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Changes in Water Chemistry Along the Course of Two Rivers with Different Hydrological Regimes

P. Zieliński*, A. Górniak, T. Suchowolec

Department of Hydrobiology, Institute of Biology, University of Białystok,
ul. Świerkowa 20 B, 15-950 Białystok, Poland

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Abstract

Chemical composition of water and dissolved organic carbon (DOC) levels were investigated over three years, along two large rivers in NE Poland, with different hydrological regimes. One river was from lakeland and the second a typical lowland river with forests and high contributions of peatlands in the catchment. The study involved hydrological (specific runoff, river discharge) effects on the variability of water chemistry and DOC concentrations. Specific runoff and discharge influence on DOC level and water quality. DOC concentrations and chemical water parameters were highest in the upper part of the lowland river and lowest in the upper course of the lakeland river. A two times lower DOC concentration was observed in the river draining lakeland with high values of specific runoff than in the lowland river. In typical lowland rivers organic compounds (mainly natural humic substances) intensified water eutrophication along the river course.

Keywords: river, DOC, water chemistry, hydrology.

Introduction

Numerous lowland rivers in Europe are contaminated and loose their characteristic biodiversity [1]. Chemical changes of their waters are brought about by different causes such as the inflow of wastes, nutrients, and pesticides from urban and agricultural areas or nutrients and dissolved forms of organic carbon from drained organic soils [2]. Dissolved organic carbon plays an important role in varied biogeochemical cycles. Nutrients and metals such as DOC-mineral complexes, can migrate in fresh water [3]. Dissolved forms of organic carbon are a source of energy for stream ecosystems [4]. Recent reports have shown concern of the intensification of DOC export from catchment to rivers [5]. Numerous data clearly show the important effect of the river basin character on carbon concentrations and their losses [6]. The influence of the hydrological parameters of rivers on water chemistry and its changes along the river course has not yet been comprehensively studied, especially in Poland [7, 8].

The aim of the present study was to examine the spatial and seasonal variation of DOC and water chemistry in two Polish rivers with contrasting basins, river flow, and catchment land-use.

Study Area and Methods

The Narew River (NR) (the largest in NE Poland) and the Czarna Hańcza River (CHR) in northeastern Poland were selected for investigation as relatively undisturbed river

*Corresponding author, e-mail: zielpi@uwb.edu.pl

ecosystems of lowland and lakeland areas (Fig. 1). The region has scarce industrial development and low human density. The aim of the regional policy is to preserve these undisturbed conditions. In the catchment of the Vistula River, the Narew River is the largest in NE Poland while the catchment of the Czarna Hańcza River is a part of the Niemen River basin, lying chiefly in Lithuania.

The investigated rivers represent two geographic regions with similar annual precipitation of 550-770 mm and a vegetation season of 190-200 days. The lowland Narew River drains a periglacial sandy-loam catchment with a different percentage of forests and wetlands (undisturbed by human activity). Multiannual discharge of the Narew River varies from 5 m^3/s in the upper course to 150 m^3/s in the lower course. The catchment of the Czarna Hańcza River in the Lithuania Lake District covers sediments from the last glaciation. It is characterized with

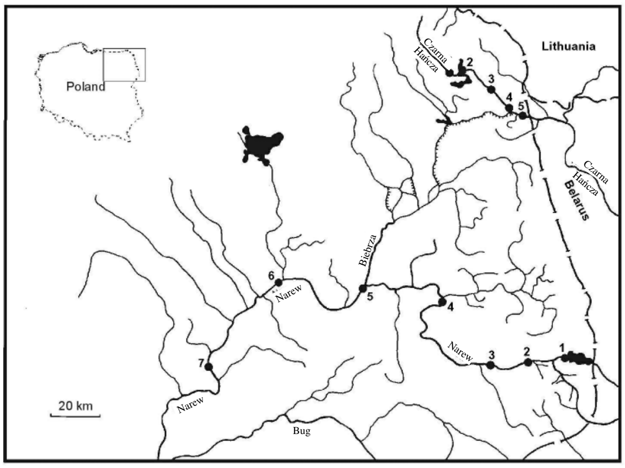

Fig. 1. Location of investigated rivers and sampling stations.

annual spring rise of waters and several lakes in the river system. The mean river discharges in Poland do not exceed 10 m^3/s, but the specific runoff from the catchment is almost two times higher then that from the Narew River catchment, the respective values being 6-10 and 4-6 $dm^3/s\ km^{-2}$. The CHR catchment area is dominated by extensive agriculture, a small degree of forestation, and high denivelations to 170 m.

In May, July and October (3 times a year in 1996-1998) water samples were collected from 12 stations located along the Narew River (7 stations) and Czarna Hańcza River (5 stations) (Fig. 1, Table 1). The samples were taken from the upper water layer, in places with maximum velocity of the water flow. At each sampling station water temperature, pH and electrical conductivity were measured. On the same day chemical parameters of the water were determined using standard methods. DOC concentrations were measured using a Shimadzu TOC-5050 A analyser in samples previously filtered through 0.45mm Nalgene SFCA filters and acidified to pH = 2. The quality of DOC was determined on the basis of spectrophotometric data as SUVA (specific ultraviolet absorbance) calculated with the ratio of absorbance 260nm (1cm of filtered water, natural pH) x 1000 to DOC concentration. The hydrological data (multiannual river discharge from 1981 to 1990 were taken from the Białystok Institute of Meteorology and Water Management (unpublished data). Statistical analyses, ANOVA rang test, and discriminant analyses, were carried out using Statgraphics and Statistica 5.0.

Results and Discussion

Throughout the entire study period mean concentrations of most parameters investigated in the two rivers were significantly different except for conductivity, potassium

Table 1. Characteristic of sample stations on Narew River (a) and Czarna Hańcza River (b).

a Sample station	River length [km]	Catchment area [km^2]	Discharge [m^3/s]	Specific runoff [$dm^3/s\ km^2$]
1	52.3	1 050	5.6	5.30
2	74.0	1 978	9.9	5.00
3	99.9	2 538	13.9	5.50
4	181.8	4 302	20.4	4.75
5	238.1	14 308	70.2	4.81
6	303.7	20 106	100	4.97
7	367.2	24 433	141	5.77

b Sample station	River length [km]	Catchment area [km^2]	Discharge [m^3/s]	Specific runoff [$dm^3/s\ km^2$]
1	8.8	40.0	0.16	4.00
2	45.2	203.2	1.50	7.38
3	54.9	504.2	3.82	7.58
4	78.8	821.2	5.99	7.29
5	105.8	883.2	6.00	6.79

and ammonia ions (Table 2). For most parameters the mean concentrations determined in the Narew River markedly exceeded those found in the Czarna Hańcza River.

Comparison of the mean water specific runoff in both investigated rivers showed that in the case of the Czarna Hańcza River catchment the mean specific runoff is one third greater than that from the Narew River basin. However, the DOC load reaching the Czarna Hańcza River is much smaller than that recorded in the Narew (Figs 2a,b). The increased annual export of DOC is associated with the leaching of dissolved organic matter from the peat-covered catchment [9]. The intensified DOC export is connected with large loads of organics immobilised in peat soils with high intensity. This particularly concerns phosphorus and ammonia ions [10], which get to waters chiefly in the form of mineral-organic complexes [11]. The average DOC concentrations gradually decrease with the course of the Narew River (Fig.3a). This record is in agreement with the data reported by Radwan et al. from the Krutynia River [7]. A negative correlation ($r= -0.97$, $p<0.001$) was determined between the average DOC concentration at different sample stations and the Narew River length. In NR decreases in DOC concentration occur owing to its gradual utilization by aquatic micro-organisms and because DOC export from middle and lower course of the river is very low. These results correspond with River Continuum Concept [12]. In the Czarna Hańcza River the concentrations of dissolved organic carbon slightly increase (Fig. 3b) owing chiefly to the autochthonous production of DOC in lakes lying in the river course.

The quality of organic matter exported by the two rivers is quite different. A comparison of the SUVA parameter data showed that organic matter, which flowed out of the peat-covered catchment of the upper Narew River, contained large quantities of aliphatic organic compounds. Hence in the initial river sector the SUVA parameter was smaller (Fig. 4a). In the river course bacteria selectively utilize dissolved organics. UV radiation penetrating the upper water layer also plays an active role in its transformation [13], affecting the biogenic spiralling of nutrients [4]. In this case the poorly decomposable dissolved organic matter of intensified aromaticity (SUVA exceeding 30) prevails. The microbiological decomposition of organic matter is probably affected by the length of time the flowing water remains in the riverbed; so the correlation coefficient between the water retention time in the Narew River channel and DOC is $r= –0.98$ ($p<0.001$). In the entire investigated sector of the Czarna Hańcza River the SUVA index constantly shows high values. Higher velocity, stony-gravel bottom, and rich water oxygenation characterizing the river are favourable for the rapid microbiological utilization of organic matter originated from syrton or peryphyton (Fig. 4b). This confirms the higher oxygen saturation of waters in the Czarna Hańcza River in comparison with the Narew (Table 2).

In the waters of the Narew River the concentrations of analysed nutrients, i.e. nitrogen and phosphorus forms, were considerably higher than in the Czarna Hańcza River (Table II). The mean concentrations of $P\text{-}PO_4$ and P_{tot} in NR are two times higher than in CHR. The main and reach source of phosphorus for NR is the hypertrophic Siemianówka Dam Reservoir (SDR), situated in the upper part of the Narew River, where cyanobacteria blooms are observed [9]. No point sources of pollution are found in the entire upper sector of the Narew River, though the investigated parameters show high concentrations. An increase in the concentration of total phosphorus, SRP and NO_3 (Figs. 5a,b) can be attributed to the decomposition of mineral-organic

Table 2. Mean values (±SD)of physico-chemical parameters in two investigated rivers. (*) – statistically significant difference, $p<0.001$.

Parameters		Narew River	Czarna Hańcza River	Signifficant differences
		n=63	n=45	
Temperature	°C	**14.6** ± 4.4	**13.9** ± 3.9	
Conductivity	µS/cm	**398.1** ± 68.2	**389.9** ± 91.1	
Reaction	pH	**7.48** ± 0.37	**7.79** ± 0.31	*
Oxygen saturation	%	**87.1** ± 18.8	**103.5** ± 20.6	*
DOC	mg/dm³	**15.88** ± 7.07	**4.45** ± 1.91	*
Ca	mg/dm³	**69.12** ± 11.8	**61.7** ± 14.3	*
K	mg/dm³	**2.43** ± 0.9	**2.61** ± 1.3	
$P\text{-}PO_4$	µg/dm³	**94.0** ± 51.7	**44.9** ± 31.1	*
P_{tot}	µg/dm³	**246.1** ± 228.4	**127.1** ± 85.5	*
$N\text{-}NO_3$	µg/dm³	**338.1** ± 234.3	**209.3** ± 214.6	*
$N\text{-}NH_4$	µg/dm³	**211.7** ± 110.0	**197.6** ± 148.0	
Fe	µg/dm³	**425.9** ± 251.6	**133.5** ± 146.9	*
SO_4	mg/dm³	**28.6** ± 12.1	**22.9** ± 7.8	*
Cl	mg/dm³	**15.2** ± 2.6	**13.7** ± 4.3	*

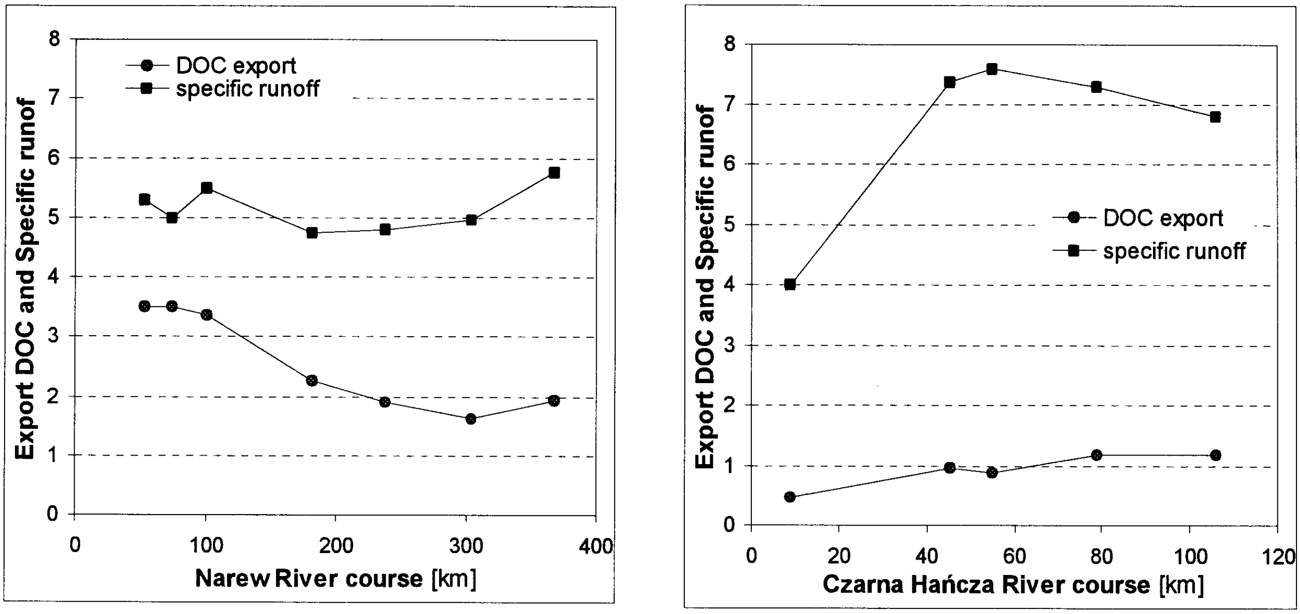

Fig. 2. Changes of DOC export from the catchment [tC/km^2 year] and specific runoff [dm^3/s km^2] along the Narew River (a), and Czarna Hańcza River (b) course. Mean data 1996-1998.

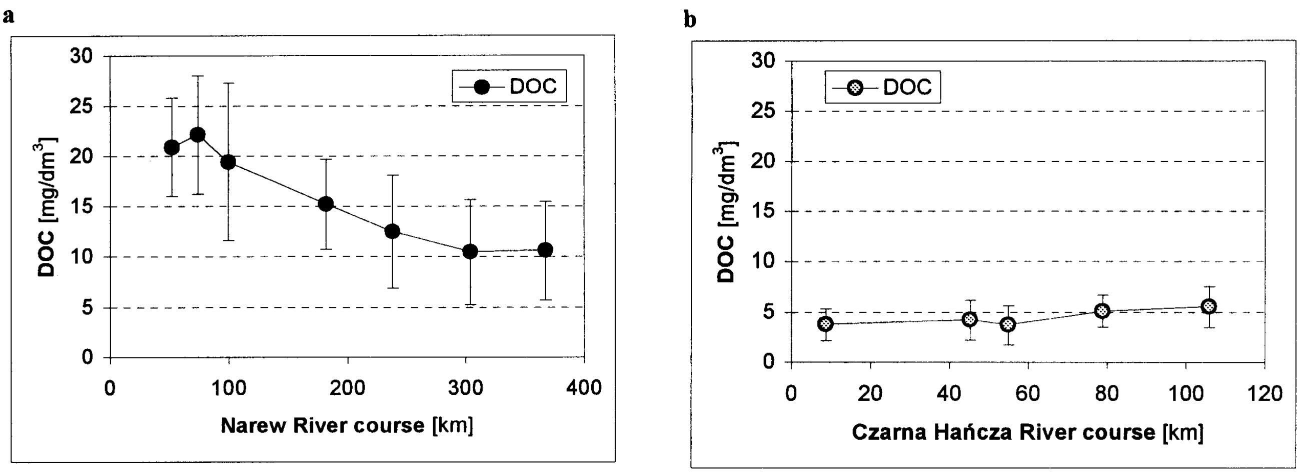

Fig. 3. Changes of DOC concentration (± SD) along the Narew River (a) and Czarna Hańcza River (b). Mean values (1996-98).

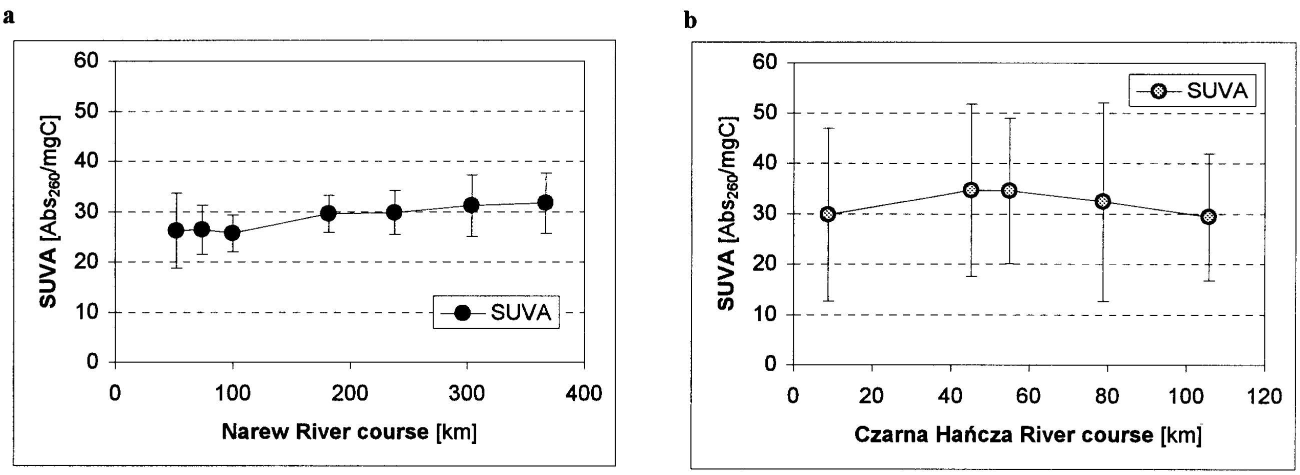

Fig. 4. Changes of SUVA parameter along the Narew River (a) and Czarna Hańcza River (b). Mean values (± SD) 1996-98.

complexes transported from very fertile peatbogs and forested areas of the Narew River valley. The gradually increasing concentrations of nutrients in the river course are probably induced by its humoeutrophication (eutrophication by humic substances) [11]. In the upper sector of the river the nitrification and transformation of nitrogen from ammonia to nitrate occur (Fig. 5a). The greater the river and its discharge the slower this process [14].

In the Czarna Hańcza River seasonal variations are observed in the concentration of nitrogen and phosphorus forms (Figs. 5c,d). The CHR looses a part of nutrients below the lakes. This is particularly evident below Lake Hańcza (station 1) and Lake Wigry (station 3). At station 2 a pronounced increase in the concentration of all the parameters is brought about by the discharge of treated wastes from the town of Suwałki. Owing to the considerable self-purification potential of the river the quality of waters is distinctly improved already at the next station. The lakes act as collectors of biogens. The more absorptive the lower their trophy. In the case of lakeland rivers the loads of nutrients reaching a river from its catchment fertilize it in a short course while above all they contribute to the eutrophication of lakes.

A distinct seasonal variability of chemical parameters was recorded in the waters of the Narew River (Fig. 6). Spring differs from the remaining seasons of the year to the greatest degree owing to the inflow of great loads, particularly in the form of dissolved organic matter and nutrients. In summer and autumn small differences in water quality are recorded at successive stations. In the summer the Narew River frequently functions owing to the inflow of groundwaters containing insignificant quantities of organic and mineral compounds. In the period of the investigation great hydrochemical uniformity characterised the Czarna Hańcza River irrespective of the season of the year. This river chiefly "feeds" on autochthonous organic matter while the inflow of mineral substances is stable.

In the Narew River the significant diversity of water quality occurs linearly along its course (Fig. 7a). In the Czarna Hańcza River the quality of waters is less variable except for station 2, whose separate character depends on the anthropogenic pollution of the water (Fig. 7b).

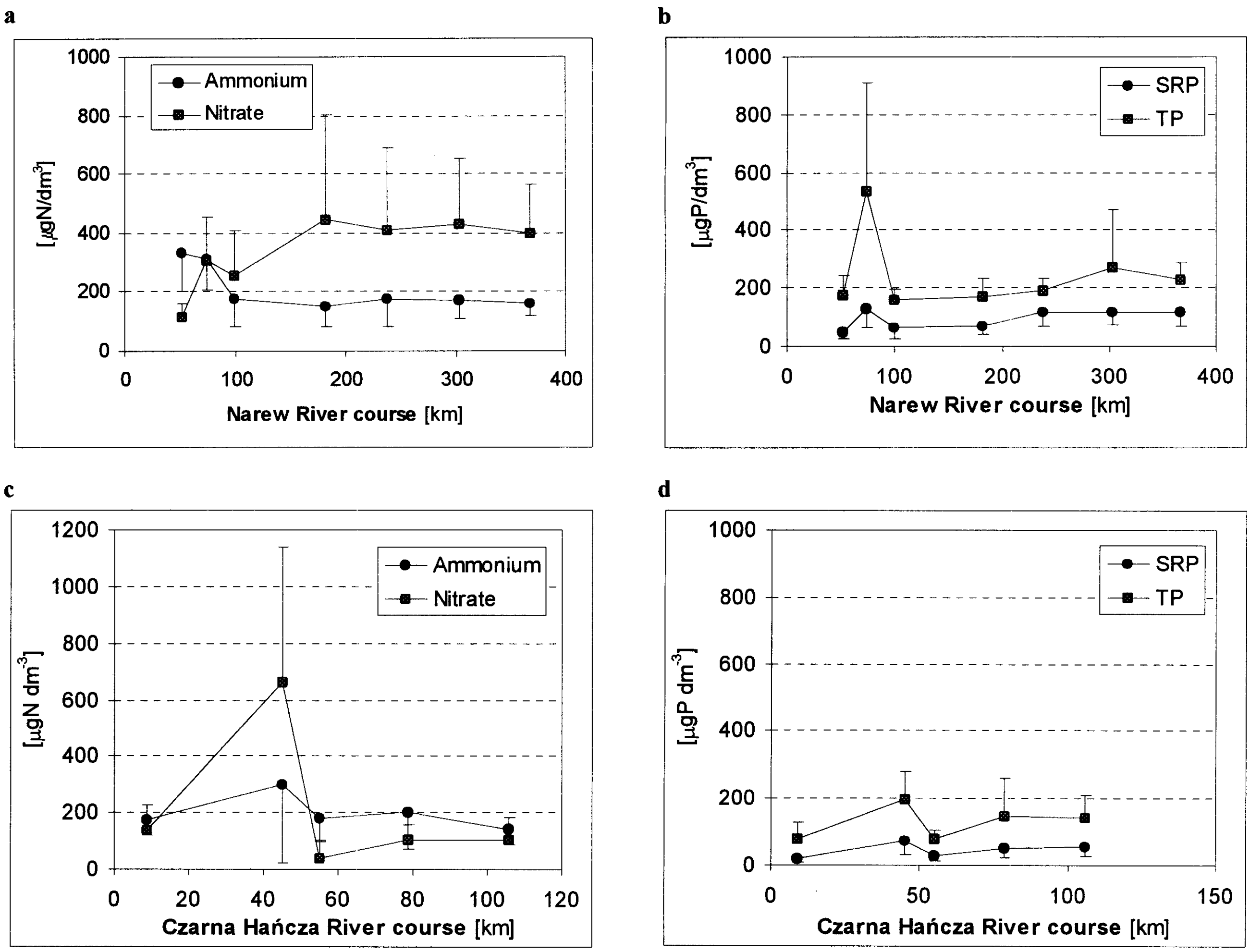

Fig. 5. Changes of nutrients concentrations (N-NO_3, N-NH_4, SRP and TP) along the Narew River (a, b) and Czarna Hańcza River (c, d) courses. Mean values (±SD) 1996-1998.

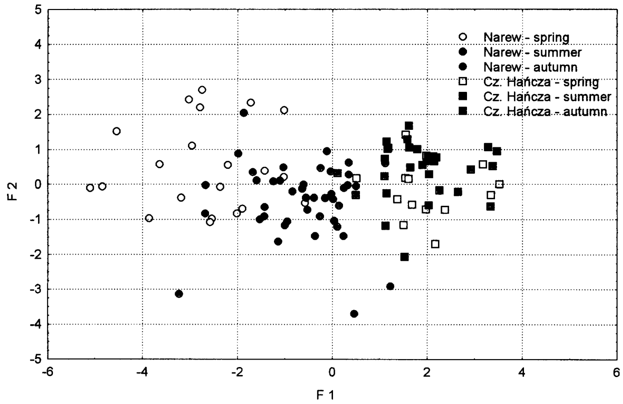

Fig. 6. Discriminant analysis of seasonal changes of physico-chemical parameters in Narew River (squeres) and Czarna Hańcza River (circles). F1, F2 – discriminant functions from main variables (DOC, oxygen saturation, Ca, P_{tot}, $N\text{-}NO_3$, Fe, SO_4).

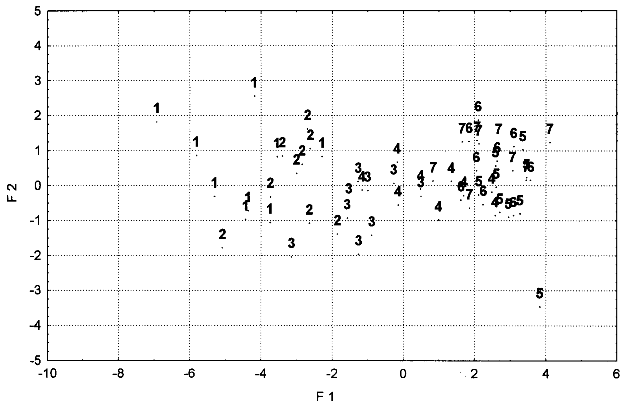

Fig 7a. Differentiation of water quality in Narew River verified with discriminant analysis. F1, F2 – discriminant functions from main variables (DOC, oxygen saturation, Ca, P_{tot}, $N\text{-}NO_3$, Fe, SO_4); numbers: 1-7 – sample stations situated along Narew River.

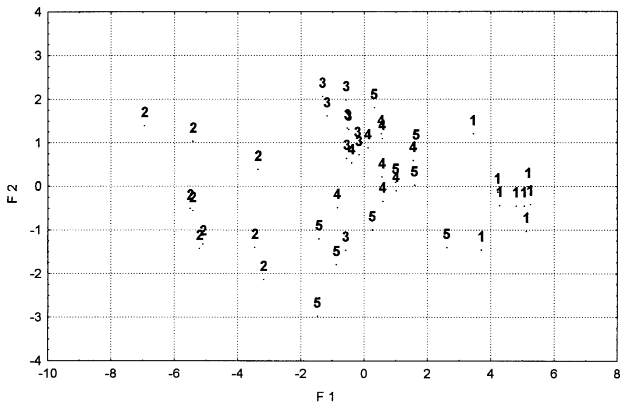

Fig 7b. Differentiation of water quality in Czarna Hańcza River verified with discriminant analysis. F1, F2 – discriminant functions from main variables (DOC, oxygen saturation, Ca, P_{tot}, $N\text{-}NO_3$, Fe, SO_4); numbers: 1-5 – sample stations situated along Czarna Hańcza River.

Conclusions

Differences in water chemistry between the River Narew and the Czarna Hańcza are statistically significant. Lowland Rivers probably are more eutrophicated than the Lake Rivers. The fluvial export DOC from the catchment to a greater degree depends on the character of the river valley than on its hydrology. Dissolved organic matter is an important carrier of nutrients in lowland riverine ecosystems. This can intensify the humoeutrophication process [11]. Increased water flow during floods increases concentrations of chemical parameters in both rivers, although the increase was less pronounced in the Czarna Hańcza, where the load of biogens is neutralised by lakes in this river system.

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