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

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Abstract: The study aimed to analyse the seasonal variability of phosphorus concentrations and phosphorus content and the impact of catchment development of the Panew Mała River. The study presents the findings of a two-year experimental investigation (comprising 17 measurement series across 12 measurement cross-sections) into the concentration of phosphorus (P) and its soluble form, orthophosphates (PO_4^{2-}). The mean phosphate concentrations were found to be low, with a range of 0.03 to 0.08 PO_4^{2-} mg·dm^{-3}. In contrast, the total phosphorus concentrations were relatively high, with a range of 0.11 to 0.43 mg·dm^{-3} P. The seasonal variability was analysed based on quarterly means and half-yearly periods covering quarters II and III (spring–summer) and quarters I and IV (autumn–winter), respectively. The analysis of spatial variability was conducted using cluster analysis according to Ward's method, with the Euclidean distance employed as a measure of distance and the results related to the utilisation of different catchment area. Due to the slight differences in the phosphate concentration, the total phosphorus concentration was analysed in detail. The analysis of variance showed no significant differences between phosphorus concentrations in certain quarters, while greater variations were obtained for half-yearly periods. The applied method of grouping the sampling sites made it possible to distinguish several groups of sampling sites, which indicate relations between the values of phosphorus concentration in the waters of Mała Panew and the type of use of the catchment area.

Keywords: catchment, phosphorus, river, seasonal pollution, water

INTRODUCTION

The contamination of surface water can be attributed to two distinct sources of pollution: point sources, which include sewage treatment discharge and stormwater runoff, industrial plants and nonpoint sources, which encompass runoff from urban and agricultural areas. The detection of nonpoint sources is particularly challenging due to their extensive coverage across watersheds and the intricate biotic and abiotic interactions they involve. The structure of land cover, especially agricultural use, can influence the quality of ground and surface water. Land use in watersheds affects the export of nutrients and sediments, particularly through streambank erosion, which can increase the export of phosphorus from riparian zones to the stream. The relationship between water quality in the catchment area and the manner of its management is challenging to ascertain due to the multitude of factors that affect water quality. This topic has been the subject of extensive research (Solbe, 1986; Sliva and Williams, 2001; Selle, Schwientek and Lischeid, 2013; Pulikowski, Pawęska and Bawiec, 2015; Kändler *et al.*, 2017; Gruss *et al.*, 2021; Thi Ko, 2021; Islam, Phoungthong and Idris, 2022; Lach *et al.*, 2023; Özalp, Yildirimerb and Erdoğan Yükselc, 2023). However, each catchment area requires an individual approach when determining the factors that most strongly affect the quality of individual water parameters.

The processes of runoff and the transport of solids and dissolved substances in catchments are significantly influenced by some factors, including vegetation cover, soil properties, land use intensity and the distribution of settlement areas. These findings are supported by a substantial body of research, as evidenced by the following references (Lerner and Harris 2009; Lúcia *et al.*, 2020; Matej-Lukowicz *et al.*, 2020; Cygan, Kłos and Wieczorek, 2021). The quality of water in a catchment area is dependent upon the mutual relations between the individual forms of development therein. A thorough analysis of the individual components of the catchment is therefore required to indicate the most important factors influencing the quality of surface waters for a given catchment (Kim *et al.*, 2011; Kändler *et al.*, 2017; Dębska, Rutkowska and Szulc, 2022; Steinhoff-Wrześniewska *et al.*, 2022). In contrast to nitrate, phosphorus in the watersheds of the small lowland catchments is not related to the indicator of soil carbon and soil phosphorus (Gardner, Cooper and Hughes, 2002), but is correlated with the proportion of arable land in the catchment. To maintain good water quality in the river, it is crucial to analyse the water in the entire course of the river, taking into account the way its surface is used (Bartnicki, 2019; Schmalz and Kruse, 2019). Nutrient concentrations and loads in rivers exert a significant influence on marine pollution, resulting in the eutrophication of these ecosystems and a deterioration in water quality.

Phosphorus is one of the most significant indicators of human activity, with a substantial impact on the quality of surface waters. Next to nitrogen, it is one of the key elements of agricultural production, also present in industrial processes and households. However, its transport by river currents has led to the eutrophication of marine ecosystems Mc Dowell and Haygarth (2024). The primary sources of this phosphorus are anthropogenic factors emanating from point sources in urban settlements and area sources of agricultural origin. The application of fertilisers to field crops results in the uptake of only a portion of the nutrients supplied. In the year of fertiliser application, the utilisation of nitrogen from mineral fertilisers is 50–70%, and from natural fertilisers 20–30%. The utilisation of phosphorus is 20–30% of the applied dose, while the utilisation of potassium is 50–60% of the applied dose (Ilnicki, 2004). Pollution from agricultural land is considered one of the main sources of phosphorus in surface waters. Sources of phosphorus loss include soil, fertilisers, crop residues, and livestock manure. The contribution of each source depends on how it is managed (Mc Dowell and Haygarth, 2024).

The dominant form of phosphorus is phosphate (orthophosphate), which plays a pivotal role in the eutrophication process due to its exclusive availability to autotrophs (bacteria, algae, and plants) for uptake (Balcerzak and Rybicki, 2011; Czaplicka-Kotas *et al.*, 2012; Cieśla and Gruca-Rokosz, 2023). Subsurface movement of P to streams is usually low because P binds readily to soil particles (Correll, 1998). Phosphorus transport is typically observed in areas of surface water movement where surface runoff occurs along an area of high soil phosphorus content. A robust correlation has been demonstrated between the phosphorus content of the surface soil layer and the concentration of dissolved phosphorus in runoff collected from upland areas within the catchment area (Sonesten *et al.*, 2018). The supply of phosphorus compounds to river waters can also be significantly influenced by factors such as stream bank erosion. This process represents a primary source of suspended sediments in stream water, and can contribute to phosphorus content during flood periods (Rahumoto, Kovar and Thompson, 2019). The primary source of phosphorus input into the Baltic Sea is river runoff. The contamination of the Baltic Sea with phosphorus is a consequence of the transport of pollutants by river currents (Armstrong *et al.*, 2012; Pastuszak, 2012; Sonesten *et al.*, 2018). It is estimated that between 95 and 99% of the total phosphorus load reaches the Baltic Sea in river runoff, with the remaining percentage originating from the atmosphere.

The Baltic Sea catchment area encompasses 99.7% of Poland and is traversed by two major rivers: the Vistula and the Odra. These rivers collect nutrients from the land and transport them to the sea. Poland, with its significant river runoff, 45% share of agricultural land and 50% share of population in the Baltic Sea catchment area, is a major contributor to the substantial phosphorus (P) loads discharged into the Baltic Sea (Jadczyszyn and Rutkowska, 2012; EEA, 2015). It is estimated that 44% of phosphorus compounds enter the Baltic Sea from the territory of Poland (Gburek and Sharpley, 1998; Sonesten *et al.*, 2018).

MATERIALS AND METODS

CHARACTERISTICS OF THE RESEARCH AREA

The research was conducted in the Mała Panew River basin, from its source point to the Turawa Reservoir. The river's source is located in the Silesian Voivodship. The river is characterised by a low flow amplitude, typical of lowland rivers. The Mała Panew catchment covers an area of 2132 km^2, with a total length of 131.8 km. The river is divided into two sections by an artificially created flow-through retention reservoir, which has resulted in the formation of two distinct sections that differ in terms of their hydrological characteristics and natural properties. The analysis presented in this article encompasses the Mała Panew River basin above the Turawa reservoir (up to the reservoir's backwater point), spanning an area of 1220 km^2. The river in question is 86 km in length. The catchment area under analysis is predominantly characterised by agricultural and forest land use. The majority of arable land is characterised by poor soil quality, classified in soil bonitation as V and VI, with a notable degree of leaching of fertiliser components into water.

The river network in the Mała Panew catchment area exhibits a notable degree of diversity for its water resources. The greatest volume of water is transported by the principal watercourse of the Mała Panew and its longest tributaries. The diversity of forms of catchment use has an impact on the quality of water in the Mała Panew, which is the main source of water for the Turawa reservoir, has multiple functions, but its primary role is to provide flood protection, store water from the Mała Panew for navigation, energy generation, fishing and recreation. (Wiatkowski and Wiatkowska, 2019). The river network in the Mała Panew catchment area is distinguished by a notable diversity in terms of water resources. The Mała Panew is a meandering river with a predominantly sandy substrate. The river is moderately polluted (Sobolewska and Wylęgała, 2012). The fundamental hydrographic network is constituted by minor catchments, which are distinguished by notable spatial variability in the chemical composition of the waters. The influence exerted by biological and geomorphological soil conditions is also considerable. The enlargement of the river using connecting small catchments leads to a reduction in the variability of local chemical component values in the stream. In connection with this, larger-scale regularities related to the dominant shape, urbanisation, and use of the catchment area become crucial.

The study aimed to assess the impact of the development of the catchment area on the content of phosphorus and its forms in the Mała Panew River and to analyse the seasonal variability of phosphorus compounds.

The partial catchments designated in the Mała Panew catchment area display a comparable pattern of land use. Forested areas represent the dominant land use type, comprising approximately three-quarters of the area of individual partial catchments. An exception is observed for the partial catchment marked with the symbol XII, where forests constitute slightly over 50% and agricultural land slightly over 40% (Tab. 1).

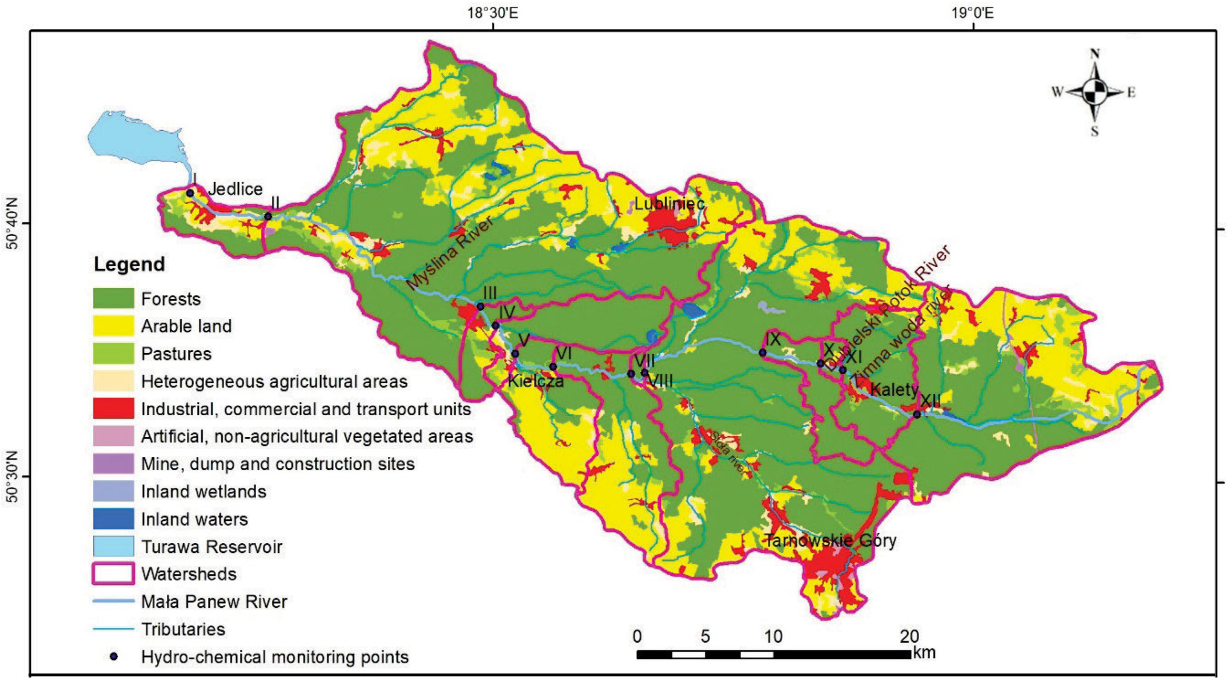


Fig. 1. Land cover structure in the Mała Panew catchment); source: GIOŚ (2018)

METHODS

The research material comprised water samples from the Mała Panew River, collected monthly at fixed monitoring points across the river section extending from the source to the closure at the backwater point of the Turawski reservoir (Fig. 1). This involved the collection of samples at 12 measurement cross-sections, designated I, II, III, IV, V, VI, VII, VIII, IX, X, XI and XII. The research was conducted throughout 17 measurement sessions between May 2019 and April 2021. The analysis of the catchment area management is presented in Table 1, which also shows the location of the selected hydrochemical measurement cross-sections. The cartographic materials from the Hydrographic and Land cover database (Geoportal, no date) were analysed to determine the location, which was chosen to ensure that the results represented the water quality of areas with a similar type of land use. In areas of the catchment with low variability in land use, monitoring points were situated at greater distances from one another. Conversely, in areas of the catchment with high variability and high density of potential pollution sources, there were more monitoring points. The aforementioned approach allows for the capture of the dynamics of changes in water quality within the Mała Panew River system. The structure of land cover in the catchment area under study is presented in Table 1, while Figure 1 shows the location of monitoring points.

Table 1. The use of partial catchments in the Mała Panew River catchment

The partial catchment area	Percentage share			
	arable land	forest	urban area	others
I – Most Jedlice huta	33.3	59.8	6.5	0.4
II – Krasiejów most	33.1	60.2	6.3	0.4
III – Zawadzkie Stadion	30.8	62.1	6.7	0.4
IV – Zawadzkie Ziaji	31.1	62.0	6.6	0.4
V – Żędowice	32.4	60.4	6.9	0.3
VI – Kielcza	30.1	62.4	7.1	0.4
VII – Krupski Młyn	27.7	64.4	7.5	0.4
VIII – Potępa	27.8	64.3	7.5	0.4
IX – Pusta Kuźnica	31.2	63.3	5.3	0.2
X – Brusiek	34.1	59.8	5.9	0.2
XI – Kalety 3-Maja	34.3	59.6	5.9	0.2
XII – Miotek	41.5	52.9	5.4	0.3

Source: own study.

The total phosphorus (P) and its soluble form, orthophosphates (PO_4^{2-}), were determined in the analysed water samples following PN-EN ISO 15681-2 using the flow colourimetric method, and phosphates according to the SKALAR procedure. The analysis of the water samples was conducted at the Chemical Laboratory of the Institute of Technology and Life Sciences – State Research Institute in Falenty (Pol.: Laboratorium Chemiczne Instytutu Technologiczno-Przyrodniczego – Państwowego Instytutu Badawczego w Falentach). The resulting data were subjected to statistical analysis using the STATISTICA 13.3 package. The analysis included average values of concentrations characterising individual sub-catchments in the annual and quarterly periods, which are discrete quantities, not continuous. The continuous value is the instantaneous concentration $C(t)$. The quarterly analysis was performed by dividing the set of results covering 188 measurements (the grouping variable was the quarter number in which the sample was taken); the number of series for total phosphorus for individual quarters ranged from 35 to 57. Data for individual quarters were analysed with a division into catchments with a predominance of agricultural land (A) and forest land (F). The division was into two parts of similar number (93 and 95) because both sub-sets covered 6 sub-catchments. The analysis of spatial variability was conducted using cluster analysis with Ward's method, assuming the Euclidean distance as the measure and linking the obtained results with the use of individual catchment areas. On this basis, two groups of catchments were distinguished, with a greater proportion of agricultural land (A), which encompasses the following sub-catchments: sub-catchments I, II, V, X, XI and XII are distinguished by a greater share of agricultural land (A), while sub-catchments III, IV, VI, VII, VIII and IX are distinguished by a greater share of forest land (F).

The water quality limits are adopted following the Regulation of the Minister of Infrastructure of 25 June 2021 on the classification of ecological status, ecological potential and chemical status and the method of classification of the status of surface water bodies, as well as environmental quality standards for priority substances (Rozporządzenie, 2021).

RESULTS AND DISCUSSION

The Mała Panew is a meandering river that facilitates the extension of the retention time. The forest areas situated close to the riverbed are characterised by deciduous forest communities. The mean phosphate concentrations during the analysed period were low, with a range of 0.03–0.08 mg·dm^{-3} PO_4^{2-}. In contrast, the concentrations of total phosphorus were relatively high, with a range of 0.11–0.43 mg·dm^{-3} P, which is consistent with the findings of previous studies (Bogdał *et al.*, 2019). The range of reported concentrations of phosphorus compounds in river waters is considerable. The mean median concentrations of dissolved mineral phosphorus and total phosphorus in rivers worldwide are 28 and 85 mg·dm^{-3}, respectively (Savenko and Savenko, 2022). The PO_4^{2-} levels in the polish river Szreniawa were found to be between 0.16 and 0.25 mg·dm^{-3}, while in the stream Korzeń, the concentration of PO_4^{2-} was significantly higher – 0.718 mg·dm^{-3} (Fudała, Bogdał and Kowalik, 2023; Lach *et al.*, 2023). The relatively low concentration of orthophosphates with total phosphorus (P) suggests that non-anthropogenic sources of phosphorus pollution may be the dominant contributor. The critical point in terms of phosphate concentration in the studied catchment was point XI (Kalety 3-Maja), where several incidents of exceeding the limit value for surface water quality class II were recorded. In the case of P, the highest concentrations occurred incidentally, in the autumn–winter period at measurement point IX (Pusta Kuźnica). The concentration values of total phosphorus and soluble forms often exceeded the limit value of class II surface water quality for lowland rivers (Rozporządzenie, 2021), which may be caused by uncontrolled sewage discharges. The origin of these discharges could not be determined.

The correlation analysis for quarterly and annual concentrations of total phosphorus (P) with the structure of use demonstrated significant correlations for annual values and the proportion of agricultural land, forests and urban areas. The obtained correlation coefficients indicate that an increased share of agricultural land exerts a favourable effect on the value of total phosphorus concentration in the studied waters, while an increased share of forests and urban areas exert a deleterious effect. The study area encompasses agricultural land situated in the northern and southern regions, in proximity to the watershed. It has been demonstrated that reduced agricultural activity in the nearness may positively influence the concentration of phosphates in the river (Burzyńska, 2015). The notable correlation between the total phosphorus concentration in the second quarter and the proportion of urbanised areas (Tab. 2), as observed in our research, is corroborated by findings of Savenko and Savenko (2022). The relationships between the proportion of a specific catchment use and the concentration of total phosphorus are illustrated in Figure 2. Subsequently, an effort was made to identify catchments with analogous types of usage. The mean proportion of each land use type within the delineated catchment areas was calculated for the identified groups (Tab. 3). The differentiation in question pertains principally to agricultural land and forest areas, representing approximately 5% in absolute terms (Tab. 3). In relative values however, it reaches 16.8% for agricultural land and 6.8% for forests.

The grouping of sub-catchments based on land cover, as determined by the Ward's method and the square of the Euclidean distance (Fig. 3).

To distinguish differences with periodic concentrations of total phosphorus, average concentrations in individual quarters and years were calculated for both groups of sub-catchments (I and VI), and the results are presented in Figure 4. The results demonstrate that, across all analysed periods, sub-catchments

Table 2. Pearson's correlation of total phosphorus (P) concentration with land cover

Land use	Correlation coefficient in quarter or year				
	I	II	III	IV	year
Arable land	−0.4276	−0.5700	−0.3699	−0.2915	**−0.7139**
Forest	0.3821	0.4913	0.4122	0.2465	**0.6680**
Urban area	0.4707	**0.6779**	0.1293	0.3872	**0.6853**
Others	0.5326	0.5610	−0.3900	0.1113	0.3724

Explanation: the highest values are bolded.
Source: own study.

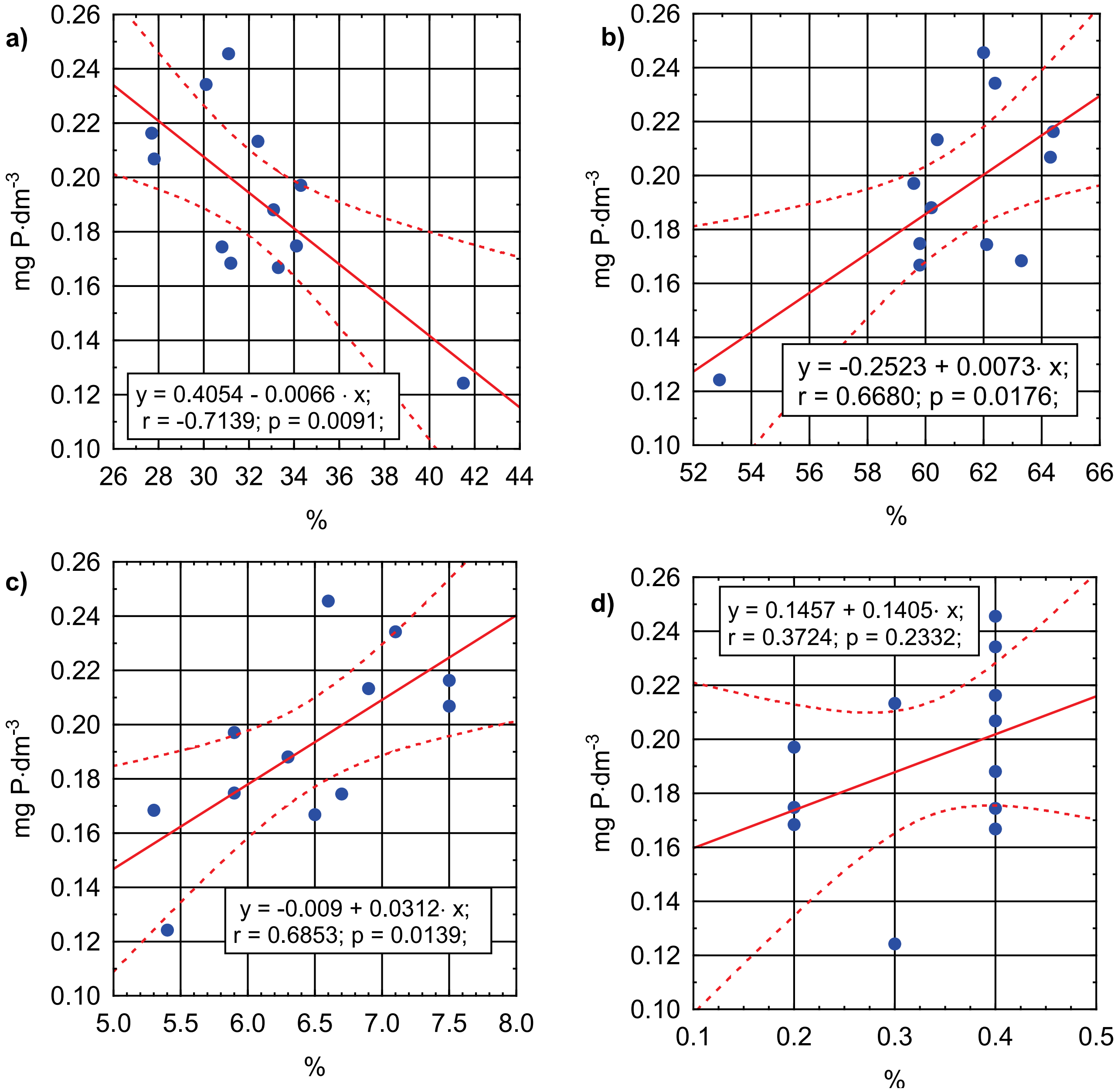


Fig. 2. The relationship between the average annual concentrations of total phosphorus and the type of use: a) arable land, b) forest, c) urban area, d) other; source: own study

Table 3. Characteristics of the catchment groups included in the individual groups

Specification	Type of area (%)			
	arable land	forest	urban area	others
The greater proportion of arable land cover of agriculture (A) – sub-catchments: I, II, V, X, XI, XII	34.8	58.7	6.2	0.3
The greater proportion of forest cover (F) – sub-catchments: III, IV, VI, VII, VIII, IX	29.8	63.0	6.8	0.4

Source: own study.

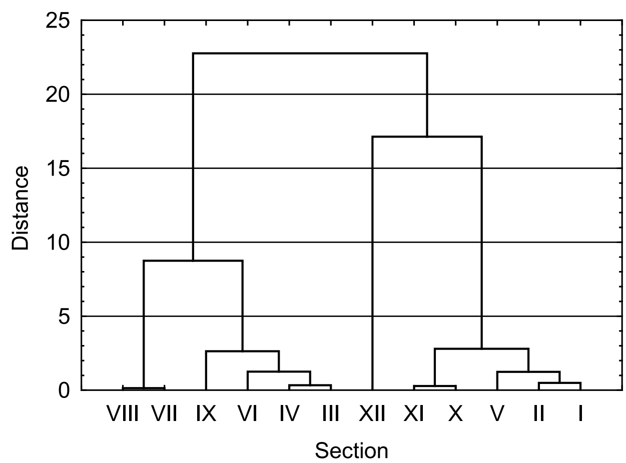


Fig. 3. Dendrogram (Ward's method – square of Euclidean distance); source: own study

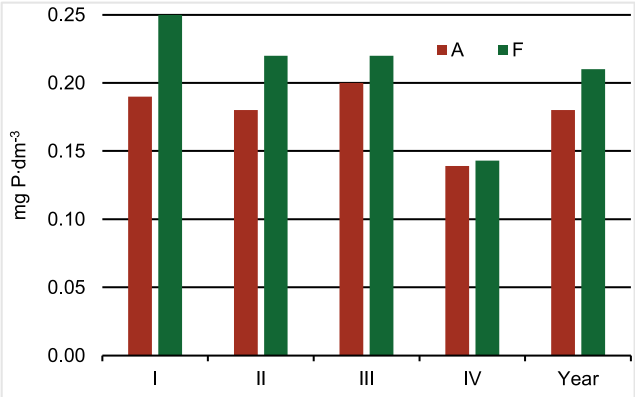
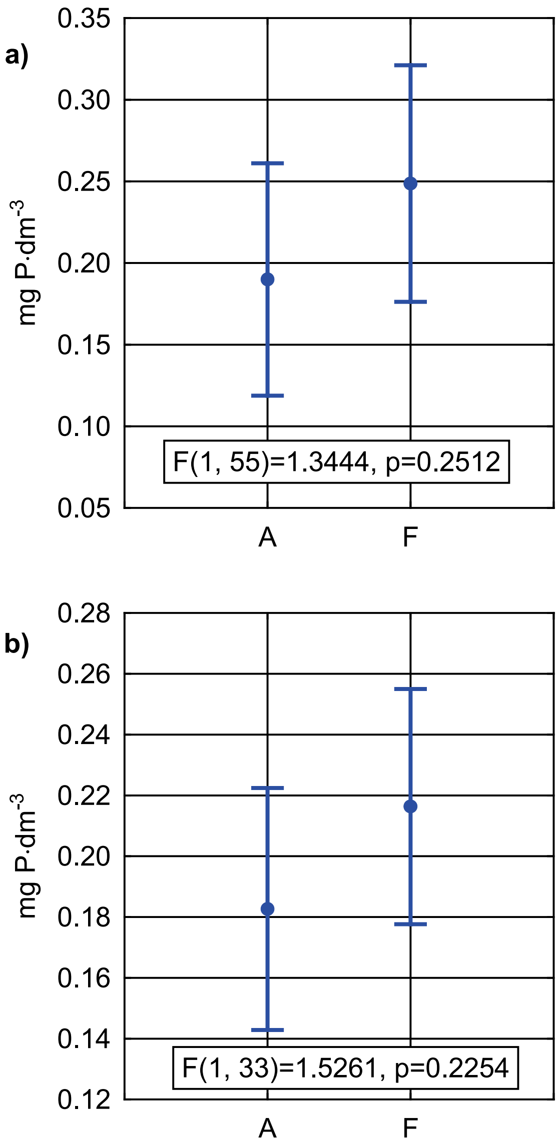


Fig. 4. Average quarterly and annual concentrations of total phosphorus; A = agricultural catchments, F = forest catchments, I, II, III, IV = quarter of year; source: own study

with a higher share of agricultural land exhibited lower values of total phosphorus concentration. Subsequently, the significance of the obtained differences was analysed using a one-way analysis of variance. The results are presented in Figure 5. Despite the one-way nature of differentiation, none of the five analysed differences



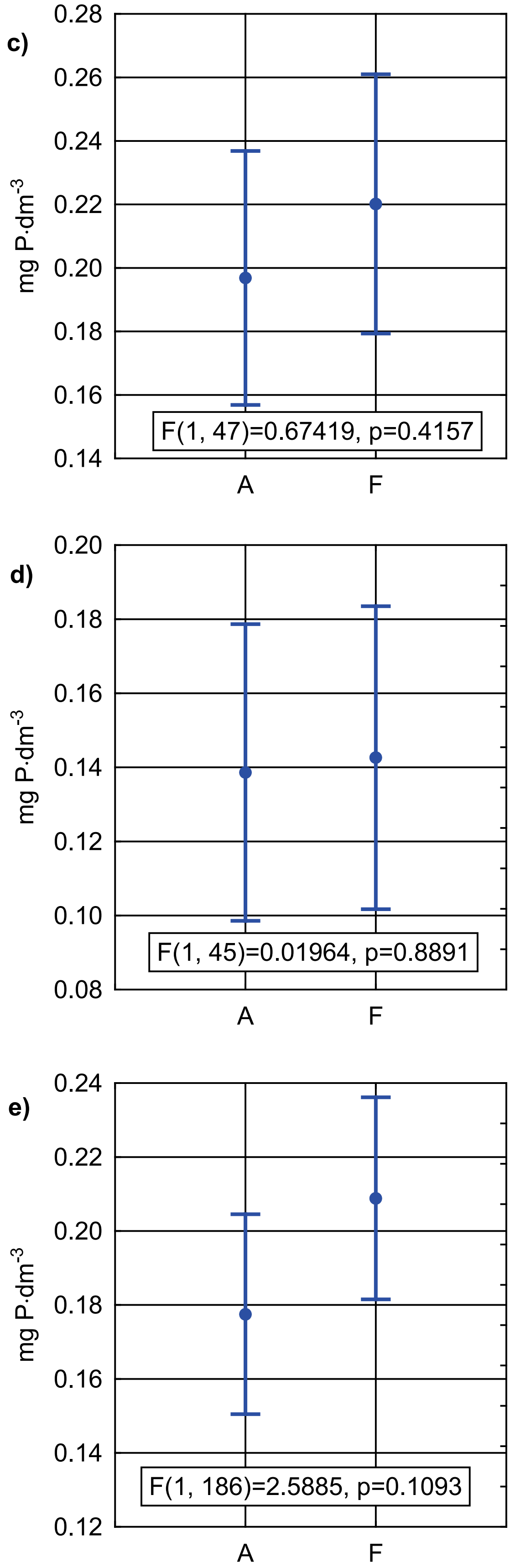


Fig. 5. The significance of differences between the total phosphorus concentrations in agricultural catchments (A) and forest catchments (F) in: a) I quarter, b) II quarter, c) III quarter, d) IV quarter, e) year; source: own study

in the concentration of total phosphorus reached a level of significance at the 0.05 level.

Next, similar analysis was performed on the concentrations of the dissolved form of phosphorus – orthophosphates. In the case of this form, no significant correlations were obtained for annual values, while significant correlation coefficients were obtained for quarter II except for forests. The nature of the correlation for phosphorus is similar to that for total phosphorus, that is, the correlation coefficient is negative for agricultural land and positive for the rest. However, a completely opposite trend was observed for quarter IV (Tab. 4).

Table 4. Pearson's correlation of total phosphorus (P) concentration with land cover

Land use	Correlation coefficient in quarter or year				
	I	II	III	IV	year
Arable land	−0.5224	**−0.6232**	−0.1942	0.0501	−0.4957
Forest	0.4348	0.5565	0.2307	−0.0363	0.4584
Urban area	**0.6852**	**0.6525**	0.0296	−0.0806	0.4917
Others	0.4484	**0.7068**	−0.4889	−0.2243	0.0849

Explanation: the highest values are bolded.
Source: own study.

The average quarterly and annual concentrations of orthophosphates are shown in Figure 6. In the first two quarters the values for agricultural areas are lower, in the remaining two quarters the trend is reversed and finally the annual values are almost the same (Fig. 6). The significance of the differences obtained was also analysed. In the case of orthophosphates, a significant difference of 0.05 was obtained for quarter III. The other differences were not significant. The results are presented in Figure 7. Due to intensive vegetation processes during this period (IV–VI), significantly lower concentrations of orthophosphates may occur in catchments with a higher proportion of agricultural land and the associated increased uptake of dissolved phosphorus compounds. The analysis of the mean annual values of the concentrations of P and phosphate and the obtained values of the correlation coefficients (Tab. 2) indicate the dominant share of the forest areas in the studied catchment area on the concentration of P and PO_4^{2-}. Similar observations of high concentrations of phosphorus and its mineral forms in surface waters in heavily forested areas have been reported in the literature (Koc and Sidoruk, 2005; Bogdał *et al.*, 2015; Janicka *et al.*, 2022). Miller *et al.* (2011) distinguished between base flow and storm flow and found that forests and urban areas influenced water quality mainly during low flow conditions and agricultural areas during storm flows. Studies of the upper Neisse catchment in the Czech Republic and Germany showed a relationship between areas with forest cover above 70%, base flow in the river and low nutrient concentrations. This situation pertains to the Mała Panew catchment area. The river in question exhibits a low irregularity coefficient and low annual flow variability, as documented in reference (Rzętała and Machowski, 2018). The extensive forested areas in the catchment contribute to the potential for phosphorus to enter the river from forest areas via surface runoff. This hypothesis is corroborated by the observation that anthropogenic phosphorus forms (orthophosphates) concentrations are low (Fig. 7). The studies demonstrate that phosphorus transport primarily occurs within the regions of surface water movement, where surface runoff occurs along areas exhibiting high soil

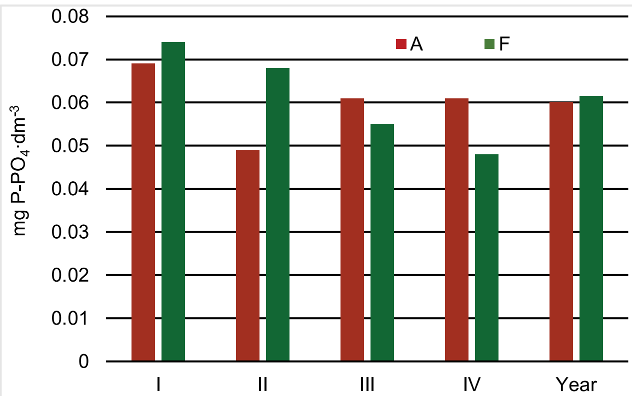
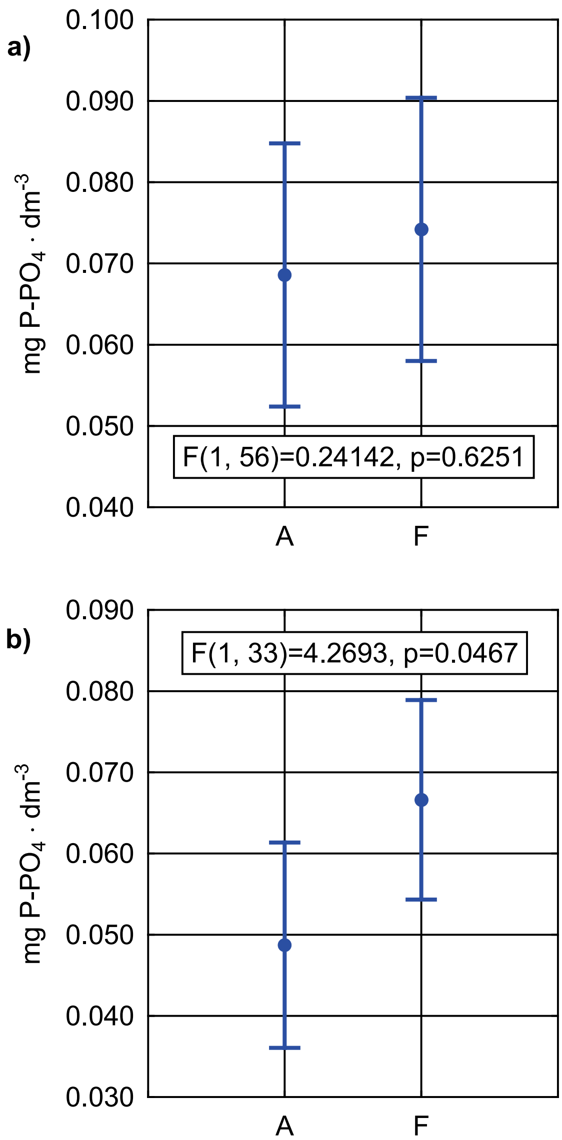


Fig. 6. The mean quarterly and annual concentrations of phosphates (PO_4^{2-}); A = agricultural catchments, F = forest catchments; I, II, III, IV – quarters of year; source: own study



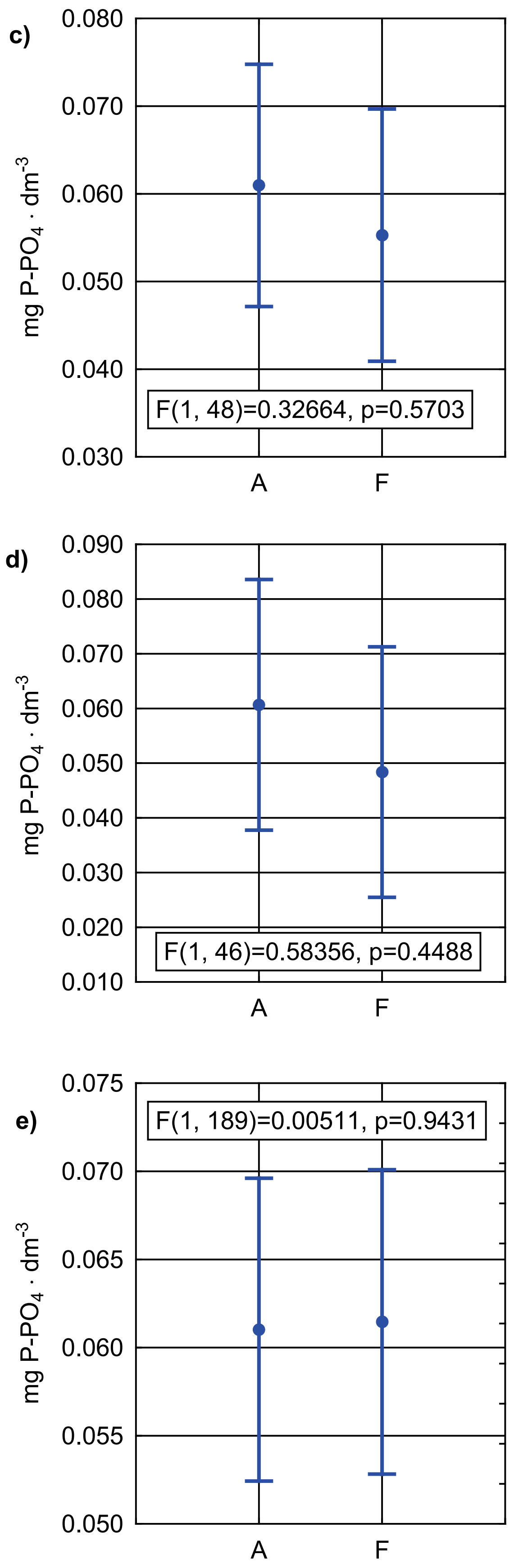


Fig. 7. The significance of differences between the total phosphates (PO_4^{2-}) concentrations in agricultural catchments (A) and forest catchments (F) in: a) I quarter, b) II quarter, c) III quarter, d) IV quarter, e) year; source: own study

phosphorus content (Gburek and Sharpley, 1998). It can proposed that the source of phosphorus compounds in the Mała Panew River may be decomposing forest organic matter. In the studied catchment area, forest areas bordering the Mała Panew River bed, which are predominantly deciduous, may be a source of phosphorus originating from decomposing organic matter.

The forest cover of the catchment area exerts a beneficial influence on the concentration of dissolved forms of phosphorus in the river. The primary river flow within the catchment area is derived from the interconnection of smaller catchments, resulting in the "averaging" of local conditions for the formation of runoff. The identification of areas with a propensity for surface runoff and the observation of a correlation between streamflow P concentration patterns and P concentrations in near-stream soils indicate that, with regard to phosphorus, the focus should be on near-stream regions rather than the entire watershed.

CONCLUSIONS

The mean phosphate concentration in the sampled catchment area was found to be relatively low, whereas the concentration of total phosphorus was found to be high. The quarterly and annual concentrations of total phosphorus in catchments with a higher proportion of agricultural land were observed to be lower than in catchments with a lower proportion of agricultural land. Nevertheless, the observed differences in concentration were not found to be statistically significant at the 0.05 level. A significantly lower concentration of this form of phosphorus was observed in the second quarter in catchments with a higher proportion of agricultural land. This may be attributed to the occurrence of intensive vegetation processes during this period (IV–VI), which result in an increased uptake of dissolved phosphorus compounds.

The forest cover of investigated area the catchment area exerts a beneficial influence on the concentration of dissolved forms of phosphorus in the river. The primary river flow within the catchment area is derived from the interconnection of smaller catchments, resulting in the "averaging" of local conditions for the formation of runoff. The identification of areas with a propensity for surface runoff and the observation of a correlation between streamflow P concentration patterns and P concentrations in near-stream soils indicate that, with regard to phosphorus, the focus should be on near-stream regions rather than the entire watershed. The catchment area under consideration encompasses a forest cover exceeding 60%. The majority of forests in the area of study are situated in proximity to the river valley. In contrast, arable land, which has the potential to exert a significant influence on the concentration of phosphates in the river (due to its agrarian use), is distributed in the catchment areas situated at a greater distance from the river valley (namely the northern and southern regions). These areas represent a relatively small proportion of the overall development structure of each catchment area. Furthermore, the concentration of phosphorus compounds demonstrates a negative correlation with the share of arable land within the total area of the partial catchments that have been subjected to analysis. The aforementioned developments in the catchment area, coupled with the relatively low concentrations of orthophosphates, suggest that their presence is largely attributable to point sources of these emissions from urbanised areas. The results of the conducted studies indicate that the flow of phosphorus in the form of a suspension of solid particles P significantly exceeds its dissolved flux.

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CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

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