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Land Cover Effects on Selected Nutrient Compounds in Small Lowland Agricultural Catchments

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Abstract: The influence of landscape on nutrient dynamics in rivers constitutes an important research issue because of its significance with regard to water and land management. In the current study spatial and temporal variability of N-NO_3 and P-PO_4 concentrations and their landscape dependence was documented in the Świder River catchment in central Poland. From April 2019 to March 2020, water samples were collected from fourteen streams in the monthly timescale and the concentrations of N-NO_3 and P-PO_4 were correlated with land cover metrics based on the Corine Land Cover 2018 and Sentinel 2 Global Land Cover datasets. It was documented that agricultural lands and forests have a clear seasonal impact on N-NO_3 concentrations, whereas the effect of meadows was weak and its direction was dependent on the dataset. The application of buffer zones metrics increased the correlation performance, whereas Euclidean distance scaling improved correlation mainly for forest datasets. The concentration of P-PO_4 was not significantly related with land cover metrics, as their dynamics were driven mainly by hydrological conditions. The obtained results provided a new insight into landscape–water quality relationships in lowland agricultural landscape, with a special focus on evaluating the predictive performance of different land cover metrics and datasets.

Keywords: nitrate nitrogen; phosphate phosphorous; land cover; metrics; lowland streams

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1. Introduction

Over the past few decades, special attention has been paid in water quality investigations to nutrient compounds, primarily nitrogen and phosphorus ions, whose excessive presence in the freshwater environment results in the accelerated eutrophication of streams and lakes [1–3]. It was broadly documented that the eutrophication process causes several negative ecological consequences, mostly affected by massive phytoplankton and algae blooms, a serious problem in the context of water supply due to its toxicity and impact on human health [4–6]. Changes in physico-chemical water properties, such as the decrease in water saturation with oxygen, the increase of water acidification, and the reduction of its transparency [7,8], were also documented as results of eutrophication. In addition, the presence of high nutrient concentrations, especially various nitrogen forms, also has a direct impact on the life-cycles of aquatic organisms in inland waters [9]. It has been documented that high concentrations of nitrate ions cause the conversion of oxygen-carrying pigments (hemoglobin, hemocyanin) to forms that are incapable of carrying oxygen (methemoglobin and methemocyanin) [10,11]. Furthermore, there is also broad evidence of the potential carcinogenic role of nitrates in mammals [12]. Numerous studies in this area indicate that the toxicity of nitrogen compounds in the aquatic environment increases with the exposure time of organisms and with the concentration of these substances [13]. Generally, values over 10 mg/L of NO_3 are proven to adversely affect fish and invertebrates [14].

The load of nutrient compounds entering the streams and rivers significantly depends on natural and anthropogenic factors, which affect the sources, mobilization, and migration of ions across the landscape [15,16]. In this context, special attention is paid to the human impact on the chemical composition of flowing waters, as such activity, related mainly to urbanization and agriculture, is responsible for pollution and negative consequences in the aquatic environment [17–20]. It is well documented that industrial and municipal sewage inflows, the use of fertilizers, and atmospheric deposition from anthropogenic emission are responsible for external ion sources affecting the streams, primarily various types of nitrogen [21–23]. Furthermore, soil erosion, which is a consequence of deforestation, cattle grazing, and agrotechnical operations, results in more intense ion mobilization [24,25]. Land cover has also a direct influence on ion migration through uptake and release processes of physical, chemical, and biological nature [26–29]. Simultaneously, river regulation, especially conducted in urbanized and industrial areas, results in a reduction of the self-purification capacity of running waters [30]. The latter is also affected by the removal of riparian buffer zones, which are an important barrier where nutrient uptake by vegetation, as well as denitrification occurs [31,32]. As a result, one of the most important predictors of the concentration of nitrogen and phosphorus ions in flowing waters is the way the area of their catchment is used, as it affects their sources, mobilization, and migration [16,33].

Investigations related to the influence of the surrounding landscape on selected river water quality parameters have a relatively long tradition in hydrological and environmental sciences [34,35]. Today, such investigations are still broadly conducted, mainly thanks to the appearance of GIS software, considered as a useful tool for relatively easy spatial data processing [36,37]. Along with the development of GIS software, the increasing availability of high-resolution spatial data made it possible to precisely quantify various types of landscape properties, such as slopes, land use, and land cover types, using different types of metrics [16,29,38]. In such a way, a number of studies linked the concentration of nutrient compounds with landscape properties and these relationships were studied at different spatial scales, from entire catchment areas [39] to buffer zones along the watercourses [40,41], sometimes with additional distance or flow accumulation scaling [42]. Most of the work in this area, however, concerned catchments of over a hundred square kilometers, including upland or highland relief and steeper slopes of the terrain, where high hydrological connectivity and intensive erosion result in increased ion migration [43–45]. Meanwhile, few studies used widely available land cover datasets [39], while in most cases land cover metrics were computed with the use of government or self-classification-based land cover maps [46,47], making the results not comparable at the European scale. Finally, the results and conclusions of such investigations were not consistent and the effects of particular land cover metrics on nutrients ranged from negative to even positive [48,49]. Therefore, there still remains a need to explore such relationships and evaluate the most accurate spatial scales of landscape predictors, calculated on different widely available and cost-free datasets. This seems to be particularly valuable in the case of small lowland catchments, where the dependence of water quality on the environment was not widely documented. For example, in Poland such studies mainly concerned shallow groundwater [50], river-lake systems [51], and selected individual watercourses, such as the Raszynka River [52] and highland streams in the proximity of Gdańsk in the Pomerania Region [53].

Thus, the paper focused on selected nutrient compounds and their land cover predictors across small agricultural catchments. The specific objectives of the study were to: (1) characterize spatial and seasonal variations of nitrate nitrogen and phosphate phosphorous concentration in lowland streams; (2) compare the performance of the relationships between nitrate and phosphate concentrations and landscape metrics estimated for different scales; and (3) evaluate the performance of landscape metrics computed with two different, but widely available and cost-free datasets.

2. Materials and Methods

The investigated area is drained by the Świder River, which is a 99-km-long right tributary of the Vistula River. Its catchment area is approximately 1160.7 km^2 (Figure 1) and according to [54], it belongs to the denudation-type Garwolińska Plain, located within the Mazovian Lowland. Superficial deposits from the Quaternary age, building the overall flat plain relief, consist mainly of sandy loam and boulder clays, while in some places aeolian sands and gravels (dune terraces), as well as silt deposits (valleys) are present [55]. The elevation of the study area is relatively uniform and ranges from approximately 108 m a.s.l. (above sea level) near the mouth of the Glinianka Stream to only 187 m a.s.l. near the springs of the Sienniczanka. The climate of the investigated area can be considered as warm temperate in the transitional zone from marine to continental [56]. The mean annual air temperature is approximately 8–9 °C, while annual precipitation amounts to 500–550 mm. The lowest mean temperature is usually observed in January, while the highest in July. The same is true for the highest monthly precipitation sum [57]. As a result, the highest streamflow rates are observed in early spring as a result of snowmelt, and the lowest usually occur during summer and autumn. Because of the agricultural character of the study area, it is dominated by croplands and meadows, while the contribution of forested areas, composed mainly of white willows (*Salix alba* L.), common aspens (*Populus tremula* L.), black alders (*Alnus glutinosa* (L.) Gaertn.), and scots pines (*Pinus sylvestris* L.), is similar to the average value for Poland (approximately 30%) [58]. It must be emphasized that the investigated area is characterized by a low degree of urbanization—according to the Corine Land Cover 2018, the contribution of anthropogenic areas does not exceed 10%, and such artificial surfaces can be identified as small- and medium-sized villages and settlements.

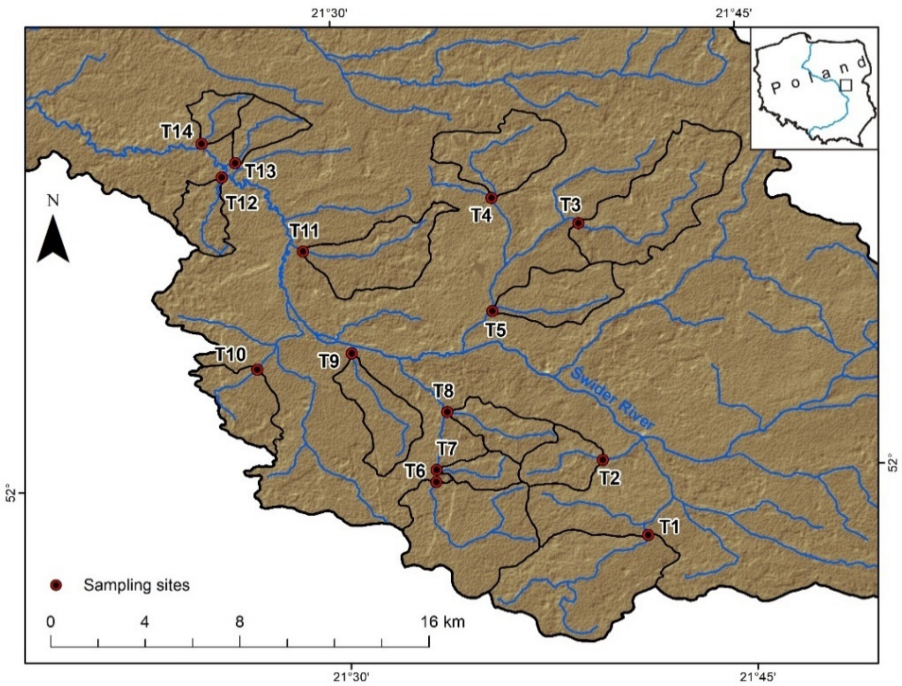

Figure 1. Location of the sampling sites in the Świder River catchment. The hillshade model was created on the basis of digital terrain model SRTM 1 Arc-Second Global (USGS).

Field investigations were carried out in twenty independent catchments drained by first- or second-order lowland streams. The sampling sites, with the catchment area ranging from 3.7 to 23.7 km^2, were selected with a view to maximizing differences between land cover properties, however, they are simultaneously characterized by relatively similar geological and climatological properties. Their location precluded direct anthropopressure reflected in the water quality, such as point sources related to sewage inflows and unstratified, through-flow reservoirs. Also, the watercourses had to be permanently flowing, which excluded six streams during the sampling period. In consequence, only 14 watercourses were adopted in the analysis (Figure 2).

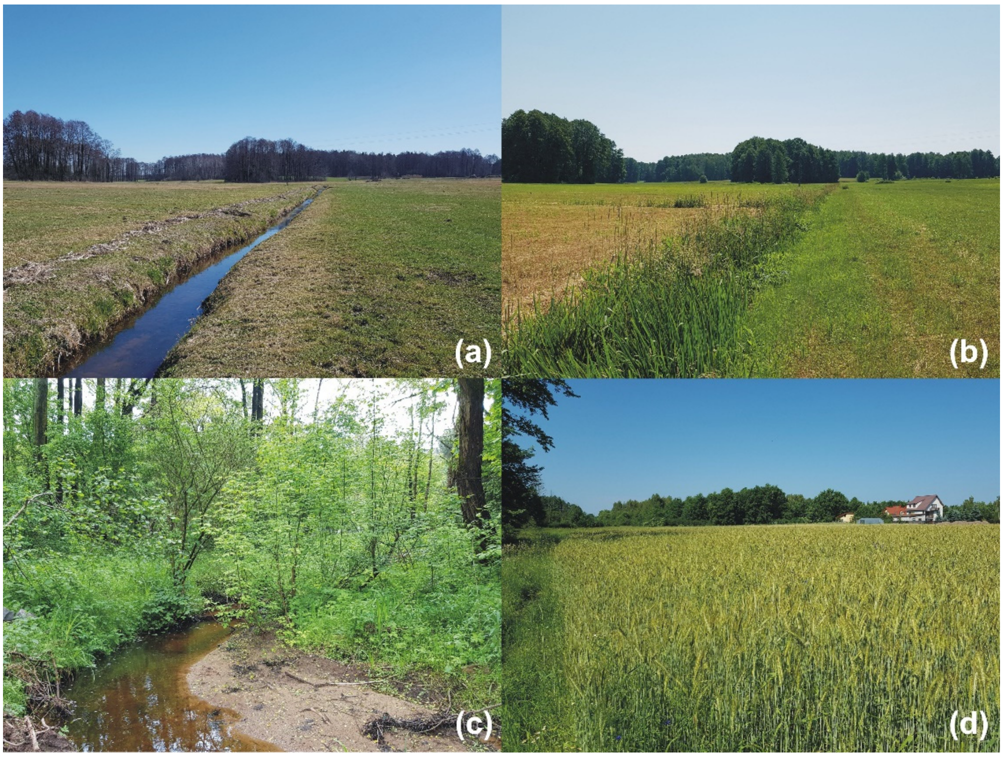

Figure 2. The channel of the Sienniczanka stream (T4) during spring (**a**); the same sampling site during summer, overgrown mainly by *Sparganium erectum* L. (**b**); the channel of the Ostrowik stream (T12) shaded, with the forest consisting of *Populus tremula* L. and *Alnus glutinosa* (L.) Gaertn. (**c**); a typical agricultural landscape with common wheat crops 10 meters from site T13 (**d**).

Water samples were collected from April 2019 to March 2020 in regular monthly intervals (in the middle of each month) into a polyethylene bottles, always from the main current of the streams. Then immediately after transportation to the faculty laboratory, the concentration of nitrate nitrogen (N-NO_3) was determined using the sulfanilic acid method, while the phosphate phosphorous concentration (P-PO_4) was determined using the molybdenum blue method, both with the use of a LF300 photometer. To determine whether the sampling sites are not directly influenced by anthropopressure during the collection of water samples, dissolved oxygen (DO) saturation (%) and conductivity (µS/cm) were measured in the field. This was conducted with portable, handheld meters Hanna Hi 98193 (resolution of 0.1 °C and ±1.5% mg/L) and Hanna Hi 9811-5 (resolution of ±2.0% µS/cm), both regularly calibrated. Such measurements confirmed the appropriate selection of sampling sites, as the spatial and seasonal variability of DO and conductivity values could be explained by natural factors. Additionally, the macrophytes coverage was assessed in the cross-section of the channels positioned 50, 100, 150, and 200 m upstream from the sampling sites. In such cross-sections, the percentage of macrophytes (from 0 to 100% with 10% of precision) was visually evaluated and then averaged. It must be noted that both measurements and water samples were collected in days characterized by stable flow rates and, whenever possible, a minimum of three days after rainfall events.

To provide a hydrometeorological background, mean monthly air temperature and monthly precipitation sums in the investigated period were presented in the context of the respective mean values from the period of 1991–2020. For this purpose, air temperature and precipitation data from the nearest representative meteorological station Warsaw-

Okęcie were acquired from the Institute of Meteorology and Water Management—National Research Institute.

Several catchment metrics were calculated with the use of raster and vector processing tools in ArcMap 10.5 GIS software (Esri, California, USA), to evaluate their influence on the spatial and seasonal variability of N-NO_3 and P-PO_4 ions in the environment. The catchment area of the sampling sites (A) was estimated with the use of the vector layers of Polish digital hydrographic maps. The contribution of selected, individual types of land cover (in %) were calculated on the basis of two cost-free and European-range datasets. The first, the Corine Land Cover 2018 vector land cover map (CLC 2018), is based predominantly on the visual interpretation of Landsat satellite imagery [59], while the second, the high-resolution Land Cover Map of Europe, is based on automatic classifications of images acquired from the Sentinel 2 satellite (S2GLC), launched by the European Space Agency [60]. Three classes of land cover—agricultural lands, meadows, and forests—were distinguished both from CLC 2018 and S2GLC datasets with the use of vector and raster processing tools. Detailed descriptions of the original classes used to compute them are reported in Table 1. Artificial (anthropogenic) surfaces, marshes, peatbogs, and water bodies were omitted from the analysis due to their sporadic occurrence and, in consequence, their possible disruption of statistical analysis due to many zeros in the dataset. In addition, artificial surfaces were excluded due to significant differences in their contribution across investigated catchments (up to dozens of times).

Table 1. Classes used to compute land cover metrics and their definitions.

Land Cover Type	CLC 2018 Classes and Definitions	S2GLC Classes and Definitions
Agricultural lands	2.1.1. Non-irrigated arable land—Cultivated land parcels under rainfed agricultural use for annually harvested non-permanent crops, normally under a crop rotation system, including fallow lands within such crop rotation.	Cultivated areas—areas managed by humans that include non-irrigated and irrigated arable land with different crops, and land under rice cultivation. It also includes temporary bare soils (e.g., fallow lands).
Meadows	2.3.1. Pastures, meadows, and other permanent grasslands under agricultural use—permanent grassland characterized by agricultural use or strong human disturbance. Floral composition dominated by graminacea and influenced by human activity. Typically used for grazing-pastures, or mechanical harvesting of grass–meadows.	Herbaceous vegetation—land covered by herbaceous vegetation, including both natural, low productivity grassland and managed grassland, used for grazing and/ or mowing.
Forests	3.1.1. Broad-leaved forest—vegetation formation composed principally of trees, including shrub and bush understory, where broad-leaved species predominate. 3.1.2. Coniferous forest—vegetation formation composed principally of trees, including shrub and bush understory, where coniferous species predominate. 3.2.4. Transitional woodland/shrub—transitional bushy and herbaceous vegetation with occasional scattered trees. Can represent woodland degradation, forest regeneration/recolonization or natural succession.	Broadleaf tree cover—land covered with broadleaved tree canopy that loses leaves seasonally, regardless of the plant height. Coniferous tree cover—land covered with needle-leaved tree canopy that do not lose needles seasonally, regardless of the plant height.

The contributions of individual land cover types were calculated for the whole catchment area, as well as for buffer zones of 100, 250, and 500 m width, extending from the sampling site upstream to the springs. To determine how land cover distance from the stream influences the relationships between metrics and ion concentrations, the inverse weighted distance method was also applied to calculate metrics. To this end, a modified formula which takes into account the Euclidean distance (ED) of each raster cell to the stream [61] was used:

$$LC = (SUM\ [Z_i\ /\ D_i]\ /\ SUM\ [1\ /\ D_i]) \times 100 \quad (1)$$

where LC is the percentage of land cover type (%); n is the total number of cells in the catchment; Z_i (n) is the presence of land cover z in cell n (1 or 0); and D_i is the Euclidean distance from cell i to the stream.

To assess the spatial and seasonal variability of nutrient compounds in the investigated lowland catchments, mean, maximum, minimum, and standard deviation of N-NO_3 and P-PO_4 concentrations were calculated both for the individual sampling sites, as well as for certain months of the sampling period. These values were presented on the mean, max, and min charts. Relationships between the concentration of N-NO_3 and P-PO_4 and computed land cover metrics were evaluated on the basis of correlation analysis. Initially, data was inspected with the Shaphiro–Wilk goodness of fit test, which indicated that nearly half of the land cover metrics do not have a normal distribution ($p < 0.05$). After normalization with the logarithmic function, the distribution was still outside of normal. Thus, the Spearman rank correlation coefficient, which is considered as definitely more resistant to outliers and more reliable in the case of a small sample size, was used instead of the Pearson coefficient. In this way land cover types both from CLC 2018 and S2GLC datasets, calculated for the total catchment area, buffer zones, and weighted by Euclidean distance, were linked with the concentration of N-NO_3 and P-PO_4. This was applied for mean concentration of N-NO_3 for the whole investigated period (IV–III) and for the four periods—spring (IV–VI), summer (VII–IX), autumn (X–XII), and winter (I–III), similar to [40,62]. A probability value of correlation of less than 0.05 was considered as statistically significant. Calculations were performed in the Statistica 13.5 software (TIBCO Software Inc., California, USA) and presented in tabular form and on the bar charts, which allowed the authors to characterize seasonal changes in the investigated relationships (Table 2).

Table 2. Detailed characteristics of the sampling sites catchments.

Stream	Site	A (km^2)	M (%)	CLC AL (%)	CLCMD (%)	CLC FR (%)	S2GLC AL (%)	S2GLC MD (%)	S2GLC FR (%)	MN DO (%)	SD DO (%)	MN CON (µS/cm)	SD CON (µS/cm)
Parysów Stream	T1	23.7	60	39.2	17.8	33.6	22.2	35.6	31.6	59	16	473	64
Stodzew Stream	T2	6.3	15	62.3	5.0	28.5	44.1	20.3	29.1	65	13	363	44
Sienniczanka	T3	20.7	70	47.4	9.8	36.5	29.0	25.6	40.4	88	11	416	67
Pogorzel Stream	T4	12.1	35	33.7	2.7	57.9	13.0	19.7	55.1	46	12	413	34
Żaków Stream	T5	9.3	80	68.6	16.3	8.0	49.4	33.2	14.1	97	15	395	34
Struga	T6	20.4	45	65.4	3.1	21.8	35.2	31.8	24.3	84	11	265	55
Żelazna Stream	T7	3.7	85	85.6	0.0	14.0	51.7	27.1	16.2	76	17	262	36
Kalonka Stream	T8	6.3	15	59.6	13.7	19.8	26.5	41.2	26.0	46	8	189	20
Bolechówek Stream	T9	7.1	50	86.5	0.3	12.1	54.2	29.1	12.6	66	13	390	58
Karpiska Stream	T10	8.2	40	30.9	0.0	61.8	17.4	11.9	59.6	46	9	531	70
Chełst Stream	T11	12.3	5	42.2	11.3	41.8	16.2	30.1	40.2	67	11	412	41
Ostrowik Stream	T12	5.4	5	37.2	6.8	55.2	5.4	22.8	58.2	72	12	209	21
Rzakta Stream	T13	4.9	40	82.6	0.0	11.6	45.5	34.6	11.6	92	8	430	69
Glinianka Stream	T14	3.7	25	70.0	5.9	19.8	33.7	34.0	22.2	70	14	455	65

Abbreviations: A—catchment area, M—macrophytes coverage, AL—agricultural lands, MD—meadows, FR—forests, CLC—Corine Land Cover 2018 dataset, S2GLC—Sentinel 2 Global Land Cover dataset, DO—dissolved oxygen saturation, CON—water conductivity, MN—mean values, SD—standard deviation.

3. Results

3.1. Hydrometeorological Background

The investigated period from April 2019 to March 2020 can be considered as very warm—the average air temperature at the Warsaw-Okęcie meteorological station reached 11.4 °C, which was 2.5 °C higher than the average from the reference period (1991–2020). The highest mean monthly temperature (21.4 °C) was observed in August, while the lowest in January (2.6 °C). During the sampling period, subzero monthly mean air temperatures were not documented. Furthermore, only in May and July was the air temperature lower than in the reference period (Figure 3a). The precipitation sum during the sampling period was, in turn, definitely lower than in the reference period (Figure 3b), which indicated extremely dry conditions. Total precipitation was only 390 mm, which accounted for only 72% of the average sum of precipitation calculated for the reference period. Except for May, September, December, and February, in the remaining months precipitation was lower than the mean values calculated for the reference period (Figure 3b).

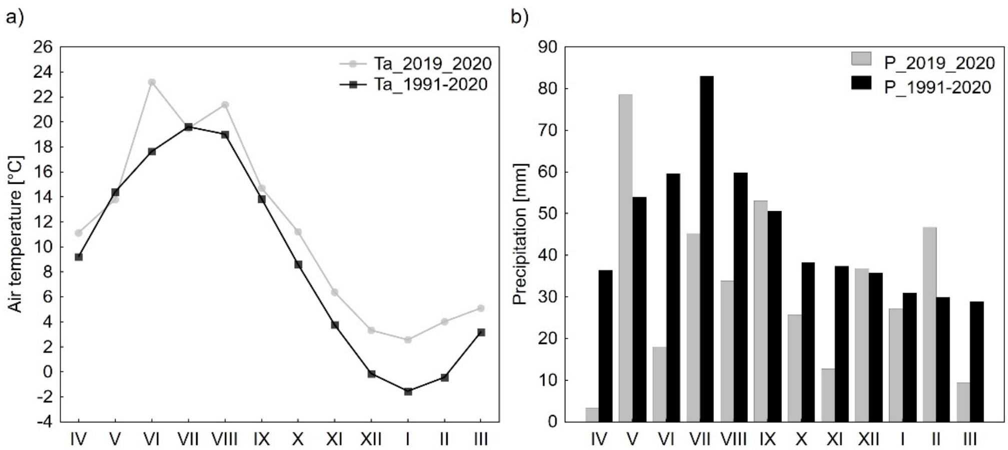

Figure 3. Mean monthly air temperature values (**a**) and monthly precipitation totals (**b**) from April 2019 to March 2020 on the background of the years 1991–2020 for Warsaw-Okęcie meteorological station. Based on data from the Institute of Meteorology and Water Management—National Research Institute.

3.2. Spatial and Seasonal Distribution of Nutrients

Clear spatial variability of N-NO_3 and P-PO_4 concentrations was found between the investigated lowland catchments (Figure 4a–d). In some catchments, the mean and maximum concentrations of N-NO_3 did not exceed 1.5 and 2–3 mg/L, respectively, while in other sampling sites values over 15 mg/L were noted, while mean values were definitely higher (Table 3). The variability of N-NO_3 concentration measured with the standard deviation was the highest in sampling sites with the highest mean concentration values, such as T2, T9, T13, and T14. In the case of P-PO_4, the spatial variability was definitely lower in comparison to N-NO_3, while their variability was also generally more aligned across sampling sites, as values of standard deviation ranged from 0.67 to 1.89 mg/L (Table 3).

The seasonal variability of N-NO_3 and P-PO_4 concentrations was also clearly outlined, as indicated by values from all sampling points, aggregated in the monthly timescale (Figure 4b,d). In the case of N-NO_3 relatively low mean and maximum concentrations (not exceed 4.0 mg/L) were mainly observed in the growing season (defined as a period with mean temperature above 5 °C)—particularly from May to as late as December. On the contrary, high values of N-NO_3 concentration were noted from January to April, representing winter and early spring months (Figure 4). The seasonal course of P-PO_4 concentrations was more complex—high concentrations were interspersed with low ones, which was documented in the summer period. However, in the hot period from May to October generally higher concentrations of P-PO_4 were measured in comparison to the winter months (Figure 4).

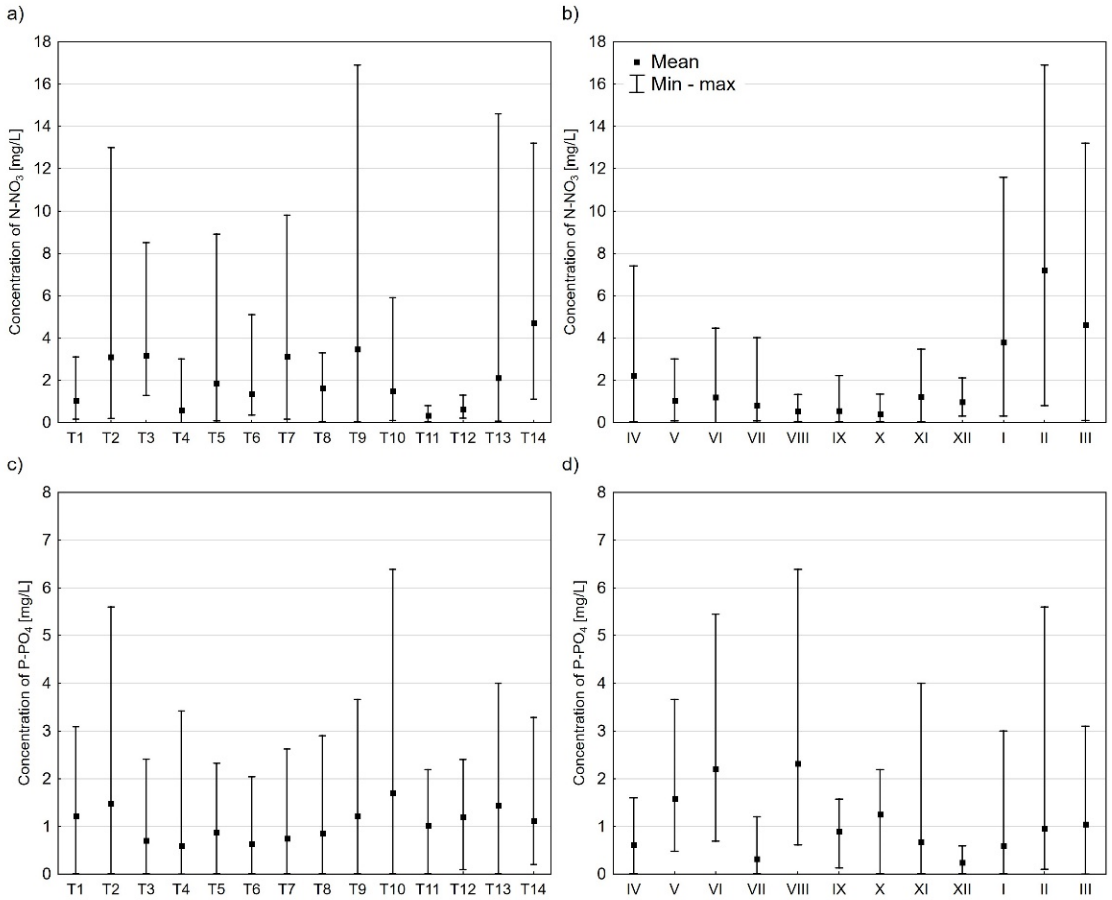

Figure 4. Spatial and seasonal variability of N-NO_3 (**a** and **b**, respectively) and P-PO_4 (**c** and **d**, respectively) across the sampling sites from April 2019 to March 2020.

Table 3. Mean and standard deviation (SD) values for N-NO_3 and P-PO_4 concentrations in mg/L in the investigated catchments, calculated for the sampling period from April 2019 to March 2020.

Parameter	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14
Mean N-NO_3	1.04	3.10	3.18	0.59	1.87	1.36	3.11	1.64	3.47	1.51	0.35	0.63	2.11	4.72
SD N-NO_3	0.97	3.56	2.25	0.85	2.51	1.40	3.21	0.87	5.40	2.10	0.25	0.34	3.96	3.56
Mean P-PO_4	1.22	1.48	0.70	0.59	0.88	0.64	0.75	0.85	1.22	1.71	1.02	1.20	1.44	1.12
SD P-PO_4	1.00	1.89	0.82	0.90	0.79	0.68	0.69	0.91	0.92	1.77	0.67	0.70	1.21	0.82

3.3. *Land Cover Effects on Nutrient Concentrations*

The overall pattern of correlation between selected land cover metrics, calculated for two different datasets, and mean concentrations of N-NO_3 and P-PO_4 was presented in Table 4. Generally, both in the case of the CLC 2018 and S2GLC datasets, the mean concentration of N-NO_3 during the investigated period was positively correlated with the percentage of agricultural lands and negatively correlated with the percentage of forest cover on $p < 0.05$ (Table 4). For meadow datasets, no statistically significant correlations were found and the relationships, as indicated by the sign of the correlation coefficients, were different depending on the dataset (Table 4). Generally, the CLC 2018 agricultural land and forest datasets provided a slightly better correlation performance with N-NO_3 concentrations compared to the respective S2GLC datasets. Across agricultural land datasets, the best performance was found for the larger spatial scales, such as 250-m-wide buffer zones and the total catchment area for CLC 2018 and 500-m-wide buffer zone for S2GLC. The opposite was true for the forest datasets, which were generally better correlated in smaller scales, such as 100-m-wide buffer zones (Table 4). For both land cover datasets, forests were correlated better with N-NO_3 concentration with additional Euclidean distance scaling, which was not evidenced for the agricultural lands. In the case of P-PO_4 concentration no statistically significant relationships were found with the use of CLC 2018 and S2GLC datasets ($p > 0.05$) Significant differences in correlation performance, as well as between signs of the correlation, indicate the accidental character of the land cover metrics relationship with P-PO_4 concentrations (Table 4).

Table 4. Spearman rank correlation coefficients linking selected land cover metrics and mean N-NO_3 and P-PO_4 concentrations across investigated lowland streams during the study period from April 2019 to March 2020. Abbreviations: T, total catchment area; 100, 250, and 500, buffer zone width; ED, Euclidean distance scaling. The * indicates statistically significant correlation at the $p = 0.05$.

Land Cover Type	Metrics	N-NO_3 CLC	N-NO_3 S2GLC	P-PO_4 CLC	P-PO_4 S2GLC
Agricultural lands	T	0.73 *	0.75 *	–0.01	0.08
	100	0.71 *	0.71 *	0.32	0.22
	250	0.82 *	0.76 *	0.18	0.11
	500	0.76 *	0.82 *	0.10	0.12
	ED_T	0.82 *	0.76 *	0.19	0.13
	ED_100	0.72 *	0.68 *	0.34	0.17
	ED_250	0.79 *	0.71 *	0.23	0.22
	ED_500	0.81 *	0.76 *	0.15	0.13
Meadows	T	–0.26	012	–0.18	–0.05
	100	–0.26	0.51	–0.47	–0.32
	250	–0.25	0.38	–0.42	–0.26
	500	–0.28	0.16	–0.33	–0.19
	ED_T	–0.21	0.36	–0.32	–0.3
	ED_100	–0.33	0.51	–0.17	–0.32
	ED_250	–0.25	0.39	–0.42	–0.33
	ED_500	–0.19	0.34	–0.41	–0.26
Forests	T	–0.59 *	–0.57 *	–0.01	–0.03
	100	–0.74 *	–0.71 *	0.17	0.02
	250	–0.66 *	–0.72 *	0.22	–0.02
	500	–0.68 *	–0.68 *	0.07	–0.07
	ED_T	–0.73 *	–0.67 *	0.07	0.04
	ED_100	–0.75 *	–0.73 *	0.19	0.02
	ED_250	–0.72 *	–0.73 *	0.20	–0.03
	ED_500	–0.70 *	–0.68 *	0.22	–0.02

Changes of the correlation performance across averaged three-month periods provide an insight into the seasonal variability of the land cover effect on N-NO_3 concentrations in lowland catchments (Figure 5). Overall, in the case of the agricultural lands dataset, the strongest positive correlation was performed in the winter and spring periods, when nearly all relationships were statistically significant (Figure 5a). The S2GLC agricultural land dataset performance during spring was slightly lower in comparison to CLC 2018 dataset. However, the situation was opposite in the winter period. In the summer and autumn periods, correlation values with agricultural land datasets were insignificant for both CLC 2018 and S2GLC ($p > 0.05$). Generally speaking, meadows had no significant impact on N-NO_3 concentration in the both CLC 2018 and S2GLC datasets ($p > 0.05$). However, during the autumn period for the buffer zone of 100 m width there was observed single significant positive correlation (Figure 5b). It seems interesting that the S2GLC meadows dataset always provided a positive relationship with N-NO_3 concentration, while in the case of the CLC 2018 dataset, the same direction of the impact was noted only in the summer and autumn periods. Additionally, in those seasons the relationship, even not significant, was the strongest. According to the correlation results, the presence of forests generally has a negative impact on N-NO_3 concentration for both CLC 2018 and S2GLC datasets in all studied periods (Figure 5c). Positive relationships were documented only in summer and autumn. However, like all of the relationships in those periods, they were found to be statistically insignificant ($p < 0.05$). The strongest, significant correlations were performed for the CLC 2018 and S2GLC dataset in the winter period. Similar to agricultural lands, in this season the best performance was provided by the S2GLC dataset. This is not true for the spring period, when the CLC 2018 forest dataset performed slightly better. In all periods, the strongest correlations were obtained for the narrowest buffer zones (100 or 250 m), with Euclidean distance scaling.

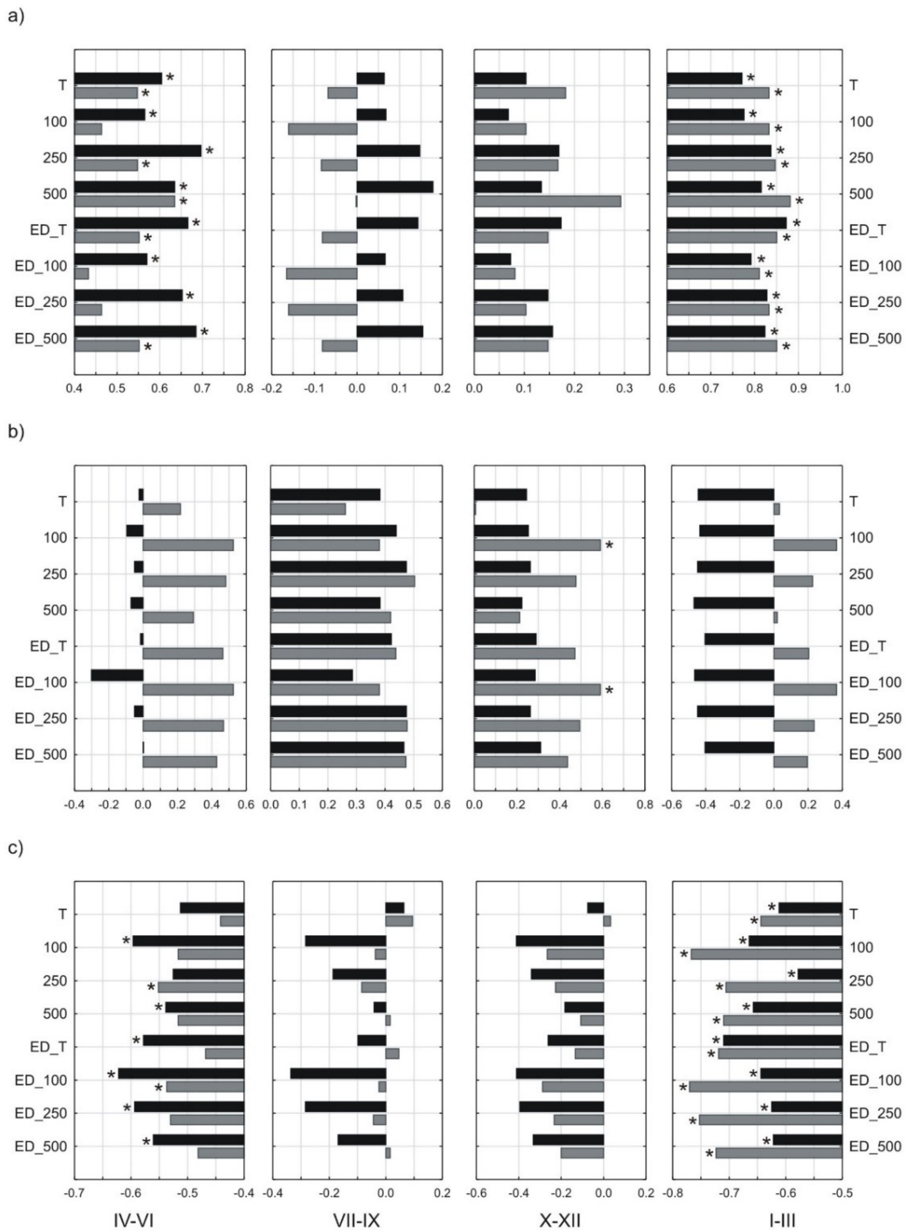

Figure 5. Correlation coefficients between N-NO_3 concentration in certain seasons and different land cover metrics calculated for agricultural lands (**a**), meadows (**b**), and forests (**c**) with the use of the CLC 208 and S2GLC datasets, respectively. Abbreviations: T, total catchment area; 100, 250, and 500, width of the buffer zone; ED, metrics computed with the Euclidean distance scaling. The * indicates significant correlation at $p = 0.05$.

Correlation performance for the P-PO_4 concentration was also seasonally varied, both in the case of agricultural land, meadows, and forest datasets (Figure 6). However, nearly all of the metrics were correlated insignificantly ($p < 0.05$) and the signs of the correlation varied between the respective CLC 2018 and S2GLC datasets. Only in the case of S2GLC meadows dataset was the direction of the relationships uniform across all of the investigated periods (Figure 6b) and the values of the correlation were relatively higher than for agricultural lands and forests. In the autumn period there was documented an even significant correlation between the P-PO_4 concentration and the percentage of meadows in a 100-m-wide buffer zone for both datasets.

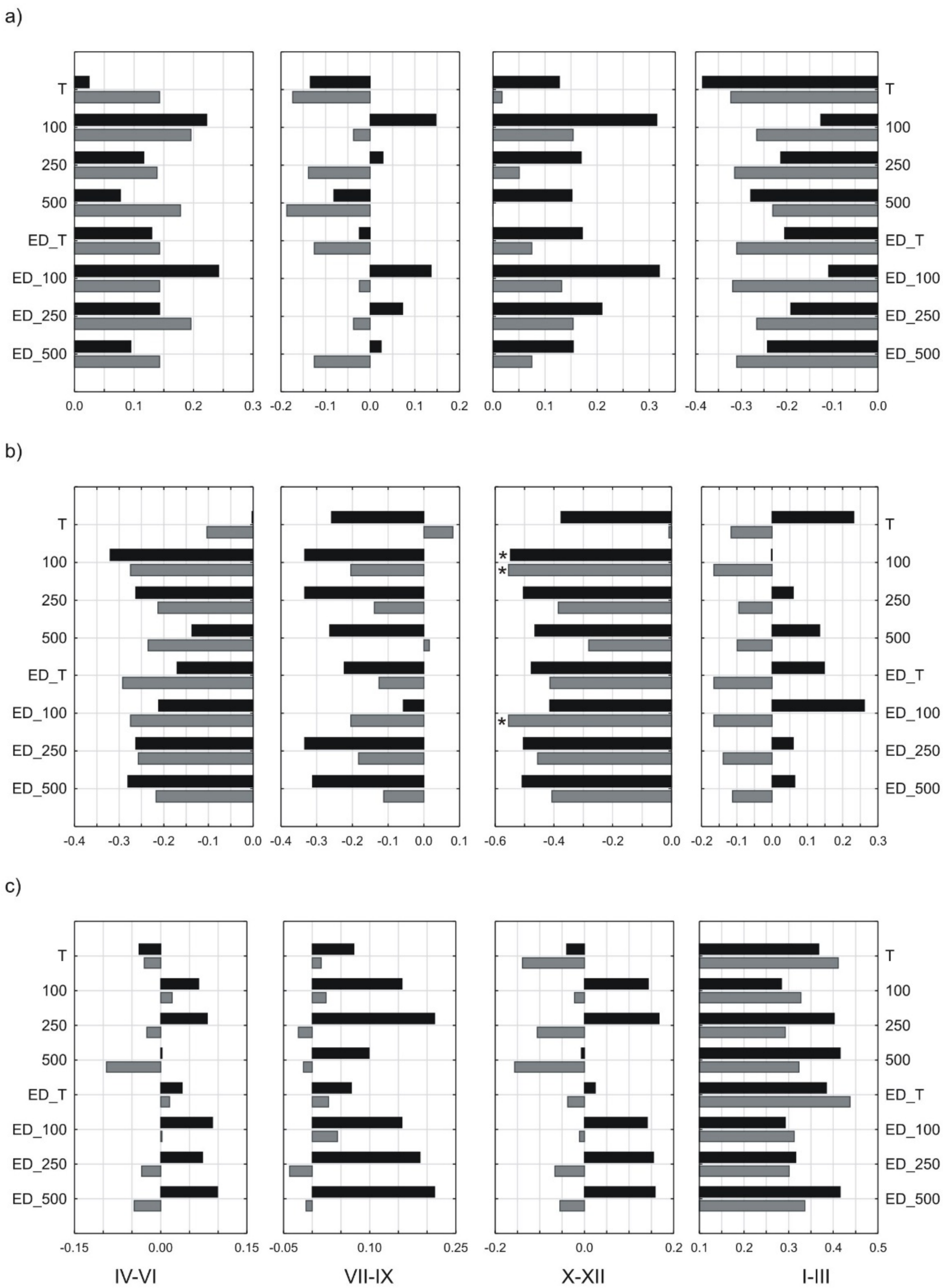

Figure 6. Correlation coefficients between P-PO_4 concentration in certain seasons and different land cover metrics calculated for agricultural lands (**a**), meadows (**b**), and forests (**c**) with the use of the CLC 2018 and S2GLC datasets, respectively. Abbreviations: T, total catchment area; 100, 250, and 500, width of the buffer zone; ED, metrics computed with the Euclidean distance scaling. The * indicates significant correlation at $p = 0.05$.

4. Discussion

4.1. Spatial and Seasonal Nutrient Dynamics

The effect of land cover on selected nutrient compounds was investigated on the example of lowland agricultural catchments located in central Poland. The sampling period was characterized by unusually hot and dry meteorological conditions compared to the long-term averages. Such conditions have a significant effect on ion sources, migration, and delivery processes in geochemical pools [63]. Nevertheless, clear seasonal and spatial patterns of nitrate and phosphate concentration were observed in the investigated sites. Overall, seasonal changes of N-NO_3 concentrations were generally consistent with the typical annual cycle, as documented and discussed previously [64–66]. However, low values of N-NO_3 concentrations were also documented during autumn, with the minimum values observed as late as in October. Such a clear shift in the annual concentration course can be explained by increased air temperature in the autumn months, even by as much as 3.5 °C in December in comparison to the reference period. Simultaneously, small precipitation totals in this period resulted in a slower rate of N-NO_3 ion migration. In comparison to values reported in the literature [67,68], in the studied sites a relatively low concentration of N-NO_3 during the summer was observed, as well as its low spatial variability. This could be related to nutrient uptake, especially by the well-developed macrophytes [69], which is an effective process at low flow velocities [70]. In fact, in some of the investigated streams (e.g. T5, T7, T9, and T13), channel beds and banks were locally overgrown by *Sagittaria sagittifolia* L., *Phragmites australis* (Cav.) Trin. ex Steud., *Sparganium erectum* L., and *Carex nigra* Reichard. In addition, such streams were characterized by greater seasonal variability of N-NO_3 than forested, solar-sheltered catchments, where macrophytes occurred only locally (e.g. T8, T10, and T11). Denitrification, which is generally effective in quasi-natural streams in the presence of moderate water temperatures, could also constitute an important process of N-NO_3 removal [71]. In the case of P-PO_4, seasonal changes of its concentrations were significantly different in comparison to N-NO_3. They could be mainly related with hydrological conditions, as during the summer period the concentration of P-PO_4 was definitely higher than in the autumn and winter periods. During such summer baseflow periods, as documented by [72], inorganic soluble phosphorus becomes a significant component in the total phosphorous budget. A decrease of P-PO_4 concentration as an effect of dilution was particularly visible in July and September, when higher streamflow rate was observed due to intensive rainfall events occurred two and three days before sampling. In can be supposed that such dynamics of P-PO_4 after storm events is characteristic for the lowland landscape, where soil and land erosion, the main natural source of P-PO_4 ion [73,74], is expected to be insignificant due to slight slopes and generally flat terrain. The presented seasonal variability of P-PO_4 concentrations, even reported previously in the literature [75–77] is not the dominant, typical pattern, as different seasonal P-PO_4 variability was also observed [78,79]. In fact, seasonal changes of N-NO_3 and P-PO_4 concentrations in the investigated lowland streams are differently driven. In the case of N-NO_3 ions, temporal variability mainly results from the biogeochemical activity of terrestrial and aquatic vegetation, while in the case of P-PO_4 ions, a clear dependence on hydrological conditions was documented. A similar response of nutrient dynamics to landscape and hydrometeorological conditions was previously reported by [80] in the Owasco Lake catchment in Northeastern USA.

4.2. Land Cover Effect on Nutrient Variability

Results of the correlation analysis confirmed that agricultural activity has a great impact on N-NO_3 released into lowland streams. The positive correlation of the contribution of agricultural lands metrics in the catchment areas and N-NO_3 concentration was also extensively documented for other geographical regions [22,34,81–83]. On the other hand, the presence of deciduous and coniferous forests resulted in the decrease of the N-NO_3 delivered to the watercourses, which could be linked with ion uptake and its retention by woodland vegetation [84–86]. However, in the current study, the landscape effect on ion concentration was dependent on the season, both for the agricultural lands and forests. The contribution of agricultural lands and forests was significantly correlated with $N\text{-}NO_3$ concentration only in the spring and winter periods. This seasonal tendency can be related to the limited uptake of the $N\text{-}NO_3$ ions due to the lack of herbaceous and crop vegetation in this period [66] and increased hydrological connectivity caused by rain or snow precipitation [87], enhanced by low evapotranspiration [88]. Artificial and natural fertilizers, used frequently by farmers, constitute additional sources of nitrogen ions in this period [51,89]. Another factor worth mentioning are decomposition processes of terrestrial vegetation and macrophytes [90], as well as leaf litter from riparian zones [91]. In the spring and summer months, when terrestrial and aquatic vegetation is responsible for an uptake in nutrients, low and more uniform intensity of ion fluxes was observed through the catchments. In the case of $P\text{-}PO_4$, the lack of significant relationships between its concentrations and landscape metrics can be explained by the combination of several factors. Apart from the clear dependence of $P\text{-}PO_4$ on hydrological conditions, low intensity of soil and land erosion seems to be crucial in such lowland catchments. Moreover, because most of the rural areas in the investigated catchments are not connected to the sanitary sewer, human activity can be an important external source of $P\text{-}PO_4$ ions. This was previously evidenced in the neighboring Wilga catchment by [50] and can be confirmed by the increased $P\text{-}PO_4$ concentrations in comparison to other investigated lowland catchments. During spring and summer, [53] found that the $P\text{-}PO_4$ concentration in three Pomeranian streams always remains below 0.5 mg/L, while in the case of the Mazovian Raszynka River, the maximum annual concentration of $P\text{-}PO_4$ only amounted to 0.83 mg/L [52]. It is worth noting that a weak correlation of the phosphorous concentrations in streams with land cover types was also reported for agricultural catchments in other geographical regions [49].

The performance of land cover metrics in water quality prediction, calculated for different spatial scales with even additional distance of flow accumulation scaling, was previously broadly discussed [42,45,92]. However, the presented results are not clear and unequivocal. For example, [81] reported that the concentration of nitrates in the studied watercourses can be equally justified by land use in the whole catchment area and in the 100-m-wide buffer zone. Different conclusions were presented by [64] and indicated that landscape characteristics of the whole catchment area were of greater importance than the characteristics of the buffer zone. In other studies, 100-meter-wide [41] and 300-meter-wide [93] buffer zones were found to be the most accurate in terms of predicting river water quality. In the current study, the use of buffer zones usually increased the performance of the correlation for mean $N\text{-}NO_3$ concentration in lowland streams, both for the CLC 2018 and the S2GLC datasets. The application of Euclidean distance in the calculation of metrics resulted in the further increase of the correlation performance, but this effect was widely present only for the forest datasets. In the case of agricultural lands dataset, an increase of the correlation coefficient value after distance weighting was only observed for the total catchment area—the difference in the performance level for buffer zone metrics (100, 250, and 500 m) was negligible or even opposite. Moreover, the performance differentiation between agricultural lands and forests became apparent depending on spatial scale. The highest correlation performance for agricultural lands datasets was reported generally for the widest buffer zone (500 m), as well as the total catchment area. Meanwhile, the presence of the forests was the most important in the narrowest buffer zone (100 m), with additional Euclidean distance weighting. This different performance tendency between land cover types can be explained by their physical nature. The forest cover effect on water quality is the most important in the closest proximity to the stream, where ion uptake, denitrification, and sediment trapping occur [94,95]. On the other hand, the influence of agricultural lands is greater, the larger the area of their drainage. Some of the previous studies also indicated that even with the same land use percentage, landscape configuration, measured with the patch density, edge density, and mean shape index, plays an important role in organic matter and nutrient runoff from catchments [39]. However, this can be more important in larger catchments, where their area is suggested to have a significant effect on metrics performance [42].

In the current study, there was also the possibility to compare metrics performance calculated on the basis of the two independent datasets, both widely accessible for nearly all of the European countries [59,60]. Overall, both CLC 2018 and S2GLC datasets provided similar correlation performance and the differences in significant correlation values usually did not exceed 0.05–0.1. However, it is worth noting that metrics based on S2GLC dataset were better correlated in smaller spatial scales, such as buffer zones of 100 and 250 m width. At such scales, high-resolution datasets seem to be favorable, although this cannot be stated for larger areas. Finally, although the results of the correlation analysis for meadows were not significant, the opposite impact of this land cover type on N-NO_3 between used datasets was observed, both for the whole study period and for specific seasons. The contribution of meadows in S2GLC dataset was definitely higher, marking in that way a small participation of agricultural lands in the comparison to the CLC 2018. This indicates that the classification algorithm in the S2GLC dataset classified some agricultural lands as meadows. Moreover, this example suggests that great carefulness is needed when evaluating the impact of meadows on water quality, as it could be overestimated in both ways. Meadows identified from the aerial or satellite level can in fact be different in their functioning, that is, grazed, fertilized, and mowed. In addition, sometimes they are not managed in any way, which makes their functioning much more similar to natural herbaceous vegetation [96]. This is reflected in their impact on water quality, which could be significantly different: from being an additional source of nutrient ions [97] to acting as a biogeochemical barrier [52]. Therefore, uncritical reliance on satellite-based datasets could lead to potentially erroneous conclusions if there is no precise information about such land cover management.

4.3. Implications for Water Quality Management

Understanding the complex relationships observed between terrestrial and aquatic environments is definitely required in appropriate management of lotic ecosystems. The obtained results provided new insight into this subject and could be representative of the other lowland agricultural catchments in the temperate climate, characterized by flat terrain and low hydrological connectivity. Overall, statistical modelling conducted on the basis of landscape predictors should take into account the strong seasonal variability of their impact, driven mainly by vegetation cover changes. As indicated, land cover metrics during summer and autumn seasons could be useless. Nevertheless, this fact points to the need to search for new predictors, which could explain nutrients variability during growing season, and such additional variables could include macrophytes density, as well as soil properties metrics [42]. Moreover, from scaling (weighting) methods presented in the literature [47,98,99], the use of buffer zones and/or Euclidean distance scaling seems to be the optimal solution for modelling purposes in lowland landscapes. Flow accumulation scaling could be difficult to apply due to blind drainage, similar to slope scaling in terms of small differences in elevation and low steeper slopes. Finally, correlation values reported for metrics based on the S2GLC dataset (10 m/pixel) and CLC 2018 dataset (minimum width of objects: 100 m) indicated that the increase of data resolution had not significantly improved modeling performance. This is an important issue in the context of the cost- and time-efficiency of investigations. It can be supposed that using high-resolution land cover maps acquired from photogrammetric low-altitudes flights could be justified only for small experimental catchments, while in such studied mesoscale catchments widely available and cost-free datasets can be used with high efficiency. Meanwhile, the results of the correlation analysis confirm the previous findings [62,95] and suggest that restoring riparian buffer zones covered with trees and woodland vegetation would have a clear impact on the N-NO_3 reduction in lowland streams. According to [94], a 30–40-meters-wide buffer zone can effectively protect the physical, chemical, and biological integrity of small streams. However, management in such streams also requires the appropriate treatment of macrophytes, such as periodic planting and cutting, as they are responsible for different effects depending on the season. Maintaining good water quality of small lowland streams is crucial not only in terms of environmental protection, but also ecology and fisheries management, as they act as a refuges for riverine species, especially valuable freshwater fish [100,101].

5. Conclusions

The effect of the land cover on selected nutrient dynamics was investigated in fourteen temperate lowland catchments in central Poland. Generally, a clear spatial and seasonal variability of N-NO_3 and P-PO_4 concentration was observed in the studied catchments, which could be mainly related with the vegetation cycle and hydrological conditions, respectively. For both the CLC 2018 and S2GLC datasets, the percentage of agricultural lands was found to have a significant positive association with N-NO_3 concentration, while the forest percentage was negatively linked with the level of nitrates. However, significant relationships were only found in the spring and winter periods, when ion release from decomposing vegetation and higher hydrological connectivity occur. Meanwhile, the effect of meadows on N-NO_3 was usually not significant and its direction was dependent on the land cover dataset. The use of buffer zones usually increased the correlation performance of agricultural land and forest datasets, whereas Euclidean distance scaling improved such performance mainly in the case of forest cover metrics. Overall, the total catchment area and 500-m-wide buffer zone provided the best correlation for agricultural lands, which was opposite to forests, appeared to be the most significant in the 100-m-wide buffer zone. In contrast, P-PO_4 concentrations were generally not significantly related with any land cover metrics. The study highlighted the importance of understanding of relationship between land cover and stream nutrient concentrations, as well as evaluating the performance of different metrics scales and datasets in such a prediction for practical implications.

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