

Original Research

Concentrations of Macroelements, Zinc and Iron Ions in Water of the Upper Narew Basin, NE Poland

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Abstract

The purpose of present research was to evaluate the dynamics of concentration changes of macroelements as well as iron and zinc ions in the upper Narew River catchment (northeastern Poland). The following rivers and streams were selected: Narew, Supraśl, Horodnianka, Ruda, Małynka, Łoknica, and Rudnia. Calcium, magnesium, sodium, potassium, iron and zinc analyses were made using the flame AAS method. A gradual increase of macroelement contents in Narew water was found, which was the consequence of water supplies and surface runoffs. Our study revealed the differentiation of macroelements, iron and zinc concentrations in water of the upper Narew River, depending on the catchment character as well as spatial distribution of their point sources.

Keywords: calcium, zinc, rivers, river basin

Introduction

Surface water quality is a matter of serious concern today. Rivers, due to their role in carrying off municipal and industrial wastewater and runoff from agricultural land in their vast drainage basins, are among the water bodies most vulnerable to pollution. Surface water quality in a region is largely determined both by natural processes (precipitation rate, weathering processes, soil erosion) and anthropogenic influences such as urban, industrial and agricultural activities, and increasing exploitation of water resources [1, 2].

Recently much hydrochemical research in headwater catchments has focused upon the dominant role of riparian zones in regulation of stream water chemistry. In terms of their spatial distribution, these zones exert a disproportionately large influence on stream water chemistry [3-7].

The ions commonly quantified include Na, K, Ca, and Mg (summed as total cations and anions). These essentially constitute the total ionic salinity of most fresh waters, as other ions make only very minor contributions [8].

Basic cations such as Ca, Mg, K, and Na commonly occur in surface water, mainly in the form of dissolved chlorides, nitrates, sulfates, hydrocarbonates and carbonates. In natural waters, minerals are their source, and their concentrations oscillate within wide ranges [9].

Iron is an important biological and geochemical trace element in estuarine ecosystems; however, excessive iron is of environmental concern in these settings due to biogeochemical recycling and ecological risks [10].

Elution of mineral and organic substances, as well as chemicals from cultivated fields, is a multifactorial process affected by geological structure of the catchment bedding, soil type, hydrological and climatic conditions [11], and on the other hand cultivation specificity [12] and structure of ecosystems on a catchment, namely dominating agroecosystems in an agricultural basin.

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Table 1. Data obtained from the meteorological station in Białystok. Monthly total precipitation in mm in 2001-05.

Year	Rainfall [mm]												Rear
	Months												
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
2001	26	15	24	44	64	44	96	63	109	42	63	22	612
2002	46	57	33	11	19	72	54	24	28	118	26	12	500
2003	36	15	17	23	93	52	47	42	48	64	52	52	541
2004	23	54	31	32	74	62	95	118	17	34	41	38	619
2005	34	32	38	7	99	46	60	69	60	12	30	59	546
1961-1995	33	27	32	40	59	72	73	70	57	45	44	41	593

Pollution of water flowing in the Narew River catchment results mainly from agricultural performance of its surface. In addition, water quality is negatively influenced by municipal residential areas and rainfall wastewater, both from villages and cities. Depending on the runoff type (sub-surface, midcover, surface), migrating water gains the traits of the environment [13].

Utilization of calcium fertilizers in Poland has recently decreased, but it has been much lower in the Podlasie region than average for the whole country. Mean potassium fertilizer utilization in the Podlasie region was 19.0 kg/ha⁻¹ (2004),

calcium ones – 59.7 kg/ha⁻¹. The sum of a precipitation measuring station in Białystok in the study period was one year, from 541 mm (2003) to 619 mm (2004) (Table 1). Detailed data on the catchment basins studied were placed in Table 2. Studies were carried out within the Narew River upper catchment area situated in northeastern Poland. The following rivers and streams were selected: Narew, Supraśl, Horodnianka, Ruda, Małynka, Łoknica, and Rudnia (Fig. 1).

The aim of the research was to evaluate dynamics of linear concentration changes of macroelements, iron, and zinc in waters of the catchment area.

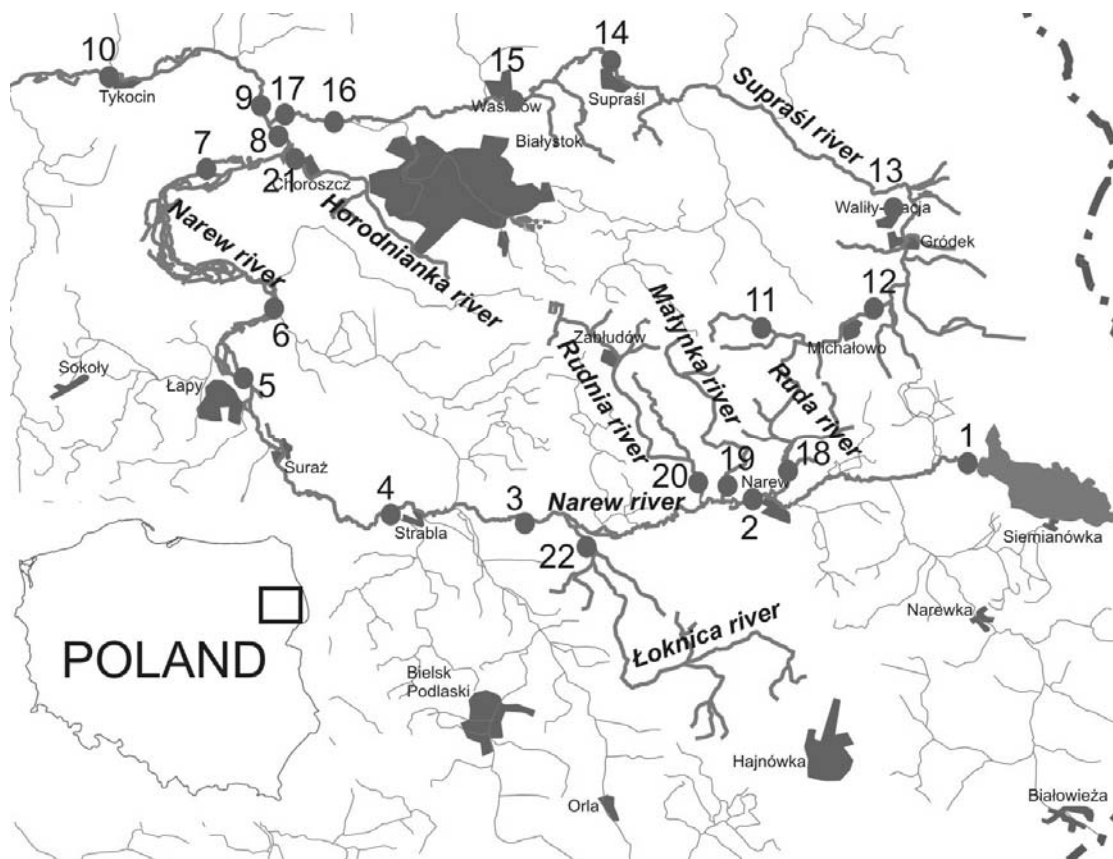


Fig. 1. River-basin of the upper Narew with points of water sampling.

Table 2. Characteristics of studied catchments flows.

Parameter/river	Łoknica	Ruda	Małynka	Rudnia	Narew	Supraśl	Horodnianka
Flow length [km]	28.0	10.5	15.0	26.2	130	93.8	18.0
Basin area [km ²]	175.0	82.0	50.0	87.0	4,500	1,844.4	77.0
Flow of SQ [m ³ ·s ⁻¹]	2.01	0.74	0.58	1.02	17	4.73	0.41
Land performance [%]:							
Meadows and pastures	22	24	4	24	20	10	28
Arable lands	60	43	40	49	39	15	40
Woods	15	30	43	22	29	70	18
Meliorations [%]	31	16	37	25	21	27	23

Table 3. Conditions and parameters of AAS and EAAS surface water determinations.

Item	Detection range	Precision	Accuracy	Wavelength	Gap width
	[mg·dm ⁻³]	%		nm	Nm
Iron	0.06-15	10	20	248.3	0.2
Zinc	0.01-2	10	20	213.9	1.0
Calcium	0.01-3	10	15	422.7	0.5
Magnesium	0.003-1	10	15	285.2	0.5
Sodium	0.002-1	10	15	589.0	0.5
Potassium	0.03-2	10	15	766.5	1.0

Material and Methods

Our study was performed in 2001, 2002, 2003, 2004 and 2005 in all seasons and all months. Ten measurement points were localized on the Narew, Supraśl – 7, Horodnianka, Ruda, Małynka, Łoknica, and Rudnia – 1 on each due to their small length as compared to other streams and rivers. Every month, one water sample was collected from the surface layer (0.5 m deep) at each measurement point in 2001-05. Water samples were stored in 1.5 l polyethylene bottles and chemical analyses were performed in a laboratory of the Department of Technological Studies, Institute of Environmental Engineering, Technical University in Białystok. After filtering through micropore filters ($d = 0.45 \mu\text{m}$), and acidification with concentrated nitric acid (1 ml $\text{HNO}_3/100$ ml of water sample), concentrations of soluble forms were determined: calcium, magnesium, sodium, potassium, iron, and zinc. Determinations were carried out by means of the AAS technique using a SpectrAA-100A device (Varian). Calcium, magnesium, sodium, potassium, iron and zinc analyses were made applying the flame method. Standards by Merck at 1,000 $\text{mg}\cdot\text{dm}^{-3}$ concentrations were used for analyses.

Analyzed samples were diluted with de-ionized water to optimum concentrations. Oxidation flame air-acetylene was used as an atomization source in AAS and EAAS tech-

niques. Precision and accuracy of methods were estimated by determining sample recovery for 5 model samples containing various concentrations of metals (Table 3).

The methodology correctness was checked on the basis of reference material analysis (SRM 1643e–Trace Elements in Water, NIST). Electrical conductivity of water within the catchment was also measured directly in rivers using HACH conductometer and results were expressed in $\mu\text{S}\cdot\text{cm}^{-1}$ units. The following numbers of results were achieved for each component studied: Narew – 510, Supraśl – 357, Horodnianka, Ruda, Małynka, Łoknica, and Rudnia – 52 for each. In total, 7,889 results were achieved for the whole study period. Median was accepted as the best measure of average value level. According to Wagner and Błaszczak [14], and Spahr and Wynn [15], as well as Johnes and Burt [16], using such a measure is justified when observations much different from mean value are present in a set. Final result estimation was based on the analysis of median values for studied metal concentrations in surface waters. Pearson's coefficients, Student's t-test, and minimum and maximum values, as well as arithmetic means, were also calculated. The data matrices were prepared and processed in Excel 2003. Factor analysis and other statistical calculations were performed using Statistica 7.1. The factor loadings were calculated using the Varimax rotation method. To interpret the factor analysis results, it was assumed that con-

nections of the primary variable with a factor are strong when its load absolute values are greater than 0.70 [17, 18]. Data clustering analysis – the Ward agglomeration method based on object or variable distances in multidimensional space – was used for results analysis.

Results and Discussion

Fairly uniform median values for calcium ions along the whole studied section were found (Fig. 2) with slight increasing tendency from point No. 1 (55.4 mg·dm⁻³ Ca) to points No. 9 (73.3 mg·dm⁻³ Ca) and No. 10 (65.2 mg·dm⁻³ Ca). The lowest content of calcium was recorded at point No. 1, the highest at point No. 9. Near point No. 9, melioration ditches flow into the Narew. It can be supposed that calcium contents in the Narew are affected by surface

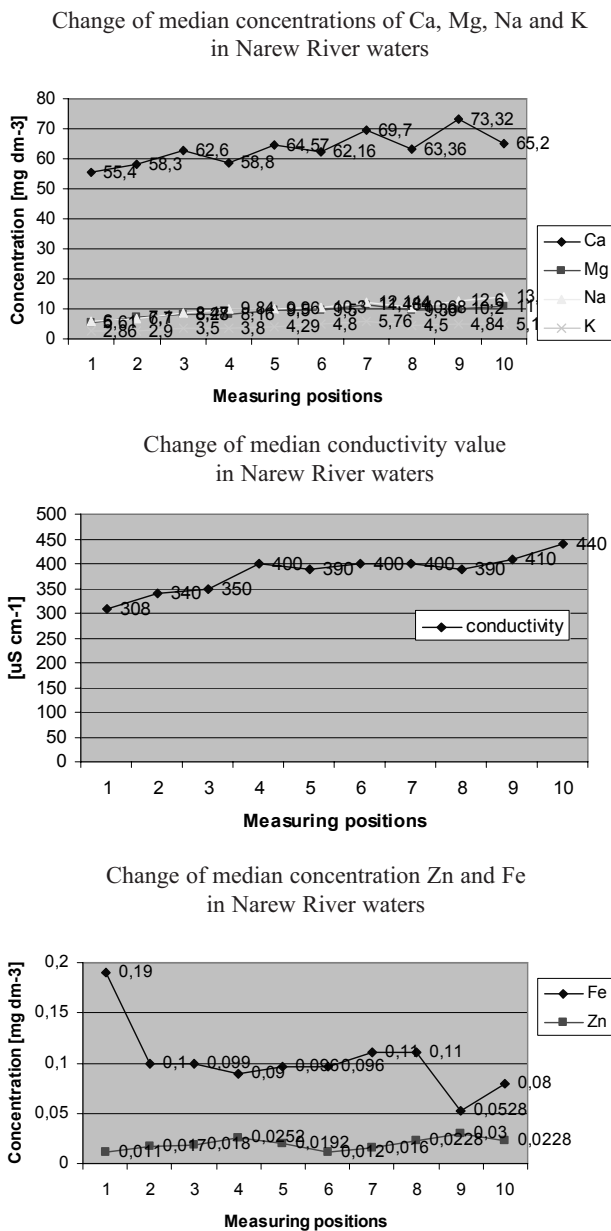


Fig. 2. Dynamics of concentration changes for studied parameters in the Narew catchment.

runoff, that is transformed in the network of melioration ditches into the point runoff, introducing significant amounts of calcium to the Narew and its tributaries. Magnesium concentration is distributed similar to that of calcium. The increasing tendency along the whole studied section of the river is apparent. The lowest Mg content was found at point No. 1 (5.6 mg·dm⁻³ Mg) and the highest at point No. 7 (11.5 mg·dm⁻³ Mg), to which values from points Nos. 9 and 10 were similar. Sodium and potassium concentrations also reveal increasing tendencies along the Narew river.

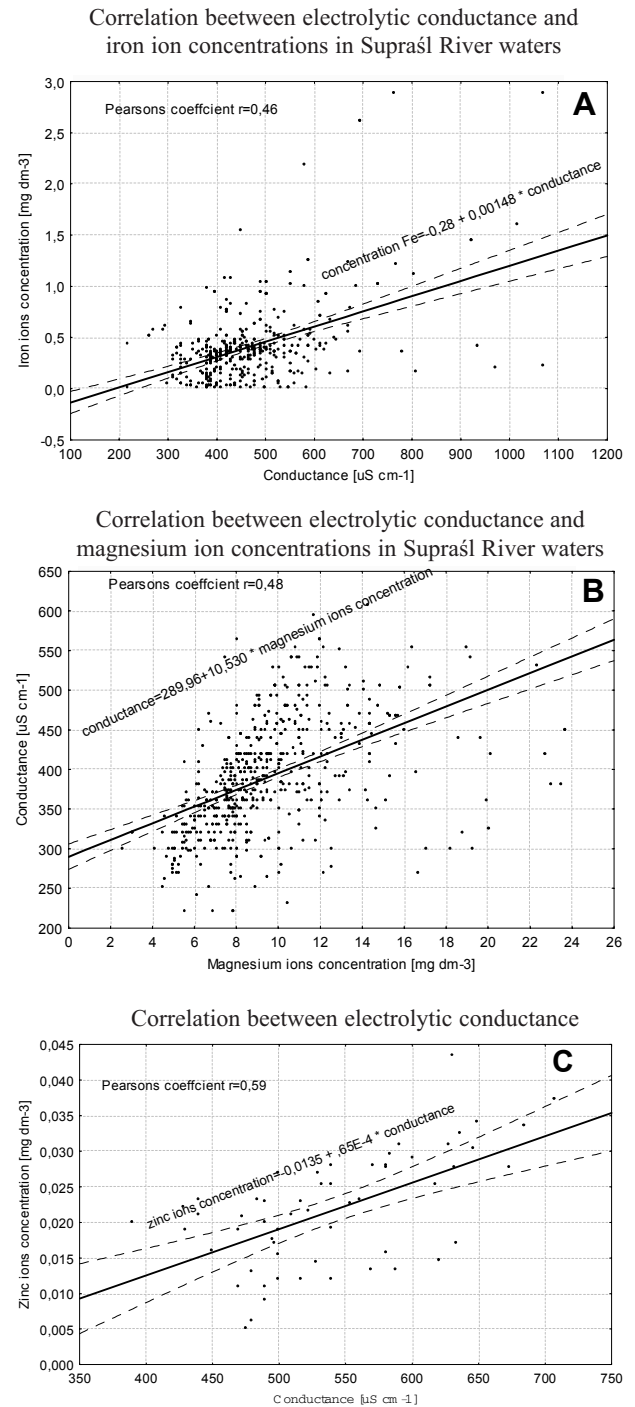


Fig. 3. Dependence of studied parameters in waters in the upper Narew catchment.

Table 4. Concentrations of studied components in Narew catchment waters, 2001-05.

Stream		Conductivity [$\mu\text{S}\cdot\text{cm}^{-1}$]	Ca	Mg	Na	K	Fe	Zn
			[$\text{mg}\cdot\text{dm}^{-3}$]					
Narew	range	220-607	20.9-136.8	2.6-23.7	2.9-31.4	0.7-14.9	0.003-2.880	0.001-0.320
	median	380	63.4	9	10.1	4.1	0.099	0.019
Supraśl	range	220-1069	8.2-107.1	1.1-111.1	0.1-59.6	0.9-21.2	0.010-2.876	0.002-0.144
	median	450	56.5	10.5	8.2	4	0.351	0.027
Horodniana	range	520-858	43.9-149.8	12.2-25.3	10.5-42.7	4.0-24.1	0.010-1.636	0.004-0.385
	median	685	100.3	18	21.7	9.5	0.083	0.096
Małynka	range	320-620	38.8-129.1	4.1-21.9	4.5-13.4	0.8-15.1	0.015-1.244	0.007-0.145
	median	460	70.4	10.3	7.4	5.2	0.502	0.038
Rudnia	range	390-708	39.1-93.3	6.4-18.6	6.3-16.2	2.7-14.4	0.012-2.620	0.005-0.043
	median	531	67.4	12.2	9.1	5.6	0.378	0.022
Ruda	range	350-660	51.0-89.3	8.1-22.8	5.5-11.2	1.7-8.0	0.022-1.020	0.002-0.062
	median	500	67.5	11.8	8.2	3.9	0.541	0.012
Łoknica	range	320-711	35.9-122.1	5.1-31.1	5.4-31.2	2.5-35.3	0.004-1.440	0.007-0.059
	median	504	84.5	18	10.9	5.1	0.295	0.021

The lowest contents of Na and K were recorded at point No. 1 ($6.0 \text{ mg}\cdot\text{dm}^{-3}$ Na and $2.9 \text{ mg}\cdot\text{dm}^{-3}$ K) and the highest for sodium at point No. 10 ($13.9 \text{ mg}\cdot\text{dm}^{-3}$ Na) and potassium at point No. 7 ($5.8 \text{ mg}\cdot\text{dm}^{-3}$ K). Specific conductivity reflects summarized contents of minerals (Ca, Mg, Na, and K) in water. Values of that trait were arranged in a similar way in Narew water as concentrations of Ca, Mg, Na, and K. The lowest conductivity was measured at point No. 1 ($308 \mu\text{S}\cdot\text{cm}^{-1}$) and the highest at point No. 10 ($440 \mu\text{S}\cdot\text{cm}^{-1}$). The study revealed existing interaction of specific conductivity and magnesium concentration expressed by Pearson coefficient $r = 0.48$ at $p=0.000$ (Fig. 3b). Fig. 4 presents changes of median value for specific Narew water conductivity in 2001-05 on a background of annual mean rainfall sum for the studied area. Values of specific conductivity were proportional to the mean annual rainfalls.

Elution of various components (macroelements in majority) from the subsoil depended on the intensity of rainfalls and formed the specific conductivity in 2001-05. Similar variability also occurred in the case of Ca, Mg, Na, and K concentrations, not only in Narew, but in other rivers under study. The highest concentration of iron ions (Figs. 1 and 2) were found at point No. 1 ($0.190 \text{ mg}\cdot\text{dm}^{-3}$) and the lowest at point No. 9 ($0.053 \text{ mg}\cdot\text{dm}^{-3}$). Point No. 1 is localized behind Siemianówka dam reservoir, the catchment of which is strongly forested. Studies by Górnjak et al. [19] have revealed that water on areas covered with woods as compared to those poorly forested are more abundant in iron ions. Catchment of Siemianówka reservoir is located on peaty soils. According to Kowda [20], large amounts of iron is the characteristic trait of peat soils developed in a river valley area.

The highest zinc level was recorded at point No. 9 ($0.030 \text{ mg}\cdot\text{dm}^{-3}$) and the lowest at point No. 1 ($0.011 \text{ mg}\cdot\text{dm}^{-3}$). Point No. 9 is located just below the Supraśl River estuary, to which the small Biała River transporting municipal wastewaters from Białystok flows. In general, a statistically significant higher zinc concentration was found in Supraśl water rather than Narew (Table 4) at the level of $p=0.0024$. Studies of Grabińska et al. [21] revealed $0.046 \text{ mg}\cdot\text{dm}^{-3}$ of zinc ions concentrations in the Narew at a point below the Supraśl tributary, which was confirmed by results of the present study. In addition, large zinc amounts are transported by the Horodniana River (Narew tributary), springs of which are located near a municipal waste dump in Hryniewiczze. Concentration of zinc ions appears to be statistically higher ($p = 0.000$) as compared to the Narew.

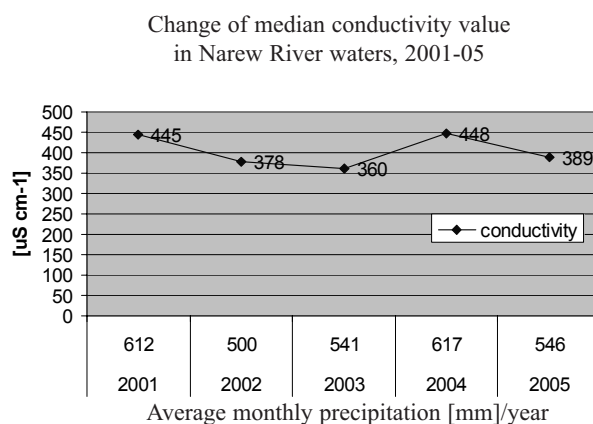


Fig. 4. Changes of median values for electrolytic conductivity in Narew River water, 2001-05.

Table 5. Load-tested indicators of water quality.

River	Point	TDS	Ca	Mg	Na	K	Fe	Zn
		[g·s ⁻¹]						
Narew	1	587.621	154.588	16.17	17.728	7.928	0.506	0.032
	2	1,433.066	387.517	45.527	45.035	18.314	1.084	0.104
	3	1,830.595	500.069	58.739	67.987	25.988	0.857	0.143
	4	2552.441	598.382	78.563	96.357	38.424	1.113	0.199
	5	3,011.487	776.746	108.091	115.558	50.343	1.526	0.265
	6	3,716.038	913.471	128.301	137.568	60.635	1.254	0.181
	7	4,157.124	1,071.138	169.775	191.127	77.3	1.471	0.274
	8	4,664.707	1159.3	163.775	195.756	77.664	1.886	0.416
	9	9,501.932	2,552.355	361.434	418.535	162.049	2.089	1.011
	10	10,111.661	2,368.656	380.367	478.589	180.316	2.731	0.804
Supraśl		2,860.747	2,025.226	115.596	75.055	35.382	4.037	0.263
Horodnianka		245.053	66.528	9.324	7.753	5.208	0.134	0.029
Małynka		127.987	33.845	5.466	2.79	1.278	0.18	0.004
Rudnia		242.942	49.084	8.332	5.994	2.853	0.4	0.008
Ruda		24.154	4.478	0.573	0.454	0.272	0.025	0.001
Łoknica		231.552	52.26	7.449	7.74	4.56	0.204	0.006

Table 6. Coefficients of variation on tested parameters in river water.

River	TDS	Ca	Mg	Na	K	Fe	Zn
	[%]						
Narew	18.9	28.6	35.0	42.4	46.5	144.1	120.7
Supraśl	24.8	33.6	70.1	77.7	71.7	90.5	71.3
Horodnianka	12.4	23.2	17.7	30.2	43.9	176.6	90.0
Małynka	13.1	29.3	32.5	29.3	56.5	50.9	70.6
Rudnia	13.6	16.2	23.0	21.6	38.2	101.9	38.0
Ruda	11.5	12.2	20.7	16.2	27.5	41.4	86.7
Łoknica	13.8	23.2	29.4	34.3	75.0	84.5	60.4

Analyzing component levels in the waters of the Narew showed about twice the increase in point No. 9 compared to No. 8 (Table 5), which is a consequence of the interaction of Supraśl water. Table 5 shows that Supraśl water flow includes large loads of tested components. Demonstrated high values of coefficients of variation for Fe and Zn (Table 6) in waters may be explained by the Narew's polluted tributaries and the presence of localized sources of pollution, and partly by the presence of natural sources of these ingredients.

On a base of multifactorial analysis, Cattel plot and Kaiser criterion, two factors representing about 64% of global variability for phenomena in the studied system were identified (Table 7). Factor I explains the variability of chemical composition of Narew River water at 44%. Positive factorial loads being "correlation coefficients" between the following variables: sodium and potassium vs. factor I (the process making Narew water more abundant in these constituents) were distinguished. Factor II elucidates about 20% of total variability of Narew river chemical

Table 7. Factor analysis of waters in the upper Narew catchment.

Factor analysis of Narew River waters Factor loadings (Varimax normalized) (> 0.7)		
Variable	Factor 1	Factor 2
Conductivity	0.62301	0.16108
Ca	0.677369	-0.294768
Mg	0.843515	0.111984
Na	0.858301	-0.19486
K	0.86049	0.09874
Fe	-0.064131	0.818808
Zn	0.081916	0.758786
Explained variance	3.046434	1.419297
Proportion of total variance	0.435205	0.202757
Factor analysis of Supraśl River waters Factor loadings (Varimax normalized) (> 0.7)		
Variable	Factor 1	Factor 2
Conductivity	0.316897	0.700255
Ca	0.811236	-0.132569
Mg	0.743776	0.059738
Na	0.641185	0.633722
K	0.759455	0.366115
Fe	-0.128408	0.816269
Zn	0.056123	0.686407
Explained variance	2.319258	2.184594
Proportion of total variance	0.331323	0.312085

composition and is correlated with zinc and iron concentrations. It is the source that supplies Narew water in zinc and iron ions.

The largest tributary of the Narew, the Supraśl, brings her the greatest number of test components as shown in previous discussions.

The highest concentration of zinc ions in Supraśl water was recorded at point No. 2 ($0.043 \text{ mg}\cdot\text{dm}^{-3}$) (Figs. 1 and 2). Point No. 2 is located within the section crossing agriculturally intensively utilized. Liquid manure is quite often used as a fertilizer and large numbers of cattle are grazing on that area. It is a peat-bog meliorated zone of about 800 ha area that shows overdrying features. A municipal wastewater treatment plant is built in Gródek, which can be a potential source of zinc ions for the Supraśl. It is indicated by zinc ions concentration at point No. 1 ($0.023 \text{ mg}\cdot\text{dm}^{-3}$) and it is a considerable, almost 2-fold, increase at point No. 2 ($0.043 \text{ mg}\cdot\text{dm}^{-3}$), below Gródek.

As commonly known, liquid manure, organic fertilizers and animal wastes contain large amounts of zinc. It is proven by numerous domestic and foreign studies.

According to Moore and Ramamoorthy [22], higher levels of zinc in water occur near sewage sources, which was also confirmed in the present study. Point No. 6 is located below the Biała River estuary. This small tributary is almost entirely within the large city of Białystok with wastewater treatment plant, heat and power plant, developed industry and road network connected with the river through a sewerage system. It seems that the infrastructure of a large city may be a zinc source for surface water, which is confirmed by studies of Grabińska et al. [21]. At point No. 5 $0.021 \text{ mg}\cdot\text{dm}^{-3}$ was recorded, which is much lower content as compared to point No. 6, indicating that the Biała transporting pollution from Białystok is a main source of contamination in this region. Zinc concentration decreases to $0.023 \text{ mg}\cdot\text{dm}^{-3}$ at point No. 7, which probably results from natural processes of self-cleaning in the Supraśl River. Points Nos. 4 and 5 are located within the Supraśl at the end of a woody zone (Knyszyńska Forest). No significant point and surface pollution sources are situated in that region. Therefore, it seems that it is the main reason for low levels of zinc ions at those points (0.028 and $0.021 \text{ mg}\cdot\text{dm}^{-3}$). The highest conductivity values recorded were found at points Nos. 2 and 6 (495 and $588 \mu\text{S}\cdot\text{cm}^{-1}$), which may be confirmation of interpreted zinc ion sources for the Supraśl.

The highest median for iron ions was found in the Supraśl at point No. 16 ($0.518 \text{ mg}\cdot\text{dm}^{-3}$) the lowest at point No. 11 ($0.281 \text{ mg}\cdot\text{dm}^{-3}$). At the same time, the highest median for specific conductivity was measured at point No. 16 in the Supraśl ($588 \mu\text{S}\cdot\text{cm}^{-1}$). Point No. 16 is located below the left-tributary of the Biała. Domestic and foreign studies have revealed that urbanized areas often are serious suppliers of iron ions to surface water and soil. Ilnicki et al. [23] claim that the worsening of water quality is a result of point pollution (cities, industry) as well as surface pollution (agricultural and forest areas). A slight increasing tendency for iron content median along a river course has been observed. It is probably the interaction effect of iron ions from point and surface sources, including the agricultural area near Gródek and Michałowo, woodland of Knyszyńska Forest, the "Lower Supraśl" area and urbanized towns and cities (Gródek, Michałowo, Białystok). According to Kabata-Pendias and Pendias H. [24], the lowest iron amounts occur in light sandy soils, higher in heavy loamy soils and silts. Above-listed pollution sources at points Nos. 12 and 16 on the Supraśl invoke abundance also in macroelements (Ca, Mg, Na, and K). values of particular medians are evidence that points Nos. 12 and 6 are elevated in relation to other points. Conductivity values were arranged in a similar way. Studies of Skorbilowicz [25] confirm these remarks. Studies revealed the dependence of iron concentration on specific conductivity in Supraśl water expressed by Pearson coefficient $r = 0.46$ at $p = 0.000$ (Fig. 3a). According to Greger and Kautsky [26], salinity increase (specific conductivity) results in an increase of heavy metals solubility, including iron. Studies upon surface water confirmed that dependence.

In Table 6, obtained high values of coefficients of variation of Mg, Na, K, Fe and Zn in the Supraśl confirms the earlier discussion about the presence of sources of pollution

of its waters. The Supraśl carries large amounts of Fe (Table 6) a consequence of the vast areas of forest in its catchment area and the emission of Fe and geogenic by anthropogenic sources of this component.

Two factors representing about 64% of global phenomena in the analyzed system have been identified (Table 7). Factor I explains the chemical composition variability in the Supraśl in 33%. Positive factorial loads between variables Ca, Mg, and K vs. Factor I (making the Supraśl abound in these elements) were distinguished. Factor II elucidates about 31% of total variability of chemical composition in the Supraśl and it is correlated with iron concentration and conductivity value. It is a source that supplies the Supraśl in iron ions and increased conductivity, which was confirmed by earlier analyses of the river water.

This paper studies water from rivers less than 30 km long: Horodnianka, Ruda, Małynka, Łoknica, and Rudnia. The highest concentrations of calcium, magnesium, sodium, potassium, and zinc ions were found in the Horodnianka River (Table 4). High contents of these elements in that flow should be partially associated with agriculture, due to the fact that 40% of agricultural area is covered by arable lands in the Horodnianka catchment. Suburban infrastructure (adjacent to Białystok) is also important in shaping the river chemistry. A municipal waste dump in the Horodnianka springs neighborhood also exert great impact. An increase of conductivity value is associated with processes of river erosion, elution, and pollutants transport in the form of surface, linear and area runoff from river basins. A high level of conductivity in studied waters may only confirm zinc origin in the Horodnianka. The highest level of iron ions was recorded in Ruda river water. Probably, it is the effect of a fairly large area covered by woods (30%). At the same time, the lowest contents of zinc were found in the river, which may be attributed to the lack of metal sources associated with agriculture, no wastewater treatment plants, and municipal waste dumps in the upper Narew catchment area.

When analyzing loads of tested components contributed by the tributaries to the Narew (Table 5), it should be noted that change in the chemical composition of water is less significant compared with changes caused by the Supraśl.

Horodnianka only recorded in the waters of the $0.029 \text{ g Zn}^{2+} \cdot \text{s}^{-1}$ markedly increases the load in the waters of Zn^{+2} Narew, which is manifested in the increase of its value at control point No. 8 with respect to point No. 7. The dependence of zinc concentration on specific conductivity in the river was also found ($r = 0.59$ at $p = 0.000$) (Fig. 3c).

Analyses of Ca, Mg, Na, K, Fe, and Zn concentrations along with specific conductivity measurements in the upper Narew river catchment allowed for making the dendrogram according to Ward agglomeration method (Fig. 5). It presents 2 apparent groups and the large distance at which arrangement II is connected with I, significantly distinguishing both bundles. Arrangement I consists of a group of rivers flowing through mainly wooded and agricultural areas. A single separate object is included in arrangement II (Horodnianka). The Horodnianka also crosses agricultural areas, but it also flows near the municipal waste dump

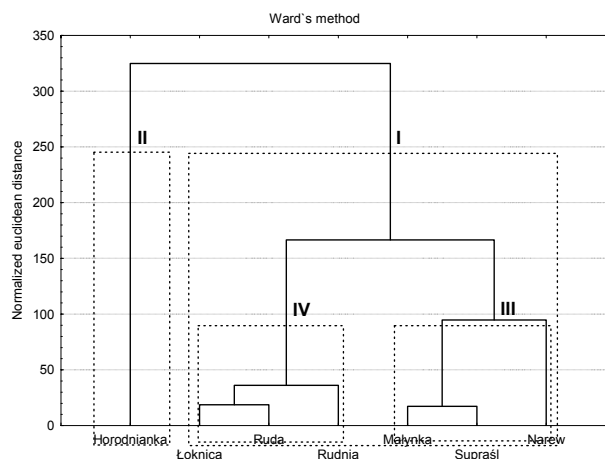


Fig. 5. Dendrogram of the CA according to Ward.

located in Hryniewicze, from where pollutants are probably eluted and transported to analyzed river during heavy rainfalls, which made the object become separate on the dendrogram. Arrangement IV includes rivers passing through mainly agricultural areas. Arrangement III consists of a group of rivers flowing through mainly wooded areas. The Ward agglomeration method confirmed earlier theses and analyses.

Conclusions

1. A gradual increase of macroelement concentrations in the Narew along its course as a consequence of river supply by surface runoff and another of its tributaries was found.
2. The study revealed different concentrations of macroelements and iron in upper Narew River catchment, depending on the basin character as well as spatial distribution of point sources.
3. Higher macroelements contents were found in Narew tributaries than in the river itself.
4. Studies and analyses allowed for identifying the main point pollution sources for the Supraśl River, i.e. Gródek and Białystok.

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