

POLISH JOURNAL OF ECOLOGY (Pol. J. Ecol.)	57	2	217–227	2009
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*Regular research paper*

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## THE EFFECT OF HYDROLOGICAL DROUGHT ON CHEMICAL QUALITY OF WATER AND DISSOLVED ORGANIC CARBON CONCENTRATIONS IN LOWLAND RIVERS

**ABSTRACT:** The effects of drought on river water quality and dissolved organic carbon (DOC) fluctuations were studied in 22 lowland rivers in north-east Poland with different size (from 3.3 km to 77.2 km), and discharge (mostly in range 1–8 m<sup>3</sup> s<sup>-1</sup>). The extensive agriculture, housing and plantation forestry (afforestation from 7% to 97%) dominate in the landuse in catchments. All investigated rivers were characterized by similar hydrological regime and relatively high natural level of organic matter in waters (10 mg DOC dm<sup>-3</sup>). The autumn 2000 drought in Poland was one of the most severe in many years when the monthly sum of precipitation in October made only 6% of average long-term norm for the region. Significant differences in concentrations of investigated chemical parameters were noted between results from wet (1996–1998) and dry (2000) autumn periods. Concentrations of ions derived from non-point sources increased in many locations, which was confirmed by increases in Ca, and HCO<sub>3</sub> concentrations. Average dissolved organic carbon concentrations, and water colour were two times higher in the wetter autumn than in dry period. The hydrological drought in autumn 2000 caused significant decrease in the range of DOC concentrations (about 30%). The largest difference in DOC concentrations between the wet autumn period and extremely dry one were recorded in the rivers flowing through dense forests. Our results indicate that dissolved organic carbon in most natural catchments de-

creased as a result of the lack of dilution. Some more natural north-east Polish rivers gradually lost contact with their catchments, and ecotone zones did not play an important role in supplying organic matter to rivers during droughts. Most of river and catchment morphological parameters became less important in shaping the amounts of DOC in rivers. The current study indicates that small and medium rivers were not resistant in hydrochemical terms to flow decreases what has environmental consequences for transport of nutrients, organic matter and finally on sediments, flora and fauna habitats.

**KEY WORDS:** drought, river, water quality, DOC, Specific UV Absorbance (SUVA)

### 1. INTRODUCTION

Long-term rainless periods in catchment areas bring about the phenomenon of hydrological drought that manifests in rivers as temporary low flow (Smakhtin 2001). Decreased amounts of flowing water do not only affect the functioning of river ecosystems, ecotone zones, and land ecosystems within catchments, but they also bring about considerable changes in water quality. Droughts dramatically reduce the surface runoff from catchments, and only ground-

waters are active in these periods. Depending on the shape and type of river beds, the ecotone zones either completely disappear or their range becomes significantly limited. Even in moderate climates, droughts result in the considerable shortening of river lengths, mainly in the upper courses. In rivers with wide, shallow channels, the bottom sometimes dries out in places, which leads to decreased macrophyte range belt, the disappearance of some benthic organisms, and the accelerated mineralization of organic matter (Langhans *et al.* 2006). Climate change and its specific symptoms in different climatic zones are seen as the events that will, within the coming century, change the general biological diversity of habitats, mainly under cool and mid-latitude climatic conditions (Hillbricht-Ilkowska 1998, Hillbricht-Ilkowska *et al.* 2000). Climate warming and the increase of mean air temperature may lead to important changes in the functioning of riverine ecosystems (Freeman *et al.* 2004) and may cause drastic shifts in the DOC load and its chemical structure (Arvola *et al.* 2004).

Periods of warming and drought have occurred more and more frequently over the past several decades. In north-eastern Poland in 2000, long periods without rain were recorded in the second half of summer and the beginning of autumn. Increase in the air temperature and evapotranspiration were recorded during autumn of 2000 in north-eastern Poland by Kożuchowski and Degirmendzić (2005). In October of that year, hydrochemical studies, including dissolved organic carbon (DOC) measurements, were carried out by the authors in 22 lowland small and medium-size rivers in north-east Poland. Data for the same locations collected under average conditions in 1996–1998 served as the reference point for the current study of atmospheric drought. Numerous studies have documented the leaching DOC from forests across the globe (McDowell *et al.* 1998). Some of the highest concentrations of DOC have been found in streams draining temperate forest catchments (Grieve 1990, Górniak and Zieliński 2000). On the other hand – presence of forests can decrease the total streamflow by 10% in growing season (Riedel *et al.* 2005, Xiaofeng *et al.*

1995). The present study focuses on changes in water quality and DOC distribution from catchments under conditions of low water levels as well as the quality of dissolved organic matter measured as UV absorbance. We expected that the DOC concentrations in the rivers are strongly related to the proportion of forests in the catchments throughout the study region, and that the DOC load and quality varies with varying climatic conditions.

## 2. STUDY AREA

Twenty-two measurement points were selected on representative rivers with different catchment and environmental conditions in north-east Poland (Fig. 1). The rivers studied drain periglacial areas with sandy-loam catchments and most of them flow in a north-westerly direction. Most of rivers studied have natural channels and flow through relatively untransformed lowland catchment areas in north-east Poland. A few of the rivers have regulated channels (like the city rivers No. 2 and 3, or typically agricultural, regulated rivers like No. 4 and 5). All of the rivers are in the River Narew watershed (Vistula drainage area) (Fig. 1). The rivers studied are of various lengths (from 3.3 km to 77.2 km), different river bed slopes (ranging from 0.16 to 3.64 ‰) (Table 1) and discharge mostly between 1.0–8.0 m<sup>3</sup> s<sup>-1</sup>. The majority of the river catchments do not exceed 100 km<sup>2</sup>, and catchment afforestation ranges from 7% to 96.9% (Table 1). The rivers studied all lie within the same geographic region with mean annual precipitation of 600 mm and a vegetation season of 190–200 days.

The 2000 year was not typical from meteorological point of view. Most of monthly average air temperature in the studied region – Białystok town, (except summer period) were much higher than long-term (1961–2000) norm (Fig. 2). Annual mean temperature for 2000 was 25% higher (8.6°C) than multiannual average (6.8°C). The drought periods were observed from August to October when the monthly sum of precipitation does not exceed average long-term (1971–2000) norm for Białystok region (Table 2). Critical situation was noted in October when monthly sum of precipitation recorded less

Table 1. Morphometrical and hydrological characteristics of 22 investigated rivers and catchments in NE Poland (numeration as in Fig. 1).

Dash mark – discharge below 0.5 and double dash mark – discharge between 0.5-1.0 m<sup>3</sup> s<sup>-1</sup>

No	River (local name)	River length (km)	River slope (‰)	Catch- ment area (km <sup>2</sup> )	Catch- ment deniv- elation (m)	Catch- ment slope (‰)	Catch- ment length (km)	Catch- ment width (km)	Catch- ment affores- tation (%)	Dis- charge (m <sup>3</sup> s <sup>-1</sup> )
1	Chwyszczaj	9.3	1.86	26.9	26.7	5.14	8.6	5.3	7	–
2	Dolistówka	6.5	3.63	16.7	42.0	10.2	5.6	4.3	12	–
3	Biała	19.9	2.02	63.1	47.3	9.85	15.7	9.4	19	0.8
4	Krzywczyk	7.7	3.64	25.4	33.4	6.68	7.6	5.4	34	–
5	Bobrówka	8.6	0.56	33.6	4.8	0.83	6.8	4.7	38	–
6	Słoja	15.7	1.94	225	55.0	3.67	22.2	12.5	38	0.8
7	Sokołda	47.2	0.91	461	110.0	5.12	28.3	14.0	50	2.3
8	Supraśl	77.2	0.16	1817	94.4	2.22	52.8	64.0	54	8.6
9	Leśna Prawa	21.7	0.61	236.4	24.3	1.58	18.1	13.6	55	--
10	Mietlica	5.4	0.67	29.1	53.8	9.96	4.4	10.0	60	–
11	Płoska	33.5	0.55	191	80.2	5.81	144.0	18.0	66	1.0
12	Łanga	7.7	2.21	28.7	53.5	9.91	9.6	5.3	71	–
13	Czarna	28.7	1.29	190	102.0	7.39	16.7	13.6	72	1.0
14	Bartoszycha	7.3	2.19	32.4	50.0	8.77	6.3	6.1	75	–
15	Narewka	62.7	0.38	710	61.8	2.32	45.6	22.4	79	3.6
16	Radulinka	5.9	3.14	18.5	49.0	11.4	6.8	3.7	92	–
17	Borsukówka	5.7	0.95	14.2	6.4	1.68	5.7	4.3	94	–
18	Jabłoniówka	6.7	2.99	25.0	23.8	4.76	9.5	6.4	94	–
19	Migówka	3.3	1.97	16.5	40.0	9.76	6.6	3.3	96	–
20	Łutownia	14.4	1.08	119.5	23.6	2.17	16.0	10.1	97	--
21	Jelonka	4.8	0.63	12.8	6.2	1.72	5.8	4.65	97	–
22	Perebel	8.7	1.24	46.1	18.8	2.77	9.5	7.6	97	–

Table 2. Actual monthly and annual norms (1961–2000) for precipitation (mm) in Białystok region and monthly and annual precipitation in 2000 Białystok meteorological station and the rate of multiannual norm; months below the norm of precipitation marked with bold numbers.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Sum
Norm	29.0	24.2	31.2	39.0	52.5	71.8	84.8	62.4	57.3	46.4	39.5	38.9	577.1
2000	34	25	46	32	9	36	88	39	30	2.9	63	31	436
%	117	103	147	<b>82</b>	<b>17</b>	<b>50</b>	104	<b>63</b>	<b>52</b>	<b>6</b>	159	<b>80</b>	<b>76</b>

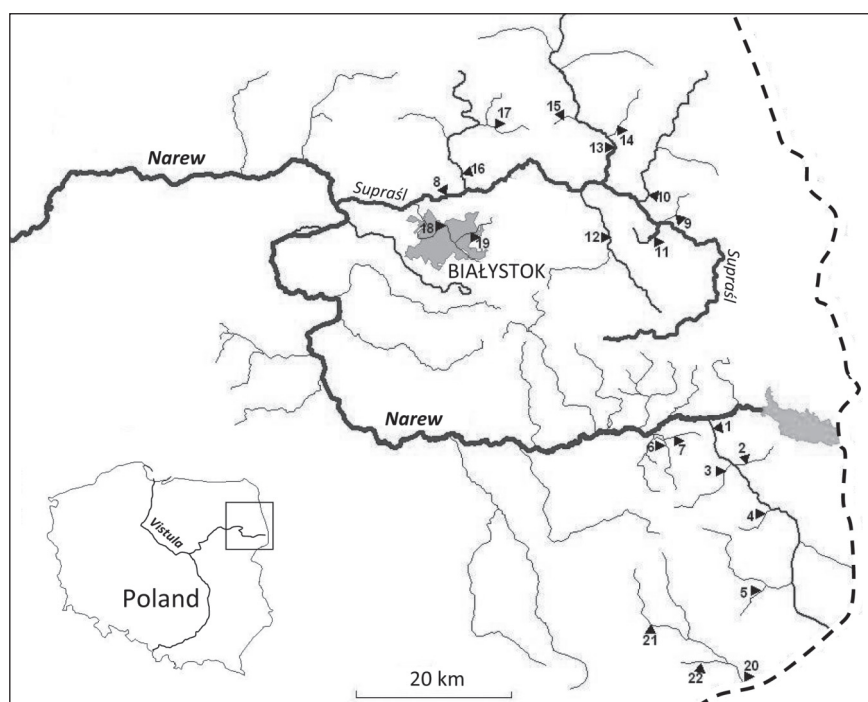


Fig. 1. Map of the study site with the location of the sampling points in north-eastern Poland (numeration as in Table 1) in the region of Białystok town.

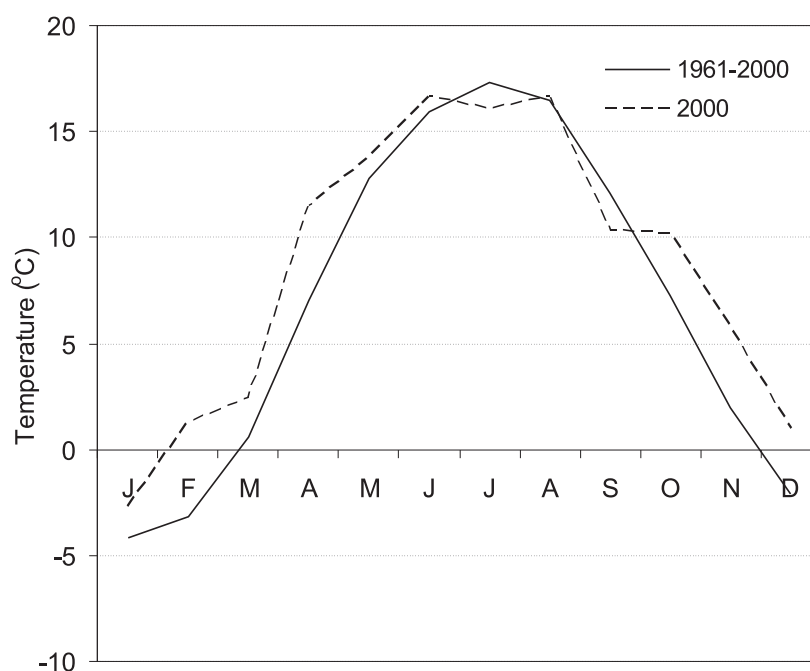


Fig. 2. Changes of monthly mean multiannual (1961–2000) temperature and mean monthly temperature recorded in 2000 at Białystok (north-eastern Poland) meteorological station.

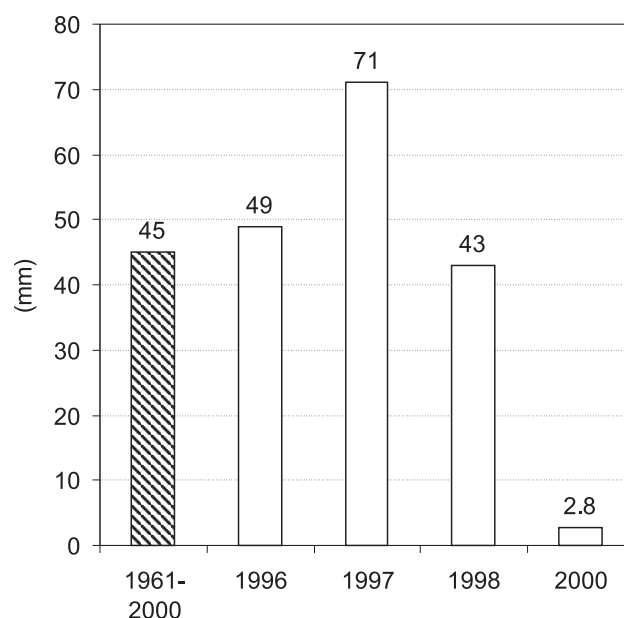


Fig. 3. Changes of monthly sum of precipitation for October in study years and mean October multiannual norm of precipitation (1961–2000), (data for Białystok, north-eastern Poland).

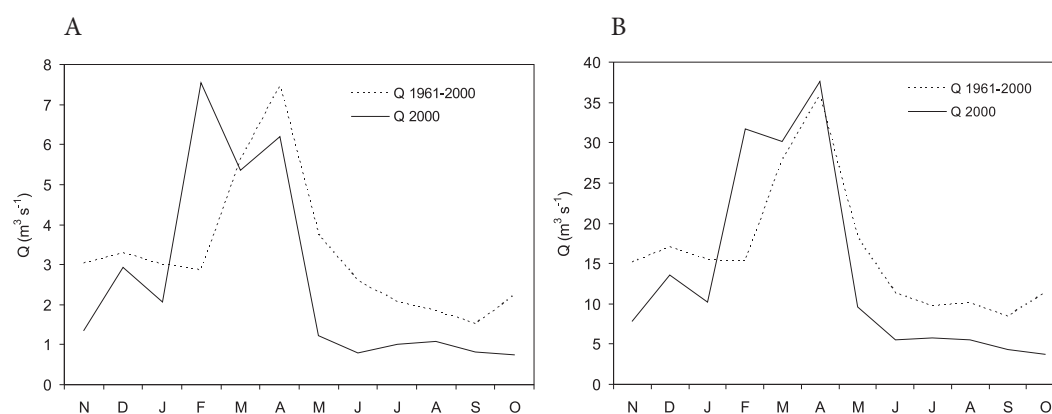


Fig. 4. Mean monthly discharge ( $Q$ ) in 2000 (hydrological year) for River Narewka (a) and River Narew (b) (Fig. 1) in comparison to mean multiannual discharge for period 1961–2000.

than 3 mm (Fig. 3). The consequences of precipitation deviations from normal values were manifested as hydrological drought and low stream flow. Mean river discharge in October 2000 in closing profile for investigated area (Narewka No 15 and Narew below Supraśl No 8 – see Table 1 and Fig. 1) was 70% lower than multiannual norm for October (Fig. 4a, b).

### 3. METHODS

Ten samples from each point (three samples: spring, summer, autumn 1996–1998 each plus one sample in 2000 during the autumn drought) were collected. Field measurements of physical parameters of water (temperature, conductivity, pH, dissolved oxygen) were recorded with a multiprobe

Table 3. Physicochemical characteristics of water from 22 lowland rivers (Fig. 1, Table 1) in north-east Poland (autumn 1996–1998 and 2000); n – number of samples. Statistical significance is marked by an asterisk ( $P < 0.05$ ).

Parameter	October 1996–1998  n=66		October 2000  n=22
Temperature (°C)	8.51 ± 1.64	*	9.82 ± 1.33
Oxygen (mg O <sub>2</sub> dm <sup>-3</sup> )	9.22 ± 3.25		9.28 ± 2.40
Oxygen saturation (%)	78.44 ± 28.83		81.49 ± 21.11
Acidity (pH)	7.45 ± 0.34	*	7.04 ± 0.25
Specific conductivity (µS cm <sup>-1</sup> )	474.1 ± 189.8		478.4 ± 157.9
Ca (mg dm <sup>-3</sup> )	78.57 ± 15.04	*	87.65 ± 15.67
Mg (mg dm <sup>-3</sup> )	8.47 ± 3.46		8.10 ± 1.92
Fe (µg dm <sup>-3</sup> )	411.4 ± 387.6		311.5 ± 197.1
HCO <sub>3</sub> (mg dm <sup>-3</sup> )	252.8 ± 53.07	*	289.4 ± 41.92
SO <sub>4</sub> (mg dm <sup>-3</sup> )	28.74 ± 10.69		33.17 ± 13.30
Cl (mg dm <sup>-3</sup> )	15.28 ± 9.66		16.63 ± 17.22
TP (µg dm <sup>-3</sup> )	377.8 ± 375.6	*	183.0 ± 208.7
P-PO <sub>4</sub> (µg dm <sup>-3</sup> )	126.8 ± 163.1		121.0 ± 171.6
N-NH <sub>4</sub> (µg dm <sup>-3</sup> )	265.7 ± 221.5		245.1 ± 201.0
N-NO <sub>3</sub> (µg dm <sup>-3</sup> )	539.7 ± 456.2		685.1 ± 870.4
DOC (mg dm <sup>-3</sup> )	12.32 ± 9.19	*	7.27 ± 5.47
SUVA (Abs <sub>260</sub> g C <sup>-1</sup> dm <sup>-3</sup> )	21.41 ± 16.83	*	41.26 ± 25.81
Colour (Abs <sub>330</sub> cm <sup>-1</sup> )	0.129 ± 0.110	*	0.064 ± 0.037

Table 4. Correlation coefficients (r) between catchment afforestation (Table 1), and mean DOC concentration in particular seasons in 1996–1998 and in October 2000; significance level (n = 22,  $P < 0.05$ ).

DOC (mg dm <sup>-3</sup> )	Catchment afforestation (%)
May (1996–98)	0.58
July (1996–98)	0.19
October (1996–98)	0.28
Drought (October 2000)	-0.17

sensor (Hydrolab<sup>TM</sup>). All samples were analyzed for dissolved organic carbon (DOC) with a Shimadzu TOC-5050A analyzer using high-temperature catalytic combustion (Sugimura and Suzuki 1988). The samples were filtered with 0.45 µm, acidified with 2 M hydrochloric acid and were sparged with nitrogen gas to remove carbonates (Zieliński and Górniak 1999). Specific UV Absorbance (SUVA) indicating of the aromatic character of organic matter

allows the aromatic biased UV 260 nm measurement to be normalized over the overall organic load in the water. A characterization of the aromaticity of the water independent from the general level of organics in the water can then be obtained.

To determine Specific UV Absorbance (SUVA), spectrophotometrical absorbance at 260 nm (Abs<sub>260</sub>) was measured and the SUVA parameter was computed using the following formula after Chin *et al.* (1994, modified)

Table 5. Correlation coefficients ( $r$ ) between morphological characteristics of rivers and catchments vs. DOC and SUVA (formula 1) in different study periods; significance level  $P < 0.05$  (marked with bold letters).

Parameter	Mean for study period October (n = 66)		October 2000 (n = 22)	
	DOC	SUVA	DOC	SUVA
Catchment area	-0.20	0.10	0.01	-0.15
Catchment afforestation	<b>0.28</b>	0.23	-0.17	0.05
River length	-0.22	0.16	0.00	-0.15
River slope	<b>-0.34</b>	0.21	-0.09	0.08
Catchment slope	<b>-0.61</b>	<b>0.34</b>	<b>-0.42</b>	<b>0.26</b>
Catchment width	<b>-0.52</b>	0.00	<b>-0.29</b>	0.22
Catchment length	-0.20	0.10	-0.05	-0.05
Catchment denivelation	<b>-0.45</b>	-0.04	<b>-0.44</b>	<b>0.40</b>

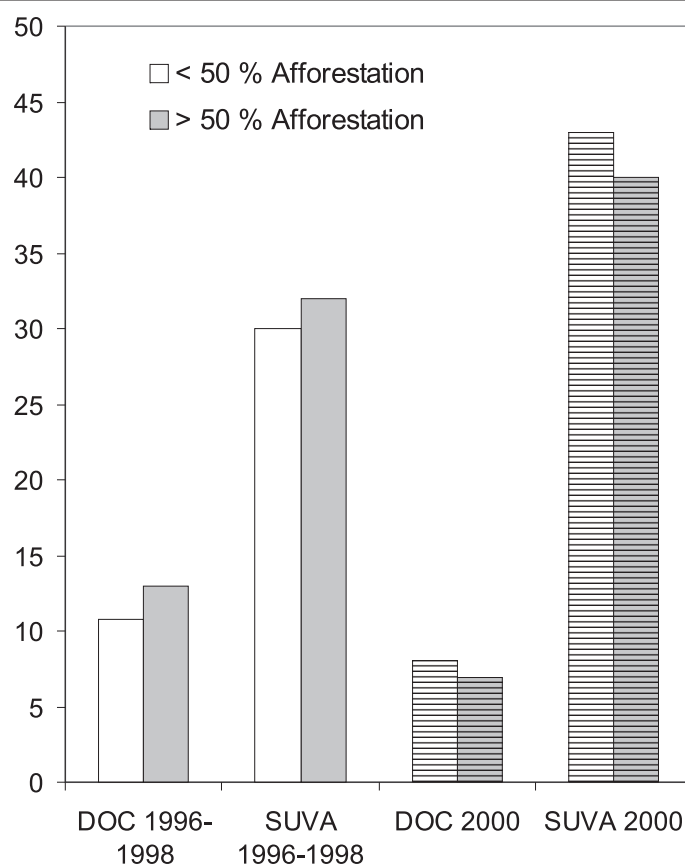


Fig. 5. Changes of DOC concentration (mg dm<sup>-3</sup>) and SUVA (Abs<sub>260</sub> g C<sup>-1</sup> dm<sup>-3</sup>) (formula 1) in two groups of catchment afforestation in wet/normal October (1996–1998) and during drought (October 2000).



$$SUVA = \frac{Abs_{260} \times 1000}{DOC} \quad (Abs_{260} \text{ g C}^{-1} \text{ dm}^{-3}) \quad (1)$$

SUVA provide complementary information about the chemical properties (aromatic moieties content) of humic dissolved organic matter (DOM) fractions and its recalcitrance. Quantification of SUVA is valuable information on the origin of DOM and whether it is allochthonous (or pedogenic) or autochthonous (or aquagenic) in the river water (Imai *et al.* 2001).

Samples for DOC and absorbance measurements were pre-filtered with GF/C filters. Water hydrochemical analyses were performed in accordance with methods described by Hermanowicz *et al.* (1999). Meteorological and hydrological data were obtained from Institute of Meteorology and Water Management, Department in Białystok.

The statistical analyses, Pearson's correlation coefficients and ANOVA range tests were conducted using STATGRAPHICS Plus 1.4 for Windows.

#### 4. RESULTS

Significant differences in parameters such as water temperature, pH, calcium ion concentration, hydrocarbonates, water colour, DOC and SUVA were noted when the physicochemical parameters of river waters collected in October 1996–1998 were compared with data obtained during the period of low flow (October 2000) in the 22 selected rivers (Table 3). Water colour in the majority of the rivers was two times higher in the wetter autumn (October 1996–1998) than in the dry period (October 2000) (Table 3).

During the autumn drought in 2000, the mean concentration of dissolved organic carbon was almost as twice as low ( $7.27 \text{ mg dm}^{-3}$ ) as the average value in the preceding study period ( $12.32 \text{ mg dm}^{-3}$ ). The largest difference in DOC concentrations between the wet autumn period in 1996–1998 and the extremely dry one in autumn 2000 were recorded in the rivers flowing through dense forests (Fig. 5). The hydrological drought in autumn 2000 caused a significant decrease

in the range of DOC concentrations (CV = 68%) in studied rivers as compared to years with higher humidity (CV >100%). As the consequence differences in organic matter quality were also observed with changes in the amount of DOC. During the drought, dissolved organic matter transported in rivers was more aromatic ( $41.26 \text{ Abs}_{260} \text{ g C}^{-1} \text{ dm}^{-3}$ ) than in wetter periods ( $21.41 \text{ Abs}_{260} \text{ g C}^{-1} \text{ dm}^{-3}$ ), and the SUVA parameter was almost twice as high as in 1996–1998 (Table 3). In the majority of the 22 highland rivers, the dissolved organic matter was characterized by higher aromaticity of dissolved organic carbon (higher SUVA value) during the drought in 2000 than in the autumn periods of 1996–1998. The exceptions were rivers that were relatively susceptible to stress with lower forests density (Fig. 5).

Although catchment afforestation has an influence on DOC concentrations in river waters mostly during wet spring and normal autumn, it had none during the hydrological drought in 2000 like in ordinary summer (Table 4). Statistical dependencies between eco-morphological parameters of rivers and catchments and DOC were different for data from the whole study period autumn (1996–1998) and October 2000 (Table 5). Calculations indicated that there were negative correlation coefficients between DOC concentrations *vs.* river and catchment slope, catchment widths, and denivelation, while the correlation coefficients for the same parameters *vs.* SUVA were insignificant or lightly positive (catchment slope). Most of correlation coefficients were lower or statistically insignificant for the results obtained during the drought 2000 (Table 5) and these morphological parameters became less important in shaping the amounts of DOC in rivers.

#### 5. DISCUSSION

Low flows are an integral part of every river regime (Smakhtin 2001). Decreases in water levels due to drought can affect catchment functioning throughout the following year or even for several years if the drought occurred in a larger area. A one-year drought not only causes water level decreases, but also results in many other changes in



river ecosystems. Although most chemical parameters of the water increased in the current study, DOC, water colour, pH, and TP decreased (Table 3). Dillon and Molot (1997) reported similar results finding that soils during the dry periods transported less organic matter, TP, and Fe. During droughts, catchments, especially extremely wet ones, stop exporting mobile phosphorus forms (Hillbricht-Ilkowska *et al.* 2000). When water levels decrease, solutions become concentrated as the amounts of water decrease in rivers, which was confirmed in the present study by the increase of Ca concentration (Table 3). This increase is associated with evaporation from rivers and the ground surface, as well as the increase of residence and contact of waters with soils during penetration of underground waters into rivers (Murdoch *et al.* 2000, Caruso 2002). All of investigated catchments soils are well permeable, and rivers gradually loose contact with catchments, and ecotone zones no longer play important roles in supplying organic matter to rivers. Surface runoff is inhibited and water flow direction changes from rivers to catchments what can be exhibited in rivers with very low slope (below 0.5‰) where in extremely situation water is standing (relatively high DOC concentrations (rivers No. 5, 8, 11). Riverine floodplains consist of a shifting mosaic of aquatic, semi-aquatic, and terrestrial landscape elements (Langhans *et al.* 2006). As the main source of DOC, catchments stop supplying new portions of OM. Droughts activate hyporheic zones where intense conversions of organic matter occur (Findlay *et al.* 2001) – especially in low catchment slope rivers (Table. 5). Soil-originated DOC (e.g., leached from river sediments) is usually considered to be recalcitrant organic matter that is older and of a high molecular weight – *i.e.* having high SUVA values (Table 3, Fig. 5). This is confirmed by data on the quality of organic matter in catchments with high forest coverage and higher catchment denivelation (Fig. 5; rivers No. 6, 19, 10). During hydrological droughts, a great part of water flows through deeper soil layers and elutes organic compounds that were deposited earlier and not bonded to soil mineral particles (Hongve 1999). In city rivers and rivers on poorly forested catchments, where

SUVA parameters during droughts are lower, the organic matter is more aliphatic (Fig. 5). This may be proof that the supply of man-made origin DOC is easily biodegradable. At higher flows, when waters reaching rivers mainly come from catchment soils, DOC concentrations are usually higher (Drever 1997). The value of the SUVA parameter twice higher was the evidence of the greater aromaticity of the DOC contained in rivers (Table 1). In rivers with densely populated catchments DOC concentrations are comparable to those in presented study and the aromaticity index (*i.e.* SUVA value) is also low (Thomas 1997). The Białystok city rivers (No. 2 and 3) (Fig. 1) have isolated beds and even under normal conditions (no drought) their contact with natural catchments is limited. These rivers recall drainage canals more than natural flows. Most of organic matter is derived from polluted sources and it isn't dependent on the water level in the catchment. In rivers with high indices of organic matter decomposition, high DOC concentrations in summer are observed both within catchments and rivers (Grieve 1990).

The highest DOC concentration differences occur in rivers flowing through catchments covered by more than 66% of forests (Fig 5). This confirms the hypothesis that forests are the main and most abundant source of dissolved organic matter. During the drought, the positive influence of afforestation on DOC concentration is much lower than under normal hydrological conditions. Polyhumic rivers are characterized by DOC deficiency during droughts (Table 3). The possibility of autochthonous organic matter production in these rivers is reduced to a minimum due to very limited light accessibility. Droughts cause thermal and oxygen stress and can also lead to DOM deficiency for microorganisms. For such lotic ecosystems, drought is a sort of ecological disaster. It is also a significant factor that reduces DOC variability in lowland rivers, where its concentration decreased from about 10 mg dm<sup>-3</sup> in autumn 1996–98 to a few mg dm<sup>-3</sup> during the drought in 2000.

Along with decreases in DOC, water colour also significantly decreases, which is associated with lower content of humic substances and iron compound loads in dry

catchments (Table 3) but the differences are not statistically important. This is confirmed by the great dependence of small and medium rivers on catchment conditions. In general, the importance of allochthonous DOM sources decreases along with the increase of autochthonous sources (Thomas 1997). Prolonged droughts are a serious threat for rivers, because DOC elution from peats intensifies greatly after droughts (Hongve 1999). This can lead to DOC loads that much exceed the maximum spring concentrations of dissolved organic matter. Hinton *et al.* (1998) found that DOC concentration in rivers depends on the water level in the wet areas in a catchment. Our results showed that also depends on the water level on forested areas. DOC from degraded peats (*e.g.* due to melioration) is more aromatic (not easily degradable) than that originating from natural peats although the loads are smaller (Kalbitz 2001). The results indicate that drought derived DOC from forested catchment is more recalcitrant than DOC exported from catchment soils during normal/wet periods. The results of the current study indicate that small and medium rivers are not resistant in hydrochemical terms to flow decreases, and that decreases in DOC concentration in rivers may occur periodically. In consequence, climate warming, lower precipitation and the increase of mean air temperature may lead to faster and pulse DOC release (with higher value of SUVA) by peat and forest soils; the first examples of which were observed in England (Freeman *et al.* 2001, Freeman *et al.* 2004, Worrall *et al.* 2004).

**ACKNOWLEDGMENTS:** We would like to thank many colleagues who participated in this study, in particular: T. Suchowolec, H. Samsonowicz, S. Płonowski. The valuable comments and suggestions from prof. A. Hillbricht-Ilkowska and anonymous reviewer improved the quality of the manuscript considerably.

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*Received after revising November 2008*