Seasonal changes of the concentrations of mineral forms of nitrogen and phosphorus in watercourses in the agricultural catchment area (Bay of Puck, Baltic Sea, Poland)

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ABSTRACT

The Baltic Region countries are obliged to meet the stringent limits of N and P discharge set by HELCOM for 2021. Area sources of pollution, including agriculture, are considered the main contributors of biogenic compounds. The Bay of Puck as an inner part of the Baltic Sea is particularly sensitive to eutrophication caused by nutrient inflow from agricultural lands. Rivers and streams inflowing to the Bay of Puck transport nitrogen and phosphorus compounds washed out from fields. The article discusses concentrations of nitrogen and phosphorus compounds measured during annual research (VII.2017 – VI.2018) at three watercourses: Płutnica, Reda and Błądzikowski Stream inflowing to the Bay of Puck. The concentrations ranged from 0.01 to 0.13 mg/L N-NO_2, from 0.39 to 7.55 mg/L N-NO_3, from 0.03 to 0.58 mg/L N-NH_4, from 0.44 to 9.51 mg/L TN, from 0.05 to 0.45 mg/L P-PO_4 and from 0.03 to 1.89 mg/L TP. Seasonal changes of nutrient concentrations were observed, with maximum concentrations of nitrates in August and September after application of fertilizers to arable land.

Key words | area pollution, Baltic Sea, eutrophication, nitrogen, phosphorus, surface runoff

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INTRODUCTION

Eutrophication of coastal marine areas and estuaries, in particular, is an increasing problem across the world (Kroeze *et al.* 2013), and is caused by nutrient enrichment. In Poland almost the entire territory (98% of the area) is located in the catchment of the Baltic Sea. The characteristic features of the Sea include the inland location, relatively low depth (53 m on average), limited exchange of waters with the Atlantic Ocean, significant inflow of river waters and rainwater and finally a large number of inhabitants in the watershed. It is estimated that the total water exchange time is about 25–30 years. During the year, an average of 400 km^3 of oceanic waters inflow to the Baltic Sea. The exchange is only 4% of its entire volume. Thus, contaminants discharged to the sea can stay in it for years, especially if sedimentation occurs to bottom sediments. The primary contributor to the eutrophication of the Baltic Sea is the agricultural sector (HELCOM 2007, 2010). The use of fertilizers causes the intensification of the global biogeochemical cycles of nitrogen (Erisman *et al.* 2013) and phosphorus (Elser & Bennet 2011). Monitoring biogenic substances is of particular importance for the purposes of improving the Baltic Sea environment and to fulfil the goals of EU directives as well as the Baltic Sea Action Plan. The surface load of nitrogen and phosphorus compounds flowing into the Baltic Sea, counted in $kg/km^{-2}{\cdot}year^{-1}$, has increased significantly in recent

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decades. The nitrogen load increased at the end of the 1990s 1.5–4.5 times compared with the period when human impact was negligibly small. In the case of phosphorus in the same reference period, there was a 2–6-fold increase in the surface load (Conley 1999). The main contributor of nitrogen compounds is river inflows, especially in the southern and south-eastern part of the Sea. The second largest source of nitrogen compounds is precipitation – Figure S1 (available with the online version of this paper) (Rahm & Danielsson 2007; Eggert & Schneider 2015). Due to the high importance of the riverine N and P inputs, monitoring of nutrient loads discharged to the Baltic Sea from agricultural catchments of small first-order rivers inflowing to the southern part of the Sea and their impact on marine waters is the issue of special concern (Dzierzbicka-Glowacka *et al.* 2018; Dzierzbicka-Głowacka *et al.* 2019). The quality of surface water is undoubtedly dependent on land use. However, due to the large number of parameters to be estimated, their temporal and spatial variability and the complexity of leaching, transport and transformational processes, the actual dependencies for a particular catchment are complex. Factors strongly affecting the quality of both surface and underground waters are, in particular, the type of vegetation, the type of soil, the intensity of land use and the distribution of settlements (Tu 2011). Previous studies on the relationship between water quality and land use have shown, inter alia, that nitrate concentrations in a humid climate are strongly related to arable land (Rothwell *et al.* 2010). According to Kersebaum *et al.* (2010) the share of agriculture in area pollution discharged to surface waters in EU countries is around 55%. Inappropriate agricultural practices can significantly contribute to increasing nutrient loads discharged into surface waters (Valle Junior *et al.* 2014; Pacheco & Fernandes 2016). In turn, for example, the presence of buffer vegetation zones along river banks greatly limits the incoming load of area pollution (Kiedrzyńska *et al.* 2014; Santos *et al.* 2015).

The main purpose of the study was to determine the concentration of nutrients in surface waters of three watercourses flowing directly to the Bay of Puck. The Bay of Puck is the most shallow, western part of the Gulf of Gdańsk. The area of the Puck Bay is 356 km^2, and the maximum depth is 55 m. The Puck Bay is separated from the Gulf of Gdańsk by the underwater sandy shoal of Mielizna Rybitwia. In combination with the inland location it is particularly sensitive to the inflow of nutrients and threatened by eutrophication.

MATERIALS AND METHODS

Research sites

The three analysed watercourses are located in the Puck municipality in Poland (Figure 1). In the area there are several small rivers flowing directly into the Baltic Sea and most of them to the Bay of Puck. Land use in the Puck municipality is diverse. The agricultural lands dominate and cover 54.1% of the area while forests (wooded and shrubbery) constitute 32.4%. Built-up and urbanized lands occupy only 7.9%. The majority of agricultural and forest lands play an important economic and environmental role. About 1,800 farms are located in the municipality. The structure is dominated by smaller farms (1–5 ha). Farmers cultivate field vegetables – 55%, field grasses – 14%, cereals – 11%, forage plants – 10%, root crops – 10%. Farmers also specialize in livestock breeding.

Measurement points:

1 – Płutnica River (54.72772N, 18.3931E) – catchment area of 84.0 km^2 and a length of 9.0 km. Average annual flow rate 0.45–0.70 m^3/s. The sampling point is located approximately 0.45 km from the outflow to the Bay of Puck, directly downstream of the bridge on road No. 216.

2 – Błądzikowski Stream (54.69582N, 18.43652E) – catchment area of 23.0 km^2. Average annual flow rate around 0.04 m^3/s. The sampling point is located about 1.50 km from the outflow to the Gulf of Puck.

3 – Reda (54.64303N, 18.45959E) - the largest river located partly in the Puck Commune. The total catchment area is 485.5 km^2, and the length of the watercourse is 45 km. The average annual flow rate is 4.44–5.71 m^3/s. The sampling point is located about 1.1 km from the outflow of the river to the Bay of Puck in the 'Beka' Nature Reserve.

Sampling and laboratory analyses

Samples were collected in the period VII.2017–VI.2018. Samples were collected at intervals of 3–4 weeks in glass bottles (2 litres in total), and immediately transported in a portable cooler to the laboratory. Samples

Figure 1 | Puck Municipality and location of measurement points (1–3) on analysed watercourses: Płutnica River, Błądzikowski Stream and Reda River.

were taken from the middle stream course using a sampler with an extension arm. The following analyses were performed: ammonium nitrogen (N-NH_4), nitrite nitrogen (N-NO_2), nitrate (V) nitrogen (N-NO_3), total nitrogen (TN), phosphorus phosphate (P-PO_4) and total phosphorus (TP). The determinations were carried out according to Polish Standards compatible with EU and US-EPA standards, immediately after the samples were delivered to the laboratory. All determinations were carried out in three replications. The results were compared with surface water purity classes defined in the Regulation of the Environmental Minister (REM) (Dz.U. 2016 poz. 1187). The limit values for the classes are given in the Figure S2 (available with the online version of this paper). First class means very good and second class good physicochemical quality of surface waters.

RESULTS AND DISCUSSION

In all three analysed watercourses a significant variability of N-NO_3 and TN concentrations was noted (Table 1). The highest average concentration of N-NO_3 was observed at sampling point no. 2 (Błądzikowski Stream). The elevated N-NO_3 concentrations occurred in September 2017 at all measurement points and in January 2018 (for nos 1 and 3). The maximum value was 7.55 mg/L of N-NO_3 for Błądzikowski Stream. For Płutnica River and Reda River the maximum values were 2.45 and 1.52 mg/L respectively in January 2018. The N-NO_2 concentrations changed in the range from 0.01 to 0.13 mg/L for measurement point no. 2, which means that they exceeded the second class of quality according to REM. The concentration of N-NH_4 exceeded the limit value for the first quality class only in July at Błądzikowski Stream (0.58 mg/L). Except for this one event, the N-NH_4 concentrations were relatively constant and varied from 0.12 to 0.19 mg/L. Taking into account the obligatory reduction limits for Baltic Sea states, Poland is obliged to reduce N and P loads to 153,600 t/year and 4,400 t/year, respectively by 2021 (HELCOM). To meet these criteria the concentrations of 2.50 mg N/L and 0.07 mg P/L in river waters should be kept, as the annual river outflow from Poland's territory is equal to 61.5 km^3. The mean concentration of TN in Błądzikowski Stream is higher while in Płutnica and Reda River the TN concentrations were half the required value. The maximum concentration of P-PO_4 was noted for measurement point no. 2 as 0.45 mg/L in August. At the same time for Reda River the concentration was 0.24 mg/L while for Płutnica River it was 0.25 mg/L. The average concentrations of TP were in the range from 0.17 to 0.33 mg/L. Analysing the annual load of nutrients from the three catchments (Table S1, available with the online version of this paper) it was calculated that Błądzikowski Stream, Płutnica and Reda discharge about 35 t P/year to the Baltic Sea (around 0.8% of the allowed TP load). As those three catchments cover 0.20% of Polish territory and assuming the equal outflow from other Polish territories the TP limit for 2021 would be exceeded almost four times.

Variation during the investigation period

The average monthly concentrations of nutrients are shown in Figure 2. According to REM all sampling points (except Błądzikowski Stream in July) in the case of N-NH_4 (Figure 2(a)) are considered clean (first class). Low concentrations of this form of nitrogen indicate lack of fecal contamination. In the research conducted by Ignatowicz & Struk-Sokołowska (2004) on the water quality of Narew River flowing through

Table 1 | Concentration of N-NO_2, N-NO_3, N-NH_4, TN, P-PO_4 and TP [mg/L] in the measurement points in Puck Commune in the period VII.2017 – VI.2018

Sampling point	Parameter	Mean concentration in the research period [mg/L]	Standard deviation	Median	Max	Min
1. Płutnica River	N-NO_2	0.03	0.01	0.03	0.05	0.01
	N-NO_3	1.09	0.69	0.86	2.45	0.69
	N-NH_4	0.13	0.04	0.12	0.21	0.04
	TN	1.34	0.77	1.09	2.80	0.53
	P-PO_4	0.12	0.05	0.13	0.25	0.05
	TP	0.17	0.03	0.17	0.23	0.03
2. Błądzikowski Stream	N-NO_2	0.05	0.03	0.04	0.13	0.03
	N-NO_3	2.76	1.99	2.34	7.55	1.99
	N-NH_4	0.14	0.14	0.12	0.58	0.14
	TN	3.36	2.38	2.90	9.51	0.50
	P-PO_4	0.14	0.10	0.10	0.45	0.10
	TP	0.33	0.48	0.18	1.89	0.07
3. Reda River	N-NO_2	0.02	0.01	0.02	0.04	0.01
	N-NO_3	0.84	0.39	0.87	1.52	0.39
	N-NH_4	0.10	0.03	0.09	0.15	0.03
	TN	1.04	0.41	1.04	1.81	0.44
	P-PO_4	0.08	0.05	0.07	0.24	0.05
	TP	0.21	0.29	0.13	1.16	0.09

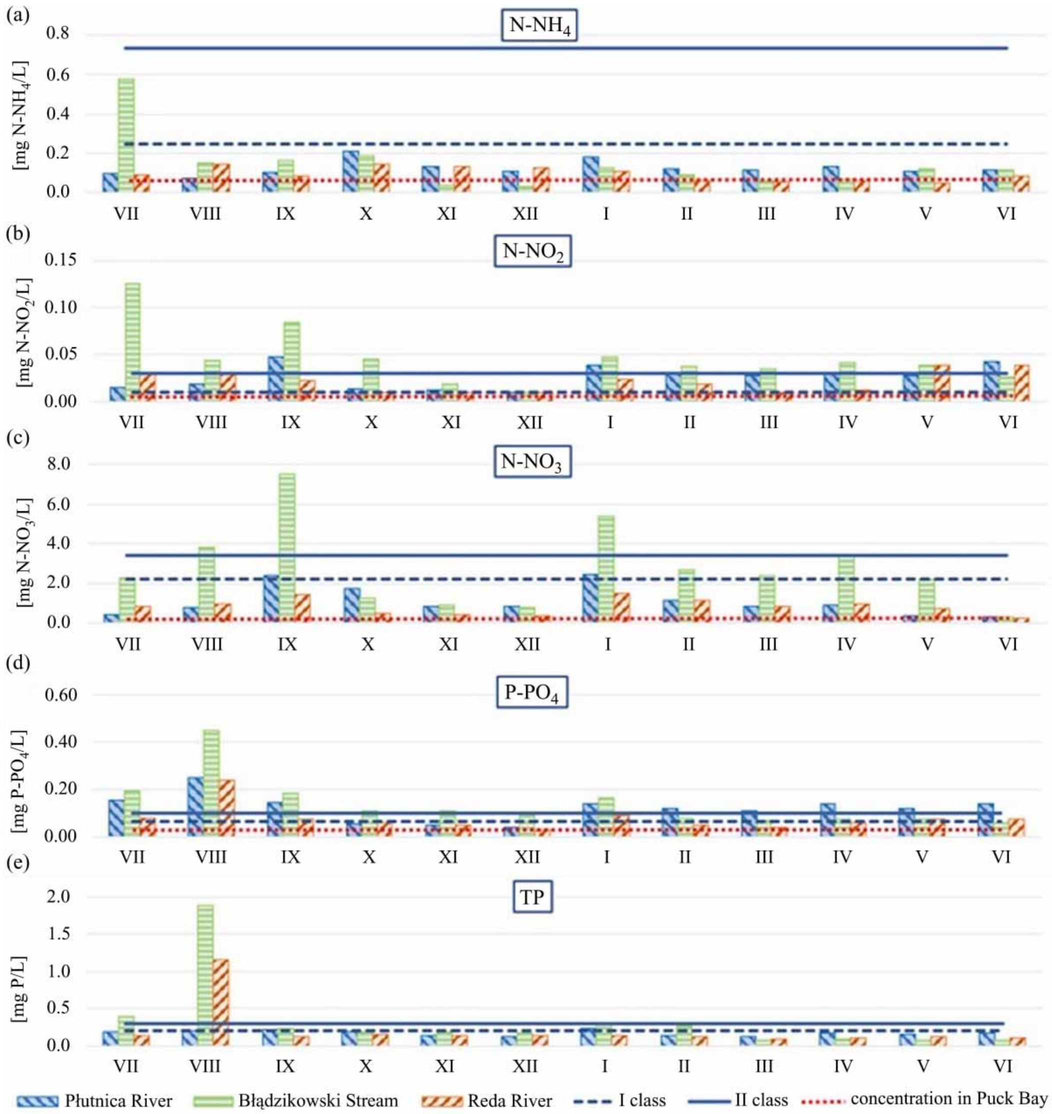

Figure 2 | Concentrations of (a) $N\text{-}NH_4$, (b) $N\text{-}NO_2$, (c) $N\text{-}NO_3$, (d) P-PO4 and (e) TP at sampling points (Płutnica River, Błądzikowski Stream and Reda River) in the period VII.2017–VI.2018.

typically agricultural areas, similar mean values were observed – in summer season – 0.14–0.21 mg/L, in autumn season – 0.075–0.22 mg/L. In the current study the seasonal average values for the three watercourses range from 0.09 to 0.30 mg/L in summer and from 0.085 to 0.15 mg/L in autumn. The concentrations of $N\text{-}NH_4$ are higher from two times (for Płutnica and Reda River) to 14 times (for Błądzikowski Stream) than the average concentrations reported in the Bay of Puck (Szymczycha *et al.* 2012).

The concentrations of $N\text{-}NO_2$ (Figure 2(b)), slightly exceeded the first class of purity for the Płutnica River in the period from July to November, while in the period from January to June they oscillated close to the second class. The same situation occurs in the summer months (July–September and May–June) for Reda River. In the case of Błądzikowski Stream the $N\text{-}NO_2$ concentrations significantly exceeded the limit of the second class in the period from July to October and from January to May they were at an average level of 0.03 mg/L. NO_2 are a transitional form in the conversion of ammonium ions into nitrate (V) ions. Even low concentrations of $N\text{-}NO_2$ are toxic to aquatic organisms. The concentrations of $N\text{-}NO_2$ measured on the Ślina River

(Poland) (Kiryluk & Rauba 2011) with the agricultural catchment changed in a wider range from 0.001 to 0.24 mg/L. The maximum concentration of N-NO_2 was twice as high as the maximum concentration in Błądzikowski Stream.

Elevated concentrations of N-NO_3 were observed for Błądzikowski Stream in the summer months (Figure 2(c)). In August and September concentrations exceeded the limit value for the second quality class (REM). In comparison with Gowienica River (Rawicki *et al.* 2015) the highest concentrations of N-NO_3 were measured in April – 5.48 mg/L and June – 12.83 mg/L. N-NO_3 concentrations in analysed samples were 19–378 times (for Reda River and Błądzikowski Stream respectively) higher than the seawater concentrations in the Bay of Puck. Elevated concentrations of N-NO_3 in aquatic ecosystems can lead to a reduction of biodiversity as a result of the disappearance of plant species from poor habitats (Jasiewicz & Baran 2006).

The dominant nitrogen form is N-NO_3 – about 81%–82% of TN. The list of concentrations of different nitrogen forms for each of the sampling points is presented in Table S2 (available online). In the research conducted for the Trzemna River (Dąbrowska 2008) flowing through intensively used agricultural lands, similar results were obtained. The N-NO_3 constituted from 78% to 82% of TN. The concentrations of other forms of nitrogen decreased in the following order: N_{org} interchangeably with N-NH_4 > N-NO_2.

In surface water samples collected in the second half of August, increased concentrations of P-PO_4 and TP were noted (Figure 2(d) and 2(e)). The concentrations of P-PO_4 in all analysed watercourses in August exceeded the values corresponding to the second class of purity (0.1 mg/L), with the highest values measured on Błądzikowski Stream and Płutnica River. In contrast, concentrations of TP exceeded the values corresponding to second class in the case of Błądzikowski Stream and Reda, while in the case of Płutnica they exceeded the admissible value for the first class of quality. High concentrations of P-PO_4 measured in August corresponded in time to the period after crop harvest, when the surface of the soil is exposed causing increased erosion and leaching of phosphorus compounds from the soil. The rainy summer of 2017, in particular intensive rainfalls in the second half of August, additionally favored the leaching of nutrients from the soil. Differences between N-NO_3 and phosphorus compound removal in August and September can be explained by strong dependence between phosphorus content in the soil and the concentration of dissolved phosphorus in the runoff (Sharpley & Kleinman 2003); thus phosphorus compounds can be detected earlier in water receivers when runoff takes place. Pietrzak *et al.* (2017) proved that erosion of phosphorus from the soil causes a rapid marker in the concentration of phosphorus in the runoff. In addition, it is recommended that phosphorus fertilization should be preceded by tests of current soil TP status. Tao *et al.* (2010) verified a strong correlation between TP and total suspended solids ($r =$ 0.97), indicating that phosphorus compounds originate primarily from sediment transport due to erosion in agricultural areas and from riverbank erosion.

Trends

TP, N-NH_4 and N-NO_3 concentration analysis showed high variability for the analysed watercourses (Figure 3). Generally the smallest dispersion of results occured for the Reda River (except for one point of TP in August) (Figure 3(c)). The analysed part of Reda River watershed consists of meadows (60%) and farmlands (35%), while forests and urbanized areas account for 3% each. Furthermore, the flow rate of Reda is quite high, thus mixing and scattering has a major impact on the overall concentration of nutrients. This thesis can also be confirmed by a relatively large catchment area compared with the other watercourses. The most significant variability especially due to N-NO_3 and TP concentrations occurred for Błądzikowski Stream. The watershed is typically agricultural (farmlands > 70%). Application of fertilizers apparently results in contamination with biogenic substances of Błądzikowski Stream waters. The manure dosage (the separate point in Figure 3(b) with N-$NH_4 = 0.58$) and the use of mineral-based fertilizer can be distinguished. A significant part of the results for Płutnica river (Figure 3(a)) was close to the values that were presented for Reda River. The watershed development is similar; meadows and farmlands constitute the majority (65%) with a significant share of forests (30%) and sole urbanized area (<5%). The impact of fertilization on streams with higher flows may be difficult to observe in surface waters, though based on Błądzikowski Stream the negative impact on watercourse quality has been recorded.

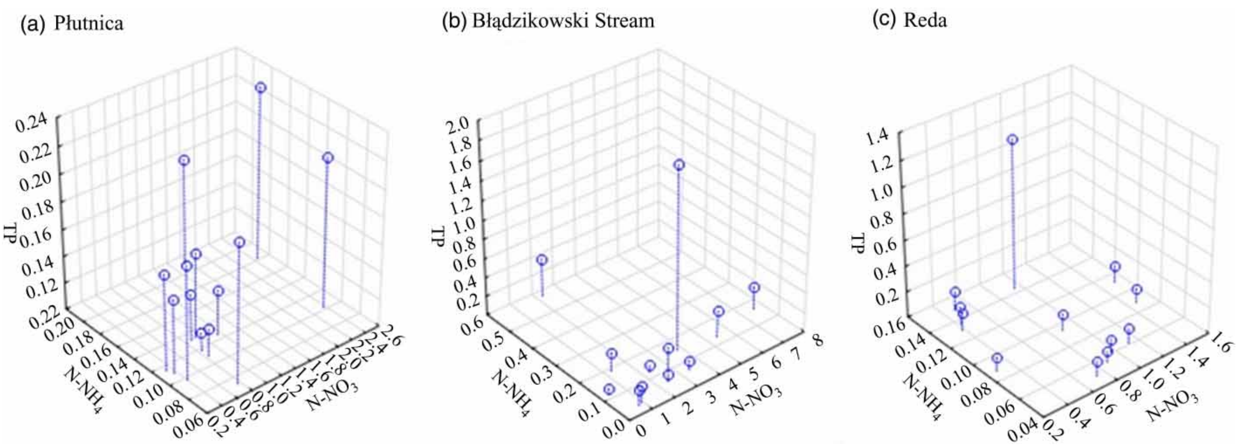

Figure 3 | 3D scatterplot distribution of TP, $N\text{-}NH_4$ and $N\text{-}NO_3$ at (a) Płutnica River, (b) Błądzikowski Stream and (c) Reda River.

Spearman's rank correlation analysis for all watercourses indicates significant positive dependence between $N\text{-}NH_4$ and TP in Błądzikowski Stream and Reda River (0.59 and 0.85 respectively). This could evidence use of manure fertilization rich in both compounds. The correlation between $N\text{-}NO_2$ and TP occurred in Błądzikowski Stream (0.63) and Płutnica River (0.40) No other correlations were recorded for the analysed period.

Comparing the obtained results with research from 2006–2008 (Table S3, available online), a decrease of 5% and 16% of mean TP was recorded for Błądzikowski Stream and Płutnica River respectively, while for Reda, a 91% increase was observed. Average concentration of $N\text{-}NO_3$ for Reda and Błądzikowski Stream decreased by 37% and 33%, and increased by 15% for Płutnica. Average concentration of $N\text{-}NH_4$ decreased by about 60% for each watercourse (http://geografia.univ.gda.pl).

Eutrophication ratio

A high concentration of nutrients in the aquatic environment is the main factor leading to increased water fertility (Wiatkowski & Paul 2009) and is the main cause of the eutrophication process and intensive blooms of cyanobacteria in the Baltic Sea and particularly in the semi-closed parts like the Gulf of Gdańsk or the Bay of Puck. Plants demand an N:P ratio of 16:1, which is called the Redfield ratio (Redfield *et al.* 1963; McGroddy *et al.* 2004). On the basis of long-term monitoring, a value of the N:P ratio exceeding 20 is considered too high (White 1989). The average values of the N:P ratio for the analysed sampling points are presented in Table 2. The highest average N:P ratio was observed at point 2 – Błądzikowski Stream – 24. It was related to the high concentration of mineral nitrogen, mainly $N\text{-}NO_3$. At the same time, the concentration of phosphorus as mineral phosphate (V) occurred at low, fairly stable levels at each of the research points. The high variability of the N:P ratio was noticed during the research period. The maximum values of this ratio were observed in October (Płutnica River – 36:1), February (Reda River – 26:1) and April (Błądzikowski Stream – 47:1). In October and in April fertilization of arable land was performed. According to the literature data, there is a high variability of the N:P ratio in rivers. Mainstone & Parr (2002) obtained a variability of this ratio from about 1 to 1,000 for data from 5,000 research points on the rivers of England and Wales. Wiatkowski & Paul (2009) for Troja River in Poland gave a range from 7 to 37, with an average of 22. From the ratio of the maximum content of mineral nitrogen to phosphorus

Table 2 | The ratio of mineral nitrogen to phosphorus mineral phosphate (V) at research points

	Ratio N:P			
Sampling points	**Mean**	**Max**	**Min**	**Standard deviation**
1. Płutnica River	13:1	36:1	3:1	9.8
2. Błądzikowski Stream	24:1	47:1	8:1	14.4
3. Reda River	15:1	26:1	5:1	6.4

phosphate (V) in the waters of the analysed rivers, it was deduced that the element limiting the growth of phytoplankton biomass was phosphorus. However the mean values of the N:P ratio for Płutnica and Reda River oscillated close to 16:1.

CONCLUSIONS

1. The nutrient concentrations in the analysed streams were obviously affected by land use. Seasonal changes were observed according to agricultural practices like fertilizer application and crop harvest. In summer, the elevated concentrations of N and P forms were observed in Błądzikowski Stream, which flows through areas intensively used for agriculture indicating the leaching of fertilizers from arable lands. The Reda River flowing through the area of the Beka Nature Reserve was characterized by significantly lower concentrations of nutrients – the limit concentrations of the second class of quality (REM) for TP was exceeded only in August, after the harvest and high rainfall.
2. The average N:P ratios for Płutnica and Reda River were close to the optimal Redfield ratio. In the case of Błądzikowski Stream the mean ratio was 24:1, indicating that phosphorus is the biomass-limiting element.
3. Fulfilling the obligatory discharge limits set by HELCOM will be difficult for typical watercourses flowing through agricultural areas unless fertilizing practices remain unchanged.

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