

HEAVY METAL POLLUTION AND TOXICITY ASSESSMENT IN A SMALL URBAN RIVER: ANALYSIS OF THE BOGDANKA RIVER CATCHMENT (POZNAŃ, POLAND)

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Abstract

Urbanization and the increasing share of impervious surfaces promote heavy metal (HM) inputs to small urban rivers, mainly via surface runoff and stormwater drainage systems. The aim of the research was to identify HM (Cd, Cr, Cu, Ni, Pb, Zn) pollution in water and bottom sediments within the Bogdanka River catchment in Poznań. Samples from 28 sites were collected in March and June 2024 and were analysed using inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS). Data evaluation included selected pollution and toxicity indices and principal component analysis (PCA). The results revealed contamination of bottom sediments in the lower river course, attributed to stormwater drainage, which represents the main HM source in the catchment. Toxicity indices showed that HMs in water and bottom sediments do not pose significant toxicological risk. Additionally, PCA suggests that organic matter content and sediment pH_{KCl} are important factors influencing HM accumulation in sediments.

Keywords

heavy metals • sediments quality • urban watercourse • pollution assessment • stormwater drainage

Introduction

Ongoing urbanization leads to increased emissions of pollutants into the environments of urbanized areas (Duh et al., 2008; Strok al et al., 2021). One of the most susceptible

components of the urban environment to pollutant absorption are small urban rivers/ watercourses (Bernhardt & Palmer, 2007; Strok al et al., 2021; Bylak et al., 2022). Studies on the pollution of small urban rivers are being conducted worldwide (e.g., Islam

et al., 2015; Decena et al., 2018; Ali et al., 2022; Pimiento et al., 2023; Springe et al., 2024), including in Poland (e.g., Borowiak et al., 2016; Aleksander-Kwaterczak & Plenzler, 2019; Wojciechowska et al., 2019). These studies are particularly important due to the multiple ecological, hydrological, and social functions played by small rivers in urban landscapes (Abramowicz & Stępniewska, 2020; Veerkamp et al., 2021). In the context of hydrochemical research, it is especially relevant that they can provide habitat for aquatic organisms within urban environments, which may significantly contribute to the maintenance of biodiversity in cities (Campos et al., 2024). Additionally, they can serve as recreational and leisure areas for local communities (Abramowicz et al., 2022) and positively influence the microclimate, which is particularly important in relation to the urban heat island phenomenon (Qi et al., 2023). These factors make the protection of small urban rivers one of the key challenges for decision-makers in contemporary cities.

The small, transformed catchments are characterized by low hydrological inertia, which makes the influence of external factors almost immediately observable, resulting in significant variability in water quality indicators (Hasenmueller et al., 2017). The increase in pollutant input to these rivers caused by progressive urbanization is associated with the expansion of impervious surfaces such as sidewalks, roads, parking lots, and rooftops (Paul & Meyer, 2001; Li et al., 2012). These surfaces reduce the infiltration potential of precipitation, resulting in increased surface runoff intensity (Shrestha et al., 2021). Pollutants also accumulate on these surfaces and are subsequently washed off (Li et al., 2012; Gunawardena et al., 2015). They can enter rivers directly or be transported through stormwater drainage systems (Sakson et al., 2018).

Stormwater runoff may contain both organic and inorganic substances, including heavy metals (HMs) (Eriksson et al., 2007; Gołdyn et al., 2018). HMs are considered one of the main environmental pollutants and remain among the most frequently studied

contaminants in natural environments (e.g., Li et al., 2012; Ma et al., 2016; Pochodyła-Ducka et al., 2023; Bełcik et al., 2024). They are detected in most surface runoff samples, regardless of city size or country (Milik & Paseła, 2018). According to the Water Framework Directive (2000), HMs are classified as priority pollutants that may have negative effects on aquatic environments and human health. Studies indicate that they often exceed toxic thresholds for aquatic organisms (e.g., Islam et al., 2015; Ali et al., 2022). However, they pose a significant threat to human health primarily when multiple HMs are present in the water simultaneously (Ma et al., 2016).

Sources of HMs in stormwater runoff include activities related to the use of winter road maintenance agents, vehicle parts and components, atmospheric deposition, chemicals used in households and offices, erosion from construction sites, discharges from industrial facilities and chemical spills (Nabizadeh et al., 2005), as well as illegal wastewater discharges and waste dumping sites (Naveen et al., 2017; Essien et al., 2022). HM concentrations can vary significantly depending on factors such as the type of surface receiving the rainfall, the length of the dry period preceding the precipitation event, and the characteristics and chemistry of the rainwater (Li et al., 2012). Additionally, the speciation of HMs in water, and thus their presence in dissolved form or adsorption or precipitation onto sediment grains, is determined by the physico-chemical parameters of water, especially redox potential and pH. Changes in these parameters may lead to the remobilization of HMs from bottom sediments, which affects their bioavailability and toxicity (Linnik et al., 2023ab). Therefore, it is recommended to conduct studies during different seasons (Taka et al., 2022).

Taylor & Owens (2009) highlight the importance of interdisciplinary research, including hydrological, urban, and chemical studies, to better understand the dynamics of pollution in environments influenced by human activity. In particular, chemical and hydrological studies enable the understanding of the complex

circulation of pollutants in urban environments and provide valuable information for social scientists, economists, and decision-makers, who are directly responsible for shaping urban systems. Conducting research at the catchment scale is especially important as it allows for an objective assessment of a given river (Sakson et al., 2018).

The aim of this study is to: (1) investigate the concentrations of HMs in water and bottom sediments of the Bogdanka catchment in Poznań, (2) assess the potential pollution and toxicity of HMs in water and bottom sediments using selected indices, (3) identify potential major sources of pollution, and (4) examine the influence of physico-chemical parameters of water and bottom sediments on the mobility of HMs.

Materials and methods

Research area

The study area was the catchment of the Bogdanka River, which covers the north-western part of the city of Poznań and part

of the neighbouring Suchy Las municipality (Fig. 1). Poznań is located in the west-central part of Poland and has a population of over 500,000 inhabitants (Statistics Poland, 2023). In the physico-geographical structure of Poland, the Bogdanka catchment is situated within the Poznań Gap of the Warta River and the Poznań Lakeland mesoregions, which are part of the Greater Poland Lakeland macroregion (Solon et al., 2018). The catchment is classified as a surface water body, delineated based on the Water Framework Directive (2000), and covers an area of 52.69 km².

The Bogdanka valley forms the Western Green Corridor, which extends from Lake Kierskie to the mouth of the Bogdanka River. Most of the catchment itself is located within highly urbanized areas, with only the western and northeastern parts differing from the typical urban landscape (Fig. 1). In its lower course, the main river and most of its tributaries are canalized. All natural tributaries (Wierzbak, Gołęcinka, Strzeszyński Strumień, Rów Złotnicki) are located to the northeast of the Bogdanka River. However, the river

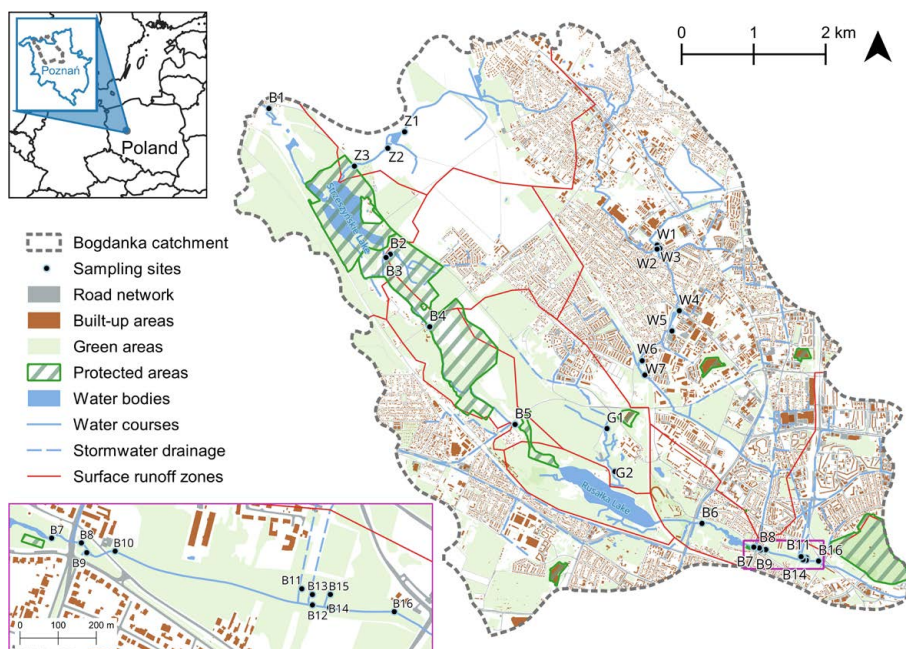


Figure 1. Location of the study area and sampling points

is largely fed by stormwater drainage systems (Fig. 1). The catchment is also partly covered by surface nature protection areas, including two ecological sites (Bogdanka I and II) and, in small sections in the northern part, Natura 2000 protected areas.

Sampling and samples preparation

Water and bottom sediment samples were collected twice: on 01.03.2024 and on 04.06.2024. Sampling points were selected throughout the catchment, including tributaries of the Bogdanka River (Wierzbak, Gołęcinka, Strzeszyński Strumień, Rów Złotnicki), inflows of the stormwater drainage system, as well as upstream and downstream of reservoirs, which can significantly affect the chemistry of the river's water (Śniady et al., 2024b). Sampling points are shown in detail in Figure 1. Water samples (250 mL each) were collected in Nalgene® polyethylene (HDPE) bottles and stabilized *in situ* with 60% Ultrapur® HNO₃. After collection, the samples were transported to the laboratory in a refrigerated vehicle at a temperature of approximately $4 \pm 2.5^\circ\text{C}$. For bottom sediment collection, an Ekman sediment grab sampler was used, and the top layer of sediment was placed in zip-lock bags. A total of 56 water samples and 56 bottom sediment samples were collected in two sampling campaigns. To prepare the sediments for analysis, they were dried at 105°C using drying oven (Digitheat, J.P. Selecta, Spain) and sieved through a 0.2 mm mesh. HMs were extracted from the prepared sediments using *aqua regia* (Lis & Pasieczna, 2005). Additionally, *in situ* measurements of basic water parameters such as pH, temperature, electrical conductivity and redox potential (Eh) were conducted. A ProDSS Multiparameter Digital Water Quality Meter by YSI (Ohio, USA) was used for this purpose.

Chemical analysis

Concentrations of HMs (Cd, Cr, Cu, Ni, Pb, and Zn) were determined by inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS 8800 Triple Quad, Agilent

Technologies, Tokyo, Japan). Assays using the ICP-QQQ-MS technique were performed using calibration curves obtained from the diluted stock multi-element standard at $100 \mu\text{g}\cdot\text{mL}^{-1}$ (VHG Labs, Manchester, NH, USA). The operating parameters of the ICP-QQQ-MS instrument and the analytical procedures are described in the works of Siepak & Sojka (2017), Siepak et al. (2020) and Sojka et al. (2024). All reagents used were ultrapure, and water was deionized to a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ in a Direct-Q® UV3 Ultrapure Water System apparatus (Millipore, France). The analytical quality control was verified by the analysis of the certified reference materials (CRMs) no. LGC 6187 used for river sediments (Manchester, England) and SRM no. 1640a used for water (National Institute of Standards and Technology, Gaithersburg, MD, USA).

Additionally, the bottom sediments were analyzed for organic matter content and pH. Organic matter in the sediments was determined using the loss-on-ignition (LOI₅₅₀) method by combustion at 550°C (e.g., Heiri et al., 2001). The pH of the sediments was measured in a 1 M KCl solution (pH_{KCl}; e.g., Al-Busaidi et al., 2005) using a Multi 350i multifunctional measuring device from WTW (Weilheim, Germany).

Water pollution and toxicity assessment

Two integrated indexes were used to assess the overall HM pollution and toxicity in the waters of the Bogdanka River catchment. The first of these, the heavy metal evaluation index (HMEI) was used to present direct exceedances of HMs concentrations in water according to the standards of the Regulation of the Minister of Infrastructure (2021) for surface waters (Śniady et al., 2024a). It is expressed as the ratio of the monitored metal concentration (HM_{Conc.}) to its maximum permissible concentration (HM_{MPC}). It was therefore calculated according to the equation:

$$\text{HMEI} = \sum_{i=1}^n \frac{\text{HM}_{\text{Conc.}}}{\text{HM}_{\text{MPC}}}$$

For the evaluation of HM pollution, 1.0 was used as a threshold value. Results above 1.0 indicate that the river's water is polluted, and results below 1.0 indicate that there is no pollution.

The second index of heavy metal toxicity load (HMTL) was used to assess the potential toxic effects of HM in the waters of the Bogdanka River catchment (Zakir et al., 2020). It is calculated by multiplying the studied content of HMs in water (C_i) by their total hazard score (HIS_i) assigned by the Substance Priority List prepared by the Agency for Toxic Substances and Disease Registry (ATSDR, 2022). It is calculated according to the equation:

$$HMTL = \sum_{i=1}^n C_i \cdot HIS_i$$

A scale following Zakir et al. (2020) was adopted for quality assessment using HMTL: $HMTL < 100$ (low toxicity), $100 \leq HMTL < 300$ (moderate toxicity), $300 \leq HMTL < 500$ (high toxicity), $500 \leq HMTL < 1000$ (very high toxicity) and $HMTL \geq 1000$ (extremely high toxicity).

Bottom sediments pollution and toxicity assessment

The geoaccumulation index (I_{geo}) and potential ecological risk index of single metal (ER) were used to assess the pollution and toxicity of individual HMs in bottom sediments, respectively. I_{geo} was created by Müller (1981) and allows to classify sediments into one of seven classes, from 0 (unpolluted) to 6 (extremely severe polluted). It was calculated according to the equation:

$$I_{geo} = \log_2 \left(\frac{C_i}{1.5 \cdot B_i} \right)$$

where:

C_i – represents the concentration of the specific HM in the bottom sediment [$\text{mg} \cdot \text{kg}^{-1}$], and
 B_i – refers to the geochemical background level.

The ER for the ecotoxicological assessment of each individual HM in sediment was developed by Hakanson (1980) and is calculated according to the following formula:

$$ER = TR_i \cdot \frac{C_i}{B_i}$$

where:

TR_i – is a toxicological response of HMs following Hakanson (1980),

C_i – represents the concentration of the specific HM in the bottom sediment [$\text{mg} \cdot \text{kg}^{-1}$], and

B_i – refers to the geochemical background level.

Following Hakanson (1980), five categories of ecological risk were distinguished: $ER < 40$ (low); $40 \leq ER < 80$ (moderate); $80 \leq ER < 160$ (considerable); $160 \leq ER < 320$ (high) and $ER \geq 320$ (very high).

To identify the overall pollution of the sites studied by HMs, the pollution load index (PLI) proposed by Tomlinson et al. (1980) was calculated according to the following formula:

$$PLI = \sqrt[n]{\prod_{i=1}^n \frac{C_i}{B_i}}$$

where:

C_i – represents the concentration of the specific HM in the sediment [$\text{mg} \cdot \text{kg}^{-1}$], and

B_i – refers to the geochemical background level.

PLI values allow the assessment of sediment pollution by HMs into one of two classes: unpolluted ($PLI = 1$) or polluted ($PLI > 1$).

To assess the overall toxicity of HMs deposited in the sediment, the potential ecological risk index (PERI) and the toxic risk index (TRI) were applied. PERI was developed by Hakanson (1980) and is calculated as the sum of ER for the investigated HMs, according to the following expression:

$$PERI = \sum_{i=1}^n ER_i$$

The following scale was adopted for PERI (Hakanson, 1980): $PERI < 150$ (low); $150 \leq PERI < 300$ (moderate); $300 \leq PERI < 600$ (high) and $PERI \geq 600$ (very high).

TRI allows for the description of the potential impact of HMs on aquatic organisms and was proposed by Zhang et al. (2016). It is calculated according to the following formula:

$$TRI = \sum_{i=1}^n \sqrt{\frac{\left(\frac{C_i}{TEC}\right)^2 + \left(\frac{C_i}{PEC}\right)^2}{2}}$$

where:

C_i – denotes the concentration of the analyzed HM in the sediment [$\text{mg}\cdot\text{kg}^{-1}$],

TEC– stands for Threshold Effect Concentration [$\text{mg}\cdot\text{kg}^{-1}$], and

PEC– refers to Probable Effect Concentration [$\text{mg}\cdot\text{kg}^{-1}$].

The PEC and TEC values for sediments were adopted from MacDonald et al. (2000). The TRI values enabled the assessment of the toxic impact of HMs accumulated in bottom sediments using a five-level scale: $TRI \leq 5$ (no toxic risk); $5 < TRI \leq 10$ (low); $10 < TRI \leq 15$ (moderate); $15 < TRI \leq 20$ (considerable) and $TRI > 20$ (very high). For the calculation of I_{geo} , ER, PLI and TRI the geochemical background was adopted based on the Geochemical Atlas of Poznań and Environs (Lis & Pasieczna, 2005) and amounted to: $1 \text{ mg}\cdot\text{kg}^{-1}$ for Cd; $7 \text{ mg}\cdot\text{kg}^{-1}$ for Cr; $8 \text{ mg}\cdot\text{kg}^{-1}$ for Cu; $5 \text{ mg}\cdot\text{kg}^{-1}$ for Ni; $13 \text{ mg}\cdot\text{kg}^{-1}$ for Pb; $51 \text{ mg}\cdot\text{kg}^{-1}$ for Zn.

Statistical analysis

The results obtained for HMs were analysed using basic descriptive statistics. Measures of central tendency (mean, median), dispersion (minimum, maximum, standard deviation, interquartile range, coefficient of variation), and distribution (skewness, kurtosis) were calculated. To visualize the distribution of the data, raincloud plots were prepared (Allen et al., 2021). The statistical significance of changes in HMs concentrations between March and June was analysed using the Wilcoxon signed-rank test (Wilcoxon, 1945).

In addition, principal component analysis (PCA) was performed to identify interrelationships among HMs as well as between HMs and sampling points. Prior to conducting PCA, the normality of the HM distributions was assessed using the W test (Shapiro-Wilk) at a significance level of $\alpha = 0.05$. The data did not exhibit a normal distribution, and due

to the right-skewed distribution of HMs in the analysed samples, the data were transformed using the Box-Cox method (Box & Cox, 1964). The Box-Cox transformation is used to transform variables so that their distribution after transformation is as approximate to normal as possible. The formula of the Box-Cox transformation is as follows:

$$c'_i = \begin{cases} \frac{(c_i + \alpha)^\lambda - 1}{\lambda}, & \text{if } \lambda \neq 0 \\ \log(c_i + \alpha), & \text{if } \lambda = 0 \end{cases}$$

where:

c_i – means original variable,

c'_i – is a transformed variable,

λ – means a primary transformation parameter and adopts values in a range from -5 to 5, and

α – is a parameter of moving variable.

The transformed data were subsequently standardized. In the PCA analysis, physico-chemical water parameters (pH, Eh, electrical conductivity, temperature) as well as LOI_{550} and pH_{KCl} were included as supplementary variables in the analysis of HMs in water and bottom sediments. Sampling points on the biplots were additionally characterized based on the parameters with the strongest influence on HM mobility. Statistical analyses were performed using Statistica 13.3 (TIBCO Software Inc., Palo Alto, CA, USA) and the R version 4.5.1 (R Core Team, 2025), with the use of the following packages: ggplot2 (Wickham, 2016), vegan (Oksanen et al., 2025), patchwork (Pedersen, 2025), ggsignif (Ahlmann-Eltze & Indrajeet, 2023), and gghalves (Tiedemann, 2022).

Results

Water composition characteristics

The conducted study indicates that the basic physico-chemical parameters measured in both March and June did not exhibit substantial spatial variability, as evidenced by the relatively low coefficients of variation compared to HMs (Tab. 1). Electrical conductivity and temperature were positively skewed in March,

Table 1. Results of statistical analysis for basic physico-chemical parameters and heavy metals in the waters of the Bogdanka River catchment area

Parameter	Temperature	Electrical conductivity	pH	Eh	Cd	Cr	Cu	Ni	Pb	Zn
Unit	°C	μS·cm ⁻¹	-	mV	μg·L ⁻¹					
Month	March 2024									
Minimum	7.61	402.0	6.30	64	0.021	0.09	1.87	0.35	1.12	3.82
Maximum	11.4	1316.0	7.69	311	0.337	2.45	12.2	4.21	19.2	82.3
Mean	8.49	688.6	7.34	208	0.090	0.49	5.41	1.60	4.13	21.9
Median	8.39	649.3	7.39	216	0.073	0.37	5.25	1.44	3.30	14.4
Standard deviation	0.78	198.2	0.30	61	0.069	0.48	2.64	0.93	3.61	19.2
Interquartile range	0.61	182.2	0.35	92	0.061	0.22	3.81	0.90	2.62	17.8
Skewness	2.20	1.55	-1.61	-0.51	2.02	3.25	0.67	1.16	2.97	2.14
Kurtosis	7.07	3.13	4.39	-0.18	5.20	11.3	0.24	1.35	11	4.89
Coefficient of variation (%)	9	29	4	29	77	99	49	58	87	88
Month	June 2024									
Minimum	13.1	282.3	6.50	-18	0.006	0.10	4.96	0.37	0.26	6.42
Maximum	20.1	1437.1	7.74	266	0.311	4.13	20.6	8.66	22.7	404.9
Mean	17.1	622.1	7.23	157	0.054	0.77	9.79	1.90	2.45	59.5
Median	17.5	603.0	7.27	176	0.026	0.45	8.75	1.25	1.15	23.1
Standard deviation	1.64	277.6	0.30	76	0.068	1.02	4.04	1.84	4.38	100.2
Interquartile range	2.11	349.6	0.43	101	0.038	0.54	5.48	1.49	1.54	41.9
Skewness	-0.84	-0.43	-1.82	-0.63	2.58	2.70	0.93	2.31	4.07	3.16
Kurtosis	0.84	-0.27	5.60	-0.49	7.21	7.12	0.46	6.12	18.1	9.45
Coefficient of variation (%)	10	45	4	48	125	133	41	97	179	168

whereas in June both parameters exhibited negative skewness. In March, the maximum electrical conductivity reached 1316 μS·cm⁻¹, with a mean value of 688.6 μS·cm⁻¹, whereas in June it amounted to 1437.1 μS·cm⁻¹ with a mean of 622.1 μS·cm⁻¹. Temperature ranged from 7.61 to 11.4°C in March and from 13.1 to 20.1°C in June. Both pH and Eh exhibited negative skewness in both sampling periods, with mean values of 7.34 for pH and 208 mV for Eh in March, and 7.23 for pH and 157 mV for Eh in June.

The results show that HM concentrations in the waters of the Bogdanka catchment followed a consistent ascending sequence of mean values in both March and June:

Cd < Cr < Ni < Pb < Cu < Zn (Tab. 1). Moreover, all HMs in both sampling periods exhibited positive skewness, which is further illustrated in the raincloud plots (Fig. 2), clearly showing prominent high outlier values. Seasonal variability assessed using the Wilcoxon signed-rank test demonstrated statistically significant changes in HM concentrations at specific points for Cd, Cu, and Pb. Although individual differences were also observed for Cr, Ni, and Zn, the Wilcoxon test indicated that these were not statistically significant ($p > 0.05$) across the study area and should be considered on a site-specific basis rather than as general trends (Fig. 2). It is also worth noting that Cd and Cu concentrations exhibited

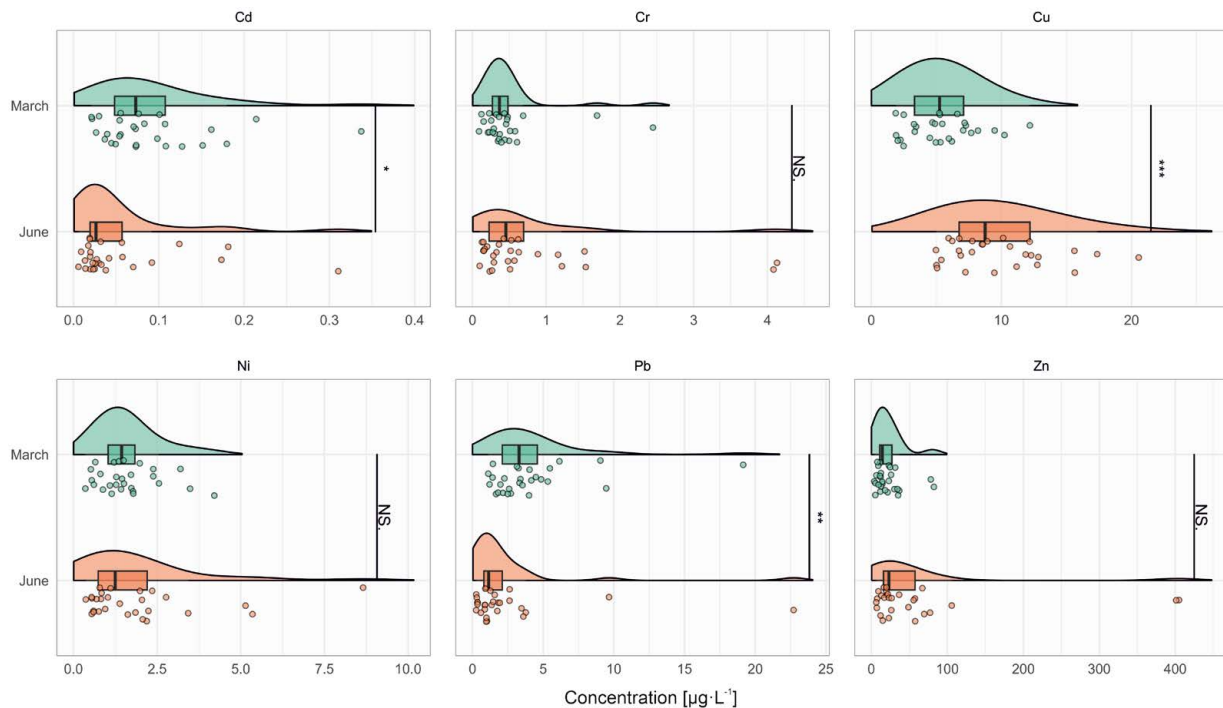


Figure 2. Raincloud showing the distribution of heavy metals in the waters of the Bogdanka River catchment and the results of the Wilcoxon signed-rank test, which indicate the statistical significance of differences in concentrations between the two sampling campaigns, where NS. is not significant ($p > 0.05$), * is significant ($p \leq 0.05$), ** is more significant ($p \leq 0.01$), and *** is highly significant ($p \leq 0.001$)

the greatest spatial variability (Fig. 2), with values ranging from 0.021-0.337 $\mu\text{g}\cdot\text{L}^{-1}$ for Cd and 1.87-12.2 $\mu\text{g}\cdot\text{L}^{-1}$ for Cu in March, and 0.006-0.311 $\mu\text{g}\cdot\text{L}^{-1}$ for Cd and 4.96-20.6 $\mu\text{g}\cdot\text{L}^{-1}$ for Cu in June. Detailed results of the statistical analysis are provided in Table 1.

Bottom sediments composition characteristics

The characteristics of the sediments (LOI_{550} and pH_{KCl}) exhibited distinct trends. Organic matter content showed high spatial variability in both sampling periods, expressed by the coefficient of variation, as well as strong positive skewness, with values ranging from 1.79 to 2.91 (Tab. 2). In contrast, sediment pH_{KCl} displayed low variability, with coefficients

of variation of 5% in both sampling periods, slightly positive skewness in March, and negative skewness in June. The mean pH_{KCl} values were 7.68 in March and 7.77 in June.

Unlike the patterns observed in the water, HM concentrations in the sediments could not be arranged into a consistent sequence across both sampling periods (Tab. 2). In March, the ascending sequence of mean concentrations was: $\text{Cd} < \text{Cr} < \text{Ni} < \text{Cu} < \text{Pb} < \text{Zn}$, whereas in June it was: $\text{Cd} < \text{Ni} < \text{Cr} < \text{Cu} < \text{Pb} < \text{Zn}$. Similar to the water samples, HMs in both sampling periods were characterized by positive skewness and the presence of distinct outliers with elevated concentrations, as illustrated by the raincloud plots (Fig. 3). Moreover, in contrast to the HMs in water, the Wilcoxon signed-rank test revealed that seasonal

Table 2. Results of statistical analysis of parameters characterizing bottom sediments and heavy metals in bottom sediments of the Bogdanka River catchment area

Parameter	LOI ₅₅₀	pH _{KCl}	Cd	Cr	Cu	Ni	Pb	Zn
Unit	%	-	mg·kg ⁻¹					
Month	March 2024							
Minimum	0.54	6.98	0.02	0.73	0.98	0.37	1.24	2.63
Maximum	74.3	8.46	0.49	18.3	38.1	58.1	33.5	152.3
Mean	14.0	7.68	0.10	4.30	8.15	5.08	9.74	43.7
Median	2.60	7.66	0.07	2.96	4.93	2.18	6.28	27.7
Standard deviation	21.2	0.36	0.10	4.20	8.34	10.9	8.47	46.1
Interquartile range	14.5	0.58	0.08	4.21	9.23	3.19	10.0	32.9
Skewness	1.79	0.17	2.70	1.95	2.05	4.63	1.42	1.52
Kurtosis	2.09	-0.67	8.97	3.79	5.04	22.8	1.26	1.01
Coefficient of variation (%)	152	5	101	98	102	214	87	106
Month	June 2024							
Minimum	0.31	6.42	0.02	0.54	0.99	0.29	1.15	1.28
Maximum	88.4	8.41	1.31	15.8	35.1	21.6	35.1	236.5
Mean	10.2	7.77	0.18	5.81	10.5	4.48	11.4	71.7
Median	1.47	7.71	0.12	4.52	6.98	3.59	9.19	51.7
Standard deviation	19.5	0.38	0.23	4.36	9.52	4.46	7.86	64.8
Interquartile range	8.21	0.38	0.08	7.26	11.3	4.09	10.3	74.7
Skewness	2.91	-1.36	4.56	0.91	1.27	2.48	1.28	1.20
Kurtosis	9.43	4.62	22.6	-0.02	0.81	7.73	1.73	0.83
Coefficient of variation (%)	192	5	133	75	90	100	69	90

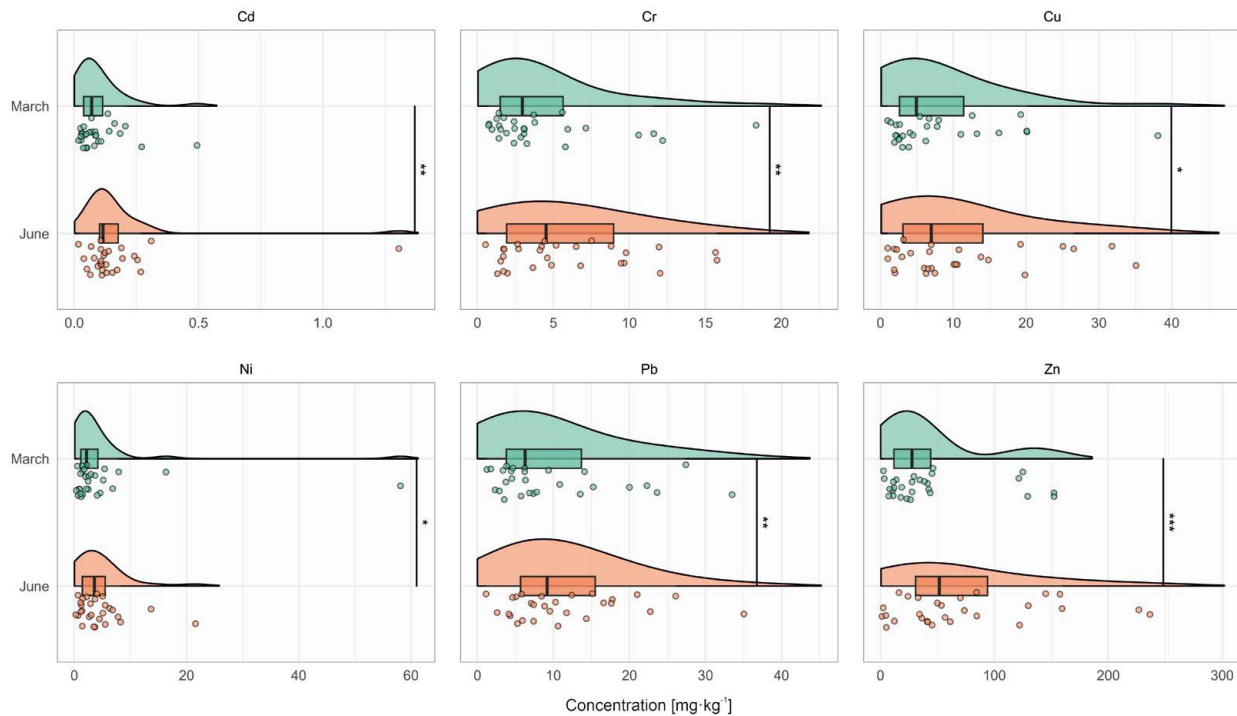


Figure 3. Raincloud showing the distribution of heavy metals in the bottom sediments of the Bogdanka River catchment and the results of the Wilcoxon signed-rank test, which indicate the statistical significance of differences in concentrations between the two sampling campaigns, where NS. is not significant ($p > 0.05$), * is significant ($p \leq 0.05$), ** is more significant ($p \leq 0.01$) and *** is highly significant ($p \leq 0.001$)

changes in concentrations for all analysed HMs were statistically significant ($p \leq 0.05$). The highest concentrations in the sediments were recorded for Zn, with maximum values of $152.3 \text{ mg}\cdot\text{kg}^{-1}$ in March and $236.5 \text{ mg}\cdot\text{kg}^{-1}$ in June.

Water pollution and toxicity assessment

The pollution assessment of water using the HMEI indicated that in March, sampling points B1, B2 and G1 were polluted, with HMEI values ranging from 1.15 to 1.65 (Fig. 4A). In June, pollution was detected at two points, with HMEI values of 1.75 at B7 and 2.73 at B9. No pollution was recorded at the remaining points, and detailed results are presented in Figure 4A. The HMEI results indicate that pollution varied between sampling periods and that the polluted sites were located throughout the catchment.

The toxicity assessment using the HMTL showed that in March no potentially toxic concentrations of HMs were found in the

water. However, in June, potentially toxic levels were observed at three locations (Fig. 4B). At points B7 and B9, the HMTL indicated high toxicity, and these were also identified as polluted based on the HMEI analysis. Additionally, moderate toxicity was recorded at point B4, for which the HMEI indicated no pollution with a value of 0.81 (Fig. 4B).

Bottom sediments pollution and toxicity assessment

The calculated I_{geo} for each HMs individually in the bottom sediments of the Bogdanka River catchment revealed that only for Cd no pollution was identified during both sampling periods (Fig. 5A). The highest I_{geo} value was recorded for Ni at point B15 in March, reaching 2.95, which classified the sample as moderately severe pollution. Moderate pollution levels were observed in individual samples for Cu, Ni, and Zn (Fig. 5A). Cr and Pb reached, at most, the level of minor pollution. Most of the detected sediment pollution was concentrated in the lower course of the Bogdanka

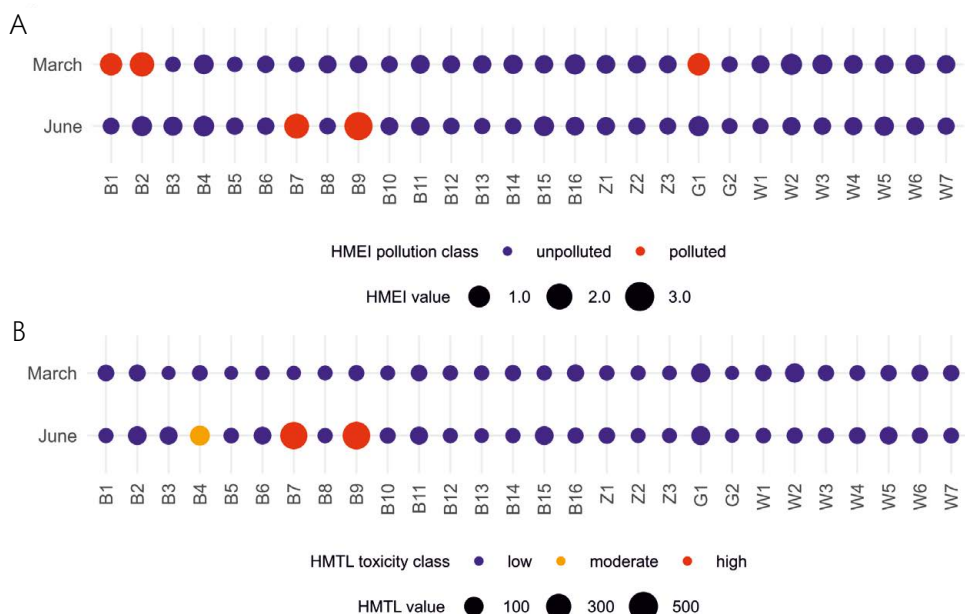


Figure 4. Results of the heavy metal evaluation index (HMEI) and heavy metal toxicity load (HMTL) for heavy metals in water at individual sampling sites in the Bogdanka River catchment area

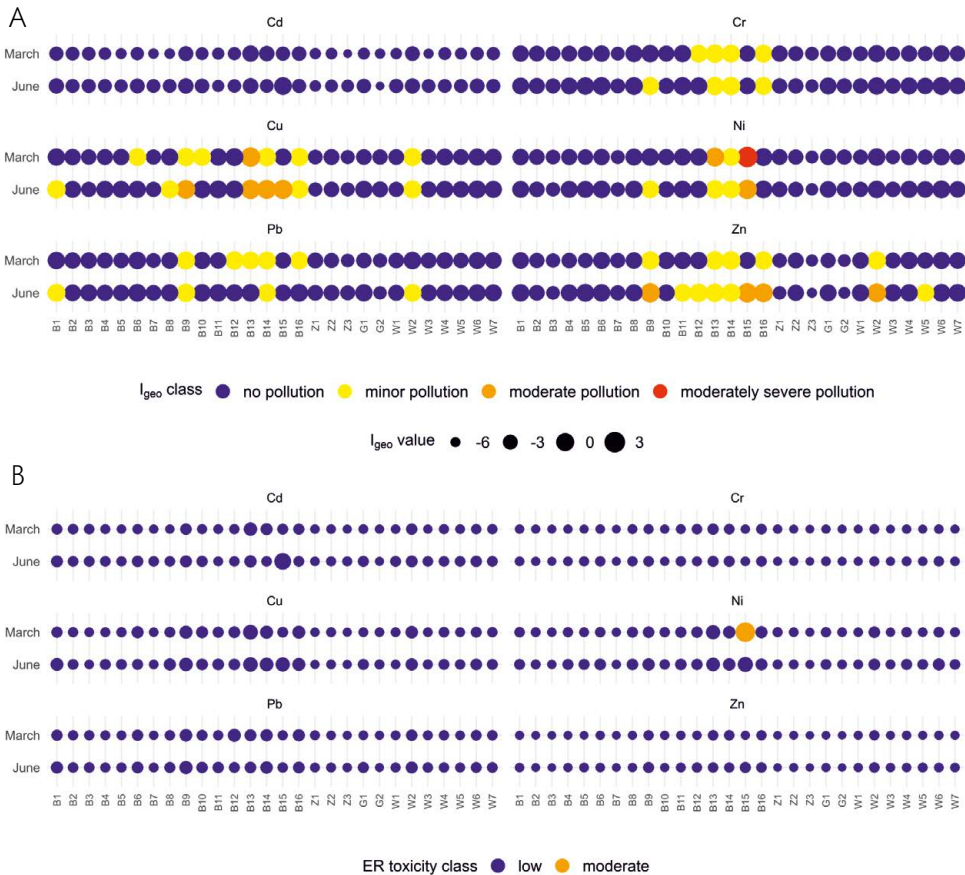


Figure 5. Results of the geoaccumulation index (I_{geo}) and ecological risk index (ER) for individual heavy metals in bottom sediments at sampling sites of the Bogdanka River catchment area

River (points B9 and B11-B16) near the storm-water drainage system (Fig. 1) and at point W2. Additionally, pollution was detected in March at points B10 and B6 for Cu, and in June at point B1 for Cu and Pb, at W2 for Zn, and at B8 for Cu.

The toxicological analysis using ER for individual HMs indicated that only at point B15 for Ni in March was potential moderate toxicity identified (Fig. 5B), which corresponds with the highest I_{geo} value at the same point. The remaining points were characterized by potential low toxicity, with detailed results presented in Figure 5B.

The calculated PLI values allowed for the description of overall HM pollution at

individual sampling points. In March, pollution was detected at points B9, B13, B14 and B16 (Fig. 5A), with PLI values ranging from 1.19 to 2.13. These points are located near the inflows of stormwater drainage systems in the lower course of the Bogdanka River (Fig. 1). In June, PLI also indicated pollution in the bottom sediments at points B9, B13, B14 and B16, as well as additionally at B15 and W2. No pollution was identified at the remaining points, and detailed results are presented in Figure 6A.

The calculated PERI and TRI values, describing the potential toxicity of deposited HMs in the bottom sediments, showed no toxicity at any of the points. The highest PERI

value was recorded at point B15, with values of 82 in March and 94 in June. The highest TRI value was identified in March at point B13 with a value of 3.44, and in June at point B15 with a value of 2.88. Detailed results for PERI and TRI are provided in Figure 6B and 6C, respectively.

Principal component analysis

The PCA analysis of HMs in the waters of the Bogdanka River catchment explained 70.3% of the data variance for PC1 and 13.5% for

PC2 in March, and 65.4% for PC1 and 16% for PC2 in June. The data analyzed in March indicated a strong correlation between the pairs Pb-Cd, Cr-Zn, and Cu-Ni (Fig. 7A). In addition, a positive correlation of Eh with the Pb-Cd pair was observed. The pH showed a weaker correlation with the Cd-Pb pair and a negative correlation with the Cu-Ni pair along the PC2 axis.

The PCA analysis of HMs in the waters of the studied catchment in June indicated a strong correlation among Cd, Cr, Ni, Pb, and Zn, whereas Cu displayed a slightly

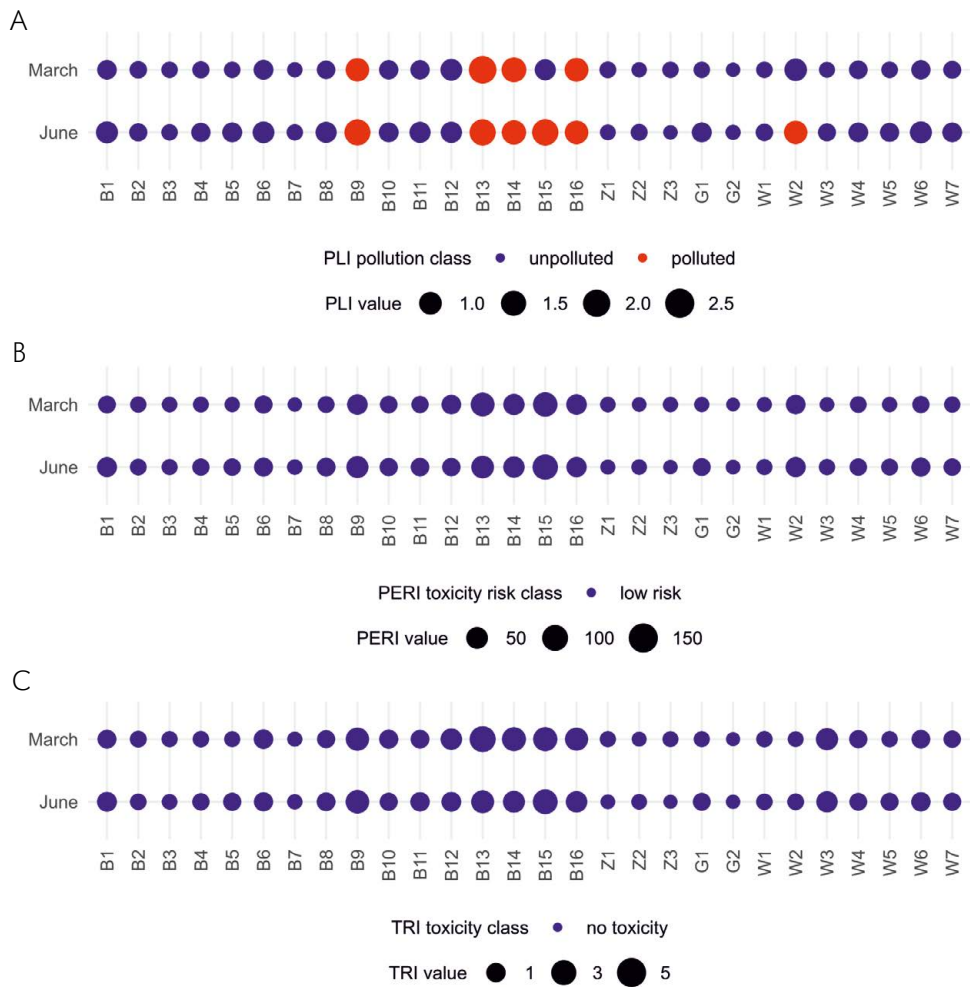


Figure 6. Results of integrated pollution and toxicity indices at individual sampling sites in the Bogdanka River catchment area: pollution load index(PLI), potential ecological risk index(PERI) and toxic risk index(TRI)

Discussion

Studies indicate that stormwater drainage systems represent a significant source of HMs pollution (Barańkiewicz et al., 2014; Stokół et al., 2018). This is also confirmed by the results obtained in the Bogdanka River catchment, particularly the contamination of bottom sediments at sites B9, B13, B14, B15, and B16, as demonstrated by the calculated PLI index (Fig. 6A). Sites B13, B14, B15, and B16 are located in the lower course of the Bogdanka River, where stormwater drainage systems discharge runoff from urbanized areas (Fig. 8A, B), while site B9 is situated at the outlet of a stormwater collector draining runoff from areas located southwest of the Bogdanka River (Fig. 8C). The study by Selbig et al. (2013) showed that HMs are also associated with fine particle fractions that are not retained in stormwater sedimentation tanks and can be transported with runoff into urban rivers. This is particularly important

in the case of road traffic-related dust, which represents one of the main sources of HMs in surface runoff reaching urban rivers (Wardas et al., 2010). Research by Ciążła & Siepak (2016) and Gałuszka & Migaszewski (2025) further confirmed that traffic-related HMs are present in the < 0.063 mm fraction.

General HMs contamination was also observed in bottom sediments in June at site W2, where sediment inflow from a construction site of a residential housing estate was recorded during sampling (Fig. 8D). Dust and building materials may constitute a significant source of HMs, particularly in the summer period, due to intensified thermal erosion (Müller et al., 2019; Yang et al., 2020), while construction activity additionally enhances soil erosion (Taylor & Owens, 2009), consequently leading to intensified sediment redeposition. As a result, areas located in the immediate vicinity of construction sites are particularly exposed to HMs input.



Figure 8. Selected points identified as polluted with heavy metals in bottom sediments: B13 (A), B15 (B), B9 (C) and W2 (D)

PCA analysis of bottom sediments confirmed the correlation of sites B9, B13, B14, B15, and B16 (Fig. 7C, D) with HMs in the Bogdanka River catchment. In addition, for most HMs (except Cd), this relationship was also confirmed by I_{geo} analysis (Fig. 5A). The study by Barańkiewicz et al. (2014) on the Cybina River in Poznań demonstrated that surface runoff from industrial and service areas is associated with the presence of HMs such as Cd, Ni, Pb, and Zn. Taka et al. (2022), based on observations from six catchments in Finland, identified Cu and Zn as well as Cr as the dominant HMs in urban runoff. Furthermore, the study by Decena et al. (2018) on the Mangonbangon River (Tacloban City, Philippines) and Pimiento et al. (2023) on the Molinos and Arzobispo rivers (Bogotá, Colombia) clearly indicated the highest bottom sediment contamination in small urban rivers by Cu and Zn on the basis of I_{geo} , which is consistent with the results obtained in the Bogdanka River catchment, where these HMs were most frequently classified as showing moderate contamination (Fig. 5A).

It is also worth noting that I_{geo} analysis for Cd did not indicate contamination at any site, and the Cd concentrations obtained in bottom sediments are lower than, for example, in Kraków (Aleksander-Kwaterczak & Plenzler, 2019) and Riga (Sprinže et al., 2024). Moreover, it should be emphasized that the dominant HMs (Zn, Pb, and Cu) in bottom sediments exhibit a distribution clearly different from that observed in small urban rivers in developing countries (Islam et al., 2015; Ali et al., 2022). It should also be stressed that the applied toxicity indices (ER, PERI, TRI) indicate no toxicity of the deposited HMs in bottom sediments. Only at site B15, during the winter period, was a moderate toxic potential of Ni recorded according to ER, which is most likely related to the incidental inflow of a large amount of pollution.

Studies on HMs in the waters of the Bogdanka River catchment revealed considerable spatial and seasonal variability of sites with detected contamination, expressed by the HMEI index (Fig. 4A), as well as the absence

of correlation between these sites and individual HMs in PCA analysis (Fig. 7A, B). Earlier research by Borowiak et al. (2016) on Cd and Pb in Bogdanka waters showed that their concentrations differ significantly throughout the year. This results from the fact that transformed catchments of small urban rivers are highly susceptible to the first flush phenomenon, i.e., the washing out of HMs accumulated on impervious surfaces during the first rainfall following a longer dry period (Lee et al., 2004; Joshi & Balasubramanian, 2010). In addition, Bełcik et al. (2024) demonstrated that in the winter season, HMs accumulate in the snow cover and are intensively released during snowmelt. The amount of HMs in surface runoff also depends on the area from which they are washed (Li et al., 2012; Teixidó et al., 2023). All these factors, together with random events (such as wastewater discharges, hazardous substance spills, etc.), contribute to considerable temporal variability of HMs concentrations throughout the year.

Nevertheless, it should be emphasized that the Wilcoxon signed-rank test for HMs in the waters of the Bogdanka River catchment indicated no statistically significant changes for Cr, Ni, and Zn (Fig. 2), which contrasts with the results for bottom sediments, where all HMs showed significant differences between seasons (Fig. 3). This may be due, on the one hand, to the presence of numerous water reservoirs through which the Bogdanka River flows (Fig. 1, Borowiak et al., 2016), which may stabilize water chemistry and retain pollutants (e.g., Sojka et al., 2018a; Śniady et al., 2024b). On the other hand, seasonal changes in the physico-chemical parameters of water (Tab. 1), such as pH, Eh, and temperature, may in the long term affect the remobilization or binding of HMs in bottom sediments (Linnik et al., 2023ab).

It should be stressed, however, that PCA analysis revealed in March a positive correlation of Eh with HMs, while in June a negative correlation (Fig. 7A, B). Such a relationship may indicate that in March the HMs supply from the analysed catchment was relatively fresh, while in June remobilization

of HMs from bottom sediments could occur under weakly reducing conditions (Linnik et al., 2023a). This thesis may be additionally supported by the decrease in mean Eh values from 208 mV in March to 157 mV in June (Tab. 1).

Furthermore, PCA analysis of bottom sediments confirmed that HMs in bottom sediments are positively correlated with organic matter (LOI_{550}) and negatively with pH_{KCl} of the bottom sediments (Fig. 7C, D). In particular, the positive correlation of HMs with organic matter, which can bind HMs in bottom sediments, is relatively well documented, with similar relationships reported by Jung (2017), Sojka et al. (2018b), and Bartoszek et al. (2022). The negative correlation of pH_{KCl} in bottom sediments confirms the well-known fact that lower pH promotes HMs mobility in bottom sediments and constitutes an important factor controlling HMs mobility in sediments (e.g., Calmano et al., 1993; Linnik et al., 2023b). The study of the relationship between pH_{KCl} in river and reservoir bottom sediments and heavy metals has, however, not been frequently undertaken, with such analyses conducted, among others, by Baran & Tarnawski (2015).

Conclusions

The study conducted in the Bogdanka River catchment, involving the analysis of HM concentrations in water and bottom sediments during two sampling periods (March and June), allowed for the following conclusions to be drawn:

1. HM concentrations in the Bogdanka River catchment varied seasonally, and the Wilcoxon signed-rank test analysis showed that changes in HMs concentrations in water were significant for Cd, Cu, and Pb, while in bottom sediments they were significant for all analyzed HMs.
2. The results obtained using pollution (HMEI) and toxicity (HMTL) indices for HMs in water indicated incidental contamination and toxicity at individual sampling sites, which varied seasonally and do not represent a significant threat.

3. The analysis based on I_{geo} for HMs in bottom sediments demonstrated that storm-water drainage inflows are the main source of contamination in the catchment, which was further confirmed by PCA.
4. The calculated toxicity indices for HMs in bottom sediments (ER, PERI, TRI) indicated no toxicity of the deposited HMs, except for one site in the winter period, where Ni contamination was detected.
5. The key factors controlling the content of HMs in bottom sediments were the organic matter content, which showed a positive correlation with HMs, and the pH_{KCl} of bottom sediments, which showed a negative correlation with HMs.
6. The results obtained may serve as a valuable source of information for decision-makers and researchers involved in spatial planning.

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Authors' contribution

- I. Śniady: Conceptualization, Data Curation, Formal analysis, Investigation, Methodology, Resources, Visualization, Writing – Original Draft, Writing – Review & Editing;
 I. Stryniak: Conceptualization, Funding acquisition, Investigation, Project administration, Resources, Visualization, Writing – Review & Editing;
 J. Szponar: Investigation, Visualization;
 M. Siepak: Conceptualization, Methodology, Supervision, Validation, Writing – Review & Editing.

Editors' note:

Unless otherwise stated, the sources of tables and figures are the authors', on the basis of their own research.

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