Wastewater as a Driver of Heavy Metal Pollution in River Catchments – a study of possible scenarios

Dominika Matuszewska [1, 2, 3,*], Edyta Kiedrzyńska [2, 3, **], Monika Harnisz[4], Marcin Kiedrzyński[5]

[1] Doctoral School of Exact and Natural Sciences, University of Lodz, Jana Matejki 21/23, 90-237 Lodz, Poland

[2] European Regional Centre for Ecohydrology of the Polish Academy of Sciences, Tylna 3, 90-364 Lodz, Poland.

[3] University of Lodz, Faculty of Biology and Environmental Protection, UNESCO Chair on Ecohydrology and Applied Ecology, Banacha 12/16, 90-237 Lodz, Poland

[4] University of Warmia and Mazury in Olsztyn, Faculty of Environmental Sciences, Department of Water Protection Engineering and Environmental Microbiology, Prawocheńskiego 1 Str., 10-720 Olsztyn, Poland

[5] University of Lodz, Faculty of Biology and Environmental Protection, Department of Biogeography, Paleoecology and Nature Conservation, Banacha 1/3, 90-237 Lodz, Poland

**d.matuszewska@erce.unesco.lodz.pl*

***e.kiedrzynska@erce.unesco.lodz.pl*

ORCID number: D.M.:0000-0002-3586-8155; E.K.:0000-0003-0649-4438; M.H.: 0000-0002-2907-4199; M.K.:0000-0002-1751-9357

Abstract

Heavy metal pollution is one of the main problems of the Baltic Sea, caused by the inflow of large loads with river waters. Heavy metals can enter rivers i.a. from point sources such as wastewater treatment plants and industrial plants with inadequately-treated wastewater. The present article examines (i) the impact of WWTPs and industrial facilities on the pollution of the Pilica River, (ii) heavy metal loads along its continuum, and (iii) the identification of common pollution patterns in wastewater and river water, and the effect of their physicochemical properties.

Among WWTPs, the highest heavy metal concentrations are generated by the smallest plants, and the highest loads by the largest ones, which is related to the size of their flow. In addition, industrial plants are significant sources of point pollution of rivers, with arsenic, tin, zinc, cobalt, copper, molybdenum, nickel, lead, chromium, mercury and barium being detected in wastewater. The most common heavy metal in the Pilica was found to be Barium, with the highest loads observed in winter (66.29-216.98 kg/day). In addition to Ba, depending on the season, arsenic, copper and nickel were also detected.

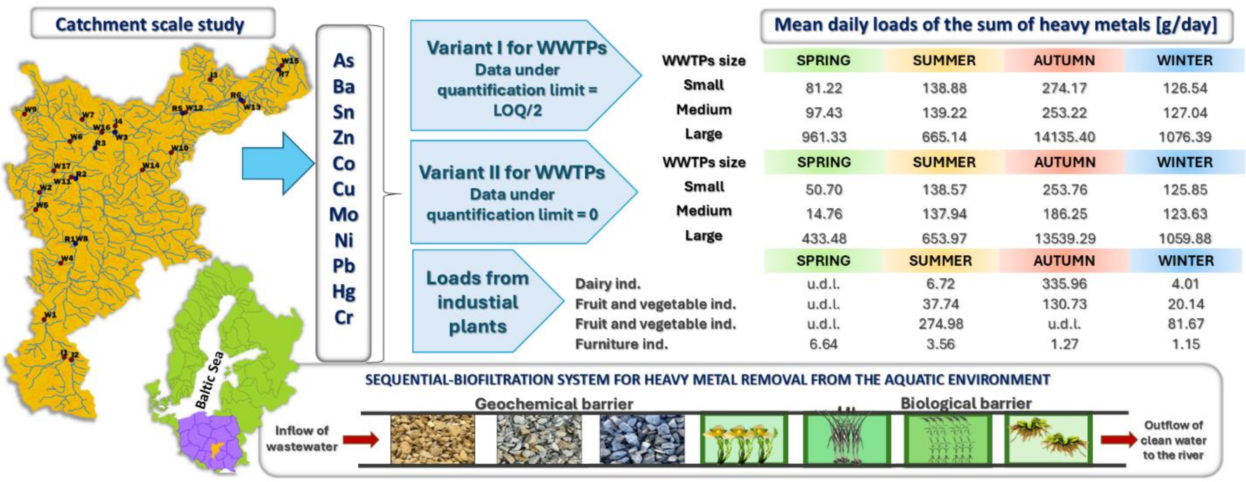
The article takes an innovative approach employing two data calculation variants, which allowed for a comprehensive analysis that captured both typical and less predictable scenarios of river pollution. It also presents an example of modification of the sedimentation-filtration system as a sustainable solution for removing heavy metals from treated wastewater.

Key words: heavy metals, wastewater, wastewater treatment plants, industrial plants, river catchment, ecohydrology

Environmental Implication

Heavy metal loads generated from municipal and industrial wastewater treatment plants located in the Pilica river catchment (seasonally 2022-2023) included As, Ba, Sn, Zn, Co, Cu, Mo, Ni, Pb, Hg and Cr. Among these, As (u.d.l.-1.94 kg/day), Ba (19.98-216.98 kg/day), Cu (u.d.l.-29.18 kg/day) and Ni (u.d.l.-2.29 kg/day) were identified in the Pilica river itself. As even slight elevations in metal levels within ecosystems can have toxic impacts on the food chain and human health, it is essential to quantify the contamination of river systems from point sources and to develop modern, environmentally-friendly solutions for their elimination.

Graphical abstract



Contents

1. Introduction

In 2024, six of the nine planetary boundaries exceeded their safe limits. These included changes in the aquatic environment and the amounts of “Novel Entities”, understood as artificial substances introduced into the environment without prior comprehensive research (Caesar, et al., 2024). Well-known sources of such emissions are sewage treatment plants. It is estimated that in 2022 alone, 268 billion m³ of domestic sewage was generated worldwide, of which only 58% was delivered to treatment plants and treated safely. Of the remainder, a significant portion arose from a lack of sewer connections or septic tanks (45%) or their inadequate emptying (24%);

in addition, approximately a fifth of sewage was subjected only to pre-treatment failing to meet discharge standards (19%) (The United Nations Human Settlements Programme, 2024).

One common group of pollutants is represented by the heavy metals. Their concentration in the environment has increased with urbanization, extraction of fossil fuels, development of motorization and intensification of various industries (Rodríguez Martín et al., 2015). In addition to natural sources of occurrence, such as weathering of rocks or soil erosion, heavy metals are increasingly identified as components of municipal and industrial sewage (Piwowarska et al., 2024).

The heavy metal loads carried with river waters from the area of Poland are received by the Baltic Sea, with a total of 5.7 t of cadmium, 49.7 t of lead and 2.5 t of mercury flowing from the Polish part of the Baltic Sea basin in the years 2012-2021. In 2021 alone, the input was 0.37 t of Cd, 13.4 t of Pb, 0.44 t of Hg; these values constituted 7.1%, 15.7% and 36.7%, respectively, of the total loads of Cd, Pb and Hg flowing into the Baltic Sea from the entire basin in this year. The transport of heavy metal loads to the Baltic Sea mainly takes place via large rivers such as the Vistula (HELCOM, 2021, 2024).

Due to their toxic properties, heavy metals pose a significant threat to both the functioning of ecosystems and human health. Although cadmium, lead, mercury, and arsenic are widespread pollutants with toxic effects, chromium, copper and zinc can also be toxic, despite being necessary for the proper functioning of living organisms in trace amounts; their toxicity is intensified by their high persistence in the environment and a tendency to bioaccumulate (Abd Elnabi et al., 2023; Walker et al., 2019).

Exposure to heavy metals has a range of negative effects, such as oxidative stress, DNA damage, neurological disorders (Jomova et al., 2025) and metabolic disorders, which result in increased mortality. Overexposure can thus disturb population structures and disrupt entire aquatic ecosystems (Mukherjee et al., 2022; Sierra-Marquez et al., 2019; Guo et al., 2018; Pandey & Madhuri, 2014). As these substances pose a serious threat to human and animal health, and freshwater and marine ecosystems, there is a need for interdisciplinary studies aimed at better understanding the sources of heavy metal pollution and the process of their transport, accumulation and blocking in the hard-to-access pool, and their degradation (Morin-Crini et al., 2022).

To fully understand the nature and extent of heavy metal pollution, there is a need for comprehensive analyses of pollutant transport in the catchment area, with a particular emphasis on the impact of municipal and industrial wastewater treatment plants. These analyses should include the identification of problem areas that significantly contribute to the deterioration of water quality in river ecosystems, and determine the effectiveness of existing treatment technologies with regard to emissions of pollutants, including heavy metals. Such catchment approaches to understanding problems occurring in ecosystems represent a key focus of Ecohydrology: a systemic framework for the use of ecosystem processes in Integrated Water Resources Management (IWRM) that acts as a complement to technical hydrological solutions and ecological engineering (Kiedrzyńska et al., 2014). This framework can serve as a foundation for the application of ecohydrological biotechnologies and Nature-Based Solutions for the elimination of pollutants such as heavy metals from aquatic ecosystems (Piwowarska et al., 2024).

The aim of the study was to quantify the scale of pollution with heavy metals from point sources in the Pilica River catchment. To this end, it takes a tripartite approach: i) an analysis of the role of municipal and industrial wastewater treatment plants in the pollution of the Pilica River, ii) an analysis of heavy metal loads carried along the Pilica River continuum from the source section to the mouth, as well as iii) a search for common patterns of pollutant occurrence in the analyzed samples with regard to the physicochemical factors characterizing the studied matrices (river water, wastewater). Moreover, the publication presents an approach for eliminating heavy metals from sewage based on a modified sedimentation-filtration system.

An innovative element of the presented article is its use of two separate data calculation variants. This approach not only yields a more comprehensive data analysis, but also provides a clearer picture of the full spectrum of the potential events and reactions occurring in the environment; it captures both the most probable and less typical variants of river pollution from point sources, in addition to any possible alternatives. The comprehensive nature of the analysis plays an important part in modeling the transport of heavy metals in the catchment. The obtained data can enable accurate prediction of surface water pollution scenarios, and the implementation of appropriate methods for mitigating the release of these pollutants into the environment.

2. Materials and methods

2.1 Characteristics of the case study

The study was conducted in the Pilica River catchment located in central Poland (Fig.1). The Pilica is the largest left-bank tributary of the Vistula River, with a length of 342 km, and a catchment area covering 9258 km^2 (Kiedrzyńska et al., 2014). In the Pilica catchment, 88% of the total sewage outflow is derived from 50 municipal WWTPs (Kiedrzyńska et al., 2014). The dominant type of land cover in the catchment is arable land, constituting over 60%, followed by forests (31%), and then a mixture of urban, industrial, and other types of land use (9%) (Harnisz et al., 2020). Importantly, out of 70 surface water bodies in the Pilica catchment, analyzed in terms of the implementation of the Water Framework Directive, 12 were classified as parts strongly modified by humans (Izydorczyk et al., 2019). This indicates strong anthropogenic pressure on the catchment.

The Pilica River begins near the town of Pilica, at an altitude of about 350 m above sea level, and flows into the Vistula at 457 km of its course. Due to the fact that the Pilica catchment area has a heterogeneous morphological structure and terrain, runoff from the catchment area is also diversified and ranges from 3 to 6 L/s/km^2 (Urbaniak et al., 2014). The river flows though twelve cities: Szczekociny, Koniecpol, Przedbórz, Sulejów, Tomaszów Mazowiecki, Piotrków Trybunalski, Spała, Inowłódz, Nowe Miasto, Wyśmierzyce, Białobrzegi and Warka. Of these, Tomaszów Mazowiecki has a developed textile, ceramic, machine, metal and leather industry and Warka a developed brewing and fruit and vegetable industry (Urbaniak et al., 2014). There are 143 municipal wastewater treatment plants in the catchment area. It is estimated that on average, 59% of the population in the entire catchment area is connected to a sewage treatment plant, however, this value varies from 51.3 to 70.5% depending on the region (Kiedrzyńska et al., 2014). Due to the numerous industrial plants in the catchment area, the river also receives a high level of polluted from many anthropogenic sources (Szklarek et al., 2021; Kiedrzyńska et al., 2014). Domestic sewage constitutes 4% of the total sewage discharge, and industrial sewage 8%. It is estimated that the mean discharge of treated sewage in the Pilica River catchment from all 143 treatment plants is 18,341,875 m^3/year (Kiedrzyńska et al., 2014).

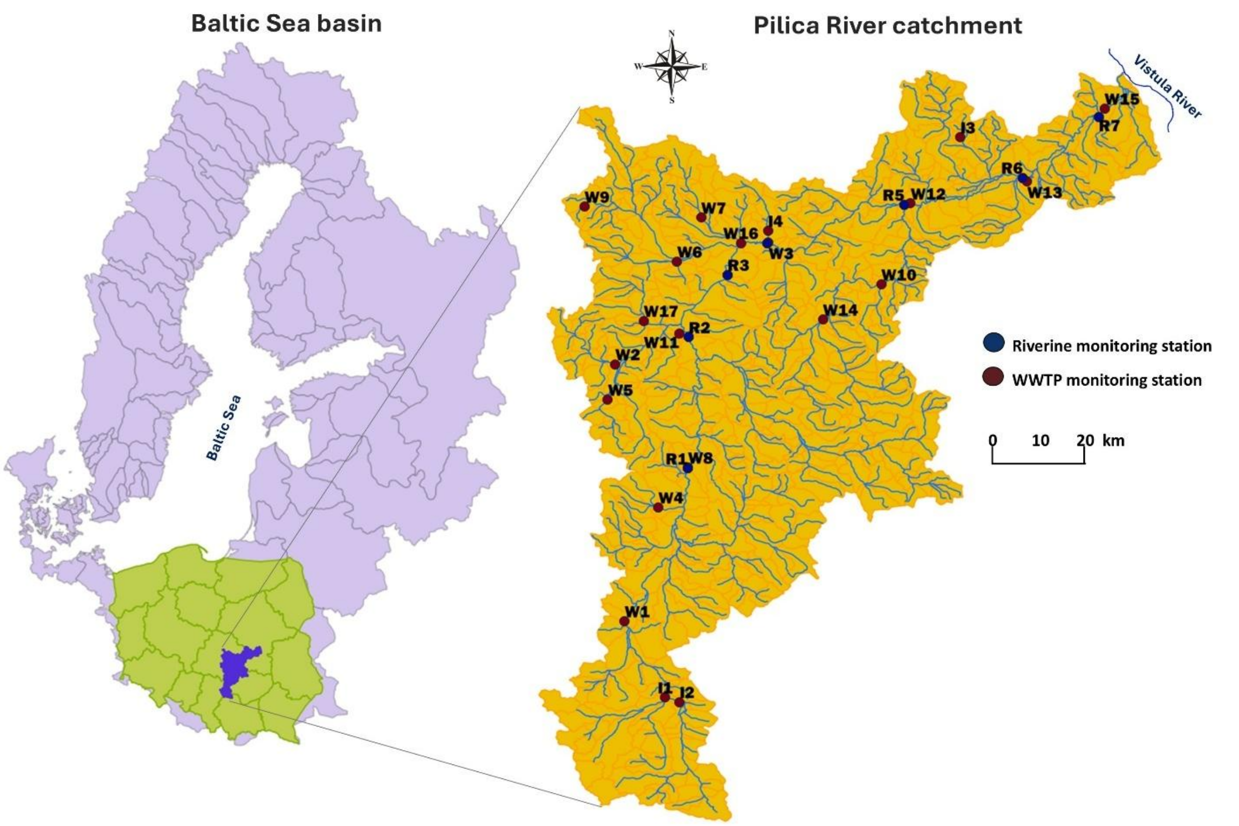


Fig.1 Location of the Pilica River catchment (Poland) and location of WWTP monitoring stations (W1–W17), industrial plants (I1-I4) and riverine monitoring stations (R1–R7) along the Pilica River continuum.

2.2. Sampling of wastewater and riverine water

Samples of treated sewage were taken directly from the outlets of 17 municipal sewage treatment plants of different sizes located in the Pilica River catchment area. These WWTPs were selected due to their dispersion throughout the entire river basin. The treatment plants (WWTPs) were divided into three size categories based on population equivalent (PE): small WWTPs (class I, <2,000 PE), medium WWTPs (class II, 2,000-9,999 PE) and large WWTPs (class IV, 15,000-99,999 PE) (W1-W17) (Tab.1). Samples of treated wastewater were collected at the outflow from the WWTP. Additionally, samples of treated sewage were also collected directly from the outlets of four industrial plants (I1- I4). These plants represented the dairy industry (I1), the fruit and vegetable industry (I2, I3) and the furniture industry (I4) (Tab.1).

Water samples were also collected from seven points along the Pilica River continuum. Samples were collected from bridges (sites R1, R2, R4, R5, R6, R7) and from a site located just below the

Sulejów Reservoir dam (R3) (Tab.1). The R1-R6 river monitoring sites (except R7) were located at the water gauge posts belonging to the Polish Institute of Meteorology and Water Management. Sampling points were located throughout the catchment area. Sampling was carried out seasonally – spring (09-10.05.2022), summer (18-19.07.2022), autumn (05-06.12.2022), winter (27-28.02.2023), in the years 2022-2023. This gave a total of 68 samples of treated wastewater from municipal treatment plants, 16 samples of treated wastewater from industrial plants and 28 samples of river water from Pilica. All samples were subjected to physicochemical analyses and the concentration of heavy metals was determined.

Tab.1 Characteristics of the monitored municipal and industrial WWTPs in the Pilica River catchment. The letter designations mean respectively: W – municipal wastewater treatment plants; I – industrial plants; R – points located along the Pilica River continuum).

Municipal WWTPs monitoring stations				
	Location of WWTPs	WWTPs size class	Population equivalent of WWTPs	Average flow [m³/s for river and m³/day for WWTPs]
W1	Koniecpol	I	600	447.3
W2	Rozprza	I	500	101.0
W3	Spała	I	350	103.5
W4	Wielgomłyny	I	1000	67.0
W5	Gorzkowice	I	700	425.9
W6	Wolbórz	I	800	399.0
W7	Ujazd	I	1500	628.3
W8	Przedbórz	II	2000	839.5
W9	Tuszyn	II	4000	788.0
W10	Drzewica	II	6000	828.3
W11	Sulejów	II	7500	1613.8
W12	Nowe Miasto nad Pilicą	II	2583	217.3
W13	Białobrzegi	IV	58,400	2148.5
W14	Opoczno	IV	75,000	4405.3
W15	Warka	IV	99,000	4187.5
W16	Tomaszów Mazowiecki	IV	80,000	9736.0
W17	Piotrków Trybunalski	IV	80,000	10243.0
Industrial plants monitoring stations				
	Location of industrial plant	Type of industry		Average flow [m³/s for river and m³/day for WWTPs]

I2	Szczekociny	dairy industry		146.75
I1	Szczekociny	fruit and vegetable industry		589.25
I3	Kozietuły Nowe	fruit and vegetable industry		1533.53
I4	Inowłódz	furniture industry		32.5
		Riverine monitoring stations		
Station	Town name of a station	Station type in the river continuum	Km of the river (from the estuary)	Average flow [m^3/s for river and m^3/day for WWTPs]
R1	Przedbórz	River	201.2	15.02
R2	Sulejów	River (inflow to Sulejów Reservoir)	161.3	21.48
R3	Smardzewice	Sulejów Reservoir (outflow)	136.3	26.58
R4	Spała	River	119.4	31.35
R5	Nowe Miasto	River	78.8	34.65
R6	Białobrzegi	River	45.3	42.05
R7	Warka	River	17.0	no data

2.3 Physical and chemical analysis

The obtained samples were first subjected to *in situ* physical analysis comprising water temperature, pH, conductivity (SPC), total dissolved solids (TDS), salinity, oxygenation, and redox potential (ORP) using a YSI-6050000 Professional Plus multiparameter meter. They were then transported to the laboratory and kept at 5°C for further analysis. In the laboratory, the samples were filtered through GF/F filters and analyzed using an ion chromatography system (DIONEX, ICS 1000) to quantify their ion content: the analysis included fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulphate anions (SO_4^{2-}), and lithium (Li^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium cations (Ca^{2+}).

The total suspended solids (TSS) value was determined for each sample by filtering a known volume of water (V) through a Whatman GF/F filter of known mass. The filter was then dried at 105 °C for about 1.5 hours and weighed on a Mettler electronic balance. Unfiltered river water and treated wastewater samples were analyzed for total phosphorus (TP) by the ascorbic acid method using the oxidative decomposition reagent Oxisolv (Merck) in a MV500 microwave system (Merck) (Kiedrzyńska et al., 2014). Total nitrogen (TN) analyses were performed using commercially-available tests with a measuring range of 0-25 mg/L (method 10071,TNT) (Hach). Chemical oxygen demand (COD) in the samples was determined using an AQUALYTIC® COD VARIO photometer using commercially-available cuvette tests with a measuring range of 0-1500 mg/L (Tintometer GmbH). The tubes with added samples were mineralized in the AL125 thermoreactor and then analyzed according to the manufacturer's instructions.

The respirometric method was used to determine the biochemical oxygen demand (BOD_5) in treated wastewater and river water. The bottles with the analyzed samples were incubated for five days using the Lovibond BD 600 measuring system (Tintometer group). The bottles with the samples were hermetically sealed with heads with sensors, and the BOD_5 result was calculated automatically by the system based on the monitored pressure changes. The samples were incubated in the dark in a Pol-ST3 Basic (POL-EKO) thermostatic cabinet at a temperature of 21 °C.

2.4 Analysis of heavy metals

The samples were tested for the presence and quantity of 11 heavy metals: arsenic (As), barium (Ba), tin (Sn), zinc (Zn), cobalt (Co), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), chromium (Cr) and mercury (Hg). However, as the levels of mercury were below the detection limit in many samples, it was not included in each analyses. The concentrations were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) by an accredited analytical laboratorium, in accordance with the PN-EN ISO 17294-2:2016-11 standard.

To objectively estimate the impact of the wastewater treatment plant on heavy metal supply and reduction in water quality of the Pilica River, two scenarios (versions) were assumed for the analysis:

(I) Variant 1 – the analysis included data below the detection limit, in accordance with Article 5 of COMMISSION DIRECTIVE 2009/90/EC of 31 July 2009 establishing, under Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for the analysis and monitoring of chemical water – LOQ/2.

(II) Variant 2 - data below the quantification limit was replaced with the value "0" (Cantoni et al., 2020).

Heavy metal loads were calculated based on the outflow of sewage from WWTPs (m^3/day) and river flows (m^3/s) at particular river gauge stations. However, no load or flow data were calculated at point R7 as no water gauge was present.

2.5 Statistical analysis

The data points were independent from each other, and the Shapiro–Wilk test confirmed them to have non-normal distributions. Correlations between heavy metal concentrations (As, Ba, Sn, Zn, Co, Cu, Mo, Ni, Pb, Hg, Cr) and other physico-chemical factors were assessed using Spearman's correlation. Principal Component Analysis (PCA) was used to investigate relationships between group of samples and physico-chemical factors. PCA and biplot visualizations were conducted using PAST 4.03. Before the correlations and PCA analysis, the data were first normalized. A chart illustrating the characteristics of heavy metal concentrations entering the Pilica River from various sources was created using Statistica ver. 13.3 (StatSoft Poland).

3 Results

3.1. Concentrations of heavy metals in wastewater and river

The median concentration values of all heavy metals identified in the analyzed samples differ depending on the adopted variant (Fig. 2A-F). In Variant 1, the highest median values of As, Sn, Mo and Pb were noted in small wastewater treatment plants (WWTPs), and the highest Cr values in small and large WWTPs (Fig. 2A); values for these metals were significantly lower in Variant 2 (Fig. 2B). In both variants, the highest median Ba values were observed in medium-sized WWTPs (Fig. 2C,D), and the highest Zn in small WWTPs (Fig. 2E,F). Among the remaining heavy metals detected in municipal wastewater, the median values were slightly lower in Variant 2 or did not differ from Variant 1. In Variant 1, industrial wastewater had similar ranges of heavy metal concentrations to wastewater from large municipal WWTPs (except for Sn and Cr), with the lowest median values being observed in river samples (except for Ba; Fig.2 A, C, E). In Variant 2, the median values for industrial wastewater and river water were lower than the medians for Variant 1 or close to these values (Fig.2B,D,F).

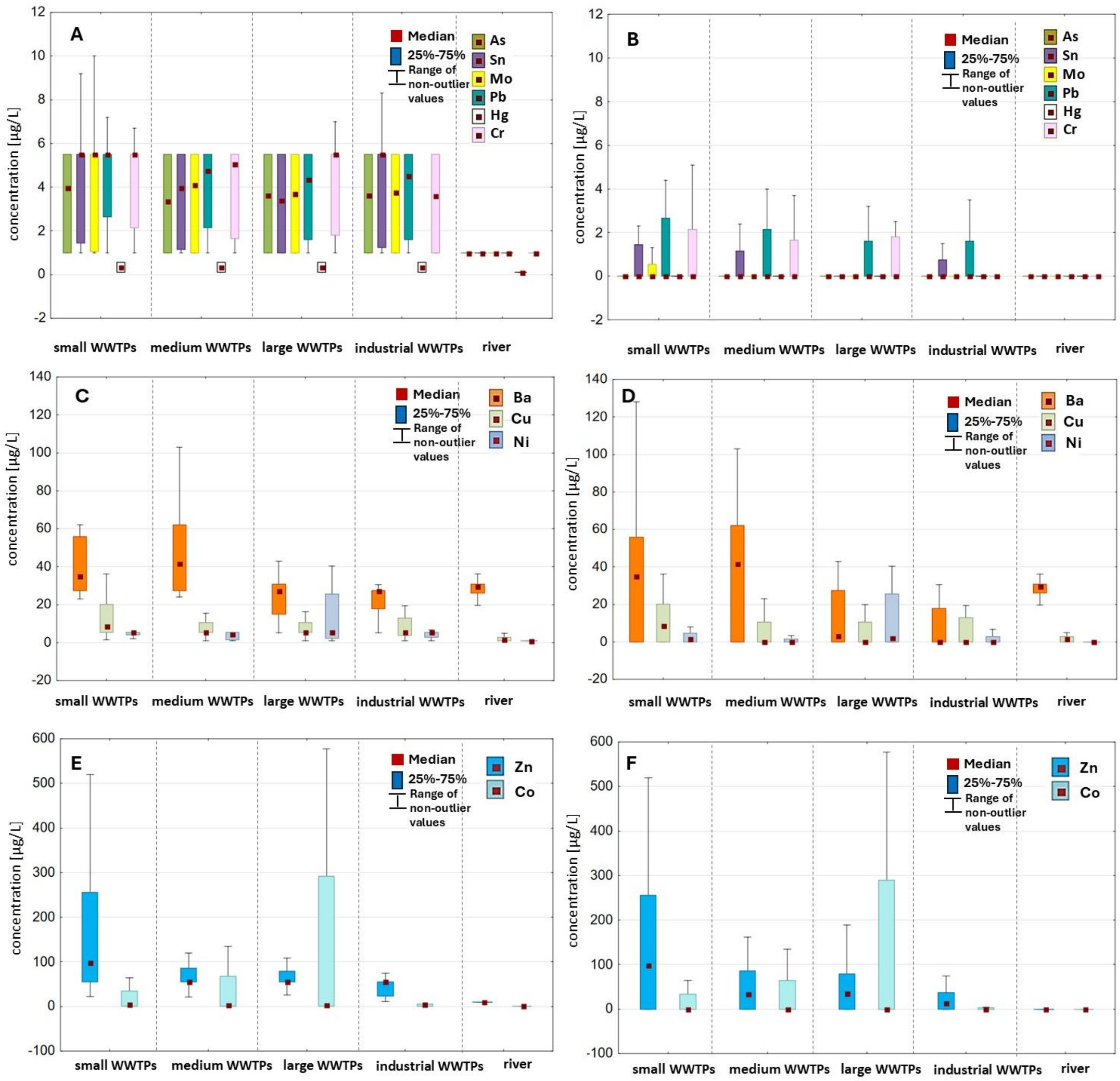


Fig.2 Median heavy metal (A-F) concentrations identified in the treated municipal wastewater (small, medium-size, large WWTPs) throughout the sampling period (May 2022-Feb.2023) compared to industrial wastewater and riverine water. Charts for Variant 1 – A, C, E; charts for Variant 2 – B, D, F.

3.1.1. Municipal wastewater – analysis of pollutant co-occurrence patterns

Spatial and temporal patterns of pollutant concentration were presented using PCA ordination, which was based on normalized data for heavy metal concentrations analyzed during seasonal sampling. In both variants, sewage treatment plants were arranged along the first axis (PC1), explaining 48.42% of variability in Variant 1 (Fig.3A) and 54.67% in Variant 2 (Fig.3B).

In Variant 1, samples collected in spring and autumn, regardless of the class of the treatment plant, were associated with high loads of Cr, Pb, Sn, Mo, Co, Hg and As. Only two samples from summer and winter, belonging to class I (small) WWTPs, are associated with high concentrations of Ba, Cu, Zn, Ni. The remaining samples of treated wastewater from winter and summer are located on the opposite side of the PC1 axis (Fig.3A).

In Variant 2, all samples from summer, and individual samples from winter, indicate high concentrations of Mo, Cu, Pb, Sn, Cr, and Ba. In contract small numbers of samples of treated wastewater from summer (one sample - class I WWTPs), winter (one sample - class IV WWTPs) and spring (one sample - class I WWTPs) were associated with Ni, Zn, Hg and As. The positions of samples from spring, autumn and winter in the PCA ordination space are driven by high Co loads with a stronger correlation with the second axis (PC2; Fig.3B).

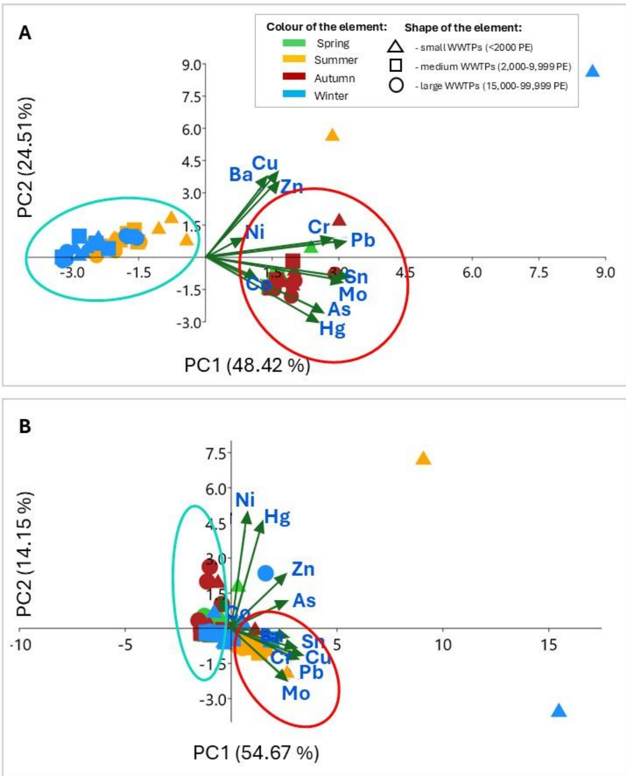


Fig.3 PCA analysis of samples of municipal wastewater collected according to season, based on normalized heavy metal data. (A) Variant 1 – data below LOQ included in analyses as LOQ/2 (B) Variant 2 - data below LOQ included in analyses as “0”; triangle – class I WWTPs, square – class II WWTPs, dot – class IV WWTPs, green elements – spring, yellow elements – summer, red elements – autumn, , blue elements – winter. Ellipses were drawn manually to illustrate groupings and do not represent statistical confidence intervals.

The physicochemical factors influencing the concentrations of the analyzed heavy metals were determined based on Spearman's correlation analysis. It was found that in the case of Variant 1 (Fig.4A), the presence of certain ions (Li^{+}, F^{-}, Cl^{-}, PO_4^{3-} and SO_4^{2-}) significantly influenced the concentration of the analyzed heavy metals in municipal sewage. For many heavy metals (As, Ba, Sn, Cu, Mo, Ni, Pb), strong correlations were also demonstrated with the presence of TSS. Inverse correlations were demonstrated between redox (ORP) values and the concentrations of As, Sn, Cu, Pb, Cr (Fig.4A).

In Variant 2, only some correlations overlap with Variant 1; Ba level demonstrated positive correlations with ORP, turbidity, TN, TP and BOD_5; Zn level positively correlated with TP, K^{+}, NO_3^{-} and PO_4^{3-} content; Co negatively correlated with pH. A significant number of analyzed metals (Sn, Cu, Mo, Ni, Pb, Cr) demonstrated a positive correlation with temperature and COD. In addition, Variant 2 exhibited more negative correlations of metals with physicochemical factors than in Variant 1 (Fig.4B).

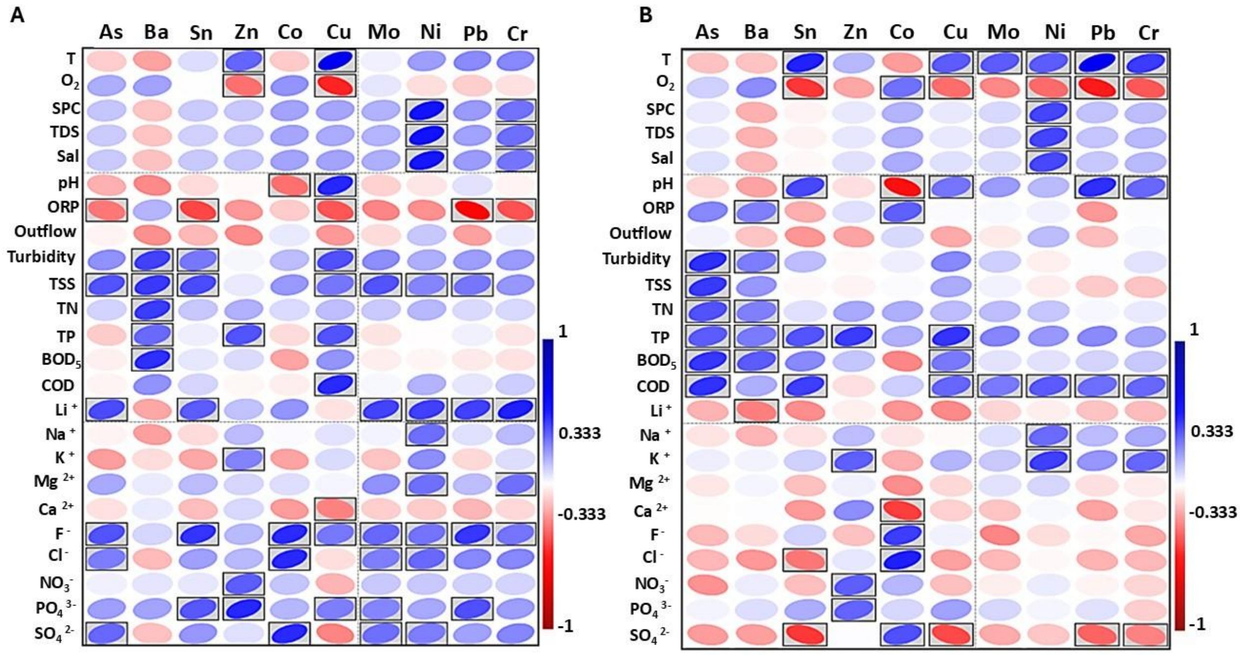


Fig.4 Spearman's correlation matrix between heavy metal concentrations in treated sewage from municipal wastewater treatment plants and physico-chemical parameters. Statistically significant values ($p>0.05$) are marked in frames. (A) Variant 1, (B) Variant 2

3.1.2. Industrial wastewater – analysis of pollutant co-occurrence patterns

The heavy metal concentrations of the outflow from industrial plants were also subjected to PCA analysis. In Variant 1, the analyzed samples arranged along PC 1 (55.09%) indicate high loads of Co, Ni, Mo, Cr, Hg and As in industrial wastewater from spring and autumn. In particular, arrowheads of Pb, Sn, Zn, Ba and Cu, indicating increasing concentrations, are directed towards spring wastewater associated with the furniture industry (plant I4). Samples collected in summer and winter are arranged on the opposite side of the PC 1 axis (Fig.5A).

In Variant 2, the samples exhibit a different orientation with respect to PCA ordination space. The PC 1 axis explains 41.76% of the variance. The arrows of Ba, Ni, As, Sn, and Cr, indicating increased concentrations, are directed towards samples collected in summer from plant I3 dealing with the fruit and vegetable industry. For Pb, Zn, Cu and Mo, the arrowheads are directed towards the remaining samples collected in summer, and the sample collected in spring from the furniture industry (I4). The remaining samples from autumn and winter are located on the opposite side of the PC 1 axis (Fig. 5B).

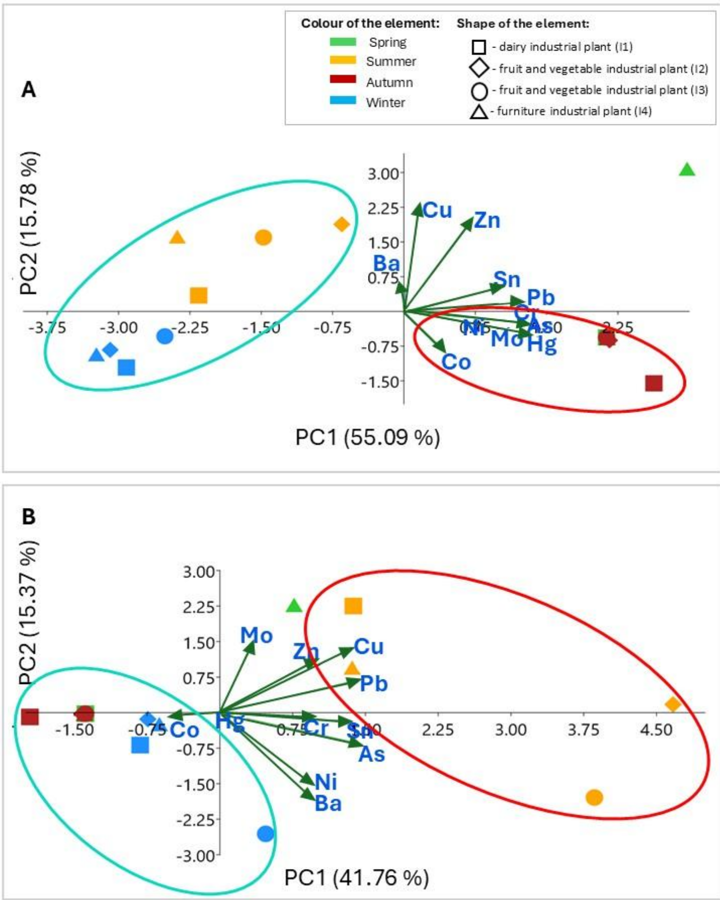


Fig.5 PCA analysis of industrial wastewater samples with regard to season of collection, based on normalized physico-chemical data. (A) Variant 1 – data below LOQ included in analyses as LOQ/2 (B) Variant 2 - data below LOQ included in analyses as “0”; square – dairy industrial plant I1, diamond – fruit and vegetable industrial plant I2, dot – fruit and vegetable industrial plant I3, triangle – furniture industrial plant I4, green elements – spring, yellow elements – summer, red elements – autumn, blue elements – winter. Ellipses were drawn manually to illustrate groupings and do not represent statistical confidence intervals.

The treated wastewater from industrial plants was also subjected to Spearman’s correlation analysis. In Variant 1 (Fig. 6A), a significant positive correlation was observed between TSS and Ba level, and between F^- anions and Mo and Co level. Negative correlations were also found between the redox potential and the concentrations of Zn, Cu, total phosphorus and Mo, and between Ca^{2+} ion content and the concentrations of Co, Mo and Pb (Fig.6A).

Variant 2 presents more statistically significant correlations, both positive and negative. TP concentrations were positively correlated with As, Ba, Sn and Cr level; TN correlated with As, Ba and Zn level; Ca^{2+} ion content correlated with Zn and Ni level; NO_3^- and PO_4^{3-} correlated with As and Cr level; pH with Sn level, and temperature with Cr level. In contrast, oxygen content correlated negatively with Pb and Cr level; pH with Co level; redox state with Cu level; TSS with Co level; BOD_5 with Cr level; Li^+ and F^- content with Ba level, and NO_3^- content with Co level (Fig.6B).

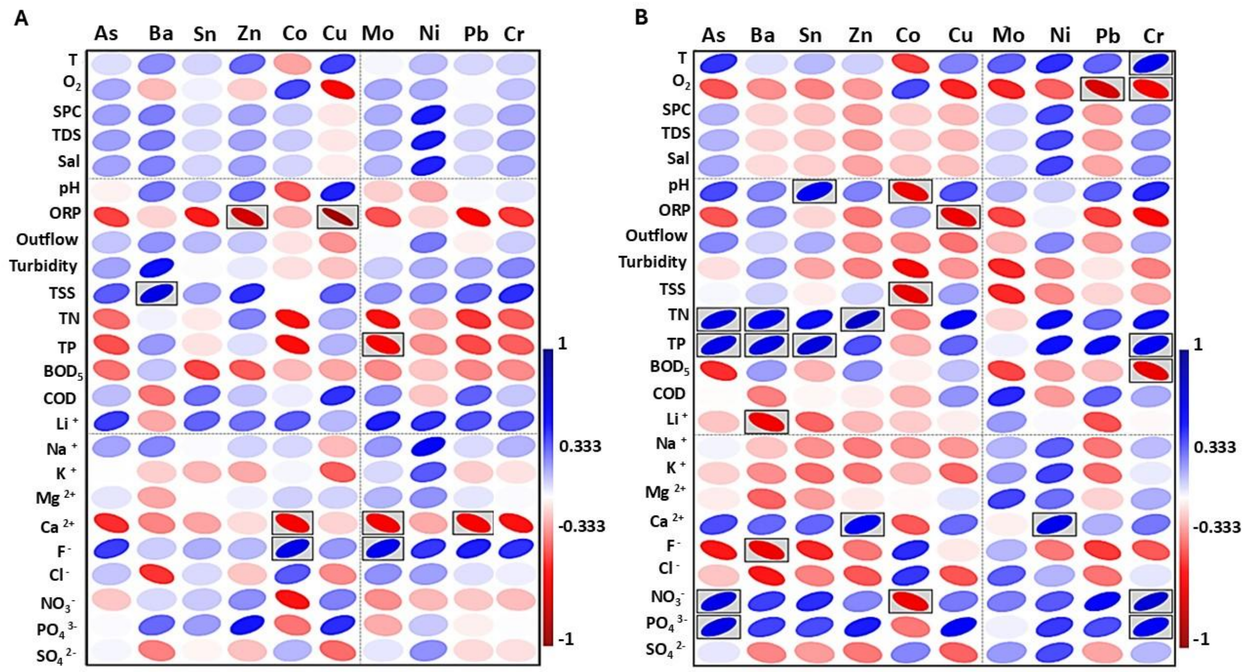


Fig.6 Spearman's correlation matrix between heavy metal concentrations and physico-chemical parameters of treated sewage from industrial wastewater treatment plants. Statistically significant values ($p>0.05$) are marked in frames. (A) Variant 1, (B) Variant 2

3.1.3. River Water – analysis of pollutant co-occurrence patterns

The heavy metal concentrations identified in river water for each season were also subjected to PCA analysis. The first PCA axis explained 51.83% of the variance in Variant 1 (Fig.7A) and 56.93% in Variant 2 (Fig.7B); the second axis explained 34.45% (Variant 1) and 28.95% (Variant 2). The vectors representing Cu are directed towards winter samples, and those representing Ba and As towards summer samples. Samples from the spring and autumn seasons lie on the opposite side of the PC1 axis (Fig.7A, B).

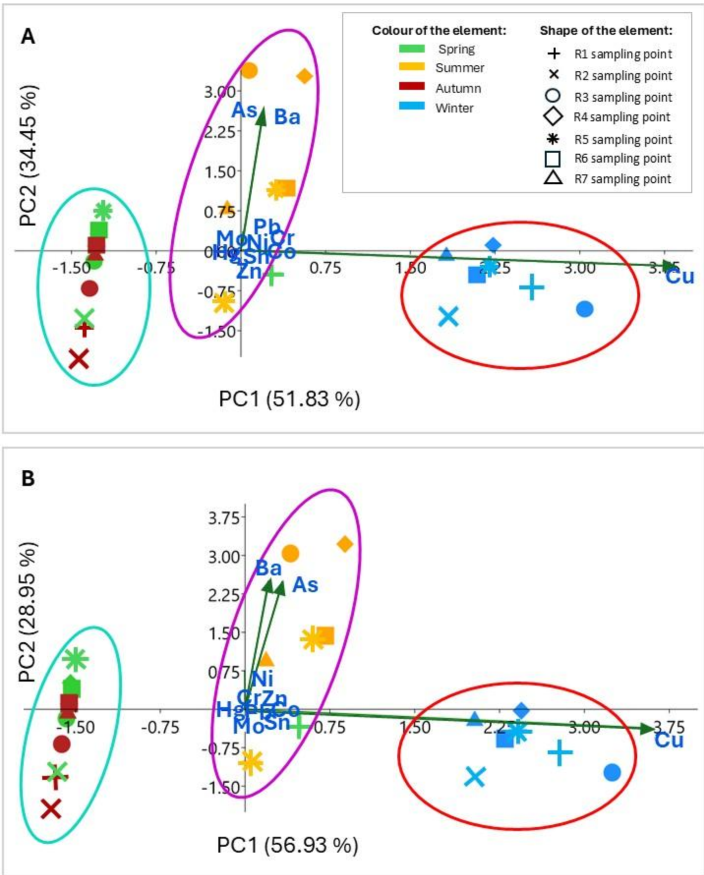


Fig.7 PCA analysis of river water samples according to season of collection based on normalized physico-chemical data. (A) Variant 1 – data below LOQ included in analyses as LOQ/2 (B) Variant 2 - data below LOQ included in analyses as "0"; plus – R1 sampling point, cross – R2, dot – R3, diamond – R4, star – R5, square – R6, triangle – R7, green elements – spring, yellow elements – summer, red elements – autumn, blue elements – winter. Ellipses were drawn manually to illustrate groupings and do not represent statistical confidence intervals.

For both variants, the Spearman's correlation analysis revealed the following correlations in river water: As level with temperature, O_2, pH, flows, TN, BOD_5, Ca^{2+}, NO_3^- and SO_4^{2-} level; Ba level with Na^+, Mg^{2+} ion level; Cu level with SPC, salinity, ORP, TSS, BOD_5, Li^+, Mg^{2+}, F^-, Cl^- and SO_4^{2-} level; Ni level with temperature. In Variant 2, Ni level was negatively correlated with redox potential and TN concentration (Fig.8A, B).

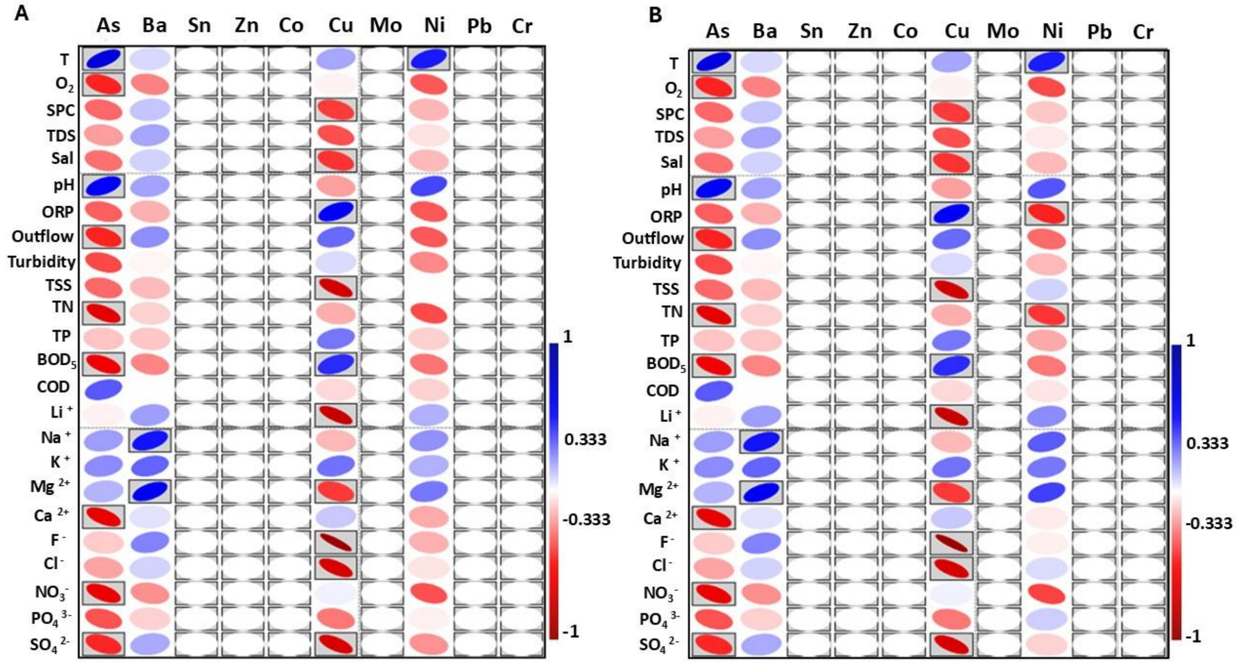


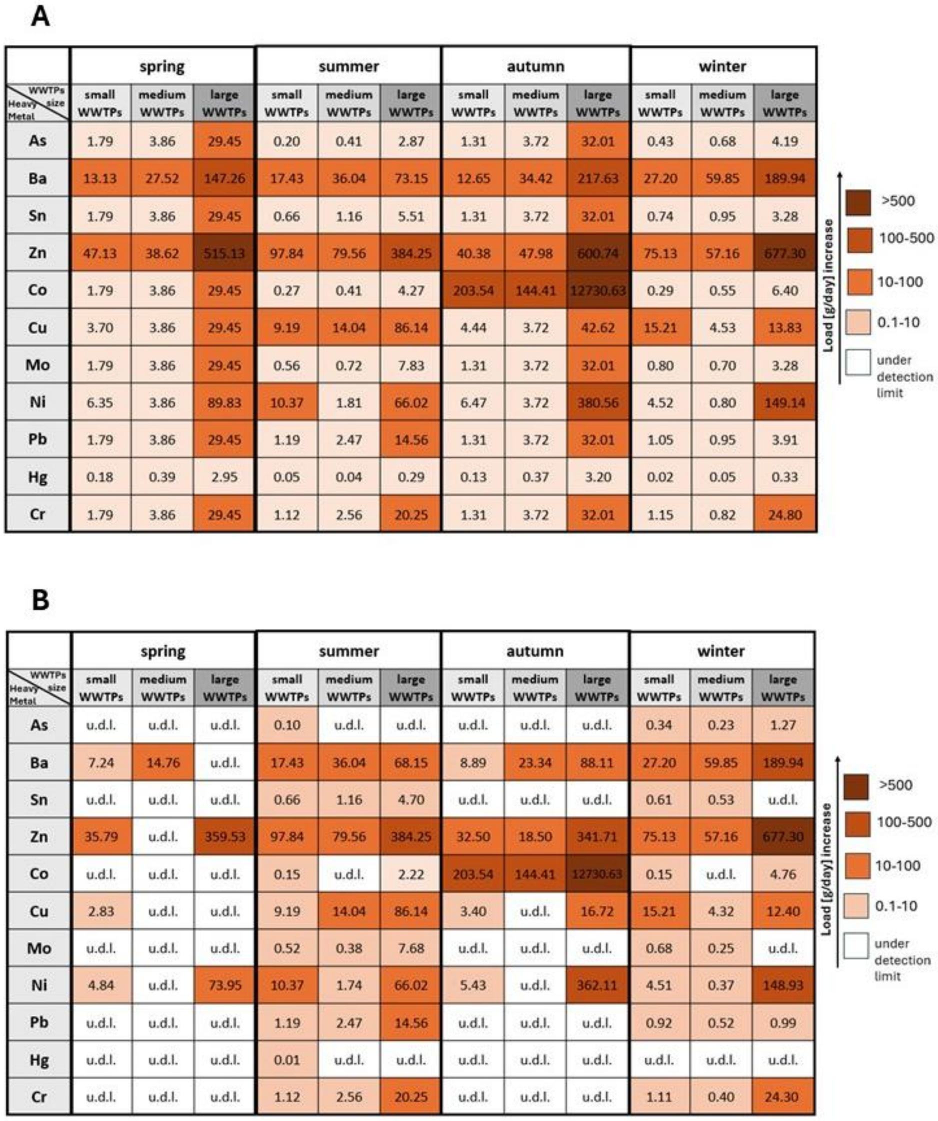
Fig.8 Spearman's correlation matrix between heavy metal concentrations in riverine water and physico-chemical parameters measured for the collected samples. Statistically significant values ($p>0.05$) were marked in frames. (A) Variant 1, (B) Variant 2

3.2. Export of heavy metal loads with wastewater effluents

3.2.1. Heavy metal loads entering the river from municipal wastewater treatment plants

Regarding the heavy metals entering the Pilica River with municipal sewage, the highest mean daily loads (g/day) were generated from large (class IV) wastewater treatment plants, for both Variant 1 (Fig.9A) and 2 (Fig.9B). This could be attributed to the high daily sewage outflows from this class of WWTPs: the mean flows in the analyzed class IV WWTPs were 5890.5 m^3/day in spring, 5730.9 m^3/day in summer, 6401.0 m^3/day in autumn, and 6553.9 m^3/day in winter. In contrast, the average flows were 357.7 m^3/day (spring), 277.2 m^3/day (summer), 262.7 m^3/day (autumn), 343.4 m^3/day (winter) in class I WWTPs, and 772.4 m^3/day in spring, 819.0 m^3/day in summer, 743.8 m^3/day in autumn, and 1094.2 m^3/day in winter in class II WWTPs.

The highest average daily load was observed for cobalt (12730.63 g/day), and occurred in autumn in class IV WWTPs; however, the data from autumn and spring also demonstrated the highest number of values below the detection limit (Fig.9B). Significant differences in average load were noted between variants 1 and 2, especially in the case of class IV (large) WWTPs (Table 2).



A

Heavy Metal \ WWTPs size	spring			summer			autumn			winter		
	small WWTPs	medium WWTPs	large WWTPs	small WWTPs	medium WWTPs	large WWTPs	small WWTPs	medium WWTPs	large WWTPs	small WWTPs	medium WWTPs	large WWTPs
As	1.79	3.86	29.45	0.20	0.41	2.87	1.31	3.72	32.01	0.43	0.68	4.19
Ba	13.13	27.52	147.26	17.43	36.04	73.15	12.65	34.42	217.63	27.20	59.85	189.94
Sn	1.79	3.86	29.45	0.66	1.16	5.51	1.31	3.72	32.01	0.74	0.95	3.28
Zn	47.13	38.62	515.13	97.84	79.56	384.25	40.38	47.98	600.74	75.13	57.16	677.30
Co	1.79	3.86	29.45	0.27	0.41	4.27	203.54	144.41	12730.63	0.29	0.55	6.40
Cu	3.70	3.86	29.45	9.19	14.04	86.14	4.44	3.72	42.62	15.21	4.53	13.83
Mo	1.79	3.86	29.45	0.56	0.72	7.83	1.31	3.72	32.01	0.80	0.70	3.28
Ni	6.35	3.86	89.83	10.37	1.81	66.02	6.47	3.72	380.56	4.52	0.80	149.14
Pb	1.79	3.86	29.45	1.19	2.47	14.56	1.31	3.72	32.01	1.05	0.95	3.91
Hg	0.18	0.39	2.95	0.05	0.04	0.29	0.13	0.37	3.20	0.02	0.05	0.33
Cr	1.79	3.86	29.45	1.12	2.56	20.25	1.31	3.72	32.01	1.15	0.82	24.80

B

Heavy Metal \ WWTPs size	spring			summer			autumn			winter		
	small WWTPs	medium WWTPs	large WWTPs	small WWTPs	medium WWTPs	large WWTPs	small WWTPs	medium WWTPs	large WWTPs	small WWTPs	medium WWTPs	large WWTPs
As	u.d.l.	u.d.l.	u.d.l.	0.10	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.34	0.23	1.27
Ba	7.24	14.76	u.d.l.	17.43	36.04	68.15	8.89	23.34	88.11	27.20	59.85	189.94
Sn	u.d.l.	u.d.l.	u.d.l.	0.66	1.16	4.70	u.d.l.	u.d.l.	u.d.l.	0.61	0.53	u.d.l.
Zn	35.79	u.d.l.	359.53	97.84	79.56	384.25	32.50	18.50	341.71	75.13	57.16	677.30
Co	u.d.l.	u.d.l.	u.d.l.	0.15	u.d.l.	2.22	203.54	144.41	12730.63	0.15	u.d.l.	4.76
Cu	2.83	u.d.l.	u.d.l.	9.19	14.04	86.14	3.40	u.d.l.	16.72	15.21	4.32	12.40
Mo	u.d.l.	u.d.l.	u.d.l.	0.52	0.38	7.68	u.d.l.	u.d.l.	u.d.l.	0.68	0.25	u.d.l.
Ni	4.84	u.d.l.	73.95	10.37	1.74	66.02	5.43	u.d.l.	362.11	4.51	0.37	148.93
Pb	u.d.l.	u.d.l.	u.d.l.	1.19	2.47	14.56	u.d.l.	u.d.l.	u.d.l.	0.92	0.52	0.99
Hg	u.d.l.	u.d.l.	u.d.l.	0.01	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
Cr	u.d.l.	u.d.l.	u.d.l.	1.12	2.56	20.25	u.d.l.	u.d.l.	u.d.l.	1.11	0.40	24.30

Fig.9 Mean seasonal loads of heavy metals [g/day] entering the Pilica River from WWTPs during the period 2022-2023.

Tab.2 Mean heavy metal loads [g/day] from wastewater treatment plants: values presenting the difference between variants 1 and 2 (based on the data presented on the Fig.9).

	spring			summer			autumn			winter		
	WWTP size											
	small	medium	large	small	medium	large	small	medium	large	small	medium	large
	The difference between mean heavy metal loads [g/day] in variants 1 and 2											
As	1.8	3.9	29.5	0.1	0.4	2.9	1.3	3.7	32.0	0.1	0.4	2.9
Ba	5.9	12.8	147.3	0.0	0.0	5.0	3.8	11.1	129.5	0.0	0.0	0.0

Sn	1.8	3.9	29.5	0.0	0.0	0.8	1.3	3.7	32.0	0.1	0.4	3.3
Zn	11.3	38.6	155.6	0.0	0.0	0.0	7.9	29.5	259.0	0.0	0.0	0.0
Co	1.8	3.9	29.5	0.1	0.4	2.0	0.0	0.0	0.0	0.1	0.5	1.6
Cu	0.9	3.9	29.5	0.0	0.0	0.0	1.0	3.7	25.9	0.0	0.2	1.4
Mo	1.8	3.9	29.5	0.0	0.3	0.2	1.3	3.7	32.0	0.1	0.4	3.3
Ni	1.5	3.9	15.9	0.0	0.1	0.0	1.0	3.7	18.4	0.0	0.4	0.2
Pb	1.8	3.9	29.5	0.0	0.0	0.0	1.3	3.7	32.0	0.1	0.4	2.9
Hg	0.2	0.4	2.9	0.0	0.0	0.3	0.1	0.4	3.2	0.0	0.1	0.3
Cr	1.8	3.9	29.5	0.0	0.0	0.0	1.3	3.7	32.0	0.0	0.4	0.5

3.2.2. Heavy metal loads entering the river from industrial plants

The analysis of industrial WWTP discharge (Fig. 10) found that in summer and winter, the highest metal loads were observed in wastewater from the fruit and vegetable industry (I3) and in sewage from one of the fruit and vegetable plants (I2) (Fig. 10). The loads depend not only on the metal concentrations but also on the volume of treated wastewater discharges, which are influenced to a large extent by the size of the industrial plant. Flows in fruit and vegetable plant I2 ranged from 315 to 838 m^3/day depending on the season, with the lowest flow being recorded in summer and the highest in autumn. In contrast the flow rate ranged from to 803 to 2109 m^3/day in fruit and vegetable plant I3, with the lowest flow recorded in winter and the highest in autumn. Also, flow rates of 30 to 35 m^3/day were noted in the furniture plant (the lowest flow was recorded in spring and the highest in summer), and 139 to 163 m^3/day in the dairy plant (the lowest flow was recorded in autumn and the highest in winter). While these flow rates differ from the received heavy metal loads, it is worth noting that the characteristics of the wastewater and its physicochemical properties also have a great influence on the composition of the grab samples, which also have a significant impact on the generated concentrations.

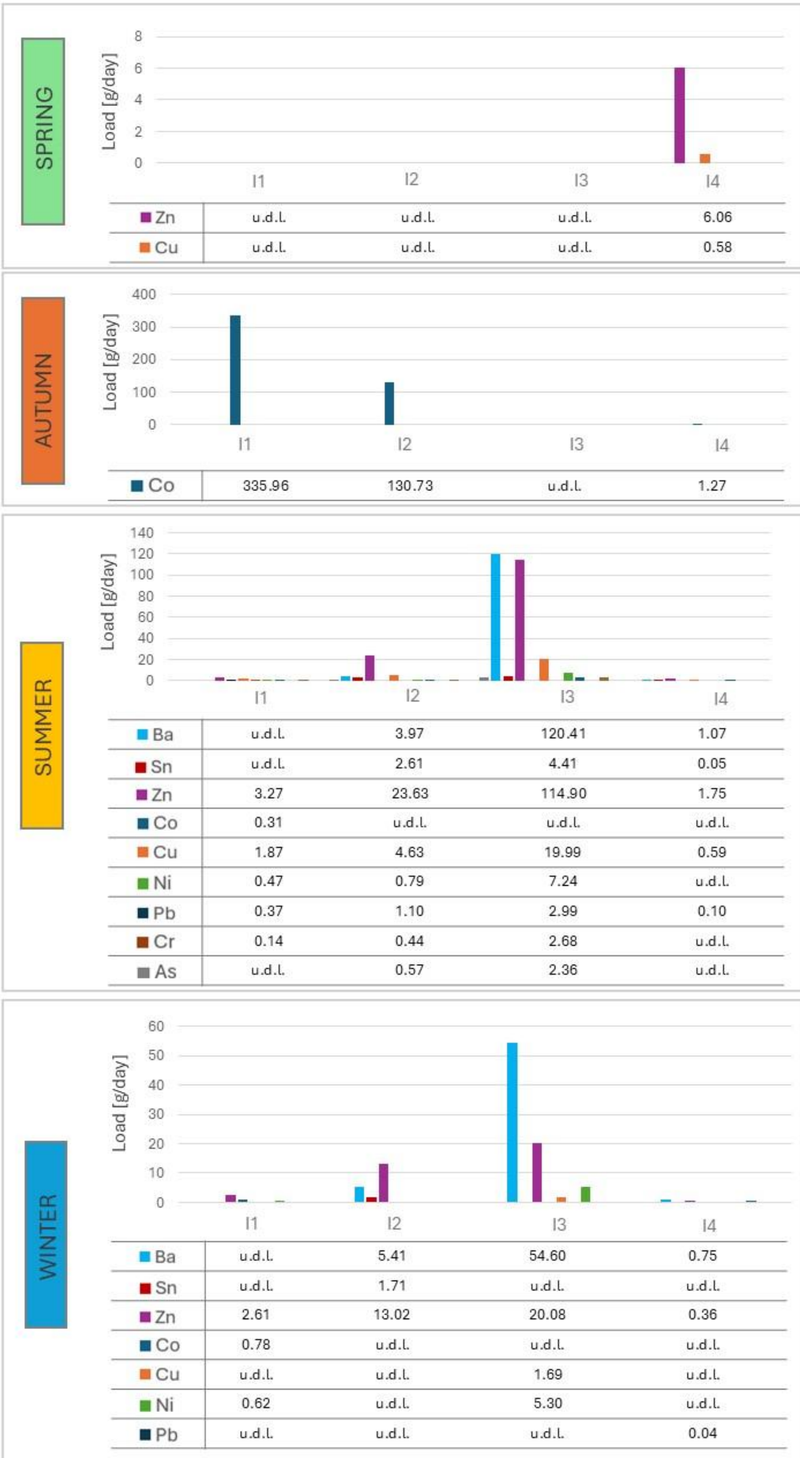


Fig.10 Loads [g/day]of selected heavy metals identified in samples of industrial wastewaters; I1 – dairy industry, I2 and I3 – fruit and vegetable industry, I4 – furniture industry.

3.3 Transport of heavy metal loads along the river continuum within a catchment

In all seasons, the most common heavy metal identified in river samples was barium. These loads increased along the river continuum, with the highest loads in all seasons detected at point R6.

The highest Ba loads were observed in winter (66.29-216.98 kg/day). In winter, copper was also present in the analyzed samples, and its concentrations also increased along the river continuum (10.42-29.18 kg/day). In spring, in addition to Ba, high Cu and Ni loads were also observed; however, no upward or downward trend was observed. In summer, increasing loads of As (u.d.l.-1.94 kg/day) and Cu (1.33-3.39 kg/day) were also observed, while in autumn, only Ba was observed, whose loads ranged from 22.95 to 89.36 kg/day (Fig.11). The highest mean flows in the river were recorded in winter (57.2 m³/s) and the lowest in summer (13.0 m³/s). Similar flow rates were observed in spring and autumn, *viz.* 21.5 m³/s and 22.3 m³/s, respectively.

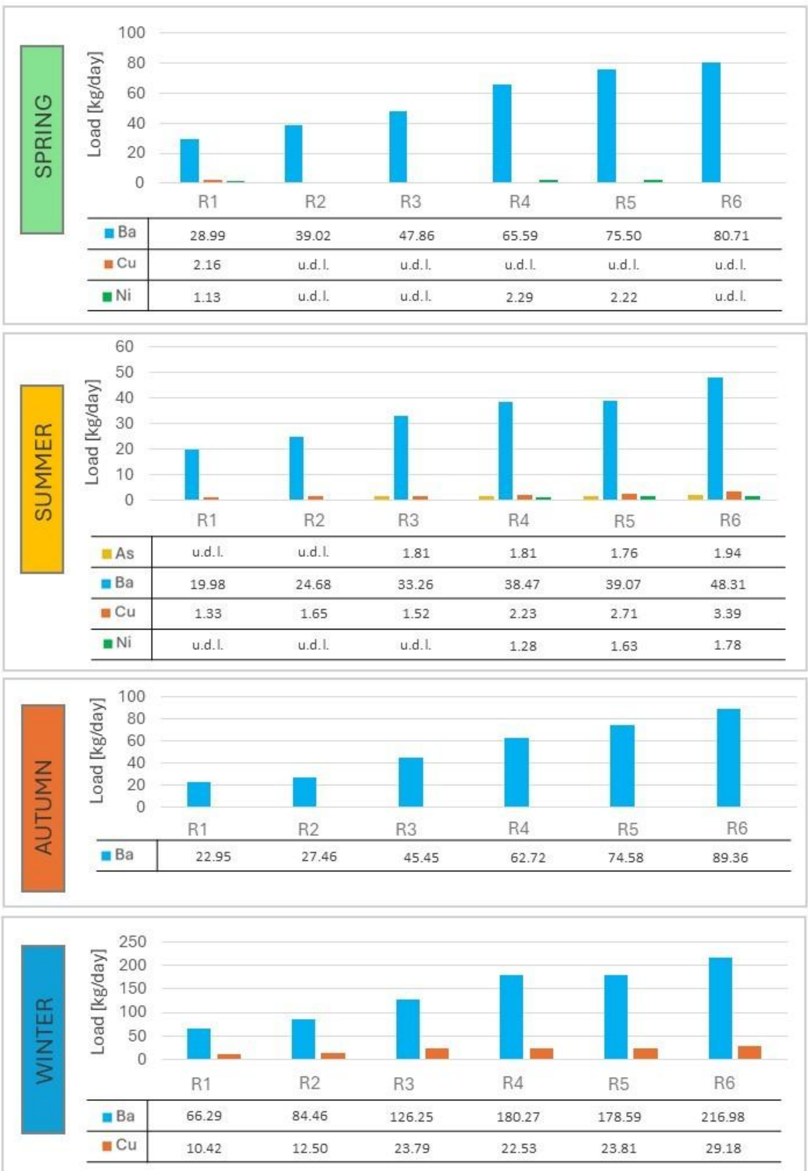


Fig.11 Loads of heavy metals from riverine sampling points [kg/day] identified seasonally during the years 2022-2023

4 Discussion

Many of the aquatic environments around the world are polluted with non-biodegradable and toxic heavy metal residues. As metals do not decompose, the pollutants not only accumulate in aquatic organisms, but also biomagnify along the trophic chain (Ahmad et al., 2010). Two significant sources of environmental heavy metal pollution are the development of industry, and progressive urbanization, which is also associated with increased population density. Wastewater from industrialized areas is characterized by higher concentrations of heavy metals than sewage from less industrialized areas, due to its higher content of municipal, industrial and hospital sewage (Hubeny et al., 2021). However, the scale of pollution of the aquatic environment and sewage remains difficult to understand due to data gaps and varying levels of determinations; furthermore, much of the data may be overestimated or underestimated. Therefore, this article takes a different approach by processing the data through two calculation variants. This procedure yielded different variants of pollution, allowing for an objective assessment of the scale of heavy metal pollution of the Pilica catchment area.

4.1 Wastewater as sources of heavy metals in river water

4.1.1 Municipal WWTPs

The presented analyses confirm the presence of heavy metals in treated wastewater from both municipal wastewater treatment plants and industrial plants. Regardless of the calculation variant, heavy metals were detected in sewage every season, with the highest median values observed in sewage from small sewage treatment plants, i.e. those with PE below 2000. These findings are consistent with previous observations indicating that the highest concentrations of

TN and TP reaching the Pilica River with treated wastewater also derived from small WWTPs (Kiedrzyńska et al., 2014).

In addition, high loads of these pollutants also reach the Pilica River from class IV (large) WWTPs (Fig.9 A,B), which is related to the high flows occurring in these plants (Tab.1). Importantly, these sewages are discharged into surface waters: the rivers in Lodz receive water runoffs from WWTPs as well as from rainwater systems and combined sewers. Sakson et al. (2017) report that approximately 48% of annual Zn, 38% Cu, 61% Pb and 40% Cd loads discharged into the studied water receivers came from separation systems, 4% Zn and Cu, 10% Pb and 11% Cd from combined sewers and the rest from wastewater treatment plants, which indicates that treatment plants have a significant impact on the quality of surface waters in this region.

The nature of the discharged sewage is also important. Analyses conducted on wastewater sludge samples from municipal and rural Polish WWTPs confirmed the presence of heavy metals. The sludge from the rural treatment plants was found to contain 0.6–9.5 mg Cd/kg of sludge, 9.3–524 mg Cu/kg, 48–90.0 mg Ni/kg, 8.8–275.2 mg Pb/kg, 575–1732 mg Zn/kg, 7.5–170.0 mg Cr/kg and 0–3.8 mg Hg/kg of dry sludge mass. In contrast, the sludge from the municipal plants contained 1.07–16.7 mg Cd/kg, 32–195 mg Cu/kg, 1.3–128.9 mg Ni/kg, 21.2–322.4 mg Pb/kg, 20–5351.1 mg Zn/kg, 12.7–2759.8 mg Cr/kg and 0.1–1.55 mg Hg/kg (Olejnik, 2024). Similar analyses carried out on sludge from the WWTP in Bytom (Poland) found the following heavy metal profile: 1.8-4.1 mg Cd/kg of sludge, 34.9-68.3 mg Cr/kg, 104.1-194.0 mg Cu/kg, 51.2-98.1 mg Ni/kg, 97.6-189.2 mg Pb/kg, 1092.2-1851.6 mg Zn/kg, and 0.3-1.1 mg Hg/kg of sludge (Tytła, 2019).

Sewage was also found to influence water quality in the Changjiang River. High concentrations of As, Cd, Zn, Pb, Hg and Cr were detected in places where the sources of river pollution were municipal and industrial sewage (Wang et al., 2011). According to Sörme and Lagerkvist (2002), sources of Cu in wastewater may be runoff from roofs and tap water, Zn-galvanized utility materials and car washes, which are also significant sources of Pb, Cr and Cd, and Ni may come from chemicals used in WWTPs. Analyses of wastewater sludge from Shanxi Province in China showed that 35.7% of the total amount of identified heavy metals came from the smelting industry, coking plants and road traffic, 29% from households and the water supply, and 16.2% from industries such as leather tanning, textile production and chemical industry (Duan et al., 2015). All this indicates a worldwide problem related to the discharge of wastewater into surface waters.

4.1.2. Wastewater from fruit-vegetable industry

Our analyses confirm the presence of heavy metals in the wastewater of the fruit and vegetable industry. The highest loads of metals, *viz.* Ba (120.41 g/day), Zn (114.90 g/day) and Cu (19.99 g/day), were observed in summer in plant I3, together with high loads of Sn, Ni, Pb, Cr and As. These metals were also present in plant I2, but their loads were much lower (Fig.10). The presence of heavy metals in the wastewater of the fruit and vegetable industry may be caused by the transfer of these compounds from the environment to the fruits and vegetables, and then to wastewater during their processing. The key role in the initial contamination of the plant products is no doubt played by the fertilizers, ripening agents, fungicides and pesticides used in their cultivation during the flowering and growth periods (Fang & Zhu, 2014).

The use of fertilizers results in the occurrence of Cd, Cu and Zn in greenhouse soils (Wei, 2020). Both Cr and Ni, as well as Zn, Cd and Pb show strong correlations with nitrogen fertilizer use, where their levels range from 3.2 to 19 µg Cr/g of fertilizer, from 7 to 34 µg Ni/g, from 1 to 42 µg Zn/g, from 0.05 to 8.5 µg Cd/g and from 2 to 120 µg Pb/g; they can also be present in phosphate fertilizers at concentrations of 66–245 µg Cr/g, 7–38 µg Ni/g, 50-1450 µg Zn/g, 0.1-190 µg Cd/g and 4-1000 µg Pb/g (Sandeep et al., 2019). Phosphate fertilizers have also been identified by the

European Parliament and the Council of the European Union as a potential source of cadmium, and their use has hence been subject to special legal regulations (European Union, 2019).

The dynamics of heavy metals in the soil and their potential to accumulate in fruits and vegetables are significantly influenced by the properties of soil, such as the presence of organic and inorganic matter, soil type, pH, mineral content, or the type of crop (Zwolak et al., 2019). Different fruits also have different accumulation potential: berries have the potential to accumulate Cu, Ni and Sb, stone fruits to accumulate Cu and Sb, pome fruits to accumulate Cu, Ni and Sb, and shell fruits to accumulate Cu (Gruszecka-Kosowska, 2019).

4.1.3. Wastewater from the dairy industry

The wastewater entering the Pilica also derives from the dairy industry. It was found to carry negligible loads of some metals, such as Zn, Cu, Ni, Pb and Cr; however, an increased cobalt load was noted in the autumn, amounting to 335.96 g/day. Cobalt is a component of vitamin B12, where it occurs as Co(III). It is an essential trace element for both ruminants and horses, which can synthesize vitamin B12 in their digestive tracts through the action of microorganisms. In addition to meeting the demand for vitamin B12 synthesis, cobalt also takes part in fermentation in ruminants, where it increases the efficiency of digestion of low-quality feed fibers. Co is excreted from animal organisms in urine or feces, or with milk (EFSA, 2009). In 2023, the EU Commission Implementing Regulation came into force, with an urgent provisional authorisation of the use of cobalt(II) acetate tetrahydrate, cobalt(II) carbonate, cobalt(II) carbonate hydroxide monohydrate (2:3) and cobalt(II) sulphate heptahydrate as feed additives for ruminants with a developed rumen, equines and lagomorphs (European Union, 2023). It has been found that heavy metals such as Pb, Cr and Co in milk persist in dairy products, although with some reduction in their level; for example, it was found that Pb content was 0.6% lower in yogurt than the original cow's milk, while Cr 0.8% was lower and Co 1.9% lower (Al-Naemi, 2018). Hence, it is highly likely that these metals may also occur in wastewater from dairy production units.

4.1.4. Wastewater from the furniture industry

In the wastewater from the furniture industry, the highest load was observed in spring for Zn (6.06 g/day), although this was accompanied by Cu, Ba, Sn, Pb and Co. Many of these heavy metals may derive from the use of pigments, dyes and resins contained in putties and paints: such products are known to include lead, cadmium, mercury and chromium in their composition (Yuan et al., 2014). One study of the air in paint factories found Pb concentrations to range from 38 to 360 ng/m^3, Ni from 5 to 41 ng/m^3, Cu 10-24 ng/m^3, Cr 1-7 ng/m^3 and Zn from 0.01 to 316 ng/m^3; this indicates the presence of heavy metals in both the production processes and the paints themselves (Yaghi & Abdul-Wahab, 2003). Interestingly, heavy metals are also identified in wood chips generated during wood processing and in post-industrial wastewater, suggesting that heavy metals can accumulate in trees and are leached during processing. In wood chips, after digestion, the concentrations of Cu can range from 1.11-1.21 mg/L, Zn 37.7-40.2 mg/L, Cd, 0.859-0.913 mg/L, Mn 80.9-88.1 mg/L, Pb 1.56-3.44 mg/L, and Al 28.2-30.7 mg/L, with higher concentrations noted in wastewater than in chips (Ayob et al., 2022).

4.2 Seasonal changes in heavy metal concentrations

Seasonality was found to have differing effects on heavy metal pollution depending on the calculation method: PCA analysis of data from municipal and industrial sewage confirmed strong relationships between heavy metals and the spring and autumn seasons (Variant 1), or between heavy metals and the summer and partially winter seasons (Variant 2). Hence, the obtained results indicate an extremely different picture of seasonality depending on the calculating method. It is also important to remember about the temporary nature of sampling.

However, a number of studies have reported seasonal variations in the levels of heavy metals in sewage. Renuka et al. (2014) report the presence of various heavy metals including Cr, Co, Pb, As and Cd in sewage. While Cr was observed throughout the year, Cd was observed in all months except December, with the concentrations peaking in September and November. While Cr, Co, Pb and As peaked in December, their values were also high in March, September, October and December; this indicates the relationship between the winter period and the occurrence of heavy metals in wastewater (Renuka et al., 2014). Seasonal analyses of treated wastewater from Manisa city identified the highest concentrations of chromium (3.44 ug/L), nickel (0.218 ug/L), arsenic (27.7 ug/L), barium (107.129 ug/L), mercury (0.027 ug/L) in winter, manganese (8.35 ug/L), cadmium (0.04 ug/L) in spring, and lead (0.533 ug/L) in summer (Sadiq et al., 2019). Seasonal variability was also observed in sewage sludge from Greece, with the highest concentrations of Cd and Cr observed in spring and the lowest in winter (in two out of three WWTPs), and Cu, Ni and Pb being highest in winter and lowest in summer (Spanos et al., 2016). This demonstrates the diversity of the composition of the analyzed matrices and the fact that the occurrence of heavy metals in a given season is influenced by co-occurring physicochemical parameters.

Our present analysis of heavy metal loads found the highest Ba (66.29-216.98 kg/day) and Cu loads in river water (10.42-29.18 kg/day) occurred in winter. Arsenic was recorded in summer (1.76-1.94 kg/day), and Ni in spring (1.13-2.29 kg/day) and summer (1.28-1.78 kg/day). During rainy seasons, pollutants may be diluted, resulting in lower levels in the aquatic environment; conversely, studies on the Han River by Li and Zhang (2010) identified the highest total heavy metal concentrations in June (1195.92 μg/L), which the authors attribute to increased water evaporation and greater anthropogenic activity.

The dry season is also characterized by reduced water flows in rivers and, consequently, higher pollutant concentrations. Eliku and Leta (2018) report higher iron concentrations during the rainy season, which the authors attribute to the high runoff occurring at this time, resulting in soil erosion and release of iron. A study of the Karnaphuli River in Bangladesh found the water to contain 13.31 to 53.87 µg As/L, 46.09 to 112.43 µg Cr/L, 2.54 to 18.34 µg Cd/L and 5.29 to 27.45 µg Pb/L. The values in the sediments were 11.56-35.48 mg As/kg, 37.23-160.32 mg Cr/kg, 0.63-3.56 mg Cd/kg and 21.98-73.42 mg Pb/kg. Higher concentrations of these metals were identified in winter. Potential sources included municipal sewage discharges (Cd, Pb), waste from the petroleum and textile industries (Cr), fertilizer and pesticide production, wood processing, tanning and runoff from mountain areas (As), atmospheric deposition, leaded gasoline, crude oil, production of chemicals, electronics, tires, and the presence of a steel mill near the studied river (Pb) (Ali et al., 2016).

In the present analysis, the barium could have been re-emitted in the winter period through *inter alia* release from river sediments. Although Ba constitutes only 0.05% of the Earth's crust, and naturally-occurring forms are rare, it is used in a range of commercial processes (Aziz et al., 2017) including the plastics, textile, paper, electronics, pharmaceutical, cosmetic, dye and tanning industries, as well as pesticide production (Kravchenko et al., 2014). All this means that Ba can occur in large quantities in the environment. As a result, it is a commonly found in the environment.

4.3 The relationships between heavy metal levels and the physico-chemical properties of wastewater and river water

In the aquatic environment, heavy metals are distributed between the water phase and bottom sediments. As such, their fate is influenced by *inter alia* precipitation, sorption or dissolution, as well as pH, temperature, mixing of water masses, the amount of oxygen dissolved in water, redox potential and ionic strength (Piwowarska et al., 2024; Yu et al., 2001). Among the binding fractions in sediments, heavy metals can be found in exchangeable fractions, bound to carbonates, Mn-oxides, Fe-oxides, organic matter, sulphides, and residues. Interestingly, the amount of heavy metals bound to organic matter does not always increase with the increase in the binding sites of the matter; this indicates that other factors such as the extent of contamination, binding competition between metals, and the type of organic matter may play a role (Yu et al., 2001).

In the treated sewage samples, zinc and copper levels were found to correlate positively with temperature and negatively with oxygen. In addition, As, Ba, Sn, Cu, Mo, Ni and Pb levels correlated positively with the presence of suspended solids, and Ba, Sn and Cu with turbidity. Ni and Cr levels correlated positively with conductivity, total dissolved solids and salinity. In contrast, As, Sn, Cu, Pb and Cr levels correlated negatively with redox potential. Positive Significant correlations were also shown between Ba and total nitrogen, between Ba, Zn and Cu and total phosphorus (TP) content, between Ba and BOD_5, and between Cu and COD.

Many positive and negative correlations were also detected between heavy metal content and the anions and cations present in the samples. For industrial plants, a positive correlation was shown only for TSS and Ba concentrations, and for fluoride ions and molybdenum. Conversely, Zn and Cu demonstrated significant negative correlations with redox index; Mo with TP content; Co, Mo and Pb with calcium ion level.

In the river samples, As and Ni had positive correlations with temperature, As with pH, and Ba with sodium and magnesium ion levels. In turn, As concentrations in water were negatively correlated with certain physicochemical parameters (oxygen, flow, TN, BOD_5, calcium ion, nitrates and sulfates), and Cu content with conductivity, salinity, TSS, lithium, magnesium, fluorine, chlorine and sulfate ion levels. Similarly, Wei et al., (2018) found Cu, Cd, As and Zn to be influenced by *inter alia* F-, TP, *E.coli* content and COD_{Cr}. The authors attribute the presence of Cu, Zn and As in the samples to industrial activity and to livestock and domestic sewage production (Wei et al., 2018). Arsenic levels has also been found to correlate with BOD (Chung et al., 2016).

The physicochemical status of surface waters significantly affect metal concentrations. Lower pH and higher temperature have been found to promote the release of heavy metals into the aquatic environment, while higher pH promotes their precipitation and their adsorption on the sediment surface (Li et al., 2013). pH has a significant influence on the form of heavy metals in the environment; for example, the hydroxide sediments of most heavy metals exhibit poor solubility under standard water pH conditions, and these complexes become soluble only at lower pH (Elder, 1988). Under conditions of lower water pH but higher salinity and temperature, the amount of Cu and Zn released from sediments increases. In contrast, an increase in pH can lead to changes in the solid fraction of Zn, such as an increase in the residual fraction and a decrease in organic matter and sulfides. An increase in temperature and salinity, on the other hand, can reverse these changes in the fraction distribution (Zhao et al., 2024).

Another important factor is the amount of dissolved oxygen, which affects the rate of release of metals into surface waters by influencing the rate of oxidation of organic matter (Li et al., 2013). Importantly, the formation of sediments is also strongly influenced by the presence of sulphides. Both forms are influenced by redox potential: the dominant heavy metal sediments are oxides in oxidation conditions, and sulfides in anaerobic conditions (Elder, 1988). In conditions of increased redox potential, reduced sulfur compounds can be oxidized to SO_4^{2-} with an efficiency as high as 40-80%. While many heavy metals in sediments become more soluble at higher redox potentials, higher concentrations of As can be observed in highly-contaminated sediments under low redox potentials (Popenda, 2014).

4.4 Transport of heavy metals along the river continuum and river self-purification

Our findings indicate that barium loads increased along the river continuum in all seasons; this may indicate a constant inflow of Ba to the waters of the Pilica River, and thus a higher concentration of pollutants. At the final measurement point located before the entry of the Pilica into the Vistula, the highest load was observed in winter (216.98 kg Ba/day). The same season was found have the highest Cu loads, with the highest value noted at point R6 (29.18 kg/day). In the remaining seasons, Ni and As were also present, with their loads increasing along the river; however, no change in Ni level was observed in the spring. The presence of heavy metals in the Pilica may be caused by their entry into the ecosystem from both diffuse and point sources.

Hydrological conditions also have a strong influence on the conditions of surface waters. High Ba and Cu loads were calculated for winter, and these may be related to the increased mean flow noted during this period (57.23 m^3/s). The levels of organic pollutants present in water are further increased by intensive atmospheric precipitation, which washes out the soil and organic matter from the river basin. Therefore, diffuse sources of pollution based mainly on water runoff from urban and agricultural areas play an important role in river pollution during periods of intensive rainfall and floods (Urbaniak et al., 2014). Importantly, due to the processes of adsorption, hydrolysis and co-precipitation occurring in water, only small amounts of metals are soluble, the rest is deposited in sediments. It is estimated that 30-98% of the total loads of heavy metals found in the river can be transported in a form associated with sediment. Moreover, if such sediments settle on the banks of a riverbed or floodplain, they will again become a potential diffuse source of environmental pollution (Piwowarska et al., 2024).

Barium can enter the atmosphere via industrial emissions, and then be passed to the aquatic environment by deposition. It can also be taken up by agricultural soils by the application of fertilizers and soil additives. Furthermore, industrial sewage and runoff from soils contaminated with fly ash are also known sources of Ba (Verbruggen et al., 2020).

Barium is released in the aquatic environment by ion exchange with solid particles. In important part in these processes is also played by salinity level, with a large part of molecular barium being desorbed within 60 minutes at salinity values above 1.7. At low salinity, water mixing and co-precipitation processes with iron and manganese hydroxides influence the release of barium from river suspensions (Coffey et al., 1997). Interestingly, during the mixing processes of fresh and salt water, the adsorbed Ba should be simultaneously displaced by cations such as Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} (Hanor & Chan, 1977). Our correlation analysis indicates a positive correlation between the presence of Ba in the river and Na^{+} and Mg^{2+} ions. Moreover, previous analyses of heavy metal (Pb, Cu, Zn, Cd, Ba) adsorption to biofilm found Ba to have the weakest bonds, resulting in easier release; this weak bond formation could be explained by its characteristic standard electrode potential, covalent radius and atomic radius (Dong et al., 2003).

Heavy metals are also widely distributed in other rivers around the world. One example is the Ona River in Nigeria was found to contain 9.2 mg/L Zn, 0.4 mg/L Cr, 0.2 mg/L Pb, 0.4 mg/L Cu, 0.1 mg/L Ni and 5.3 mg/L Fe, which are believed to derive from both human activities such as the use of chemicals and zinc-based fertilizers, and natural geological conditions (Adefemi & Awokunmi, 2010). The Turkish Dipsiz stream, which is polluted by *inter alia* the Yatagan Thermal Power Plant, contains 0.17 µg Cd/L, 0.37 µg Cu/L, 0.41 µg Pb/L, 1.05 µg Zn/L, 0.09 µg Cr/L (Demirak et al., 2006). The Powa River, Poland, was found to carry 0.28-0.62 mg Cr/kg, 0.33-0.61 mg Ni/kg, 0.41-1.23 mg Cu/kg, 3.05-6.18 mg Zn/kg, 0.16-0.39 mg Cd/kg, 0.64-1.03 mg Pb/kg of sediment (Sojka et al., 2018). In Italian rivers (Angitola, Mesima, Crati, Esaro) the mean annual heavy metal concentrations ranged from 0.9 to 6.3 µg As/L, 0.014 to 0.045 µg Cd/L, 0.25 to 1.09 µg Pb/L, 0.31 to 0.53 µg Hg/L in river water, and from 9.3 to 20.9 mg As/kg sediment, 0.1 to 0.22 mg Cd/kg, 7.41 to 13.10 mg Pb/kg, 0.006 to 0.044 mg Hg/kg in the sediments (Protano et al., 2014).

Studies of the Tembi River found differences in the concentrations of metals between its upper and lower reaches. The mean concentrations were 0.17 mg Cd/L, 0.19 mg Cr/L, 0.47 mg Cu/L, 0.45 mg Mn/L, 0.48 mg Ni/L, 1.13 mg Pb/L and 0.2 mg Zn/L in the upper section of the river, and 0.25 mg Cd/L, 0.29 mg Cr/L, 0.57 mg Cu/L, 0.94 mg Mn/L, 0.68 mg Ni/L, 1.4 mg Pb/L and 0.35 mg

Zn/L in the lower section, i.e. the concentrations increased along the river continuum (Shanbehzadeh et al., 2014).

4.5 Different approaches to environmental data analysis

The quality of data obtained in environmental studies is influenced by a range of variable factors, such as changing environmental conditions or differences in the equipment used. In addition, matrix effects, the concentrations of contaminants, such as heavy metals, in the samples, and miscellaneous factors such as instrument sensitivity and purity of the reagents used, can further complicate analyte detection and quantification (Saadati et al., 2013).

Studies of environmental pollution commonly obtain data sets containing values lower than the *limit of quantification* (LOQ). According to the European Union (2009) *the quantification limit* refers to a defined multiple of the detection limit at a given concentration of the analyte, which can be determined with acceptable accuracy and precision. Therefore, it is necessary to establish an appropriate approach to account for this censored data during the analysis.

Two such approaches were used in the present article: replacing a data point without a value with half of the LOQ value (Variant 1) and replacing the LOQ value with the value "0" (Variant 2). These methods have their advantages and disadvantages, and thus influence the obtained research results. The use of Variant 2 means that the calculated values are lower than the actual values due to the use of sets of artificially low numbers. In the case of Variant 1, the conversion error is lower (Cantoni et al., 2020).

Variant 1 was used, among others, in data analyses of the presence of contaminants (including heavy metals) in humans urine and complements (Becker et al., 2003), as well as during creation and validation the method for detecting 24 analytes representing a broad spectrum of illicit drugs and several of their key urinary metabolites in wastewater samples (González-Mariño et al., 2012). Variant 1 also has been used in, *inter alia*, assays of PFAS compounds in water, sediments and organisms collected in Beibu Bay in southern China for the values between LOD and LOQ (Pan et al., 2021) and in studies of estrogenic activity of water from freshwater ponds and water reservoirs affected by blooms (Procházková et al., 2018). The approach based on Variant 1 is also recommended by the European Commission and is included in Commission Directive 2009/90/EC (European Union, 2009). The Variant 2 approach has been used in, *inter alia*, calculations conducted during a clinical trial on the concomitant use of atorvastatin and ximelagatran (Sarich et al., 2004), as well as in evaluation of the cefiderocol pharmacokinetics in clinically stable subjects with mild, moderate, and severe renal impairment and in subjects undergoing hemodialysis (Katsube et al., 2017).

The combination of variants (1 and 2) in parallel with other calculation methods was used in the analysis of databases on water quality monitoring in 28 drinking water treatment plants. 19 pollutants, including metals, volatile organic compounds, pesticides and perfluorinated compounds, were analyzed. The authors emphasized that the use of the method of conversions with the value "0" causes the obtained results to be underestimated, and conversions from LOQ/2 give overestimated results; as such, caution should be exercised in assessing the obtained results (Cantoni et al., 2020).

4.6 The sedimentation-biofiltration system as a solution supporting the elimination of heavy metals from the aquatic environment

Due to the widespread pollution of the aquatic environment from point sources, it is important to limit these pollutants before they reach aquatic ecosystems. An increasingly popular solution is the use of ecohydrological biotechnologies and nature-based solutions (NBS); these approaches are cheap and environmentally friendly, and are currently included in various programs of the European Commission (e.g. Horizon Europe), as well as within the framework of the IX phase of the UNESCO Hydrological Program (Piwowarska et al., 2024). Nature-Based

Solutions are a group of biotechnological and ecohydrological tools aimed at increasing the potential of sustainable development. Since NBS are based on processes naturally occurring in ecosystems and their properties, they can be used both on a micro scale (e.g. in the areas of individual households) and on a macro scale (e.g. on the scale of the entire landscape) (Piwowarska & Kiedrzyńska, 2022). Implementing the concepts of ecohydrological biotechnologies to reduce anthropogenic pollution from WWTPs has been demonstrated to increase the sustainable development of surface waters; in addition, due to their low cost and non-invasive nature, such approaches represent a promising natural solution which is attractive to society (Kiedrzyńska et al., 2014; Kiedrzyńska et al. 2017).

One attractive group of solutions close to nature are sequential sedimentation-biofiltration systems (SSBS), which combine various processes such as sedimentation, filtration and adsorption, as well as phytoaccumulation and rhizofiltration (Jarosiewicz et al., 2024).

A good example of a functioning SSBS system with a horizontal arrangement was constructed in a ditch discharging purified sewage from the municipal WWTP in Rozprza (central Poland) to the Dąbrówka River, a tributary of the Pilica. The Rozprza WWTP is a small treatment plant with 500 PE, whose mean daily, multi-year wastewater outflow is 107 m^3. The SSBS system was constructed on a slope, so that the sewage flows through individual barriers by gravity (Kiedrzyńska et al., 2017). While this system was found to be effective, we propose a modification (Fig.12) based on present results concerning the presence of heavy metals in sewage and literature data (Tab.3).

Tab.3 Examples of effective elimination of heavy metals with the use of selected geochemical and biological elements of the proposed modification of sequential biofiltration system.

Element of the system	**Heavy metal**	**Removal efficiency**	**Reference**
dolomite	As	Up to 92% in concentration	Shah et al., 2019
	Cu	Up to 97% in concentration	Sočo et al., 2023
	Co	Up to 80% in concentration	Ivanets et al., 2016

zeolite	Ba	Up to 40.3% in concentration	Baldermann et al., 2020
	Cu	Up to 86% in concentration	Filatova et al., 2021
	Ni	Up to 89% in concentration	
	Zn	Up to 85% in concentration	
	Cr	Up to 82% in concentration	Álvarez et al., 2021
limestone	Cu	Up to 100% in concentration	Yao et al., 2009
	Ni	Up to 47.8% in concentration	
	Zn	Up to 36.8% in concentration	
Limnocharis flava	Hg	Up to 90% in concentration	Marrugo-Negrete et al., 2017
Limnocharis flava + Typha angustifolia	Cu	Up to 79.07% in concentration	Syukor et al., 2016
	Cr	Up to 69.17% in concentration	
	Ni	Up to 74.87% in concentration	
	Pb	Up to 62.07% in concentration	
	Zn	Up to 63% in concentration	
Phragmites australis + Typha latifolia	Pb	Up to 61% in concentration	Kumari & Tripathi, 2015
	Cu	Up to 78% in concentration	
	Cr	Up to 68.1% in concentration	
	Ni	Up to 73.8% in concentration	
	Zn	Up to 61% in concentration	
Phragmites australis	Mo	0.5-2.1% in concentration	Hua et al., 2019
	Hg	Up to 79.8% in concentration	Soto-Ríos et al., 2018
	Cu	68-87% in concentration	Guzman et al., 2022
	Zn	53-95% in concentration	
	Pb	20-55% in concentration	
Salvinia natans	Zn	Up to 84.8% in concentration	Dhir & Srivastava, 2011
	Cu	Up to 73.8% in concentration	
	Ni	Up to 56.8% in concentration	
	Cr	Up to 41.4% in concentration	

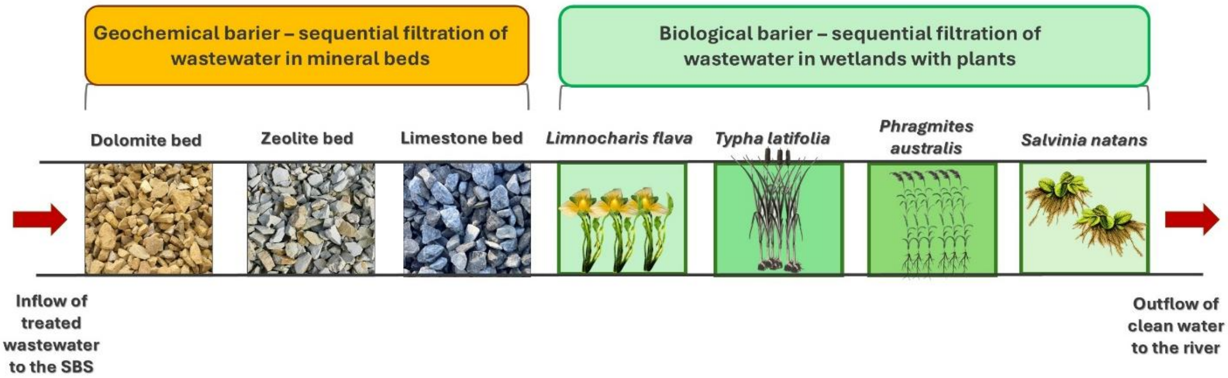


Fig.12 Modification proposal of the sequential biofiltration system built at the wastewater treatment plant in Rozprza (Kiedrzyńska et al., 2017, modified).

5. Conclusions

The article presents the results of physicochemical analyses of river water and treated sewage originating from point sources of pollution located in one of the largest sub-basins of the Vistula River: the Pilica River basin. Both the Vistula and the Pilica flow through some of the most industrialized and polluted areas in Europe (Kiedrzyńska, et al., 2014). In order to stop the transport of heavy metals to such large water bodies as the Baltic Sea, it is important to identify their the sources. Our findings indicate that:

- Both wastewater treatment plants and industrial plants discharging treated effluents directly into rivers constitute significant point sources of pollution of aquatic ecosystems such as the Pilica River;
- An objective analysis of the case is complicated by the choice of calculation variant: this decision will influence the data obtained on the relationship between heavy metals and seasonality, with the results potentially being overestimated or underestimated;
- The loads of heavy metals entering the river from point sources of pollution and transported along the river continuum depend primarily on the size of the flows;

- The distribution of heavy metals in the aquatic environment and in wastewater samples is determined by the physicochemical properties of the matrix, which determine both the form of occurrence and the potential mobility and toxicity of these elements.

The obtained results can be a basis for understanding the participation of point sources of pollution in the contamination of river ecosystems and the transport of pollutants in the areas of entire catchments; therefore, these results article can be interpreted on both the local and international scale. As our research indicates, sustainable management of point sources of pollution should be based on frequent, more complex analysis of the efficiency of eliminating heavy metals and other compounds from both municipal and industrial wastewater. As the physical, chemical and biological methods used by treatment plants are insufficient to obtain purified wastewater completely free of toxic compounds, it is recommended to support them with technologies of increased pollutant capture, such as the sequential biofiltration system indicated in the article. In the face of increasing anthropogenic pressure and thus increased pollutant production, there is a need to integrate modern wastewater treatment technologies with ecohydrological solutions based on phytoremediation to inhibit environmental degradation and improve the quality of inland waters.

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