J. Elem. s. 779–794 DOI: 10.5601/jelem.2014.19.2.522

CONTENTS OF Cu, Zn, Cd, Pb AND Fe IN RAINWATER EFFLUENTS DISCHARGED TO SURFACE WATERS IN THE CITY OF POZNAŃ

Barbara Szpakowska[1], Dariusz Świerk[1], Ryszard Gołdyn[2], Danuta Barałkiewicz[3]

[1]Department of Landscape Architecture
Poznań University of Life Sciences
[2]Department of Water Protection
[3]Laboratory Trace Elements Analysis by Spectroscopy Method
Adam Mickiewicz University in Poznan

Abstract

Progressing urbanization results in the potential increase of pollution sources such as wastes, industrial or municipal sewage, which may contain hazardous inorganic pollutants such as e.g. metal ions and their compounds. Urbanization has a negative effect also on soil, as a consequence of an increasing share of impermeable surfaces such as pavements, parking lots, housing developments and public buildings. The area of a hardened (impermeable) surface is exposed to intensive surface runoff during rain and as a result pollutants are transported through the storm drainage system directly to surface waters.

The aim of this study was to determine the effect of metals contained in rainwater discharged from subcatchments of various land use types on the quality of surface waters (the Cybina River and the Antoninek reservoir) in the city of Poznań, as well as investigate whether metal contents in rainwater effluents depend on the relief and character of the immediate catchment.

Investigations were conducted in 2009 along the lower section of the Cybina River. Water samples from the river and reservoir were collected each time when collecting rain water samples. Water and sewage samples were collected 15 times within a year. Analyses were conducted on 5 selected catchments (with different land uses) drained by storm water drainage system discharged to the Cybina River and the Antoninek reservoir. Water was collected from 13 sampling points (5 of which were sewer outfalls and 8 were situated on the river or the reservoir above and below the sewage discharge).

Higher concentrations of all tested elements were recorded in rainwater in comparison to the water samples coming from the river or the reservoir. Canonical Variate Analysis (CVA) model presenting differences between water concentrations of Cu, Zn, Cd, Pb and Fe and environmental variables (rainfall intensity measured in a four-point scale, location as divided into industrial areas multi- and single-family housing as well as location of sewage discharge to the river on the reservoir) showed elevated concentrations of these elements especially in water

Dariusz Świerk, PhD, Department of Landscape Architecture, Poznań University of Life Sciences, Dąbrowskiego 159, 60-594 Poznan, Poland, e-mail: darius@up.poznan.pl

collected directly from the storm water sewer. Elevated metal concentrations in storm system effluents did not have a significant effect on the content of these pollutants in the river or the reservoir. It could have been caused by the intensive immobilization of elemental ions in bottom deposits followed by the metal uptake by aquatic organisms, mainly plants.

Key words: rainwater, pollution, surface waters, copper, zinc, cadmium, lead, iron.

ZAWARTOŚĆ Cu, Zn, Cd, Pb I Fe W ŚCIEKACH DESZCZOWYCH ODPROWADZANYCH DO WÓD POWIERZCHNIOWYCH MIASTA POZNANIA

Abstrakt

Postępujący proces urbanizacji powoduje potencjalne zwiększenie źródeł zanieczyszczeń, jak odpady, ścieki przemysłowe czy komunalne, które mogą zawierać groźne zanieczyszczenia nieorganiczne, m.in. jony metali oraz ich związki. Proces ten oddziałuje niekorzystnie także na glebę, powodując zwiększenie udziału powierzchni nieprzepuszczalnych, jak chodniki, parkingi, budynki mieszkalne i użytkowe. Teren o powierzchni utwardzonej (nieprzepuszczalnej) jest narażony na intensywny spływ powierzchniowy podczas deszczu i transport substancji zanieczyszczających kanalizacją deszczową bezpośrednio do wód powierzchniowych.

Celem badań było określenie wpływu metali zawartych w wodzie deszczowej odpływającej ze zlewni cząstkowych o różnym użytkowaniu gruntów na jakość wód powierzchniowych (rzeki Cybiny i zbiornika Antoninek) na terenie Poznania, a także zbadanie, czy zawartość metali w ściekach deszczowych zależy od ukształtowania i rodzaju zlewni bezpośredniej.

Badania prowadzono w 2009 r. wzdłuż dolnego odcinka rzeki Cybiny. Próbki wody pobierano z rzeki i ze zbiornika Antoninek podczas opadów deszczu, 15 razy w ciągu roku. Do badań wybrano 5 zlewni (o odmiennym sposobie użytkowania) odwadnianych kanalizacją deszczową uchodzącą do rzeki Cybiny i zbiornika Antoninek. Wodę pobierano z 13 stanowisk (5 to wyloty z kanałów, 8 usytuowano na rzece lub zbiorniku powyżej i poniżej ujścia ścieków).

W wodzie deszczowej stwierdzono większe stężenie wszystkich badanych pierwiastków w porównaniu z wodą pochodzącą z rzeki lub zbiornika. Analiza CVA (Canonical Variate Analysis), która umożliwia określenie zależności między stężeniami Cu, Zn, Cd, Pb i Fe oraz zmiennymi środowiskowymi (intensywność opadów atmosferycznych mierzona w 4-stopniowej skali, lokalizacja uwzględniająca tereny przemysłowe, zabudowa wielo- i jednorodzinna, lokalizacja punktów poboru wody deszczowej) jednoznacznie wskazała na wyższe stężenie badanych pierwiastków w wodzie pobranej bezpośrednio z kolektorów deszczowych. Podwyższone stężenie metali w ściekach deszczowych nie wpłynęło znacząco na zawartość tych zanieczyszczeń w rzece i zbiorniku. Mogło to być spowodowane intensywną immobilizacją jonów pierwiastków w osady denne, a następnie pobraniem metali przez organizmy wodne, głównie rośliny.

Słowa kluczowe: ścieki deszczowe, zanieczyszczenie, wody powierzchniowe, miedź, cynk, kadm, żelazo.

INTRODUCTION

As a consequence of spatial management and urbanization the urban space is being gradually developed by roads, pavements, housing and public buildings (WARDAS et al. 2010). This leads to an increased percentage share of impermeable surfaces such as concrete or asphalt in the urban space at the simultaneous reduction of permeable and semi-permeable surfaces such as natural subsoils, tree and shrub plantings. This phenomenon results in the accelerated surface runoff and promotes migration of pollutants to surface waters (Göbel et al. 2007).

Numerous pollutants may be found in rainwater, e.g. compounds of metals such as arsenic, mercury, chromium, lead, cadmium, nickel, barium, zinc, vanadium, tin, silver, strontium, aluminium, copper or iron. Quality of rainwater depends to a considerable degree on the type of catchment, season of the year, type of pavements, intensity of vehicle traffic, but also dry and wet deposition within a given catchment (Shirasuna et al. 2006).

Metals in rainwater in urbanized areas originate mainly from dusts from combustion plants, iron and steel industry, non-ferrous metallurgy, waste incineration plants, cement or glass-making industries (Göbel et al. 2007).

Significant sources of certain metals such as Cu and Zn include impermeable roof surfaces, which are most frequently produced from materials containing these metals, additionally roofing materials, roof gutters or downpipes may be covered by special coatings containing Al or Pb.

Pavements of roads and parking lots with intensive vehicle traffic are important potential sources of metals. Direct pollutant sources include products formed as a result of abrasion of pavements, tires, brake shoes as well as leaks of gear oil, lubricant, brake fluid or corrosion products. Tire wear leads to the release of oxides of such metals as Zn, Pb, Cu, Cr and Ni, while wear of brake shoes produces mainly oxides of Ni Cr, Cu and Pb. In turn, Fe may originate from worn brake drums.

Rainwater quality to a considerable degree depends on the form of pollutants. The stronger a metal is bound with solid particulates, the greater the effect of intensive, but short-term precipitation on total load (Dougherty et al. 2006, Budai, Clement 2007).

In Poland for many years rainwater flowing to the receiving water tank was considered clean. As a result, precipitation water discharged to the sewerage system was analyzed extremely rarely and those analyses concerned only several indexes such as pH, BOD_5, COD, chlorides, sulfates or electrolytic conductivity. Only recently rainwater has been included in the sewage category, resulting in the necessity of its treatment prior to its discharge to surface waters (*Ordinance of the Minister of the Environment* 2006).

The aim of the presented study was to determine the effect of metals contained in rainwater sewage flowing in from subcatchments differing in land use types (single- and multi-family housing development, industrial areas) on quality of surface waters (the Cybina River and the Antoninek reservoir) in the city of Poznań.

MATERIALS AND METHODS

Site description

Investigations were conducted in 2009 along the lower section of the Cybina River, being a right-bank tributary to the Warta River. The analyzed section of the Cybina is situated in the city of Poznań, between Lakes Swarzędzkie and Maltańskie, i.e. between 4.3 and 8.7 km of the river course, counting from its confluence to the Warta. Mean multiannual flow rate in the river at this section is 0.67 $m^3 s^{-1}$. In the river course at this section four small dam reservoirs were constructed or reconstructed in the 1980's, which main objective was to intensify the process of water self-purification.

Analyses concerning the effect of rainwater sewage on surface waters were conducted on five selected catchments drained by storm water drainage systems discharged to the Cybina and the small Antoninek reservoir located in its area. Catchment no. 1 draining the single-family housing district is 42.7 ha in area, of which paved areas occupy 28.9% (Figure 1*a*). A settlement

Fig. 1*a*. The location map of water sampling points below Lake Swarzędzkie

tank and a separator for sewage pre-treatment are located in front of the outfall sewer outlet to the Cybina. Catchment no. 2 covers the area of a vehicle manufacturing plant (Volkswagen), including parking lots for new cars and employee parking plots as well as a section of an expressway of approx. 800 m. The drained catchment is 56.8 ha in area, of which 51.6% are paved surfaces (Figure 1a). Before being discharged to the Cybina sewage is pre-treated in an Imhoff tank, adapted for this purpose after a former domestic sewage and process wastewater treatment plant. Plot no. 3 covers mainly the Antoninek Glassworks. It is 4.78 ha in area, of which 88% are paved (Figure 1*b*). Rainwater sewage is discharged to the Antoninek reservoir. Plot no. 4 occupies the area of workshops, a car showroom and parking lots of Polcar,

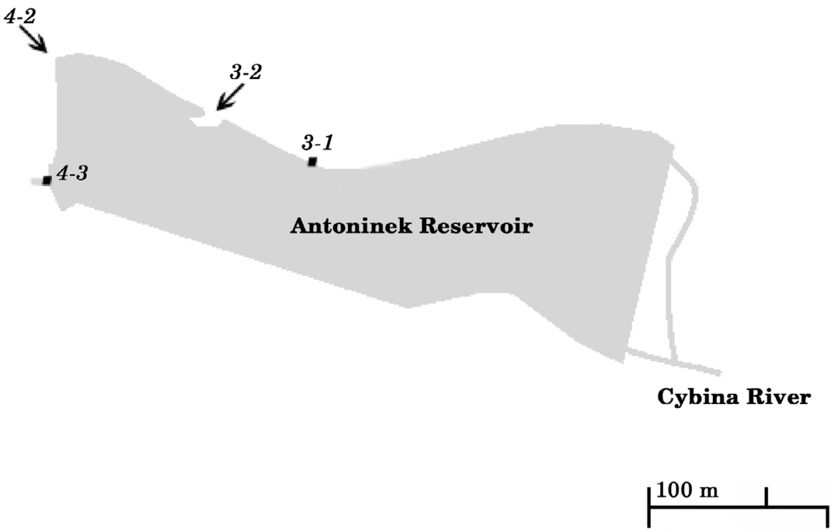


Fig. 1*b*. The location map of water sampling points in the Antoninek reservoir

a car dealer also offering automobile repair services. The catchment area is 4.33 ha, of which 76% are paved. Rainwater is also discharged to the Antoninek reservoir (Figure 1*b*). Plot no. 5 covers the area of a small multi-family housing district. This catchment is 7.37 ha in area, with only 26.7% being paved (Figure 1*c*). The limited paved area and a slight inclination of the area results in the amount of discharged waters being lower than those of the other catchments.

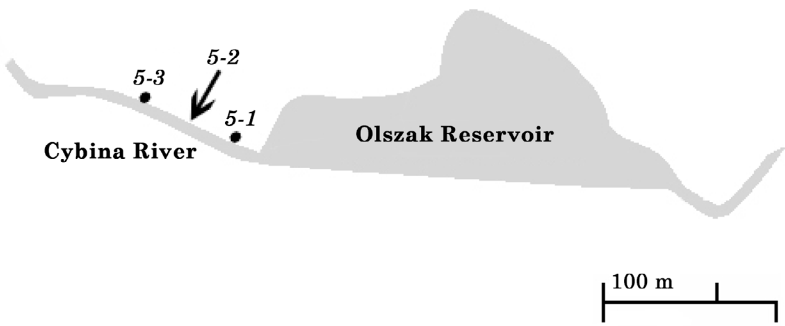


Fig. 1*c*. The location map of water sampling points below the Olszak reservoir

Sampling

Water samples from the river and reservoir were collected each time when collecting rain water samples. Water and sewage samples were collected 15 times within a year. A total of 13 sampling points were established in the river in the vicinity of rainwater sewage outfalls from the identified subcatchments and directly on these outfalls. Five of them were storm water sewage outfalls (denoted with black arrows), 8 were situated on the river and the water reservoir constituting storm water receiving waters. The sampling points on the river were always situated above and below sewage outfalls (denoted with black points); however, in the case of the reservoir due to the location of sewage outfalls in close vicinity only one station was established above and below both outfalls (Figure 1*b*).

Analytical methods

Water samples from the river and reservoir were collected from the current from the subsurface water layer. Storm water sewage was collected directly from the outflow from the sewer. Samples for chemical analyses were collected at each sampling point in three replications and they were analyzed separately.

Five metals (Cu, Zn, Cd, Pb and Fe) were detected in water and sewage samples. Quantitative analyses of elements were performed by flame atomic absorption spectrometry FAAS (ISO 9964-1-1993) as well as inductively coupled plasma mass spectrometry ICP-MS (ISO 17294-2-2003). Specification and parameters for individual methods were presented below (Tables 1, 2).

Statistical analysis was performed using the analysis of variance (Anova). In analysis parametric test Matched Anova for normal data was used. This test is used to compare two or more sets of matched data, and it tests the null hypothesis that the mean difference between the sets is zero.

Table 1

Instrumental characteristics and setting for ICP-MS

Spectrometer	**ELAN DRC II (Perkin Elmer Sciex, Canada)**
Nebulizer	Meinhard
Spray chamber	Cyclonic
Interface	Pt cones
Mass analyzer	Quadrupole
RF power (W)	1200
Ar gas flow rates (L min^{-1}): plasma auxiliary nebulizer	 15 1.2 0.94
Internal standard	Sc^{45}, Y^{89}, Tb^{159}

Table 2

Operating parameters for F-AAS

Ion	Wavelength (nm)	Lamp intensity (mA)	Split (nm)
Fe	248.3	10.0	0.2
Zn	213.9	10.0	1.0

If $p < 5\%$ then the null hypothesis is rejected and at least one of the sets is significantly different.

In order to indicate which explanatory variables are the best predictors of sampling points, taking into account also types of catchment area as well as rainfall intensity discriminatory analysis was used, which made it possible to construct the CVA [canonical variation analysis – a linear variant of Fisher's discriminatory analysis (LDA)]. Calculations using the Canoco 4.5 for Windows program were presented graphically in the CanoDraw for Windows program. Thanks to this statistical method it may be stated which environmental variables [rainfall intensity measured in a four-point scale, location as divided into industrial areas, multi- and single-family housing development as well as the position of sewage discharge to the river or the reservoir (above the storm sewer, directly from the sewer and below the storm sewer)] determine the distribution of concentrations for analyzed elements in storm water sewage and in surface waters. Explanatory variables used in discriminatory analysis in Canoco as environmental variables. Then a canonical correspondence analysis (CCA) was selected using Hill's scaling.

In order to determine the boundary level of significance the Monte Carlo permutation test was performed. All variables were analyzed and next these variables were included in the model, which contributed the most to the discrimination of groups based on the values of p and F for the analyzed variable. This process was repeated to the time when the value of p dropped below 0.05 for the tested variable.

Differencies between the catchments were tested using an analysis of variance on repeated measures using that general linear models approach and Tukey' s test. Statistical analyses were done Statistica version 6.0 software.

RESULTS

Analysis of distribution for concentrations of selected elements (Cu, Zn, Cd, Pb and Fe) in the Anova test

The analysis given below was conducted for elements, which values within a given group were statistically significantly correlated ($p < 0.05$) – Table 3. The Anova test was applied in order to compare three and four paired groups of variables with a distribution consistent with a normal distribution.

The figures given below (1 - 5) illustrate the distribution of concentrations for Cu, Zn, Cd, Pb and Fe. Definitely the highest concentrations of all the elements were recorded in water collected from rainwater sewers. In case of copper the highest value (amounting to over 120 μg l^{-1}) was observed in the water from sewer no. 1 (Figure 2*a*). A greater effect on the concentrations of copper in river water was observed for water from sewer no. 2, which is connected with a greater amount of rainwater influents. Concentrations in river water below that sewer were so high that they exceeded acute

Table 3

Mean and calculated values of p in the Anova test for Cu, Zn, Cd, Pb and Fe (μg l^{-1})

Catchment		Single-family housing district			Area of a vehicle manufacturing plant			Antoninek Glassworks		Area of workshops		Area of a multi-family housing district		
		1-1.	**1-2.**	**1-3.**	**2-1.**	**2-2.**	**2-3.**	**3-1.**	**3-2.**	**4-2.**	**4-3.**	**5-1.**	**5-2.**	**5-3.**
Cu	average	2.75	32.56	3.26	2.59	15.88	8.00	2.37	10.23	19.87	2.35	1.60	8.65	2.94
	***p*- value**	0.011*			0.001*			0.049*				0.007*		
Zn	average	16.25	52.97	16.32	25.84	246.82	90.90	20.14	870.70	156.91	11.55	7.73	87.20	15.93
	***p*- value**	0.046*			0.001*			0.019*				0.020*		
Cd	average	0.01	0.10	0.02	0.02	0.21	0.07	0.16	0.44	0.31	0.03	0.01	0.21	0.04
	***p*- value**	0.049*			0.035*			0.011*				0.007*		
Pb	average	0.39	5.18	0.71	0.43	4.63	2.45	10.43	15.68	18.58	7.06	1.35	17.55	3.15
	***p*- value**	0.016*			0.004*			0.164				0.044*		
Fe	average	143.53	441.28	150.86	244.18	460.84	292.68	278.17	649.11	652.04	315,87	432.18	2049.21	317.50
	***p*-value**	0.045*			0.014*			0.050				0.046*		

values for some aquatic animals, e.g. cladocerans *Daphnia pulicaria* and *Ceriodaphnia dubia*. Phytoplankton species, especially cyanobacteria, are very sensitive to copper. That is a reason of the frequent use of copper as an algicide (PADOVESI-FONSECA, PHILOMENO 2004). These high concentrations of copper are probably one of the reasons of the observed cyanobacteria decline in the Antoninek Reservoir (GOŁDYN et al. 2010). More evident differences in the concentration levels were shown for zinc. In sewer no. 3 maximum

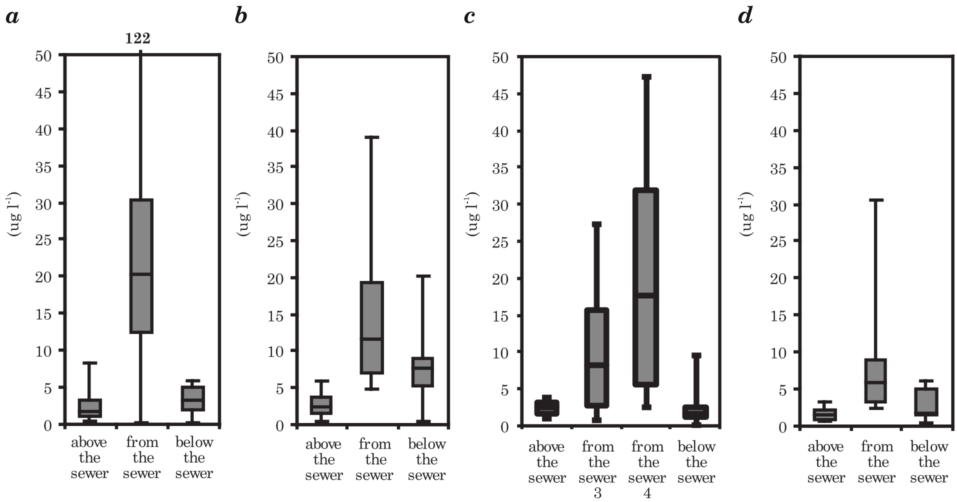


Fig. 2. The distribution of Cu concentrations in the annual cycle: *a* – catchment of the single-family housing district, *b* – catchment of the area of a vehicle manufacturing plant, *c* – catchments of the Antoninek Glassworks and the area of workshops, *d* – catchment of the area of a multi-family housing district

values exceeded 7 mg l[-1] (Figure 3*c*). It is the value exceeding the criteria of organoleptic effects for pollutants, listed by the US EPA (2009). Also for cadmium the highest concentration was observed in waters from sewers nos. 3 and 4 (Figure 4*c*) located in industrial areas. Discharge of these waters to the reservoir in Antoninek resulted in a rapid precipitation of cadmium to bottom deposits, since at testing station 4.3 in the vicinity of the outflow of water from the reservoir the concentration of this element was much lower, never exceeding the chronic value of 0.25 μg l[-1] (EPA 2009).

When analyzing the distribution of lead concentrations it may be stated that the greatest differences in concentrations were found at sewer no.

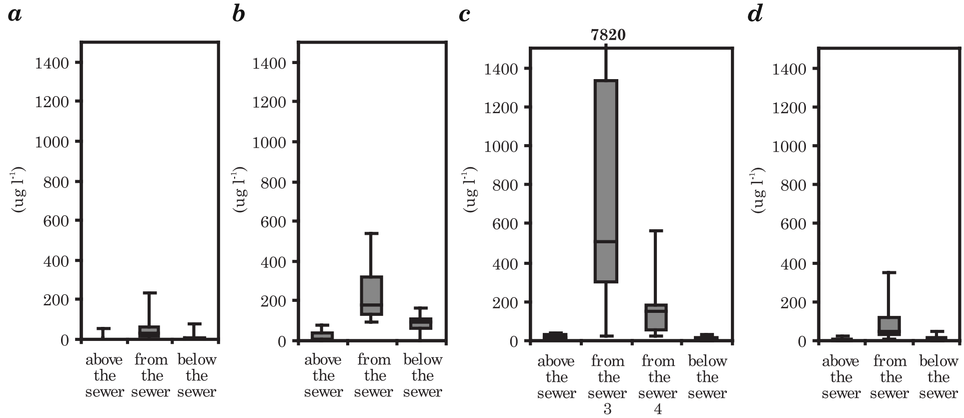


Fig. 3. The distribution of Zn concentrations in the concentrations in the annual cycle: *a* – catchment of the single-family housing district, *b* – catchment of the area of a vehicle manufacturing plant, *c* – catchments of the Antoninek Glassworks and the area of workshops, *d* – catchment of the area of a multi-family housing district

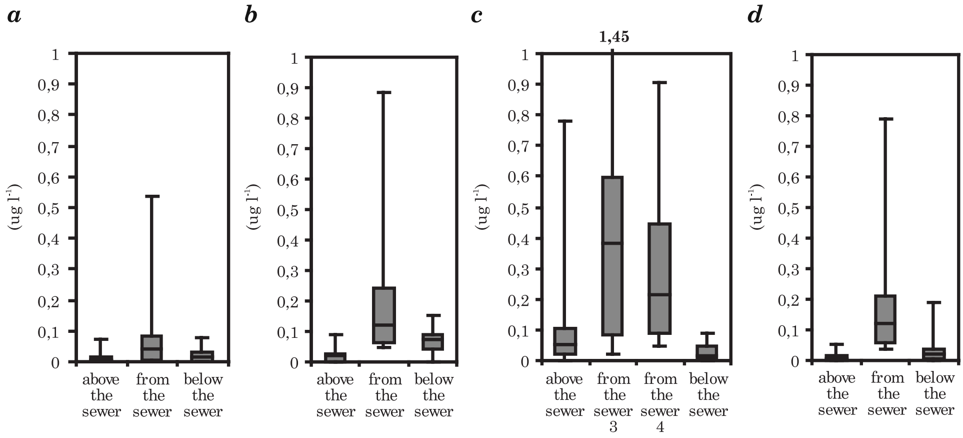


Fig. 4. The distribution of Cd concentrations in the annual cycle: *a* – catchment of the single-family housing district, *b* – catchment of the area of a vehicle manufacturing plant, *c* – catchments of the Antoninek Glassworks and the area of workshops, *d* – catchment of the area of a multi-family housing district

5 in comparison to the concentrations of this element in samples of water coming from the river above and below the sewer (Figure 5*d*). An analogous situation occurred in case of iron, when the highest concentrations were also recorded at sewer no. 5 (Figure 6*d*). In most cases high concentrations of these parameters in sewers had an effect on elevated levels of concentrations in water sampled below the sewer Only in case of the Antoninek reservoir usually instead of an increase in the concentrations their levels were found

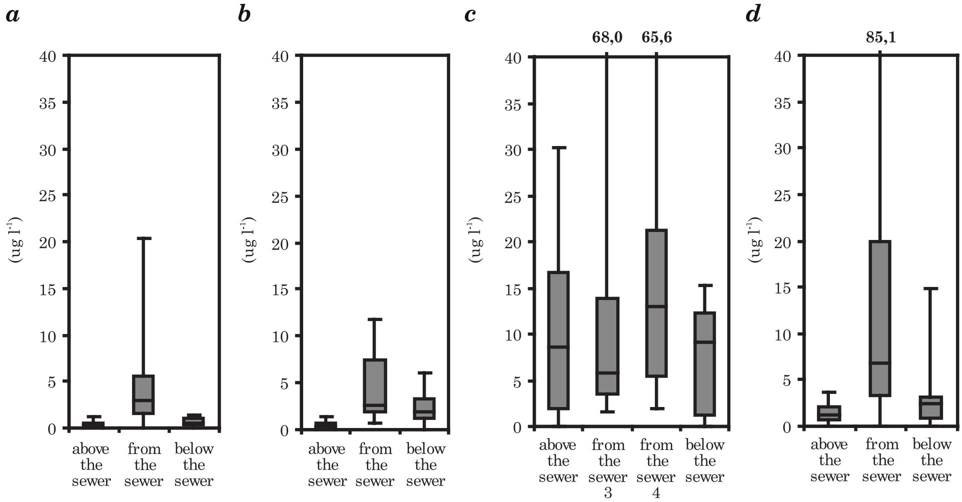


Fig. 5. The distribution of Pb concentrations in the annual cycle: *a* – catchment of the single-family housing district, *b* – catchment of the area of a vehicle manufacturing plant, *c* – catchments of the Antoninek Glassworks and the area of workshops, *d* – catchment of the area of a multi-family housing district

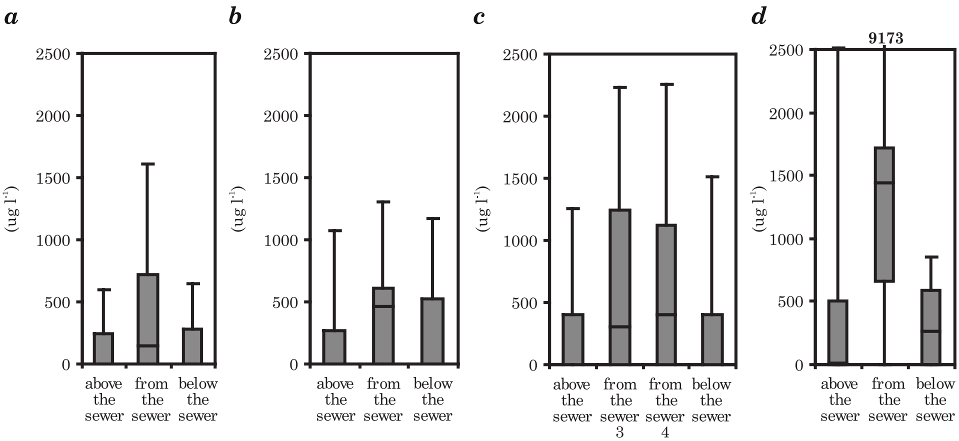


Fig. 6. The distribution of Fe concentrations in the annual cycle: *a* – catchment of the single-family housing district, *b* – catchment of the area of a vehicle manufacturing plant, *c* – catchments of the Antoninek Glassworks and the area of workshops, *d* – catchment of the area of a multi-family housing district

to decrease in its waters, despite the high values in discharged stormwaters. This indicates that in the reservoir there occurs a rapid sedimentation of pollutants supplied both with stormwater and river waters, connected with the lothic conditions being replaced by lenthic conditions.

Canonical Variate Analysis (CVA) model – a canonical variant of Fisher's linear discriminatory analysis (LDA)

This model was constructed based on the discriminatory analysis. The aim of the conducted analyses was to verify which environmental variables may influence the distribution of concentrations of tested elements in waters of the Cybina River as well as the Antoninek reservoir. Canonical Variate Analysis (CVA), a canonical variant of Fisher's linear discriminatory analysis (LDA) was used in the construction of the model.

The discriminatory analysis compared the effect of different variables on the distribution of concentrations of tested elements in water. The following parameters were included in the analyses: rainfall intensity measured in a four-point scale, location as divided into industrial areas, multi- and single -family housing as well as the location of sewage discharge to the river or the reservoir (above the sewer, directly at the sewer and below the storm water sewer).

Forward stepwise analysis was performed in order to verify which variables to the highest degree determine the distribution of concentrations of the tested elements.

The model given below (Figure 7) presents dependencies between tested parameters (Cu, Zn, Cd, Pb and Fe) and variables included in the analysis. All analyzed elements were characterized by elevated concentrations in water collected directly from the storm water sewer, with higher concentrations of investigated pollutants in storm water sewage. For lead and cadmium

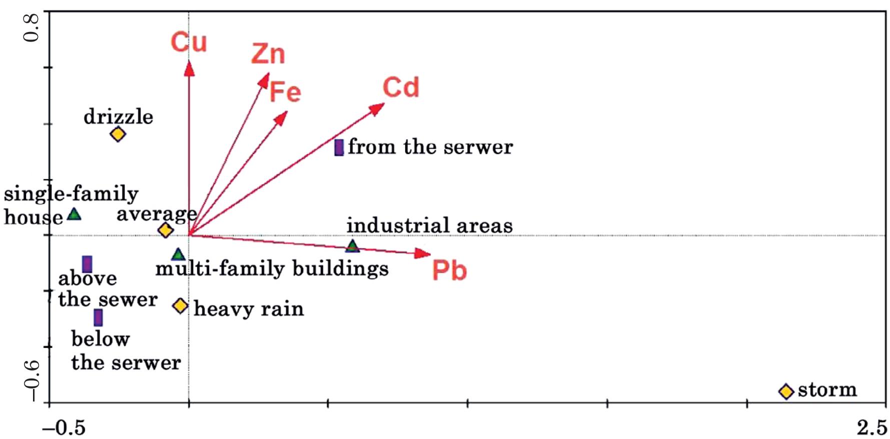
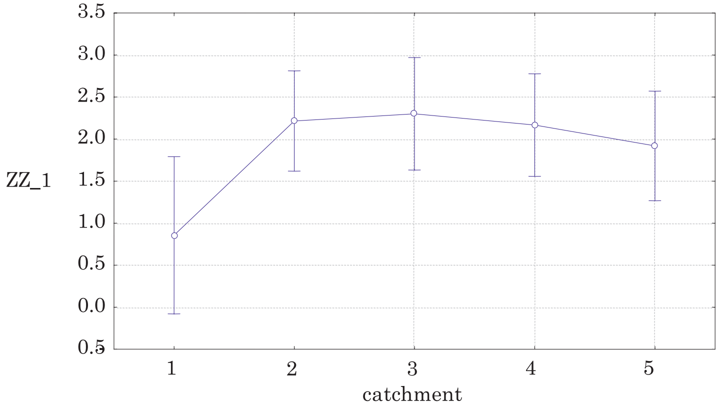


Fig. 7. The CVA model (n = 137) – dependencies between analyzed elements and variables (rainfall intensity, location as divided into industrial areas, multi- and single-family housing development as well as the location of sewage inlet to the river or the reservoir (above the sewer, directly at the sewer and below the storm water sewer, $p < 0.05$

the highest concentrations were recorded during the most intensive rainfall in industrial areas. Higher copper concentrations were detected in water coming from the catchments with predominant single-family housing development during the least intensive rainfall.

The analysis of variance on repeated measures using that general linear models approach was done (Figure 8). The model tests two factors (catchment, concentration of examined metals) and interaction between analysed factors. In the analysis Tukey's test was applied which made it posssible to find the difference between the catchments with respect to the level of examined metals. It was shown that catchment no. 1 draining the single-family housing district differ significantly from the other studied catchments.



ZZ_1 – expected boundary values

Fig. 8. The differencies between the catchments no 1-5 with respect to the level of examined metals [$F(4, 160)=5.0811$, $p = 0.0007$]

DISCUSSION

When analyzing recorded data it may be stated that rainwater contained a considerable load of metals such as Cu, Zn, Cd, Pb or Fe in comparison to water collected from the Cybina River or the Antoninek reservoir. The highest values were found for Fe, while the lowest for Cd. The highest levels for Cu were recorded in rainwater collected from catchment no. 1 (mean 32.56 μg l^{-1}), which could probably have been caused by the frequent use of copper roof finish elements in single-family housing. In countries of Central Europe the mean copper emission from roof surfaces was 1.1 g m^{-2} $year^{-1}$, while for zinc it was 3.0 g m^{-2} $year^{-1}$. Water coming from catchment no. 3 had the highest Zn and Cd values, which is typical of industrial areas, i.e. the Antoninek Glassworks in this case. Such high values were obviously a consequence of the high share of paved area (impermeable) in the catchment, amounting to as much as 88%. The highest Pb concentration was recorded in rainwater coming from catchment no. 4 (workshops, showrooms, parking lots), with the mean lead level in rainwater at the storm water sewer amounting to 18.58 μg l^{-1}. Catchment no. 5 with multi-family housing development was characterized by rainwater with an elevated Fe concentration. This area had a slight percentage (26.7%) of paved areas, which may indicate that this element is only partially immobilized with the soil sorption complex.

When referring the recorded results to literature data similar trends may be found in the distribution of concentrations for the tested elements. Studies conducted by GÖBEL et al. 2007 concerned rainwater collected from an unpaved catchment (gardens, green areas), roofs and roads with varying degrees of vehicle traffic. It was shown that water flowing directly from roofs had higher concentrations of such elements as Zn or Cu, while water collected from traffic arteries had higher Pb concentrations in relation to the other tested locations. In the case of Pb and Zn, the above mentioned findings were confirmed in a study by GNECCO et al. (2005). A study by GÖBEL et al. (2007) showed a considerable effect of the type of pavement, from which rainwater flows to the receiving waters on its pollution with metals.

Studies conducted by KANG et al. in the years 2005 - 2007 were connected with the evaluation of water quality in the Yeongsan River in the vicinity of the city of Gwangju (Korea) depending on the weather. Results showed a marked effect of precipitation intensity on pollution of tested waters. This was the case particularly with such metals as Cd, Cu or Zn.

Metal pollution of rainwater is also influenced by the manner of catchment use. Analyses conducted in Queensland State, Australia, showed that water rich in Zn abd Pb flows from areas with housing land use. In contrast, rainwater collected from industrial areas had higher Pb and Fe concentrations in comparison to water collected from the other sampling points (HERNGREN et al. 2005).

In recent years much attention has been focused on disposal methods for metals polluting waters (SHRESTHA et al. 2003). One of the methods to remove metals from water may be connected with the establishment of a series of flow-through ponds with a total length adapted to the river water flow rate. Effectiveness of this method was specified for Cu at 70%, while for Zn it was 94 - 95% (WALKER, HURL 2002). In turn, in the experiment conducted by JANG et al. (2005) 3 types of mulch were evaluated as potential sorbents of heavy metals from water flowing from urbanized areas. It was shown that mulch from bark of deciduous trees is the best sorbent of heavy metals in urban areas. It seems that establish the biological barriers can increase the inflow of heavy metals because some plants and algae, called hyperaccumulators, such as *Thlaspi caerulenscens* J. Presl & C. Presl*, Salix vilminalis, Brassica juncea* (L.) Czern.*, Ceratophyllum demersum* L., *Potamogeton crispus* L. and *Oenanthe aquatica* (L.) demonstrate a particularly high ability to accumulate metals in unusually high concentrations (SALT et al. 1998, Obarska-Pempkowiak, Kołecka 2005, Senze et al. 2009, Świerk, Szpakowska 2011, RAJFUR 2013). Also common reed (*Phragmites australis* (Cav.) Trin. ex Steud.), which is a widely distributed species worldwide, proves useful in cleaning eutrophic lakes and waste waters (Kozłowska et al. 2009).

CONCLUSIONS

1. Elevated concentrations of all tested metals were found in water collected from storm water sewers. The highest concentrations in rainwater were recorded for Fe (max. 7820 μg l^{-1} – catchment no. 5) and for Zn (max. 7820 μg l^{-1} – catchment no. 3), while the lowest concentration in rainwater was detected for Cd.

2. Rainwater coming from catchments of industrial and commercial land use (catchments nos. 3 and 4) had higher concentrations of such elements as Zn, Cd and Pb, while rainwater coming from catchments with predominant single-family housing developments had higher Cu concentrations in comparison to water collected from the other catchments.

3. Values of measured concentrations were most probably influenced by the share of paved surfaces in the total area of the immediate catchment and by the land use of the catchment.

4. No significant negative effect of rainwater was found on surface waters in the city of Poznań. This may indicate intensive immobilization of these elements into bottom deposits and tissues of aquatic vegetation, mainly hydromacrophytes.

5. The CVA model presenting dependencies between water concentrations of Cu, Zn, Cd, Pb and Fe and environmental variables showed that all analyzed elements were characterized by elevated concentrations in water collected directly from the storm water sewer.

REFERENCES

Budai P., Clement A. 2007. *Estimation of nutrient load from Urban diffuse sources: Experiments with runoff sampling at pilot catchments of lake Balaton, Hungary*. Water Sci. Technol., 56(1): 259-302. DOI:10.2166/wst.2007.464

Dougherty M., Dymond R.L., Grizzard Jr.T.J., Godrej A.N., Zipper C.E., Randolph J. 2006. *Quantifying long-term NPS pollutant flux in an urbanizing watershed*. J. Environ. Engin., 132(4): 547-554. DOI:10.1061/(ASCE)0733-9372(2006)132:4(547)

EPA 2009. *National Recommended Water Quality Criteria*. US EPA, Office of Water. http://www.epa.gov/ost/criteria/wqctable

Gnecco I., Berretta C., Lanza L.G., La Barbera P. 2005. *Storm water pollution in the urban environment of Genoa, Italy*. Atmospheric Res., 77: 60-73. DOI:10.1016/j.atmosres.2004.10.017

Göbel P., Dierkes C., Coldewey W.G. 2007. *Storm water runoff concentration matrix for urban areas*. J. Contaminant Hydrol., 91: 26-42. DOI:10.1016/j.jconhyd.2006.08.008

Gołdyn R., Dondajewska R., Szeląg-Wasielewska E., Szyper H. 2010. *An appraisal of changes* *in seasonal water quality during passage through a shallow reservoir in Western Poland.* Environ. Monit. Assess. 151: 181-188.

Herngren L. Goonetilleke A., Godwin A. 2005. *Understanding heavy metal and suspended solids relationships in urban stormwater Rusing simulated rainfall.* J. Environ. Manage., 76, 149-158. DOI:10.1016/j.jenvman.2005.01.013

ISO 9964-1, 1993(E). *Water quality. Determination of sodium and potassium.*

ISO 17294-2, 2003. *Water quality – Application of inductively coupled plasma mass spectrometry (ICP-MS).* Part 2. *Determination of 62 elements.*

Jang A., Seo Y., Bishop L. 2005. *The removal of heavy metals in urban runoff by sorption on mulch.* Environ. Pollut., 133:117-127. DOI:10.1016/j.envpol.2004.05.020

Kang J-H., Lee Y.S., Ki S.J., Lee Y.G., Cha S.M., Cho K.H., Kim J.H. 2009. *Characteristics of wet and dry weather heavy metal discharges in the Yeongsan Watershed, Korea.* Sci. Total Environ., 407: 3482-3493. DOI:10.1016/j.scitotenv.2009.02.021

Kozłowska M., Jóźwiak A., Szpakowska B., Goliński P. 2009. *Biological aspects of cadmium and lead uptake by Phragmites australis (cav. Trin ex steudel) in natural water ecosystems.* J. Elem., 14(2): 299-312. DOI: 10.5601/jelem.2009.14.2.10

Obarska-Pempkowiak H., Kołecka K. 2005. *Experiences from application of salix viminalis for water and sewage treatment.* Rocz. Ochr. Środ., 7: 55-69. (in Polish)

Ordinance of the Minister of the Environment of 24 July 2006 on conditions to be met when discharging wastewater to waters or soil and on substances particularly noxious to the aquatic environment. (Journal of Laws no. 137, item 984).

Padovesi-Fonseca C., Philomeno M.G. 2004. *Effects of algicide (Copper sulfate) application on short-term fluctuations of phytoplankton in Lake Paranoá, Central Brazil.* Braz. J. Biol., 44(4): 819-826.

Rajfur M. 2013. *Algae – Heavy metals biosorbent.* Ecol. Chem. Eng., 20(1): 23-40. DOI: 10.2478/eces-2013-0002.

Salt D.E., Smith R.D., Raskin I. 1998. *Phytoremediation.* Ann. Rev. Plant Physiol. Plant Mol. Biol., 49: 643-668.

Senze M., Kowalska-Góralska M., Pokorny P. 2009. *Metals in chosen aquatic plants in a lowland dam reservoir.* J. Elem., 14(1): 147-156. DOI: 10.5601/jelem.2009.14.1.15

Shirasuna H., Fukushima T., Matsushige K., Imai A., Ozaki N. 2006. *Runoff and loads of nutrients and heavy metals from an urbanized area.* Water Sci. Technol., 53(2): 203-213. DOI:10.2166/wst.2006.054

Shrestha R., Krebs P., Roeske I. 2003. *A study on environmental improvement of the River Bagmati of Kathmandu Valley, Nepal.* Rocz. Ochr. Środ., 5: 59-65. (in Polish)

Świerk D., Szpakowska B. 2011. *Occurrence of heavy metals in aquatic macrophytes colonizing small aquatic ecosystems.* Ecol. Chem. Eng., 18(3): 369-384. http://tchie.uni.opole.pl/SECE/index.php/ece-s/ece-s-183

Walker D.J., Hurl S. 2002. *The reduction of heavy metals in a stormwater wetland.* Ecol. Engine., 18 407-414.

Wardas M., Aleksander-Kwaterczak U., Jusik S., Hryc B., Zgoła T., Sztuka M., Kaczmarska M., Mazurek M. 2010. *An attempt to assess the impact of anthropopressure on the ecological state of urbanised watercourses of Krakow Conurbation and the difficulties encountered.* J. Elem., 15(4): 725-743. DOI: 10.5601/jelem.2010.15.4.725-743