RECOGNITION OF MAIN PROCESSES FORMING CHEMICAL COMPOSITION OF THE SUPRAŚL RIVER WATER

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ABSTRACT

The aim of the study was to identify and define the processes that affect the variability of the chemical composition of Supraśl river water at selected measuring points. One of the recognized multivariate statistical methods was used for identification. The research area covered the Suprasl river. Four measuring points were selected on the river – Michałowo, Gródek, Nowodworce, Dzikie. The measuring points were selected in such a way to take into account the impact of the most intense interaction located along the river. Changes in concentration were determined on the basis of monthly analyzes of water samples collected from the Supraśl river in 2003–2012 by the Regional Inspectorate for Environmental Protection (RIEP) in Białystok. The analyses were performed in the RIEP laboratory in Bialystok, which has implemented and maintained a management system that meets the requirements of the norm PN-EN ISO/IEC 17025 + Ap.1:2007 approved by the certificate AB 165. The water samples were subject to determinations of dissolved oxygen concentration, BOD_5, COD_{Mn}, COD_{Cr}, NH_3, $N-NH_4^+$, $N_{Kieldahl}$, NO_3^-, $N-NO_3^-$, NO_2^-, $N-NO_2^-$, $N_{tot.}$, PO_4^{3-}, P_{tot} and electrical conductivity value. The monthly sum of precipitation was read based on data from the Weather Service "IMGW-PIB Monitor". The research and analysis results allowed to identify the self-cleaning, nitrification, and de-nitrification processes, as well as enrichment affecting the variability of the chemical composition of the Supraśl river water. The results from the factor analysis showed some prevailing of enrichment processes over internal changes in the aquatic environment of the Supraśl river.

Keywords: chemical composition, river water, multivariate statistical method.

INTRODUCTION

The study upon factors affecting the variability of chemical composition of water outflow from the upper Narew river catchment, including Supraśl river, and determination of their sources were conducted by Banaszuk and Wysocka [1996], Mioduszewski [1997], Banaszuk H. [2004] and Banaszuk P. [2007]. Other research carried out by Grabowska et al. [2003], Górniak [2006], as well as Zieliński and Jekaterynczuk-Rudczyk [2009] the most often related to the catchment fragment associated with selected river or reservoir. According to Skorbiłowicz and Kiryluk [2005], the quality of the Supraśl river water periodically changes, mainly in relation to the content of $N-NH_4^+$, NO_2^- and NO_3^-. The authors argue that indirectly, the quality of the Supraśl river water is influenced by methods of adjacent land use, mainly including the post-bog meadows, as well as the migration of pollutants from other, non-agricultural sources. Prevailing part of the Supraśl river catchment is abundant in moorshed muck soils characterized by a high content of nitrogen forms released by mineralization of soil. Skorbiłowicz [2006] conducted a factor analysis of the results of the items concentrations in water samples from the whole Supraśl river. The analyses allowed to identify two factors, the first of which explained 57% of the chemical composition variation of the Supraśl river and the other 30%. The factor analysis also performed

by Skorbiłowicz [2010], involving results of the Supraśl river water, enabled the identification of two factors. Factor I explained the variability of chemical composition of the Supraśl river waters in 76%, while factor II in 14%. The author identified sources of minerals in the catchment area of the river Supraśl, which included among others, wastewater produced mainly in Michałowo and Gródek. Skorbiłowicz and Ofman [2015] showed that the unit loads of Ca^{2+} and Mg^{2+} in the Supraśl river water were positively correlated ($r = 0.79$ and $r = 0.85$) with the amount of liming in soils of the Supraśl river catchment that is closed by Dzikie intersection.

The aim of the study was to identify and define the processes affecting the variability of the chemical composition in Supraśl river water at selected measuring points. One of the recognized multivariate statistical methods was used for identification.

METHODS

The Supraśl river with a length of 93.8 km and catchment area of 1844.4 km^2 is the right tributary of the Narew river with an estuary of 299.8 km. The springs of the river are located north of the village Topolany, in the area of extensive peat bogs. The catchment area up to the village Gródek is of a lowland nature with marsh-peat subsoil. The catchment area of the river is covered with The Knyszyńska Forest Landscape Park. Its borders surround a prevailing fragment of Knyszyńska Forest – one of the best preserved forest complexes in Poland. Forests cover 80% of the Park area. They have a remarkably Boreal character, similar to that of the southern taiga. Pines and pine-spruce trees, sometimes older than a century, dominate. The Knyszyńska Forest with

area of 132,372 hectares is Natura 2000 protected area. The Suprasl river is a source of drinking water supply for Bialystok agglomeration, therefore its catchment is covered by the indirect protection zone. Annual precipitation ranges from 500 to 600 mm. The studied valley contains mainly hydrogenic soils – moorshed ones occupying approximately 70% of the area. Organic soils predominate on the broad, flat valley sections of Upper and Lower Supraśl river, where they cover about 70% of the area. They occupy 56% of the area within a relatively narrow Middle Supraśl river valley. On this stretch of the river, the catchment areas are dominated by forests (approximately 63% of the total area).

The study area included the Supraśl river. Four measuring points were selected on the river – Michałowo, Gródek, Nowodworce, Dzikie (Figure 1).

The measuring points were selected in such a way to take into account the impact of the most intense interactions located along the river. Changes in the concentration were determined on the basis of monthly analyzes of water samples collected from the Supraśl river in 2003–2012 by the Regional Inspectorate for Environmental Protection (RIEP) in Białystok. Analyses were performed by RIEP laboratory in Bialystok, that has implemented and maintained a management system, which meets the requirements of the norm PN-EN ISO/IEC 17025 + Ap.1:2007 confirmed by the certificate AB 165. The water samples were subject to determinations of dissolved oxygen concentration, BOD_5, COD_{Mn}, COD_{Cr}, NH_3, $N\text{-}NH_4^+$, $N_{Kieldahl}$, NO_3^-, $N\text{-}NO_3^-$, NO_2^-, $N\text{-}NO_2^-$, $N_{tot.}$, PO_4^{3-}, P_{tot} and electrical conductivity.

The monthly sum of precipitation was read based on a data from the Weather Service "IMGW-PIB Monitor" [http://monitor.pogodynka.pl/#map/19.533,52.1384,7,false,true,0].
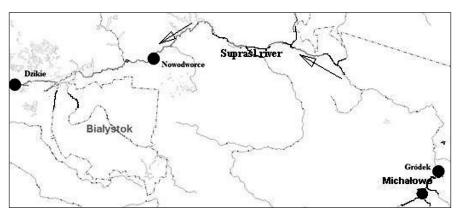

Figure 1. Localization of the measuring points on the Supraśl river

Statistical processing of the test results used the factor analysis that belongs to the group of multidimensional analysis and is used to describe and explore a large number of data. The hydrochemical studies use it to describe the processes occurring in surface waters and groundwater and identification of the supply sources as well as the origin of substances affecting the chemical composition of water. In order to interpret the results of factor analysis, it was assumed that the association of the primary variable with the factor is strong when the absolute values of its loads are greater than 0.70. Values of so-called general statistics were also calculated, in particular: arithmetic mean, standard deviation, and variation coefficient. The licensed software package StatSoft Statistica 12 was applied for all calculations.

RESULTS AND DISCUSSION

The largest spread of the test results of Supraśl river water samples occurred at point Michałowo in the case of BOD_5 (variability coefficient – 330.41%), while the smallest – for electrical conductivity of water (variability coefficient – 10.21%). Quite significant result dispersion was recorded for NH_3 and $N-NH_4^+$ (156.90%) and for PO_4^{3-} and P_{tot} (105.72% and 102.60%, respectively) (Table 1). The remaining variability coefficients reached lower, yet very similar values. A great scatter of results around their mean value

may indicate some factor or process that invokes them. The water quality indicator expressed as BOD_5 is a measure of readily-decomposable organic matter content. The results of factor analysis (Table 2) also indicate the presence of factor I correlated with factorial loads of variables BOD_5, NH_3, $N-NH_4^+$, $N_{Kieldahl}$, as well as PO_4^{3-}, P_{tot}. This factor is associated with penetration of readily-decomposable organic matter (BOD_5), nitrogen and phosphorus compounds being the components of poorly purified municipal wastewater into the water of Supraśl river before point Michałowo. The other factor is negatively correlated with dissolved oxygen and with NO_3^- and $N-NO_3^-$, while positively with NO_2^- and $N-NO_2^-$, which may suggest de-nitrification processes occurring in water of that fragment of Supraśl river. The former factor explains up to 50% of processes that site, whereas the latter only 18%, indicating a great surplus of Supraśl river water enrichment against the conversion of components that entered the aquatic environment.

At the measuring point Gródek, the largest scatter of results related to the Supraśl river water was recorded for PO_4^{3-} and P_{tot} (88.57% and 76.15%) as well as $N-NH_4^+$ (70.82%) (Table 3), which may result from the discharge of insufficiently purified wastewater in that region. These may be wastewater discharged to the Supraśl river by municipal sewage treatment plants in Michałów and Gródek. A slight dispersion of results (10.41%) for electrical conductivity of the

Table 1. Mean concentration of components in the Supraśl river water at the measuring point Michałowo

Parameter	Unit	Number of samples	Arithmetic mean	Minimum	Maximum	Standard deviation	Variability coefficient [%]
Precipitation	[mm]	84	54.62	0.08	225.20	35.13	64.31
Dissolved oxygen	[mgO$_2$·dm^{-3}]	46	5.71	0.60	10.20	2.71	47.42
BOD$_5$	[mgO$_2$·dm^{-3}]	46	5.82	0.90	133.00	19.22	330.41
COD$_{Mn}$	[mgO$_2$·dm^{-3}]	46	18.54	9.00	78.00	10.09	54.41
COD$_{Cr}$	[mgO$_2$·dm^{-3}]	46	72.08	24.00	279.40	35.45	49.18
NH$_3$	[mg·dm^{-3}]	44	1.91	0.15	16.10	3.00	156.90
N-NH$_4^+$	[mg·dm^{-3}]	44	1.48	0.12	12.50	2.33	156.90
N$_{Kieldahl}$	[mg·dm^{-3}]	46	2.85	1.20	12.80	2.51	87.90
NO$_3^-$	[mg·dm^{-3}]	45	16.17	0.66	49.10	9.60	59.36
N-NO$_3^-$	[mg·dm^{-3}]	33	3.35	0.15	8.41	1.91	57.04
NO$_2^-$	[mg·dm^{-3}]	46	0.21	0.05	0.53	0.13	64.89
N-NO$_2^-$	[mg·dm^{-3}]	34	0.06	0.02	0.16	0.04	66.19
N$_{tot}$	[mg·dm^{-3}]	46	6.50	2.80	13.10	2.39	36.77
PO$_4^{3-}$	[mg·dm^{-3}]	46	0.98	0.15	4.96	1.03	105.72
P$_{tot}$	[mg·dm^{-3}]	46	0.41	0.06	1.76	0.42	102.60
Electrical conductivity	[μS·cm^{-1}]	46	469.04	383.00	648.00	47.90	10.21

Table 2. Results of the factor analysis (rotation method – normalized varimax, determined loads are >0.7). Measuring point Michałowo

Variables	Factor I	Factor II
Precipitation	-0.15	0.66
Dissolved oxygen	-0.49	**-0.75**
BOD_5	**0.75**	0.12
COD_{Mn}	-0.57	-0.19
COD_{Cr}	-0.59	-0.07
NH_3	**0.95**	0.16
$N-NH_4^+$	**0.95**	0.16
$N_{Kieldahl}$	**0.94**	0.16
NO_3^-	-0.45	**-0.78**
$N-NO_3^-$	-0.45	**-0.78**
NO_2^-	0.10	**0.79**
$N-NO_2^-$	0.10	**0.79**
N_{tot}	0.65	-0.51
PO_4^{3-}	**0.85**	0.35
P_{tot}	**0.87**	0.35
Electrical conductivity	0.69	-0.03
Explanation of chemical composition in the Supraśl river water by factor I and II [%]	50	18

Supraśl river water was observed. Based on the factor analysis (Table 4), two factors were identified, of which the first explains 37% of the chemical composition of the Supraśl river water, while the other 20%. The former factor indicates the self-cleaning processes occurring in water of the studied river. Significant factorial load representing the water-dissolved oxygen indicates a factor making its supply to the Supraśl river water. At the same time, the analysis suggests nitrification processes due to probable internal correlation at the level of the factor between dissolved oxygen vs. NO_3^-, $N-NO_3^-$. The analysis has shown negative factorial loads representing phosphorus compounds (PO_4^{3-}, P_{tot}), which may be a consequence of the self-cleaning processes in the studied water. This can be explained by the oxygen produced due to photosynthesis and the use of phosphorus compounds by developing mono and multicellular plant organisms. The latter factor indicates the processes of enriching in $N-NH_4^+$ resulting from the discharge of insufficiently treated wastewater.

Water of the Supraśl river (point Nowodworce) contained the most variable concentration of NO_2^- (267.03%), which may indicate the intense nitrification processes occurring in water before this point. A slight scatter of dissolved oxygen results (23.35%) seems to confirm this phenomenon. A subsequent case of very slight variability of electrical conductivity (7.07%) for studied water, was recorded (Table 5).

Factor analysis (Table 6) indicates the supply of organic matter expressed as COD_{Mn}, COD_{Cr}, including the hardly decomposable one, as well as $N_{Kieldahl}$, NO_3^-, $N-NO_3^-$ and $N_{tot.}$ along with the decrease in water electrical conductivity. The enrichment in these components can happen due to the penetration of runoff from surrounding fields into the Supraśl river. At the point Nowod-

Table 3. Mean concentration of components in the Supraśl river water at the measuring point Gródek

Parameter	Unit	Number of samples	Arithmetic mean	Minimum	Maximum	Standard deviation	Variability coefficient [%]
Precipitation	[mm]	84	54.62	0.08	225.20	35.13	64.31
Dissolved oxygen	$[mgO_2 \cdot dm^{-3}]$	75	6.95	0.60	13.70	2.49	35.79
BOD_5	$[mgO_2 \cdot dm^{-3}]$	75	3.24	1.20	14.30	2.05	63.37
COD_{Mn}	$[mgO_2 \cdot dm^{-3}]$	58	22.78	7.00	73.10	11.31	49.63
COD_{Cr}	$[mgO_2 \cdot dm^{-3}]$	58	85.66	20.50	243.00	36.82	42.98
NH_3	$[mg \cdot dm^{-3}]$	63	0.55	0.08	2.00	0.37	67.37
$N-NH_4^+$	$[mg \cdot dm^{-3}]$	66	0.41	0.06	1.55	0.29	70.82
$N_{Kieldahl}$	$[mg \cdot dm^{-3}]$	73	1.93	0.67	4.80	0.72	37.56
NO_3^-	$[mg \cdot dm^{-3}]$	70	9.51	2.10	32.30	5.92	62.17
$N-NO_3^-$	$[mg \cdot dm^{-3}]$	60	1.99	0.05	6.71	1.11	55.78
NO_2^-	$[mg \cdot dm^{-3}]$	73	0.12	0.01	0.42	0.08	66.69
$N-NO_2^-$	$[mg \cdot dm^{-3}]$	60	0.04	0.00	0.13	0.03	66.09
N_{tot}	$[mg \cdot dm^{-3}]$	73	3.97	0.80	10.00	1.64	41.36
PO_4^{3-}	$[mg \cdot dm^{-3}]$	73	0.58	0.16	3.64	0.52	88.57
P_{tot}	$[mg \cdot dm^{-3}]$	75	0.29	0.07	1.69	0.22	76.15
Electrical conductivity	$[\mu S \cdot cm^{-1}]$	74	392.81	206.00	479.00	40.88	10.41

Table 4. Results of the factor analysis (rotation method – normalized varimax, determined loads are >0.7). Measuring point Gródek

Variables	Factor I	Factor II
Precipitation	-0.33	-0.24
Dissolved oxygen	**0.82**	0.01
BOD_5	0.13	0.57
COD_{Mn}	0.58	-0.12
COD_{Cr}	0.59	0.00
NH_3	-0.06	**0.92**
$N-NH_4^+$	-0.06	**0.92**
$N_{Kieldahl}$	0.60	0.55
NO_3^-	**0.85**	0.09
$N-NO_3^-$	**0.85**	0.09
NO_2^-	-0.55	0.34
$N-NO_2^-$	-0.55	0.34
N_{tot}	**0.89**	0.28
PO_4^{3-}	**-0.77**	0.39
P_{tot}	**-0.71**	0.49
Electrical conductivity	-0.29	0.39
Explanation of chemical composition in the Supraśl river water by factor I and II [%]	37	20

worce, any remarkable sources of $N_{Kieldahl}$, NO_3^-, $N-NO_3^-$ and N_{tot} cannot be found, but meadows with post-bog soils and their intense performance methods can be the only reason for the water enrichment in nitrogen compounds due to washout by precipitation water. This fact was also reported by Kiryluk (2003) as well as Skorbiłowicz and

Kiryluk (2005). It should be noted that the point in Nowodworce lies in the protection zone of the surface intake of drinking water for Bialystok. The other factor indicates the self-cleaning processes, the consequence of which is decreasing PO_4^{3-} combined with the dissolved oxygen supply. Positive, high factorial loads representing forms of $N-NH_4^+$ may prove the presence of unknown source of these compounds above that site. Perhaps wastes of grazing farm animals are the main cause of the ammonia penetration into the Supraśl river water.

The last measuring point Dzikie is situated directly after the Biała river estuary to the Supraśl river. Therefore, there was a significant dispersion of results related to the water tests in the case of: NH_3, $N-NH_4^+$, NO_2^-, $N-NO_2^-$ and PO_4^{3-} (Table 7). Diversity and variability of the chemical composition of water may result from the enrichment of the Biała river water due to the infrastructure of Białystok it flows through. The first and second factor in factor analysis (Table 8) confirm the processes of enrichment in these components. The processes of nitrogen leaching from the post-bog soils present in that region of the Supraśl river catchment can occur at this point.

CONCLUSIONS

1. The study and test results allowed for identification of the self-cleaning, nitrification, de-nitrification, and enrichment processes affecting the

Table 5. Mean concentration of components in the Supraśl river water at the measuring point Nowodworce

Parameter	Unit	Number of samples	Arithmetic mean	Minimum	Maximum	Standard deviation	Variability coefficient [%]
Precipitation	[mm]	84	54.62	0.08	225.20	35.13	64.31
Dissolved oxygen	$[mgO_2 \cdot dm^{-3}]$	117	9.77	3.30	16.30	2.28	23.35
BOD_5	$[mgO_2 \cdot dm^{-3}]$	117	2.04	0.70	5.80	0.89	43.63
COD_{Mn}	$[mgO_2 \cdot dm^{-3}]$	57	12.63	5.30	23.30	4.49	35.56
COD_{Cr}	$[mgO_2 \cdot dm^{-3}]$	99	39.39	0.00	93.00	21.14	53.67
NH_3	$[mg \cdot dm^{-3}]$	89	0.17	0.05	0.50	0.09	50.31
$N-NH_4^+$	$[mg \cdot dm^{-3}]$	59	0.14	0.04	0.39	0.08	53.05
$N_{Kieldahl}$	$[mg \cdot dm^{-3}]$	101	0.90	0.33	1.70	0.29	32.13
NO_3^-	$[mg \cdot dm^{-3}]$	100	4.91	0.50	19.50	3.18	64.90
$N-NO_3^-$	$[mg \cdot dm^{-3}]$	84	1.08	0.00	4.41	0.69	63.94
NO_2^-	$[mg \cdot dm^{-3}]$	86	0.70	0.01	9.70	1.87	267.03
$N-NO_2^-$	$[mg \cdot dm^{-3}]$	62	0.01	0.00	0.02	0.01	46.55
N_{tot}	$[mg \cdot dm^{-3}]$	80	1.96	0.00	6.00	1.06	54.06
PO_4^{3-}	$[mg \cdot dm^{-3}]$	102	0.22	0.10	0.56	0.09	38.93
P_{tot}	$[mg \cdot dm^{-3}]$	87	0.15	0.04	0.33	0.05	35.53
Electrical conductivity	$[\mu S \cdot cm^{-1}]$	117	383.56	249.00	447.00	27.13	7.07

Table 6. Results of the factor analysis (rotation method – normalized varimax, determined loads are >0.7). Measuring point Nowodworce

Variables	Factor I	Factor II
Precipitation	-0.21	-0.55
Dissolved oxygen	0.33	**0.78**
BOD_5	0.44	0.64
COD_{Mn}	**0.81**	-0.21
COD_{Cr}	**0.70**	-0.13
NH_3	-0.05	**0.84**
$N-NH_4^+$	-0.05	**0.84**
$N_{Kieldahl}$	**0.81**	0.31
NO_3^-	**0.84**	0.40
$N-NO_3^-$	**0.84**	0.40
NO_2^-	0.62	0.25
$N-NO_2^-$	0.63	0.24
N_{tot}	**0.88**	0.39
PO_4^{3-}	0.24	**-0.72**
P_{tot}	0.19	-0.07
Electrical conductivity	**-0.80**	0.16
Explanation of chemical composition in the Supraśl river water by factor I and II [%]	42	20

Table 8. Results of the factor analysis (rotation method – normalized varimax, determined loads are >0.7). Measuring point Dzikie

Variables	Factor I	Factor II
Precipitation	-0.44	0.16
Dissolved oxygen	0.46	-0.60
BOD_5	0.67	0.32
COD_{Mn}	0.25	0.09
COD_{Cr}	0.05	0.43
NH_3	**0.75**	0.48
$N-NH_4^+$	**0.73**	0.49
$N_{Kieldahl}$	**0.73**	0.26
NO_3^-	**0.88**	-0.20
$N-NO_3^-$	**0.89**	-0.20
NO_2^-	0.01	**0.72**
$N-NO_2^-$	0.01	**0.72**
N_{tot}	**0.94**	0.00
PO_4^{3-}	-0.08	0.59
P_{tot}	0.35	0.65
Electrical conductivity	0.32	0.51
Explanation of chemical composition in the Supraśl river water by factor I and II [%]	35	19

Table 7. Mean concentration of components in the Supraśl river water at the measuring point Dzikie

Parameter	Unit	Number of samples	Arithmetic mean	Minimum	Maximum	Standard deviation	Variability coefficient [%]
Precipitation	[mm]	94	55.44	0.08	225.20	35.00	63.13
Dissolved oxygen	$[mgO_2 \cdot dm^{-3}]$	96	9.92	5.30	17.60	2.11	21.23
BOD_5	$[mgO_2 \cdot dm^{-3}]$	96	2.70	0.60	10.00	1.37	50.80
COD_{Mn}	$[mgO_2 \cdot dm^{-3}]$	95	12.45	6.60	24.80	3.78	30.32
COD_{Cr}	$[mgO_2 \cdot dm^{-3}]$	84	44.93	4.53	96.30	21.90	48.75
NH_3	$[mg \cdot dm^{-3}]$	84	0.26	0.05	1.70	0.26	102.26
$N-NH_4^+$	$[mg \cdot dm^{-3}]$	96	0.18	0.04	1.32	0.20	108.55
$N_{Kieldahl}$	$[mg \cdot dm^{-3}]$	96	1.24	0.44	3.30	0.45	35.79
NO_3^-	$[mg \cdot dm^{-3}]$	84	8.21	2.10	22.10	2.84	34.63
$N-NO_3^-$	$[mg \cdot dm^{-3}]$	96	1.88	0.48	5.20	0.78	41.32
NO_2^-	$[mg \cdot dm^{-3}]$	96	0.13	0.03	0.93	0.13	98.66
$N-NO_2^-$	$[mg \cdot dm^{-3}]$	95	0.04	0.01	0.28	0.04	98.66
N_{tot}	$[mg \cdot dm^{-3}]$	96	3.18	1.70	8.60	1.10	34.49
PO_4^{3-}	$[mg \cdot dm^{-3}]$	96	0.29	0.10	3.04	0.31	104.53
P_{tot}	$[mg \cdot dm^{-3}]$	96	0.19	0.04	1.00	0.12	62.55
Electrical conductivity	$[\mu S \cdot cm^{-1}]$	96	479.72	315.00	986.00	85.88	17.90

variability of chemical composition in the Supraśl river water.

2. At the measuring points Gródek and Michałowo, sources of BOD_5, NH_3, $N-NH_4^+$, PO_4^{3-}, P_{tot} were identified. It was the effect of the discharge of insufficiently purified wastewater from municipal sewage treatment plants.

3. The analyses allowed to find the processes of nitrogen leaching from bog-hydrogenic soils into the Supraśl river water at some points.

4. Results of the factor analysis revealed the prevalence of the enrichment over internal conversion processes in the aquatic environment of the Supraśl river.

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