



Possibilities for reduction of selected pollutants in urban area rainfall wastewater with the use of ditches

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ABSTRACT

Wastewater composition depends on a variety of factors, including the type of catchment and the method of catchment development, methods of black ice control, parameters of atmospheric precipitation and the season. The major pollutants of rainfall wastewater are heavy metals, animal waste, mineral hydrocarbons, salts, de-icers, leaves and other plant parts, but the volume of pollution may vary even within one catchment. From the viewpoint of rainfall wastewater pretreatment, in urban areas, ditches are significant facilities since they are inhabited by a variety of flora species, mainly ruderal and reed bed vegetation, which have a capacity for accumulating heavy metals such as chromium, copper, nickel, lead, cadmium and zinc. The focus of the present study is a ditch located in the western part of the city of Kielce, which collects rainfall wastewater from closed stormwater drainage of Skrajna, Malików and Kolejarzy Streets, then removes it to the pretreatment facility and finally—to the Sufraganiec river. The material for analysis was collected between November 2012 and April 2013, following atmospheric precipitation of varying intensity, as well as after snowmelt. In the collected material, the pH, electrolytic conductivity, suspension, bicarbonates, as well as concentrations of selected heavy metals (Pb, Cd, Zn, Cu, Ni, Cr) were determined.

Keywords: Rainfall wastewater; Ditch; Urban area; pH; Heavy metals

1. Introduction

Rainfall wastewater appears as a consequence of rainfall water transformation due to surface runoff and is then introduced into the stormwater drainage system. Therefore, the quality of rainfall wastewater is characterised by values of indicators different from those of rainwater quality indicators. The major sub-

stances which cause it are mineral hydrocarbons, i.e. oils, fuels, lubricants, salts, de-icers, heavy metals, animal waste, leaves and other plant parts or street waste [1]. The composition of rainfall wastewater depends on a number of factors, including the catchment type and the method of catchment development, black ice control, atmospheric precipitation parameters, the season and many others [2]. The type of the rainfall determines its quality which may vary due to high

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concentrations of physicochemical and bacteriological pollutants. Within one catchment, pollutant indicators may fluctuate depending on the duration and intensity of precipitation, the degree of industrialisation in a given area, as well as the apparatus used for wastewater treatment [1,3,4]. Major pollutants of rainfall wastewater are heavy metals and aromatic hydrocarbons originating from unburnt fuel fractions and as products of asphalt road surface or car tyre wear [2]. Heavy metals are most commonly found in dusts suspended in the atmosphere. Rainfall wastewater contains largest amounts of lead and zinc as well as nickel, copper and arsenic [5]. They occur in the form of dissolved salts or insoluble compounds. Their occurrence is directly linked to both natural sources, such as volcanic eruptions, erosion and others, and anthropogenic sources. These include traffic routes, strongly urbanised and industrialised areas, as well as corrosion of building materials such as copper and zinc which are used in roof coverings [6,7]. This is why concentrations of trace elements in rainfall wastewater depend mainly on land development, as well as the types and characteristics of human activity in a particular area [8].

Together with the growth of urbanised areas, there appears the problem of wastewater removal and management in a particular area, linked directly to the degree of surface sealing, which disables water seepage into the soil [9]. Stormwater drainage systems enable removal of large amounts of water over a short period of time with simultaneously limited infiltration. However, this solution is linked with a negative influence on the natural environment because stormwater drainage systems are not effective during heavy torrential rainfall [10,11]. Consequently, in urban areas, actions are taken to manage rainfall wastewater locally. In this way, the formation of entirely new groundwater is supported, and water removal in small watercourses—as a result relieving the wastewater network during heavy rains and lowering high water levels. Thanks to that the negative impact of harmful substances on water ecosystems can be neutralised. However, the manner of water management is determined by local subsurface conditions [11].

Ditches prove to be significant facilities for wastewater pre-treatment in urban areas [12,13]. Ditches are used to reduce the load of some pollutants in cities [10,14]. In order to enhance pollutant reduction, a variety of flora species (mainly ruderal and reed bed vegetation) are introduced to some systems [15,16]. These species have a capacity for accumulating pollutants, including heavy metals such as chromium, copper, nickel, lead, cadmium and zinc [10,17].

2. Materials and methods

The present study concerns a ditch situated in the western part of the city of Kielce, between Skrajna and Piekoszowska-Malików Streets (Fig. 1). The total length of the ditch is 2.95 km; the wastewater passage rate equals 0.37 ms^{-1} . The ditch collects rainfall wastewater from the closed stormwater drainage of Skrajna, Malików and Kolejarzy Streets, and then removes it to the Sufraganiec river. The wastewater is pre-treated at the rainfall wastewater pre-treatment facility situated in Jarząbek Street. The majority of the ditch crosses the catchment in non-built-up areas, but some parts of it pass through a batching plant where a section of the ditch is covered with concrete slabs. The direct impact zone of the ditch includes other industrial or storage facilities, including a cement plant.

The study covers rainfall wastewater samples collected both at the inlet (1 pk), and at the outlet (2 pk) of the ditch (Fig. 1). The material for the analysis was collected over six months between November 2012 and April 2013, following atmospheric precipitation of varying intensity and snowmelt. Two water samples were collected in 1.5 dm^3 containers at each point. Wastewater flowing into the ditch and caused by both rainfall and snowmelt has been analysed. This made it possible to determine the role of the ditch in the reduction of pollutants in different temperature conditions.

The flow rate was measured over a preset distance of 10 m, and it was found that the average flow rate through the analysed ditch was 0.37 m s^{-1} , while the rainfall wastewater flow time was the 27 s. If we assume that the length of the ditch is 2.95 km, the flow time from the ditch inlet (1 pk) to the ditch outlet (2 pk) will be about 2.25 min. The flow time of rainfall wastewater is an estimate because the selected part of the ditch where the flow rate was measured is a straight section, not overgrown by any water plants which would prevent the passage of precipitation wastewater.

The material was collected with a grab sampler in accordance with the PN-ISO 5667-10:1997 standard. The collected material was analysed for pH, conductivity, suspension (as in PN-72/C 04559.0) and bicarbonate concentrations (as in PN-C-04540-01:1990). In order to determine the concentrations of heavy metals, i.e. Pb, Cd, Zn, Cu, Ni and Cr, as well as the amounts suspended and dissolved, a 25 cm^3 sample was taken from the collected material and 5 cm^3 of concentrated HNO_3 was added. The remaining part of the collected material was filtered through a filter of $0.45 \mu\text{m}$ diameter. From the obtained solution, 25 cm^3 samples were collected, to which 5 cm^3 of concentrated HNO_3 was

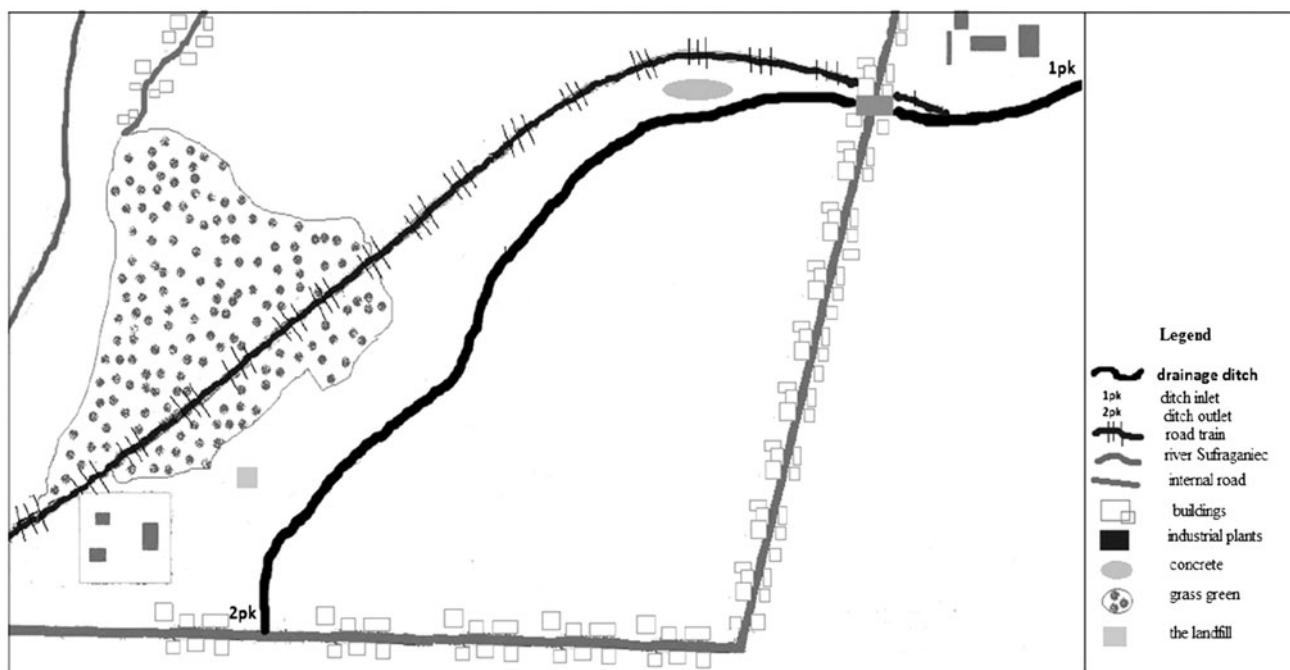


Fig. 1. The situation of the drainage ditch in the city of Kielce and rainfall wastewater sampling points: ditch inlet—1 pk, ditch outlet—2 pk.

added. The prepared solutions were subjected to two-stage microwave enhanced mineralisation:

Stage 1: growth 5 min, retention 25 min, power 100 W,

Stage 2: growth 0 min, retention 15 min, power 0 W.

The cooled solutions were transferred to 100 mL volumetric flasks and the solutions were diluted to volume with ultrapure water. All reagents and acids were suprapure or of pro-analysis quality. The total element concentrations in the water samples were determined with UV–Vis spectrophotometry. The correctness of the determinations was verified by means of the standard addition method, providing $\pm 2.3\%$ accuracy.

3. Results

The results of the conducted rainfall wastewater sample analysis are presented in Table 1.

4. Discussion of the results

Situated in the western part of Kielce, the studied facility forms a part of the city's stormwater drainage system. In the ditch, heavy metals are to a large extent of local origin, as a result of paved surface runoff as

well as deposition within a small distance from the emission source. The metals which belong to one group may have a shared origin or, as has been claimed by Csavina et al. [18], fine particles can form larger particles consisting of several heavy metals due to coagulation. The origin of Pb, Cd, Cu, Ni and Zn is connected with road transportation, wherein in consequence of fuel combustion, tyre and brake wear, heavy metals are emitted [19]. Another factor which influences the presence of heavy metals in the studied area is raw rock materials processing. Devonian limestone, processed at a nearby cement plant, contains lead ore—galena. Lead emission may occur during mechanical crushing of the rock material and during the cement manufacturing process. High Pb concentrations correlate with the close proximity of the cement plant.

Another source of heavy metals may be the fuels used in nearby production plants and households, where car tyres and plastics are burnt as fuel. The values of heavy metal deposition are related to those from industrialised areas of eastern Asia and Europe [20–24]. Contamination with heavy metals in these areas is due to emissions from fossil fuel combustion, metalworks operation and road transport. In particular, the impact of the latter factor in urban areas with poor air exchange contributes to increased rainfall wastewater levels. Regrettably, the metals present in

Table 1
Analysis results of selected heavy metal concentrations in rainfall wastewater

Analysed	Sampling point		S_D
	1	2	
pH	7.74 (7.49–7.97)	7.79 (7.65–7.93)	0.75
Conductivity, $\mu\text{S cm}^{-1}$	1104.417 (580–2,543)	985.75 (637–1808)	12.26
HCO_3^{2-} , mol dm^{-3}	11.67 (9.48–15.4)	8.81 (5.98–12.24)	1.31
SPM, $\text{mg}\cdot\text{dm}^{-3}$	392.5 (160.0–630.0)	315.0 (60.0–71.0)	5.33
Cd	Total ($\mu\text{g dm}^{-3}$)	61.58 (11.01–137.0)	1.14
	Soluble ($\mu\text{g dm}^{-3}$)	34.05 (7.01–134.8)	3.09
	SPM (%)	43.96 (1.61–80.22)	2.16
Cu	Total ($\mu\text{g dm}^{-3}$)	25.60 (7.70–96.03)	0.43
	Soluble ($\mu\text{g}\cdot\text{dm}^{-3}$)	16.75 (2.80–91.71)	0.66
	SPM (%)	44.64 (4.50–75.57)	0.54
Cr	Total ($\mu\text{g dm}^{-3}$)	159.7 (37.61–552.6)	3.11
	Soluble ($\mu\text{g dm}^{-3}$)	127.8 (35.90–402.0)	3.41
	SPM (%)	18.54 (2.68–53.39)	1.55
Ni	Total ($\mu\text{g dm}^{-3}$)	8.759 (2.971–22.27)	0.17
	Soluble ($\mu\text{g dm}^{-3}$)	6.528 (2.781–22.06)	1.06
	SPM (%)	29.35 (0.94–60.44)	2.21
Pb	Total ($\mu\text{g dm}^{-3}$)	625.3 (100.2–2658.7)	2.96
	Soluble ($\mu\text{g dm}^{-3}$)	216.4 (29.92–835.3)	3.01
	SPM (%)	57.11 (6.16–91.62)	1.86
Zn	Total ($\mu\text{g dm}^{-3}$)	43.82 (3.44–215.03)	2.66
	Soluble ($\mu\text{g dm}^{-3}$)	24.25 (2.31–186.5)	3.03
	SPM (%)	44.95 (5.88–84.16)	1.97

rainfall wastewater may influence the toxicological effect in surface waters and soils directly, and—indirectly—in underground waters.

The presence of mobile metal forms in the bottom sediment deposited in the ditch is significant for plants. Several processes thank to which plants activate and obtain nutrients from the substratum occurring in the root–substratum contact zone, i.e. in the rhizosphere—a very thin layer close to the roots, with rich fungal and bacterial flora. Plant roots can release complexing agents, which facilitates metal absorption by the roots and enhances the mobility of a particular element in the substratum [25–27]. The presence of plants is, therefore, one of the factors conditioning reduction possibilities for pollutants present in rainfall wastewater passing through the ditch. The following plant species commonly overgrow ditch banks:

- (1) macrophytes (from the heliophyte group), e.g. common bulrush (*Typha latifolia*), common reed (*Phragmites communis*), reed mannagrass (*Glyceria aquatica*), sweet flag (*Acorus calamus*),
- (2) perennial plants, e.g. hygrophyte yellow iris (*Iris pseudacorus*), geophyte Jerusalem artichoke (*Helianthus tuberosus*), hemicrypto-

phytes: common nettle (*Urtica dioica*) and tansy (*Tanacetum vulgare*),

- (3) trees, e.g. common osier (*Salix viminalis*), black locust (*Robinia pseudoacacia*) Fig. 2

The diversification and domination of particular communities and species along the ditch are due to the presence of landscape development features, such as roads, batching and cement plants as well as households. They are also influenced by types and pollution of the rainfall wastewater introduced into the ditch.

The studied samples of solutions collected both at ditch inlet and outlet displayed pH values above 7, due to the presence of cement and batching plants in the immediate vicinity of the ditch. Yet in the autumn and winter seasons the pH value at ditch inlet was higher than spring values recorded during snowmelt (Fig. 3). In autumn and winter, lower pH values were observed as a result of wastewater passage through the ditch, whereas in spring, a small increase was noted. In December, the samples collected at inlet and outlet displayed very similar pH values.

The volume of dissolved pollutants is determined by the value of electrolytic conductivity, which remained within the range up to $2,543 \mu\text{S cm}^{-1}$ at inlet

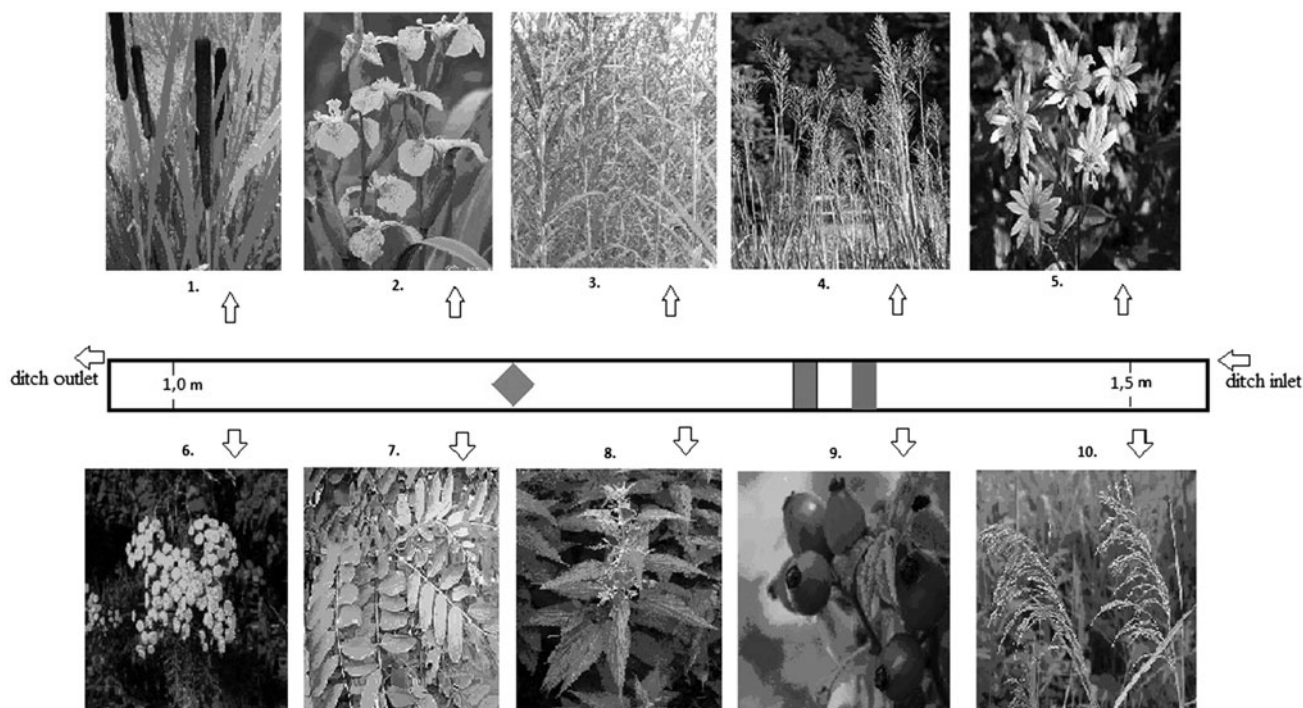


Fig. 2. Diagram of the drainage ditch with overgrowing vegetation (1) common bulrush, (2) yellow iris, (3) common osier, (4) common reed, (5) Jerusalem artichoke, (6) tansy, (7) black locust, (8) common nettle, (9) dog rose, and (10) reed mannagrass; road, bridge, batching plant.

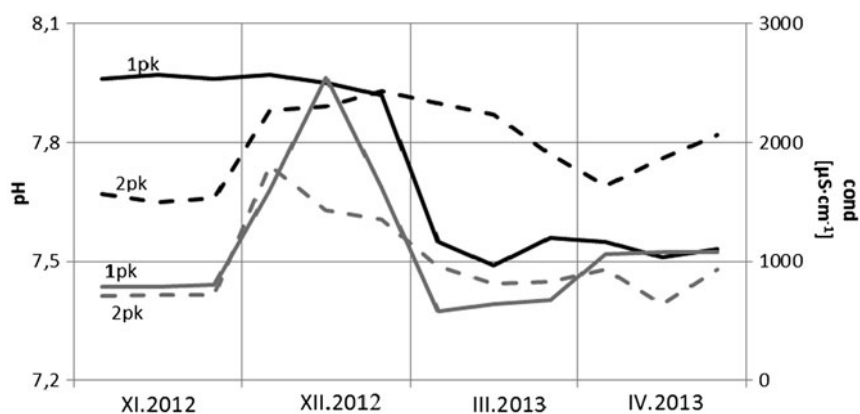


Fig. 3. Changes to pH values (black) and cond (grey) in rainfall wastewater samples.

and up to $1,808 \mu\text{S}\cdot\text{cm}^{-1}$ at outlet (Fig. 2). Over the entire study period, the 1pk samples had higher cond values than those found in the 2pk material, with the exception of March 2013, when the volume of dissolved substances at ditch outlet was higher than at ditch inlet. In this case, cond values ranged from 580 to $956 \mu\text{S}\cdot\text{cm}^{-1}$ at ditch inlet and outlet, respectively. The largest amounts of substances in ion form were observed in December and in April, when values

amounting to $2,543\text{--}1,082 \mu\text{S}\cdot\text{cm}^{-1}$, respectively, were recorded. It is believed that the degree and form of pollution depend on air quality. Rainfall waters in the vicinity of cement plants are more subject to pollution, as is the case with the studied location. Under these conditions, the predominant form of the buffering system ($\text{H}_2\text{CO}_3\text{--HCO}_3^{2-}\text{--CO}_3^{2-}$) is bicarbonate ions which determine water acidity/alkalinity. This affects the processes which occur in the water medium, including

precipitation, formation of hardly soluble salts, as well as determining the suspension and metal bioavailability. In the studied cases, the amount of HCO_3^{2-} as a result of passage through the ditch was on average lowered by 23.66%, lesser reduction being noted in December (12.75%) and the highest in October 2012 (34.25%). The presence of free carbon dioxide, which determines the carbonate equilibrium, significantly affects metal solubility in water. When the content of free CO_2 is negligible in proportion to bonded CO_2 , water does not dissolve metal (e.g. Pb and Zn) compounds. But when the content of free CO_2 is equal to the content of bonded CO_2 , the process of dissolution occurs, and when free CO_2 preponderates, the gas displays aggressive properties, leading to appearance of metal bicarbonates, e.g. $\text{Pb}(\text{HCO}_3)_2$ and $\text{Zn}(\text{HCO}_3)_2$.

In high salinity, in the presence of HCO_3^{2-} and CO_3^{2-} and in a slightly alkaline medium, hardly soluble salts of Pb, Cd, Zn, Cu, Ni and Cr are precipitated [28–32]. Thus, metals are built into the suspension structure, and then—under slow flow conditions and occurrence of the sedimentation process—also into the bottom sediment [24,33]. It must be noted that metals in carbonate and bicarbonate forms supply the fraction which is characterised by considerable bioavailability, due to which the metals can be easily absorbed by ditch plants. The change to metal forms is also affected by reduced pH values in the near-bottom zone, which may unsettle the carbonate equilibrium, in consequence of which metals are released into the water.

The major element of surface waters, responsible for metal migration in the medium, is suspension. This is why, in the studied rainfall wastewater, the degree of studied metal bonding with the suspended material was assessed. The suspension consists of both organic and inorganic substances, which means that the suspended matter is built of particles varying in size. Yet only the fraction with particle diameter $< 1 \mu\text{m}$ remains in the suspended state and fosters the transport of adsorbed substances over long distances. Substance transport as well as sedimentation processes therefore depend on the adequate agglomerate size, the water flow rate and the presence of chemical compounds such as chlorides or sulphates [34,35], which determine the value of conductivity and degree of water alkalisation/acidification.

Bonded to the suspension, metals are passively carried in the water medium, and under conductive hydrodynamic conditions, they are subject to sedimentation processes, due to which their volume in water samples decreases. The movement of a chemical compound may also occur due to reasons unrelated to the presence of the substance in the transport medium.

Some examples of this type of processes are the deposition of a chemical compound bonded to suspended matter, which falls to the bottom of the water column, or re-formation of the suspension [36,37].

The amounts of suspension in the studied rainfall wastewater samples ranged widely from 0.07 to 0.69 g dm^{-3} . In the majority of cases, the amount of the suspended material was reduced as a result of wastewater passage through the ditch. The highest reduction (63%), was recorded in March 2013, whereas the lowest (ca. 25%)—in December 2012. In November 2012, as a result of heavy flows, the material collected in the sediment was moved upwards, and consequently the volume of suspension increased by 19% at ditch outlet as compared to the material introduced with rainfall wastewater at inlet.

The areas surrounding the ditch contain industrial facilities, warehouses and fallow fields, from which, as a result of heavy rainfall, pollutants are flushed, including large amounts of suspended material. That is why high autumn and winter values of the suspension, of the order of 400 mg dm^{-3} , both at the inlet and outlet of the analysed ditch, could be due to significant rainfall intensity. The latter contributes to increased flow velocity and increased material accumulation which builds the sediment.

It must be stressed that the observed reduction of suspension volume also caused a reduction of the total metal volume in wastewater samples. However, the conducted analyses have demonstrated that, depending on the metal, the quantitative distribution of the suspension-bonded and dissolved forms varies (Fig. 4).

Heavy metals, like a few other inorganic compounds, have strong adsorption properties. They are halted at phase boundary, such as the bottom or bank surface, water vegetation, hydrotechnical structures,

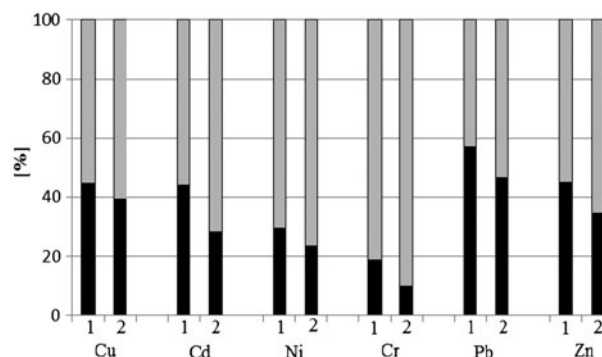


Fig. 4. Metal forms: suspension-bonded (black) and dissolved (grey) in rainfall wastewater samples from 1 pk (1) and 2 pk (2).

suspension particles and other solids located in the water. They can precipitate as a result of chemical processes in natural waters, such as oxidation. This is why the metal content in individual components of surface waters varies, the decrease starting from the suspension, through sediment, down to the water itself [38–40].

Metal ions in the water medium are coordinated by water particles, hence reactions of these molecular entities with organic donors and other ligand groups require displacement of one or more water particles, depending on the number of donor ligand groups. But the capacity for metal binding by, for instance, humic matter may be significantly affected by the solution's salt concentration. A high degree of salinity may inhibit the process [7,41]. Moreover, this type of phenomenon is not the same for all metal cations, which is suggested by, for example, the decay chain of metal and SH complexes: $Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Mg^{2+}$ [37,42].

A higher suspension content, according to the literature, adsorbs a large part of metals, and small amounts of analytes remain in the water, in the form of free ions [39]. Apart from the ion form, the most toxic for living organisms, they appear in the form of ions bonded to a variety of ligands (complex compounds) as well as precipitated particles of a chemical compound, suspended in the liquid phase, adsorbed on the suspension and colloid particle surface [43]. But the diversity of metal forms occurring in the water medium is conditioned by the metal's chemical properties, its compounds' capacity for adsorption on solid particles, formation of hydrated ions, ion pairs, hydrolysed forms and complex compounds as well as physicochemical conditions of the water medium such as temperature, pH or biological activity of organisms [44,45]. In slightly alkaline solutions, for example, with a high oxygen content, metal ions are transformed into poorly soluble forms, with a simultaneous tendency for adsorption on suspensions present in the water [46,47], as has been observed during the present study.

When comparing metal content in the ion form and in the suspension at both sampling points, different chains which reflect the growing rank of metals in the bonded form are obtained:

- (1) 1 pk: Cr < Ni < Cd < Cu < Zn < Pb.
- (2) 2 pk: Cr < Ni < Cd < Zn < Cu < Pb.

A similar correlation, wherein chromium and nickel were the metals least bonded to the suspension, was obtained by Rabajczyk [35] for a strongly alkalised area, within the Sitkówka–Nowiny cement plant

impact zone. In the natural water-head environment with large amounts of humic matter, bonded lead predominates [35].

Considering the pH of the studied rainfall wastewater samples, which pointed to the alkaline reaction, as well as high values of carbonate hardness, it is likely that the process of precipitation of, for example, carbonates and hydroxides of the studied metals occurs. These are poorly soluble compounds and, under favourable conditions, they are subject to the sedimentation process. In this way, various metal forms, including biodigestibles, are introduced into the bottom sediment structure.

According to the study by Czamara et al. [17], plants overgrowing the entire length of the ditch demonstrate capacity for accumulation of heavy metals such as chromium, copper, nickel, lead, cadmium and zinc. Vascular water plants take in metals and cumulate them in their tissues. The mechanism of plant intake of excess heavy metals, i.e. redundant in terms of plant development, is mostly due to lack of a biological barrier, causing passive and non-selective sorption. This is why, with several heavy metals, a simple correlation between their participation in the medium and the amount accumulated in plants is observed.

With regard to selected heavy metals, higher water plants, i.e. macrophytes, have developed a mechanism for active and selective intake adjusted to their physiological needs. Most frequently, the actively acquired metals are needed for plant development, as is the case with copper and zinc. However, even in these cases, a correlation between their concentration in a plant and in the medium is observed. Heavy metal content in water plants is seasonal and depends on metal mobility [18]. Mobile metals, such as zinc, display a reduced content during the vegetative season, while in plants, the content of less mobile metals, such as Pb and Cd, remains unchanged, with copper, chromium and nickel contents markedly increasing during the vegetative season [18]. It must also be said that Cr (VI), once assimilated by plants, becomes easily reduced to Cr(III) [25–27].

It must be stated that the cadmium ion, which displays high mobility, is easily desorbed into water, from where it can be taken in by living organisms. Copper, in turn, is taken in as Cu^{2+} ions in either an active or a passive manner. Excess copper is accumulated primarily in plant roots. Copper biodigestibility is affected by the presence of amorphous Fe, Mn and Al hydroxides, which causes small amounts of copper to appear in soluble or exchangeable forms [47].

Data from the literature show that nickel digestibility by plants increases if the medium contains mobile forms and if the pH value decreases [48].

A factor which fosters plants' metal intake is temperature increase, as demonstrated by Olaniran [49]. In the spring season, when the activity of many micro-organisms intensifies, release and increased solubility of some metal (Pb, Cd and Zn) compounds found in the sediment are observed. In this form, these compounds may be taken in by plants, which can contribute to reduced concentrations of studied metals in rainfall wastewater samples.

In urban areas, the presence of open channels, such as pollution-reducing ditches, may play another significant role. Study results suggest that urbanisation causes uncontrolled changes to the environment and the microclimate fostering allergic diseases and asthma, classified by the WHO as civilisational diseases [50]. Ecosystems such as ditches contribute to water flow stabilisation as well as microclimate enhancement in urban areas. In this way, they condition higher and steadier humidity of city air and decrease dust levels, which in turn limits the risk of asthma, allergy and other diseases related to air pollution [51,52].

5. Conclusion

The downflowing rainfall waters, particularly in industrial and services areas, wash away numerous surface pollutants. Land development determines not only chemical composition, but also forms of pollutants introduced into the sewage network. Ditches, used in stormwater drainage systems, perform several functions. Yet one of the most important issues remains the reduction of pollution from rainfall wastewater, including heavy metals Pb, Cd, Cr, Ni, Zn and Cu.

The conducted study, with its contribution to further research into the role of ditches in urban systems, has shown that as a result of passage through the ditch the volume of the suspended material, the concentration of bicarbonate ions, pH values and conductivity, as well as the volume and form of metal occurrence in rainfall wastewater are all subject to change. Yet it must be said that the degree of reduction in the volume of pollution introduced to the sewerage receiver is conditioned by many factors, including the pollutant type, temperature, precipitation intensity, plant species grown with their seasonal activity, the season, land development and use of the facility. The possibility of using ditches in urban area stormwater drainage systems enables not only reduction in pollutant load. It also contributes to sustainable urban development, based on water resources as a major determinant of other environmental and social issues, including health, pollutant migration and water retention.

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