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Methods of assessment of stormwater sediments quality

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Abstract. Concentration of heavy metal (cadmium, copper, chromium, nickel, lead and zinc) in sediments collected from the stormwater treatment plant located in the urbanised catchment were investigated using geo-accumulation index and enrichment factor to determine metal accumulation and pollution status. Total metal concentrations varied widely in studied materials and the mean values were higher than their background values. The I_{geo} results indicate that tested sediments were uncontaminated with respect to Cd. The study area is moderately to strongly contaminated with Zn, Pb and Cu. The other elements are within the scope moderate contamination.

1 Introduction

The sediments found in urban areas are composed of a diversity materials that range from mineral compounds and biogenic materials to organic and inorganic materials of human origin [1]. Atmospheric particles deposited on impermeable surfaces of cities are the main sources of urban sediments. This type of sediment may take various routes, including atmospheric, soil, or bodies of water, depending on some specific conditions both natural and anthropogenic processes thus, it carries associated pollutants along with it, such as metals, especially zinc (Zn), lead (Pb), copper (Cu), nickel (Ni), cadmium (Cd), and chromium (Cr), which are frequently used in industrial activities and discharged without any control into the rainwater or sewage system [2, 3].

Metals are a group of pollutants of high ecological significance. They are not removed from water by self-purification, but accumulate in suspended particulates and sediment [4–6]. Sources of metals in aquatic sediments are natural or anthropogenic sources. Main natural sources are weathering of soils and rocks and atmospheric deposition. Discharging agricultural, municipal, residential or industrial waste products into water bodies are anthropogenic sources [7]. Moreover, the long-term environmental monitoring requires an evaluation of the degree of contamination in urban areas with particular emphasis upon understanding the environmental processes controlling sediment distribution in the assessment of trace elemental studies [8–9].

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2 Materials and methods

2.1 Study site

Analyzed catchment, with a total area of 82 hectares, from the east and the northern part is limited by the open ditch running along the city boundaries and receiving rainwater flowing down from the dense forest complex. The sedimentation tank, which collected sediments for testing, is a open horizontal settling chamber of stormwater treatment plan named OWD Witosa. This property was built in the seventies. Currently, after reconstruction realized in 2009, it consists of separation chamber, open horizontal settling chamber length of 50 m, coalescence separator of ϕ 3.0 m, water pumping station and drainage system. Technical parameters of the settler shown in Table 1. Wastewater is delivered to the separation chamber with storm overflow by the ferroconcrete collector ϕ 1400 mm from the northern part of the city of Kielce. Sewage system consists of a main collector with a diameter ϕ 1200 and 1400 mm (L = 762 m) and lateral channels (ϕ 300–800 mm) with a total length of approx. 7.0 km. It receives wastewater from estate area, in which is located 400 single and multi-family residential. At present residential buildings covers an area of 36.5 ha, which represents approx. 44.5% of dewatered area, the 13.6 ha of these terrains are sealed surfaces (roads, parking lots, squares, roofs). The remaining part of the catchment are green areas – 45.5 ha (55.5%), of which the majority are meadows and wasteland (31.5 ha), forests – 12.2 ha and 1.8 ha are orchards. Treated wastewater is discharged into the Silnica river via channel having the diameter ϕ 1400 mm at km 11 + 580 [10].

Table 1. Technical parameters of sedimentation tank OWD Witosa.

Parameter	Value	Unit
Bottom surface	1268.0	m^2
Water surface area at normal water mirror	1387.0	m^2
Total depth of settling chamber	3.45	m
Depth at the maximum water mirror	3.00	m
Depth at normal water mirror	1.50	m
Active capacity of settling chamber	2080	m^3

2.2 Sampling

The sediment samples were collected during two months of spring season (May – June) 2014, in accordance with the PN-EN ISO 5667-15:2009 standard method [11]. Within sedimentation tank, sediments were collected from two sites in this open reservoir, namely inlets and outlets. Three sampling points in inlet and another three in outlet – 18 sediment samples. Samples were collected using a stainless steel standard bottom grab sampler, or Eijkelkamp equipment for sites with difficult access, and placed in acid-washed plastic containers (~1L). Between the series of sample collecting, all equipment was rinsed with water from the reservoir. Then, the samples were transported to the laboratory and homogenized using a solvent-cleansed stainless steel bucket and a spoon. The physical and chemical parameters were measured immediately afterwards.

2.3 Determination of heavy metal

The sediment samples for heavy metal determination were oven-dried at 105°C on glass dishes until the constant weight, homogenized with a pestle and mortar, and each of the weighed samples (approximately 0,2 g) were transferred into Teflon vessels, digested with 7 ml HNO_3 in a microwave oven (Multiwave 3000, Anton Paar). The digestates were left to cool at room temperature and then filtered through nitrocellulose membrane filter. The filtered digestates were diluted with distilled water to 100 ml in a volumetric flask. Total metal concentration of lead, chromium, cadmium, copper, nickel and zinc was determined using by atomic emission spectrometry with inductively coupled plasma ICP Optima 8000 (Perkin Elmer) with certified multi element standards [12]. All the reagents were of high quality and analytical grade. All solutions were prepared using double distilled water. All plastic, quartz and glassware were soaked in 10% nitric acid for at least 24 h hours and rinsed with ultra pure water. Total heavy metal concentrations were expressed in mg per kg of dry mass of sediments.

2.4 Geoaccumulation index (I_{geo})

Geoaccumulation index (I_{geo}) was developed by Műller [13] and had widely been used in trace elements studies of sediments [3,7,14]. To quantify the degree of heavy metal pollution Igeo was calculated using Eq. (1):

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 B_n} \right) \quad (1)$$

where: C_n is the measured concentration of the metal n in the urban sediment and B_n is the geochemical background value of given metal in the shale [15,16] and the 1.5 factor was introduced for the purpose of assessing the natural fluctuations in the content of a given substance in the environment with minimum anthropogenic influence. I_{geo} classes are given in table 2.

2.5 Enrichment factor (*EF*)

Normalized enrichment factor is applied to differentiate metal source originating from anthropogenic and natural means. This involves normalization of the sediment with respect to reference elements such as Al, Fe, Mn, Ti, Sc, Li and Cs [14]. Normalized EF of metals in urban sediments from OWD Witosa of each site was calculated using Eq. (2).

$$EF = \left(\frac{C_n}{C_{Fe}} \right)_{sample} \Bigg/ \left(\frac{C_n}{C_{Fe}} \right)_{background} \quad (2)$$

where (C_n/C_{Fe})sample is the ratio of concentration of the element of concern to that of Fe in the sediment sample (mg/kg dry weight) and (C_n/C_{Fe})background is the same ratio in an unpolluted reference material [17]. According to Chen et al. [18] the EF values were categorized into seven classes where EF < 1 indicates no enrichment, EF < 3 is minor enrichment, EF = 3–5 is moderate enrichment, EF = 5–10 is moderately severe enrichment, EF = 10–25 is severe enrichment, EF = 25–50 is very severe enrichment, and EF > 50 is extremely severe enrichment (Table 2). Enrichment factor values between 0.5 and 1.5 indicate the metal is entirely from natural processes, whereas values greater than 1.5 suggest that the sources are more likely to by anthropogenic [19].

Table 2. Enrichment factor (EF) and I_{geo} classes in relation to sediment quality.

EF	Sediment quality	I_{geo}	I_{geo} classes	Sediment quality
< 1	No enrichment	≤ 0	0	Unpolluted
< 3	Minor enrichment	0 – 1	1	Unpolluted to moderately polluted
3 – 5	Moderate enrichment	1 – 2	2	Moderately polluted
5 – 10	Moderately severe enrichment	2 – 3	3	Moderately to highly polluted
10 – 25	Severe enrichment	3 – 4	4	Highly polluted
25 – 50	Very severe enrichment	4 – 5	5	Highly to very highly polluted
> 50	Extremely severe enrichment	5 – 6	6	Very highly polluted

3 Results and discussion

3.1 Heavy metal concentrations

Total metal concentrations varied widely in studied materials. The minimum, maximum, average, standard deviations (SD) and background concentrations for each element are presented in Table 3. Mean values were higher than their background values, suggesting that these metals in stormwater sediments from OWD Witosa were influenced by anthropogenic sources, except cadmium that was no detected in all sediment samples. The results showed that zinc (Zn), copper (Cu) and lead (Pb) with the highest concentrations (983.43±103.09 mg/kg d.w., 69.39±12.46 mg/kg d.w., 124.87±5,87 mg/kg d.w.) and these values exceeds the values of background several times. Mean concentration of Cr is 36.31 mg/kg d.w. and of Ni 23.75 mg/kg d.w., respectively. Values exceeding the standards presented in the next decreasing order Zn>Cu>Pb>Cr>Ni>Cd. It was also observed differences in the metal concentrations on the inlet and outlet of the sedimentation tank. For each element the concentration values were less than a few to several percentage points at the inlet than at the outlet of the reservoir. Elevated concentrations of zinc and lead may result from many processes that occur in the aquatic environment; to a large extent, they depend on sediment composition, thus on the character of the catchment.

Table 3. Heavy metal concentrations in sediments compared with local background values.

Study site	**Parameter**	**Concentration, mg/kg dry weight**					
		Cd	**Cu**	**Cr**	**Zn**	**Pb**	**Ni**
Inlet	Average	n.d.	60.07	27.97	894.55	119.38	19.70
	Min	n.d.	51.27	25.00	887.38	117.63	18.57
	Max	n.d.	70.46	31.25	902.46	121.04	21.10
	SD	n.d.	7.14	2.40	6.64	1.43	0.80
Outlet	Average	n.d.	78.71	44.64	1072.31	130.36	27.79
	Min	n.d.	66.99	42.37	998.55	127.37	26.07
	Max	n.d.	90.37	47.03	1196.37	132.69	30.00
	SD	n.d.	9.15	1.51	69.02	1.84	1.67
Total	Average	n.d.	69.39	36.31	983.43	124.87	23.75
	Min	n.d.	51.27	25.00	887.38	117.63	18.57
	Max	n.d.	90.37	47.03	1196.37	132.69	30.00
	SD	n.d.	12.46	8.79	103.09	5.87	4.36
Background		0.5	7	6	73	15	5

3.2 Index of geoaccumulation I_{geo}. Pollution status

The geoaccumulation index includes seven grades ranging from 0 to 6 (unpolluted to very strongly polluted). The geoaccumulation factor results indicate that tested sediments were uncontaminated with respect to Cd (cadmium was not detected in all samples), therefore not even placed on bloxplot diagram (Fig. 1). The Zn accumulation level is 3.16 which indicates to strong contamination. Tested sediments are moderately to strongly contaminated with Pb (2.47) and Cu (2.70). The other elements are within the scope moderate contamination (1<Igeo<2). The high contents of lead, zinc and copper are probably a result of anthropogenic activity in watershed area. Many of these terrains are sealed surfaces (roads, parking lots, squares, roofs) and more than half of the area (55.5%) are the green areas where can be used plant protection products as a chemical fertilizers and pesticides - a potential source of heavy metal contamination.

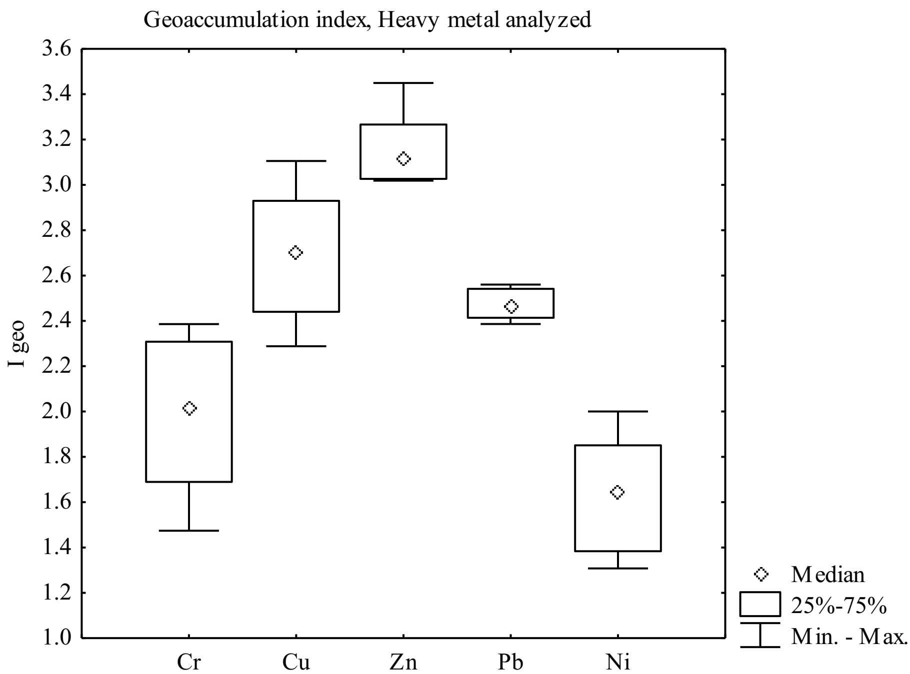

Fig. 1. Boxplot diagram of the geoaccumulation index (I_{geo}) values.

3.3 Enrichment factor (EF). Pollution status

In present study, the enrichment factor (EF) was used to assess the level of contamination and the possible anthropogenic impact in the sediments collected from urbanised stormwater treatment plant. To identify anomalous trace metal concentrations, the normalization of element is required. Several authors used the iron (Fe) to normalize contaminants [17,20] therefore in the present study concentration of Fe has been used as a normalization standard. Table 4 shows enrichment factor (EF) values for Cd, Cu, Cr, Zn, Pb and Ni. The values of EF suggest that all trace elements except cadmium originate from anthropogenic inputs and tested sediments are very enriched with them. The EF values for Zn are the highest among the metals and it has severe enrichment (EF from 13.54 to 23.76). Slightly lower values but still within the scope of this class have been obtained for Cu and

Pb (13.08±3.82 and 10.88±1.91, respectively). Results for Ni and Cr indicate to moderately severe enrichment (6.35±1.91 and 8.21±2.85, respectively). The enrichment of heavy metals in this study has been observed to be relatively high. The differences in individual EF values may result in the nature of heavy metals, their pollution loads, as well as speciation forms of trace elements occurrence in sediment-water complex. Therefore so high content of heavy metals due to ability to sorption on fine particle which are forming deposits.

Table 4. Enrichment factor (EF) values of selected heavy metals in stormwater sediments.

Parameter	Enrichment factor (EF)					
	Cd	**Cu**	**Cr**	**Zn**	**Pb**	**Ni**
Average	<1	13.08	8.21	17.75	10.88	6.35
Min	<1	8.38	4.56	13.54	8.62	4.09
Max	<1	18.68	11.28	23.76	12.98	8.81
SD	<1	3.82	2.85	4.01	1.91	1.91

4 Conclusion

The present study is a assessment of the stormwater sediment contamination by geochemical indicators – geoaccumulation index Igeo and the enrichment factor (EF) for six selected heavy metals (cadmium, copper, chromium, zinc, lead and nickel). Results showed that the heavy metal concentration are very high and it has been reported a significant excess of a geochemical shale. The results indicate that zinc (Zn), copper (Cu) and lead (Pb) had the highest means concentrations exceeds the value of background several times. Cadmium was no detected in all sediment samples. It was also observed differences in the metal concentrations on the inlet and outlet of the sedimentation tank. For each element the concentration values were less than a few to several percentage points at the inlet than at the outlet of the reservoir.The Igeo results indicate that tested sediments were uncontaminated with respect to Cd. The Zn accumulation level is 3.16 which indicates to strong contamination. The study area is moderately to strongly contaminated with Pb (2.47) and Cu (2.70). The other elements are within the scope moderate contamination ($1<Igeo<2$). The high contents of lead, zinc and copper are probably a result of anthropogenic activity in watershed area. Many of these terrains are sealed surfaces (roads, parking lots, squares, roofs) and more than half of the area (55.5%) are the green areas where can be used plant protection products as a chemical fertilizers and pesticides – a potential source of heavy metal contamination. Additionally, the enrichment of heavy metals in this study has been observed to be relatively high – from moderately severe enrichment (Cr, Ni) to severe enrichment (Zn, Pb, Cu). The differences in individual EF values may result in the nature of heavy metals, their pollution loads, as well as speciation forms of trace elements occurrence in sediment-water complex. These findings indicate that more attention should be paid to metal contamination in urban sediments and its regular monitoring. Particularly, with the use of geochemical tools.

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