Relationship between selected pollution indicators of stormwater from urban catchments

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ABSTRACT

The article presents the results of studies on stormwater quality in two urban catchments located in Kielce, differing in the area and land use. Precipitation water samples were taken in stormwater drainage during runoff events in order to determine concentrations of the following heavy metals (HM): Cd, Cu, Cr, Ni, Pb, Zn, Co, Mn, Fe, as well as the concentration of total suspended solids (TSS) and total organic carbon (TOC). Completed analyses proved that maximum TSS and TOC concentrations were higher in the Jesionowa stormwater treatment plant (SWTP) catchment (10,621 and 71.6 mg dm$^{-3}$, respectively) compared to the Witosa SWTP catchment (627 and 21.9 mg dm$^{-3}$, respectively). The analysis of the values of mean concentrations of HMs (the ANOVA test) shows that a substantially higher mean value of Cu concentration (0.133 mg dm$^{-3}$) was found only for the Jesionowa SWTP. For the sake of comparison, in stormwater flowing from the catchment of the Witosa SWTP, this value was 0.029 mg dm$^{-3}$. The lack of statistically significant differences between the mean values of the indices of concern may reveal similarities between factors that determine deposition processes and pollutant wash-out in the catchments examined. The modified contamination index ($mC_d$), calculated in the study, allows a statement that for both catchments, stormwater is very highly contaminated with respect to HMs. That is confirmed by the enrichment factors, that attribute the category extremely severe enrichment or severe enrichment for Cd (Witosa/Jesionowa), severe enrichment for Zn (Witosa) and moderately severe enrichment for Pb, Ni and Cr (both facilities). The principal component analysis was applied to assess the correlation between the analyzed pollution indices. For the Jesionowa catchment, the occurrence of strong positive relationships was found between Ni, Co, Mn, Cu and Zn. As regards the other catchment, a single strongly correlated group of HMs (Cu, Pb, Zn, Co, Mn, Fe) and TSS ($r = 0.65-0.94$) was observed. That may indicate a major TSS role in the transport of the pollutants examined, whereas the rate of their wash-out depends on the hydrological conditions prevailing in the catchment (precipitation intensity).

Keywords: Stormwater; Heavy metals; Total suspended solids; Principal component analysis; Urban catchment

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1. Introduction

Control of precipitation water is one of the more important determinants for effective water management within catchments. Considerable pollution of stormwater carried away from urban areas has a decisive influence on temporary water quality deterioration, and it destabilizes biological balance in the receiving water. Particular attention should be given to heavy metals (HM) concentration in precipitation waters due to their bioaccumulation in plants and organisms, as well as in sediments accumulating in stormwater treatment plant (SWTP) facilities. HMs appear most often in stormwater as dissolved salts, ions or undissolved compounds [1]. Field analyses of stormwater quality carried out in urbanized catchments [2–5] show considerable diversity in concentrations of individual pollutants contained in them. They most often originate from street traffic (wear of vehicle parts, including tires and brake shoes, petrol leaks, exhaust gas, corrosion of metallic and galvanized surfaces, road surface abrasion), atmosphere (dust and suspended particles contained in it), and to a lesser extent green spaces (fertilizers, insecticides and fungicides). The primary factors that influence pollution indices include season, the location of the land, land surface type and humidity, wind velocity, precipitation characteristics, rain front movement direction, and vehicular traffic volume [6–9]. These factors determine the content of total suspended solids (TSS) and HM accumulated and washed out from the catchment surface. The studies carried out in Poland and abroad [10–17] show that TSS and HM concentrations in stormwater flowing out of urban catchments change very considerably, even if the areas are used in much the same way. This observation allows putting forward a thesis that it is not possible to find a typical constitution of storm and thaw waters. A lot of practical information on the process of accumulation of HM and volatile organic compounds can be found in the study of Mahbub at al. [18]. The authors analyzed road surfaces in catchments (single-family housing, industrial areas and city centers) in the south-eastern part of Queensland State in Australia. Among other issues, the studies covered the following: concentrations of HM (Ni, Al, Mn, Cu, Zn, Cd, Cr), total and dissolved organic carbon (TOC and DOC), particle size distribution (PSD), pH, electrical conductivity, average daily traffic (ADT), total and dissolved suspended solid (TSS and TDS). The principal component analysis (PCA) was applied to interpret the obtained results. The analysis confirmed the substantial impact of PSD on the relationship between ADT and the analyzed pollutants. Moreover, it has been observed that land use has no effect on the process of accumulation of the analyzed pollutants on road surfaces [18]. On the other hand, in case of road catchments (sized 0.392–1.280 ha) located in the USA, the studies carried out by Stenstrom and Kayhanian [19] proved strong correlations between concentrations of the selected HMs (Cu and Ni, Pb and Zn, Cd and Zn, Ni and Cr) and chemical oxygen demand values, and concentrations of total Kjeldahl nitrogen and total phosphorus (TP). The changes in pollution concentrations during the deposition and washing out processes were also analyzed by Wicke et al. [9], although these studies were limited to car park areas only. The researchers proved strong dependence between HM (Zn, Cu, Pb) content and TSS deposited on different car park surfaces and dry period duration.

The aim of this paper is to specify the relationship between concentrations of HMs (Cd, Cu, Cr, Ni, Pb, Zn, Co, Mn and Fe), TSS and TOC in stormwater with the use of PCA. The ranges of variation of individual pollutant indices were also discussed. The degree of stormwater pollution with HMs was specified for two urban catchments showing different land use.

2. Materials and methods

2.1. Study area

The investigations into stormwater quality and quantity were conducted for two urban catchments in the city of Kielce, Poland (Fig. 1). In the catchments, which differ in land use, five characteristic surface types with respect to runoff were identified (Table 1): asphalt and gravel road surfaces, roofs, car parks and green spaces. The first catchment, having a total area of 83 ha, is located on the outskirts of the city. On the east, and partially north side, the catchment is surrounded by an open ditch collecting stormwater flowing from a dense forest area. The ditch turns into a ø 800 mm closed sewer which is connected to sewer conveying the effluent from the Witosa SWTP – Fig. 1b. All the stormwater is piped (ø 1.4 m) to the receiving water of the River Silnica. Land development includes primarily one- and multi-family housing and the share of impervious surfaces is 25.9% of the total catchment area (Table 1). The highest point in the catchment is 365.5 m a.s.l., and the lowest is 291.25 m a.s.l. The average slope of the land is 8.2% [20].

The second catchment belonging to the Jesionowa SWTP (Fig. 1c) covers a much larger area (A = 400 ha). It is located in the north-western part of Kielce and includes highly urbanized areas. The catchment land use is dominated by industrial zones with large commercial buildings and low residential buildings. As a result, the share of impervious surfaces is 42.4% (169.6 ha). The highest point in the catchment is 315 m a.s.l., and the lowest is 25.9 m a.s.l. The average slope of the land is 2.68%.

In the analyzed catchments, a separate sewage system is used, in which drains collect stormwater and sanitary wastewater is carried by sewers.

2.2. Measurement apparatus

Measurement apparatus was installed in sewer chambers built in inflow channels entering individual SWTPs. Stormwater samples were taken using automatic samplers ISCO 6712 from Teledyne ISCO (Lincoln, NE, USA), complying with requirements of the United States Environmental Protection Agency (EPA). The instruments were configured so as to allow their activation immediately after exceeding the pre-set stormwater level in the channel (5–8 cm), recorded by channel filling probe. Sample taking frequency (24 max.) was determined individually (every 5–30 min), depending on the predicted rainfall duration.

Modular flowmeters ISCO AV 2150 from Teledyne ISCO (Lincoln, NE, USA) were used to measure stormwater volume. Their operation is based on the measurement of water-column pressure and mean flow velocity in the channel, recorded by the AV probe. The measurement frequency during the peak runoff event ranged 15–30 s, and prior to the event 1–5 min, depending on the instrument setup.
It was possible to find the relation between stormwater volume and the volume and progress of precipitations through the analysis of data recorded by a tipping-bucket rain gauge, RG50 type, from SEBA Hydrometrie GmBH (Kaufbeuren, Germany) (Fig. 1a). The measurement frequency was 1 min for 0.1 mm resolution.

2.3. Stormwater quality analysis

Unstabilized samples were immediately transported to a chemical laboratory in order to determine the following quality indicators, that is, pH, HM (Cd, Cu, Cr, Ni, Pb, Zn, Co, Mn, and Fe), TSS and TOC. The pH value was measured...
in accordance with the PN-EN ISO 10523:2012 method using SevenMulti™ meter (Mettler Toledo, Greifensee, Switzerland) [21]. Samples were digested in nitric acid using a microwave oven (Multiwave 3000, Anton Paar, Graz, Austria). Concentrations of HM were determined by atomic emission spectrometry with inductively coupled plasma ICP Optima 8000 from Perkin Elmer (Waltham, Massachusetts, USA) with certified multi-element standards (Perkin Elmer, Waltham, Massachusetts, USA) [22]. The TSS determination was performed according to the PN-EN 872:2007 standard [23]. The TOC was determined according to the PN-EN 1484:1999 [24].

2.4. Assessment of HM stormwater pollution

In order to evaluate the level of stormwater pollution with HMs, the following indicators were employed:

- Contamination factor (Cf) [25,26], which expresses the ratio of the content of a given element in the water sample (Cn) to the background value, or the reference value (Cef) (the content of a given element in an unpolluted sample):

\[
C_f = \frac{C_n}{C_{ef}}
\]  

(1)

The factor values are interpreted as follows [26]: 
- Cf < 1 – low contamination factor, 1 ≤ Cf < 3 – moderate contamination factors, 3 ≤ Cf < 6 – considerable contamination factors and Cf ≥ 6 – very high contamination factor.

- Contamination index (Cc), used by many researchers for the assessment of the quality of water or wastewater [25,27], is determined based on the equation:

\[
Cc = \sum_{i=1}^{n} C_{f_i}
\]  

(2)

where \(C_f\) – contamination index for an individual HM.

The degree of contamination can be described as follows [25,27]: 
- \(C_c < 1\) – low contamination, \(1 < C_c < 3\) – medium contamination and \(C_c > 3\) – high contamination.

The modified version of Eq. (2), developed by Abraham and Parker in their study [28] for the description of the overall degree of pollution, goes as follows [27]:

\[
mC_c = \frac{\sum_{i=1}^{n} C_{f_i}}{n}
\]  

(3)

where \(n\) – number of elements examined.

The values of \(mC_c\) fall into five categories [27,28]: 
- \(1.5 < mC_c < 2\) – low contamination, \(2 < mC_c < 4\) – moderate contamination, \(4 < mC_c < 8\) – high contamination, \(8 < mC_c < 16\) – very high contamination, \(mC_c > 16\) – extremely high degree of contamination.

- Enrichment factors (EF) were developed to speculate about the origin of HMs in the atmosphere or precipitation [29]. The factor application was extended to include other components of the natural environment [30]. The EF is calculated from the equation:

\[
EF = \frac{C_{ef,\text{sample}}}{C_{ef,\text{dual}}}
\]  

(4)

where \(C_e\) and \(C_{ef}\) – contents of individual HMs and iron in the examined stormwater samples and in the geochemical background.

The factor values EF ≤ 1.0 indicate the lithogenic origin of a given HM, whereas the values EF > 1.0 show anthropogenic enrichment of stormwater with HM [31] (Table 2).

2.5. Data analysis

During the first stage of analyses of the obtained pollution index values, their ranges (minimum and maximum) were determined for particular runoff events, as well as mean values and medians for individual catchments (Table 3). Then, they were compared with the results of studies from other urbanized catchments [1,14,32–39]. Later, box plots were developed (Figs. 2 and 3), presenting ranges of non-outliers, median, and lower and upper quartile (25% and 75%).

In order to compare the mean values of pollutant indicators, the variance analysis was carried out (ANOVA), which was preceded by the Brown–Forsythe variance homogeneity test. For statistically significant ANOVA results, the Tukey’s multiple comparisons (for different N) was used. When the assumption on variance homogeneity was not satisfied, the non-parametric Kruskal–Wallis test was performed. Variance analyses were preceded by the tests of normality of distribution of the variables of concern (the Shapiro–Wilk test). When the distribution of a given feature did not comply with normal distribution, the Box–Cox transformation was performed [40].

In the next step, the PCA was applied to evaluate the dependencies between individual variables. It is a method used to reduce the multi-dimensionality of data containing a considerable volume of correlated variables. The reduction is achieved through the transformation of input data to new variables (principal components), which are orthogonal (uncorrelated). The dimensionality reduction in the space of properties, and ordering them into subsets (principal

<table>
<thead>
<tr>
<th>EF classes</th>
<th>Stormwater quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>No enrichment</td>
</tr>
<tr>
<td>&lt;3</td>
<td>Minor enrichment</td>
</tr>
<tr>
<td>3–5</td>
<td>Moderate enrichment</td>
</tr>
<tr>
<td>5–10</td>
<td>Moderately severe enrichment</td>
</tr>
<tr>
<td>10–25</td>
<td>Severe enrichment</td>
</tr>
<tr>
<td>25–50</td>
<td>Extremely severe enrichment</td>
</tr>
</tbody>
</table>
Table 3

Statistics characterizing concentrations of selected stormwater pollution indices

<table>
<thead>
<tr>
<th>Event number</th>
<th>TSS (mg dm⁻³)</th>
<th>TOC (mg dm⁻³)</th>
<th>Cd (mg dm⁻³)</th>
<th>Cu (mg dm⁻³)</th>
<th>Cr (mg dm⁻³)</th>
<th>Ni (mg dm⁻³)</th>
<th>Pb (mg dm⁻³)</th>
<th>Zn (mg dm⁻³)</th>
<th>Co (mg dm⁻³)</th>
<th>Mn (mg dm⁻³)</th>
<th>Fe (mg dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range (Jesionowa SWTP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J1</td>
<td>295–844</td>
<td>17.9–22.3</td>
<td>0.010–0.127</td>
<td>0.107–0.200</td>
<td>0.102–0.143</td>
<td>0.080–0.095</td>
<td>0.032–0.487</td>
<td>0.084–1.560</td>
<td>0.005–0.010</td>
<td>0.681–2.151</td>
<td>8.10–22.26</td>
</tr>
<tr>
<td>J2</td>
<td>315–10,621</td>
<td>32.7–71.6</td>
<td>0.001–0.009</td>
<td>0.047–0.405</td>
<td>0.096–0.910</td>
<td>0.076–0.304</td>
<td>0.019–0.425</td>
<td>0.483–3.542</td>
<td>0.004–0.232</td>
<td>0.988–9.434</td>
<td>3.51–74.80</td>
</tr>
<tr>
<td>J3</td>
<td>47–286</td>
<td>39.6–49.0</td>
<td>0.000–0.089</td>
<td>0.044–0.145</td>
<td>0.021–0.236</td>
<td>0.014–0.097</td>
<td>0.013–0.152</td>
<td>0.319–1.266</td>
<td>0.004–0.008</td>
<td>0.199–1.098</td>
<td>1.67–9.96</td>
</tr>
<tr>
<td>J4</td>
<td>35–827</td>
<td>38.9–49.0</td>
<td>0.002–0.469</td>
<td>0.057–0.660</td>
<td>0.140–0.872</td>
<td>0.056–0.108</td>
<td>0.039–0.758</td>
<td>0.007–3.064</td>
<td>0.004–0.015</td>
<td>0.352–2.174</td>
<td>5.15–23.79</td>
</tr>
<tr>
<td>J5</td>
<td>60–1,829</td>
<td>14.4–54.1</td>
<td>0.004–0.150</td>
<td>0.005–0.300</td>
<td>0.009–0.950</td>
<td>0.006–0.083</td>
<td>0.010–0.520</td>
<td>0.469–5.731</td>
<td>0.001–0.030</td>
<td>0.031–3.718</td>
<td>5.06–63.14</td>
</tr>
<tr>
<td>Mean</td>
<td>1,089</td>
<td>35.7</td>
<td>0.014</td>
<td>0.134</td>
<td>0.162</td>
<td>0.074</td>
<td>0.168</td>
<td>1.144</td>
<td>0.011</td>
<td>1.313</td>
<td>15.31</td>
</tr>
<tr>
<td>Median</td>
<td>315</td>
<td>38.4</td>
<td>0.007</td>
<td>0.006</td>
<td>0.009</td>
<td>0.007</td>
<td>0.013</td>
<td>0.844</td>
<td>0.007</td>
<td>0.912</td>
<td>9.91</td>
</tr>
<tr>
<td>S.D.</td>
<td>1,857</td>
<td>12.3</td>
<td>0.050</td>
<td>0.112</td>
<td>0.175</td>
<td>0.038</td>
<td>0.162</td>
<td>1.044</td>
<td>0.024</td>
<td>1.426</td>
<td>14.15</td>
</tr>
</tbody>
</table>

Range (Witosa SWTP)

| W1 | 177–384 | – | 0.005–0.007 | 0.069–0.106 | 0.100–0.115 | 0.079–0.151 | 0.064–0.184 | 1.023–2.370 | 0.001–0.008 | 0.210–2.092 | 3.82–24.08 |
| W2 | 168–627 | 5.4–11.7 | 0.005–0.008 | 0.009–0.149 | 0.085–0.135 | 0.056–0.135 | 0.040–0.171 | 0.445–1.413 | 0.002–0.008 | 0.277–1.255 | 5.24–19.33 |
| W3 | 65–303 | 11.6–21.9 | 0.006–0.068 | 0.005–0.031 | 0.012–2.723 | 0.015–0.087 | 0.027–0.108 | 0.537–1.267 | 0.001–0.005 | 0.275–1.150 | 3.03–18.40 |
| W4 | 38–611 | 1.6–10.5 | 0.013–0.139 | 0.003–0.262 | 0.013–0.193 | 0.008–0.207 | 0.038–0.190 | 0.319–3.160 | 0.001–0.021 | 0.147–1.909 | 1.75–20.54 |
| Mean | 230 | 10.7 | 0.019 | 0.049 | 0.134 | 0.043 | 0.101 | 0.970 | 0.004 | 0.578 | 7.48 |
| Median | 176 | 10.5 | 0.017 | 0.024 | 0.085 | 0.017 | 0.103 | 0.718 | 0.003 | 0.418 | 5.36 |
| S.D. | 156 | 4.8 | 0.022 | 0.054 | 0.412 | 0.037 | 0.045 | 0.703 | 0.004 | 0.464 | 5.44 |

Other researchers

<table>
<thead>
<tr>
<th>Source</th>
<th>Range (Witosa SWTP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1] 10–40,000</td>
<td>– 0.006–0.009 0.050–0.800 0.010–0.600 0.010–0.080 0.100–2.000 0.200–6.000 – – –</td>
</tr>
<tr>
<td>[32] 64–794</td>
<td>– – 0.023–0.320 – – 0.010–0.126 0.041–1.057 – – –</td>
</tr>
<tr>
<td>[33] 119–254</td>
<td>89.0–164 – 0.054–0.124 – – 0.015–0.042 0.128–0.500 – – –</td>
</tr>
<tr>
<td>[34] 11.0–430</td>
<td>– 0.007–0.008 0.030–0.220 &lt;0.01–0.045 &lt;0.01–0.129 0.130–0.520 – – –</td>
</tr>
<tr>
<td>[35] 189–4,820</td>
<td>0.008–0.009 0.067–1.820 0.074–1.350 0.003–0.010 0.003–0.006 0.284–6.200 4.5–112.8</td>
</tr>
<tr>
<td>[36a] 50–348</td>
<td>– – 0.011–0.059 0.002–0.032 0.027 – 0.001–0.033 0.042–0.261 – – –</td>
</tr>
<tr>
<td>[36b] 103–450</td>
<td>– – 0.002–7.861 – – 0.0–0.108 0.005–2.369 – – –</td>
</tr>
<tr>
<td>[37a] 103–450</td>
<td>109–408 0.006–0.008 0.010–0.250 0.002–0.095 0.011–0.037 0.012–0.427 0.390–4.400 – – –</td>
</tr>
<tr>
<td>[38] 12–1,400</td>
<td>– – 0.009–0.110 0.001–0.020 0.003–0.040 0–0.035 0.043–0.690 – – –</td>
</tr>
<tr>
<td>[39] 29–3,359</td>
<td>13–33.0 – 0–0.656 0–0.222 0–0.125 0–0.098 0–1.937 0–0.100 0.001–2.088 –</td>
</tr>
</tbody>
</table>

Range concerns average values from different types of surfaces (city center, roads, highways, industrial, commercial, residential areas);

Range concerns the mean values of 11 rainfall events;

S.D. – standard deviation.
Fig. 2. Box plot of HM concentration for the studied rainfall-runoff events.
components) is useful – mainly due to the possibility to interpret the relationships between components, graphical presentation of comparable variables configuration, and at last – ordering these variables according to the selected properties. PCA is a method commonly used to analyze qualitative and quantitative data [41,42].

3. Results and discussion

The studies covered 9 runoff events, observed between April and June 2018. In the Jesionowa SWTP catchment, the analysis included 5 rainfall events (J1–J5), and in the Witosa SWTP catchment – 4 rainfall events (W1–W4) – Table 3. During the occurrence of runoff events, the number of collected stormwater samples ranged from 8 to 24 (for a single event). In total, 94 samples from the Jesionowa SWTP catchment and 41 samples from the SWTP Witosa catchment were subjected to laboratory tests. The maximum stormwater flows in inflow channels entering both SWTPs were: 4.53 and 0.5 m³ s⁻¹, respectively, and the total amount of precipitation ranged 2.3–20.0 mm.

3.1. Total suspended solids and total organic carbon

Based on the analysis of the ANOVA results, it can be observed that the mean TOC values are much higher for the Jesionowa SWTP catchment (35.7 mg dm⁻³) than for the Witosa SWTP catchment (10.7 mg dm⁻³). As regards mean TSS values, the catchments of concern did not show major differences. The comparison of Table 3 data, however, shows that the TSS maximum values for the equivalent precipitation events were much higher in the case of the Jesionowa SWTP catchment. That is undoubtedly related to differences in land use and road transport volume in both localities. The Jesionowa SWTP catchment contains a much higher percentage of impervious surfaces, including those industrial in character, such as storage and handling yards, which are the main source of fine-grained mineral suspensions. The major source of anthropogenic emission of organic pollutants in the examined catchments is the combustion of fuels (coal) for energy in household furnaces and boiler plants, and to a lesser extent, road transport. Pollutants from these surfaces are easily flushed away by stormwater, with which they travel to the stormwater drainage systems. In the Jesionowa SWTP catchment, this system is decidedly more advanced (approx. 15.2 km of sewer network with main sewer diameters ranging from 0.5–1.5 m).

Especially in the case of TSS, it seems to be well-grounded to use medians, which represent stormwater qualitative characteristics better than mean values. The maximum TSS concentrations (10,621 mg dm⁻³) observed in the J2 event of May 16, 2018, resulting from the rainfall of total amount (Pₜₒₜ) reaching 20 mm, fit within the range specified by Królikowski et al. [1] for an urban catchment in Białystok. The maximum TSS concentrations more than twice higher than those observed in Serbia (the studies were carried out in Belgrade Centre, in the car park of the University of Belgrade [35]). If we eliminate the outliers, the upper quartile for TSS (Fig. 3) in J2 does not exceed 2,500 mg dm⁻³, for a median near 855 mg dm⁻³. On the other hand, in J3 recorded on May 17, 2018, in spite of rainfall reaching Pₜₒₜ = 14.2 mm, the maximum concentration of TSS was only 286 mg dm⁻³, due to short interval between rainfall events (6 h). This value corresponds with the studies carried out in Paris (max. 254 mg dm⁻³) [33] and Lahti (max. 348 mg dm⁻³) [36].

The highest TSS concentrations in the Witosa SWTP catchment were observed on May 16, 2018 (W2) and June 12, 2018 (W4) – 627 and 611 mg dm⁻³, respectively, and were almost 17 times lower than the TSS concentrations during J2. On the other hand, if we analyze median values for W1–W4, the highest was noted in the event of May 14, 2018 (W1) – 294 mg dm⁻³. It can be observed that it is higher than during the events J3 (139 mg dm⁻³), J4 (130 mg dm⁻³) and J5 (281 mg dm⁻³) for the Jesionowa SWTP catchment (Fig. 3).

The maximum TOC concentrations in J2–J5 was much the same, ranging within 49.0–71.6 mg dm⁻³), and only for a single event J1 they did not exceed 22.3 mg dm⁻³. For the Witosa SWTP catchment, they were lower, ranging from 10.5 to 21.9 mg dm⁻³ (W2–W4) – Table 3. The measured ranges were close to a range specified by Valtanen et al. [39] for Lahti (1.3–33.0 mg dm⁻³), yet they were much lower.
3.2. Heavy metals

The occurrence of HMs in storm and thaw waters is largely connected with washing out of pollutants from the surface of the analyzed catchments, including streets, car parks, storage areas, building roofs [43]. These pollutants are brought into the environment through fuel combustion processes (petrol, fuel oil, diesel oil, coal) – primarily Pb, Zn, Fe, Cu, Cd, Cr, Co and Ni [44–46]. The urban surface is the place, where airborne dust are deposited, brought from remote or less distant sources [47,48]. It should be emphasized here that there are a heat and power plant located in the Jesionowa SWTP catchment, and its surface is crossed by major transport routes characterized by high traffic intensity. The occurrence of HMs is closely related to transportation and traffic as they are brought into the environment with the abrasion of vehicle tires (Zn, Pb, Cd), electrolytic coating (Zn, Cr, Ni), moving engine parts (Mn), wear of metallic coatings (Cu), accumulators (Ni, Co), leaks of oil, grease (Zn), or corrosion products (Fe) [46,49–51].

Another source of Zn, Cu, Pb and Cd is the corrosion of roofs in buildings (zinc-coated sheet, roofing paper, sheet copper) [52]. Street dust is found to contain Cd, even up to few dozen mg kg–1; Cu, Cr, Ni and Pb – up to few hundred mg kg–1; and Zn – sometimes more than 1,000 mg kg–1 [45,53–55]. Cu may also result from the use of fungicides and insecticides in green spaces [45].

Based on the analysis of the mean values of HMs concentrations (the ANOVA test), it can be concluded that most of the analyzed concentrations belong to the same homogeneous groups, meaning that statistically, the values do not differ significantly (p = 0.05). Only in the Jesionowa SWTP catchment, a much higher mean Cu content (0.133 mg dm–3) was found. It was more than 4.5 times higher than the mean Cu content in stormwater flowing out of the Witoswa SWTP catchment (0.029 mg dm–3). The lack of statistically significant differences between the mean values of the examined indicators may indicate the similarity of factors determining the processes of deposition and wash-out of pollutants in the examined catchments.

The highest concentration ranges were observed for Fe (waves J1–J5: 1.67–74.8 mg dm–3, waves W1–W4: 1.75–24.08 mg dm–3), and the lowest for Co (0.001–0.232 mg dm–3 and 0.001–0.021 mg dm–3, respectively), and Cd (0–0.469 mg dm–3 and 0.005–0.139 mg dm–3, respectively). In the case of Cd, it should be observed that maximum concentrations in selected waves (J1: 0.127 mg dm–3, J2: 0.469 mg dm–3, J5: 0.150 mg dm–3, W4: 0.139 mg dm–3) considered exceeded the values specified by other researchers [1,34,35,37] – Table 3. The same is for waves J1 and W4, if we consider only ranges limited by lower and upper quartile (Fig. 2). The maximum concentration of Co in wave J2: 2.322 mg dm–3 can be treated as the outlier, which is confirmed in Fig. 2, where upper quartile (75%) does not exceed 0.018 mg dm–3.

As regards the analyzed waves, high values were also reached for Zn concentrations (maximum J5: 5.731 mg dm–3, J2: 3.542 mg dm–3, W4: 3.160 mg dm–3, J4: 3.064 mg dm–3), while in the first case they fitted into the range specified by Królkowski et al. [1] for Białystok, and Džukić et al. [35] for Belgrade, and in the other cases they did not exceed upper value ranges given by Gan et al. [37] – 4.400 mg dm–3 (Table 3). Manganese was sporadically analyzed in stormwater runoffs, and apart from wave J2, its concentrations corresponded to the data obtained from the area covered with high-rise buildings in Lahti [39]. The highest Mn concentrations were observed in wave F2, where the maximum reached 9.434 mg dm–3 (Table 3), and upper and lower quartile was: 3.298 mg dm–3 and 1.187 mg dm–3, respectively (Fig. 2).

The highest Cu value was observed in the Jesionowa SWTP catchment, in wave J4 (0.660 mg dm–3), which is more than twice higher than the maximum observed in the Witoswa SWTP catchment (wave W4 = 0.262 mg dm–3) – Table 3. The difference between the Cu concentrations in individual catchments was significant (0.107 and 0.024 mg dm–3, respectively). The obtained variation ranges were close to the values reported in the literature [34,37,39].

In the case of Cr and Ni, it can be observed that the lowest values of concentration medians for these elements were found in waves J5 and W4 (Fig. 2), induced by rainfall reaching 12.2 mm, recorded on June 12, 2018. On the other hand, Cr maxima in most of the waves (J2: 0.910 mg dm–3, J4: 0.872 mg dm–3, J5: 0.950 mg dm–3, W3: 2.723 mg dm–3) were much higher than the values specified by Zgheib et al. [34] for Paris, Järveläinen et al. [36] for Lahti, Gan et al. [37] for Guangzhou, and Valte [38] for Santa Monica. If the outliers were rejected (Fig. 2), the upper Cr limit did not exceed 0.38 mg dm–3, and the median for the waves J1–J3 and W1–W3 ranged within 0.10–0.13 mg dm–3. Then, for Ni, median for the waves J1–J4 and W1–W3 ranged from 0.08 to 0.09 mg dm–3 (Fig. 2), whereas the maximum in wave J2: 0.304 mg dm–3 was lower than in the other studies [1,35–39].

The maximum Pb concentration in the J4 runoff from the Jesionowa SWTP (0.758 mg dm–3) catchment was almost four times higher than the maximum in the Witoswa SWTP catchment (wave W4: 0.190 mg dm–3). These values are far below those provided by Królkowski et al. [1] and correspond to the studies carried out by Taebi and Droste [14], Sakson et al. [32], Zgheib et al. [34] and Gan et al. [37]. On the other hand, mean values and medians of Pb concentrations calculated globally for the analyzed areas were much the same 0.131 and 0.101 mg dm–3 (SWTP Jesionowa), and 0.107 and 0.103 mg dm–3 (SWTP Witosowa), respectively (Table 3).

Table 4 shows mean values of $C_f$, $C_i$ and $mC_f$ indices for individual events (J1–J5, W1–W4), and also mean and median values from all samples collected in both catchments. The analysis of $C_i$ for the mean values from all tested samples shows they are arranged in a similar order for both catchments: namely for the Jesionowa SWTP (Cd > Zn > Cr > Ni > Pb > Co > Cu > Mn > Fe), and for the Witoswa SWTP (Cd > Zn > Cr > Pb > Ni > Co > Cu > Fe > Mn). These series differ slightly in the location of the neighboring Ni–Pb and Mn–Fe elements. As regards the value of $C_i$ medians from all tested samples, these series are as follows: Zn > Ni > Cd > Cr > Pb > Co > Cu > Mn > Fe and Cd > Zn > Pb > Cr > Ni > C > Fe > Mn, respectively. The mean $C_i$ values obtained for the Jesionowa SWTP catchment show a very high degree
of stormwater pollution with respect to Cd, Cu, Cr, Ni, Pb, Zn, and Co, and also a significant degree of pollution with Mn and Fe. As regards the Witosa SWTP catchment, a very high degree of pollution with Cd, Cr, Ni, Pb, Zn, a significant degree of pollution with Co, and a moderate degree of pollution with Mn and Fe were found. The calculated \( m_{\text{Cd}} \) values confirm an extremely high degree of contamination for J1, J4 and J5 events, and very high contamination for J2 and J3, and also W1, W3 and W4. It was only for the W2 high-water event, that the contamination was termed as high (Table 4).

Mean values of EF with respect to HMs in stormwater (Table 5) coincide with the sequence \( \text{Cd} > \text{Zn} > \text{Ni} > \text{Cr} > \text{Pb} > \text{Co} > \text{Cu} > \text{Mn} \) (the Jesionowa SWTP), and \( \text{Cd} > \text{Zn} > \text{Pb} > \text{Cr} > \text{Ni} > \text{Co} > \text{Cu} > \text{Mn} \) (the Witosa SWTP). As regards EF median values, the sequence is slightly altered for the first catchment, namely: \( \text{Zn} > \text{Cd} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Co} > \text{Cu} > \text{Mn} \). Among the examined HMs, the highest values of EF were noted for Cd in high-water events of J3 and W4, which indicates an extremely severe enrichment. It should be emphasized that for the Witosa SWTP catchment, this category concerns the mean and the median values calculated by aggregating the values from all collected samples.

Enrichments with Cr (events J3, J4, J5, W3), Ni (J3, W1), Pb (W4), and Zn (J3, W1, W3, W4) are categorized as severe.

With respect to the Jesionowa SWTP catchment, the analysis of EF medians (Table 5) for Cd, Cr, Ni, Zn resulted in the category of moderately severe enrichment, whereas for Pb and Co, it was moderate enrichment. In a similar manner, with respect to the other catchment, severe enrichment was found for Zn, moderately severe enrichment for Pb, and moderate enrichment for Ni and Cr. Higher mean and median EF values for Cd and Zn in the Witosa SWTP catchment may be related to the corrosion of roof coverings (galvanized sheet) in single-family residential buildings.

The lowest enrichments (categories of minor enrichment and no enrichment) were found for Mn (both facilities), Cu (the Witosa SWTP catchment), and for Co (the Witosa SWTP catchment – except for the event W4) – Table 5.

### 3.3. Results of the PCA

Eigenvalues were determined in the first stage of the PCA, individually for the data from each analyzed catchment. These values were necessary to find the number of components. The Kaiser criterion was applied for this purpose. The factors with eigenvalues above 1.0 should be chosen according to this criterion (Fig. 4). Considering the above, only the first 3 principal components were further considered. The calculations performed indicate that in case of the Jesionowa SWTP catchment, the first, second and third components account for 43.85% of the variance (concentrations of Mn, Fe, and TSS are decisive), 17.72% of the variance (mainly TOC, Cd, Ni, Pb, Co), and 10.58% of the variance (mainly Fe, Cd, TOC), respectively. Concentrations of Pb, Zn, Co, Cu, Mn, TSS and Fe have a considerable effect on the first component, while those of Cr, Fe – on the second, and TOC and Cd – on the third.

In the case of runoffs from the SWTP Jesionowa area, a strong negative relationship is visible between the first factor and the variables: Cu, Ni, Pb, Zn, Co, Mn, Fe, and TSS. As regards the second factor, its strong negative relationship with Cd and positive with TOC was observed (Fig. 5).
respect to the Witosa SWTP catchment, a strong positive correlation was found between the first factor and Fe, Co, Cu, M, Zn, Pb, TSS concentrations. The second factor strongly correlates with Cr, whereas the third factor is negatively correlated to Cd and TOC (Fig. 6).

Based on the graphs, it is also possible to draw conclusions regarding the correlation of variables. The closer the vectors are located, the greater is the positive correlation between the variables. In the Jesionowa SWTP catchment, strong positive relationships are observed between Ni, Co, Cu, Zn (r = 0.62–0.84). This clearly shows that these elements come from similar sources in the same period of time. The source of those HMs could be roof coverings from galvanized sheet or copper. A different situation was observed in the Witosa catchment area. The analysis of Fig. 6 shows the occurrence of one strongly correlated group of HMs (Cu, Pb, Zn, Co, Mn, Fe) and TSS (r = 0.65–0.94). In the Witosa SWTP catchment, TSS plays a major role in the transport of the pollutants of concern while the rate of their wash-out depends on the hydrological conditions in the catchment (precipitation intensity). Additionally, the occurrence of strong correlations between the contents

### Table 5
Enrichment factor (EF) for HM in rainfall events

<table>
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<tr>
<th>Event number</th>
<th>Cd</th>
<th>Cu</th>
<th>Cr</th>
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<th>Zn</th>
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<tr>
<td>J1</td>
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<td>8.5</td>
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<td>13.1</td>
<td>5.6</td>
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<td>9.6</td>
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</tr>
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<td>13.4</td>
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<td>7.1</td>
<td>9.6</td>
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<tr>
<td>Mean</td>
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<tr>
<td>Median</td>
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<td>5.7</td>
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<table>
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<th>Event number</th>
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<td>W1</td>
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<td>7.6</td>
<td>15.1</td>
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<td>3.7</td>
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<td>1.8</td>
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</tr>
<tr>
<td>W3</td>
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<td>7.3</td>
<td>3.8</td>
<td>10.5</td>
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</tr>
<tr>
<td>W4</td>
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<td>20.3</td>
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<tr>
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<td>38.8</td>
<td>1.8</td>
<td>8.2</td>
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<td>9.9</td>
<td>16.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Median</td>
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<td>1.2</td>
<td>4.5</td>
<td>3.6</td>
<td>7.9</td>
<td>11.4</td>
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![Fig. 4. Scree plot of PCA (a) for the Jesionowa SWTP catchment and (b) for the Witosa SWTP catchment.](image-url)
of individual HMs in stormwater indicates a number of geochemical relationships between them. In general, Cu, Pb and Zn present in stormwater are mainly derived from traffic emissions.

Similar to the Jesionowa SWTP catchment, the statistical relationship was not found to exist between HMs under analysis and TOC. That confirms a presumption about the different origins of those pollutants in the stormwater from the two catchments.

4. Conclusions

In highly urbanized areas, one of the main challenges is to minimize the negative impact of stormwater on the aquatic environment of the receivers. Water quality deterioration results from the point and diffused sources of pollution. In addition to air pollution, generated by industries and combustion of fossil fuels, transportation and traffic are the primary HM sources in stormwater. The presence of HMs in the receiving water is particularly dangerous because they do not undergo biodegradation in natural river self-purification processes. Moreover, they slow down these processes due to their toxic effect on micro-organisms. On the basis of studies and analyses, it is possible to draw the following conclusions:

- The ANOVA results analysis shows that the mean TOC concentration is significantly higher in the Jesionowa SWTP catchment than in the Witosa SWTP catchment. TSS mean concentrations in both catchments do not
differ substantially. The comparison of the maximum TSS values for precipitation events indicates higher concentrations in the Jesionowa SWTP catchment, which is caused by differences in land use and road transport volume in the catchments. The Jesionowa SWTP catchment has a higher percentage of impervious areas, including the industrial ones (storage and handling yards), which are the main source of fine-grained mineral suspensions.

- The analysis of the ANOVA test results for HMs shows that for the majority of cases, the values do not show statistically significant differences (p < 0.05). The mean Cu concentration (0.133 mg dm⁻³) in the Jesionowa SWTP catchment, over 4.5 times higher than in the other catchment (0.029 mg dm⁻³), makes an exception to the rule. The lack of statistically significant differences between mean values of the examined indicators may indicate that similar factors decide pollutant deposition and washout in the examined areas.
- The ranges of the majority of HM concentrations coincide with those reported in the literature. The mean and maximum Cu values (0.014 and 0.469 mg dm⁻³, respectively), maximum Cr values (2.723 mg dm⁻³), and also maximum Mn and Co values, which are rarely examined, (0.232 and 9.434 mg dm⁻³, respectively), do not follow the pattern.
- The maximum values of concentrations of the pollutants of concern occur mostly as extreme values or outliers. Regarding concentrations, it seems more reasonable to rely on the median values rather than mean ones.
- The assessment of the contamination index Cₜ and modified index mCₜ indicates very high contamination of stormwater with HMs in both catchments.
- The mean values of the Cₜ factor in the two catchments show the highest pollution with Cd and Zn.
- The analysis of the EF values reveals the category of severe enrichment can be assigned to the Jesionowa SWTP catchment with respect to Cd concentrations and the category of severe enrichment for Cr, Ni, Pb and Zn. In the Witosa SWTP catchment, one degree of higher categories of enrichment is attributed to Cd and Zn. The lowest category of EF, namely minor enrichment, was ascribed to Mn (both catchments) and Cu (the Witosa SWTP catchment).
- Based on PCA results, with respect to the quality of stormwater in the Jesionowa SWTP catchment, the occurrence of strong positive relationships between the following HMs was observed: Ni, Co and Mn, and also Cu and Zn (r = 0.62–0.84). This may indicate a probable source of those HMs in stormwater, namely roof coverings made from galvanized or copper sheet.
- For the Witosa SWTP catchment, the analysis of PCA results indicates a substantial role of TSS in pollutant transport, while the rate of their wash-out depends on the hydrological conditions (precipitation intensity). Additionally, the occurrence of strong correlations between the content of individual HMs (Cu, Pb, Zn, Co, Mn, Fe) may suggest a number of geochemical relationships among them. In general, the sources of Cu, Pb and Zn in stormwater are mainly associated with traffic emissions.

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