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Assessment of the degree of pollution of sediments from the rainstorm sewer system in the urbanised catchment

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ABSTRACT

The study presents the results of tests aimed at determining variations in concentrations of polycyclic aromatic hydrocarbons and heavy metals (copper, cadmium, chromium, nickel, lead and zinc) in the sediments from the stormwater sewer system depending on the study period. The sediments were sampled in four periods that altogether extended over the hydrological year. They were collected from the settler chamber in the stormwater treatment plant located in the 804.6 ha urbanised catchment. The results of investigations show differences in the sediment grain size distribution. The dust-clay fraction is dominant as it constitutes up to 84% of the samples. The remaining part of the samples is composed of the mineral material, mainly of the psammite fraction grains (3–25%) and organic material (10–13%). The results concerning the content of heavy metals show that the lowest values were found for cadmium, namely 0.8 mg kg^{-1}, and the highest for zinc −627.9 mg kg^{-1}. As regards organic pollutants, a growing trend in total concentrations of PAHs was observed over the study period. The initial concentration in the winter period was 48.1 mg kg^{-1}, whereas in the last sampling session it was as much as 87.8 mg kg^{-1}, which indicates a continuous accumulation of pollutants in the material. An attempt was made to classify the sediments taking into account the Regulation of the Minister of Environment on soil and land quality standards (J. of Laws No. 165, item 1359) and geochemical classification.

Keywords: Stormwater sediments; Heavy metals; PAHs; Particle size distribution

1. Introduction

Sources of pollution of natural waters include, among many others, stormwater and sediments that accumulate in the stormwater sewer system. Pollutants, such as heavy metals or persistent organic pollutants (POPs), found in stormwater and stormwater sediments, pose a serious hazard to living organisms that occur in the adjacent aquatic environment. Stormwater, however, constitutes a part of water resources, which provide for the sustainability of surface waters. In urbanised areas, stormwater should therefore be protected from pollution and properly managed.

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The composition of stormwater and of sediments accumulated in the system depends on many factors. Those include the type of the catchment management programme, the roadway system, the vehicular traffic volume, the occurrence of failures and environmental disasters, the frequency and manner of cleaning of the catchment (roads, squares) surface, the application of de-icing agents during winter months, parameters of atmospheric precipitation, season of the year, the sewer system hydraulics and the structure and its facilities (separators, sedimentation tanks, street gullies and sumps), the way of the sewer system operation, and also the fraction green belts constitute in the drained area. Sediments not only hamper flow, they also increase the pollutant load transported to the stormwater treatment plant, stormwater overflow structures, or directly to the receivers, where they create a major hazard to the biosphere and the adjacent land environments. Due to the chemical and biochemical processes, a part of pollutants may migrate to the waters again [1,2].

Presently, regulations binding in Poland [3] require that the stormwater originating in the catchment area should be tested for suspended solids and petroleum-derived substances, and delivered, after treatment, to the receiver. The legislation does not account for sediments formed in the sewer system facilities. However, it should be emphasised that the assessment of the degree of pollution of sediments from the sewer system is important to specify the possibility and the method of their removal and disposal. Sediment pollution evaluation is also crucial for modelling the transport of the pollutant load in the sewer system, and related issues of secondary pollution of the aquatic environment. General characteristics of sediment structure and properties should also be known at the stage when the sewer system components are designed. Presently, because of the lack of the data, it is extremely difficult to state the composition of stormwater pollutants and of sediments accumulated in the stormwater sewer system by means of forecasting. It is therefore necessary to monitor them for quantity and quality on cyclic basis.

It is hard to make an assessment regarding the degree of toxicity of stormwater sediments and the hazard they pose. That results, among others, from the fact that a clear-cut classification of those sediments as wastes is not available. As regards regulations in force on waste management in Poland [4], stormwater sediments can be classified as wastes having similar properties, most often coded as 13 05 (wastes from oil/water separators). Due to a certain similarity, sediments from street gullies could be coded as 19 08 02, or 19 08 99, as it happens for sediments from grit chambers in domestic wastewater treatment facility. Alternatively, as found in the literature, those could be classified as "other municipal wastes", having a code 20 03. Differences in coding prove to be of major importance as they significantly affect the costs of operation of the stormwater sewer system. Different procedures are required for the collection, transport and disposal of hazardous wastes and municipal wastes [5].

In West European countries, a classification of sediments accumulated in the sewer system has been established. It comprises the following:

(A) Non-cohesive inorganic sediments.
(B) Sediments that have inorganic skeleton.
(C) Organic sediments that slide over the surface of non-cohesive inorganic sediments.
(D) Biofilm growing on the sewer walls.

Additionally, two groups of sediments can be differentiated, namely (E) and (F), which fit the characteristics of stormwater sediments:

(E) Sediments from detention tanks, the structure of which corresponds to that of sediments from tanks of stormwater treatment plants.
(F) Sediments from street gullies.

E-type sediments are characterised by high fineness; as a result, they have large area of grains in a unit volume. That, in turn, causes significant adsorption of sparingly soluble organic pollutants and heavy metals. Group F is characterised by variable composition, depending on the season of year and atmospheric conditions [6].

Another approach, adopted to assess the quality of stormwater sediments is found in literature [5]. It involves a classification based on the Regulation of the Minister of Environment concerning soil and land quality standards [7]. The regulation sets the standards for soil and land quality with respect to the following types of ground:

(1) Group A. Land properties located in the areas that are subject to protection by provisions of the laws—the Water Act, and land protected under the Nature Conservation Act.
(2) Group B. Properties classified as agricultural land, excluding the land under water bodies or ditches, forest land and also wooded and shrubbed land, wasteland and also built-up and urbanised areas excluding industrial land, mining land and transportation routes.

(3) Group C. Industrial land, mining land and transportation routes.

In the literature on bottom sediments and stormwater sediments, the geochemical criterion is used to assess the degree of pollution. The criterion is one of the chemical methods of evaluating the sediment quality. Chemical methods utilise the content of trace elements and chemical properties of sediments, which determine the potential capacity of sediments to bind toxic components, or the mobilisation of the latter from sediments. The criterion involves the comparison of the pollutant content in the sediment with that found in natural or low-polluted sediments, which provides the so-called geochemical background [8,9].

Recent years have witnessed some developments in ecotoxicological investigation methods for the aquatic environment, and also in assessing the hazards related to pollutant occurrence in water bodies receiving wastewater and surface runoff. In many countries, ecotoxicological criteria have entered legislation on sewage and hazardous wastes. Numerous methods have been developed to determine quality standards for bottom sediments. Sediment quality guidelines (SQGs) are based on both chemical and biological aspects. Poland still lacks legal regulations on the assessment of the harmful effect of chemical compounds in water sediments for the organisms that inhabit this environment. Many approaches have been made to establish SQGs. They rely on different theoretical or empirical basis used to assess the hazard posed by the presence of organic compounds and heavy metals in bottom sediments. The most widely used are threshold effects level (TEL) and probable effects level (PEL) parameters, which are components of the empirical method applied to benthic organisms [10]. The TEL specifies the upper limit of pollutant concentration range below which the harmful effect on aquatic organisms is found relatively seldom. The PEL is defined as the lower limit of pollutant concentration, which may significantly adversely affect the living organisms [11].

Sediment classification proposed by Bojakowska [12] incorporates ecotoxicological parameters TEL and PEL used in the USA and Canada. Sediments are categorised in a four-level scale, where:

(I) Unpolluted sediments (none of the harmful component content exceeds the TEL parameter).
(II) Low-polluted sediments (the content of at least one harmful component is higher than the TEL parameter, the content of all components is lower than the PEL parameter).
(III) Polluted sediments (the content of at least one harmful component exceeds the limit of Class (II)).
(IV) Strongly polluted sediments (the content of at least one harmful component exceeds the limit of Class (III)).

Sediments categorised as Class (I) and Class (II) can be freely applied to both aquatic and land environments. They are most often used as soil fertilisers, or to restore damaged banks of water reservoirs and rivers. Class (III) sediments can be relocated to designated sites and managed to a limited extent. Due to the elevated concentrations of hazardous compounds, those can be applied to industrial crops, or may be excluded from agricultural use. Strongly polluted Class (IV) sediments should be treated before they are placed in the environment, or they should be stored at protected refuse sites under controlled conditions.

The study aims at assessing the degree of pollution of sediments from the stormwater sewer system for urbanised area. That is done on the basis of tests run in cycles over a complete hydrological year. In view of environmental hazards, it is justifiable to assess the actual risks related to the occurrence of sediments in different parts of the sewer system. The evaluation included the content of selected heavy metals (zinc, lead, cadmium, copper, chromium and nickel) and organic pollutants (polycyclic aromatic hydrocarbons PAHs). The results of tests were referred to the standards on soil and land quality, and also to geochemical and ecotoxicological criteria.

2. Materials and methods

2.1. Study site

The analysis covered sediments collected from the stormwater treatment plant located in the 804.6 ha catchment area shown in Fig. 1. The facility treats stormwater and snowmelt from low-rise residential housing estates and from unbuilt open areas situated in the southern and south-western part of the catchment. Meadows and arable land constitute about 250 ha. Forests, made up of separate pine stands (Fig. 1) occupy the area of 8.3 ha, and are found in the southern part of the catchment. In the remaining part of the catchment (546.3 ha), single-family houses, housing estates, institutional buildings, main and side roads and industrial areas (approx. 70 ha in the northern part of the catchment) are found. The highest point in the area, (Mount Karczówka), is located at 335.40 m above the mean sea level (AMSL), and the lowest at 243.66 m AMSL. The average surface slope

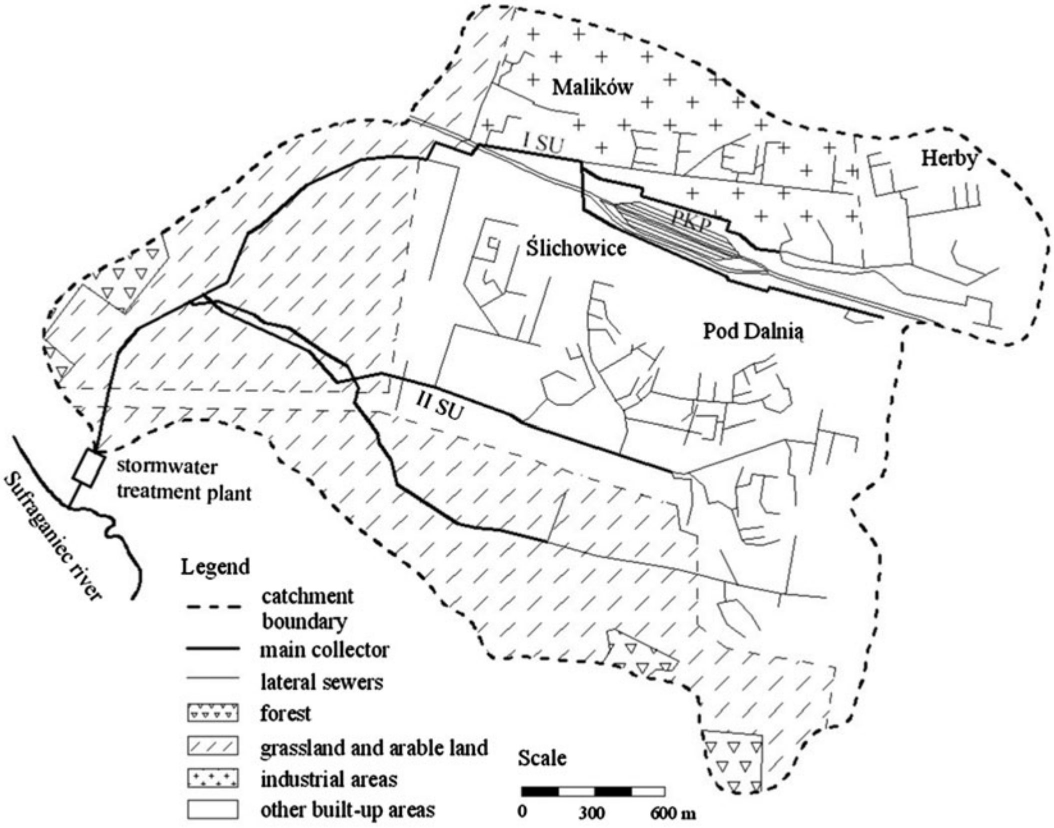

Fig. 1. The catchment of the stormwater treatment plant with the stormwater sewer system.

is 3.2%. Wastewater is delivered to the facility by the system of sewers (ϕ 200–1,800 mm) 11 965 m in length, and ditches that are 3,970 m in length. The treatment plant was put into operation in 1992. It consists of two tanks of the first wave of pollutants (FWP), two AWAS–type coalescence separators and a relief sewer. FWP tanks are 84 × 20 m (bottom dimensions) open settlers, each with a useful volume of 2,800 m^3. Treated wastewater is discharged into the Sufraganiec river via two covered channels having the diameters ϕ 1,800 mm—at km 2 + 230, and ϕ 400 mm—at km 2 + 110 [13].

2.2. Sampling

The sediment samples were collected four times per one hydrological year, described as a winter, spring, summer and autumn season, in accordance with the PN-EN ISO 5667-15:2009 standard method [14]. Within sedimentation tank, sediments were collected from two sites in this open reservoir, namely inlets and outlets. Sediment 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 divided into two parts. The first part was analysed for particle size distribution and the other was homogenised using a solvent-cleansed stainless steel bucket and a spoon. The physical and chemical parameters were measured immediately afterwards.

2.3. Analytical techniques

The pH and temperature were measured promptly after sample's homogenisation in accordance with the PN-EN 12176:2004 method using SevenMulti™ metre (Mettler Toledo) [15]. The organic content, measured as a loss of ignition (LOI), was determined in accordance with the PN-78/C-04541 method [16], which involved drying the sediment at 105°C to a constant weight, and then heating it at 550°C for 2 h. Sediment particle size distribution was examined using a laser diffraction analysis (Mastersizer 3000, Malvern).

Sediment samples from storm water were dried to constant weight in an electric dryer at 105°C and passed through a sieve with 2 mm mesh prior to heavy metal analysis. Sediment samples of 0.2 g were mineralised in 7 ml nitric acid using microwave oven (Multiwave 3000, Anton Paar). Concentrations of heavy metals: cadmium, copper, chromium, nickel, lead and zinc were determined by atomic emission spectrometry with inductively coupled plasma ICP Optima 8000 (Perkin Elmer) with certified multi element standards. Sediment samples with a mass of 1 g were extracted in dichloromethane to determine the total sum of PAHs. These compounds are grouped in two categories based on their molecular weights and these are low and high. Low molecular weight PAHs (LMW) containing two- and three-rings with molecular weight from 152 to 202 g mol^{-1} include: naphthalene (NAPT), acenaphthylene (ACNY), acenaphthene (ACEN), fluorene (FLUR), phenanthrene (PHEN) and anthracene (ANTH). The high molecular weight (HMW) PAHs have four-rings to seven-rings with molecular mass ranging from 228 to 278 g mol^{-1} include: fluoranthene (FLTH), pyrene (PYR), benzo[a]anthracene (B(a)A), chrysene (CHRY), benzo[b]fluoranthene (B(b)F), benzo[k]fluoranthene (B(k)F), benzo[a]pyrene (B(a)P), dibenzo[a,h]anthracene (D(ah)A), benzo[g,h,i]perylene (B(ghi)P) and indeno[1,2,3-c,d]pyrene (INPY). Concentrations of PAHs were identified in samples in accordance with the PN-EN 15527:2008 method [17]. To determine the reliability of the PAH data, including the efficiency of extraction methods and interferences that may be introduced during sample preparation, deuterated internal standards were used (d-8 NAPHT and d-12 B(a)A). These standards ensure that the accuracy of the results obtained is independent of the recovery degree. The next step included wetting the sediment sample with acetone, adding acetone with deuterated standards, intensive stirring of the sample and undisturbed evaporation of the acetone. This procedure makes it possible to achieve a similar binding form between standards added and the sediment matter [18]. All PAH concentrations were reported on a dry weight basis. In order to verify whether mean values of pollution indicators were statistically significant in different seasons, the analysis of variance (ANOVA) was performed (preceded by a test of homogeneity of variance Brown-Forsyth). The ANOVA Tukey's multiple comparison test was performed—most often used to study the aquatic environment [19]. The ANOVA tests were preceded by the normal distribution of the variables tested in each group (Kolmogorov–Smirnov test with Lilliefors correction and test the W Shapiro–Wilk). In the case where the distribution of the tested attribute was not compatible with the normal distribution, logarithmic transformation was performed according to the function the variable log X.

3. Results and discussion

The sediments were collected from the settler chamber following the established methodology and put to physical and chemical analyses. Irrespective of sample collection time, the sediments demonstrated homogeneous consistency, dark grey or black colour and a specific smell of petrol. After drying, they showed a strong cementation trend. The measured mean pH, the content of mineral (SM) and organic matter described as a LOI together with the moisture content in the sediment samples are shown in Table 1. For the treatment facility of concern, the pH values ranged 7.14–8.02. They were comparable with those of silts from inland water bodies, in which about neutral pH conditions (6.5–7.5) are maintained, however, they can also be slightly alkaline [2]. In each season, sediments were characterised by a high moisture content of 64–72%, a mineral matter content up to 90%, and an organic matter content ranging from 10% (winter collection) to ~13.5% (autumn collection). The amount of organic matter resembles that in bottom sediments, in which it does not exceed 15% [20]. The content of organic matter is important as regards pollutant sorption. In the sediments, organic matter can be found in a number of forms, namely small particles which occur independently of mineral particles, thin film covering mineral particles and as a kind of gel found in pores of mineral particles. Due to its hydrophobic nature, it is the preferred sorption matrix for nonionic organic pollutants [20].

In the next stage of investigations, the particle size distribution of the sediments was determined. The content of individual grain fractions is one of the factors of major importance that determine pollutant sorption in the sediment matrix [21]. Grain-size

Table 1
Comparison of the pH values, moisture content, mineral substances content and LOI in stormwater sediments

	Sampling season			
	Winter	Spring	Summer	Autumn
pH	7.14	7.59	8.02	7.42
Moisture (%)	64.88	72.17	68.56	71.28
SM (%)	90.02	88.47	87.38	86.64
LOI (%)	9.98	11.53	12.62	13.36

Notes: SM—mineral substances, LOI—loss of ignition.

distribution curves in Fig. 2 indicate that the sediments had similar particle size distribution. Dust-clay fraction, with grain diameters below 63 µm, constituted, on average, approx. 78%, the clay fraction alone with grain diameters below 2 µm, made up ~3%. The remaining fractions were set up by grains of the psammite fraction (fine and medium sand). Such a high content of the finest fraction is related to the character of the catchment, type of the surface found in the area, and also the hydrological characteristics of the catchment.

3.1. Heavy metals

In the aquatic environment, heavy metals can occur in two basic forms; they can either be solved, or bound to the solid phase particles. Metal occurrence in either of those forms depends on many factors including: the chemical form of metals delivered to the aquatic ecosystem, conditions prevailing in the liquid phase (pH, redox potential, temperature, biological activity), surface reactivity and grain composition of the solid phase. Tests on aquatic sediments are very often conducted to assess the environmental pollution with heavy metals because after they get into the stormwater, a majority of them migrate to the sediments.

In polluted aquatic sediments, elevated concentrations of cadmium, chromium, copper, nickel, zinc or lead are found most often. Their presence in the aquatic environment may result both from natural processes occurring in the atmosphere, which provides a dispersed source of pollutants, and from anthropogenic processes (transportation, industries, mining, municipal and industrial sewage and also agriculture) which constitute point emission sources [22].

The content of selected heavy metals (zinc, cadmium, chromium, nickel, lead and copper) in the sediments from the selected tank are presented in Fig. 3. The data indicate that the sediments of concern showed varied metal content. The highest average concentrations were recorded for zinc and lead. The zinc content ranged from 142 mg kg^{-1} in the winter period, to 627.9 mg kg^{-1} in autumn. The lead content was 123.3 mg kg^{-1} in the summer, and 198.3 mg kg^{-1} in the spring. The concentrations of other metals were markedly lower. For copper, chromium and nickel, the highest average concentrations, namely 94.4, 69.2 and 29.6 mg kg^{-1}, respectively, were found in the spring. The lowest content was noted for cadmium, as its concentration did not exceed 0.8 mg kg^{-1}.

The statistical analysis of the results, performed on the basis of the ANOVA test, showed that the zero hypothesis concerning the equality of the mean content of the parameters of concern should be rejected. Instead, an alternative hypothesis on the occurrence of significant seasonal variations should be assumed. Cadmium was an exception, because the test for the uniformity of variance was not satisfactory in that case. As regards the Tukey test, for copper, the results made it possible to identify spring, summer and winter (together with autumn) measurements as statistically significant. For zinc and chromium, three statistically significant groups of measurements, namely summer, autumn and winter together with spring ones were identified.

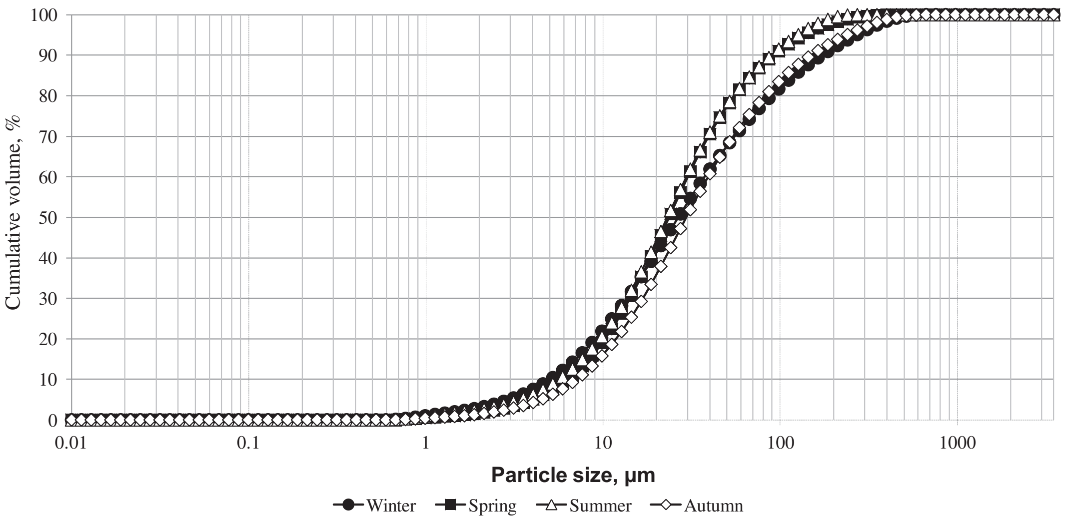

Fig. 2. Particle size distribution of stormwater sediments.

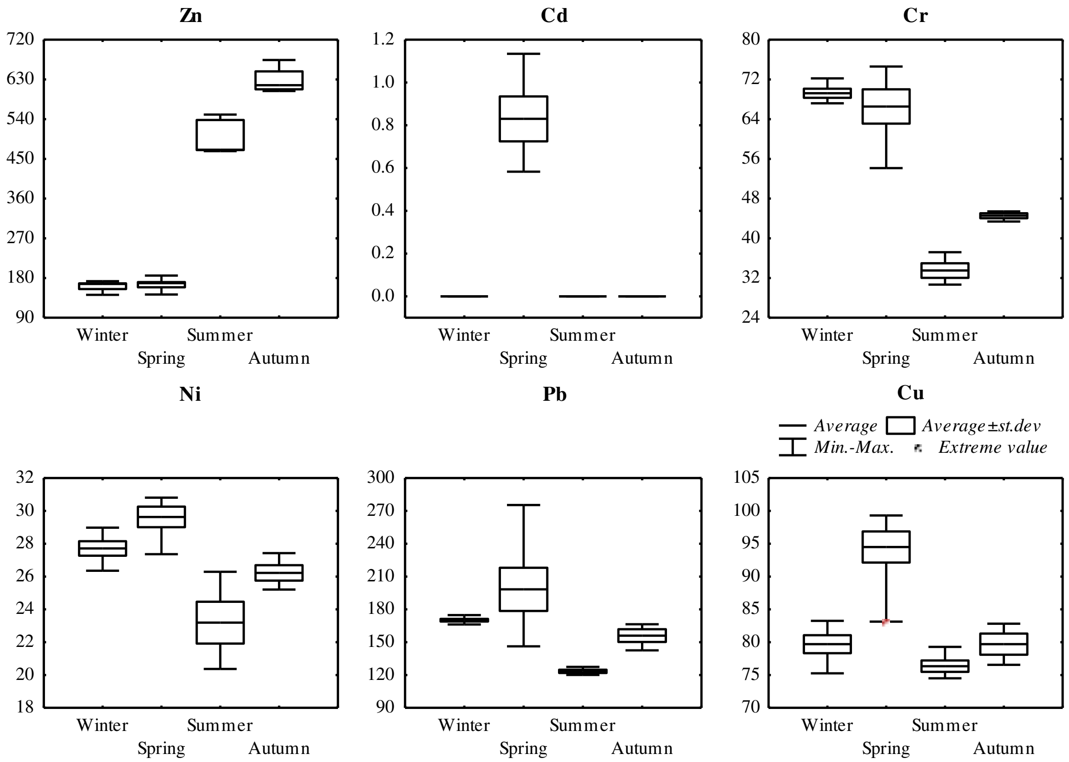

Fig. 3. Heavy metal sediment concentrations with the average in the sedimentation tank (mg kg^{-1} dry weight).

Mobility and bioavailability of heavy metals strongly depends on chemical and mineralogical forms in which they can occur. As a result, the measurement of the total concentrations of heavy metals can be used as a tool to generally estimate the heavy metal contamination. Their mobility, however, depends on how they are bound to the matter of the sediment. Depending on the way heavy metals are bonded to individual components of the sediment, and on the effect which sediment properties have on this process, four basic fractions can be differentiated [23]:

(I) Soluble (carbonate) fraction. Metals are bound, in the exchangeable way, to constant or variable charges of mineral and organic solids in the sediment components. Their amount depends on sorption and desorption processes on the sediment particles. Metals bound to carbonates, sulphates and phosphates, released from this phase, are sensitive to changes in the environment (primarily pH and the lowering of it). Adsorption of metals of this fraction depends on the amount of carbonates, and on the dimensions of the sediment particles.

(II) Reducible fraction. Metals bound to oxides and hydroxides of iron and manganese Fe/Mn occur in the co-precipitated, or adsorbed form, or as complex compounds.

(III) Oxidisable fraction. Metals are bound to organic matter and sulphides, most often in organo-metallic complexes. Under natural conditions, this fraction shows low mobility.

(IV) Residual fraction. Metals are retained within the crystal lattice of minerals. The fraction is completely immobile, and it does not produce a significant ecotoxicological effect.

Fig. 4 shows the relative content of the selected metal (mass percentage) determined for each fraction relative to the total content in fractions (I)–(IV). On the basis of the investigations into the types of bonding of metals, it can be stated that in the sediments of concern, metals most often occur in fractions (III) and (IV), i.e. they are strongly bound to the sediment matter. Such a dependence can be best observed for lead; 25% of forms in which it occurs are bound to organic matter and sulphides, the other 75% are retained in the crystal lattice. Zinc is found in fractions (III) (66%) and (IV) (26%). The mobile (carbonate) fraction, however, constitutes only 7%. Also, cadmium (6%), copper (21%) and nickel (6%) demonstrate a small amount of mobile forms; so when the conditions in the system

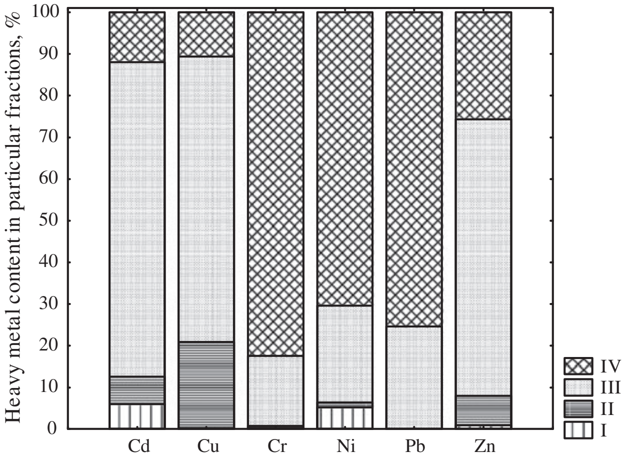

Fig. 4. Average percentage of heavy metals in particular fractions of the stormwater sediments.

change, these metals can be released into the environment, thus creating a contamination hazard. However, it should be noted that zinc and copper are the least toxic for the environment.

Comparing the results of tests on metal concentrations in the analysed sediments with the quality standards for soil and land stipulated in the Regulation of the Minister of Environment (J. of Laws No. 165, item 1359), it can be stated that concentrations of all examined heavy metals are much lower than the permissible values for urbanised areas categorised as Group B. In accordance with the regulation, the concentrations range as follows, for zinc: 300–720 mg kg^{-1}, cadmium: 4–10 mg kg^{-1}, lead: 100–200 mg kg^{-1}, copper: 100–200 mg kg^{-1}, nickel: 50–210 mg kg^{-1} and chromium: 150–380 mg kg^{-1}.

The geochemical classification of the sediments under consideration was presented in Table 2. As regards cadmium, chromium, nickel and copper, the sediments were classified as unpolluted or low-polluted, i.e. belonging to Class (I) and (II), respectively. With respect to the content of zinc and lead, however, the sediments were categorised as Class (III). Taking into account geochemical parameters, the whole tested material can be considered medium-polluted, i.e. the sediments may pose an immediate hazard to the aquatic environment and the organisms living there. 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. In the examined sediments, zinc constituted from 30% of the total content of heavy metals in the cold period, to almost 70% during the warm period. Lead made 36% of the total content of heavy metals in the cold period, whereas in the warm period, the amount of the element dropped to approx. 16%. In the summer-autumn period, the volume of wheeled traffic in the catchment is much higher than in the autumn-winter period, so the potential source of zinc may be the products of abrasion of road surfaces, brake discs and tyres. In other studies [24], it was demonstrated that elevated concentrations of heavy metals are also closely related to the occurrence of the finest fraction in the sediments, as pollutants of that kind readily sorb to surfaces of particles. As regards the sediments of concern, zinc was most closely bound to the dust-clay fraction.

3.2. Polycyclic aromatic hydrocarbons

Currently, in the water sediments, the content of POPs is often elevated several times. Those can be PAHs or xenobiotics: organochlorine pesticides and polychlorinated biphenyls. PAHs are on the list of the 129 most dangerous substances, which was compiled by the American Environmental Protection Agency. The list is updated and adjusted to the environmental conditions in many countries [25,26]. PAHs are commonly classified into one of two groups based on their molecular structure. LMW PAHs have three or fewer

Table 2
Geochemical assessment of stormwater sediments wg Bojakowska [12]

Elements	Winter	Spring	Summer	Autumn	Class I	Class II	Class III	Class IV
(mg kg^{-1})					(mg kg^{-1})			
Zinc	160.9	165.8	499.3	627.9	125	300	1,000	>1,000
Cadmium	0	0.8	0	0	0.7	3.5	6	>6
Chromium	69.2	66.5	33.5	44.5	50	100	400	>400
Nickel	27.7	29.6	23.1	26.2	16	40	50	>50
Lead	170.1	198.3	123.3	156.0	30	100	200	>200
Copper	79.6	94.4	76.3	79.7	20	100	300	>300

aromatic rings, while HMW PAHs have four or more rings. Differences in the structure and size of individual PAHs result in substantial variability in the physical and chemical properties of these substances. The toxicity of PAHs depends on a number of factors, including the species, route of exposure and molecular structure of the PAH. In general, LMW-PAHs are considered to be acutely toxic and noncarcinogenic to aquatic organisms, whereas, HMW-PAHs are generally not acutely toxic to aquatic organisms, but a number of them are carcinogenic [27]. A natural source of PAHs are forest fires and volcano eruptions. In recent year, however, the concentrations of those compounds in the environment have increased much because of anthropogenic activities (production of energy from the combustion of oil, synthetic fuels, hard coal and biomass, the use of oil and its derivatives and accidental spills of those substances, the production and use of coal) [20]. In the anthropogenic activity, two types of potential sources of PAHs can be differentiated, namely pyrogenic and petrogenic ones. The former is related to the incomplete combustion of organic matter. The latter is connected with oil and its derivatives [28].

In the material tested for the study, fifteen PAH compounds were measured. The total content of PAHs in the examined sediments was presented in Fig. 5. The data indicate the sediments were characterised by high time differentiation. The highest concentrations were observed in the summer and autumn periods, 57.0 and 87.8 mg kg^{-1}, respectively. The lowest concentrations were found for samples collected in the winter and spring, 40.5 and 51.4 mg kg^{-1}, respectively.

Comparing the results with the standards on soil and land quality [7], it can be stated that as it was the case with heavy metals, the values reported were below the permissible ones, specified as 200 mg kg^{-1}. Consequently, the sediments do not pose a hazard to the natural environment.

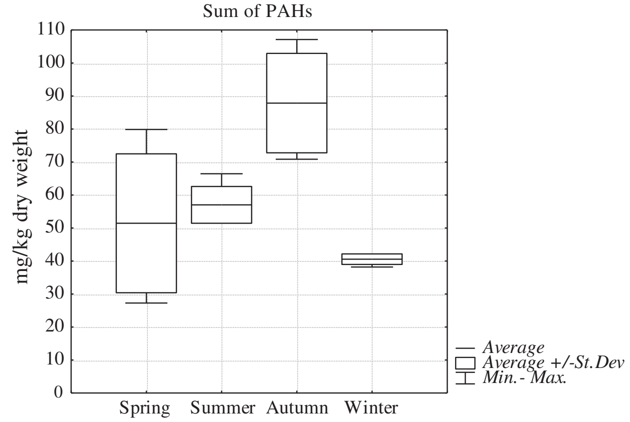

Fig. 5. PAHs sediment concentrations in the sedimentation tank (mg kg^{-1} dry weight).

The results of the ANOVA test show the occurrence of significant seasonal variations in the mean content of the PAHs. The exceptions were: anthracene, naphthalene, acenaphthene, fluorene and dibenzo(a,h) anthracene, for which the test for the uniformity of variance was not satisfactory, and also phenanthrene and benzo(a)anthracene, which showed no seasonal changes. In different seasons of the year, the statistics values F and probability levels p were: $F = 1.0079$, $p = 0.4165$ and $F = 1.7165$, $p = 0.2064$, respectively. For acenaphthylene and pyrene, two groups of measurements were identified, namely winter, together with spring and summer and also autumn ones. In the latter group, the highest concentrations of those compounds were observed, 12.1 and 23.3 mg kg^{-1}, respectively. With respect to chryzene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d) pyrene and benzo(g,h,i)perylene, as earlier, two groups were observed (the Tukey test). The difference was they were autumn, and winter together with spring and also summer measurements. The highest mean content of those compounds, statistically different from the mean values for the remaining seasons, occurred in the summer and was 4.0, 5.5, 5.1, 3.7 and 2.1 mg kg^{-1}, respectively. For benzo(k)fluoranthene, the highest concentrations were observed in the samples collected in the summer and autumn (1.0–1.9 mg kg^{-1}).

The detailed assessment of sediments from the stormwater sewer system with respect to geochemical characteristics, presented in Table 3, shows a different classification. In addition to the total content, also the content of individual PAH compounds were taken into account. The material of concern was most often categorised as Class (III)—26% of the samples, or as Class (IV)—64% of the samples. The procedures applicable to Class (III) deposits were discussed in the section on heavy metals. As regards Class (IV), i.e. strongly polluted sediments, it is recommended that they should be treated before they are disposed of into the environment. Otherwise, they should be stored at protected refuse sites under controlled conditions.

Additionally, five PAH isomer ratios with equal molecular mass but different thermodynamic stability (FLTH/PYR, PHEN/ANTH, FLTH/ΣFLTH:PYR and ANTH/∑ANTH:PHEN) and the ratio of LMW to HMW (LMW/HMW) were calculated for the sediment samples to determine probable PAH sources (Table 4).

Generally, pyrogenic or combustion sources of PAHs are indicated by high FLTH/PYR, FLTH/ΣFLTH:PYR and ANTH/ΣANTH:PHEN ratios (>1, >0.5 and >0.1, respectively) and low PHEN/ANTH < 10 and

Table 3
Geochemical assessment of stormwater sediments wg Bojakowska [12]

PAHs	Winter	Spring	Summer	Autumn	Class I	Class II	Class III	Class IV
Results, (mg kg^{-1})					(mg kg^{-1})			
ACEN	0.2	0.5	0.2	0.4	0.01	0.1	0.5	>0.5
ACNY	2.0	2.7	2.9	12.1	0.01	0.15	0.5	>0.5
PHEN	6.5	9.9	6.0	7.6	0.05	0.5	1	>1
FLTH	13.3	14.2	11.0	24.2	0.1	1.5	3	>3
FLUR	0.7	2.1	0.8	1.7	0.02	0.15	0.5	>0.5
ANTH	1.5	1.8	0.7	4.6	0.05	0.25	1	>1
PYR	11.1	12.2	8.7	23.3	0.1	1.5	2.5	>2.5
CHRY	0.8	1.0	4.0	1.6	0.1	0.75	2.8	>2.8
B(a)A	0.5	1.0	0.6	0.5	0.1	0.7	1.6	>1.6
B(b)F	0.8	1.3	5.5	2.1	0.1	0.75	3	>3
B(k)F	0.1	0.6	1.9	1.0	0.1	0.75	3	>3
B(a)P	0.8	1.0	5.1	1.5	0.1	0.75	1.6	>1.6
D(ah)A	0.0	0.7	2.0	0.4	0.01	0.15	0.25	>0.25
B(ghi)P	0.5	0.9	2.1	1.2	0.05	0.2	0.4	>0.4
INPY	0.5	0.7	3.7	1.2	0.05	0.2	0.4	>0.4
∑PAHs	40.5	51.4	57.0	87.8	1	7.5	15	>15

Table 4
Isomer ratios of PAH concentrations

Isomer ratio	Pyrogenic source	Petrogenic source	Winter	Spring	Summer	Autumn
LMW/HMW	<1.0	>1.0	0.41	0.51	0.26	0.53
PHEN/ANTH	<10	>10	4.34	5.31	8.57	1.66
FLTH/PYR	>1.0	<1.0	1.20	1.16	1.27	1.04
FLTH/ΣFLTH:PYR	>0.5	<0.5	0.54	0.54	0.56	0.51
ANTH/ΣANTH:PHEN	>0.1	<0.1	0.19	0.16	0.10	0.38

LMW/HMW PAH ratios (<10 and <1, respectively). By contrast, petrogenic and other non-combustion sources of PAH are indicated by low FLTH/PYR ratios (<1) and high PHEN/ANTH and LMW/HMW ratios (>10 and >1, respectively). A single ratio can often be misleading, so multiple ratios are often used. These ratios were calculated using the average concentrations of individual PAH compounds sampled from a sedimentation tank (each sampling season). All calculated ratios indicate a pyrogenic source, so PAHs are formed and emitted primarily during incomplete combustion processes of organic matter from different sources.

4. Conclusions

The sediments accumulated in the stormwater sewer system cause problems that are related not only to the system operation, but also to the hazard they may pose when delivered to the receiver. Because of their properties, the sediments are characterised by a high affinity for accumulating and storing toxic pollutants in their structure, such as heavy metals and also organic compounds. When the sediment structure is disturbed, or the physicochemical conditions are altered, pollutants may be released and they may migrate to the environment. A hazard of this kind may be encountered when the stormwater sewer system is cleaned, or when settlers and separators in the treatment facility overflow.

Although the awareness of the hazard posed by stormwater sediments exists, the unambiguous classification of this material has not been developed yet. The data on the assessment of their actual toxicity level are not available either. Consequently, the guidelines on the procedures of dealing with this material, or management options have not been drawn up. Hence, a need arises to continue research into those issues.

In the present study, the analysis covered the samples collected from the chamber of the settler in the stormwater treatment plant located in the 804.6 ha urbanised catchment. They were collected during four periods over the hydrological year. The results of tests show some significant differences in the physico-chemical composition of the sediments of concern. As expected, the analysis of the pollutant content revealed the occurrence of heavy metals, namely zinc, cadmium, chromium, nickel, lead and copper, and also of PAHs. The results describing metal concentrations in the sediments were referred to the soil and land quality standards stipulated in the Regulation of the Minister of Environment (J. of Laws No. 165, item 1359). The comparison shows that the concentration values of all analysed heavy metals are much lower than the permissible values for urbanised areas categorised as Group B. In accordance with the geochemical classification, however, the sediments of concern were categorised as Class III, which is medium-polluted. Consequently, they may pose an immediate hazard to the aquatic system and the organisms inhabiting it. At the same time, the speciation analysis indicates that the metals under investigation occur mostly in the unstable sulphide forms and oxide forms, retained in the crystal lattice of minerals, and as such are characterised by low mobility under natural conditions.

The analysis of the content of PAH organic compounds shows growing concentrations of those substances from 40.5 to 87.8 mg kg^{-1}, which indicates their accumulation in the examined sediments. Comparing the test results with the soil and land quality standards [7], it can be concluded that, as it was in the case of heavy metals, the values are lower than the permissible ones, i.e. 200 mg kg^{-1}. As a result, the sediments cannot be considered to be causing any environmental hazard. A detailed geochemical assessment of the stormwater sediments, however, indicates a different classification. Sediments are categorised as Class (IV), i.e. strongly polluted, which means it is recommended to treat them before disposal into the environment or to store them at protected refuse sites under controlled conditions.

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