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Spatial and Seasonal Dynamics of Inorganic Nitrogen and Phosphorous Compounds in an Orchard-Dominated Catchment with Anthropogenic Impacts

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Abstract: The influence of various types of agricultural activities on the dynamics of biogenic compounds of flowing water was broadly recognized in many spatial and temporal scales. However, relatively minor attention was paid to the hydrochemical functioning of horticultural catchments despite their importance and dominance in some regions of Europe. Thus, the current study investigated spatial and seasonal variations in inorganic nitrogen and phosphorous compounds in stream water in the Mogielanka River catchment, with 72% covered by apple orchards. Water samples were collected from fifteen sites distributed across the catchment in the monthly timescale from March 2020 to February 2021. Concentrations of NO_3^-, NO_2^-, NH_4^+, and PO_4^{3-} were determined photometrically, while in situ water temperature, oxygen saturation, electrical conductivity, and pH, were measured with the use of portable devices. The impact of horticulture was mainly documented in the higher concentration of NO_3^- during the winter months; however, maximum values did not exceed 15 mg·dm^{-3} and were relatively low in comparison to catchments dominated by arable lands. The authors also found a clear impact of unstratified reservoirs and inflows from wastewater treatment plants on the dynamics of biogenic compounds. The correlations of PO_4^{3-} with the sums of precipitation suggested, in turn, that increased PO_4^{3-} concentration mainly results from poor sewage management. The results provided preliminary but unique and spatially extensive insight into the functioning of an orchard-dominated lowland catchment and allowed the researchers to point out the main recommendations for improving water quality in similar regions.

Keywords: biogenic compounds; agriculture; orchards; lowland catchment; human activity

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1. Introduction

Because of the significant effect of various forms of nitrogen and phosphorus on aquatic organisms and human activity, water quality investigations in terms of nutrient compounds have been an important research issue for several decades [1,2]. Overall, nitrogen and phosphorus contamination of flowing waters is linked with numerous anthropogenic factors related to agriculture, industry, and municipal activity [3–6]. Agriculture usually contributes to an increase in the concentration of nutrients in flowing waters through the excessive use of artificial and natural fertilizers [6,7], especially nitrates, due to their easy flushing by infiltrating water [8]. On the other hand, livestock farming areas were documented to increase the concentration of free ammonia in the air [9,10], which may further affect NH_4^+ levels in rainwater [11]. Nutrient enrichment is also accelerated by municipal activity, as septic tanks, in turn, are responsible for phosphorus, organic nitrogen, and ammonium releases to the aquatic environment [12–14]. Finally, another source of biogenic pollutants in water is outflows from landfills [15,16]. An increased level of nutrients resulting from such human activity was broadly documented to accelerate the eutrophication of rivers and lakes [6,17]. This process is related to the development of excessive phytoplankton and macrophytes [3]. In addition, high concentrations of nutrients negatively affect many species of freshwater fish and macroinvertebrates and cause the release of toxins harmful to human health [18]. It is worth noting that eutrophic waters are a very important problem from the perspective of water supply—high concentrations of nitrate are dangerous, particularly for young children, as they cause methemoglobinemia [19,20].

Investigations related to environmental dependence on nutrient compounds were conducted in urban [21–23], forested [24,25], and agricultural [26–30] catchments. Studies concentrated mainly on the landscape predictors of the spatial variability of nutrients, as the way of land use/land cover is important in the context of mobilization, source, and delivery of ions into the aquatic environment [31]. Most of the studies in this field were based on statistical relationships described by regression models, which linked land use/land cover predictors, calculated in various configurations, and selected biogenic compound concentrations [32–34]. In most cases, clear relationships between the dominant type of catchment land use and nitrate concentration were documented, which were generally positive in the case of agricultural areas [35–38]. The opposite effect was broadly observed in the case of forested buffer zones, as their presence limited nitrate concentration [14,39], although such influence was seasonally differentiated [14]. Another common research issue was the prediction of nutrient concentration as an effect of non-point pollution with the use of the hydrological models, such as the SWAT model, or even with the use of an artificial neural network [40–42]. Such investigations related to landscape dependence of nutrient dynamics were mainly focused on areas with the dominance of cereal crops [43,44], rice [45], and livestock farming, especially dominated by cattle, sheep, and poultry [27,28,44,46]. Less attention was definitely paid to horticultural catchments, and such studies were conducted only in bilberry-dominated areas in Australia [37,47] and Martinique in the Lesser Antilles archipelago, dominated by pineapple, banana, and spike crops [48]. The reason for such small scientific recognition is that fruit production is concentrated only in selected, specific regions of the world. For example, such production in Poland—the country that produces the most apples in the whole European Union [49]—is concentrated only in the vicinity of Grójec, Sandomierz, Nowy Sącz, and Opole Lubelskie [50], and such horticultural regions do not exceed an area of thousands of square kilometers. Thus, there is a need to explore spatial and seasonal patterns of biogenic compound dynamics in such catchments, as fruit production, apples, in particular, is still growing not only in Poland [49] but also in other countries [51]. Such investigations could be particularly valuable for the appropriate management of such horticultural catchments in the context of potential eutrophication.

Thus, the current study concentrates on biogenic compound dynamics in a small lowland catchment dominated by orchards in its land cover and considered as the main apple production region in Europe. Specific objectives of the study were: (a) characterize spatial and seasonal patterns of water quality parameters, particularly inorganic nitrogen and phosphorus compounds, affected by fruit production; (b) evaluate the effect of anthropogenic disturbances located in the catchment on spatial and seasonal biogenic compounds patterns; (c) assess the relationships between biogenic compounds and rainfall amount in the catchment.

2. Study Area

Investigations were carried out in the agricultural Mogielanka River catchment, located in central Poland, almost entirely in the Wysoczyzna Rawska (Rawa Heights) mesoregion [52,53]. The catchment area covers 225.4 km^2 and is drained by the Mogielanka River, a 37 km-long left tributary of the Pilica River. The hydrological regime of the river, similar to the vast majority of rivers in the Central Polish Lowlands, can be considered as nival, with the highest streamflow rates observed in the spring months as a result of snowmelt, and the lowest usually occurring during the hot summer, mainly from July to September [54,55]. The Mogielanka catchment is mainly built of weathered boulder clays of the Wartanian Glaciation (northern and central parts), as well as fluvioglacial sands and gravels (southern parts) [56]. The analyzed area is characterized by a temperate, warm, transitional climate; data from the meteorological station in Dąbrówka Stara (located in the catchment area) indicated that the average annual precipitation sum in the years 2003–2019 was 612 mm, while the average annual air temperature in the years 2007–2019 reached 8.7 °C. The studied area is intensively used for agriculture—almost 90% of the catchment area can be qualified as agricultural lands (Figure 1). Such areas are mostly (72%) occupied by orchards concentrated in the northern and central parts of the catchment, with the dominance of apple trees (Figure 2a) and sour cherry trees. The cultivation of sweet cherries, plums, pears, blueberries, and strawberries is of less importance [57]. Approximately 12% of the total area is classified as arable lands, concentrated mainly in the southern part of the catchment near Mogielnica. Forests constitute only 10% of the total catchment area and are concentrated mainly along the Mogielanka River valley (Figure 2b) and its largest tributary—the Machnatka River. Such riparian communities are dominated by species typical for this type of forest in the Central Polish Lowlands [58], such as common alders *Alnus glutinosa*, marsh marigolds *Caltha palustris*, and perennial forbs. Although the studied areas are is characterized by a low degree of urbanization (only 3%), in the catchment, several anthropogenic objects exist, which can significantly modify selected chemical water quality parameters of rivers [59–63]. These are mainly weirs, for example, located in Błędów, as well as inflows from municipal wastewater treatment plants in Błędów and Mogielnica (Figure 1).

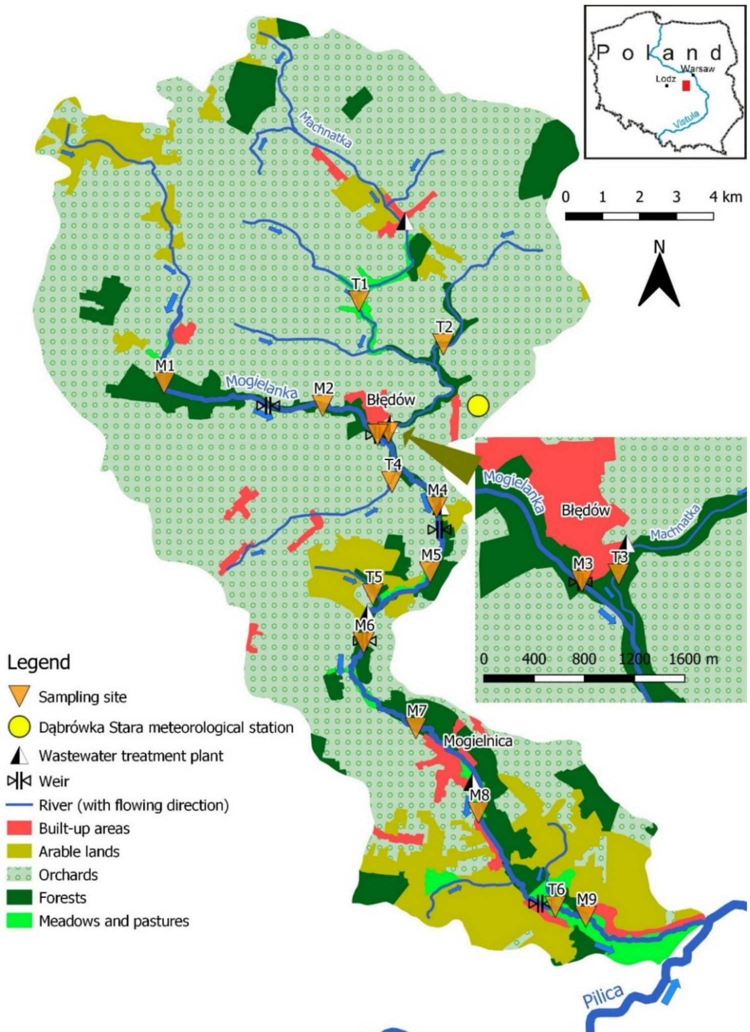


Figure 1. Location of the sampling sites in the Mogielanka River catchment. Weirs and wastewater treatment plants were also indicated. Own elaboration based on CORINE Land Cover 2018 data and digital Hydrographical Map of Poland.

Figure 2. An apple orchard in Golianki, near site T2 (**a**), the Mogielanka River near Wólka Dańkowska (site M4), with a riparian buffer zone dominated by *Alnus glutinosa* (L.) *Gaertn.* (**b**).

3. Materials and Methods

The monitoring of selected chemical parameters in the Mogielanka River catchment was conducted from March 2020 to February 2021. In a regular monthly cycle (always in the first decade of each month), water samples were collected into 0.5-L polyethylene bottles, and immediately after the transportation to the laboratory, the concentrations of nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}) (in mg·dm^{-3}) were determined with the use of an LF 300 photometer. Together with collecting samples, basic physicochemical properties were measured directly in the field. Water oxygen saturation (%) and water temperature (°C) were determined using the Hanna Hi 98193 oxygen meter with an accuracy of ± 0.1% and 0.2 °C, respectively, while electrical conductivity (μS·cm^{-1}) and pH were determined with the Hanna Hi 9811-5 **meter**, with an accuracy of 0.1 pH and ± 2.0% μS·cm^{-1}. This set of water quality parameters is relatively easy to measure and interpret, which makes it a good background for the initial assessment of the eutrophication of the orchard-dominated catchment. It is also well comparable due to common use in similar studies, and simultaneously, it clearly shows the impact of varied human alternations such as wastewater treatment plants and reservoirs. Spatially, the investigations were carried out in 15 measurement sites, with nine located along the Mogielanka River course (belonging to "M" series) and six located across the tributaries (the "T" series) with a different land cover (Figure 1); in order: M1–M2–T1–T2–T3–M3–T4–M4–M5–T5–M6–M7–M8–T6–M9. The measurement sites were distributed proportionally in the lower, middle, and upper reaches of the Mogielanka River with respect to several anthropogenic influences, such as weirs in Błędów and Główczyn-Towarzystwo, as well as inflows from wastewater treatment plants in Błędów and Mogielnica (Table 1). Water samples were always collected from the main current of the rivers, a minimum of three days after rainfall events.

To assess the spatial and seasonal variability of measured parameters, statistical measures—mean, median, maximum, minimum, and interquartile range—were calculated both for the individual sampling sites, as well as for certain months of the investigated period. These values were presented on the box plots, similar to [36]. Catchment properties were calculated in the QGIS 3.4.4 software on the basis of the Digital Hydrographic Maps and the Corine Land Cover 2018 map. Five classes of land cover were distinguished from the dataset with the use of vector processing tools: arable lands (class 2.1.1), orchards (class 2.2.2), meadows (class 2.3.1), and forests (sum of the classes 3.1.1, 3.1.2, 3.1.3., and 3.2.4) and anthropogenic surfaces (class 1.1.2).

Table 1. Detailed characteristics of the measurement sites.

Sampling Site	River/ Stream	A [km^2]	Land Cover Classes					Site Description
			FOR	MEAD	ORCH	ARA	ANTR	
M1	Mogielanka	30.5	4.6	0.8	77.9	15.8	0.9	Regulated reach
M2	Mogielanka	44.6	9.3	0.6	78.7	10.8	0.6	Natural reach
M3	Mogielanka	53.0	9.1	0.5	80.3	9.1	1.0	Site located directly below a dam reservoir, regulated reach
M4	Mogielanka	158.7	7.4	0.8	84.9	5.1	1.8	Natural reach
M5	Mogielanka	162.3	7.7	0.8	84.5	5.2	1.8	Natural reach
M6	Mogielanka	171.1	8.0	0.9	82.5	6.9	1.7	Site located directly below a dam reservoir, regulated reach
M7	Mogielanka	182.5	8.3	1.0	82.5	6.5	1.7	Natural reach
M8	Mogielanka	192.5	9.1	1.2	81.1	6.3	2.3	Site located circa 700 m below an effluent discharge, regulated reach
M9	Mogielanka	218.8	10.0	1.7	74.4	11.4	2.5	Natural reach
T1	Machnatka	52.6	9.5	1.1	83.5	4.4	1.5	Regulated reach
T2	Rębowola Stream	13.4	3.0	0.0	93.3	3.7	0.0	Site located circa 200 m below a small pond, tributary was regulated during investigation
T3	Machnatka	84.7	7.5	1.2	86.3	3.3	1.7	Site located 250 m below an effluent discharge, end of regulated reach
T4	Huta Błędowska Stream	16.5	0.0	0.0	92.5	2.0	5.5	Regulated reach
T5	Dańków Stream	1.6	10.5	0.0	13.7	75.8	0.0	End of natural reach
T6	Jastrzębia Stream	10.1	18.4	4.2	31.9	45.5	0.0	Site located below a peat bog, natural reach

Abbreviations: A—catchment area, FOR—forests, MEAD—meadows and pastures, ORCH—orchards, ARA—arable lands, ANTR—anthropogenic (built-up) areas.

The influence of precipitation in the Mogielanka River catchment on biogenic compound concentration in streams was evaluated with the use of the Spearman rank correlation coefficient. The correlation was performed between cumulative precipitation sums 5, 10, 15, and 30 days before the measurement day (from Dąbrówka Stara meteorological station) and the difference between the concentration of certain biogenic compounds between the two measurement days for all sampling sites. Such a procedure was applied throughout the whole investigated period, as well as only during the growing period, in which Central Poland lasts from April to November [64]. Due to the lack of other meteorological stations, even in close proximity to the studied catchment, it was assumed that the precipitation sum from the Dąbrówka Stara meteorological station is representative of all sampling sites. The Spearman rank correlation coefficient was also used for the evaluation of the relationships between all water quality parameters. In both cases, a probability value of correlations of less than 0.05 was considered statistically significant. Calculations and graphical content were performed in the Statistica 13.3 software and Microsoft Excel 2016. In order to provide a hydrometeorological characteristic of the study period, mean daily air temperature and daily precipitation sums were acquired from the Dąbrówka Stara meteorological station, operated by the Institute of Meteorology and Water Management—National Research Institute. Such daily values were averaged to the monthly time scale and presented on the charts along with the long-term mean values from March 2003 to February 2020 and from March 2006 to February 2020 for air temperature and precipitation, respectively.

4. Results

4.1. Hydrometeorological Background

The investigated period from March 2020 to February 2021 can be considered relatively warm. The average air temperature at the Dąbrówka Stara meteorological station reached 9.1 °C, which was 0.4 °C higher than the average from the 2006–2020 period. The highest mean monthly temperature (19.4 °C) was observed in August, while the lowest was in February (−2.3 °C) (Figure 3). The precipitation sum during the sampling period was definitely higher than in the reference period (Figure 3), which indicated wet conditions. Total precipitation was 715 mm, which accounted for 116% of the average sum of precipitation calculated for the 2003–2020 reference period (615 mm). However, the distribution of precipitation was not typical—the highest precipitation sum of as much as 194 mm was noted in June, while the lowest was in April, which turned out to be the driest month with a precipitation sum of only 3.9 mm.

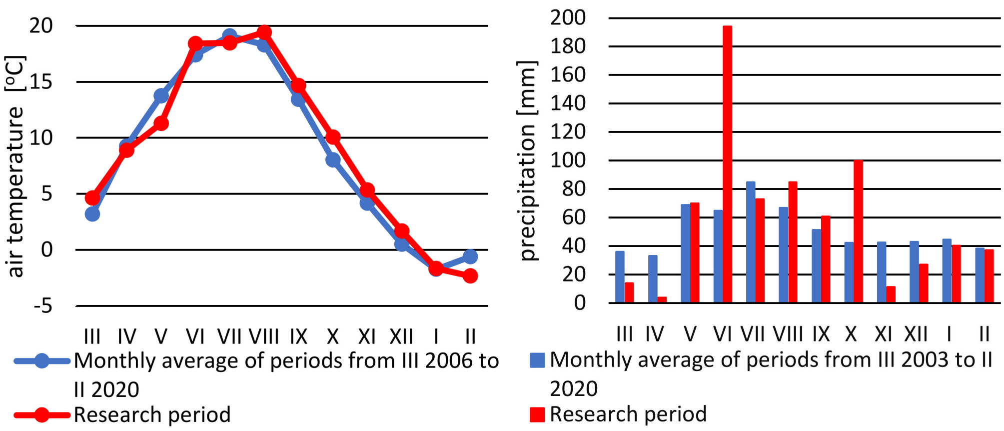


Figure 3. Mean monthly air temperature values (**left** site) and monthly precipitation totals (**right** site) from March 2020 to February 2021 on the background of the years 2006–2020 and 2003–2020, respectively, for the Dąbrówka Stara meteorological station. Based on data acquired from the Institute of Meteorology and Water Management—National Research Institute.

4.2. Seasonal and Spatial Differentiation of Selected Water Quality Parameters

The seasonal variability of the investigated water quality parameters was clearly outlined, as indicated by values from all sampling sites in the Mogielanka River catchment, aggregated in the monthly timescale (Figure 4). The concentration of NO_3^- was generally lower in the growing season, particularly from May to October. In contrast, higher values of NO_3^- concentration were noted from December to February, representing winter and early spring months, as well as in July. The opposite cycle was documented in the case of NO_2^- and PO_4^{3-}, which exhibited the highest concentrations during the summer months (Figure 4). The variability of NH_4^+ was more complex, with no seasonal tendency. Oxygen saturation of the water was related to water temperature, and the highest saturation, above 80% on average, was noted in spring and winter. In the case of electrical conductivity and pH, there was no seasonal tendency in the Mogielanka River catchment; however, it is worth noting that in November and December, the lowest pH values were observed, while the highest, on average, values of electrical conductivity were measured during the autumn (Figure 4). Spatially, the highest variability of water quality parameters was reported between sampling sites located along the Mogielanka River and its tributaries. This was particularly documented in the case of NO_3^-, PO_4^{3-}, and electrical conductivity. Generally speaking, some measurement sites distributed along the Mogielanka River displayed similarity with respect to the concentrations of inorganic biogenic compounds, as well as oxygen saturation, EC, and pH, measured with mean values. This was visible especially in the section from M4 to M7, below the confluence with the biggest tributary (Figure 5). In the case of small tributaries, great variability was noted, as some of the streams (T1 and T3) experienced increased mean and maximum concentrations of NO_3^- and PO_4^{3-} during the sampling period. In addition, the tributaries were clearly different in terms of electrical conductivity and pH. The impact of some tributaries, especially the highly contaminated T3, resulted in a visible increase in NO_3^-, NO_2^-, and NH_4^+ in the Mogielanka River below the confluence.

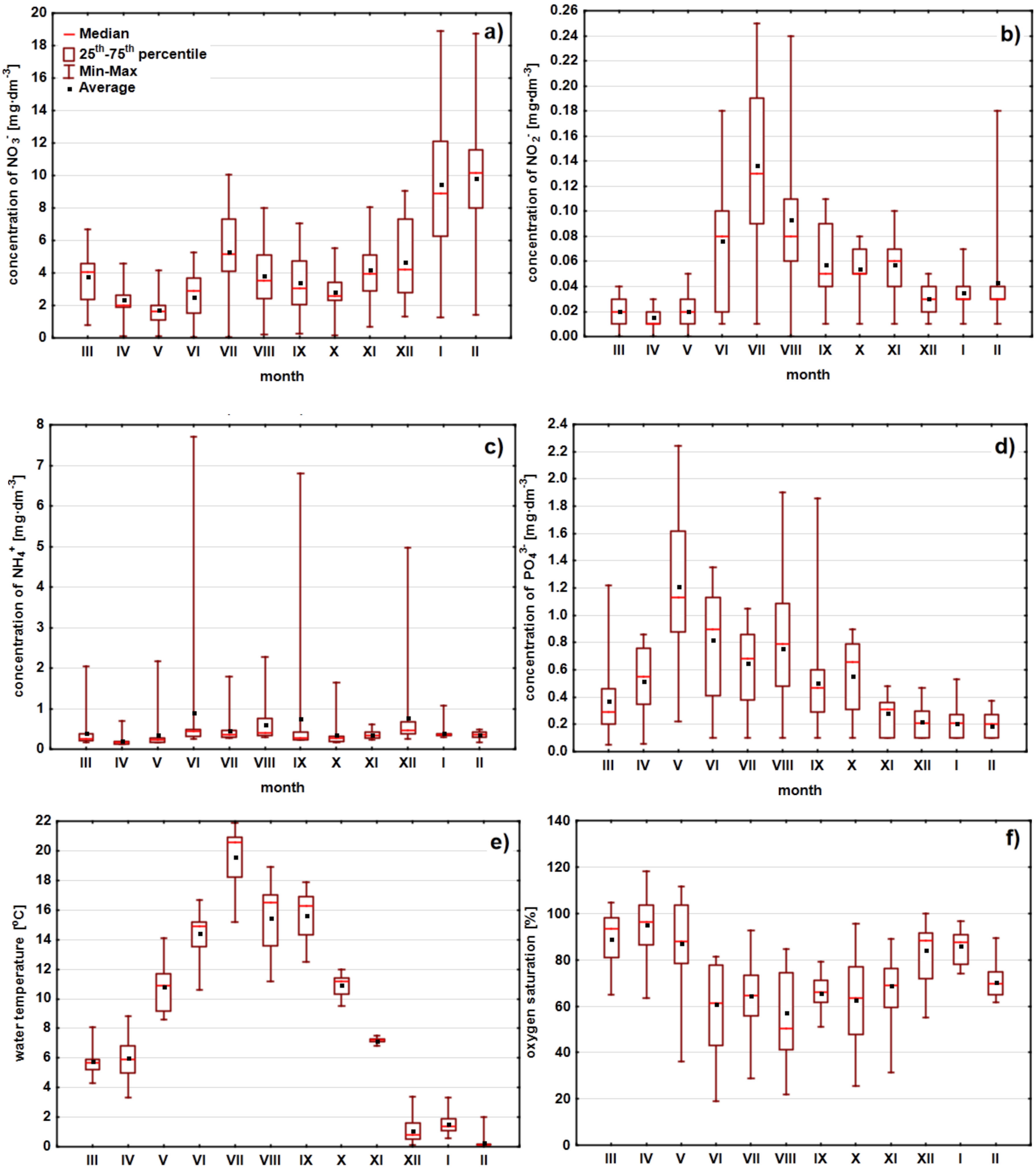


Figure 4. *Cont.*

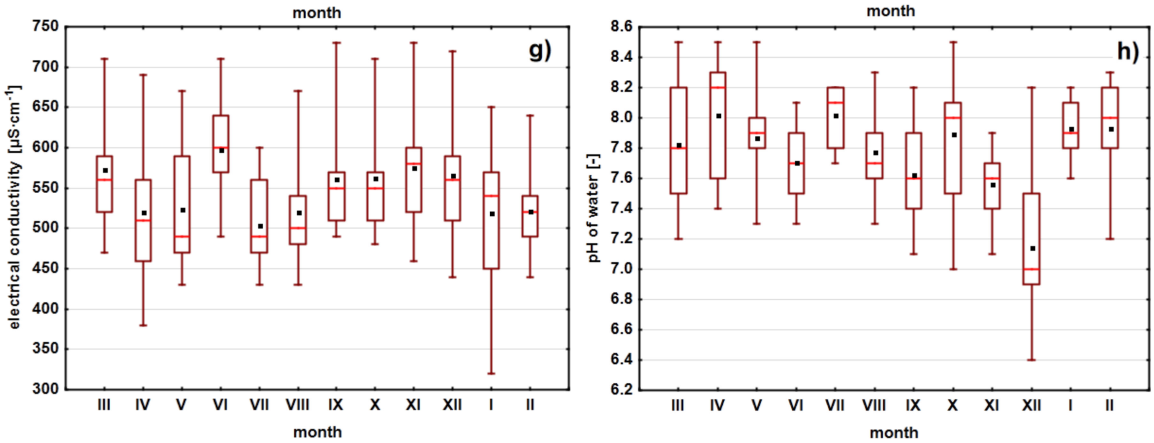
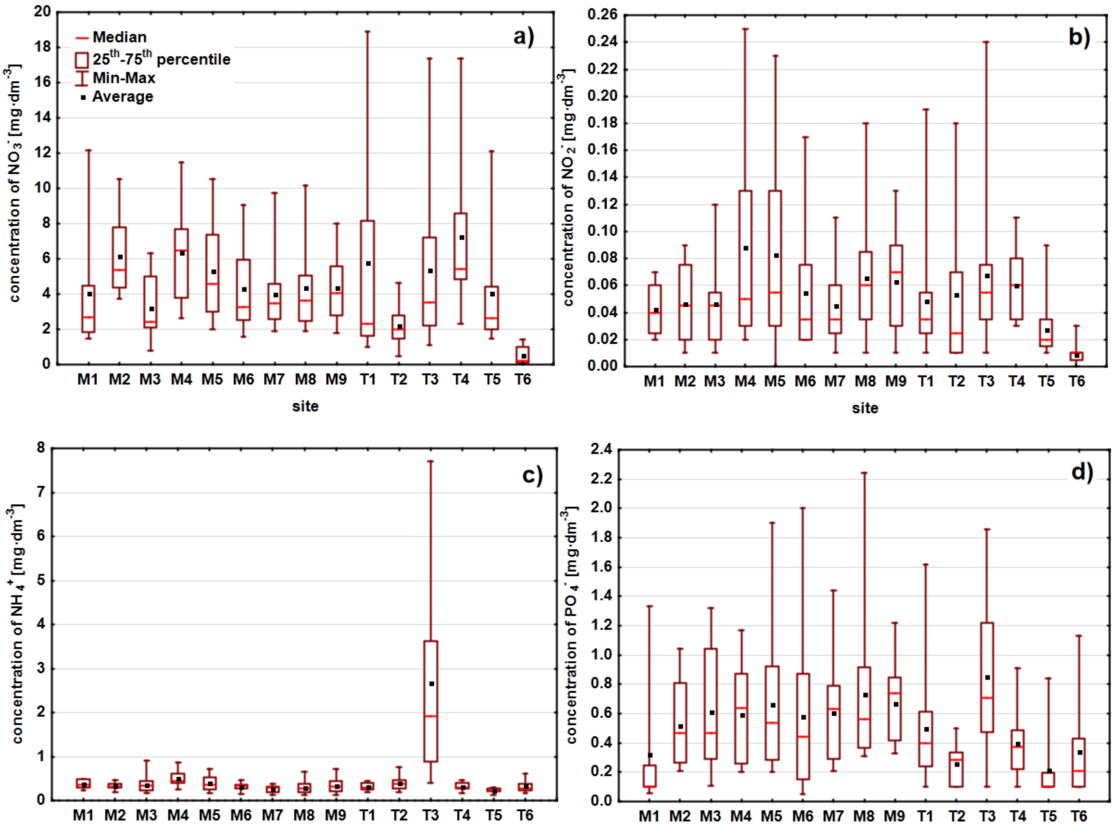


Figure 4. Seasonal variability of NO_3^- (**a**), NO_2^- (**b**), NH_4^+ (**c**), PO_4^{3-} (**d**), water temperature (**e**), oxygen saturation (**f**), electrical conductivity (**g**), and pH (**h**) in all sampling sites across the Mogielanka River catchment in certain months from March 2020 to February 2021.

4.3. Anthropogenic Influences on Stream Water Quality

The natural continuum of the hydrochemical regime of the Mogielanka River was primarily disrupted by the flow-through water reservoir in Błędów, located between the M2 and M3 sampling sites. The reservoir caused a decrease in the NO_3^- level, on average by 2.94 mg $\cdot dm^{-3}$ (Figure 6), as well as an increase in electrical conductivity (on average 42 µS $\cdot cm^{-1}$). No changes were found in the case of the concentration of NO_2^-, while slight increases of 0.04 mg $\cdot dm^{-3}$ and 0.09 mg $\cdot dm^{-3}$ were observed below reservoir for NH_4^+ and PO_4^{3-}, respectively. The oxygen saturation of water was definitely higher below the reservoir weir, with the biggest difference of 36.5% of saturation measured in May. The same can be said of water temperature, which was higher below the reservoir in each month (Figure 6).



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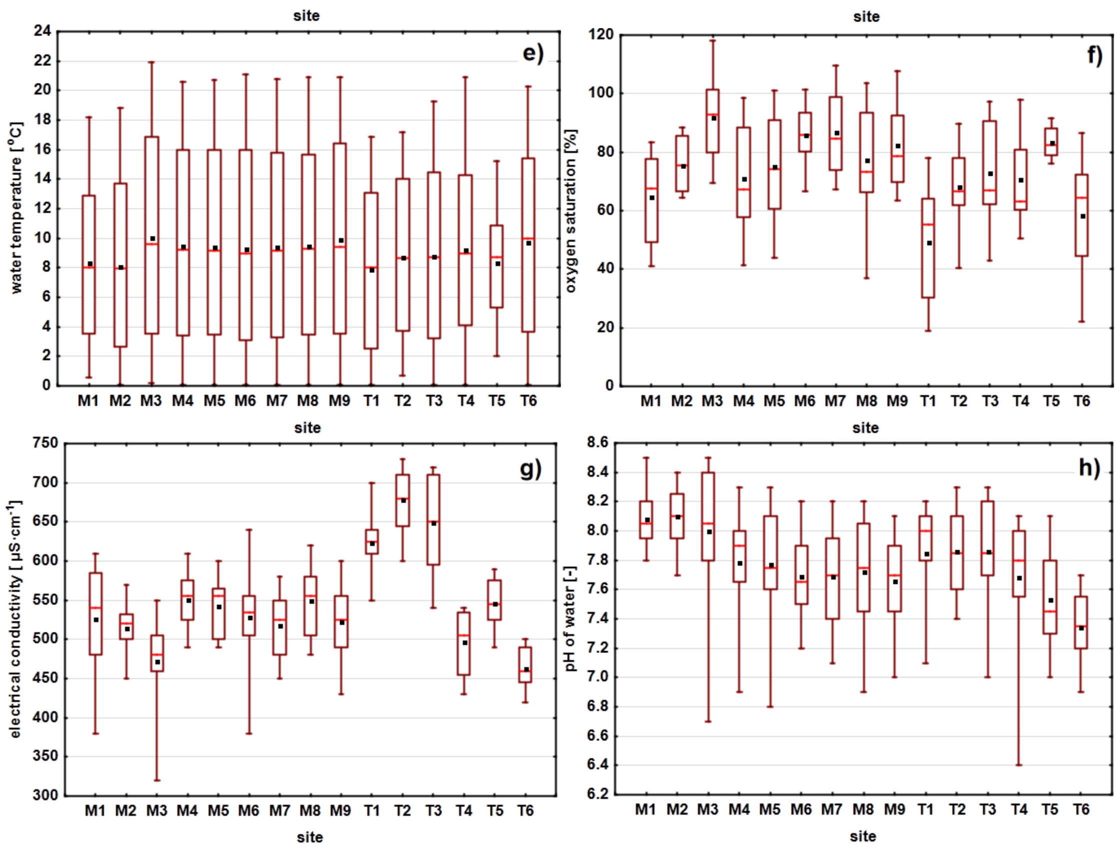

Figure 5. Spatial variability of NO_3^- (**a**), NO_2^- (**b**), NH_4^+ (**c**), PO_4^{3-} (**d**), water temperature (**e**), oxygen saturation (**f**), electrical conductivity (**g**), and pH (**h**) in certain sampling sites across the Mogielanka River catchment.

Sewage inflows from wastewater treatment plants (WWTP) were also found to affect the stream water quality; however, the impact was dependent on the season. The WWTP in Błędów, which serves approximately 1600 people, modified nearly all of the investigated water parameters, not only below the inflow but also over the downstream parts of the Mogielanka River. Particularly, an increase in the NO_3^-, NO_2^-, and NH_4^+ was observed below the sewage inflow (Figure 7). The impact of the sewage treatment plant was also marked by a decrease in water oxygen saturation, which was particularly visible in the warm period of the year (Figure 7). The influence of the WWTP in Mogielnica, serving almost 3000 people, was less prominent but nonetheless noticeable. Below the inflow in site M8, a higher value of EC was documented, as well as increased concentrations of PO_4^{3-} and NO_2^-. Moreover, similar to the Błędów WWTP, lower oxygen saturation was noted (Figure 7).

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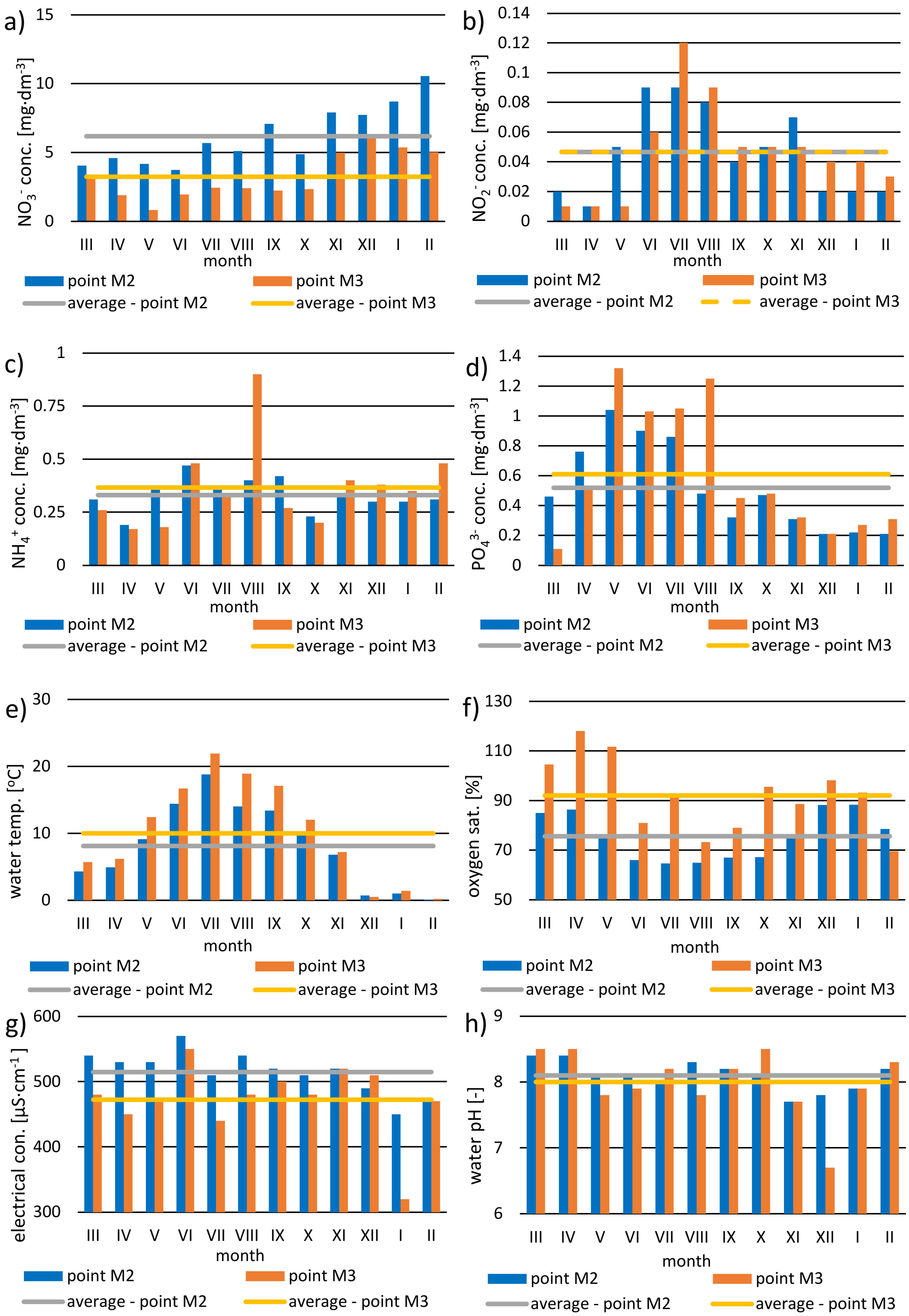

Figure 6. Seasonal variability of NO_3^- (**a**), NO_2^- (**b**), NH_4^+ (**c**), PO_4^{3-} (**d**), water temperature (**e**), oxygen saturation (**f**), electrical conductivity (**g**), and pH (**h**) in the Mogielanka River above and below the Błędów reservoir.

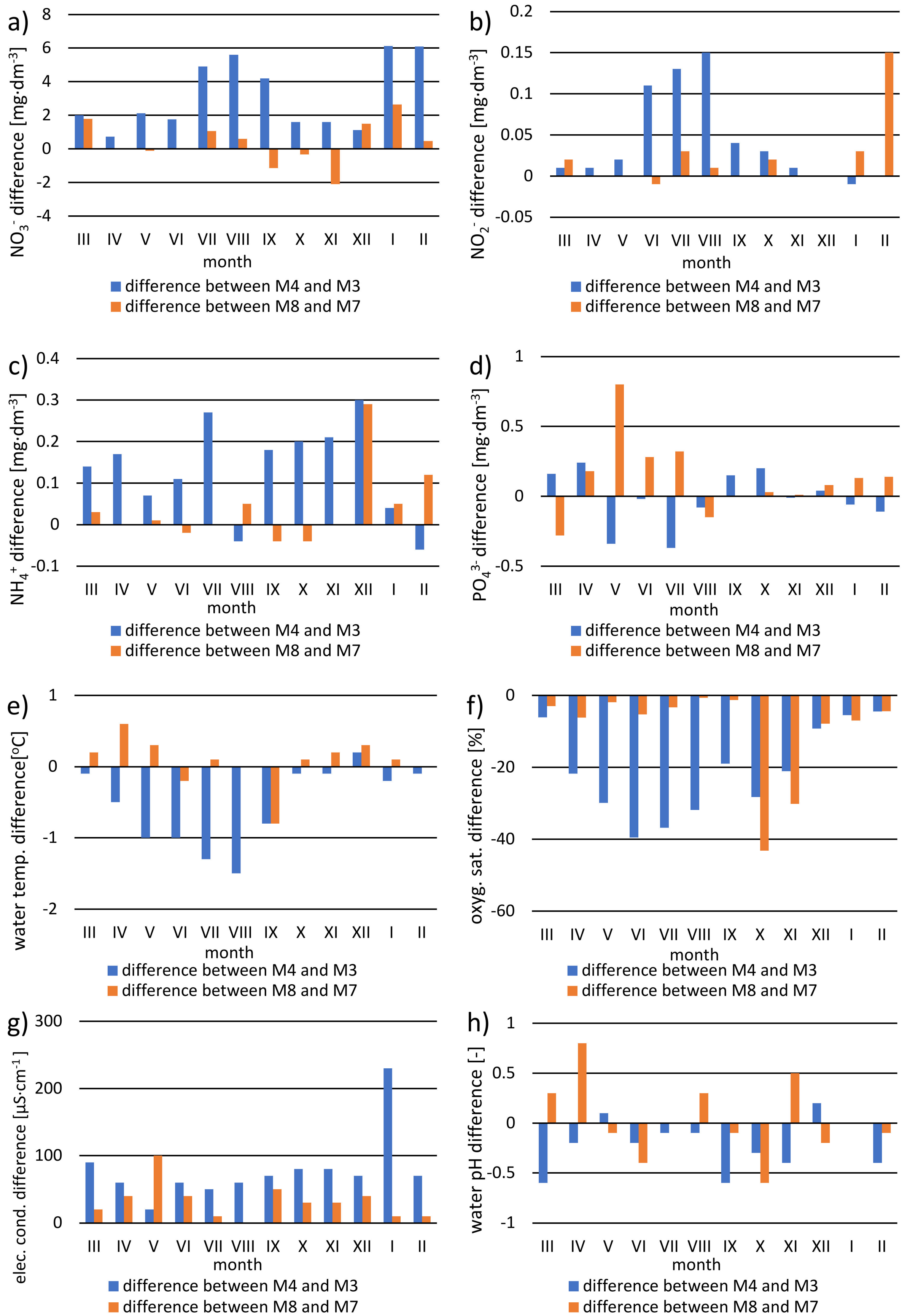

Figure 7. Differences in the measurements of NO_3^- (**a**), NO_2^- (**b**), NH_4^+ (**c**), PO_4^{3-} (**d**), water temperature (**e**), oxygen saturation (**f**), electrical conductivity (**g**), and pH (**h**), which document the impact of the Machnatka River (polluted by sewage effluent from the WWTP in Błędów and non-point agricultural sources—blue boxes) and the WWTP in Mogielnica (orange boxes) on the Mogielanka River.

4.4. Relationships between Precipitation and Biogenic Concentrations and between Chemical Compounds

The statistically significant correlations between the differences in mean biogenic compounds concentrations and the sum of precipitation (Table 2) were found in the case of NO_3^-, NO_2^-, and PO_4^{3-}. Such relationships were not documented only in the case of NH_4^+. The correlations were generally stronger for the growing period from April to November (Table 3). Furthermore, in the case of NO_3^- and NO_2^-, significant correlations were generally reported for cumulative precipitation sums of 5 and 10 days, while in the case of PO_4^{3-} it was only for the longest 30-day period of cumulative precipitation. It must be emphasized that correlation was positive in the case of nitrogen forms, while in the case of phosphates, the relationships were negative (Table 3). Statistically significant, negative correlations were also found between mean values of selected water quality parameters (Table 4).

Table 2. Precipitation sum before the measuring days. Based on data acquired from the Institute of Meteorology and Water Management—National Research Institute.

Month	Sum of Precipitation			
	5 Days	10 Days	15 Days	30 Days
IV	0.0	0.0	0.6	8.7
V	17.9	17.9	17.9	18.1
VI	16.6	36.0	42.0	64.8
VII	33.8	59.1	138.5	222.1
VIII	0.6	0.6	14.2	36.9
IX	6.4	18.4	54.0	82.6
X	8.3	28.3	63.3	63.3
XI	6.0	8.0	9.2	93.8
XII	0.0	0.0	2.5	3.2
I	16.7	2.6	25.9	45.1
II	11.6	15.4	22.3	34.4

Table 3. Spearman's rank correlation coefficients describing the relationship between the mean and median concentrations of selected biogenic compounds and the cumulative precipitation sum for the various time periods. Statistically significant correlation values at the level of p <0.05 were marked in bold.

Parameter	Metric	5 Days		10 Days		15 Days		30 Days	
		IV-II	IV-XI	IV-II	IV-XI	IV-II	IV-XI	IV-II	IV-XI
NO_3^-	Mean	0.460	0.571	0.487	**0.714**	0.345	0.500	0.509	**0.905**
	Median	**0.606**	**0.714**	0.497	0.667	0.327	0.429	0.473	**0.810**
NO_2^-	Mean	**0.806**	**0.810**	**0.642**	0.690	0.436	0.405	0.327	0.429
	Median	**0.749**	**0.762**	**0.666**	0.667	0.409	0.333	0.451	0.357
NH_4^+	Mean	−0.141	0.143	−0.196	0.071	−0.327	−0.190	−0.164	0.071
	Median	−0.123	0.214	−0.141	0.095	−0.300	−0.214	−0.145	0.048
PO_4^{3-}	Mean	−0.077	−0.143	−0.360	−0.500	−0.318	−0.262	**−0.655**	**−0.762**
	Median	0.014	0.048	−0.223	−0.262	−0.227	−0.119	**−0.664**	**−0.810**

Table 4. Spearman's rank correlation coefficients describing the relationship between the mean values of selected water quality parameters. Statistically significant correlation values at the level of $p < 0.05$ were marked in bold.

Parameter	O_2	EC	pH	NO_3^-	NO_2^-	NH_4^+	PO_4^{3-}
O_2	1.000						
EC	−0.095	1.000					
pH	0.260	**−0.740**	1.000				
NO_3^-	−0.098	−0.319	0.081	1.000			
NO_2^-	**−0.907**	−0.042	−0.165	0.298	1.000		
NH_4^+	−0.476	0.308	**−0.628**	0.077	0.480	1.000	
PO_4^{3-}	−0.371	0.011	0.046	**−0.720**	0.270	0.196	1.000

5. Discussion and Conclusions

5.1. Seasonal and Spatial Differentiation of Water Quality Parameters

The study provided unique, spatially extensive insight into biogenic compound dynamics in small lowland horticultural catchments. The obtained results could be considered representative because the research was conducted during varied hydrometeorological conditions, from dry to extremely wet, while precipitation is one of the main factors affecting ion mobility [65]. However, it must be emphasized that because of the grab sampling method with a monthly timescale, which was commonly performed in previous water quality investigations [66–68], the preliminary results obtained in the current study only reflect general seasonal tendencies. Short-term dynamics of biogenic compounds in streams are currently also investigated with the use of automatic sensors, although such studies are usually not spatially extensive [69,70].

A clear seasonal pattern of NO_3^- concentration was observed in the horticultural Mogielanka River catchment, which was generally consistent with the reported dynamics for typical arable lands, as the lowest concentrations occurred in the summer months while the highest in the winter [12,14,30,67]. However, an increase in NO_3^- concentration was documented in July, which can be related to the mobilization of such ions due to rainfall events. This can be confirmed by the positive, statistically significant correlation between various timescale precipitation sums and the concentration of NO_3^-, performed with the assumption of rainfall homogeneity across the whole catchment but based on the variable period in terms of its sum. Similar results were documented by [28] using the example of springs in the Funshion River catchment and [47] in the Double Crossing Creek catchment. It is worth noting that at some measurement sites (T1, T3, T4), the maximum values of NO_3^- concentration in the winter and spring exceeded 15 $mg \cdot dm^{-3}$. Such values are relatively small in comparison to values reaching 50 $mg \cdot dm^{-3}$, which were recorded in the studies conducted in the Samica Stęszewska River catchment [71], Theel River catchment [72], and Gowienica Miedwiańska River catchment [30]. Despite the high hydrological connectivity in the investigated period, it must be stated that the concentrations of biogenic compounds in the Mogielanka River catchment were relatively low, which could be connected with the lower use of fertilizers in orchards. According to [73], conducted by Statistics Poland in the Błędów and Mogielnica communes (the majority of their areas are located in the conducted catchment), the use of nitrogen fertilizers therein amounted to appropriately 39,9 $kg \cdot ha^{-1}$ and 33,8 $kg \cdot ha^{-1}$, respectively, while in the case of catchments studied by [30,71] it even exceeded 90–100 $kg \cdot ha^{-1}$.

In the case of NO_2^- concentrations, the highest values were noted in the summer months, as reported previously by [36]. This should be related to the lower level of water oxygen saturation in those months, which was documented as a significant negative correlation between both parameters. The temporal differentiation of PO_4^{3-} concentration was similar to NO_2^-, but its highest concentrations occurred in May after intense rainfall preceding the 1.5-month dry period. Similar results were documented by [38] and explained by the accumulation of phosphorus in the catchment during drought and its rapid activation as a result of surface runoff. However, the current study revealed a negative dependence of PO_4^{3-} concentration on the precipitation sum in a 30-day timescale, as well as a negative correlation between NO_3^- and PO_4^{3-} concentrations. This suggests that the presence of PO_4^{3-} ions is generally related to numerous areal pollution sources located across the catchment, which can be linked with a poorly developed sewage system and leaky septic tanks, as also reported in the case of the Slapanka River in central Bohemia [12]. Infiltration from such septic tanks contributes an additional source of biogenic compounds for groundwater and streams [74], which was reflected in the Mogielanka River catchment also by increased phosphate concentrations, despite the relatively low use of phosphorous fertilizers of only 15.9 kg·ha^{-1} in the Błędów commune and 13.3 kg·ha^{-1} in the Mogielnica commune [73].

Seasonal changes in water temperature were generally closely related to the air temperature pattern [75,76]; however, the results should be treated with caution due to the clear diurnal water temperature dynamics observed in rivers and streams [77] which the grab sampling method does not take into account. Nevertheless, attention could be paid to the Dańków stream (site T5), which was characterized by a lower annual temperature range compared to other sites. The fact that the minimum water temperature of this stream was 2 °C (while in the remaining sites the values were close to 0 °C), as well as the fact that a low range of temperature was recorded throughout the whole year, prove that this stream is intensively draining groundwater [78,79]. The results of the temporal differentiation of water oxygen saturation were related essentially to research conducted by [80,81]. The lowest concentrations in the summer could be explained by the mineralization of organic matter by microorganisms, which use more oxygen than aquatic plants can produce in the photosynthesis process [81].

The spatial differentiation of the biogenic compound concentrations was also clearly outlined, especially across the tributaries of the Mogielanka River, characterized by different land cover and human modifications. Thus, in the Jastrzębia stream (site T6) very low concentrations of NO_3^- were documented, which was caused by the bioaccumulation of these ions in a wetland located above the investigated site. Similarly, the stream from Golianki (site T2) also exhibited low NO_3^- values, but this could be related to the presence of a small flow-through reservoir located above the site. It was recognized that wetlands and small reservoirs (ponds) could be effective in reducing nutrient concentrations [82,83]. On the other hand, high maximum values of NO_3^- were found in some tributaries, such as the Machnatka River and the stream from Huta Błędowska, characterized by narrow riparian buffer zones and intensive horticultural activity. Finally, stable concentrations of NO_3^-, NO_2^-, and NH_4^+ along the Mogielanka River between Błędów and Mogielnica could be related to wider buffer zones on this section (in the form of alder carrs and wetlands), as well as the lack of significant point sewage inflows. These occurred in Błędów and Mogielnica, and they significantly modified the chemistry of the Mogielanka River.

5.2. Human Impact on Water Quality

In addition to areal source contamination, such as nitrate and phosphate inflows from the landscape with groundwater, the obtained results allowed the authors to quantify two types of typical human impacts on water quality for small lowland rivers. The most significant impact was observed due to the presence of a flow-through, unstratified reservoir in Błedów, which resulted in changes in NO_3^- concentrations, water temperature, oxygen saturation, and electrical conductivity. Average values of nitrates were definitely lower below the reservoir, which was also documented in the case of the reservoir in the Čermná Stream [84] and in the case of the Turawa reservoir [85]. This could be related to nitrate absorption by aquatic macrophytes and phytoplankton [60,61]. Lower values of electrical conductivity, measured below the reservoir, were in turn documented previously by [86,87] and linked to the accumulation of calcium, magnesium, and chloride ions, as well as selected trace metals in bottom sediments of reservoirs. It is also worth paying attention to higher NH_4^+ concentrations in August below the reservoir, documented previously by [61] and explained by the decomposition of organic matter after summer. No influence on water quality was detected in the case of the weir in Główczyn, probably because the river is only locally stacked up and there is no typical reservoir as in Błędów. This was clearly visible in water temperature, which in site M6 was similar to adjacent sites. By contrast, a clear impact of wastewater treatment plants (WWTP) on selected physico-chemical water parameters was found in the Mogielanka River catchment. Each month, the WWTP in Błędów (except February) caused an increase in NH_4^+ concentration in the Machnatka River and further on in the Mogielanka River below the confluence. It is also important to mention that lower oxygen saturation and higher PO_4^{3-} concentration were noted below both wastewater treatment plants, and such influence, usually negative, was broadly discussed in numerous studies [59,62,88].

5.3. Recommendations for Improving Water Quality

Interpretation of the obtained results made it possible to distinguish some main recommendations aimed at improving water quality in the Mogielanka catchment. Despite the relatively low consumption of nitrogen fertilizers in the area in question, which provided a low potential for eutrophication, in orchard-dominated catchments, there is a risk of increased NO_3^- values, which can be generally related to the lack of riparian buffer zones along the streams. This was particularly visible in the case of the Machnatka and the stream from Huta Błędowska, which were the most loaded with nutrients. In such cases, riparian buffer zones in the form of trees or extensive meadows should be used to prevent nutrient inflow (including nitrogen forms) into surface waters [89]. It was proven that 30–50-m-long buffer strips could already be of sufficient length as to be effective in limiting nitrogen inflows [90,91]. Overall, maintaining the natural character of not only buffer zones but also of river channels seems to be crucial, as it increases the ability to self-purify—it was documented that the most efficient self-purification process took place in natural riverbeds with forested riparian buffer zones [92]. Moreover, rational use of fertilizers is also important because overfertilization is the main reason behind high nitrate concentration in ground and surface water [93]. The second recommendation should be to modernize wastewater treatment plants, which may contribute to the improvement of water quality, as in the case of the research by [94], where the sewage was additionally redirected to a larger river, and [95] in the case of Niegocin Lake. The authors of [96] also linked the decrease in nitrogen and phosphorus concentrations to numerous modernizations of wastewater treatment plants in the Odra basin. However, such modernization should be carried out with a view to the future increase in the number of inhabitants; for example, following the modernization of the wastewater treatment plant in Bukowina Tatrzańska, no significant changes were observed with respect to water quality, which even deteriorated due to the rapid increase in the number of people and tourist activity [63]. The significant challenge is also to construct an extensive sewage system connected to WWTP. The dominant method of sewage disposal in most Polish rural areas is still the storage of sewage in closed reservoirs (so-called septic tanks) and their periodic transport by specialized companies [97]. It should be emphasized, however, that infiltration from such septic tanks contributes an additional source of biogenic compounds for groundwater and streams. This was reflected by relatively high concentrations of PO_4^{3-} in the Mogielanka River catchment, as well as in a negative correlation between the sum of precipitation and differences in PO_4^{3-} concentrations between individual months, which indicate numerous areal source contaminations. Such applications should preserve the eutrophication process not only in similar orchard-dominated catchments but also in other agricultural lowland regions. Finally, as the current study reported the preliminary results about biogenic compound dynamics in a horticultural catchment, further investigations are advisable, based on high-frequency monitoring and concentrated on other ions (K^+, Ca^{2+}, Mg^{2+}, and Na^+) responsible for eutrophication.

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