organic Matter in Urban Fountains

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Abstract. Optical properties of dissolved organic carbon compounds (DOC) in selected fountains in Olsztyn (Poland) were investigated. The DOC fraction was isolated by using a membrane filter (Sartorius, pore size 0.45 µm). The amount of absorption for the DOC fraction was determined using the UV spectrophotometry method (UV range) at wavelength: 203 nm (A203), 250 nm (A250), 254 nm (A254) and 365 nm (A365). Then the absorption ratios were determined: A250/A365 and A254/A203. The aim of the study was to determine the contribution of macromolecules (hardly biodegradable, having an aromatic character) in the fraction of DOC. The variability of DOC compounds in the water of fountains was investigated depending on the water supply method (also subjected to disinfection) and depending on the period of research (season of the year) or the impact of the environment. It was shown that the average A250/A365 values were three times lower in fountains not subjected to disinfection than in artificial fountains. The A254/A203 parameter was on average several times lower in artificial fountains where the water was chlorinated. The Kruskal-Wallis test confirmed that the differences between the artificial objects and the other two in the average values of A250/A365 and A254/A203 ratios are significant. The values of these quotients indicate that natural and semi-natural fountains are characterized by a high share of aromatic compounds with high molecular weight. For artificial objects, the effect of the study period on differences in average values of A250/A365 and A254/A203 was not confirmed. The U Mann-Whitney test showed that there are differences in the mean values of A254/A203 between the semi-natural and natural fountain, and the changes of A250/A365 in these fountains are related to the date of sampling. After examining the influence of the catchment and anthropogenic pressure, it was found that in the semi-natural fountain, the quality of the DOC fraction changed due to the supply of allochthonous organic matter (leaves, waterfowl and its feeding by resting people). In the case of a fountain on a natural reservoir, the relatively high primary production and allochthonous inflow of DOC had significant influence on the DOC character (leaching from slopes with rainfall, groundbaits using by anglers).

1. Introduction

The study of absorption spectra of DOC compounds using UV-VIS spectrophotometric method can explain the origin and nature of dissolved organic matter. The different wavelengths are used for calculating the absorption ratios [1]. Physical and physicochemical properties of DOM can be defined indirectly on the basis of $A_{\lambda 1}/A_{\lambda 2}$ ratios (A- absorption, λ - wavelength): the relative molecular mass,



degree of aromatic rings condensation. Basing on these absorption quotients the participation of compounds with a high relative molecular mass (which are resistant to biodegradation) can be estimated [2]. The study of the optical properties by the spectrophotometric method is often used to assess the quality of the dissolved organic matter from landfill leachate [3] and in the lake's water, rivers, springs or peats [4, 5, 6, 7, 8].

Until now no information about qualitative research of dissolved organic matter in the urban fountains using absorption spectra in the UV radiation exists in the literature. But considering the fact that people passing nearby fountains are exposed to contact with fountain water and aerosols, the research of water quality of such objects can give information, which can be important for human health [9].

The aim of this study was to investigate of qualitative changes of dissolved organic carbon fraction in the urban fountains in Olsztyn (North East Poland). The interpretation of the absorption spectra (UV range) has been used to identify the characteristics of organic matter. Basing on the absorption analysis, the $A_{\lambda 1}/A_{\lambda 2}$ ratios were determined. Afterwards, the determination of the relationship between the studied parameters, and their variability for each of the quality parameters of organic matter was carried out. Moreover, the analysis of the impact of the surrounding area to transformation of the quality and contribution of macromolecular compounds in DOC fraction in fountain's water was made. They were the first of this type of qualitative research on DOC compounds in fountains in Poland.

2. Material and methods

The research was carried out from May to October 2017 (every 2 or 3 weeks) in five fountains. Three artificial fountains were selected for the study - they were supplied with water from waterworks (permanently or periodically chlorinated). The fourth was located on a natural reservoir. The fifth fountain had a semi-natural character and was supplied with water from waterworks (without disinfection) and with rainwater. The investigated fountains in this work were called and numbered as follows:

- artificial fountains: 1 – Central Park, 2 – Old Town, 3 – Fish with a child,
- natural fountain: 4 - Jakubowo Park,
- semi natural fountain: 5 - Kusocinski Park.

The DOC fraction was obtained through microfiltration. The Sartorius membrane filter (0.45 μm pore-size) was used for separation of the suspended matter. Before filtration the filter was rinse with deionized water to remove the organic matter. The values of absorption at: 203 nm (A_{203}), 250 nm (A_{250}), 254 nm (A_{254}), 365nm (A_{365}) wavelengths were measured by spectrophotometric method (Shimadzu UV-1601PC spectrophotometer). Deionized water was used as reference and absorption path was 1 cm (quartz cuvette). Absorption ratios have been calculated as follows: A_{250}/A_{365} and A_{254}/A_{203} .

The Kruskal-Wallis test was carried out to check if there are differences between the average value of absorption quotients tested in urban fountains. The U-Mann Whitney test was carried out to check differences the average value of A_{250}/A_{365} and A_{254}/A_{203} between artificial fountains and semi- and natural (Statistica 13.1).

3. Results

Mean values of A_{250}/A_{254} ratio changed from 7 in Kusocinski Park to 22 in Old Town. The artificial objects were distinguished by a wider range of changes of this parameter. The average value of A_{250}/A_{254} was similar in the group of artificial objects and in the group of semi and semi-natural fountains (figure 1).

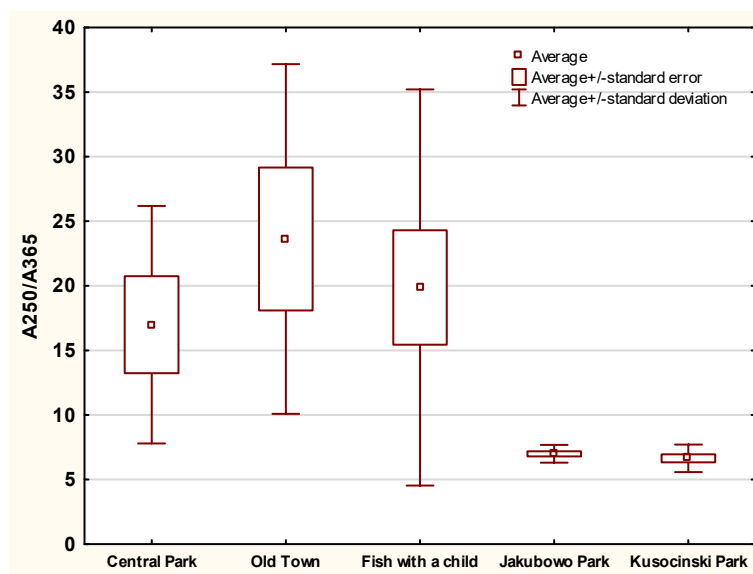


Figure 1. The range and average values the A250/A365 ratio in urban fountain's waters in 2017 (for 1 and 2 objects: $n=6$; for 3,4, 5 in each case $n=12$)

The research revealed that the average A254/A203 values were several times higher in fountains not subjected to disinfection than in artificial fountains. In artificial fountains they changed from 0,07 in Old Town to 0,11 in Fish with a child. In semi-natural Kusocinski Park and natural Jakubowo Park average A254/A203 ratios were very similar (figure 2).

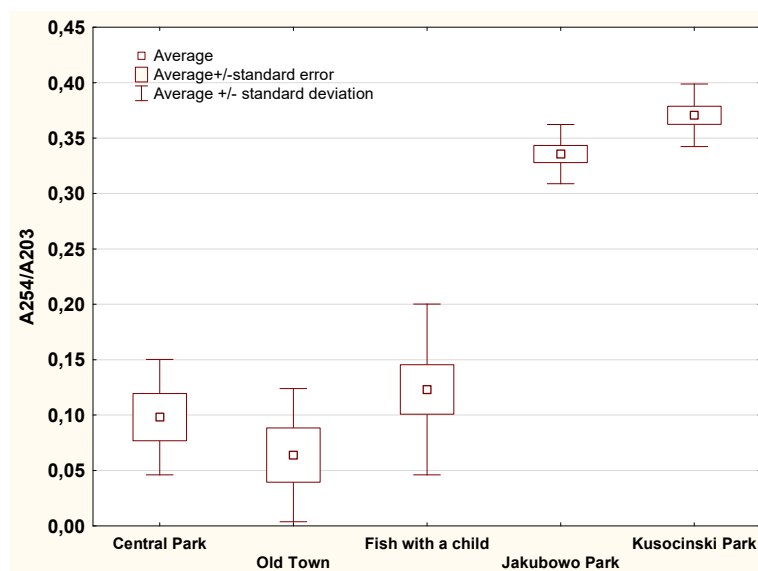


Figure 2. The range and average values the A254/A203 ratio in urban fountain's waters in 2017 (for 1 and 2 objects: $n=6$; for 3,4, 5 in each case $n=12$)

The Kruskal-Wallis test confirmed that the differences in the average values of A250/A365 and A254/A203 between investigated fountains are significant (table 1). In the group of artificial objects, no differences between average value for both of absorption ratio were found. The artificial objects and the group of other two differed from each other in highly important way (table 2).

Using the Kruskal-Wallis test ($n=24$, for $p < 0.05$) was checked if in the artificial fountains the absorption quotients studied significantly change with the date of sampling. This correlation was not confirmed for both parameter A250/A365 ($p=0.186290$) and A254/A203 ($p=0.473328$).

The U Mann-Whitney test ($n=24$, for $p < 0.05$) showed that there are differences in the mean values of A254/A203 between the semi-natural and natural fountain ($p=0.010194$), and the changes of A250/A365 in these fountains are related to the date of sampling ($p=0.030384$).

Table 1. The Kruskal-Wallis test – comparison of mean values of A250/A365 and A254/A203 in fountain water (p values; for $p < 0.0500$).

Fountain:	Central Park (N=6)	Old Town (N=6)	Fish with a child (N=12)	Jakubowo Park (N=12)	Kusocinski Park (N=12)
A250/A365					
Central Park		1.000000	1.000000	0.023997**	0.013077**
Old Town	1.000000		1.000000	0.003392**	0.001686**
Fish with a child	1.000000	1.000000		0.003540**	0.001501**
Jakubowo Park	0.023997**	0.003392**	0.003540**		1.000000
Kusocinski Park	0.013077**	0.001686**	0.001501**	1.000000	
A254/A203					
Central Park		1.000000	1.000000	0.051481	0.001093**
Old Town	1.000000		1.000000	0.002574**	0.000023**
Fish with a child	1.000000	1.000000		0.017199**	0.000087**
Jakubowo Park	0.051481	0.002574**	0.017199**		1.000000
Kusocinski Park	0.001093**	0.000023**	0.000087**	1.000000	

** significant difference for $p < 0.0500$

Table 2. The U Man-Whitney test – comparison of mean values of A250/A365 and A254/A203 between group of artificial and other fountains (p values).

Semi-natural and natural fountain (N=24)	
A250/A365	
Artificial fountains (N=24)	0.000000**
A254/A203	
Artificial fountains (N=24)	0.000000**

** significant difference for $p < 0.0500$

4. Discussions

The fraction of dissolved organic carbon (DOC) is a mixture of organic compounds of different molecular structure, and thus different chemical and functional properties [2, 10]. As a labile fraction, it is responsible for transporting in geochemical cycle related forms of elements, determining the volume of production. The biogenic elements can be transported in that way, but the all forms of toxic metals as well, that have an inhibitory effect on the biological processes, limiting the possibilities of self-purification of water [11].

The role of organic matter in water bodies as a substrate for heterotrophic microorganisms is indisputable. The bacteria can shape the environmental conditions in the lakes [12, 13]. In water disinfected by chlorination, the role of bacteria in DOM utilization is limited.

Nature of the molecules of these compounds can also be specified by setting relations absorption wavelengths ($A_{\lambda 1}/A_{\lambda 2}$) from the UV and VIS [2, 14]. On this basis it is possible to estimate not only the participation of high relative molecular mass compounds, which are resistant to biodegradation,

but to describe the transformation of the structure of the particles, which has an effect on the optical properties and, consequently, to changes in the physicochemical properties [3]. UV absorbance at 254 nm has been used effectively to determine concentrations of organic carbon in drinking water supplies for the purpose of monitoring DBP precursors [15]. Therefore, it is important to monitor qualitative changes in DOC fraction in order to demonstrate the new conditions caused by reclamation of fountain's water. Such changes can be observed by spectrophotometric measurements.

Studies of water in five fountains in Olsztyn (Poland) showed that the qualitative parameters were very different. Three artificial fountains were supplied with water from waterworks (permanently or periodically chlorinated). In these cases, the A250/A365 ratios were the highest. The higher A250/A365 ratios inform about the lower molecular weight of DOC compounds than in the other objects. The water of artificial fountains was characterized by high transparency. Facilitated penetration of light into the bottom of the fountain bowl (shallow objects) supports the abiotic decomposition of the organic matter [16]. In addition, the water of these fountains was aerated and mixed, which accelerates the decomposition of easy biodegradable DOC compounds [17].

In semi- and natural fountains very high A254/A203 and lower than in the other objects A250/A365 was observed. The values of these quotients indicate that natural and semi-natural fountains are characterized by a high share of aromatic compounds with high molecular weight. Changes in A250/A365 and A254/A203 ratios were caused by inflows from the catchment (allochthonous DOC) [7, 18]. After examining the influence of the catchment and anthropogenic pressure, it was found that in the semi-natural fountain, the quality of the DOC fraction changed due to the supply of organic matter: leaves, waterfowl (droppings) and its feeding by resting people.

In the case of a fountain on a natural reservoir, the relatively high primary production and allochthonous inflow of DOC had significant influence on the DOC character (leaching from slopes with rainfall and from groundbaits using by anglers). Therefore, changes in the proportion of compounds with lower or higher molecular weight were related to the sampling time (season of the year) [19].

5. Conclusions

In semi-natural fountain the changes in A250/A365 and A254/A203 ratios were mainly caused by inflows from the catchment (allochthonous DOC). It was found that the water of the natural fountain is additionally supplied in organic matter originating from primary production. However, in artificial objects quality changes in the DOC fraction were observed, which are not connected with season of year.

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