



Phosphate dynamics in the drinking water catchment area of the Dobromierz Reservoir

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ABSTRACT

Surface waters polluted by nutrients from agricultural sources or sewage can change their trophic state into high productive and rich in nutrient content. In particular, phosphates are often regarded as the main hazard because they may activate eutrophication. This article presents the studies conducted in order to understand better the process of phosphate build-up in surface waters of Strzegomka River at the inflow and outflow from Dobromierz Reservoir, Lower Silesia, Poland, Central Europe. The Dobromierz Reservoir is the source of drinking water for over 25,000 people. Daily changes in phosphate concentrations were analysed during the hydrological year XI 2000–X 2001 and in the long-term monthly changes over the period of 15 years (2000–2014). Phosphate concentrations monitored in Strzegomka River showed great changeability. Peak phosphate concentrations reaching 1.70 mg PO₄³⁻/L were noted in the catchment in the autumn of the hydrological year 2000/2001. The mean concentration of phosphates on the inflow to the Dobromierz Reservoir (2000–2014) was 0.33 mg PO₄³⁻/L. No statistically significant decreasing trends were detected for phosphorus compounds concentrations at the inflow of the Dobromierz Reservoir. This means that the problems with the quality of water collected from the reservoir and with the treatment thereof are continuing. Additionally, the research results indicated that treatment processes take place during water flow through Dobromierz Reservoir. A significant reduction of phosphate concentrations up to 66% was confirmed and the possibility of eutrophication of the Dobromierz Reservoir was pointed out. The analysis shows that the most important factors influencing P-PO₄ loads in the Strzegomka River are precipitation and thus also water discharge.

Keywords: Agricultural water pollution; Drinking water; Eutrophication; Phosphate; Surface water quality

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1. Introduction

The degradation of freshwater ecosystems resulting from excessive supply of biogens is a problem known throughout the world [1,2]. Phosphorus is the key nutrient factor in freshwater systems; while in the oceans, primary production is controlled by nitrogen [3–7]. The European Union has developed a series of regulations that support the protection and rational use of water resources. The concentration of phosphorus as a vital factor affecting water quality has been regulated by the EU, among others, in the Water Framework Directive (WFD), Drinking Water Directive and Urban Wastewater Treatment. The WFD obliges EU Member States to achieve a good ecological and chemical status of surface waters by 2015, which involves the necessity to significantly limit the inflow of biogenic substances to rivers and water reservoirs [8–10]. The waters of the Baltic Sea are classified as having unacceptable eutrophication status. For total inputs of phosphorus to the Baltic Sea in 2010, Poland is the greatest contributor with 37%, followed by Russia (16%) and Sweden (9%) [11,12].

Phosphorus compounds enter the waterways from human and animal excreta, phosphorus rich bedrock, wastewater containing detergents, industrial wastewater and pollutants, runoff from agriculture. Agricultural area pollution is considered the main source of phosphorus in surface waters. Phosphates (orthophosphates) are the dominant form of phosphorus, which is also most important for the course of the eutrophication process as it is the only form that autotrophs (bacteria, algae and plants) are able to absorb [3,4,6,10,13–19].

Increased concentration of phosphates in surface water may lead to eutrophication, which is a serious problem connected with the quality of surface waters. Eutrophic waters are characterised by a high concentration of biogenic compounds, chlorophyll *a*, high opacity and frequent occurrence of oxygen deficits [9,15,20–22]. Other factors that significantly influence eutrophication include the capacity of the reservoir, mean depth, retention time and water exchange degree, temperature, nutrients and light availability [23–25]. Shallow water reservoirs reach the eutrophic state more quickly, and intensive water exchange may support the supplementation of deficits of phosphates that are necessary for the development of phytoplankton [23]. The sediment plays an important role in shallow lakes. High internal phosphorus loading from the sediment and phosphorus retention can have strongly negative impact on water quality [14,26–28]. Negative consequences of eutrophication include the blooming

of blue-green algae, which produce toxins and thus create a threat for people and other organisms but also lead to difficulties in water treatment and limit the possibility of economic usage of surface water resources [21,29].

The concentration of biogenic compounds in surface waters is influenced by a series of factors, which include apart from the physiographic conditions of the catchment: soil and crop management, livestock management, landscape management and surface water management, wastewater and waste management. Similarly to other European countries, the USA and China, Poland has also witnessed the development of sewage networks and wastewater treatment systems in the recent decade, but these developments have been accompanied by a rapid increase in the use of phosphate fertilisers and an increasing frequency of occurrence of extreme hydrological conditions [4,10,19,30,31]. Thus, it is difficult to determine the mitigation options that should be chosen in order to protect water effectively from eutrophication without a detailed analysis of the processes that take place in the given catchment.

The objective of this study was to evaluate the changes and trends in the concentration of phosphates in the water course in the agricultural sub-mountain catchment and to determine the sources of pollutants that affect water quality in the Strzegomka River and the Dobromierz Reservoir. Daily changes in phosphate concentrations were analysed during the hydrological year XI 2000–X 2001. The authors conducted an analysis of surface water quality in a 15-year period (2000–2014). Measurements were taken on the Strzegomka River on the inflow and outflow from the Dobromierz Reservoir, to demonstrate the influence of a dam reservoir on the concentration of phosphates.

As far as small agricultural catchments in most countries are concerned, the lack of water quality data to support water quality assessment and decision-making is a significant problem. Even if water quality is monitored, data are still collected irregularly, and they are often incompatible with hydrological data. This study is based on a relatively rare research approach: high-frequency (daily) analysis of monitoring data for the purposes of recognition of processes that determine the concentration of phosphates in surface waters and its seasonal fluctuations as well as the analysis of long-term monthly data in order to recognise trends.

The possibility to meet WFD requirements concerning the concentration of phosphates and the possibility to achieve good water quality by 2015 were assessed.

2. Study area

The Dobromierz Reservoir (Fig. 1) was constructed from 1977 to 1986. An earth dam was erected across the valley of Strzegomka River on a 58.2 km stretch. The first filling took place in the years 1987–1989. The main planned objectives of the reservoir included supplying water to the settlements Świebodzice and the commune Dobromierz and anti-flood protection of areas located below the reservoir (flood reserve capacity 1.35 million m³, maximum capacity 11.75 million m³) [32].

In 1998, a water treatment plant was constructed directly next to the reservoir. Algae caused numerous issues with water treatment plant operations; their blooms appeared so often that the water treatment filtration and purification system had to be adapted appropriately. The process of treatment of water collected from the reservoir consists of double filtration with use of disc and gravel filters, followed by coagulation and final disinfection. As a result, during harmful algal blooms, it is possible to collect water at various depths of the reservoir. Currently, due to economic changes in the region, daily water production is

lower than planned and amounts, on the average, to approx. 4,500 m³.

Dobromierz Reservoir is situated in the Lower Silesia Region (south-western Poland, 50°54'N 16°14'E). The catchment area of the reservoir is 80.7 km², 60% of the area is located in the Bolkowsko-Wałbrzyskie Hills, 40%—in the Wałbrzyskie Mountains (The Sudety Mountains region). The catchment is built of semi-permeable and impermeable rocks, which cause intensive surface runoff and a fast increase in the water flows in streams [33].

The Strzegomka catchment is a part of the drainage basin of Bystrzyca River, a tributary of the Odra River. An average catchment slope gradient is $i_{av} = 5.2\%$; the inclination of the right part of the catchment is 12.3% and of the left one 5.7%. The Dobromierz Reservoir is supplied by the upper part of Strzegomka River (15.6 km long). Its spring is in Łysica Mountain—666 m.a.s.l. and its estuary to Dobromierz Reservoir—285.5 m.a.s.l. The right-side tributaries of the Strzegomka are Chwaliszówka and Czyżynka and the left one is Sikorka. Multi-annual discharges in Strzegomka are: SWQ = 12.19 m³/s (mean flood flow); SQ = 0.781 m³/s (mean); (SNQ) = 0.108 m³/s (the average low discharge); NNQ = 0.04 m³/s¹ (the lowest). The catchment area is inhabited by approx. 3,000 people [31–34]. The Dobromierz Reservoir is the source of drinking water for over 25,000 people. The mean monthly precipitation and air temperatures are presented in Table 1.

The catchment is of an agricultural type with intensive poultry farming. In 2001, 320,000 poultry were bred, including 300,000 in large farms [34]. A significant increase in the number of poultry in the study area had been noted; at the end of the analysed period, 850,000 poultry were bred [31]. The load of phosphorus excreted by poultry with faeces is equivalent to the load from the faeces of 400,000 humans, so it is several times higher than that produced by inhabitants of the catchment. The dominant types of soil are permeable soils, arable lands account for 36% of the catchment area, while 9.5% are meadows, 14.5% pastures, 32% forests [34].

The factors influencing the concentration of phosphates in surface waters in the years 2000–2014 include, in particular, a significant increase in the use of fertilisers in this region. Poultry manure is used mainly as a fertiliser in the catchment. It is an efficient, low cost enrichment if used properly. Between 2000 and 2008, an 88.7% increase in the use of chemical phosphorus fertilisers was noted. In 2013, it was 56.2% higher than in 2000 [31]. Other analysed climatological and economic factors were not characterised by such noticeable, long-term changes.

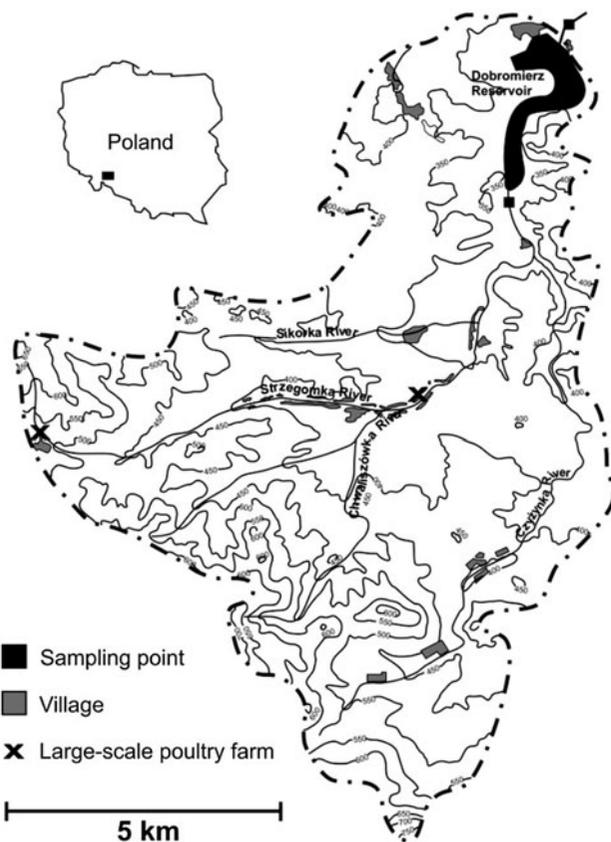


Fig. 1. The catchment of the Dobromierz Reservoir.

Table 1

Mean monthly precipitation (mm) and air temperatures ($^{\circ}\text{C}$) in the hydrological year 2000/2001 and multi-annual data 2000–2014 (meteorological station Szczawno-Zdrój)

	XI	XII	I	II	III	IV	V	VI	VII	VIII	IX	X
<i>Hydrological year 2000/2001</i>												
Precipitation	45.3	20.4	34.4	40.3	70.0	76.6	50.2	79.5	201.4	113.6	122.2	21.2
Temperature	6.3	1.4	-0.6	0.3	2.5	6.7	13.4	13.8	17.9	18.1	11.0	11.9
<i>Multi-annual data 2000–2014</i>												
Precipitation	43.7	40.4	43.1	34.6	47.0	45.5	85.8	80.0	121.4	113.4	71.6	39.0
Temperature	4.4	-0.4	-1.6	-0.8	2.4	8.1	13.0	16.0	18.1	17.2	12.4	8.3

3. Methods

In order to determine the amount of nutrient contaminants dissolved in the water of Strzegomka River more precisely and to assess the seasonal changeability, in the hydrological year 2000/2001, daily measurements of phosphate and Strzegomka discharge above and below reservoir were carried out. The samples were collected by observers in PP bottles and preserved with sulphurous acid every morning at 7 AM. Fortnightly, concentration of TP at the inflow and outflow was measured. All analyses were carried out with use of the standard method, pursuant to ISO 6878: 1998 at the Institute of Environmental Engineering of the former Agricultural University of Wrocław (now the Wrocław University of Environmental and Life Sciences).

The data from The State Environmental Monitoring database were used to conduct a long-term analysis of phosphate concentrations. All available data series from the years 2000–2014 for the analysed area were obtained from The Voivodeship Inspectorate for Environmental Protection in Wrocław. Data from two measurement points on the Strzegomka River located above and below the Dobromierz Reservoir were used. Tests were carried out periodically, as the measurement point below the reservoir was removed in 2007. Full monthly data on the inflow and outflow from the reservoir were recorded in the years 2000, 2004, 2005, 2007, a number of determinations: phosphates on the inflow to the reservoir (2000–2014) $N = 123$, total phosphorus (TP) $N = 120$, phosphates on the outflow from the reservoir (2000–2007) $N = 59$, TP $N = 59$. The provided total phosphorus (TP) concentration is ancillary, with the aim to demonstrate the dominant role of phosphates for the analysed water course and reservoir.

The data concerning the analysed catchment obtained from the Central Database of Climatological Data from the Institute of Meteorology and Water Management—National Research were also used.

The trends in the concentration of phosphates and TP were identified using the Mann-Kendall non-parametric test with XLSTAT 2014 statistical software. The statistical significance of the difference between concentrations of phosphates above and below the reservoir was evaluated with the use of the non-parametric Mann-Whitney U test. Calculations were performed using Statistica 10 software.

4. Results and discussion

4.1. Phosphate concentrations and loads 2000/2001

Phosphate concentrations monitored in Strzegomka River above the reservoir during the hydrological year 2000/2001 are characterised by a great changeability (Figs. 2 and 5). The highest changeability was noted in September and October. In September, high concentrations of phosphates occurred immediately after rainfall events and then decreased fast. The lowest changeability was noticed in January and February when the soil was frozen and the discharge in Strzegomka River was low. Low changeability was also noted in May during vegetation season as a result of small levels of

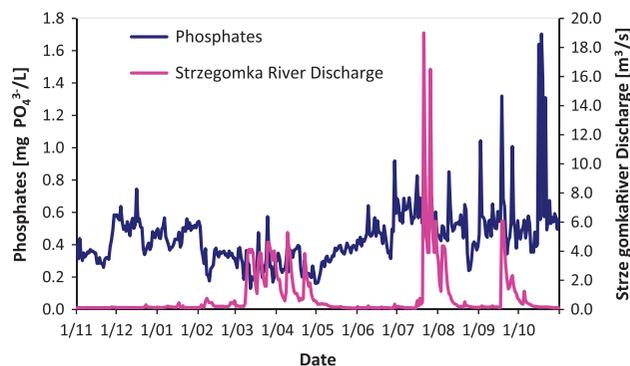


Fig. 2. Daily phosphate concentrations and discharge in the Strzegomka River at the inflow of the Dobromierz Reservoir in the hydrological year 2000/2001.

rainfall. In general, the highest phosphate concentration was found in October (1.70 mg PO₄³⁻/L) and the lowest one (0.13 mg PO₄³⁻/L) in March. Mean annual concentration was 0.44 mg PO₄³⁻/L, median 0.43 mg PO₄³⁻/L.

Phosphate loss often reached peak values during storm and runoff events. Phosphates can be washed out during rainfall, whereas in the vegetation season, phosphates were most available for plant uptake and algal growth, and the soil was overgrown with vegetation protecting it from runoff. In the autumn (when runoff is at its peak), high concentration of phosphates is observed as it was in the Dobromierz catchment. This is usually caused by an increase in runoff from soil that is not overgrown by plants even if the rainfall is low and by remobilisation of P from organic matter dying back after the end of the vegetation season [4,7,35]. Research conducted in the USA demonstrated that over 90% of annual P export from watershed occurred in one or two severe storms events [4].

Daily changes in phosphate concentration identified in the Strzegomka River below the Dobromierz Reservoir during the hydrological year 2000/2001 are presented in Fig. 3. The highest phosphate concentration was noted in August 2001 (0.66 mg PO₄³⁻/L) and the lowest one in May 2001, when the concentration of phosphates approached zero. The mean annual concentration was 0.15 mg PO₄³⁻/L, median 0.13 mg PO₄³⁻/L. The highest changeability of phosphate concentration was monitored in September. In the first 20 d of the month, phosphate concentrations were decreasing to zero. The depletion of mineral forms of phosphorus observed in the reservoir was induced by phytoplankton growth. At the end of September, the phosphate concentrations increased. This was noticed immediately after intensive rainfall. The Strzegomka River was carrying a lot

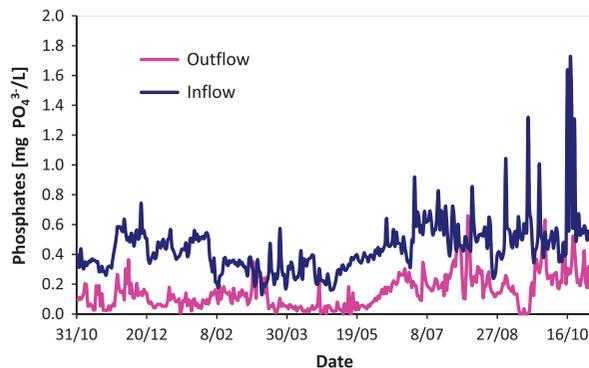


Fig. 3. Daily phosphate concentrations in the Strzegomka River at the inflow and outflow of the Dobromierz Reservoir in the hydrological year 2000/2001.

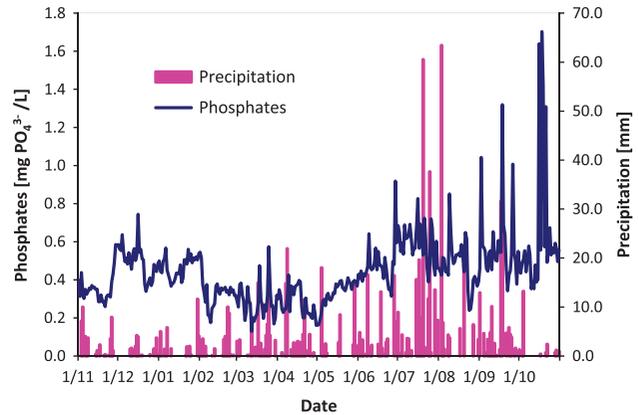


Fig. 4. Daily phosphate concentrations in the Strzegomka River at the inflow and outflow of the Dobromierz Reservoir and precipitation in the hydrological year 2000/2001.

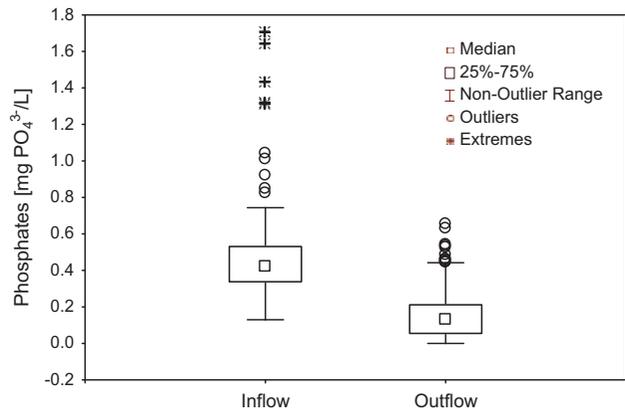


Fig. 5. Phosphate concentrations in the Strzegomka River at the inflow and outflow from the Dobromierz Reservoir in the hydrological year 2000/2001.

of phosphates, which caused an increase in the concentration of phosphates on the outflow of the reservoir.

Results of the U Mann–Whitney statistical test prove the existence of statistically significant differences between the concentrations determined above and below the Dobromierz Reservoir in the hydrological year 2000/2001 ($\alpha = 0.05$, $p = 0.0000$).

The concentration of phosphates during water flow through the reservoir was reduced by 66%. At the same time, 50% reduction in TP concentration in the reservoir was noted, while the mean concentration on the inflow to the reservoir amounted to 0.22 mg P/L and on the outflow—0.11 mg P/L.

An inflow and outflow analysis of the influence of Dobromierz Reservoir on the phosphate concentration in the Strzegomka River was carried out basing on the

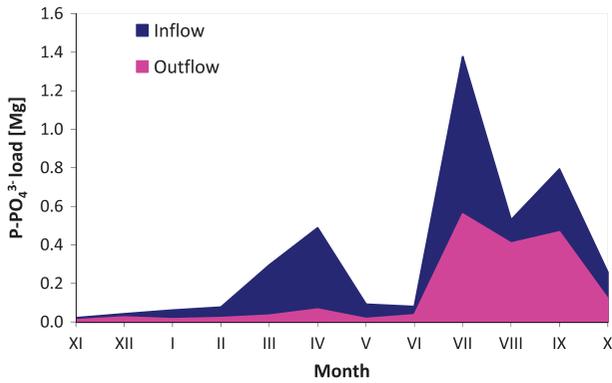


Fig. 6. Monthly P-PO₄ loads on the inflow and outflow to the reservoir during the hydrological year 2000/2001.

mean loads of P-PO₄ identified during the hydrological year 2000/2001. The lowest loads of P-PO₄ were noted in late autumn and winter (Fig. 6), while the highest were observed in July 2001 as a result of a flood that occurred in the area of research basin at that time. High correlation coefficients prove that rainfall ($r = 0.93$) and discharge ($r = 0.88$) have the most important influence on P-PO₄ loads in the Strzegomka River (Figs. 7 and 8).

Monthly loads of P-PO₄ on the outflow of the reservoir were lower than on the inflow throughout the year (Fig. 6). The reduction of P-PO₄ loads in the hydrological year 2000/2001 reached 57% which corresponds to over 2.3 Mg of P-PO₄. This reduction was a result of the decrease in phosphate concentrations described above. The highest reduction of load occurred in April, May and June (about 80%). The lowest one (23%) was noted in August when July flood waters were emptying from the reservoir. At the

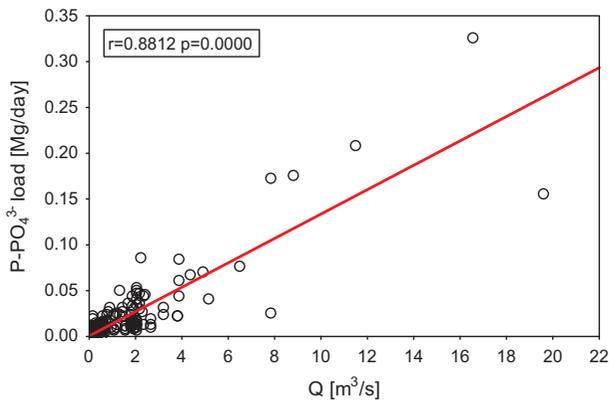


Fig. 8. Dependence between the mean monthly loads of P-PO₄ on the inflow to reservoir and total monthly precipitation in the hydrological year 2000/2001.

same time, the phosphate concentration on the inflow was decreasing.

The annual load of P-PO₄ remaining in the reservoir, calculated basing on precise measurements taken in the hydrological year 2000/2001 is 2.3 Mg. The summer 2001 floods played important role in the circulation of catchment phosphate and influenced the annual load of P-PO₄. Research carried out in Central Europe showed, that flood events play important role in the circulation of catchment phosphate [7]. The significant P-PO₄ retention in Dobromierz Reservoir has a favourable impact on water quality in Strzegomka River below the reservoir. However, the reduction of phosphate concentration affects the water quality in the reservoir. It leads to an increase in the phosphorus compounds concentration in the ecosystem of Dobromierz Reservoir and thus in a growing risk of its eutrophication.

Fig. 7. Loads of P-PO₄ as a function of discharge in Strzegomka River on the inflow to reservoir during the hydrological year 2000/2001.

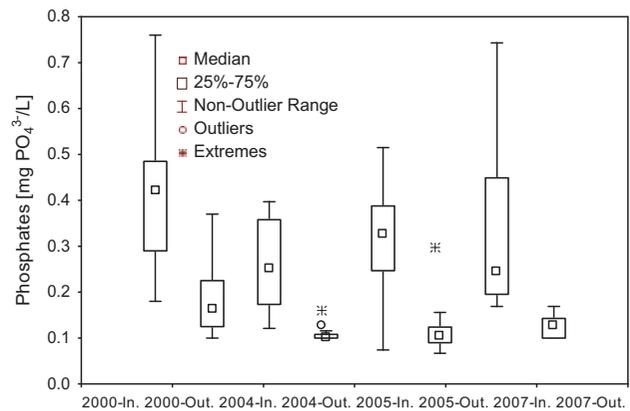


Fig. 9. Phosphate concentrations in the Strzegomka River at the inflow (In.) and outflow (Out.) of the Dobromierz Reservoir (selected years in the 2000–2014 period).

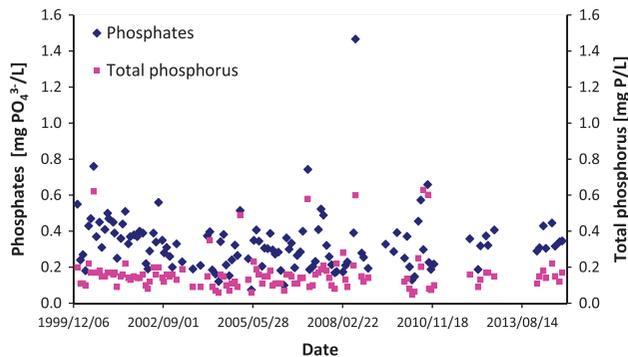


Fig. 10. Phosphate and total phosphorus concentrations in Strzegomka River on the inflow to Dobromierz Reservoir over the period 2000–2014.

4.2. Long-term trends and perspectives (2000–2014)

The concentration of phosphates (monthly data) in the waters of Strzegomka River over the period of 2000–2014 also showed a large changeability (Figs. 9, 10, and Table 2). The analysis was conducted based on the time series characteristic for small agricultural catchments, with irregular or missing values from state monitoring. Data below the reservoir are available only for the period before 2007.

Results of the U Mann–Whitney statistical test prove the existence of statistically significant differences between the monthly concentrations (Fig. 9 and Table 2) determined above and below the Dobromierz Reservoir. Both for phosphates and for phosphorus, the value $p < 0.05$ ($p = 0.0000$) was obtained. This means that the reduction in the concentration of phosphorus compounds in the reservoir was a long-term phenomenon. The impoundment of water in a dam reservoir may have either a negative or a positive influence on water quality in the water course [17,36–38]. The Dobromierz Reservoir has a positive influence on the reduction of phosphate and total phosphorus concentration in Strzegomka River, although the accumulation of phosphate loads in the reservoir is not beneficial for the quality of retained water resources. Significant improvement in water quality below the reservoir results from the retention of phosphorus compounds, not from a lowered emission or limitation of the inflow of pollutants to water environment.

Mann-Kendall non-parametric test was used for the purposes of trend analysis for phosphates and TP. This test is recommended for the purposes of detecting trends in monthly hydrological data. These data are non-normal by nature, there are missing values and periods of irregular sampling [39].

Table 2

Concentrations of phosphates ($\text{mg PO}_4^{3-}/\text{L}$) and TP (mg P/L) in the Strzegomka River at the inflow (inf.) and outflow (out.) of the Dobromierz Reservoir (selected years from the long-term period 2000–2014)

Year	Parameter	Mean	Min	Max	SD	P- PO_4 as a % of TP ^a	Reduction (%)	
							PO_4^{3-}	TP
2000	Inf. PO_4^{3-}	0.412	0.180	0.760	0.156	74.9	54.1	44.9
	Inf. TP	0.196	0.100	0.620	0.138			
	Out. PO_4^{3-}	0.189	0.100	0.370	0.088	57.2		
	Out. TP	0.108	0.070	0.170	0.030			
2004	Inf. PO_4^{3-}	0.263	0.121	0.397	0.098	72.9	58.6	54.3
	Inf. TP	0.127	0.060	0.350	0.078			
	Out. PO_4^{3-}	0.109	0.100	0.159	0.018	63.2		
	Out. TP	0.058	0.040	0.090	0.016			
2005	Inf. PO_4^{3-}	0.314	0.074	0.515	0.121	59.0	61.1	44.3
	Inf. TP	0.185	0.060	0.490	0.117			
	Out. PO_4^{3-}	0.122	0.067	0.296	0.063	38.9		
	out. TP	0.103	0.070	0.170	0.029			
2007	Inf. PO_4^{3-}	0.327	0.169	0.743	0.179	62.6	61.5	43.2
	Inf. TP	0.185	0.080	0.580	0.133			
	Out. PO_4^{3-}	0.126	0.100	0.169	0.025	46.8		
	Out. TP	0.105	0.060	0.250	0.061			

^aTP—measure of all the forms of phosphorus, phosphate phosphorus concentration $\text{P-PO}_4^{3-}/\text{L}$ = phosphate concentration $\text{PO}_4^{3-}/\text{L}$ multiplied by the conversion factor 0.3262.

Table 3

The Mann-Kendall non-parametric test results for TP and phosphates monthly concentrations 2000–2014 (significance level $\alpha = 0.05$)

Parameter	Kendall's tau	S	Var (S)	p-value (two-tailed)	Trend nature	Trend significance
Phosphates inflow	-0.113	-846	209,230	0.065	decreasing	No
TP inflow	-0.040	-279	193,318	0.527	decreasing	No

The Mann-Kendall trend test is based on the correlation between the ranks of a time series and their time order [40].

The Mann-Kendall trend analysis requires to consider several factors: Mann-Kendall statistic S , Kendall's tau and p -value. A positive value of the Mann-Kendall statistic S indicates an increasing trend and a negative decreasing trend. In order to illustrate the correlation between two variables, the Kendall's tau is calculated. It is a measure of correlation for this non-parametric test and it may adopt the values from -1 to $+1$. Kendall's tau equal to non-zero value is a proof of the existence of a trend. A positive value of Kendall's tau demonstrates that the analysed variable has a tendency to increase in time, while negative value indicates some tendency to decrease in time. As the p -value falls, the statistical significance of Kendall's tau becomes greater [41,42].

No statistically significant trends were detected for phosphate and total phosphorus concentrations (Table 3). High average annual phosphate concentrations are still noted in the waters of Strzegomka on the inflow to the reservoir, exceeding the threshold value $0.31 \text{ mg PO}_4^{3-}/\text{L}$. The mean concentration of phosphates on the inflow to the reservoir was $0.33 \text{ mg PO}_4^{3-}/\text{L}$. This results in a failure to achieve the WFD objectives (including good chemical status of surface water) by 2015. Mean annual TP concentrations do not exceed the threshold value of 0.40 mg P/L [43].

The presented values are characterised by a high annual changeability, which is typical for phosphates and nitrates in surface waters [36,44,45]. The observed concentrations of phosphates and TP are slightly lower than the average values obtained as a result of analyses carried out in agricultural catchments [2,37,38,45–48]. The main issue in the Strzegomka catchment is a surface runoff after intense rainfall. The solution of this problem requires, first of all, to rationalise agricultural management—to apply cultivation to minimise P loss. Proper stormwater and landscape management will help to eliminate the negative influence of extreme conditions.

5. Conclusions

Phosphate concentrations in Strzegomka River are characterised by great changeability during the hydrological year 2000/2001 and over the long-term period 2000–2014 as well. Noted phosphate levels are average in comparison to analyses carried out in agricultural catchments. Significant problems in the drinking water catchment that affect water quality and water treatment plant operations include the agricultural runoff caused by storm events. Phosphate presence in Strzegomka River depends on climatic conditions. High correlation coefficients show that rainfall and discharge have the most important influence on P- PO_4 loads in the Strzegomka River. P- PO_4 loads in the hydrological year 2001 were reduced by 57%, which corresponds to over 2.3 Mg of P-PO_4 . In addition, the results of empirical research developed by statistical methods confirm that significant retention of phosphate and total phosphorus occurs in Dobromierz Reservoir. It is favourable for water quality in Strzegomka River below the reservoir but it also increases the risk of eutrophication of the Dobromierz Reservoir. High average annual phosphate concentrations noted in the waters of Strzegomka on the inflow to the reservoir exceeded the threshold value $0.31 \text{ mg PO}_4^{3-}/\text{L}$, which results in a failure to meet the WFD objectives for 2015.

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