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Identification of catchment areas with nitrogen pollution risk for lowland river water quality

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Abstract: The article presents the results of research aimed at determining the catchment areas that pose a risk of nitrogen pollution of the waters of the Mała Panew river. The research was carried out in 13 permanent monitoring points located on the Mała Panew. The location of the points ensured the representativeness of the water quality results for parts of the catchment area with a homogeneous type of land use. Concentrations of nitrate-nitrogen (NO_3-N) and total nitrogen (TN) were determined in the samples taken. The content of (NO_3-N) in the third quarter of the year and its relation to the value obtained for the first year quarter may be an indicator of the impact of agricultural activities on the quality of water in streams. In the case of agricultural catchments, the lowest concentrations of NO_3-N and TN occur in the third quarter of the year and are significantly lower than in the first quarter of the year. The demonstrated seasonal variability of nitrate nitrogen concentrations in agriculturally used areas may be used to determine the type of pressure not allowing to achieve good water status in the surface water body. It was shown that the highest unit increments occurred in areas with a high proportion of forest.

Introduction

One of the main causes of terrestrial water quality degradation is the introduction of intensive agricultural practices (nutrient runoff from agricultural fields, intensive livestock rearing) and urban development (pollution by municipal and industrial wastewater) (Grizetti 2017, Sutton et al. 2011). Eutrophication caused by the increase in the content of nitrogen and other nutrients, its harmfulness to aquatic ecosystems has become one of the key problems of society (Poikane 2019, Grizetti 2021, Wiatkowski 2013). It is believed that an effective approach to preventing river pollution is to control nutrient pollution by, inter alia, controlling the loads of these pollutants entering the water.

The physicochemical properties of water in rivers are influenced by many factors, e.g., landscape, land development, functioning of hydrotechnical devices, presence of natural lakes or artificial anthropogenic water reservoirs in the catchment area (Bo et al. 2018, Pohl and Kostecki 2020, Tomczyk and Wiatkowski 2020, Tomczyk and Wiatkowski 2021, Kostecki 2021, Mazierski and Kostecki 2021). The influence of agricultural areas on the quality of surface waters is quite complex and, as research shows, it is not obvious (Sliva and Williams 2001). As a result of fertilization, nutrients flow into water bodies and may contribute to the formation of river pollution (Hus and Pulikowski 2011, Wiatkowski 2015). An important source of surface water pollution may also be poorly functioning individual household water treatment plants, in particular in the areas of communes with a high percentage of such installations and communes with a low percentage of sewerage (Kurek et al. 2019, Micek et al. 2021). The source of nutrients is mainly runoff from agricultural land or point pollution of domestic wastewater (Gruss et al. 2021, Hus and Pulikowski 2011, Pulikowski et al. 2012), however, rivers have effective mechanisms and a high self-cleaning potential (Bian et al. 2019, Shi et al. 2019). The analyzes results showed a significant relationship between land use and water quality in the stream, especially in the case of nitrogen (Yong and Chen 2002). As part of the diagnostic monitoring of Polish rivers, it was found that almost 90% of them have poor water conditions, and agriculture is responsible for 45% of nitrogen discharged by Polish rivers to the Baltic Sea (Helcom 2018, Environment 2020).

The Mała Panew is a secondary tributary of the Odra River. Due to the size of the river basin and its length, it is classified as a small river, however, its importance is significant as it flows through areas with strong anthropogenic influence (industrialized and agricultural areas) and at the same time strongly forested. The analysis of the influence of the way in which the Mała Panew catchment area is developed on the quality of the river's water is of considerable importance for the quality of water in the Turawa reservoir through which the Mała Panew flows. The Turawa reservoir is one of the two largest water reservoirs in the Opole region of strategic importance (flood control, recreation).

The aim of the study was to identify partial catchments that pose a risk of nitrogen pollution in the Mała Panew River. An attempt was made to classify the type of catchment use (agricultural/forestry) as a potential source of water pollution in the river. The hypothesis on the relationship between seasonal variability in the content of nitrogen compounds, especially in the form of nitrate, and agricultural use of the sub-catchment area was verified.

Materials and methods

The Mała Panew is a river whose total length is 131.8 km and it flows through the provinces of Silesia (54 km) and (77.8 km). The river is divided by the Turawa reservoir into two separate sections with different hydrological and natural properties. Before the reservoir, the stream is close to natural, while downstream to the estuary of the Odra, flows are regulated as a result of water management carried out on the reservoir.

The Mała Panew is a right-bank tributary of the Odra river. It begins in the vicinity of the village of Markowice in the Silesian province, Myszków district, draining the gentle and forestless slope of the Woźnicki Progress lying in the Silesian Upland. Below the Woźnicki Threshold it flows out onto a flat plain covered with pine forests. The left-bank watershed runs along a flat area made of sandy Quaternary formations. This can be one of the factors contributing to the release of pollutants into the aquatic environment. The river network is intricate with numerous connections of watercourses with other catchments (Hydrographic classification of Poland 1983). The catchment of the Mała Panew is 2132 km^2. The article analyzes the catchment of the Mała Panew river upstream the Turawa reservoir (until the backwater point of reservoir). This area is 1220 km^2, and the length of this river is 86 km. The catchment area is agricultural and forestry. A significant part of it is covered by mixed forests, in the upper and middle flow reaching the very banks of the river, the forest cover to the Turawa reservoir is about 67%. Grasslands cover over 11% of the catchment. Sparse afforestation in the marginal zones of the catchment in the areas of predominantly agricultural use pose a threat to surface and ground waters. The river network in the Mała Panew catchment is characterized by quite significant diversification in terms of water abundance. The largest volumes of water are carried by the Mała Panew itself and its longest tributaries: the Dubielski Potok, the Zimna Woda, the Lublinica, the Bziniczka, the Myślina, the Stoła, and the Bziczka. There is also an extensive network of ditches in the catchment which carry water periodically, after the spring thaw and during prolonged rainfall. In the middle reaches of the section, above the Turawa reservoir, the river flows largely through urbanized areas where production facilities have been located in Kalety, Kielcza and Jedlina. The Mała Panew river is also the main source of water for the Turawa Reservoir, which significantly affects the quality of its waters (Wiatkowski and Wiatkowska 2019) (Fig. 1).

The material for the study was water samples from the Mała Panew river collected at permanent monitoring points. The study was conducted from May 2019 to April 2021 at the following measurement points (A, B, C, D, E, F, G, H, I, J, K, L, M,) (Fig. 2).

The location of the sample points was determined on the basis of spatial land use analysis based on cartographic materials (Topographic Object Database 2015). Their location ensured representativeness of water quality results for fragments of the catchment with homogenous land use type. In the northern part of the catchment, with forest character and low land-use variability, monitoring points were located at longer distances from each other. In parts of the catchment with high dynamics of variability and high concentration of potential sources of pollution, there were more monitoring points, which allows us

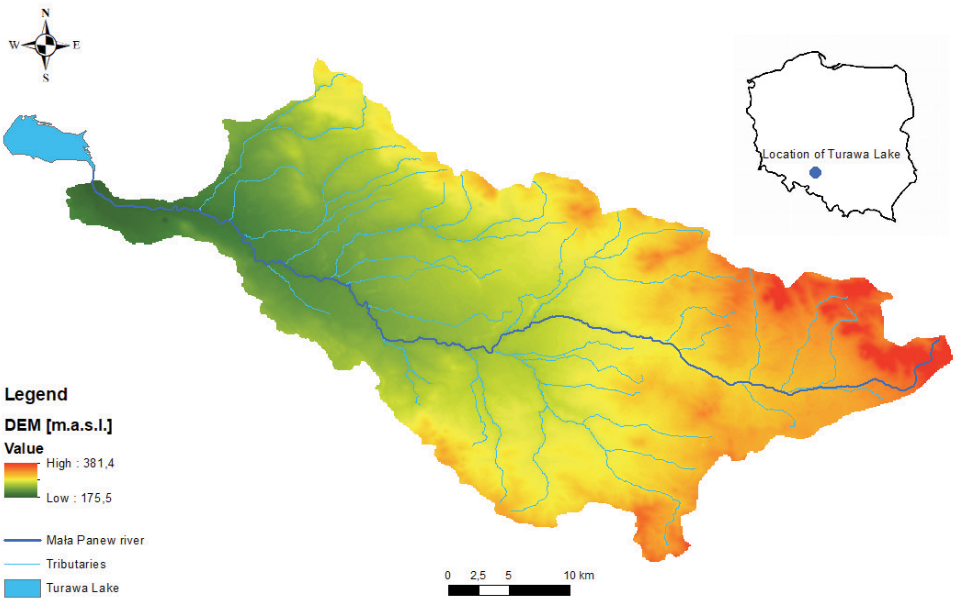

Fig. 1. Digital elevation model of research catchment, river network and location of Mała Panew catchment in Poland

to capture the dynamics of changes in water quality of the Mała Panew river. Next of the four categories was assigned to each sample points taking into account the topographic map of the catchment (Tab.1). On this basis, an agricultural section (H, I, J, K and L), a forest section (D, E, F), a headwater section (M) and an estuarine section (A) were identified, whereas the results obtained for sample points B, C and G did not allow us to assign them to separate groups or create another one.

To determine the loads of pollutants in the water of the Mała Panew river, the mean flow of the multi-year Q (m^3/s) was determined. The flow rate is derived from the linear velocity of the watercourse, and it is this rate that determines the load of pollutants carried away. On the Mała Panew river there are three water gauges: Turawa, Staniszcze Wielkie, and Krupski Młyn. The catchment areas in these three water gauge sections change as follows: 1.424 km^2; 1.101 km^2; 667 km^2. For each station, the Q from the multi-year period of 1971–2019 was determined. The data were obtained from the Institute of Meteorology and Water Management – National Research Institute and were processed. The interpolation and extrapolation methods were used to determine Q for the sample points. The catchments of sample points were determined in the Mała Panew river above the Turawa reservoir. Sample points have ungauged catchments. On the one hand, when the sample point was located above or below to the water gauge, the extrapolation method was used. On the other hand, the

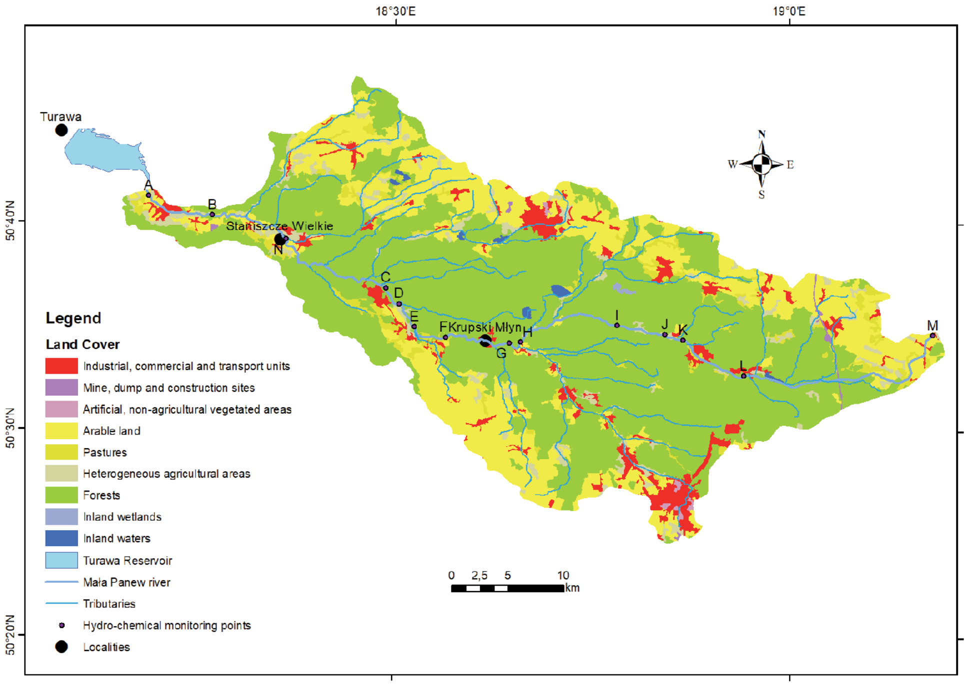

Fig. 2. Catchment area management and location of measurement points

Table 1. Division of the Mała Panew catchment into areas

Number of sample	NO_3-N			TN			Character of the area
	summer	winter	year	summer	winter	year	
A	E	E	E	E	E	E	E
B	E	F	–	E	F	–	E/F
C	F	E	E	F	E	E	E/F
D	F	F	F	F	–	F	F
E	F	F	F	F	–	F	F
F	F	F	A	F	F	A	F
G	F	F	A	A	F	A	F/A
H	A	A	A	A	A	A	A
I	A	A	A	A	A	A	A
J	A	A	A	A	A	A	A
K	A	A	A	A	A	A	A
L	A	A	A	A	A	A	A
M	H	F	D	H	H	D	H

E – estuarial, F – forestry, A – agricultural, H – headwaters of a river, D – difficult to qualify interpolation method was used when the sample point was between water gauge sample points located on the same stream (Banasik et al. 2017).

Water samples were taken at a frequency of once a month (12 times a year, for two years). The frequency at which water samples were taken was considered sufficient due to the relatively good water quality record for this river. This methodology is applied in intensive monitoring points by Inspection for Environmental Protection in Poland. There are opinions that indicate the benefits of increasing the frequency of control measurements even to 24 per year (Loga et al. 2018). A large number of analyses carried out at the same cross--section over a longer period reflect the water quality status in the catchment located upstream of the cross-section quite well. Such methodology is commonly used in water monitoring studies and it is assumed that such a result is representative for the entire surface water body or groundwater body.

Water samples were analyzed in the Wrocław Branch Laboratory of the Institute of Technology and Life Sciences – National Research Institute. Nitrate nitrogen (NO_3-N) was determined in the studied samples by the indophenol colourimetric method preceded by distillation separation of ammonia (PN-82C-04576/08). Total nitrogen (TN) was calculated as the sum of nitrate nitrogen and total nitrogen according to Kjeldahl nitrogen determined by the indophenol colorimetric method.

The obtained results were subjected to statistical analysis. In order to identify river sections characterized by similar dynamics of changes in concentration of the analyzed nitrogen compounds, an attempt was made to group the measurement sample points.

For this purpose, cluster analysis was performed using Ward's method with the Euclidean distance as the criterion. One-way analysis of variance was performed to determine the significance of the differences between concentrations of these nitrogen forms depending on the adopted nature of the catchment section. Differences for which the significance level is less than 0.05 were considered significant. Calculations were performed with the use of the STATISTICA 13.3 package. On this basis, a possible method for distinguishing areas characterized by pollution with nitrogen compounds originating from agricultural activities was indicated.

Results

Mean annual nitrate nitrogen (NO_3-N) concentrations in the studied sample points ranged from 1.37 mg/dm³ in sample points H, to 4.20 mg/dm³ (D). The analysis showed a clear tendency for changes in average quarterly concentrations of nitrate nitrogen at points G, H, I, J, K, L (these are the areas where agricultural land use prevails), whereas the values of concentrations in the 3rd quarter of the year are clearly lower than in the remaining periods (Fig.3.) and vary from 0.50 mg/dm³ at point L to 1.49 mg/dm³ at point G. During the vegetation season, the mineral reserves supplied to the soil in spring are largely used up. As a result, the content of mineral nutrients in soil and their outflow to waters decreases. At the same time, these sample points have significantly lower concentrations of nitrate nitrogen than the remaining monitoring points. Thus, the conducted research has not confirmed the often-heard opinion that agriculture is the main source of nitrate pollution of rivers (HELCOM 2018), while it indicated the seasonal dynamics of concentrations of this nitrogen form. The highest quarterly mean value of nitrate nitrogen concentration was recorded at the monitoring point E (4.89 mg/dm³). In the vast majority of monitoring points, higher mean values occurred in the 1st or 4th year quarter. At the remaining sample points (in areas of non-agricultural land use) no such clear seasonal dependencies of nitrate nitrogen concentration changes in the waters of the Mała Panew river were found, and their values were definitely higher (on average two times higher than in agricultural areas).

Analyzing the mean content of TN in the discussed sample points (Fig. 4), it is clearly visible that the seasonal variability is similar to that in the case of nitrate nitrogen (Fig. 3). This is due to a significant share of this nitrogen

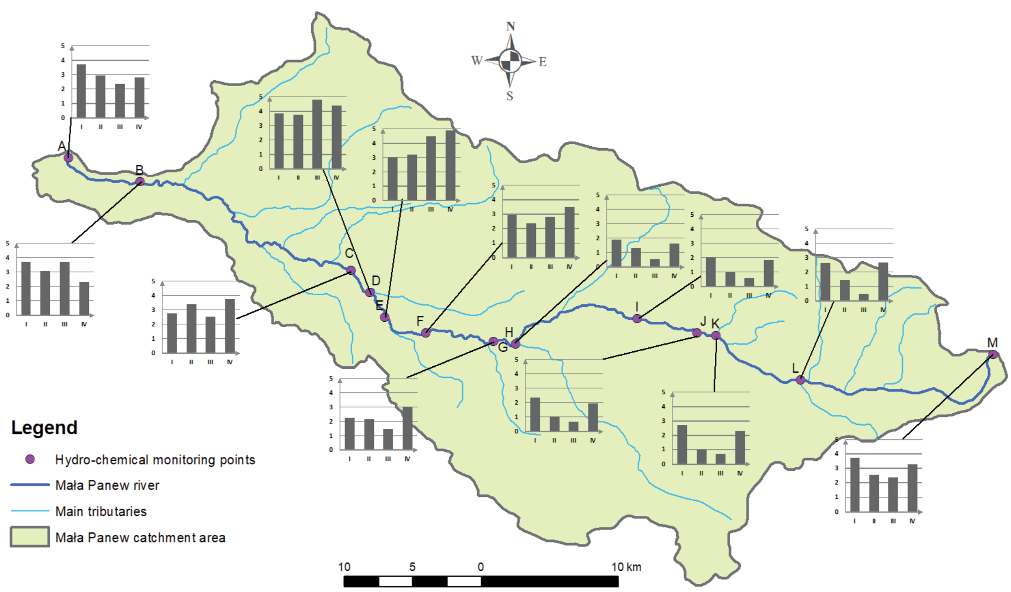

Fig. 3. Average quarterly values of nitrate nitrogen (NO_3-N) concentrations at selected hydrochemical sample points

form in TN. Mean annual TN concentrations ranged from 3.83 mg/dm³ at points H and I to 8.94 mg/dm³ at point D. For monitoring points located in areas of agricultural character (Tab. 1) the average value of TN concentration in the study period was 4.25 mg/dm³, while for the remaining areas – 6.96 mg/dm³. The summer period from 7th to 9th month (3rd quarter of the year) is the period when nitrogen pollution of the Mała Panew waters is the lowest. The large loss of mineral forms, mainly NO_3-N, is due to the intensive uptake by crops and low water outflow, and thus to the minimized supply of these compounds to river waters. Such a situation occurred in 10 out of 13 monitoring points. These were both at points located in agricultural areas (G, H, I, J, K, L) and at some other hydrochemical sample points (A, C, F, M). In waters of the investigated river, definitely higher concentrations of TN occurred in the 1st and 4th quarter. Only at point D the maximum occurred in the 3rd year quarter.

In the case of area-based pollution, several factors are assumed to increase the pollution, e.g., increase of nitrogen compounds in watercourses, changes in land use, increase in the share of urban areas, and finally, the activation of pollution deposits resulting from, e.g., atmospheric phenomena (heavy precipitation causing leaching of components or increase in groundwater level) or incorrect decisions resulting from land use transformation. Taking action to prevent the deterioration of water quality requires the correct identification of the factor responsible for the adverse changes. In the case of area-based pollution, there is a supposition of several factors causing an increase in pollution, e.g., an increase in nitrogen compounds in the streams. Taking action to prevent a deterioration in water quality requires the correct identification of the factor responsible for the adverse change.

In assessing the impact of agriculturally used areas on water pollution with nitrogen compounds (especially the nitrate form), it is very important to take into account the seasonality of this phenomenon, which poses a threat in the first quarter of the year (even before the start of the growing season and field work) and practically disappears in summer. Early outflow accumulations should rather be associated with a long post-vegetation period of accumulation of soluble nitrogen from nitrogen in soil profile than with direct nitrogen supply in the form of spring crop fertilization. Counteracting nitrogen runoff should consist in reducing as much as possible the period during which the soil is left without plant cover and minimizing runoff in early spring only to the extent necessary to carry out field work.

Based on studies on nitrogen content at 13 measurement sample points (hydrochemical) located in the Mała Panew river, an attempt was made to identify sections with different dynamics of nitrate and TN concentrations. Analysis of quarterly values (Figs. 3 and 4) suggested performing this procedure for the following periods: summer half-year (IV–IX), winter half-year (X–III) and the whole year (Fig. 3). A detailed analysis of the obtained results was carried out based on the land use classification (based on the results of a baseline analysis allowing delineation of areas and interpretation of differences in nitrogen supply to the river) presented in Tab. 1. Preliminary analysis of the individual diagrams made it possible to distinguish four areas: estuarine, forest, agricultural and spring areas. With this assumption, the similarity between the areas was analyzed in six cases presented in Fig. 5. In some cases (especially for annual concentration values) the result did not allow for making a full classification, so these cases were identified as difficult to determine.

At this stage, they were classified as transitional E/F and F/A respectively (transition zones difficult to classify unambiguously and directly). Analysis of the obtained results and utilization of the catchment showed that intensive agricultural impact is still evident in sample points situated below in the forested area, and only in the next sample points the change of character from agricultural to forest is evident (Tab. 1). The most unambiguous separation of groups was obtained for nitrate nitrogen concentrations in the summer half-year (Fig. 5a).

The analysis allowed us to formulate a thesis that periodic dynamics of nitrate nitrogen (NO_3-N) concentration may

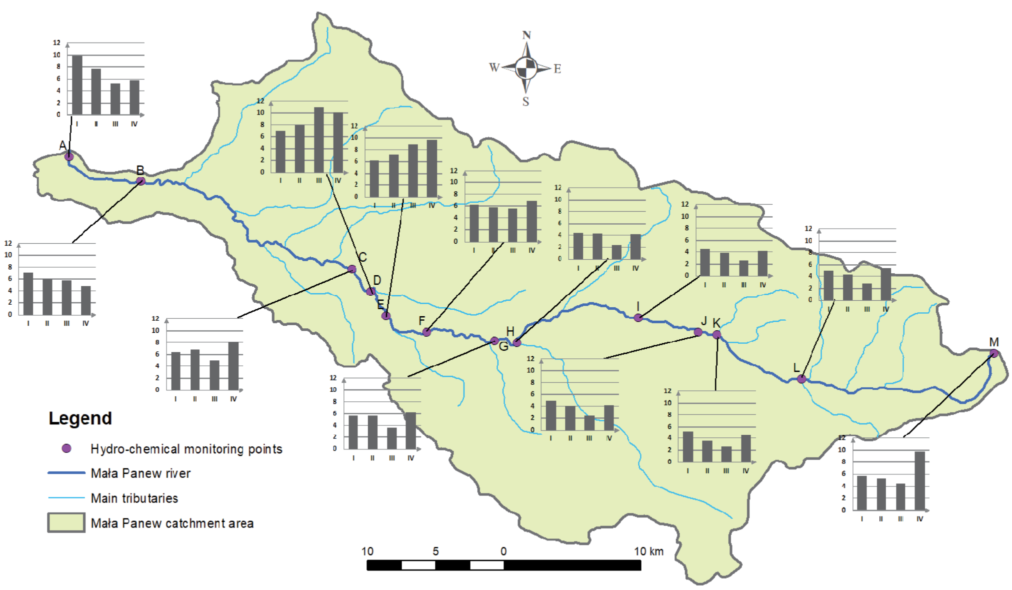

Fig. 4. Average quarterly values of TN concentrations in selected hydrochemical sample points

be useful for identification of streams sections where water quality is dependent on agricultural activity. The analysis comprised quarterly values of concentrations of both forms of nitrogen in four designated zones. Significance values of level of differences between nitrate nitrogen (NO_3-N) concentrations are presented in Tab. 2, while for TN – in Tab. 3. It is noteworthy that significant differences were obtained for the spring area, which clearly constitutes a distinct group (Fig. 5), but is also of agricultural character.

Figure 6 presents an analysis of the differences for the agricultural catchment and it can definitely be seen that the greatest, and significant, variation in concentration for both forms occurs between quarter1 and quarter 3 of the year. Significant differences were also obtained for nitrate nitrogen between quarter 1 and quarter 2. The concentration of both forms of nitrogen was always highest in the first year quarter. Figure 7 presents the results of the analyses for differences between quarter1 and quarter 3 for other section types. In the

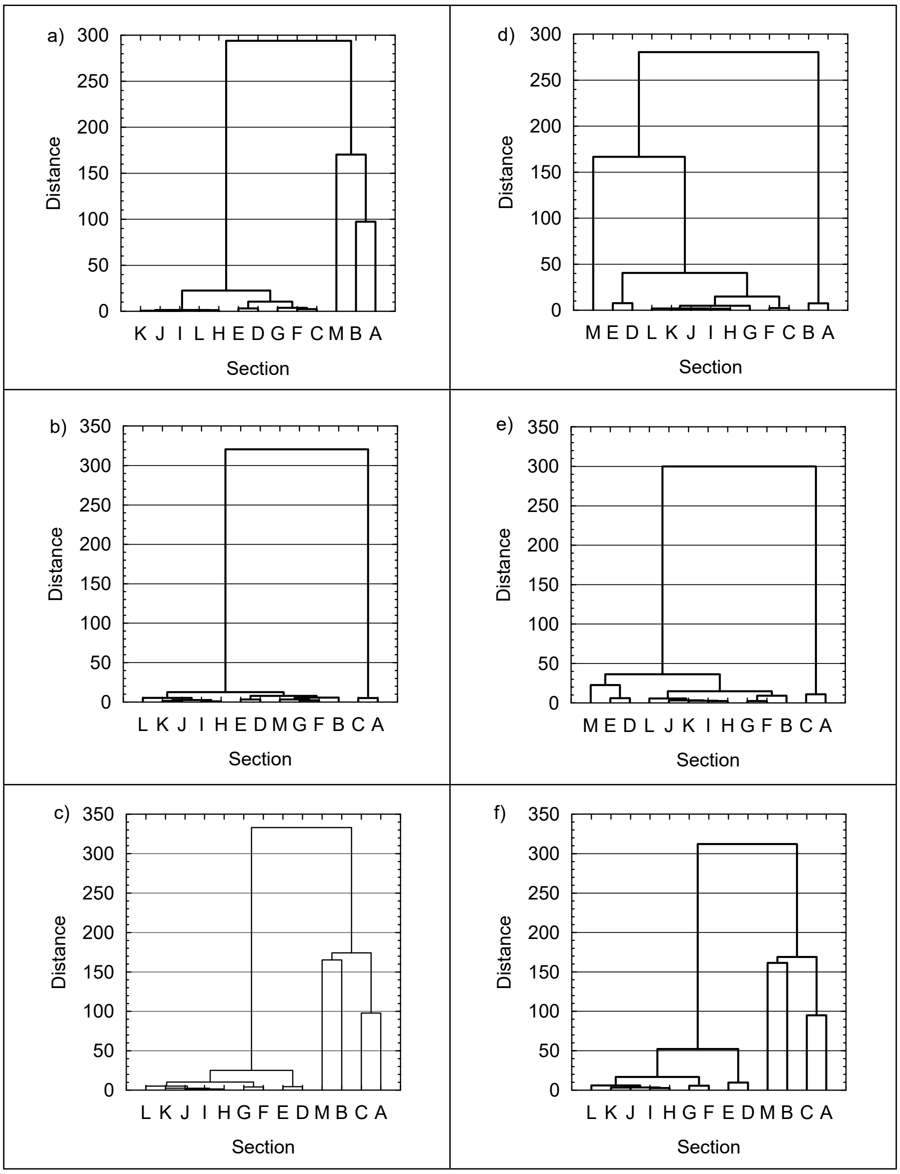

Fig. 5. Grouping of measurement sample points based on nitrate nitrogen concentration (NO_3-N) a) summer half-year, b) winter half-year, c) year; TN: d) summer half-year, e) winter half-year, f) year

Table 2. Significance of differences between nitrate nitrogen (NO_3-N) concentrations in quarter 1 of the year and subsequent quarters depending on nature of the catchment

Nature of section/quarter of the year	I–II	I–III	I–IV
estuarial	0.53828	0.16582	0.52830
forestry	0.69850	0.16178	0.02792
agricultural	0.00004	<0.00001	0.45637
headwaters of a river	0.03091	0.00404	0.46887

case of the estuary and forest sections, these differences are not significant, while they are significant for the headwater section, as it is also of agricultural character. It is worth noticing that there are different relations between values obtained for the forest area, where concentration in the 3rd quarter is higher than in the 1st quarter of the year.

The analysis indicates that a characteristic feature of streams sections fed by pollutants of agricultural origin is the concentration of nitrate nitrogen (NO_3-N) in the 3rd year quarter, which is significantly lower than in the 1st quarter. This is an indicator which allows for the identification of streams subjected to anthropopressure connected with agricultural use of the catchment. In order to confirm this thesis, values for the 3rd year quarter were analyzed and on their basis sample points were grouped (Fig.8). On the basis of this period, an unambiguous confirmation of the correctness of the adopted division based on semi-annual and annual values was obtained. The obtained results suggest that transitional areas may be

Table 3. Significance of differences between TN concentrations in quarter 1 and subsequent year quarters depending on nature of the catchment

Nature of section/quarter of the year	I–II	I–III	I–IV
estuarial	0.48457	0.11234	0.23072
forestry	0.63672	0.05259	0.01886
agricultural	0.05406	<0.00001	0.48410
headwaters of a river	0.48457	0.11234	0.01018

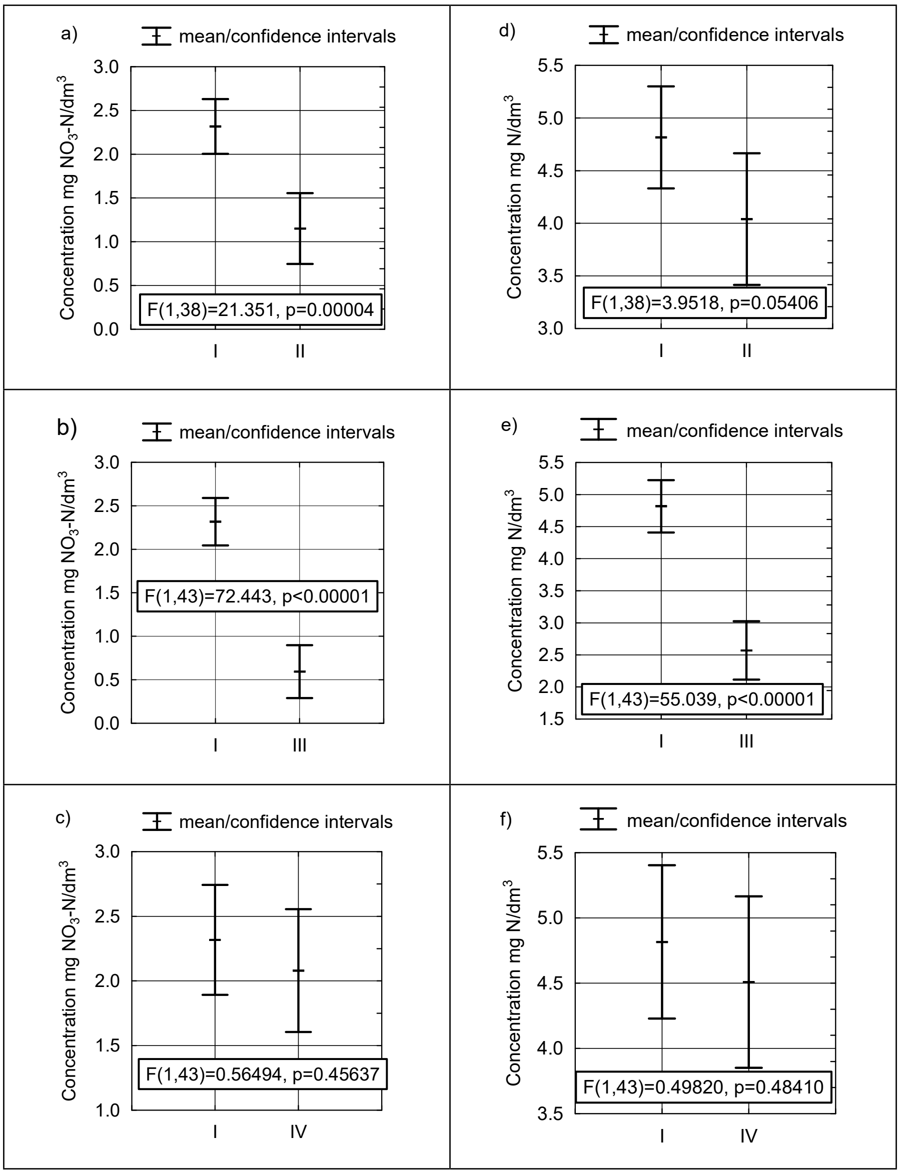

Fig. 6. Differences between concentrations in the first and consecutive quarters in sample points of agricultural character: nitrate nitrogen (NO_3-N): a) I–II, b) I–III, c) I–IV; TN: d) I–II, e) I–III, f) I–IV

eliminated. The area represented by sample points B (E/F – Estuarial/Forestry) is included in E, area C (E/F – Estuarial/ Forestry) in while area G (F/A – Forestry/Agricultural) in A.

Based on the determined mean annual flow and mean concentration values at the measurement sample points the loads of nitrate nitrogen flowing away with the waters of the Mała Panew river were calculated (Fig. 9). In the upper part of the catchment, which is a headwaters of a river section and an area with prevalent agricultural use, the load increase is small. In the sample points H – km 81.11 it amounts to 5.11 g

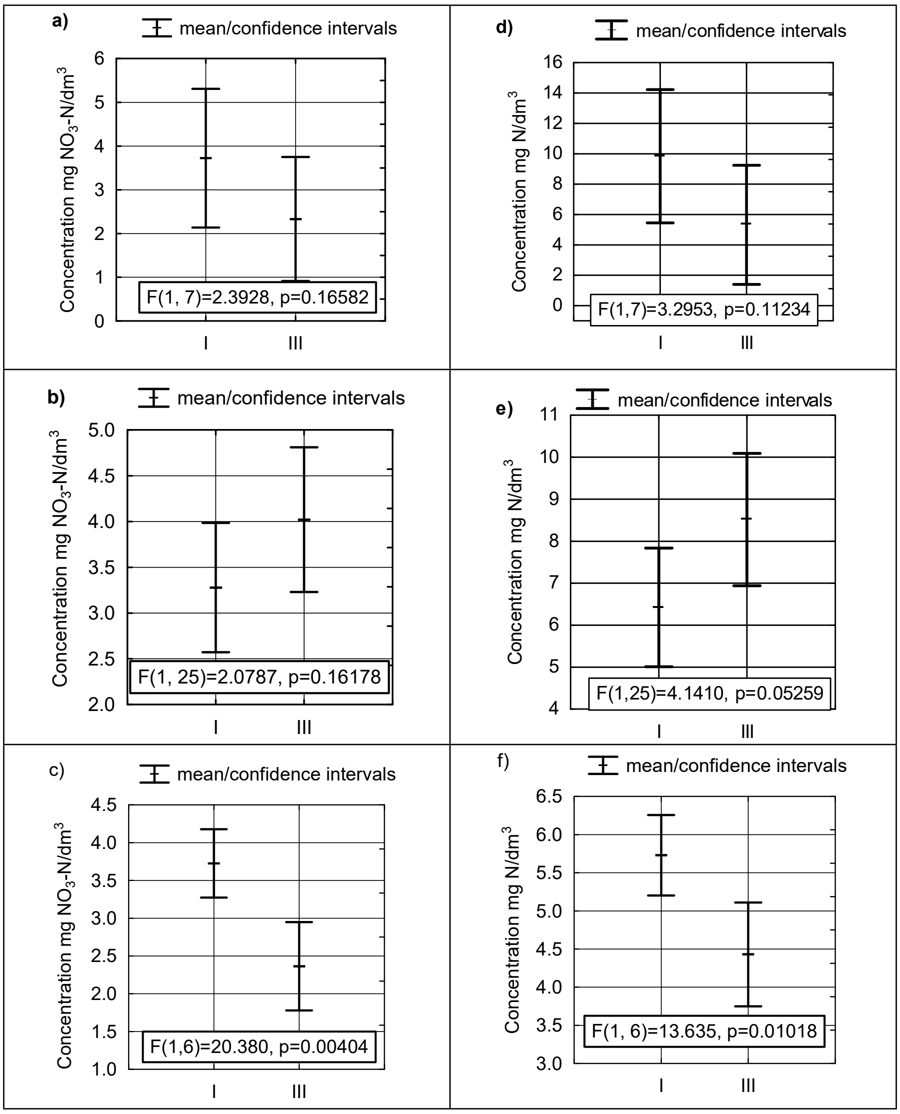

Fig. 7. Differences between first and third quarter concentrations in non-agricultural sample points: nitrate nitrogen (NO_3-N): a) estuarial, b)forestry, c) headwaters of a river; NT : d) estuarial, e) forestry, f) headwater of a river

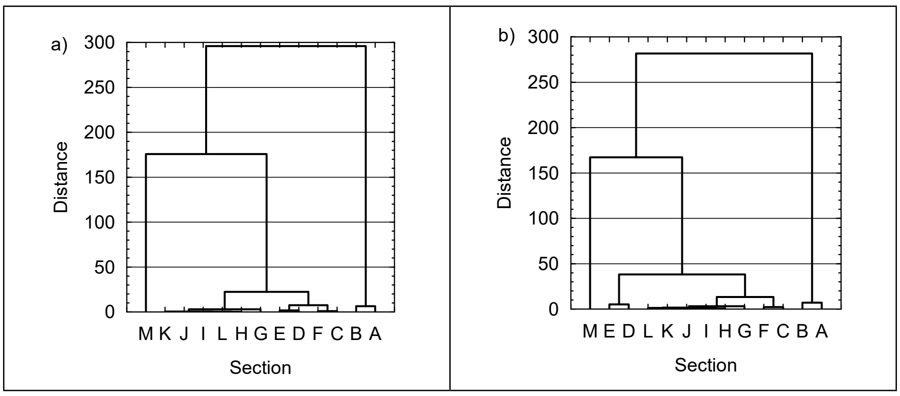

Fig. 8. Grouping of measurement sample points based on concentration in year quarter 3:
a) nitrate nitrogen (NO_3-N), b) TN

NO_3-N/s. Then, the river flows through areas with high share of forests – from sample points G to D (Fig. 10). Despite the fact that the increase in flow shows a nearly linear character, significant increases in concentration of this form of nitrogen in the studied sample points cause a large increase in the load, which in sample points D - km 63.36 reaches the value of 20.22 g NO_3-N/s. The values obtained show an almost 4-fold increase of the load in the forest area, while the flow increases only by about 1.00 m^3/s, i.e., approximately 25%. Further river course the dynamics of nitrate nitrogen loads discharged with the waters of the Mała Panew river do not show unidirectional trends. In order to better illustrate the dynamics of nitrate nitrogen loading, the obtained loading values were related to the surface area of the analyzed sub-catchments and the unit loading related to surface area was determined (Tab. 4). Without taking into account possible point sources, a large variation in this value can be seen, ranging from negative values to a maximum value of 1.54 mg/(km^2·s). Taking into account that there is a continuous increase in flow, this means that in some catchments (KJ, DC and BA – parts of the Mała Panew catchment defined as the differences of the sub--catchments at the measurement points) nitrogen loss through natural processes combined with low nitrogen inflow causes a decrease in the outflow nitrate nitrogen load. However, the highest values were obtained for the area classified as forest and on its border with agricultural land, which is confirmed by the absolute values of the load presented in Figure 9.

The study and analysis of the results showed that the highest unit increases in nitrate nitrogen loads occurred in areas with a high proportion of forests, which is due to the relatively high mean annual value of concentrations of this nitrogen form. Areas used for agricultural purposes are characterized by high maximum values of concentrations of this nitrogen form, usually in the first quarter of the year, but the average annual values reach low concentrations, due to very low values found in the third quarter.

Discussion

The annual average values and seasonal changes in concentrations of nitrate nitrogen (NO_3-N) and TN indices in river's water showed in the literature by other authors are diverse and fall within wide ranges. Gruss et al. (2021) showed that the mean concentrations of the nitrate nitrogen (NO_3-N) in the Mała Panew river above the Turawa reservoir was 2.59 mg/dm^3. They found that TN, nitrate nitrogen, and

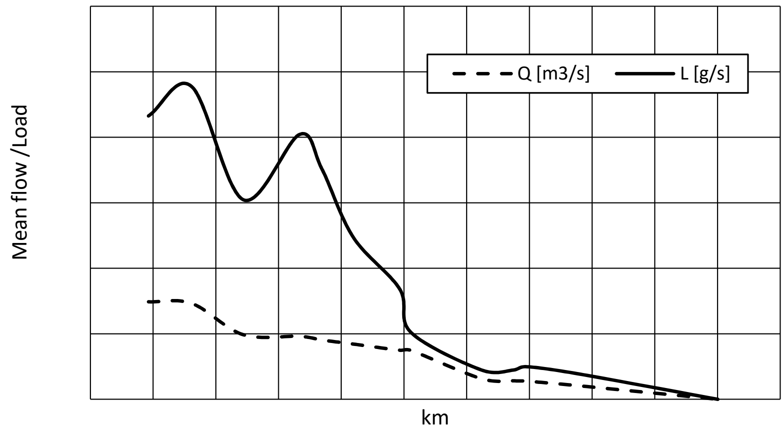

Fig. 9. Average multi-year flow and load of nitrate nitrogen and nitrate nitrogen removal

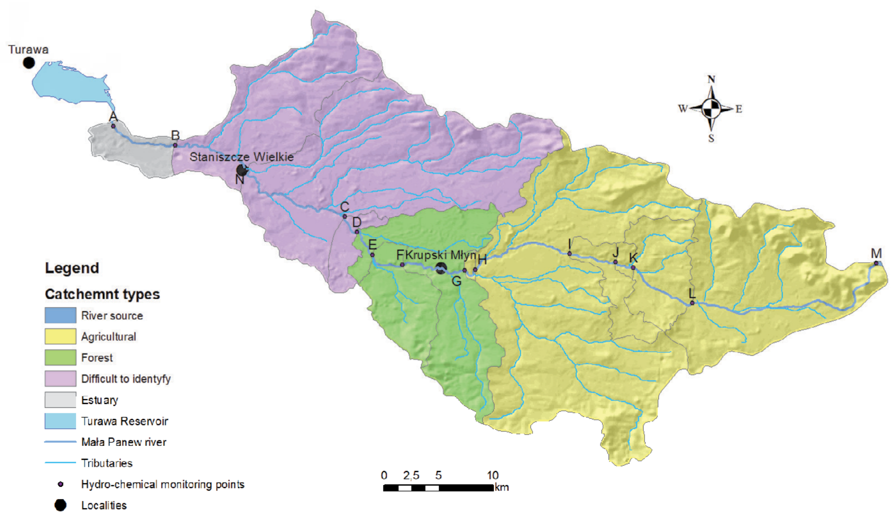

Fig. 10. Distinct areas characterising the dominant catchment use

Table 4. Unit outflow and unit load of nitrate nitrogen in parts of the sub-catchments of the Mała Panew designated at control points

Designation of area*	Character of area	Unit outflow $dm^3/km^2 \cdot s$	Unit load mg NO_3-N/ $km^2 \cdot s$
BA	E	4.96	-0.08738
CB	D	5.64	0.02178
DC	D	6.39	-0.28136
ED	F	6.39	0.05903
FE	F	6.39	0.10736
GF	F	4.17	0.05300
HG	A	6.28	1.54430
IH	A	6.25	0.00826
JI	A	6.23	0.00041
KJ	A	6.21	-0.05524
LK	A	6.10	0.00937
ML	A	5.81	0.01081
H	Q	5.35	0.01370

* parts of the Mała Panew catchment defined as the differences of the subcatchments at the measurement points

nitrite nitrogen concentrations were higher above the Turawa reservoir and decreased after passing through this reservoir. This may be due to better water oxygenation in the river than in the reservoir and more intensive nitrification process. Brysiewicz et al. (2019) report that the mean concentrations of nitrate nitrogen (NO_3-N) in the studied rivers were 2.023 and 7.321 mg/dm^3. The nitrate concentrations of the Szreniawa river waters, depending on the season, ranged from 0.13 to 13.46 mg/dm^3 (Kowalczyk and Kopacz 2019). The comparison of changes in seasonal values of pollution indicators in rivers showed that the highest concentrations of nitrate nitrogen were recorded in summer (Kowalczyk and Kopacz 2019, Żarnowiec et al. 2017, Kiryluk and Rauba 2009). Observed in our study the lowest pollution with nitrogen compounds occurred in the third quarter of the year in the parts of the catchment located at points of agricultural use. The large loss of mineral forms, mainly NO_3-N, should be attributed more to the intensive uptake by crops and low water outflow, and hence the minimized supply of these compounds to river waters, rather than to river smothering processes (associated with a change in the concentration of nitrogen compounds). On the other hand, Wilk et al. (2017) showed that the highest concentrations occurred in early spring, similar to our studies of the Mała Panew river waters. A long-term study (1958–2016) of nitrogen pollution of the Warta river showed a downward trend in the values of nitrogen compound concentrations as a result of more rational use of fertilizers after economic changes in Poland, but detailed analyses showed that agricultural activities are responsible for nitrogen pollution of the river waters (Górski et al. 2019). Similar conclusions were reached by Crooks (2021), who showed that the absence or lower proportion of intensively managed agricultural land in the catchment leads to higher water quality in rural catchments. The results of the analyses of nitrogen compound concentrations of the Mała Panew river water do not fully confirm this observation, as the study points within the catchment with agricultural character had lower nitrogen concentrations than those with non-agricultural characteristics. So far, agriculture and human activities have been indicated as the main sources of nitrate pollution. However, as studies on the waters of the Mała Panew catchment have shown, areas with high forest cover were responsible for the largest unit increases in nitrate nitrogen loads. Forest areas do not show much annual dynamics of concentration and outflow, therefore they are an important source of load of this nitrogen form throughout the year. One source of nitrate ions may be atmospheric precipitation – up to 10 kg N/ha, but the main source are nitrification processes occurring in the profile of forest soils. Increased supply of nitrogen compounds from forested areas of the catchment was also observed by Shi et al. 2019. The study catchment area is in more than 65% covered by forests. Soil characteristics of the study area (State Forests: Brynek, Koszęcin, Opole, Zawadzkie 2014 – on line) indicate that more than half of the area is covered by swamp, wet and riparian forest habitat types. Recent Chinese studies (Li et. al. 2022) indicate that water content increase in soil may raise the amount of nitrate forms in meadow and forest soils, especially in the forest soil. This can be the negative environmental effects of forest and grassland soils, especially forest soils, which not only emit considerably more N_2O but are also exposed to leaching of nitrate nitrogen. In this case, the forest becomes a source of significant nitrogen emissions to the river water.

Conclusions

Concentrations of nitrogen compounds in river waters show high seasonal dynamics. It is especially visible in parts of catchments used for agricultural purposes. The content of nitrate nitrogen (NO_3-N) in the third quarter of the year and its relation to the value obtained for the first quarter of the year may be an indicator of the impact of agricultural activities on the quality of water in streams. In the studied catchment, sections of agricultural use had lower concentrations of nitrogen compounds compared to the non-agricultural part of the catchment. The demonstrated seasonal variability of nitrate nitrogen concentrations in agriculturally used areas may be used to determine the type of pressure not allowing to achieve good water status in the surface water body. Analysis of the increase in nitrate nitrogen load along the course of the Mała Panew river showed that the highest unit increases occurred in areas with a high proportion of forests, which is due to the relatively high mean annual concentration of this nitrogen form.

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Identyfikacja obszarów zlewni stwarzających zagrożenie zanieczyszczenia związkami azotu dla jakości wody w rzece nizinnej

Streszczenie: Celem pracy było wyznaczenie zlewni cząstkowych, które stwarzają zagrożenie zanieczyszczenia wód Małej Panwi azotem. Podjęto próbę sklasyfikowania typu użytkowania zlewni (rolniczy/leśny) jako potencjalnego źródła zanieczyszczenia wody w rzece. Zweryfikowano hipotezę dotyczącą związku sezonowej zmienności zawartości związków azotowych, szczególnie w formie azotanowej, z rolniczym użytkowaniem obszaru zlewni cząstkowej. Materiał do badań stanowiły próbki wody z rzeki Mała Panew pobrane w 13 stałych punktach monitoringowych. Lokalizację punktów poboru próbek wyznaczono na podstawie analizy przestrzennego zagospodarowania terenu w oparciu o materiały kartograficzne. Ich lokalizacja zapewniła reprezentatywność wyników jakości wody dla fragmentów zlewni o jednorodnym typie użytkowania terenu. W celu określenia ładunków zanieczyszczeń w wodzie Małej Panwi wyznaczono przepływ średni z wielolecia Q ($m^3 \cdot s^{-1}$). W pobranych próbkach oznaczono stężenia azotu azotanowego (NO_3-N) i azotu ogólnego (TN). W przypadku zlewni rolniczych najniższe stężenia azotu azotanowego (NO_3-N) i TN występują w III kwartale i są znacznie niższe niż w I kwartale. Zawartość azotu azotanowego w trzecim kwartale roku i jego stosunek do wartości uzyskanej dla pierwszego kwartału może być wskaźnikiem wpływu działalności rolniczej na jakość wody w ciekach. Wykazana sezonowa zmienność stężeń azotu azotanowego na terenach użytkowanych rolniczo może być wykorzystana do określenia rodzaju presji nie pozwalającej na osiągnięcie dobrego stanu wód w danej jednolitej części wód powierzchniowych. Wykazano, że najwyższe przyrosty jednostkowe występowały na obszarach o dużym udziale lasów.