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DISSOLVED ORGANIC CARBON AND BIODEGRADABLE DISSOLVED ORGANIC CARBON DETERMINATION IN RIVER WATER OF THE STRUG BASIN

The aim of the study was to determine Dissolved Organic Carbon (DOC) and Biodegradable Dissolved Organic Carbon (BDOC) concentrations, as well as the correlation between them, in the river water of the Strug basin located in the Carpathian Foothills. The Strug river's hydrographic basin was chosen for the study as it is a typical catchment area, which allows ease of measurement. DOC concentrations in the streams (tributaries) and the Strug ranged from 2.71 to 4.88 mgC/dm^3 and from 3.62 to 4.19 mgC/dm^3, respectively. BDOC concentrations in the streams and the Strug ranged from 0.40 to 1.09 mgC/dm^{3}and from 0.64 to 0.77 mgC/dm^3, respectively. BDOC, expressed as the percentage of DOC (%BDOC) ranged from 14.76 to 24.78% in the streams, and from 17.68 to 20.11% in the Strug. The procentage of BDOC is independent of DOC concentrations. The season of the year and the size of the watercourse had the greatest impact on DOC and BDOC concentrations.

Keywords: organic carbon, water quality, natural waters, water protection

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1. Introduction

Surface water in Poland is a significant source of water used for consumption and industrial purposes. Organic matter is its typical component, which is important from the point of view of water treatment processes [1]. Even though it does not have a direct impact on human health, organic matter decreases the efficiency of disinfectants and leads to the formation of harmful disinfection by-products [2,3]. Knowledge of the DOC biodegradable fraction content is also very important in the context of water stability in water distribution systems [4,5,6].

The major source of organic matter in temperate surface water is the terrestrial contribution [7]. The main factor affecting organic carbon concentration is net primary productivity, rather than direct biomass decomposition. It has been estimated that the fluvial export of organic matter from a given region is about 1% of the net primary productivity [8]. The content of clay minerals in catchment soils is also of great importance. In places where clay content is high, water contains less carbon [9] due to the sorption capacity of soils [10]. Atmospheric precipitation is also an important factor influencing DOC concentrations. It has been estimated that the mean concentration of organic carbon in rainwater is 1.932 mgC/dm^3. In warm seasons, DOC concentrations in continental precipitation were higher than in cold seasons [11]. Similar trends have been observed in analyses performed for areas near Rzeszow [12]. The median values recorded for spring, summer and autumn were 2.9, 2.8 and 1.83 mgC/dm^3, respectively.

Research carried out for over ten years has shown a gradual increase in DOC concentrations in surface water. In some regions of the UK, this content increased by an average of 91% in the years 1989–2004, and in the USA – by 10% in the years 1990–2000 [13]. The reason for this phenomenon is unknown. It is assumed that it is driven by climate change and the related cycles of excessive drying and moistening of soil, as well as changes in the soil sorption complex caused by continuous mineral acid inflow [14,15].

Although studies on the content of biodegradable fraction of DOC have been conducted for over a dozen years all over the world, so far no such research has been performed in Poland in the context of surface water.

The aim of the present study was to determine the concentration of DOC and determine the concentration of BDOC in the waters of the Strug River.

2. Materials and methods

2.1. Study area

The Strug basin is located on the border of two physical and geographical units:

1. Outer Carpathians (Flysch Carpathians)
2. Carpathian Foredeep

In terms of the hydrographic division, the area discussed is classified as the Upper Vistula water region, forming a combined water body marked with code GW0821, composed of two Surface Water Bodies (SWB). Table 1 presents basic information on the catchment area discussed.

Table 1. Register characteristics of the Strug river basin [16]

SWB code	SWB name	SWB type	SWB code	Catchment area [km^2]
RW2000122265689	"The Strug to the Chmielnicka river"	Flysch stream	12	238
RW2000142265699	"The Strug from the Chmielnicka river to the estuary"	Small flysch river	14	31.82

[Source: http://bip.rzeszow.rdos.gov.pl/files/artykuly/48023/Rejestr_JCWP.xls]

A part of the area discussed, located in the Carpathian Foredeep, filled with Tertiary formations and Miocene clays, lies at an elevation of 210-260 meters above sea level and is characterized by a small diversity of terrain. It is an area gently sloping towards the northwest, cut by the valleys of the Wislok river's tributaries.

Within the Wislok Valley, there are Pleistocene and Holocene river formations in the form of silty clays, sandy dusts and dusts, gravels and sands.

The Carpathian Foothills are built of low- and medium-resistant Carpathian flysch of the Skole unit with a layered structure. Deep valleys covered with Holocene river formations: sands, gravels and alluvial soils, were carved in the flysch formations. The Foothills consist of quite extensive plateaux and ridges at c. 300–460 meters above sea level. Relative elevation differences in this area reach up to 150 meters. Mass wasting occurs in the form of landslides and downhill creeps. The inclined areas, especially arable land, are prone to erosion. Locally, the valley bottoms are waterlogged.

A large part of the basin, i.e. approximately 90% of its area, is covered with saprolitic and slope soils of low permeability, such as clays and sands of varying thickness.

The average annual air temperature for the study area is 7.1–7.4°C, and the total annual precipitation amounts to 627–643 mm.

The sampling sites were located in the Ryjak, Chmielnik and Nieborow streams, and at the estuary of the Strug, upstream of where the river flows into the Rzeszow Reservoir. The sampling sites for stream water were located upstream of the sewage treatment plants. The site location is presented in Figure 1.

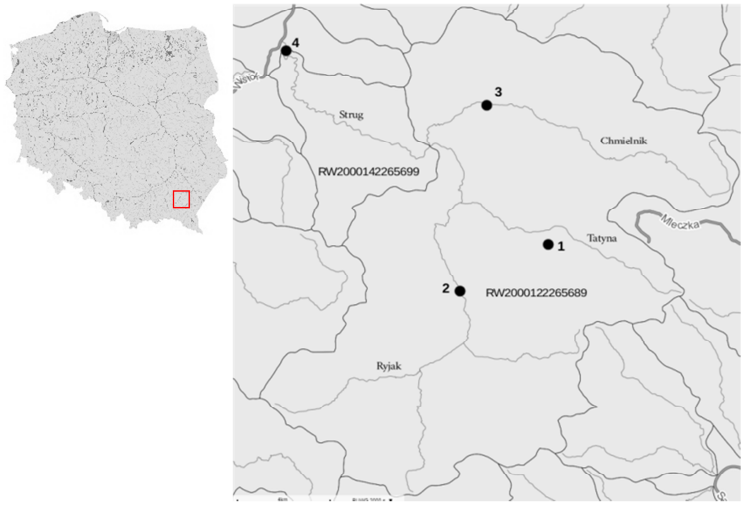

Figure 1. Sample collection sites within the Strug catchment area: 1–Nieborow stream, 2–Ryjak stream, 3–Chmielnik stream, 4–Strug River [Source: https://polska.e-mapa.net/]

2.2. BDOC and DOC determination methodology

Samples were collected quarterly with a Bürkle scoop with a telescopic rod adjusted to 500 ml bottles with a ground socket. Water samples were transported to the laboratory at refrigeration temperatures. The time between sample collection and the beginning of tests did not exceed 5 hours.

Servais' modified method for determination of BDOC in water was used in the analysis [17]. This method involves sterilizing the water sample by filtration, inoculating it with an autochthonous bacterial population, and incubating it for 28 days. The BDOC value is determined based on the difference between the DOC concentration before and after incubation.

$$BDOC = DOC_0 - DOC_i \quad (1)$$

where: BDOC – biodegradable dissolved organic carbon,
DOC_0 – dissolved organic carbon before incubation,
DOC_i – remaining dissolved organic carbon after incubation.

The analysis started with filtration of 200 ml of the sample analysed through a 0.2-µm-pore-size membrane filter (Whatman) which was first rinsed

with distilled water and then with the water sample. Two mililiters of inoculum containing autochthonous bacteria was added to the filtrate. The inoculum was a water sample filtered through a 0.2-µm-pore-size syringe filter (Whatman). This size of pores prevents the development of protozoa in the sample analysed.

The next stage of the analysis involved the determination of baseline DOC content in the sample (DOC_0). For that purpose, 40 ml of the water was collected and then analysed using a Sievers 5310 C TOC Analyser (GE) in accordance with the manufacturer's methodology. The remaining sample was incubated for 28 days in the dark, at 20°C, in a cone flask with a stopper allowing for gas exchange. After this time, DOC content was again determined in the sample (DOC_i).

The adopted method of BDOC analysis was verified with a test, which involved adding increasing doses of an organic carbon standard to water samples. These samples were a mixture of dechlorinated tap water and raw water from the Wislok river. The volume ratio was adjusted in such a way as to obtain a baseline DOC concentration of c. 0.5 mgC/dm^3. Increasing amounts of sodium acetate (source of easily biodegradable organic carbon) were added to the samples to increase DOC concentration (and, at the same time, BDOC concentration) by 0.5, 1.0 and 2.0 mgC/dm^3.

Before each use, the laboratory glassware was sterilised and cleaned to remove organic matter by heating for 4 h at 550°C in a muffle furnace. The steel filtration system was rinsed with a 10% solution of sodium persulfate at 50°C and then sterilised via autoclaving.

3. Results and discussion

The results of the method verification tests are presented in Table 2.

Table 2. Results of tests verifying the BDOC determination method

Day of incubation	BDOC dose [mgC/dm^3]			
	0	**0.50**	**1.00**	**2.00**
0	0.54	1.01	1.61	2.65
28	0.45	0.45	0.52	0.56
Difference	0.09	0.56	1.10	2.09

BDOC concentration in the water samples was 0.09 mgC/dm^3 i.e. 16.7% of the total DOC content. Data presented in Table 2 indicate that a corresponding increase of concentration was obtained for each BDOC dose after incubation. Importantly, the differences in DOC concentrations before and after incubation also reflect the BDOC fraction present in the test water.

The test results for DOC concentrations (average of two measurements) in the river water of the Strug catchment area are presented in Table 3.

Table 3. Seasonal variability in DOC

Season	DOC [mg/dm^3]			
	Nieborow stream	Ryjak stream	Chmielnik stream	Strug River
Spring (Sp)	2.71	3.20	3.38	3.62
Summer (Sm)	4.53	4.88	3.56	3.74
Autumn (A)	3.35	3.80	3.77	4.19
Winter (W)	2.78	3.06	2.93	3.78

The greatest seasonal variability in DOC concentrations was observed for water samples from the Nieborow and Ryjak streams – 1.82 mgC/dm^3. A slightly lower value was noted for the Chmielnik stream, and with the Strug, the seasonal variability was the lowest – 0.57 mgC/dm^3.

The season of the year influenced DOC concentrations in the waters analysed. The lowest concentrations in all sample collection sites were recorded in the winter and spring months. For the Nieborow stream and the Strug, the lowest concentrations were recorded in spring (2.71 and 3.62 mgC/dm^3, respectively). For the Ryjak and Chmielnik streams, on the other hand, the lowest values were observed in winter (3.06 and 2.93 mgC/dm^3, respectively).

Generally, DOC concentrations <3.0 mgC/dm^3 were found in 18.75% of the samples, 3.1-3.5 mgC/dm^3 in 25% of the samples, 3.5-4.0 mgC/dm^3 in 37.5% of the samples, and >4.0 mgC/dm^3 in 18.75% of the samples.

The results of BDOC concentration analysis for river water from the Strug catchment area are presented in Figure 2.

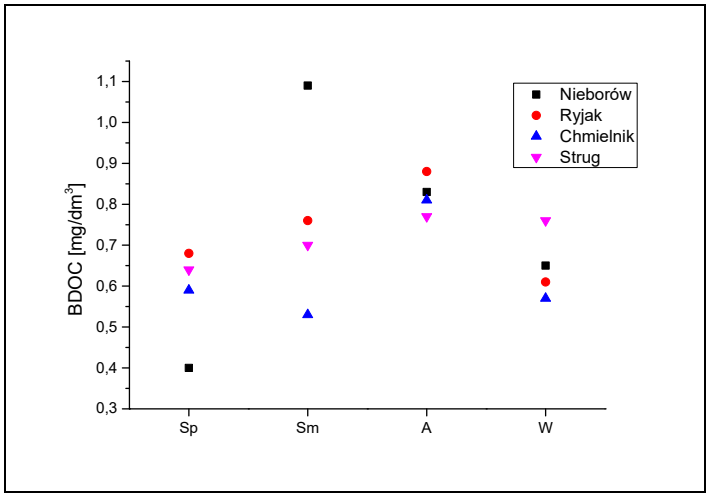

Figure 2. BDOC concentration [mgC/dm^3] Sp–spring, Sm–summer, A–autumn, W–winter

BDOC concentrations in the Strug basin streams ranged between 0.40 and 1.09 mgC/dm^3. Interestingly, these minimum and maximum values both pertained to the smallest flow i.e. the Nieborow stream. The range for the Strug was 0.64–0.77 mgC/dm^3. The %BDOC was 14.76–24.78% in the streams, and 17.68–20.11% in the Strug. As for seasonal changes, the lowest BDOC concentrations were recorded in spring and winter, and the highest – in autumn.

Figure 3 presents the general relation between DOC concentrations and BDOC expressed as the percentage of DOC. No correlation was found between these variables.

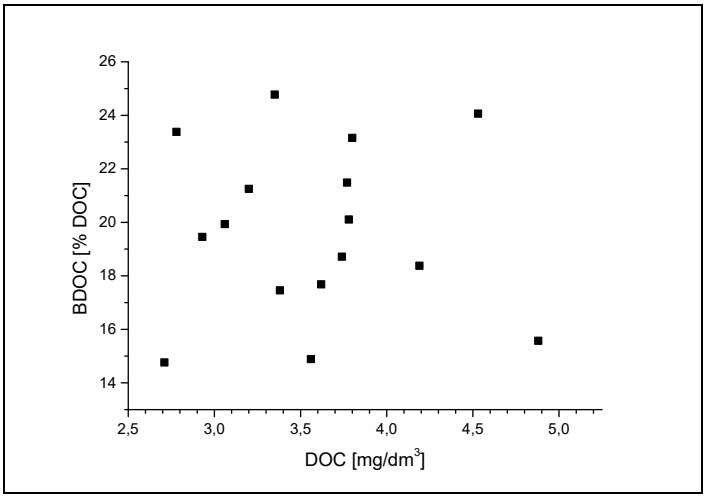

Figure 3. BDOC as the percentage of DOC in relation to DOC concentrations

DOC concentrations in flowing surface water change depending on the size of the watercourse, climate, type of the vegetation cover in the catchment area, and season of the year. The highest DOC concentrations of up to 50 mg mgC/dm^3 are found in watercourses beginning at marshes and peat-bogs [8]. In cool temperate climates, the typical range of DOC concentrations in rivers is 2–8 mgC/dm^3, with a mean of 3 mgC/dm^3. In their analysis, Servais et al. [17] demonstrated that DOC concentration in a river with a low level of pollution was c. 3.5 mgC/dm^3. Similar results were obtained in the present study. High variability in DOC concentrations has also been observed in catchment areas outside of Europe. In a study of the White Clay Creek watershed (North-eastern region of the USA), DOC concentrations ranged from 0.7 to 15.5 mgC/dm^3, with the peak %BDOC reaching 37.8% [18]. In the paper by Servais et al. [17], the BDOC fraction expressed as the percentage of DOC ranged between 19 to 34%. Similar results (20–25%) were obtained in the present study. A more extensive range has been observed for waters in areas closer to the North Pole. The %BDOC recorded by Fellman et al. [19] in three watersheds in Alaska ranged between 7 and 38%.

The present study demonstrated that DOC and BDOC concentrations varied depending on season. This was due to both accelerated organic matter decomposition at high temperatures and higher total precipitation in the summer and autumn months. DOC concentrations are also significantly affected by the size of watercourse – the smaller stream is, the greater the DOC concentration fluctuations. In the present study, this was observed in the Nieborow stream. The opposite was found for the estuary section of the Strug, where concentration fluctuations were the lowest.

4. Conclusions

1. DOC concentrations in the Strug and its tributaries (streams) ranged from 3.62 to 4.19 mgC/dm^3 and from 2.71 to 4.88 mgC/dm^3, respectively.
2. Seasons of the year and the size of the watercourse affect DOC concentrations in the river water of the Strug basin.
3. Except for the summer months, the greatest DOC concentrations were recorded at the sampling site located in the estuary section of the Strug.
4. The procentage of BDOC ranged between 14.76 and 24.78%.
5. In the Strug river basin, procentage of BDOC is independent of DOC concentrations.
6. Tests verifying the BDOC determination method proved its usefulness in analyses of natural waters.

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