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Research Article

THE SOURCES OF NUTRIENTS IN WATERS OF RIVERS IN THE WETLAND AREAS OF NAREW NATIONAL PARK IN NORTH-EASTERN POLAND

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ABSTRACT
The study aimed at the attempt to identify and to evaluate the interaction intensity, and to classify the sources of river waters nutrients in the catchment of upper river Narew within Narew National Park (north-eastern Poland). The studies were carried out on Narew river within borders of Narew National Park, where 5 measurement-control points were localized as well as one near estuaries of its 5 tributaries (Awissa, Czaplinianka, Horodnianka, Turośnianka and Supraśl). Factor analysis (FA) from multi-dimensional group was applied for statistical processing of study results, because it is commonly used to describe and explore a large number of data. concentrations of analyzed chemicals depended on a water sampling point that was under anthropopression and geogenic conditions. Studies and results from analyses (FA and CA) allowed for identifying the main sources of river Narew nutrients within Narew National Park. These are: tributaries of river Narew, point and distributed runoffs, as well as shallow ground waters that transport components having anthropogenic and partially geogenic-lithologic origin. River Turośnianka supplies the largest loads of studied parameters to river Narew within Narew National Park boundaries. River Supraśl is the most contaminated tributary of river Narew.

Key words: rivers, sources of nutrients, factor analysis, Narew.

INTRODUCTION

Water quality is considered the main factor controlling health and state of disease in both men and animals. Surface water quality in a region is largely determined by both natural processes (weathering and soil erosion) and by anthropogenic impacts (municipal and industrial wastewater discharges). The anthropogenic discharges constitute a constant polluting source, whereas surface runoff is a seasonal phenomenon, largely affected by climate within the basin [Singh et al. 2004; Vega et al. 1996].

Urbanization and agricultural intensification have led to the pollution of surface waters causing a range of environmental, social and economic problems at regional and local levels encompassed under the term eutrophication. Rivers are particularly vulnerable due to their proximity to population centers, sensitivity to land use change and ubiquitous exploitation [Malmqvist and Rundle 2002; Walsh et al. 2005].

The multivariate statistical techniques such as cluster analysis (CA), factor analysis (FA), principal component analysis (PCA) and discriminant analysis (DA) have widely been used as unbiased methods in the analyses of water-quality data for drawing meaningful information [Helena et al. 2000; Bengraine and Marhaba 2003; Voncina et al. 2002; Liu et al. 2003; Reghunath et al. 2002; Wunderlin et al. 2001; Simeonov et al. 2003]. The multivariate treatment of data is widely used to characterize and evaluate surface and freshwater quality and it is useful for evidencing the temporal and spatial variations caused by natural and anthropogenic factors linked to seasonality [Helena et al. 2000].

There are many wetlands localized in flow valleys and area depressions, and their large part is used as green lands in north-eastern Poland.

Many rivers and flows sections in the Narew river catchment are contaminated due to the disposal of unpurified or insufficiently purified sewage from agriculture, food industry, and municipal ones. Disturbances of natural water chemistry associated with human activity and colonization are apparent in boggy river Narew valley. Relatively intensive agriculture performed near the valley, meadow management on part of the peat area and the processes of organic forms mucking in that part of bogs make significant changes in migration processes within the landscape. Agriculture is seen as one of the main and the most important contamination and surface water eutrophication sources, and survey on typically agricultural areas indicated quite great differentiation of the concentrations of the studied chemicals in surface waters of the discussed area.

Narew National Park is characterized by high level of naturalness, individuality of hydrological and habitat systems as well as flora and fauna abundance. A wide, filling almost the whole valley, bog ecosystem with a complexity of river beds, mosaic system of backwater, as well as swamp and land habitats can be found there. Within the National Park, river Narew has following tributaries: Liza, Szeroka Struga, Grądówka, Awissa, Turośnianka, Czaplinianka, Wygonówka, Kurówka. Out of the Park, river Horodnianka flows into the river Narew from its right and near Choroszcz. From that point, river Narew turns west and there are no swamps and backwaters, the area is well meliorated, green lands prevail near the river, while cultivated fields and forests are localized farther. From Choroszcz to Tykocin, major tributaries of river Narew are Supraśl and Jaskranka. The NNP area represents a specific type of river known as anastomosing river.

The study aimed at the attempt to identify and to evaluate the interaction intensity, and to classify the sources of river waters nutrients in the catchment of upper river Narew within Narew National Park (north-eastern Poland).

METHODS

The studies were carried out on Narew river within borders of Narew National Park, where 5 measurement-control points were localized as well as one near estuaries of its 5 tributaries (Awissa, Czaplinianka, Horodnianka, Turośnianka and Supraśl) (Figure 1 and Table 1). The flow rate of river Narew (SNQ) amounts to 0.5 $m^3 \cdot s^{-1}$. The annual fall is estimated to about 500–600 mm. Water was sampled once a month in 2001, 2002, 2003, 2004, and 2005 at 0.5 m depth into 1.5-liter polyethylene bottles. Water chemical analyses were performed on the day of sampling in a laboratory at Technical University in Białystok, Poland. The following items were determined: $N\text{-}NH_4^+$, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, $P\text{-}PO_4^{3-}$,

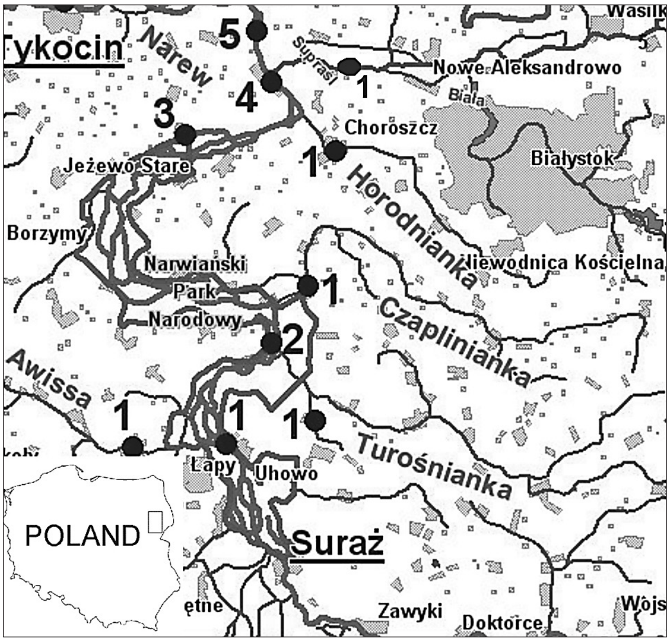


Fig. 1. Localization of sampling and measurement points on river Narew and its tributaries (Narew National Park), Poland NE

Table 1. Characterization of studied rivers' catchment

River	Forests [%]	Agricultural area [%]		Urbanized area [%]	River length [km]	Catchment area [km^2]
		Arable lands [%]	Pastures and meadows [%]			
Awissa	14	57	21	8	15	130
Czaplinianka	18	43	28	5	17	80
Horodnianka	18	40	26	15	18	76
Turośnianka	12	53	30	5	22	144
Supraśl	33	37	26	4	94	1856

SO_4^{2-}, Cl^-, by means of colorimetry, conductivity (CE) and acidity by means of potentiometry, Na^+ and K^+ applying EAS, while Ca^{2+}, Mg^{2+}, $Fe^{2+/3+}$, and Zn^{2+} concentrations by means of AAS technique. An oxidizing air-acetylene flame was used in EAS and AAS as atomization source. The soluble forms of particular ions were determined in water samples filtered through micropore filters (d = 0.45 μm). Correctness of applied methodology related to Ca^{2+}, Mg^{2+}, Na^+, K^+, $Fe^{2+/3+}$, and Zn^{2+} determinations was verified on a basis of referential material analysis (SRM 1643e, Trace Elements in Water, NIST). Factor analysis (FA) from multi-dimensional group was applied for statistical processing of study results, because it is commonly used to describe and explore a large number of data. To separate factors, the prime components analysis (PCA), which uses a primary correlation matrix for calculations was applied . It is used in hydrochemical studies to describe processes occurring in surface and underground waters as well as to identify the supplying sources and origin of substances that determine the chemical composition of waters. In order to interpret FA results, it was accepted that associations of primary variable with an experimental factor are strong when absolute values of its loads are greater than 0.70. Also cluster analysis (CA, Ward agglomeration method) that is based on the notion of objects or variables distance in multi-dimensional space was applied.

RESULTS AND DISCUSSION

The concentrations of analyzed chemicals depended on a water sampling point that was under anthropopression and geogenic conditions. The acidity (not listed in the table) ranged from 6,5 to 8.5 pH.

Survey of river Narew water revealed negligible fluctuations of $N\text{-}NH_4^+$ concentration (from 0.26 to 0.32 mg·dm^{-3}) (Table 2). Similarly slight concentration variability was also observed for $N\text{-}NO_2^-$ (from 0.007 to 0.008 mg·dm^{-3}). In the case of $N\text{-}NO_3^-$, the lowest concentration was recorded in water from point 1 (0.65 mg·dm^{-3}). At other points, concentrations were close to 0.90 mg·dm^{-3}. The highest $P\text{-}PO_4^{3-}$ concentration was recorded in water from point 2 (0.69 mg·dm^{-3}), while at other ones, the concentration oscillated around 0.40 mg·dm^{-3}. Water from point No 5 contained 39.3 SO_4^{2-} mg·dm^{-3}, which was the maximum. Other sampling-measurement points revealed more uniform concentrations of SO_4^{2-} that oscillated around 32.5 mg·dm^{-3}. Variability of Cl^- concentrations at control points was low and usually reached about 19.0 mg·dm^{-3}. The CE values in water from all points were similar - below 400 μS·cm^{-1}. The highest Ca^{2+} concentration (72.5 mg·dm^{-3}) was recorded at point 5. At other ones, it was close to 66 mg·dm^{-3}. The concentration of Mg^{2+} showed similar pattern reaching 10.1 mg·dm^{-3} at point No 5 and 11.2 mg·dm^{-3} at point

Table 2. Concentrations of determined parameters in waters of the upper Narew river in 2001–2005

Basic Statistics	Position measurement	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	$P\text{-}PO_4^{3-}$	SO_4^{2-}	Cl^-	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	$Fe^{2+/3+}$	Zn^{2+}
		[mg·dm^{-3}]						[μS·cm^{-1}]	[mg·dm^{-3}]					
Median	1	0.31	0.007	0.65	0.47	32.7	16.8	383	65.2	9.5	9.9	4.2	0.099	0.019
	2	0.32	0.007	1.09	0.69	32.4	19.0	393	62.2	9.5	10.2	4.3	0.094	0.012
	3	0.30	0.007	0.83	0.45	33.6	17.9	393	69.6	11.2	12.1	5.8	0.105	0.016
	4	0.28	0.008	0.87	0.34	32.2	18.7	384	63.0	9.1	10.4	4.3	0.104	0.023
	5	0.26	0.007	1.10	0.42	39.3	20.2	408	72.5	10.1	12.4	4.6	0.053	0.029

No 3. The levels of Na^+ and K^+ did not oscillated much: Na^+ - 10 mg·dm^{-3}, K^+ - 4.8 mg·dm^{-3}. The $Fe^{2+/3+}$ concentration in water from points No 1 – 4 fluctuated around 0.100 mg·dm^{-3}, whereas at point No 5, value of 0.053 mg $Fe^{2+/3+}$·dm^{-3} was recorded. The highest concentration of Zn^{2+} was found in water from point 5 (0.029 mg·dm^{-3}). At other points, the concentration was near 0.018 mg·dm^{-3}.

The highest level of $P\text{-}PO_4^{3-}$ (1.19 mg·dm^{-3}) along with CE value (678 µS·cm^{-1}) was recorded in water of river Awissa (Table 3). Water of river Czaplinianka contained the highest Ca^{2+} (135.9 mg·dm^{-3}), Mg^{2+} (24.2 mg·dm^{-3}), and K^+ concentrations (10.5 mg·dm^{-3}). Water of river Horodnianka was characterized by the highest SO_4^{2-} (70.5 mg·dm^{-3}), Na^+ (21.2 mg·dm^{-3}), and Zn^{2+} levels (0.091 mg·dm^{-3}). Maximum concentration of $N\text{-}NO_2^-$ was recorded in river Turośnianka (0.063 mg·dm^{-3}). In turn, river Supraśl contained high levels of $N\text{-}NH_4^+$ (0.58 mg·dm^{-3}), $N\text{-}NO_3^-$ (2.52 mg·dm^{-3}), and $Fe^{2+/3+}$ (0.349 mg·dm^{-3}).

In order to identify the sources of river Narew water contamination within Narew National Park and to evaluate their influences, the factor analysis (FA) and cluster analysis (CA) were applied. Based on factor analysis, namely "scree test" and "Kaiser's criterion", three explaining factors were identified: PC1 59%, PC2 21%, and PC3 15%, that makes up 95% of a global variability of phenomena in the analyzed system (Table 4).

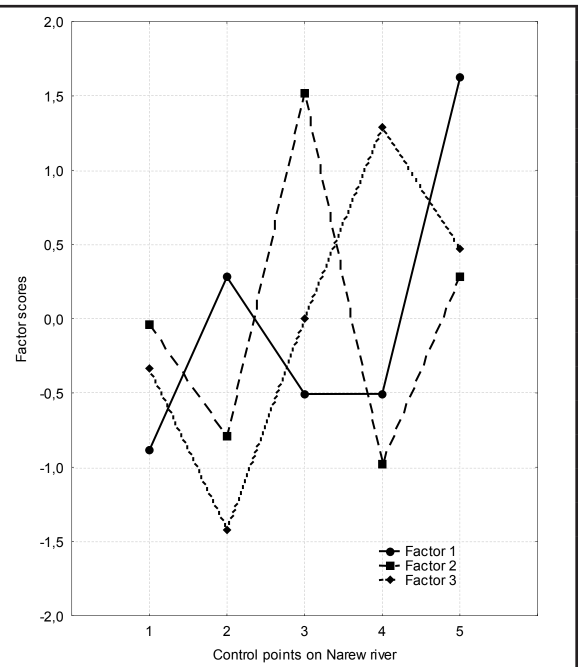
Factor I explains the variability of chemical composition in river Narew water in 59%. Positive factorial loads are apparent that are some kind of "correlation coefficients" between the following variables: flow rate (Q), $N\text{-}NO_3^-$, Cl^-, EC and factor I. $Fe^{2+/3+}$ is negatively correlated to it. Factor I may be interpreted as a process of shifting ions $N\text{-}NO_3^-$ and Cl^- during high flow rates, which is also associated with the increase of CE value

Table 3. Concentrations of determined parameters in waters of tributaries in 2001–2005

River	Basic statistics	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	$P\text{-}PO_4^{3-}$	SO_4^{2-}	Cl^-	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	$Fe^{2+/3+}$	Zn^{2+}
		[mg·dm^{-3}]						[µS·cm^{-1}]	[mg·dm^{-3}]					
Awissa	Median	0.34	0.034	1.87	1.19	78.7	32.7	678	105.0	19.8	14.8	8.6	0.132	0.011
Czaplinianka		0.22	0.037	1.81	0.36	60.3	26.4	541	135.9	24.2	17.9	10.5	0.158	0.021
Horodnianka		0.32	0.006	2.30	0.40	70.5	40.0	650	99.3	17.3	21.2	9.0	0.080	0.091
Turośnianka		0.48	0.063	1.58	0.52	69.6	19.9	560	99.3	16.2	11.3	8.3	0.214	0.027
Supraśl		0.58	0.041	2.52	0.67	45.0	18.5	440	54.6	10.3	8.0	3.9	0.349	0.026

Table 4. Results of factor analysis (normalized rotation method–varimax); marked values are >0.7) and dynamics of factorial values changes at control points on Narew river

Variable	Factor 1	Factor 2	Factor 3
Q	0.89		
$N\text{-}NH_4^+$			-0.97
$N\text{-}NO_2^-$			-0.85
$N\text{-}NO_3^-$	0.99		
$P\text{-}PO_4^{3-}$			-0.97
SO_4^{2-}			0.73
Cl^-	0.75		
EC	0.89		
Ca^{2+}		0.76	
Mg^{2+}		0.94	
Na^+			
K^+		0.96	
$Fe^{2+/3+}$	-0.94		
Zn^{2+}			0.82
Explanation of the variability in chemical composition of river Narew waters by factor I. II and III [%]	59	21	15



in the studied waters. Large amounts of $N\text{-}NO_3^-$ may be also washed out from organic soils that are present in river Awissa valley.

A strong association between nutrients' concentrations and agricultural cover also has been found in European catchments [Moreno et al. 2006; Skoulikidis et al. 2006; García-Pintado et al. 2007; Lassaletta 2007; Tisseuil et al. 2008].

Negative correlation of $Fe^{2+/3+}$ indicates its maximum concentration during low water flow rates. At elevated flow rates, concentration of $Fe^{2+/3+}$ decreases due to its dilution. Some environment features are also detrimental, because they are associated with redox potential and acidity changes that determine mobilizing the analyzed ions from sediments into the water. Commonly known diagram of pH-Eh variability indicates a strong dependence of redox potential on pH. According to the diagram, higher Eh or increased pH is needed to oxidize Fe^{2+} to Fe^{3+}. Sometimes, only pH change is sufficient. In general, higher pH value favors oxidation reactions.

The factor reached its highest value at measurement point No 5 that was localized below river Supraśl tributary, the water which contains large amounts and loads of $N\text{-}NO_3^-$. Point No 2 is another distinguishing site: rivers Awissa and Turośnianka tributaries above it carry great quantities of these components. These tributaries are additional point suppliers of the analyzed components.

Factor 2 explains 21% of chemical composition of river Narew water and it is positively correlated with Ca^{2+}, Mg^{2+}, and K^+. Probably, the processes associated with soil runoff within Narew National Park during heavy rainfalls are the cause of these components increased supply to river Narew. Their large amounts can be transferred through the drainage system to river Narew on that area. Its tributaries are also important, because they often carry quite high concentrations of these components, as well as water supply by more shallow water-carrying layers in some periods near seasons change. In early spring thawing snow and quite intensive rainfalls wash out nitrates and other easily water-soluble ions from soils [Evans et al. 1996, Pionke et al. 1996, Witkowski 1997].

Maximum influences of that factor occurred at point No 3. River Czaplinianka, despite the fact its estuary is localized farther, it may be a main supplier of Ca^{2+}, Mg^{2+}, and K^+ ions. It was indicated by studies upon these components' concentrations that they reached their maximum levels. That siteis an additional point source of the ions. High levels of macro-components in river's longitudinal profile is a resultant of influences of both anthropogenic and geogenic factors.

Factor 3 is negatively correlated with $N\text{-}NH_4^+$, $N\text{-}NO_2^-$ and $P\text{-}PO_4^{3-}$. Probably the flow rate change along with the change of supplying conditions of long-distance underground waters may be a cause of such a result. Intensive biological processes as well as nitrification under such conditions are also the cause of these components' concentration decrease in river Narew water. Instead, SO_4^{2-} i Zn^{2+} are positively correlated with factor 3. These ions can penetrate the river Narew water also due to washing out from soil surface, where organic fertilization is applied. As it is well known, organic fertilizers such as manure and sewage sludge contain large amounts of zinc that may be transported with rainfall water from fertilized surface. High value of the factor observed at point No 4 may indicate additional supply of SO_4^{2-} and Zn^{2+} ions by river Narew tributary – river Horodnianka. The flow water contained large quantities of these ions and that is why it is their point source.

The fact of common anthropopression within Narew National Park can be confirmed by studies of 46 wells, from which waters in 70% were not suitable for consuming due to elevated levels of $N\text{-}NO_3^-$, $N\text{-}NO_2^-$ and $P\text{-}PO_4^{3-}$ [Banaszuk 2004].

On dendrogram (Figure 2), the grouped measurement points on upper river Narew under monitoring are presented on abscissa. The analyses allowed for distinguishing 4 groups of points. The first group (cluster) is formed of points No 1, 2, 3, and 4. In addition, it forms two sub-clusters composed of points No 1 and 2 as well as No 3 and 4. The latter group consists of only one separate point – No 5. Applied classification allowed for identifying points on the river that are under the influence of different sources of studied components. The first group is localized in the area where Narew National Park territory has its impact. Additional sub-clusters differentiating points No 1 and 2 from 3 and 4 carry contaminants from agricultural-urban areas situated within and out of studied area. Another group was found in an influence zone of living areas, including cities and villages. In particular, point No 5 is localized in the zone where river Supraśl has its influence and that transports pollution from Białystok city.

Five tributaries of river Narew were also studied in the research. The result analyses for the

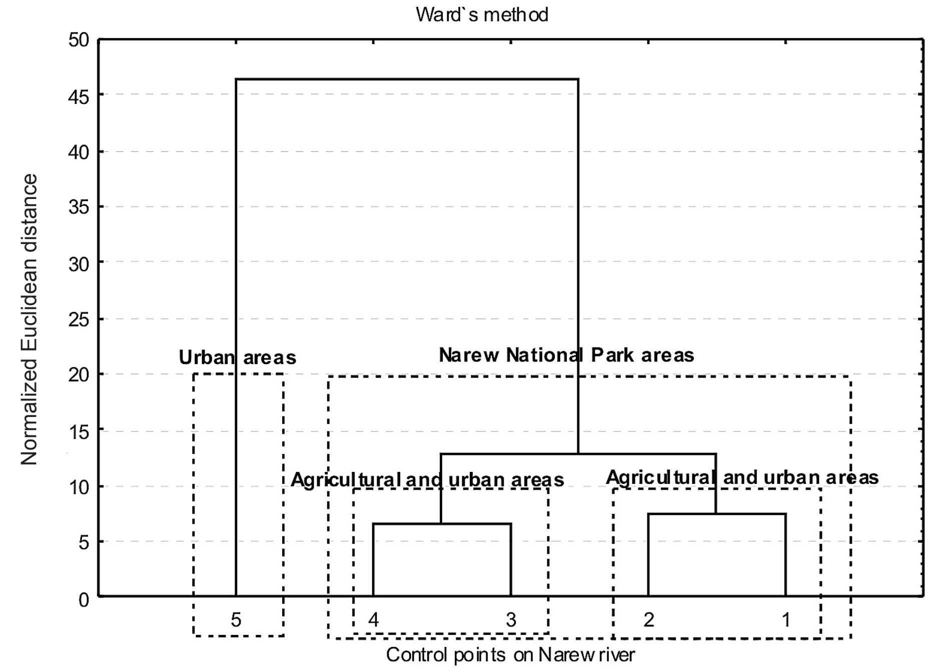


Fig. 2. Dendrogram of the CA according to Ward Monitoring locations of the Narew river

Fig. 3. Ward cluster analysis. River Narew tributaries

above rivers were made on the basis of Ward's cluster analysis (CA). There are 4 river groups formed due to the analysis of generated clusters on dendrogram (Figure 3).

The first group of rivers is localized on urbanized areas (Awissa and Horodnianka), while the second (Supraśl, Turośnianka, and Czaplinianka) on urban and agricultural ones. The latter contains agricultural areas with rivers Turośnianka and Czaplinianka as well as urbanized areas, including tributary – river Supraśl.

CONCLUSIONS

1. Studies and results from analyses (FA and CA) allowed for identifying the main sources of river Narew nutrients within Narew National

Park. These are: tributaries of river Narew, point and distributed runoffs, as well as shallow ground waters that transport components having anthropogenic and partially geogenic-lithologic origin.
2. River Turośnianka supplies the largest loads of studied parameters to river Narew within Narew National Park boundaries.
3. River Supraśl is the most contaminated tributary of river Narew.
4. The cluster analysis (CA) – based on given variables – allowed for classifying the catchments of 5 river Narew tributaries to 4 general groups: urbanized areas, areas with prevailing agricultural activity and mixed areas.
5. Study and results of the analyses (applying mulitdimensional methods – FA and CA) can be helpful in determining the level of river contamination, identifying their natural and anthropogenic sources, as well as determining the level of their influence on wetlands.

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