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CHEMICAL COMPOSITION OF BOTTOM SILTS AS AN INDICATOR OF ENVIRONMENTAL CONTAMINATION IN A SMALL RIVER BASIN

SUMMARY

Pollution of small river basins contributes to the deterioration of larger river systems, leading to the degradation of aquatic ecosystems and exerting a negative impact on the environment. Bottom sediments play an important role in the functioning of ponds and can serve as indicators for assessing the composition, intensity, and scale of environmental pollution. This study was conducted in the basin of the small river Tlumachyk, a right tributary of the Dniester River, within the Tlumach territorial community of Ivano-Frankivsk region (Ukraine). The research aimed to assess the impact of anthropogenic pressure on the qualitative composition of bottom sediments and evaluate their potential use as an agronomic resource for restoring soil fertility. The results revealed the influence of anthropogenic activities on the chemical state of bottom sediments in open ponds of the Tlumachyk River basin, including its tributaries, ponds, and lakes. The average content of total nitrogen in the bottom sediment samples ranged from 0.3% to 0.5%, phosphorus from 0.2% to 0.3%, and potassium from 0.7% to 0.8%, which is comparable to typical values found in farmyard manure. No exceedances of maximum permissible concentrations were detected for main micronutrients and heavy metals in the bottom sediments, indicating their suitability for use as an agronomically valuable resource. Therefore, these sediments may be considered for local use as fertilizers to aid in the restoration of soil fertility.

Keywords: small river basin, biogenic elements, nitrates, micronutrients, heavy metals, bottom sediments, pollution

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INTRODUCTION

Bottom sediments are deposits of various mineral and organic particles that accumulate over time on the beds of rivers, ponds, lakes, and reservoirs. Analysis of their chemical composition is crucial for assessing the level of water pollution and for monitoring the ecological status of aquatic ecosystems. The detection of elevated concentrations of biogenic elements or heavy metals in bottom sediments may indicate intense anthropogenic pressure on the catchment area and highlight the need to develop mitigation measures.

Research on the growing impact of anthropogenic load on the ecological state of aquatic ecosystems-particularly on bottom sediments as a key component-has gained increasing attention in the context of Ukraine's alignment with the European Green Deal. The core provisions and EU directives in this domain include the Water Framework Directive (2000/60/EC), the Groundwater Directive (2006/118/EC), the Nitrates Directive (91/676/EEC), and Regulation (EC) No 1107/2009 concerning the sustainable use of pesticides. In line with the European course, Ukraine must implement monitoring systems for the chemical composition of bottom sediments, adapt EU quality standards for sediment in terms of pollutant content, and develop and enforce programs aimed at reducing agrochemical pressure on aquatic ecosystems.

The possibility of use of water resources is closely linked to factors such as water and sediment quality, eutrophication, overgrowth, hydrological processes, and extreme natural phenomena, all of which are influenced by anthropogenic sources and climate change (Jaskuła *et al.,* 2021; Litvinova *et al.,* 2021; Pavlichenko *et al.,* 2023). It is well-established that the majority of pollutants in aquatic ecosystems migrate from water to bottom sediments (Sapronova *et al.,* 2024). The location and depth of a pond significantly influence both water quality and the composition and properties of sediments. Pollutant concentrations in sediments are often several times higher than in the overlying water, making them effective indicators of contamination even at low pollution levels (Ziemińska-Stolarska *et al.,* 2020; Dehodiuk *et al.,* 2024).

Contamination of bottom sediments can adversely affect the life processes of many aquatic flora and fauna species. Therefore, monitoring the quality of bottom sediments in open ponds -particularly with regard to various toxicants, including heavy metal ions-is vital for preserving biodiversity (Yakovchuk & Perepelytsia, 2017; Nawab *et al.,* 2021; Tykhonova *et al.,* 2021; Khan *et al.,* 2025).

The accumulation of heavy metals in aquatic ecosystem components is a key indicator of the environmental condition of a given territory (Kolesnyk, 2014; Litvinova *et al.,* 2019; Litvinova *et al.,* 2020). Due to their toxicity, persistence, and ability to bioaccumulate in food chains, heavy metals are considered one of the most hazardous pollutants in river ecosystems. Upon entering aquatic systems, heavy metals may cause harm to aquatic organisms and, through processes such as chemical adsorption and physical sedimentation, tend to accumulate in bottom sediments (Zhang *et al.,* 2016).

Bottom sediments act as potential secondary sources of heavy metals in aquatic environments, as metals readily bind to sediment particles. However, under changing hydrodynamic or environmental conditions-such as fluctuations in pH or redox potential-there is a risk of remobilization of these metals back into the water column, resulting in secondary contamination. These pollutants originate from both natural and anthropogenic sources, including mining and metallurgical industries, the use of pesticides and fertilizers in agriculture, sewage sludge disposal, and industrial sewage discharges (Yadav *et al.,* 2002; Baran *et al.,* 2016; Szara *et al*., 2020; Kluska & Jabłońska, 2023).

Higher concentrations of heavy metals are typically found in sediments rich in silt and clay, which is attributable to both the chemical properties of clay particles and their capacity to adsorb metals from the water column (Miroshnychenko, 2012). Another major concern is the presence of organic pollutants in sediments, as they often act as sinks for hydrophobic, persistent, and toxic compounds (Perelo, 2010).

Due to their physicochemical properties, bottom sediments may also serve as an alternative source of nutrients for agricultural applications. Such reuse is aligned with the principles of the circular economy and the European Green Deal. The agricultural use of dredged sediments is primarily justified by their high organic matter content, neutral to alkaline pH, and significant levels of available phosphorus, potassium, and magnesium, all of which contribute to their agronomic value (Kazberuk *et al.,* 2021; Litvinova *et al.,* 2023). Consequently, bottom sediments hold potential for use in agriculture, horticulture, or the reclamation of degraded lands (Szara-Bąk *et al.,* 2022). Under appropriate quality conditions, silt sediments have proven to be effective soil conditioners for agricultural purposes (Chushkina *et al.,* 2022; Kovalenko *et al.,* 2024).

The application of bottom sediments in agriculture may enhance soil fertility, reduce the need for chemical fertilizers, and limit sediment accumulation in water bodies. Nonetheless, concerns remain regarding contamination with heavy metals and organic pollutants, which may restrict their safe use as fertilizers (Bohynia, 2020; Rudenko, 2024).

This study aims to assess the impact of anthropogenic pressure on the chemical composition of bottom sediments from open water bodies within the Tlumachyk River basin, a tributary of the Dniester River system, and to evaluate the feasibility of using these sediments as an agronomic resource for restoring soil fertility.

MATERIAL AND METHODS

The Tlumachyk River is located within the administrative boundaries of the Tlumach United Territorial Community (UTC) of Ivano-Frankivsk Region, Ivano-Frankivsk Oblast, and serves as a right tributary of the Dniester River. It has a total length of 35 km and a catchment area of 254 km^2. The river valley floodplain has a V-shaped profile, ranging in width from 50 to 300 meters. The riverbed is meandering, approximately 6–7 meters wide and 1.2 meters deep near the confluence with the Dniester, and exhibits signs of channel displacement in certain sections.

To determine the agrochemical composition of bottom sediments, samples were collected from various aquatic bodies within the Tlumachyk River basin. These included the Tlumachyk River itself, its first-order tributaries (right tributaries: the Dustriv and Mlynivka rivers; left tributaries: the Khrust and Brzezina rivers), and a second-order tributary (Solonyk River, a left tributary of the Mlynivka River). Additionally, sediments were sampled from ponds and lakes situated along these watercourses (Figure 1). The investigated water bodies are located within the city of Tlumach and the surrounding rural settlements: Ozeryany, Lokitka, Hrynivtsi, Melnyky, Nadorozhna, Kolintsi, Honcharivka, Palahychi, Ostrynia, Oleshiv, and Nyzhniiv.

Tlumachyk River (700 m downstream from the wastewater treatment facilities): *Coordinates:* 48.884307, 25.019761

Mlynivka River (3.0 km from the source): *Coordinates:* 48.810594, 25.044870

Pond (800 m from the Tlumachyk River channel): *Coordinates:* 48.879816, 25.027899

Figure 1. Sampling locations of bottom sediments in the Tlumachyk River basin

Bottom sediment samples were collected using a sediment corer at depths of 0–20 cm and 0–40 cm, depending on the thickness of the deposits, in 2022. Mixed composite samples were used for analysis. Analytical determinations of sediment composition were conducted in accordance with Ukrainian national standards, including: moisture content (DSTU EN 12048:2005), pHsol. (DSTU ISO 10390:2007, DSTU EN 13037:2005); organic matter content (humus) (DSTU 4289:2004; nitrate nitrogen (DSTU 4725:2007); ammonium nitrogen (DSTU 4729:2007); light hydrolyzable nitrogen (DSTU 7863:2015).

Mobile potassium and phosphorus (Chirikov method – DSTU 4115-2002; Machihin method – DSTU 4114-2002); total nitrogen (DSTU 7911:2015), total phosphorus (DSTU EN 15959:2015), total potassium (DSTU 7949:2015); available compounds of manganese (DSTU 4770.1:2007), available compounds of zinc (DSTU 4770.2:2007), available compounds of cadmium (DSTU

4770.3:2007), available compounds of iron (DSTU 4770.4:2007), available compounds of copper (DSTU 4770.6:2007), available compounds of nickel (DSTU 4770.7:2007), available compounds of lead (DSTU 4770.9:2007); exchangeable calcium and magnesium (DSTU 7861:2015).

The assessment of nutrient availability and contamination levels in bottom sediments was performed in accordance with Ukrainian regulatory documents: DSTU 4362:2004 and Resolution of the Cabinet of Ministers of Ukraine No. 1325 of December 15, 2021, “On the Approval of Maximum Permissible Concentrations of Hazardous Substances in Soils.”

Agrochemical studies of bottom sediment quality were carried out in the Laboratory of Agroecology and Analytical Research at the Institute of Agriculture of the National Academy of Agrarian Sciences of Ukraine, using methodologies compliant with national regulatory standards.

Statistical analysis.

The least significant difference at $P<0.05$. Statistical processing was performed by Microsoft Excel in combination with XLSTA.

RESULTS AND DISCUSSION

The environmental situation in the basins of small rivers is a critical issue today. As noted by Bakalo *et al.* (2018), the difference between small rivers and medium or large ones lies not only in their length or catchment area, but in the degree to which bioprocesses in them depend on the surrounding watershed. While in large rivers the hydrological and hydrochemical regimes and overall ecological condition are mostly influenced by climatic conditions and in-channel or floodplain processes (hydrological, hydrochemical, and self-purification mechanisms), the water quality of small rivers is predominantly determined by the condition of the catchment area and the prevailing terrestrial processes within their basins.

Small rivers contribute to the volume and quality of water in large rivers and play a role in shaping natural landscapes. At the same time, the functioning of small river basins is determined by the state of regional landscape complexes.

Under conditions of intensive anthropogenic pressure-both in many countries around the world and in Ukraine-the study of bottom sediments in small rivers is highly relevant for ensuring the environmental safety of water resources. These studies are also essential for understanding the functioning of river ecosystems, assessing their condition, and developing measures for their protection and restoration. The chemical composition of bottom sediments reflects the ecological condition of both aquatic systems and their catchment areas (Lyuta, 2018; Voitovyk *et al.,* 2023).

The assessment of bottom sediment quality is a component of evaluating the ecological and geochemical state of the geological environment, including river basin territories, for which monitoring programs for surface and groundwater are developed in accordance with the EU Water Framework Directive 2000/60/EC (Lyuta & Sanina, 2023).

Pollution of rivers with industrial, agricultural, and domestic wastewater leads to the accumulation of contaminants in bottom sediments (Miroshnichenko, 2013; Kong *et al.,* 2015; Wang *et al.,* 2021; Pavlović *et al.,* 2016). Anthropogenic pressure on water bodies is evident in both urban areas, at sewage discharge sites, and in rural areas, through diffuse pollution from surface runoff from agricultural land (Vystavna *et al.,* 2015).

In a study by Zhang *et al.* (2018), the assessment of pollution sources in the bottom sediments of the Zijiang River (China) showed that Co, Zn, Cd, and Cu mainly originated from agricultural activities, As, Sb, Mn, and Pb from mining and smelting operations, and Cr and Ni from natural sources.

Deforestation, land plowing, and intensive agricultural activity within the watershed can increase soil erosion and lead to the influx of large amounts of solid particles into rivers, altering the composition and rate of bottom sediment accumulation (Pichura, 2016; Snytinsky *et al.*, 2020). Additionally, the extraction of mineral resources from riverbeds and floodplains can result in contamination of bottom sediments with heavy metals and the silting of rivers.

Dams and reservoirs can influence the hydrological regime of rivers and sedimentation processes, leading to sediment accumulation upstream of the dam and sediment deficiency downstream. Enhanced accumulation of sediment and pollutants is especially observed near dam structures (Sojka *et al.,* 2019). In small and shallow reservoirs, the zones of heavy metal accumulation depend on several factors, including the flow of the main river, reservoir depth, water turbulence, reservoir shape (e.g., constrictions, bays/inlets), and the type of water outflow (Smal *et al.*, 2015).

Research by Polish scientists on bottom sediments of the Powa River, which is part of the Oder River basin, showed that concentrations of heavy metals in the sediments of the reservoir (Stare Miasto) within the river channel were higher than in bottom sediments of the downstream river section. The decisive factors influencing heavy metal concentrations in bottom sediments were the content of silt, clay, and total organic matter (Sojka *et al.*, 2018). Findings from the Panyang River (China) indicated that over the past 100 years, the content of trace elements in bottom sediments was lower in the upper reaches compared to the middle and lower reaches of the river (Deng *et al.,* 2020).

A study of the concentration of biogenic compounds and heavy metals in bottom sediments of the Sulejow Reservoir (Central Poland) revealed that agricultural activities had a significant influence on the distribution of the studied substances. The highest accumulation of biogenic components occurred in sediment layers from deeper zones with slow water flow, in stagnation zones, areas adjacent to arable land, and zones dominated by fine-grained sediment fractions. Bottom sediments collected from the reservoir in 2018 showed no toxicological contamination in terms of cadmium, lead, or chromium content (Ziemińska-Stolarska *et al.*, 2020).

Although the issue of anthropogenic influence on the chemical composition of bottom sediments has been addressed in the works of many researchers, it still requires more detailed investigation, particularly in small river basins. To this end, studies were conducted in the basin of the small Tlumachyk River. Its riverbed begins at the confluence of the Khrust, Dustriv, and Brzezina rivers near the town of Tlumach.

Table 1. Agrochemical characteristics of bottom sediments in the Tlumachyk River channel

№	Sampling Location	Exchangeable Acidity, pH (1M KCl)	Organic Matter, Carbon (C), %	Available forms, mg kg^{-1}								
				Cu	Zn	Pb	Ni	Cd	Mn	Fe	exchangeable Calcium (Ca)	exchangeable Magnesium (Mg)
1	100 m upstream from the wastewater treatment plant, Tlumach	7.3	1.16	1.30	3.6	3.5	1.5	0.24	138	392	45.1	2.6
2	At the wastewater outlet (discharge pipe), Tlumach	7.5	0.82	2.32	5.2	3.9	1.5	0.28	121	503	28.6	2.0
11	200 m downstream from the plant, Honcharivka	7.2	3.44	0.92	12.7	5.4	3.3	0.37	148	438	75.4	2.3
3	700 m downstream from the plant, Lokitka	7.3	0.74	0.60	4.6	3.9	1.3	0.22	169	284	25.4	1.8
23	8 km from the source, Ostrynia	7.7	1.44	1.36	6.9	7.3	4.3	1.23	148	57.1	244	1.9
24	Mouth (confluence with the Dniester River), Nyzhniw	7.7	1.62	1.84	5.1	2.6	3.0	0.72	119	386	57.8	3.2
$\overline{X} \pm S\overline{x}$		*7.5±0.1*	*1.54±0.41*	*1.40±0.25*	*6.4±1.3*	*4.4±0.7*	*2.5±0.5*	*0.50±0.16*	*140±7*	*343±64*	*79.4±33.8*	*2.3±0.2*
V, %		2.9	64.6	44.6	51.8	37.7	49.5	78.04	13	46	104.3	23.0
Least Significant Difference (LSD)$_{05}$		*0.3*	*1.47*	*0.3*	*4.9*	*2.5*	*1.8*	*0.59*	28	*234*	*122.8*	*0.8*
Maximum Permissible Concentration (MPC)		–	–	***3***	***23***	***6***	***4***	***0.7***	***140***	–	–	–

To assess the anthropogenic impact on the agrochemical indicators of bottom sediments, samples were collected 100 meters upstream from the municipal wastewater treatment facilities as a reference for environmental monitoring. The sediment consists of sandy, silty, and organic fractions that include both autochthonous and allochthonous deposits enriched with macro- and micronutrients, which reflect their ecological condition. Bottom sediments should be considered as indicators for identifying the composition, intensity, and scale of environmental pollution.

Bottom sediments from the Tlumachyk River channel varied significantly depending on the sampling location (Table 1).

The bottom sediments collected upstream of the wastewater treatment facilities exhibited a slightly alkaline reaction (pH 7.3). The organic matter content, recalculated as carbon (C), was 1.16%; nitrate nitrogen ($N\text{-}NO_3$) – 11.0 mg kg^{-1}; ammonium nitrogen ($N\text{-}NH_4$) – 14.2 mg kg^{-1}; and total mineral nitrogen – 25.2 mg kg^{-1}. These values correspond to an elevated supply level based on the DSTU 4362:2004 soil assessment standard.

The wastewater treatment plant on the Tlumachyk River treats municipal sewage contaminated with both chemical and biological pollutants. In the bottom sediments sampled near the discharge pipe of the treatment facilities, the dry matter content and exchangeable acidity remained nearly unchanged. However, the organic matter content (recalculated as carbon) decreased by a factor of 1.4, while copper compound concentrations increased by 1.7 times (Table 1). The total mineral nitrogen content in bottom sediments near the outlet pipe increased 1.8 times, and the nitrate content increased nearly 2.3 times (Figure 2).

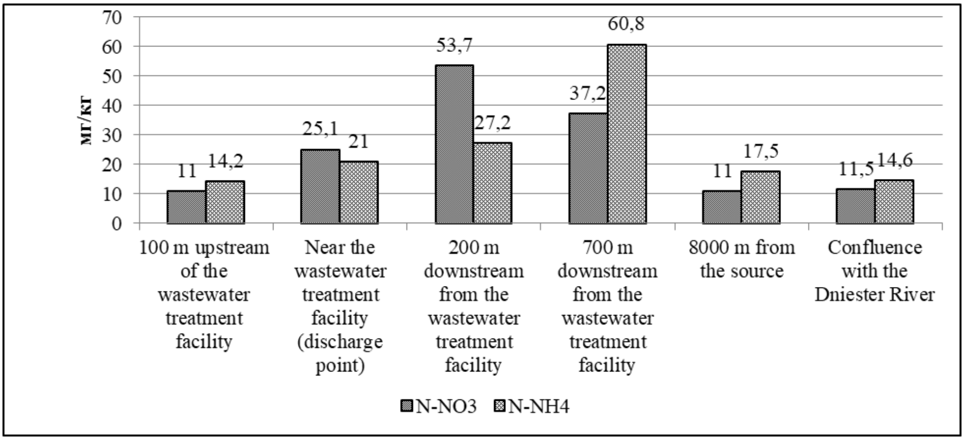

Figure 2. Content of mineral nitrogen forms in the bottom sediments of the Tlumachyk River channel

At a distance of 200 meters downstream in the river channel near the village of Honcharivka, due to sedimentation and the influence of local wastewater discharges, the dry matter content in bottom sediments decreased by 1.4 times compared to those near the outlet pipe-from 68.4% to 49.2%. In contrast, the organic matter content increased nearly threefold compared to the sediments upstream of the treatment facilities. The nitrate nitrogen content increased nearly fivefold and exceeded the maximum permissible concentration (MPC) by 1.8 times-reaching 130.0 mg kg^{-1} of NO_3, as regulated by the Order of the Ministry of Health of Ukraine "Hygienic standards for the permissible content of chemical substances in soil" (Document No. 1595). Ammonium compound levels were observed to rise to almost double those recorded in sediments prior to the treatment plant's influence, clearly reflecting the human-driven effect of treated wastewater inputs on the chemical profile of riverbed sediments.

Within the protected territory of the Madrid Autonomous Community in Spain, researchers investigated the presence of ammonium in deposits of a stream connected to the Tagus River basin. This stream has been subject to wastewater discharges from treatment facilities for more than 50 years. The study revealed that clay-rich layers function as effective sinks for ammonium, serving as indicators of historical pollution. Statistical analysis confirmed a direct relationship between higher total ammonium concentrations and clay content. Furthermore, the study indicated that the downward migration of ammonium was halted by a clay-enriched sediment barrier at depths of 60–70 cm, which acted as a natural retention layer (Martín *et al.,* 2023).

Further downstream, within the boundaries of the village of Lokitka (700 m from the wastewater treatment facilities), a decrease in nitrate and organic matter content by 1.4 and 4.6 times, respectively, was observed. The concentration of ammonium compounds increased by a factor of 2.2 compared to the values recorded in the sediments within the village of Honcharivka. Eight kilometers downstream, after the river passes through the villages of Palahychi and Ostrynia, an increase in alkalinity to pH_{sol} 7.7 was recorded, along with an increase in organic matter content to 1.44% (1.9 times higher), and a decrease in nitrate and ammonium nitrogen concentrations by 1.4 and 3.5 times, respectively, compared to the sediments in Lokitka. In the composite sample of bottom sediments from this section, exceedances of the maximum permissible concentrations (MPCs) for lead (by 1.2 times; MPC = 6.0 mg kg^{-1}) and cadmium (by 1.7 times; MPC = 0.7 mg kg^{-1}) were recorded. These exceedances are associated with local anthropogenic pressure and the characteristics of the underlying lithology, historically impacted by peat extraction.

Further downstream at the mouth of the Tlumachyk River, beyond the residential areas of Oleshiv and Nyzhniw (12.0 km from Ostrynia), the pH_{sol} remained stable at 7.7. The organic matter content increased by 1.1 times. The mineral nitrogen content decreased slightly (by 1.1 times), although the concentration of mobile cadmium compounds slightly exceeded the MPC.

In the bottom sediments of the Tlumachyk River, microelements and heavy metals such as copper, zinc, lead, nickel, cobalt, and cadmium were detected at various concentrations. The average copper concentration in the sediments was 1.39 mg kg^{-1} (with an MPC of 3.0 mg kg^{-1}). The highest copper level-2.32 mg kg^{-1}-was recorded near the outlet of the Tlumachyk wastewater treatment plant. This concentration decreased to 0.6 mg kg^{-1} 700 meters downstream and then increased again to 1.36 mg kg^{-1} in Ostrynia village, suggesting localized input of copper. At the river mouth (village of Nyzhniw), the copper concentration rose to 1.84 mg kg^{-1}. The average concentration of mobile zinc compounds in the bottom sediments was 6.3 mg kg^{-1} (coefficient of variation V = 51.8%), well below the

MPC of 23.0 mg kg^{-1}, indicating moderate accumulation of trace elements such as copper and zinc.

Iron and manganese are common components of municipal sewage, though typically present at concentrations that pose no significant environmental threat. However, their chemical forms are crucial due to interactions with other wastewater constituents such as phosphorus, sulfur, and heavy metals. It is well established that Fe and Mn hydroxides adsorb or co-precipitate trace metals under oxidizing conditions, while under reducing conditions, these metals may be remobilized following the dissolution of Fe/Mn hydroxides. Additionally, iron and manganese compounds serve as important electron acceptors during the decomposition of organic matter (Vymazal & Švehla, 2013).

Manganese compounds tend to accumulate only weakly in water solutions but intensively in silty fractions of bottom sediments. In the bottom sediments, their average concentration was 140 mg kg^{-1} (V = 13%), ranging from 119 to 169 mg kg^{-1}-close to the soil MPC for manganese (140 mg kg^{-1}). Iron accumulation in silty fractions averaged 343 mg kg^{-1} (V = 46%), with a range from 57.1 to 503.0 mg kg^{-1}; no official limit has been established for this element. The carbonate composition of Tlumachyk River silts was determined by the heterogeneous contents of calcium and magnesium, with average values of 79.4 mg kg^{-1} (V = 104.3%) and 2.3 mg kg^{-1} (V = 23.0%), respectively.

Thus, the silts of the Tlumachyk River generally meet environmental standards in terms of mobile forms of trace elements and heavy metals, except for one sample which requires further investigation.

The assessment of total forms of nitrogen (N), phosphorus (P), and potassium (K) in bottom sediments provides insight into the feasibility of their use as fertilizers (Figure 3).

The total nitrogen content in all analyzed bottom sediment samples ranged from 0.22% to 0.44% (V=26.2%, $LSD_{0.05}$ = 0.13), while in solid manure it is about 0.5%. The highest nitrogen concentration (0.44%) was recorded in the sediments collected at the river mouth within the village of Nyzhniv, although the C:N ratio was 3.7. In contrast, the C:N ratio in the sediments near the village of Ostrynia was 6.5, and in the sediments located 200 m downstream from the sewage treatment plant – 14.3.

Total phosphorus content ranged from 0.11% to 0.36% (V=45.9%, $LSD_{0.05}$ = 0.15), while in solid manure it is about 0.25%. The highest phosphorus content (0.36%) was found in the sediments 200 m downstream from the treatment plant – twice the concentration found upstream (Figure 3). The total potassium content ranged from 0.56% to 1.29% (V=34.9%, $LSD_{0.05}$ = 0.40), which in most cases exceeds that found in manure (0.6%).

Thus, the bottom sediments of the Tlumachyk River exhibit NPK content comparable to that of manure, making them a promising source of local fertilizer.

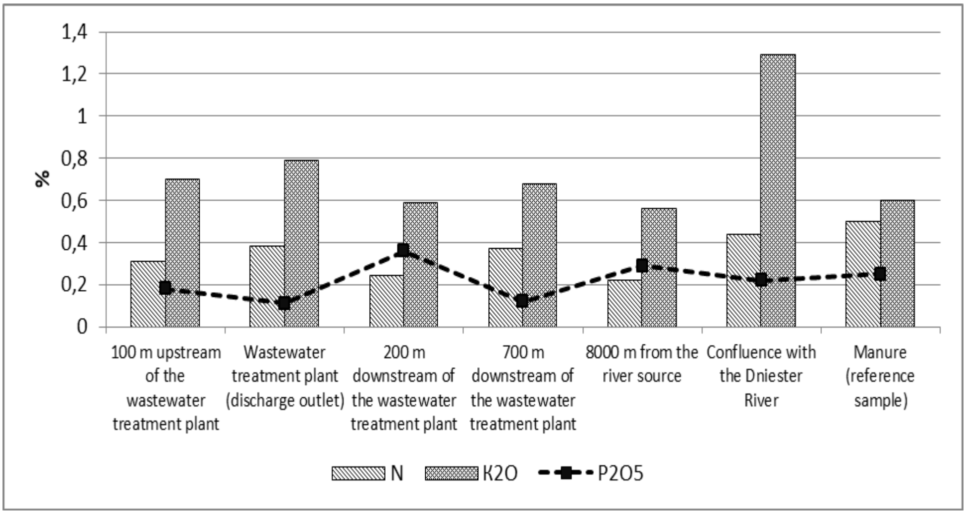

Figure 3. Content of essential nutrients in the bottom sediments of the Tlumachyk River compared to solid manure, %

The chemical composition of the Tlumachyk River sediments, as an indicator of environmental contamination, clearly reflects the direct impact of human activity, such as the inefficiency of existing wastewater treatment facilities and the lack of centralized sewage systems in some settlements. Under current conditions, anthropogenic pressure on the environment is likely to increase over time and may reach critical levels, posing a threat to the functioning of the river basin.

It is also crucial to assess the state of bottom sediments in the first- and second-order tributaries of the river, as their condition directly affects the water quality in the main channel. In the upper reaches of the Tlumachyk River, there is a second-order tributary – the Solonyk River – which flows into the Mlynivka River near the wastewater treatment facilities. Here, several rivers converge: Mlyniv, Dustriv, Khrust, and Brzezina, forming the Tlumachyk River. All these rivers and their tributaries originate in rural areas and are subject to increasing anthropogenic pressure as rural households approach the riverbeds.

The Solonyk River originates from a lake near the village of Bortnyky. At a distance of 4.5 km from its source, in the village of Melnyky, the following parameters were recorded: dry matter content – approximately 60%, organic matter (expressed as carbon) – 3.02%, nitrates – 6.8 mg L^{-1}, and ammonium nitrogen – 56.0 mg L^{-1} (Table 2).

Downstream at the confluence of the Solonyk and Mlynivka rivers, a 6% decrease in dry matter content was recorded, while the amount of organic matter increased by 13.6% compared to the previous sampling point. Nitrate content rose significantly from 6.8 to 28.8 mg kg^{-1} (Figure 4).

Table 2. Agrochemical characteristics of silt in the channels of Tlumachyk River tributaries

№	Sampling Location	Exchangeable Acidity, pH_{salt}	Organic Matter, Carbon (C), %	Available forms, mg kg^{-1}								
				Cu	Zn	Pb	Ni	Cd	Mn	Fe	Exchangeable Calcium (Ca)	Exchangeable Magnesium (Mg)
14	Mlynivka River, 3.0 km from source, Ozeryany village	7.7	3.83	0.99	6.8	7.6	3.4	0.61	98	67.6	296	1.6
9	Mlynivka River, confluence with Tlumachyk River, Tlumach town	7.5	1.86	0.80	3.3	5.6	2.8	1.13	168	312	80.9	2.6
15	Dustriv River, source Hrynivtsi village	7.7	1.90	0.86	3.1	3.5	3.2	1.14	109	401	29.4	2.6
17	Dustriv River, 4.0 km from source, Hrynivtsi village	7.4	2.82	0.70	4.4	2.5	3.4	0.50	353	919	31.7	4.3
10	Dustriv River, mouth Tlumach town	7.3	1.03	0.58	6.2	3.8	2.4	0.65	151	469	36.5	4.7
20	Khrust River, 3.0 km from source, Nadorozhna village	7.5	2.78	0.61	2.6	2.9	3.5	0.42	276	775	43.0	4.8
21	Khrust River, 7.0 km from source, Kolintsi village	7.4	1.62	0.65	7.7	3.6	2.8	0.35	183	872	36.6	3.0
7	Solonyk River, 4.5 km from source, Melnyky village	7.5	3.02	0.46	1.9	3.7	1.2	0.22	80.2	161	54.3	2.6
8	Solonyk River, confluence of 2 tributaries, Melnyky village	7.4	3.43	1.01	6.8	8.4	3.7	0.27	139	113	298	1.8
21	Brzezina River, confluence with Dustriv River, Kolintsi village	7.4	1.62	0.65	7.7	3.6	2.8	0.35	183	872	36.6	3.0
$\overline{X} \pm S\overline{x}$		*7.5±0.04*	*2.40±0.9*	*0.70±0.06*	*6.1±1.4*	*4.5±0.6*	*2.9±0.2*	*0.60±0.10*	*174±27*	*496±107*	*94.3±34.1*	*3.1±0.4*
V, %		1.8	38.04	4.61	1.8	44.4	24.9	58.59	48	68	114.4	36.6
Least Significant Difference ($LSD_{0.05}$)		*0.1*	*0.92*	*0.18*	*4.4*	*2.0*	*0.7*	*0.33*	*85*	*341*	*109.0*	*1.1*
Maximum Permissible Concentration (MPC)		–	–	***3***	***23***	***6***	***4***	***0.7***	***140***	–	–	–

As the Mlynivka River flows toward the town of Tlumach (at its mouth) through a sparsely populated floodplain, partial self-purification processes of the sediments from anthropogenic loads were observed: the content of organic matter decreased by 1.8 times, nitrate nitrogen by 1.4 times, and ammonium nitrogen by 3.4 times. However, the total nitrogen content increased by 35% and potassium by 80%, while phosphorus remained at its previous level (Figure 5).

This serves as an example of the natural environment's capacity for self-restoration of ecological potential under reduced anthropogenic pressure on small river basins. In contrast, 3 km from the source of the Mlynivka River, where it flows directly through the village of Ozeryany, the sediment moisture content increased by 30%, pH rose from 7.4 to 7.7 (pH in salt extract), organic matter content doubled, total nitrogen content increased by 1.2 times, and total phosphorus by 1.9 times-indicating the inflow of biogenic elements from domestic sewage and drainage into the river channel.

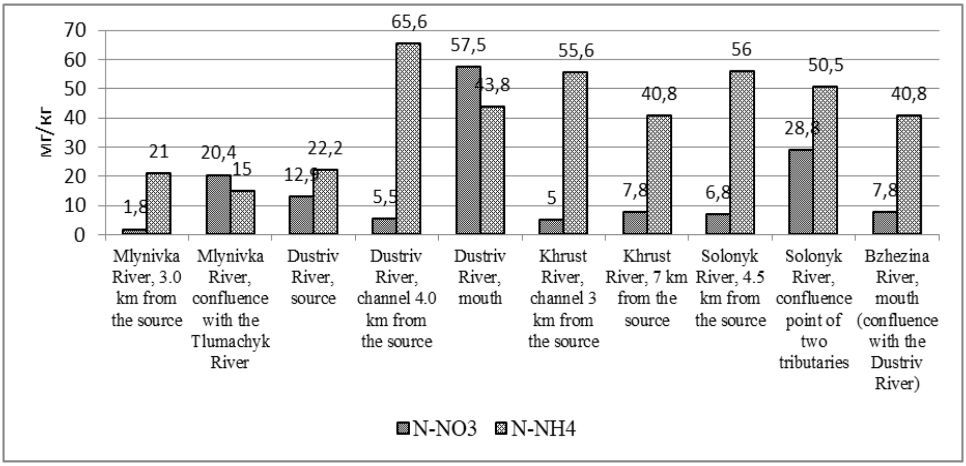

Figure 4. Content of mineral nitrogen forms in the bottom sediments of the Tlumachyk River tributaries

The tributaries Dustriv, Khrust, and Brzezina converge near the town of Tlumach. The Dustriv River originates near the village of Hrynivtsi, flows through the village of Kolintsi, and discharges into the Tlumachyk River. The headwaters of the Dustriv are subject to moderate chemical impact, so the levels of key indicators in the bottom sediments are close to the average for the basin. However, with increasing anthropogenic pressure in the village of Hrynivtsi, key environmental pollution indicators rose noticeably: organic matter content in the sediments increased by 1.5 times compared to the river source, ammonium nitrogen by 3 times, and hydrolyzed nitrogen by 1.6 times.

The nutrient content (NPK) in the sediments increased by factors of 1.0, 2.2, and 1.6 respectively, with phosphorus and potassium concentrations exceeding those in solid manure by 60% and 62%, respectively (Figure 5). With a reduction in chemical pollutant inflow after the village of Hrynivtsi, and just before the confluence with the Tlumachyk River, organic matter content decreased by 2.7 times. However, there was a marked increase in nitrogen-containing compounds: nitrate nitrogen rose by more than an order of magnitude (10.4 times), and hydrolyzed nitrogen by 1.4 times-indicating that the river channel passes through a densely populated urban area.

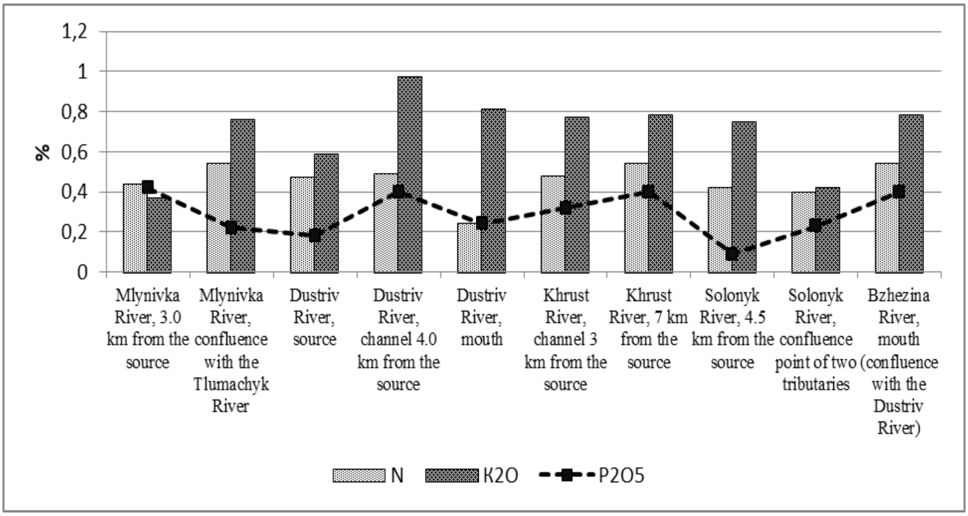

Figure 5. Content of essential nutrients in the bottom sediments of the Tlumachyk River tributaries compared to cattle manure, %.

The small Khrust River originates near the village of Nadorozhna. At 3.0 km from its source, within the village, the organic matter content in the sediment reached up to 2.78%, with nitrogen compounds at 0.48%, phosphorus at 0.32%, and potassium at 0.77%, which in some cases exceeds the NPK content of cattle manure. At 7.0 km from the source, near the village of Kolintsi, with increasing chemical pressure on the environment, the content of nitrate nitrogen increased by 1.6 times, and total phosphorus by 1.2 times. This indicates a progressive chemical load on the Khrust River catchment area, posing a threat to the ecological integrity of its basin.

Analysis of bottom sediments from the mouth of the Brzezina River indicates environmental stress in its basin, evidenced by signs of depletion in the silt fraction. The content of total nitrogen, phosphorus, and potassium in the sediments was 0.54%, 0.4%, and 0.78%, respectively-comparable to values in high-quality manure-suggesting contamination of the environment by wastewater discharges (Figure 5).

The analysis of sediments from the tributaries for micronutrients and heavy metals revealed copper concentrations ranging from 0.46 to 1.01 mg kg^{-1}, with an average of 0.70 mg kg^{-1} (maximum permissible concentration, MPC = 3.0 mg kg^{-1}). Zinc levels ranged from 2.6 to 16.8 mg kg^{-1}, averaging 6.1 mg kg^{-1} (MPC =

23.0 mg kg^{-1}), comparable to concentrations in the Tlumachyk River sediments. No exceedances were detected for nickel, but manganese levels in tributary sediments exceeded the MPC (140.0 mg kg^{-1}) by 40%, reaching up to 353.0 mg kg^{-1}. Iron compound levels ranged from 67.6 to 919.0 mg kg^{-1}, with an average of 496.0 mg kg^{-1}. These elevated values are attributed to lower flow rates and greater sedimentation of silt fractions in the tributary beds, indicating their accumulation in bottom deposits.

The average organic matter content in tributary sediments, as an indicator of pond eutrophication, was 1.6 times higher than in the Tlumachyk River. On average, nitrate nitrogen levels in the bottom sediments of the tributaries were 1.6 times lower than in the Tlumachyk River. However, ammonium compounds increased 1.5 times, and the total content of nitrogen and phosphorus compounds increased by 1.7 and 1.5 times, respectively. This highlights the vulnerability of first- and second-order small river sediments to anthropogenic pressure and their susceptibility to chemical contamination due to technological shortcomings and the lack of centralized wastewater collection and treatment systems.

Ponds are among the most ecologically important freshwater habitats, capable of alleviating anthropogenic pressure and conserving aquatic biodiversity (Hill *et al.,* 2021). They play a crucial role in the structure of surface waters and perform various economic (e.g., fish farming, water recreation, flood protection, reception of drainage from reclamation systems) and eco-landscape functions (e.g., water stabilization, water protection, biostation, aesthetic-landscape roles) (Kovalchuk *et al.,* 2024).

The Mlynivka River originates from a village pond in Ozeryany, which is subject to considerable human use within its catchment area. Taking the pond near the village of Bortnyky as an ecological reference site, the bottom sediments of the Ozeryany pond show signs of deterioration in environmental quality. Specifically, dry matter content in the sediment decreased by 1.2 times, while organic matter content doubled to 3.42% (Table 3). The amount of nitrate nitrogen increased by 2.1 times (Figure 6). Total nitrogen content increased by 1.8 times, phosphorus doubled, and potassium rose by 1.1 times, exceeding their respective contents in cattle manure bedding by 26%, 72%, and 63% (Figure 7).

As the river approaches the settlement areas of Tlumachyk and surrounding villages, the concentration of biogenic elements in the bottom sediments increases. In particular, in the rural pond of the village of Hrynivtsi, located 4 km from the source of the small river Dustriv, a further reduction in dry matter content (54.8%) was recorded in the bottom sediments, along with an increase in alkalinity up to pH_{sol}. 7.7.

This may indicate an intensification of the eutrophication process, evidenced by increased levels-compared to the sediment of the pond in the village of Ozeryany (within the Mlynivka River channel)-of organic matter, mineral nitrogen compounds (NO_3^- and NH_4^+), and total forms of NPK, exceeding the benchmark values found in cattle manure bedding (Figures 6 and 7).

Table 3. Agrochemical characteristics of silt in ponds and lakes of the Tlumachyk River basin

№	Sampling Location	Exchangeable Acidity, pH_{salt}	Organic Matter, Carbon (C), %	Available forms, mg kg^{-1}								
				Cu	Zn	Pb	Ni	Cd	Mn	Fe	Exchangeable Calcium (Ca)	Exchangeable Magnesium (Mg)
4	Source of Brzezina River, pond, Klubivtsi village	5.5	1.52	0.66	1.9	2.8	2.4	0.35	232	1065	11.1	2.3
5	Brzezina River channel, pond, Popeliv village	6.3	0.88	0.83	1.1	3.7	4.7	0.19	1637	889	11.6	2.5
6	Brzezina River, Tlumach Lake, 4.5 km from source, Tlumach town	5.9	1.19	0.59	1.5	3.5	1.7	0.24	117,8	360,6	13.8	3.0
13	Source of Mlynivka River, pond, Ozeryany village	7.6	3.42	0.84	11.7	3.7	2.8	0.24	200	108	50.8	3.2
16	4 km from source of Dustriv River, pond, Hrynivtsi village	7.7	3.49	1.06	15.9	10.0	3.1	0.40	131	136	268	2.9
19	Khrust River, pond, Nadorozhna village	6.2	0.60	1.27	1.5	4.0	1.7	0.33	135	490	8.2	2.3
18	Khrust River, pond 7 km upstream from confluence with Dustriv River, Nadorozhna village	7.2	0.81	0.31	1.6	2.2	1.1	0.27	62,2	225	9.2	2.1
12	Source of Solonyk River, Bortnyky Lake, Bortnyky village	6.6	1.64	0.31	1.3	2.6	0.7	0.68	169	143	13.9	4.4
$\overline{X} \pm S\overline{x}$		*6.6±0.3*	*1.70±0.40*	*0.70±0.12*	*4.6±2.1*	*4.1±0.9*	*2.3±0.4*	*0.30±0.05*	*335±187*	*427±129*	*48.3±31.8*	*2.8±0.3*
V, %		12.1	67.44	46.07	127.5	61.0	56.0	45.73	157	86	185.9	26.1
Least Significant Difference (LSD$_{0.05}$)		*0.9*	*1.35*	*0.40*	*6.9*	*2.9*	*1.5*	*0.18*	*626*	*433*	*106.5*	*0.9*
Maximum Permissible Concentration (MPC)		–	–	***3***	***23***	***6***	***4***	***0.7***	***140***	–	–	–

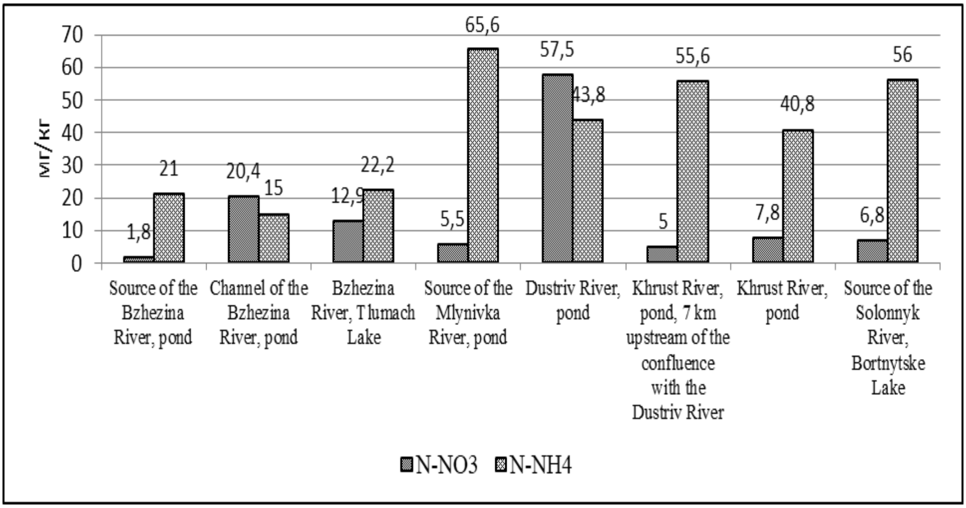

Figure 6. Content of mineral nitrogen forms in bottom sediments of ponds and lakes within the Tlumachyk River basin

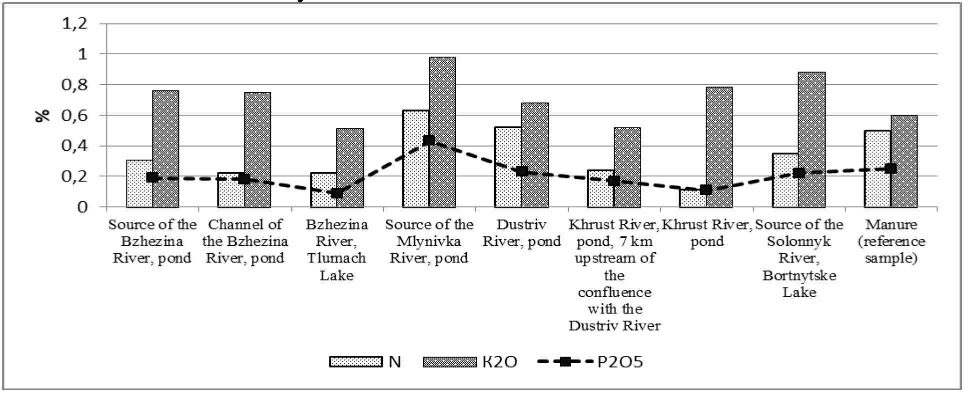

Figure 7. Content of major nutrients in bottom sediments of ponds and lakes within the Tlumachyk River basin compared to manure, %

River-lake systems, as hydrographic units, are subject to complex interactions, particularly in contact zones. One such interaction concerns the role of rivers in distributing microelements entering and exiting the lake system. Research on the flow-through Lake Simsar, located in the valley of the Simsarna River (northeastern Poland), revealed that the river flowing through the lake is a key factor contributing to the input of bioavailable fractions of heavy metals (Zn, Mn, Cd, and Ni) and their accumulation along the river's flow path within the lake. Lakes function as filters and facilitate the self-purification of water passing through them (Kuriata-Potasznik, 2016).

To determine the content of trace and heavy metals and the carbonate composition of sediments, three samples were taken from each of eight ponds. Due to the weak flow conditions, the microelemental and carbonate composition of pond sediments differs from those of flowing surface waters. On average, the accumulation of zinc was 1.3 times lower, lead-1.1 times lower, nickel-1.3 times lower, cadmium-twice as low, and calcium-1.9 times lower compared to the sediments of inflowing ponds.

The basin of the small Khrust River is characterized by forest cover and low settlement density. Therefore, the quality of bottom sediments in the pond near the village of Nadorozhna is marked by a moisture-to-dry matter ratio of 30:70, slightly acidic to neutral water reaction ($pH_{sol.}$ 6.2–7.2), low organic matter content (0.60–0.81%), and low nitrate nitrogen levels (3.0–4.3 mg kg^{-1}). The total NPK content in the forest pond was 0.11%, 0.11%, and 0.78%, respectively; while 7.0 km downstream, at the confluence with the Dustriv River, it increased to 0.24%, 0.17%, and 0.52%. This illustrates how anthropogenic pressure increases nutrient loading in pond ecosystems, including their bottom sediments.

At the source of the Bzhezina River near the village of Klubivtsi, located in a forested area, the sediment shows a moisture-to-dry matter ratio of 35:65, a slightly acidic water reaction ($pH_{sol.}$ 5.5), moderate organic matter content (1.52%), and a high concentration of ammonium nitrogen (131.0 mg kg^{-1}).

The sediment in a private pond in the village of Popeliv is ecologically balanced due to the absence of intensive land use in its catchment. It is characterized by a neutral reaction ($pH_{sol.}$ 6.3), organic matter content of 0.88%, low nitrate nitrogen content (1.2 mg kg^{-1}), and total NPK content of 0.22%, 0.18%, and 0.75%, respectively.

Located 4.5 km from the Bzhezina River's source, within a forested area, the largest water body in the Tlumachyk River basin-Lake Tlumachke-features sediments with moderate concentrations of biogenic elements, yet exhibits signs of intense accumulation of organic matter and nitrogen compounds compared to the ecologically balanced ponds of the Khrust and Solonyk rivers.

Thus, the chemical properties of pond and lake bottom sediments are directly dependent on the anthropogenic pressure on their catchment areas. Indicators of environmental pollution include a decrease in dry matter content, increased alkalinity of the aquatic environment, elevated levels of organic matter and mineral nitrogen, and excess total nitrogen, phosphorus, and potassium content above the average levels found in cattle bedding manure.

The carbonate composition of the bottom sediments in the surveyed ponds within the Tlumachyk River basin was highest in the ponds located along the Mlynivka and Dustriv rivers, which is attributed to the carbonate content of the underlying bedrock-50 and 26.8 mg kg^{-1} of silt, respectively, with an average calcium content across the group of ponds of 48.3 mg kg^{-1}.

The average magnesium content was 2.8 mg kg^{-1}, showing a uniform distribution across the ponds (coefficient of variation $V = 26.0\%$).

It should be noted that the carbonate levels in the ponds are significantly lower compared to the flowing waters of the Tlumach River (79.4 mg kg^{-1} Ca) and its tributaries (94.3 mg kg^{-1} Ca).

The microelement composition of the sediments showed an average copper content of 0.70 mg kg^{-1} (V = 46.1%), with a tendency to increase in ponds located on the Mlynivka River (0.84 mg kg^{-1}), Khrust River (1.27 mg kg^{-1}), and Dustriv River (1.06 mg kg^{-1}).

The average zinc content in bottom sediments was 4.6 mg kg^{-1}, with the highest concentration of 15.9 mg kg^{-1} recorded in the pond near the village of Hrynivtsi on the Dustriv River, indicating an anthropogenic origin of this element. Nickel levels in the sediments demonstrated a relatively uniform distribution, with an average concentration of 2.3 mg kg^{-1}.

Lead content averaged 4.1 mg kg^{-1} (V = 61.0%), with an exceedance of the maximum allowable concentration (MAC) by a factor of 1.7 in the pond near Hrynivtsi village on the Dustriv River. A notable feature of manganese distribution in the sediments is its sensitivity to external anthropogenic influences. While the average manganese content across the pond group was 335.0 mg kg^{-1}, in the pond near the village of Popeliv, the concentration reached 1637 mg kg^{-1}, significantly exceeding the MAC of 140 mg kg^{-1}.

The accumulation of iron in the sediments was fairly intensive and showed a trend of increased concentration in those ponds where magnesium levels were also elevated. The average iron content across the pond group was 427.0 mg kg^{-1}, with a maximum concentration of 1065.0 mg kg^{-1} recorded in a forest pond at the headwaters of the Brzezina River near the village of Klubivtsi. However, iron is not considered a limiting factor in terms of chemical contamination of the sediments.

Cadmium concentrations in the pond sediments were relatively low, with an average of 0.3 mg kg^{-1}, which is 2.3 times below the MAC. Thus, the sediments of the examined ponds and lakes within the Tlumachyk River basin are comparable to standard bedding manure in terms of average total nitrogen, phosphorus, and potassium content.

Considering the levels of major microelements and heavy metals, which generally do not exceed established maximum allowable concentrations, and with proper agrochemical monitoring, the bottom sediments of the ponds and lakes can be used as local fertilizers and for the preparation of soil mixtures.

CONCLUSIONS

1. Agrochemical analysis of the chemical composition of the bottom sediments of the Tlumachyk River, as an indicator of environmental pollution, demonstrates the direct impact of anthropogenic activities, particularly the presence of inadequate wastewater treatment facilities and the lack of centralized sewage systems in certain settlements. It has been established that bottom sediments of small rivers of the first and second orders are highly vulnerable to anthropogenic pressures and are subject to chemical contamination due to technological deficiencies and the absence of centralized sewage gathering and treatment systems. The chemical properties of pond and lake bottom sediments

are directly influenced by the anthropogenic load on their respective catchment areas.

2. The bottom sediments of the Tlumachyk River channel are, on average, characterized by weak alkalinity (pH in 1M KCl = 7.5), a high content of dry matter (64.4%), and a low content of organic matter (1.54%). In the sediments of the river's tributaries, the average organic matter content was 1.6 times higher, and in the sediments of ponds and lakes – 1.1 times higher. The highest organic matter content was observed in the sediments of the tributaries, where it averaged 2.40%, followed by ponds and lakes – 1.70%. The content of mineral nitrogen forms in the bottom sediments of the Tlumachyk River, its tributaries, ponds, and lakes were 50.8, 56.5, and 60.8 mg kg^{-1}, respectively. Unlike in flowing waters, ammonium nitrogen accumulates to a greater extent in the sediments of ponds and lakes, while nitrate nitrogen concentrations decrease-averaging 9.5 mg kg^{-1}, compared to 15.4 mg kg^{-1} in the tributaries and 24.9 mg kg^{-1} in the Tlumachyk River.

3. It should be noted that the carbonate content in ponds is significantly lower compared to the flowing waters of the Tlumach River (79.4 mg kg^{-1} Ca) and its tributaries (94.3 mg kg^{-1} Ca). In the sedimentary muds of ponds and lakes, the accumulation of zinc decreased on average by a factor of 1.3, lead by 1.1, nickel by 1.3, cadmium by 2.0, and calcium by 1.9 times compared to the bottom sediments of tributary waters. Cd and Pb represent the main ecological hazards, as their concentrations occasionally exceed regulatory limits, while manganese requires enhanced control due to above-threshold levels in tributaries. Sediments with Zn, Cu, and Ni within permissible concentrations may be considered suitable for use as organo-mineral fertilizers and soil amendments.

However, bottom sediments enriched in Cd and Pb should be restricted from agricultural application and used only for land reclamation under strict monitoring. In the Tlumachyk River basin, regular monitoring of Cd, Pb, and Mn is recommended, as well as modernization of wastewater treatment facilities to reduce the input of heavy metals into aquatic ecosystems.

4. In the samples of bottom sediments from the Tlumachyk River, its tributaries, ponds, and lakes, the average total nitrogen content ranged between 0.3–0.5%, phosphorus 0.2–0.3%, and potassium 0.7–0.8%, which are comparable to the generally accepted levels in bedding manure. On average, the concentrations of key microelements and heavy metals in the bottom sediments did not exceed the established maximum allowable concentrations, which indicates their potential use as an agronomically valuable resource for soil fertility restoration, local fertilizer production, and soil mixture preparation.

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