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COMPARISON OF MINERAL AND ORGANIC NITROGEN FORMS IN REGULATED AND RESTORED SECTIONS OF A SMALL LOWLAND RIVER

The lower, ending part of a small lowland Rudnia River (RR) in NE Poland was restored in 1999 and transformed into a meandering river. In this study, a few years after the natural connection between the main channel and its historic floodplain was restored, we examined the impact of river channel restoration on nitrogen dynamics and its biogeochemistry. Data were collected over a period of a year at monthly intervals from two sections of the river located on the regulated and restored sections. Spatial and temporal variations in the occurrence of mineral (NH_4^+ , NO_2^- , NO_3^-) and organic forms of nitrogen were investigated. Much higher average concentrations of organic nitrogen forms were found in the water from the restored part of the river than in the regulated one. Mineral nitrogen contribution to the total nitrogen (TN) pool was the highest, and the total organic nitrogen (TON) to total inorganic nitrogen (TIN) ratio exceeded $2 \text{ mg} \cdot \text{dm}^{-3}$ in the restored river section. The seasonal trend in concentration of organic nitrogen forms for the restored section was higher and statistically significantly different from the data recorded at the regulated river section. Geological, hydrological, and biogeochemical factors caused elevated organic nitrogen concentrations in the water at the restored part. The most important environmental parameters for nitrogen dynamics are geological structure of river valley, formation and condition of river banks ecotone zone, and water retention time in the river channel. Results from this study suggest that properly restored lowland river floodplains can be effective nitrate sink for mineral forms of nitrogen.

1. INTRODUCTION

In aquatic ecosystems, nitrogen is one of biogenic elements whose excess in water bodies may distort the balance and intensify the process of biomass creation [1]. Increased nutrient loading from anthropogenically disturbed catchments caused eutrophication of many fresh water environments including rivers. Nitrogen is present in surface

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waters in organic or inorganic binding forms (as NH_4^+ , NO_2^- and NO_3^- ions). Nitrogen forms penetrate to surface waters from natural (decomposition of organic matter or excretion) and anthropogenic (supply from municipal and industrial sewage, runoff from the fertilized fields, and depositions of atmospheric pollution) sources [2]. Water mixing from external sources, e.g. surface runoff, tributaries, and ground water infiltration, can also affect the in-stream water quality and nitrogen pool [3].

In the 20th century, river channels were intensively straightened which tended to suppress natural fluctuations in water flow [4]. Most European and North American rivers became canalized and ramparted to prevent floods, and to ensure whole-year navigation in the case of major rivers. Since then, natural lowland “river corridors” were damaged in many places and drastically fragmented [5]. Isolation of the river channel from its floodplain alters the natural geomorphology and biogeochemistry of the fluvial systems [6]. Also, natural catchment-river connectivity is completely changed by disturbance of the organic and inorganic matter biogeochemical exchange [3, 6, 7]. Regulated rivers are characterized by a straight course, narrower bed, lower sediment accumulation, and accelerated water outflow. River modification also made lotic ecosystems ecologically and biologically poorer, expressed in lower levels of biodiversity, uniform water flow, and lower retention capacity. For the last 20 years, restoration of the primary river’s character has been more often undertaken. Nature rehabilitation along and in the rivers seems to be of crucial importance for the restoration of their natural function – self purification of surface water, flood protection, ground water recharge, species protection and distribution [7–10].

The aim of the study was to evaluate the influence of river channel restoration on the concentrations of different nitrogen forms in a small lowland river. Analysis of seasonal changes in concentrations of different nitrogen forms was also performed in the context of different hydrological conditions in the restored river.

2. MATERIALS AND METHODS

Study area. The Rudnia River (RR) is a right tributary of the Narew River (NR) which is the largest lotic system in North Podlaska Lowland (NE Poland). The RR catchment covers the area of 88.6 km², and has a total length of 23.2 km. The catchment inclination is very low (1.2‰), being typical of this region. The mean flow in the river mouth profile during the study period was 0.2 m³ · s⁻¹, which contributes to a low specific discharge (from a catchment) (about 2.3 dm³ · s⁻¹ · km⁻²). According to the classification developed by Horton and Strahler, RR can be classified as having first and second order flows rates.

The RR was regulated, mainly in the upper and middle sections, in the 1970’s. In the river mouth section, the natural channel (going parallel to NR) was shortened by 250 m long artificial canal leading water directly to the Narew River (Fig. 1). A cut-

off river channel fragment (4 km long) has been remained and for over 25 years, has functioned as an oxbow lake. In 1998–1999, the North-Podlaskie Association for Birds Protection (PTOP) commissioned a project designed to restore the cut-off river part of RR. As a part of this project, the natural course of lower river section was restored by damming the artificial canal built in the 70's.

The Rudnia River basin is dominated by agricultural fields in 70% of the catchment area in total. More than a half of this agricultural areas are covered with arable lands (58%), meadows and pastures (41%) and orchards (1%). The afforestation coefficient within the catchment reaches 21% [7]. The fallow lands cover 9% of the RR catchment with domination dense and dispersed rural areas as well as urban development – Zabłudów town. The agricultural management can be described as extensive, which contributes to slight changes in surface water quality within the catchment. The only significant source of the pollutions for investigated river is Zabłudów town with less than 2500 inhabitants. However this town has a new sewage network with modern sewage treatment plant.

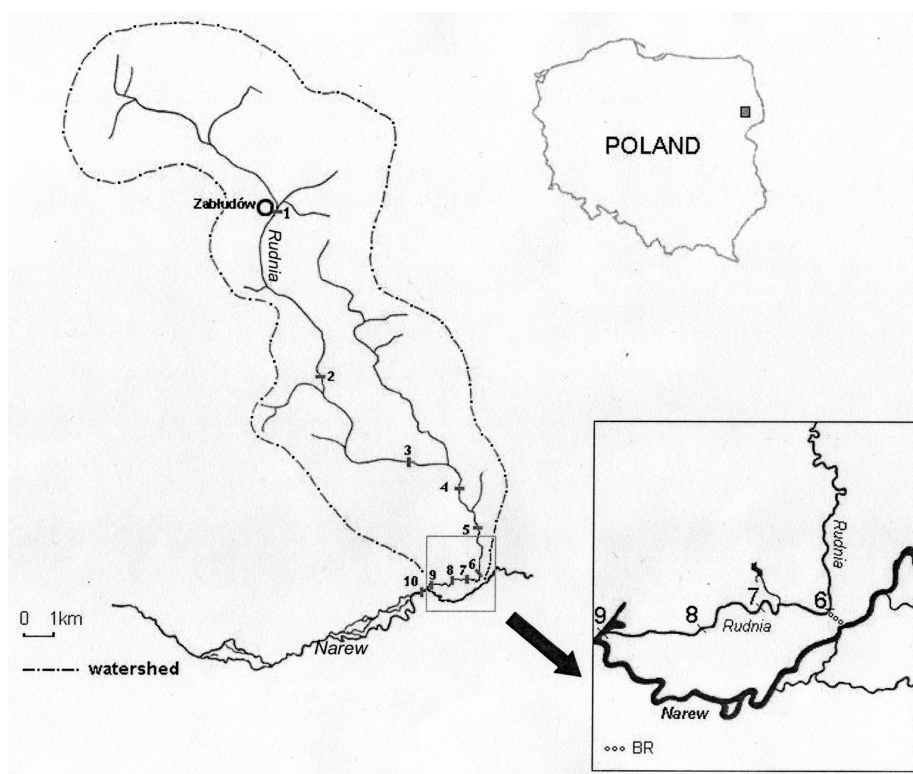


Fig. 1. Location of the study area and sampling sites:

1–5 regulated part of the Rudnia River; 6–9 restored part, 10 – transit river (Narew).

BR – the previous connection of the Rudnia River with Narew River before the restoration

Sampling procedure and chemical analysis. Samples were collected every month at 9 measurement points situated along the course of the Rudnia River (1–5 regulated, 6–9 restored channel). In addition, water samples were taken from the Narew River 100 m below the mouth of the Rudnia River (Fig. 1). Hydrochemical investigations have been carried out between February and December 2006, except restored part of the river in February and March when sampling points were flooded, and there was no access to the river. The water quality of the transit Narew River (NR) was considered as a good example of typical surface waters for investigated region.

Measurements of physical parameters (temperature, electrolytic conductivity, pH, and dissolved oxygen concentration) were carried out using a Hydrolab DataSonde (Hydrolab Corp., Austin, TX) probe in the field. Main cations and anions were determined the same day in the laboratory according to methods proposed by Hermanowicz et al. [11]. Investigated nitrogen forms were analyzed, using reagents by Riedel–deHäen, according to following methods: NH_4 – colorimetrically by the indofenol blue method, NO_2 – colorimetrically with sulphanilic acid by the chromotropic acid method, NO_3 – colorimetrically with N-(1-naphthyl)-ethylenediamine by the zinc catalyst method. Total nitrogen was determined using the Kjeldahl analyzer Tecator 2300 (Sweden) by the titration method PN-EN 25663:2001. Total inorganic nitrogen concentration (TIN) was calculated as the sum of $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NO}_3\text{-N}$. Total organic nitrogen (TON) was calculated by subtracting the ammonium from the total Kjeldahl nitrogen amounts. Total nitrogen (TN) was considered as a sum of the TIN and TON forms. Samples taken in August and September for the Kjeldahl nitrogen were not determined.

Concentration of dissolved organic carbon (DOC) was determined by the catalytic combustion at high temperature using a Shimadzu 5050A carbon analyzer (Shimadzu, Japan). Specific UV absorbance (SUVA) was used to evaluate aromatic compounds complexity of organic matter. This parameter refers to UV absorbance normalized for the concentration of dissolved organic carbon of a sample and was calculated from [12]:

$$\text{SUVA} = \frac{\text{Abs}_{260} \times 1000}{\text{DOC}}$$

Statistical computations were performed using Statgraphics v. 5.0 software package (Statistical Graphics Corporation). Data were analyzed using standard analysis of variance (ANOVA) and multivariate procedures. For statistical analysis, the Spearman rank correlation test was employed for further interpretations of our results with the significance level of $p < 0.05$.

3. RESULTS

Water in the Rudnia River was characterized by a slight variability in hydrochemical parameters in 2006. Many aspects of water quality, such as concentrations of

biogenic substances, were significantly different in the regulated section compared with the restored part (Fig. 2, Table 1). Most of the statistically different parameters were lower in the restored part compared with the regulated section of the RR (Table 1). Much lower mean values of electrical conductivity were recorded in the Narew River than in the Rudnia River (Table 1). A similar relationship was noted for mean biogenic ion concentrations. Only the level of dissolved organic carbon was slightly higher at very similar aromaticity of organic matter (SUVA) at all measurement points.

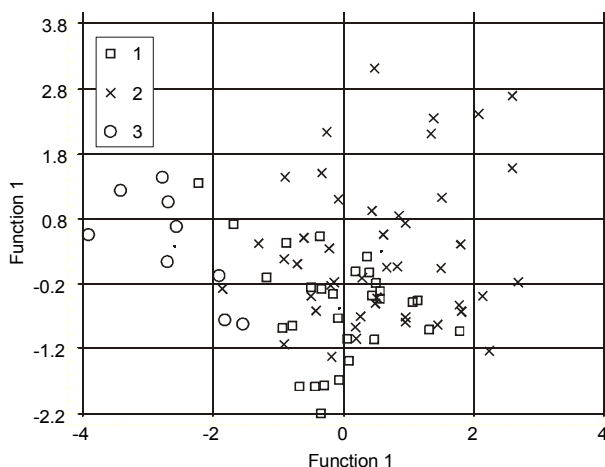


Fig. 2. Differentiation of water quality verified with discriminant analysis generated on various parts of restored river and Narew River in 2006:
1 – restored part of the Rudnia River, 2 – regulated part of the Rudnia River, 3 – Narew River

Table 1

Hydrochemical characteristics of the Rudnia River and Narew River in 2006

Parameter	Restored part of the Rudnia River		Regulated part of the Rudnia River		Narew River	
	Average	Range	Average	Range	Average	Range
Temperature, °C	12.4	0.1–22.1	10.0	0.1–20.8	11.7	0.2–21.4
pH	6.98	6.88–8.28	7.05	6.98–8.25	7.14	6.88–8.30
Conductivity, $\mu\text{S}\cdot\text{cm}^{-1}$	476	386–594	512	348–623	384	288–445
Oxygen saturation, %	88	53–153	86	32–128	91	35–143
DOC, $\text{mg}\cdot\text{dm}^{-3}$	12.1	4.1–22.8	13.1	7.7–26.5	13.9	7.0–22.0
SUVA, $\text{m}^3\cdot\text{g}\cdot\text{C}^{-1}\cdot\text{m}^{-1}$	37	17–104	36	13–62	35	19–60
TN, $\text{mg}\cdot\text{dm}^{-3}$	2.62	0.98–7.65	3.01	1.08–8.25	2.30	1.24–2.99
TON, $\text{mg}\cdot\text{dm}^{-3}$	1.81	0.03–6.97	1.71	0.31–6.48	1.49	0.17–2.47
TIN, $\text{mg}\cdot\text{dm}^{-3}$	0.81	0.18–2.32	1.31	0.48–3.82	0.77	0.23–1.88
TP, $\text{mg}\cdot\text{dm}^{-3}$	0.17	0.07–0.99	0.25	0.08–0.95	0.16	0.08–0.23

DOC – dissolved organic carbon; SUVA – specific UV absorbance; TN – total nitrogen; TON – total organic nitrogen; TIN – total inorganic nitrogen, TP – total phosphorus.

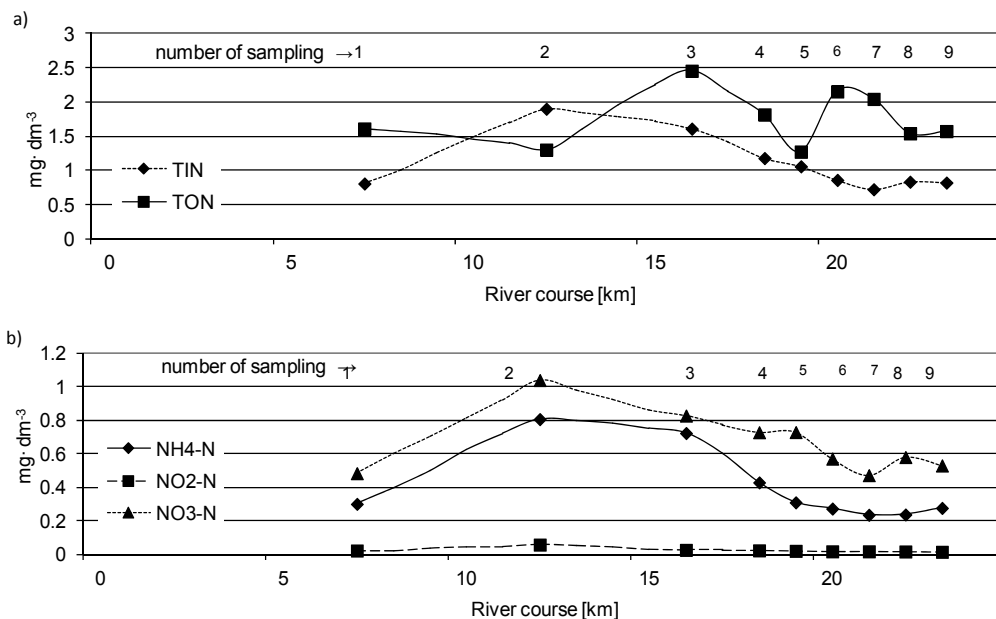


Fig. 3. Concentrations of nitrogen forms along the Rudnia River course – last 4 km constitute restored part of the river (mean values 2006): a) mineral and organic nitrogen; b) mineral nitrogen forms

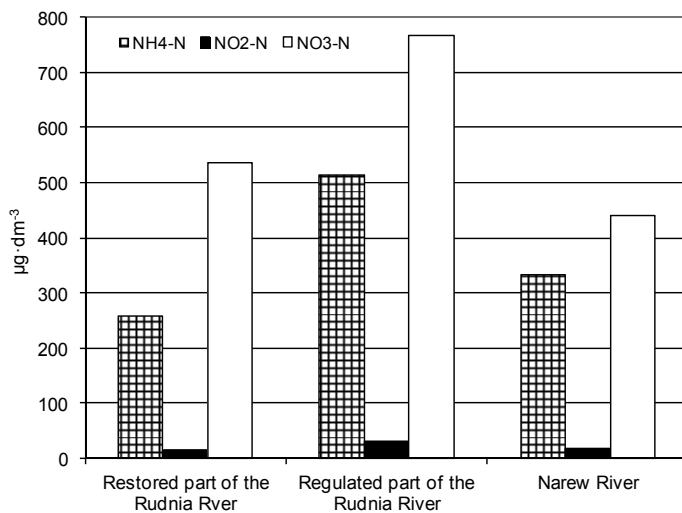


Fig. 4. Mean concentrations of mineral nitrogen forms in the Rudnia and Narew Rivers in 2006

A statistically significant decrease in concentration of mineral nitrogen was found in the restored section of the studied river (Fig. 3). Concentrations of organic nitrogen within the restored section increased, while a decrease was observed around the river's

mouth (Fig. 3a). Among mineral nitrogen forms, the concentrations of nitrites and nitrates were significantly lower in the restored section (Fig. 3b). Only the mean concentration of nitrates along the river course did not show significant statistical differences ($p = 0.274$).

Lower levels of total and mineral nitrogen were found in the restored river section. Mean organic nitrogen concentration in the restored part was slightly higher than in the regulated fragment of the same river (Table 1). Of the mineral nitrogen forms, the least ammonium ion concentrations were recorded in the restored section (Fig. 4).

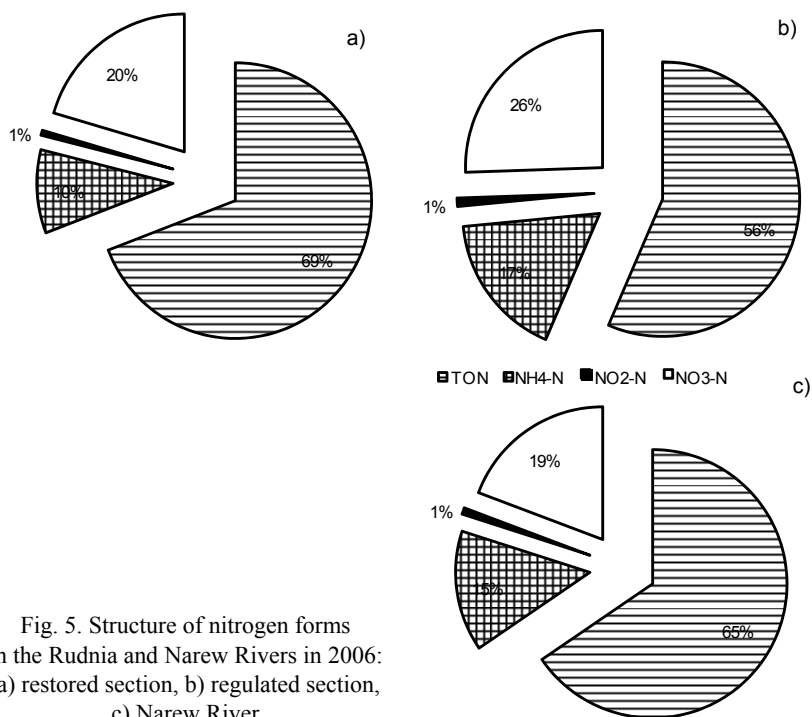


Fig. 5. Structure of nitrogen forms in the Rudnia and Narew Rivers in 2006: a) restored section, b) regulated section, c) Narew River

In the analyzed water from the restored part of the river, the total organic nitrogen (TON) made up almost 70% of the total nitrogen pool, and only 56% in the regulated section. In the water of the Narew River (as the background), total organic nitrogen made up 66% of the total nitrogen pool (Fig. 5).

The seasonal dynamics of concentrations of nitrogen forms at the studied sites showed statistically significant differences. Only similar levels of mineral nitrogen forms were found. Nitrate concentrations have increased in the Rudnia River since spring. The highest mean values for this parameter were recorded in winter time. Similar mean nitrate concentrations were recorded in the Narew River in spring and winter (Fig. 6a).

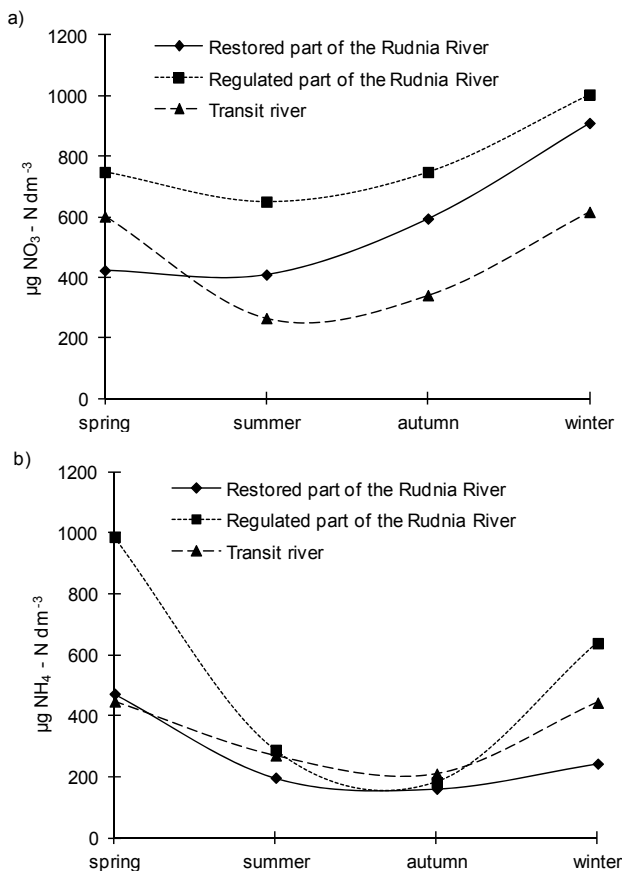


Fig. 6. Seasonal mean values of selected nitrogen forms in the Rudnia and Narew Rivers in 2006: a) nitrates; b) ammonium

Seasonal variability of ammonium also showed similarity at the studied measurement stations (Fig. 6b). The lowest mean concentrations of NH₄-N were recorded at the end of summer and the beginning of autumn. The largest variability in ammonium ion concentration was recorded between points in the regulated river section. Organic nitrogen forms varied not uniformly at the studied points. The highest concentrations of TON in the Rudnia River were observed in summer, whereas peak concentrations in the Narew River occurred in autumn. Seasonal variations in TON were highest in the restored section of the river with coefficient of variation exceeding 70%.

4. DISCUSSION

Nitrogen is an important biogenic element which is present in all natural environments and is a significant component of the biosphere. Nitrogen atoms are incorpo-

rated into chemical compounds mainly as a result of biochemical processes involving microorganisms [13]. Decomposition of biomass produces inorganic nitrogen substances, mainly in a form of ammonium ions. In turn, ammonium is oxidized to nitrites(III) and nitrates(V), by *Nitrosomonas* and *Nitrobacter* bacteria, respectively, during nitrification processes. Under anaerobic conditions, denitrification processes may occur leading to nitrogen losses in aqueous environments [14] and a very active place for such processes is hypohoreic zone of the river [15].

Recorded concentrations of nitrogen forms in the water of studied rivers were relatively low compared with other rivers from that region [16] but typical of rivers flowing through extensive agricultural areas of North-Eastern Poland.

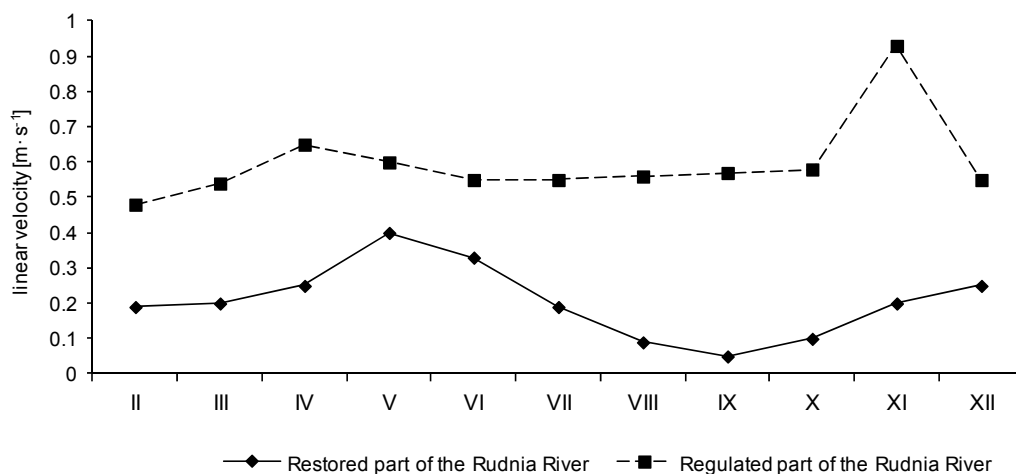


Fig. 7. Annual dynamics of water flow rates in regulated and restored parts of the Rudnia River in 2006

Obtained mean annual concentrations of total nitrogen (TN) in the investigated river sections did not show statistically significant differences (Table 1). Significant differences were found for mineral nitrogen contents between the regulated and restored part of the RR (Table 1, Fig. 4), similar differences were noted for Olentangy River, Ohio, USA [17]. Among other mineral forms, the largest differences were recorded for nitrates, followed by ammonium. No differences were observed for nitrites. The difference between mean nitrate and ammonium levels resulted from various water flows, which determines the water retention in a river bed. The higher the retention time, the more intensive the nitrogen transformations occur, including losses by denitrification [14]. Within the restored part of the Rudnia River, the water flow throughout the year was consistently lower than in the regulated section (Fig. 7). This is due to intensive transformations of mineral nitrogen forms in the section of the river with a wider and better preserved, peaty floodplain (Fig. 3). Lower water flow also caused an overgrowth of macrophytes in the river bed which has created a very appar-

ent ecotone in the coastal zone. This acts as a buffer for biogens supplied to the river bed. Plants growing in the ecotone zone uptake large amounts of mineral nitrogen during their development. In the cooler seasons and during river bed rinsing due to high surface water flow (mainly in spring), it may supply considerable organic nitrogen loads. Relocation of the Rudnia River bed within the Narew catchment may be another reason for increasing organic nitrogen concentration in the restored section. Within the restored section, the Rudnia River flows through a peaty area of the Narew catchment running parallel to the main NR channel. Periodically organic sediments of which are an important source of organic matter [15], including nitrogen, reaching the surface water where lowering oxygen level [14]. In all types of fresh waters bottom sediments play crucial role in nitrogen circulation [1]. This is confirmed by a significant correlation between mean organic nitrogen concentrations within restored section and mean water temperature ($r = 0.543$, $p < 0.05$) as well as mean organic nitrogen concentrations and mean POC levels ($r = 0.504$, $p < 0.05$). This observation was not recorded at other sampling points. N loss may be due primarily to the high organic matter content of the soil and its ability to mineralize N [18].

In the regulated river section, a significant relation has been found between mineral nitrogen forms and other ions, and reflexes typically agricultural catchment coverage [19]. This is confirmed by the statistically significant coefficients of linear correlation between TIN vs. Na, K, Cl, and P concentrations (Table 2). A similar relationship between N and P was observed by Smith et al. [2]. These elements are basic components of mineral fertilizers used in agriculture. Despite extensive agricultural use in the upper and middle sections of RR, a major pool of nitrates and ammonium in the regulated section of the river has a natural, catchment origin. The gradient is the largest one in this part of the catchment, which increases the possibility for surface runoff during rainfall events. In the northern part of the catchment, impermeable geology and a loamy soil structure [7] also increases surface runoff. Another factor responsible for rapid surface runoff in this catchment is the considerable surface tension of the first water-carrying layer within the regulated section of the river [7]. Dissolved ion loads are transported within the catchment water.

Concentrations of different forms of nitrogen in the water are characterized by considerable temporal oscillations, even in a short term scale [20]. In summer, due to intensive algae and macrophytes growth, a significant decrease in nitrogen concentration in the water may occur. This relationship was most obvious in the Narew River, where summer concentrations of ammonium were much lower than for the rest of the year (Fig. 6b). There may be establishment of riparian vegetation that will take up nitrate and contribute to the soil organic matter pool, and floodwater that will inundate the riparian zone leading to anaerobiosis [15, 21]. In the winter, the nitrate amounts in all zones apparently increased, which may be associated with their lack of utilization by plankton organisms (Fig. 6a). Despite the difference between mean nitrate concentrations during the year at the measurement sites, the general trend was similar.

Ammonium nitrogen present in surface water usually originates from the biochemical decomposition of organic nitrogen forms contained in plants and animals such as proteins, and its decomposition products, urea, etc. Its high concentration in the winter-spring period is associated with the whole-year ammonification process [22, 23].

Table 2

Statistically significant dependences (Spearman's linear correlation coefficient) between nitrogen forms and water quality features in the restored and regulated parts of the Rudnia and Narew Rivers in 2006

Parameter	Restored part of the Rudnia River (n = 30)		Regulated part of the Rudnia River (n = 44)		Narew River (n = 8)	
	TIN	TON	TIN	TON	TIN	TON
pH	-0.55 ^a	0.54 ^a	–	–	–	–
Temperature	–	–	–	–	-0.53 ^a	–
Conductivity	–	-0.54 ^a	–	–	–	–
Oxygen saturation	–	–	–	–	–	0.78 ^a
HCO ₃ ⁻	–	–	–	–	0.62 ^a	–
Ca ²⁺	–	–	–	–	0.52 ^a	–
Na ⁺	–	–	0.63 ^b	–	0.82 ^a	–
K ⁺	–	–	0.67 ^c	–	0.80 ^a	–
DOC	-0.53 ^a	–	–	–	-0.66 ^a	–
POC	–	0.50 ^a	–	–	0.66 ^a	-0.56 ^a
Cl ⁻	0.51 ^a	–	0.57 ^c	–	0.82 ^a	–
SiO ₂	–	–	–	–	-0.81 ^a	0.56 ^a
SRP	–	–	0.66 ^c	–	0.69 ^a	–
TP	0.58 ^c	–	0.69 ^c	–	0.64 ^a	-0.51 ^a

^aSignificant at the 0.05 probability level.

^bSignificant at the 0.01 probability level.

^cSignificant at the 0.005 probability level.

DOC – dissolved organic carbon, POC – particulate organic carbon, SRP – soluble reactive phosphorus, TP- total phosphorus.

Seasonal TON changes at the analyzed sections of the river varied due to differences in the catchment character and its management. In the Narew River, concentrations of organic nitrogen showed a sinusoidal trend as a consequence of nitrogen circulation within the catchment and river bed functioning. Increased spring concentrations should be associated with a catchment, allochthonous supplies. Minimal levels in summer are caused by an intensification of the mineralization processes as a result of increased water temperatures. In contrast, increased TON concentrations in autumn are the result of the decay of organisms remains in the river bed;

allochthonic nitrogen sources do not contribute significantly during the autumn. The decrease in TON in winter is related to the ammonification of organic nitrogen [22]. High TON concentrations were recorded in the Rudnia River in summer. Seasonal dynamics of organic nitrogen concentrations in water is a good indicator of the river bed transformation (Fig. 8).

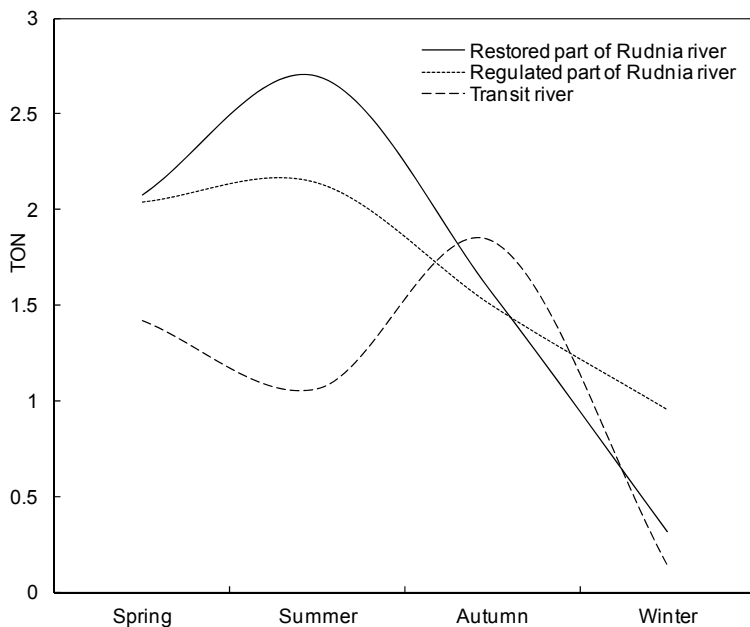


Fig. 8. Seasonal variability of TON concentrations ($\text{mg}\cdot\text{dm}^{-3}$) in restored, regulated parts of the Rudnia River and transit Narew River (cf. Fig. 1)

The calculated molar ratio of particular nitrogen forms may reflect a river's hydrological character. In restored rivers, the organic to mineral nitrogen ratio (TON/TIN) greatly exceeds the value of 2.24, whereas in the seminatural Narew River, the ratio is 1.81, and in the anthropogenically regulated part of the Rudnia River it is only 1.3. Much higher ratio values were observed in small forest streams in the North-Podlaska Lowland as a result of the catchments' afforestation [24]. The high TON/TIN ratio in the outlet of the Rudnia River results from the valley and river bed hydrogeological structure, as well as from the intensity of biogeochemical transformations occurring in water. In the restored part of the river, the $\text{NH}_4^+/\text{NO}_3^-$ ratio was the lowest and amounted to about 0.5, whereas the value of approximately 0.7 was observed at the other measurement points. The molar ratio of nitrates(V) to nitrites(III) did not significantly differ along the river course and remained 0.03–0.04 at all sampling sites.

Changes of studied parameters greatly depended on the river's hydrogeological regime [19, 22]. The water flow rate determining the water retention time in river

channel seems to be the most important hydrological feature that affects the concentrations of nitrogen forms and their variations. Greater water retention in the river channel leads to intensive nitrification, the effect of which are lower $\text{NH}_4\text{-N}$ concentrations in water. Decreasing the water flow makes the water body more stable, which leads to increased plankton organism numbers and the creation of a wide ecotone zone [25]. Population of larger microorganisms is responsible for an intensive utilization of mineral nitrogen forms dissolved in the water. Nitrates are the most important nitrogen source for green plants. Preferential nitrate intake is metabolically proven. Nitrates regulate the activities of assimilation enzymes.

5. CONCLUSIONS

- Recorded concentrations of various nitrogen forms in studied river water were relatively low as compared to other rivers from that region, being typical of those flowing through extensively performed agricultural areas of North-Eastern Poland.

- Significant decrease of mineral nitrogen concentrations was found in restored section of the Rudnia River. Mean organic nitrogen concentration at the restored part was slightly higher than in the regulated part.

- Present study indicates an important role of TON in river biogeochemistry. Seasonal dynamics of TON content in the running water can be a good indicator of condition of the river channel and the level of its transformation.

- The ratio of TON to TIN concentrations may characterize many biogeochemical processes occurring in the river channel and ecotones.

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