DOI: 10.2428/ecea.2012.19(01)012 ECOL CHEM ENG A. 2012;19(1-2):113-121

Marcin NIEMIEC[1], Barbara WIŚNIOWSKA-KIELIAN[1]
and Monika ARASIMOWICZ[1]

CONTENTS OF COPPER, NICKEL AND CHROMIUM IN THE SEDIMENTS OF RAINWATER RESERVOIRS SITUATED ALONG THE NATIONAL ROAD No. 4

ZAWARTOŚĆ MIEDZI, NIKLU I CHROMU W OSADACH ZBIORNIKÓW WÓD DESZCZOWYCH USYTUOWANYCH WZDŁUŻ DROGI KRAJOWEJ Nr 4

Abstract: The paper aimed at determining heavy metal pollution level of the sediments collected from reservoirs that retain rainwater, localized along the national road No. 4. The sediments were sampled from 11 reservoirs on three dates: in May 2007, in April 2008 and in June 2008 in the Sulkow, Biskupice, Bodzanow and Suchoraba villages, along the *ca* 10 km section of this road. The sediments were dried in the open air, dry-mineralized and dissolved in a mixture of nitric and chloric acids (3:2, v/v). The contents of copper, chromium and nickel were assessed in the obtained solutions by means of ICP-AES method.

Copper contents in the analyzed sediments ranged from 9.29 to 102 mg $\cdot$ kg^{-1}, with an average for all samples 34.94 mg Cu $\cdot$ kg^{-1}. Chromium contents in the studied sediments comprised in limits 12.6–58.1 mg Cr $\cdot$ kg^{-1}, with an average value of 27.7 mg Cr $\cdot$ kg^{-1}. Nickel quantities assessed in sediments from rainwater reservoirs were within the range of 7.57–25.62 mg Ni $\cdot$ kg^{-1}, with an average value of 13.71 mg $\cdot$ kg^{-1}. Changeability (RSD) of the studied metal contents between individual reservoirs fluctuated from 18 to 58 %. The amounts of analyzed elements in the sediments from reservoirs receiving runoffs from the road were much smaller than assessed in similar sediments from various cities worldwide. The investigated sediments do not pose any hazard in view of pollution with copper, chromium or zinc. A regular diminishing of copper content in the sediments was observed with increasing distance from Krakow agglomeration. The closest reservoir is situated in Sulkow, 7 km from the Krakow boundaries, near the boundaries of the Wieliczka town. On the other hand, the reservoir in Suchoraba village is about 17 km far from Krakow. Along this stretch copper content in sediment taken from reservoirs that retain rain water diminished several times, what points at a considerable effect of pollution coming from urban centre on this metal level in the sediments. No such dependence was observed for nickel or chromium.

Keywords: rainwater reservoirs, sediments, metals content, Cu, Ni, Cr

[1] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone: +48 12 662 43 47, fax +48 12 662 4341, email: niemiecm@tlen.pl, rrkielia@cyf-kr.edu.pl

Advanced level of urbanization increases the number of hard surfaced areas. With growing area of anthropogenically transformed terrains the hazard of area pollution source is more serious. *Environmental Protection Agency* (EPA) attaches more attention to this type of pollution which may locally lead to environment degradation. Many researchers of this problem state that in the areas with high coefficient of urbanization rainwater is currently the gravest threat to both surface and underground water quality [1–3]. Rainwater running off from hard surfaced areas may contain considerable amounts of pollutants posing a hazard to natural ecosystems [4]. The most important impurities polluting the runoffs are organic matter, heavy metals, oil derivatives, chlorides which can be extracted with petroleum spirit [5]. The Directive of the Minister of Environment of 29 November 2002 [6] determines the necessity to clean rainwater from the road drainage to make it parameters would meet the standards formulated in the Directive of the Minister of Environment of 24 July 2006 [7]. One of the ways of pretreatment is the use of sedimentation pools and infiltration and evaporation tanks. Various physical and physicochemical phenomena are used in these devices to remove the pollutants from rainfall wastewater and transform them to sediments [8]. It is thought that bioretention reservoirs are the most efficient method of cleaning rainwater runoffs of heavy metals, because the physical and chemical processes are supplemented with biological sorption of pollutants. Another problem is treatment and disposal of water from the pretreatment reservoirs. Inappropriate exploitation and utilization of the reservoirs may after some years cause mobilization of toxicants bound in the sediments posing a hazard to the natural environment. With increasing number of facilities pretreating stormwater sewage the pressure of roads and other urbanized areas on the environment will be diminishing, but also considerable amount of sediments will be generated and their management may prove problematic. The annual deposition of sediments from surface runoffs in France is estimated for 5 million Mg (tons) and potentially increasing in future [3].

Heavy metals are constant component of rainfall water. Emission of these elements to the environment is connected with all kinds of human activity. Metals are emitted to the atmosphere, absorbed on dust particles fall to the ground from where are washed away by rainwater. Considerable amounts of nickel find their way to the environment with burning fuels and this element leaching from the road surface, but also due to corrosion of vehicle parts coated with this element. Chromium in rainfall sewage also comes from fuel burning and in result of leaching from chromium plated vehicle surfaces.

The investigations aimed at determining the extent of copper, chromium and nickel pollution of sediments from the reservoirs of rainwater running from the surface of national road No. 4.

Material and methods

In 2007 and 2008 sediments were sampled from evaporation reservoirs which receive rainwater runoffs from the national road No. 4 along *ca* 10 km section of this road between Sulkow and Suchoraba villages. The parameters of the reservoirs and the catchment were given in Table 1.

Table 1

Characteristic of stormwater ponds

No.	No. of object	Localization	Capacity of reservoir [V]	Retention time of water in pond [t]	Total catchment area		Flow [Q]
					sealed [F_1]	green areas [F_2]	
			[m^3]	[min]	[ha]	[ha]	[$dm^3 \cdot s^{-1}$]
1	20	Sulkow	118.4	31.1	0.29	1.85	71
2	21	Sulkow	176.9	29.4	0.29	5.97	119
3	22	Sulkow	86.2	29.7	0.18	2.67	58
4	33	Biskupice	93.0	24.2	0.39	2.58	77
5	32	Przebieczany	81.5	37.8	0.17	1.29	45
6	36	Bodzanow	98.0	25.8	0.62	0.69	87
7	37	Bodzanow	127.0	30.4	0.39	4.08	127
8	41	Suchoraba	101.6	27.2	0.36	2.64	95
9	43	Suchoraba	—	—	0.37	3.88	94
10	45	Suchoraba	194.8	32	0.36	5.17	119
11	55	Suchoraba	218.0	27.7	0.53	9.91	156

The samples were collected on three dates: in May 2007, in April 2008 and in June 2008 in the Sulkow, Biskupice, Bodzanow and Suchoraba villages. Sediments for analyses were sampled from 11 reservoirs situated in: Sulkowice – 3 reservoirs, Biskupice – 1 reservoir, Przebieczany – 1 reservoir, Bodzanow – 2 reservoirs and Suchoraba – 4 reservoirs. Average sample was composed of primary samples collected from the whole area of the reservoirs. A laboratory sample was representative for the whole reservoir. The sediments were gathered from the top layer to the depth of 10 cm. Collected sediments were dried in the open air, dry mineralized in a muffle furnace at 450 ^{o}C and digested in a mixture of $HClO_4$ and HNO_3 acids (2:3, v/v). Material prepared in this way was dissolved in HCl and the contents of copper, chromium and nickel were assessed in obtained solution using ICP-AES method on JY 238 ULTRACE apparatus (Jobin Yvon Emission). Organic matter content was determined on the basis of weight loss during calcinations at 550 ^{o}C. The methods were validated on the basis on internal reference materials.

Rainwater sewage pollution with copper is mainly connected with fuel burning in engines. It has been estimated that cars emit about $4.5 \cdot 10^{-5}$ g per 1 kilometre of the way they pass [8]. Considerable amounts of this element are frequently noted in runoffs from roads and highways. Nordeidet et al [9] emphasize great importance of copper as a factor polluting runoffs from roads and highways.

Average copper content in the sediments from rainwater reservoirs was 34.94 $mg \cdot kg^{-1}$, fluctuating from 9.29 to 102 $mg\ Cu \cdot kg^{-1}$ (Table 2). The greatest quantities were registered in the sediments from the third sampling, where the amount was almost

Table 2

Parameters of heavy metals quantity in sediments from stormwater ponds

Element	Following sampling	Minimum	Maximum	Mean	Median	RSD* [%]
		[mg · kg^{-1} d.m.]				
Cu	I	9.29	60.64	30.34	30.96	59
	II	12.18	57.30	29.43	26.94	57
	III	11.82	102.0	45.06	46.56	55
Cr	I	16.38	58.08	34.20	29.60	37
	II	12.62	26.31	20.89	18.06	35
	III	17.19	38.94	28.52	27.31	26
Ni	I	7.57	15.52	11.65	11.63	18
	II	11.31	25.62	16.88	14.56	30
	III	8.37	18.19	12.77	12.03	22

* RSD – *Relative standard deviation.*

twice greater than in the 1st or 2nd sampling. The highest concentrations of copper were determined in the reservoirs situated closest to Krakow (Fig. 1). The average for 1–6 objects for all three samplings was 42.26 mg · kg^{-1}, whereas for reservoirs 7–11 it reached 26.62 mg · kg^{-1}. With growing distance from the city agglomeration copper level in the sediments was decreasing regularly. Standard deviation for sediments from all reservoirs fluctuated from 50 to 60 % between the successive samplings.

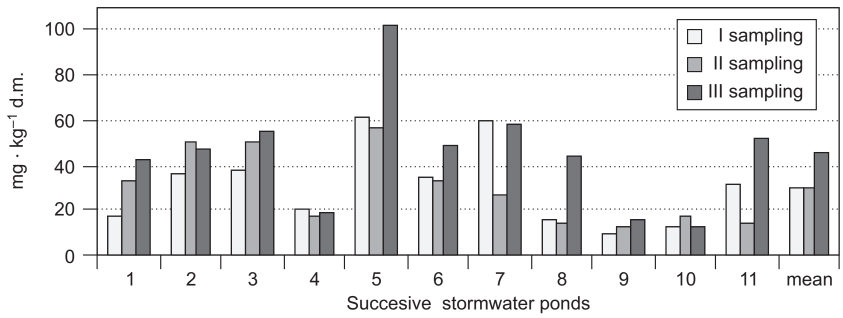

Fig. 1. Copper content in sediment from successive stormwater ponds

Copper contents in the analyzed sediments indicate their anthropogenic enrichment. This metal quantities registered by Neal et al [10] in the Thame River water (the Thames tributary) reached several mg · dm^{-3}. Wisniowska-Kielian and Niemiec [11] reported diversified copper contents in the sediments from the Dunajec River bottom and retention reservoirs: from 3.5 mg · kg^{-1} in the unpolluted areas to 28 mg · kg^{-1} in the regions under strong anthropopressure. However, copper concentrations assessed in the investigated sediments do not pose a hazard to the environment because they do not exceed the permissible contents of this element in soil or protected ground [6]. Nogaro et al [12] found that copper concentrations in reservoirs accumulating rainwater in the Lyon area reached the level of 113 mg · kg^{-1}. On the other hand, Rozenkrantz et al [13] assessed the copper contents in the sediments from rainwater infiltration pools in the vicinity of Melbourne similar to obtained in the presented research, amounting from 9.6 to 124 mg Cu · kg^{-1}, whereas Datry et al [14] observed a much higher concentration of this metal, between 241–503 mg · kg^{-1}, in the infiltration pools of rainwater runoffs in Lyon neighbourhood. Petavy et al [3] also registered high contents of copper in the sediments from infiltration pools in western France reaching from 122 to 334 mg · kg^{-1}, depending on the fraction. These authors pay attention to a considerable copper affinity to organic matter and the finest sediment fractions. These properties of copper cause that its removal from sediments depends the sedimentation conditions in reservoirs. Ikenaka et al [15] stated much higher quantities of copper in sediment of Kafue River, which ranged from 23 to 12906 mg · kg^{-1}, 4745 mg · kg^{-1} on average, whereas recommended value amounts 50 mg Cu · kg^{-1}. This phenomenon is a result of heavy metals transportation from the Copper Belt area to downstream areas. Krolikowski et al [16] noted copper concentrations amounting 6.8–60 mg · kg^{-1} in storm inlets in Bialystok, approximate to presented in this paper. Murakami et al [17] point to possible copper contamination of underground runoffs. These authors state that copper concentrations in the dust from the heavily loaded highways may reach even 990 mg · kg^{-1}. Mayer et al [18] report that this element concentrations in the sediments from reservoir receiving stormwater in Toronto range from 56 to 114 mg · kg^{-1}, *ie* are a bit higher than presented in the paper. Birch and McCready [19] investigated copper content in street dust and in the sediments from reservoirs accumulating rainwater in Sydney. Average copper content in street dust was 160 mg Cu, whereas in the sediments reached over 200 mg Cu · kg^{-1}. It evidences a considerable copper binding by organic matter and suspension particles. Obtained results of copper contents in sediments of the investigated reservoirs are much lower than presented by various authors.

Chromium content in sediments from the analyzed reservoirs ranged from 123.6 to 58.1 mg · kg^{-1} d.m. (Fig. 2) and was on average of 27.7 mg · kg^{-1}. The highest contents of this element were registered in the sediments collected in June 2008, whereas the lowest in sediments of the second sampling (April 2008).

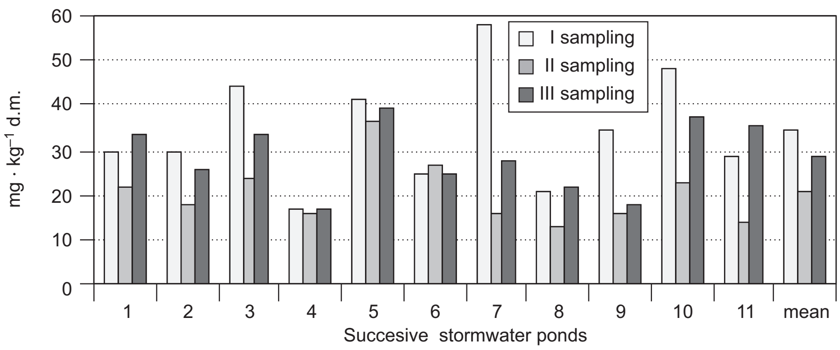

Fig. 2. Chromium content in sediment from successive stormwater ponds

No dependence of chromium concentration in sediments on the reservoir distance from Krakow was registered, as it had place in case of copper. Variability (RSD) of this element content in individual reservoirs was quite equal considering the sampling date and in all analyzed sediments fluctuated from 26 to 37 % (Table 2). Chromium contents in sediments of the studied reservoirs were not high and much lower than the literature data. No exceeded permissible content of this element was registered either in the soil or ground under protection [6]. Datry et al [14] determined chromium content in sediments from infiltration pools of rainwater runoffs in Lyon vicinity on the level of 68–129 $mg \cdot kg^{-1}$, whereas Petavy et al [3] registered this metal contents in sediments from western France ranging from 33–113 $mg \cdot kg^{-1}$. Birch and McCready [19] in their study determined chromium content in sediments originating from urbanized areas in Syndey amounting 31 $mg \cdot kg^{-1}$. The same authors reported that this element content in street dust in Syndey equaled 34 $mg \cdot kg^{-1}$. Jartun et al [20] assessed an average content of chromium in runoffs in Bergen, Norway as 30 $mg \cdot kg^{-1}$, while McKenzie et al [21] report 122 $mg \cdot kg^{-1}$ as an average content of this metal in dust from highways in California. On the other hand, Krolikowski et al [16] registered average amounts of chromium in storm inlets in Bialystok ranging from 1.17 to 3.84 $mg \cdot kg^{-1}$, whereas sediments from lamella separators from this city contained much larger amounts, 19.2–63.2 $mg\ Cr \cdot kg^{-1}$. Chromium contents in the analyzed reservoirs sediments were small, much smaller than assessed in similar objects from the other parts of the world.

Nickel content in the researched sediments fluctuated from 7.57 to 25.62 $mg \cdot kg^{-1}$ and on average was 13.71 $mg \cdot kg^{-1}$ (Fig. 3). Average quantities of this element in sediments from all reservoirs differed slightly. The greatest amount of nickel was determined in the sediments collected in April 2008. No such relationship as in case of copper was noted between this element accumulation in the sediments and the reservoir distance from Krakow city agglomeration. Higher contents were registered only in sediments from the second sampling in the reservoirs numbered 1, 2 and 3. Variability of this element contents in individual reservoirs between sampling dates was slight and in all studied sediments fell within 18–31 % range (Table 2).

Nickel contents in the investigated sediments were low and did not exceed values permissible for soil or ground under protection [6].

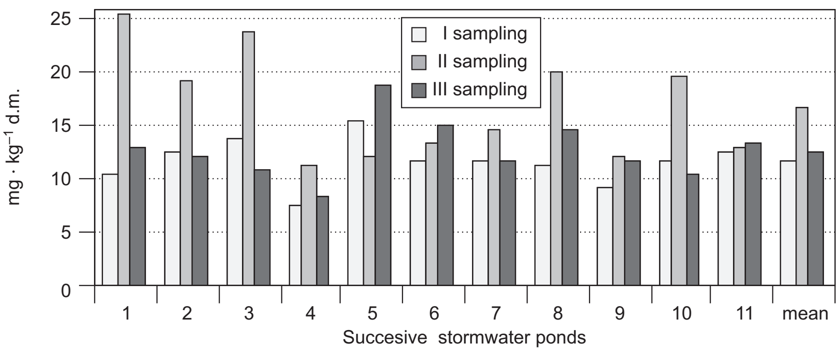

Fig. 3. Nickel content in sediment from successive stormwater ponds

Nickel is fairly common in the environment and is always a component of rainwater. This element contents in the analyzed sediments remained on a level formerly assessed by Wisniowska-Kielian and Niemiec [11] in bottom sediments of the Dunajec River and its tributaries. Nickel contents in sediments from the studied reservoirs were not high and much lower than presented in literature. Datry et al [14] stated this element content in sediments from infiltration pool of rainwater runoffs in the vicinity of Lyon ranging from 50 to 114 $mg \cdot kg^{-1}$, whereas Murakami et al [17] reported average concentrations of nickel of about 50 $mg \cdot kg^{-1}$ in street dust, which reached even 100 $mg \cdot kg^{-1}$ but only on highways with high traffic load. Birch and McCready [19] assessed 31 $mg\ Ni \cdot kg^{-1}$ in sediments originating in the urbanized areas in Sydney, whereas nickel content in street dust in this city was 34 $mg \cdot kg^{-1}$. Rozenkrantz et al [13] noted nickel contents of 5.7–21.5 $mg \cdot kg^{-1}$ in the sediments from rainwater infiltration pools in the vicinity of Melbourne, similar to obtained in the Authors' own research. Jartun et al [20] reported 24 $mg \cdot kg^{-1}$ as mean nickel content in the sediments from runoffs in Bergen, Norway. On the other hand, in research conducted by Krolikowski et al [16] average contents of this element in the sediments from storm inlets in Bialystok ranged from 0.98 to 12.8 $mg \cdot kg^{-1}$, but the amounts of this element assessed on lamella separators were 13–43 $mg \cdot kg^{-1}$.

The contents of the investigated metals in sediments from road runoffs were not high and it may be supposed that they do not pose any environmental hazard. The levels of copper, chromium and nickel in the sediments were much lower than observed by other authors in various cities in the world, however assessed ranges of these elements contents indicate anthropogenic enrichment of the sediments. The share of hard surfaced catchment in total area of the investigated reservoirs catchment is only from 5 to 10 %. The remaining part consists of green areas. Such considerable share of natural areas in total catchment area of the reservoirs leads to dilution of pollutants running off roads and their uptake by grass plants, which may explain lower contents of the studied impurities. Runoffs from city centres with considerable share of hard surfaced areas in catchment are always more burdened with pollutants. Barret et al [2] point to a considerable variability of the chemistry of runoffs from roads during rainfall. Sewage of the first phase of the runoff is the most concentrated. Its pollutant concentrations may be compared with those noted in industrial sewage, therefore retention reservoirs counteract the discharge of highly concentrated sewage to the natural, particularly water environment and their most important role is receiving the pollutants carried by the first phase of the runoff.

Conclusions

1. Sediments from the investigated rainwater reservoirs were characterized by a much lower content of copper, chromium and nickel than the sediments collected from rainwater reservoirs in various cities worldwide.

2. A high share of green areas in total catchment area of the studied reservoirs might favour lower accumulation of the studied metals in the sediments because waters filtering through green areas always contain lesser amounts of pollutants.

3. Copper contents in sediments of the analyzed reservoirs depended on the localization of the reservoir and were diminishing systematically with increasing distance from Krakow agglomeration boundaries. No such relationship was assessed for chromium and nickel.

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ZAWARTOŚĆ MIEDZI, NIKLU I CHROMU W OSADACH ZBIORNIKÓW WÓD DESZCZOWYCH USYTUOWANYCH WZDŁUŻ DROGI KRAJOWEJ Nr 4

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem pracy było określenie poziomu zanieczyszczenia metalami ciężkimi osadów pobranych ze zbiorników zlokalizowanych wzdłuż drogi krajowej nr 4 przyjmujących wody deszczowe. Osady pobrano z 11 zbiorników w trzech terminach: maj 2007 r., kwiecień 2008 r. i czerwiec 2008 r. z miejscowości: Sułków, Biskupice, Bodzanów i Suchoraba na odcinku ok. 10 km. Osady wysuszono na powietrzu i zmineralizowano na sucho i roztworzono w mieszaninie kwasów azotowego(V) i chlorowego(VII) w stosunku objętościowym 3:2. W uzyskanych roztworach oznaczono ogólną zawartość miedzi, chromu oraz niklu metodą ICP-AES.

Zawartość miedzi w badanych osadach mieściła się w granicach od 9,29 do 102 mg · kg^{-1}. Średnia dla wszystkich próbek wynosiła 34,94 mg · kg^{-1}. Stężenie chromu w badanych osadach wahało się w granicach 12,6–58,1 mg Cr · kg^{-1}, a średnio wynosiło 27,7 mg · kg^{-1}. Ilości niklu oznaczone w osadach ze zbiorników wód opadowych mieściły się w zakresie 7,57–25,62 mg Ni · kg^{-1}. Średnia zawartość tego pierwiastka wynosiła 13,71 mg · kg^{-1}. Zmienność (RSD) stężeń badanych metali pomiędzy poszczególnymi zbiornikami wahało się w granicach 18–58 %. Ilości badanych pierwiastków w osadach ze zbiorników przyjmujących spływy z drogi były znacznie mniejsze niż stwierdzane w podobnych osadach w innych miastach na świecie. Badane osady nie stanowią zagrożenia ze względu na zawartość miedzi, niklu i chromu. Zaobserwowano regularne zmniejszanie zawartości miedzi w miarę oddalania się od aglomeracji krakowskiej. Zbiornik usytuowany najbliżej Krakowa w Sułkowie oddalony jest o ok. 7 km od rogatek Krakowa i znajduje się przy granicy z miastem Wieliczka, natomiast zbiornik w Suchorabie jest oddalony o ok. 17 km od Krakowa. Na tym odcinku zawartość miedzi w osadach ze zbiorników wód deszczowych zmniejszyła się kilkakrotnie, co wskazuje na znaczny wpływ zanieczyszczeń napływających z ośrodka miejskiego na poziom tego metalu w osadach. W przypadku niklu i chromu nie zaobserwowano takiej zależności.

Słowa kluczowe: zbiorniki wód deszczowych, osady, zawartość metali, Cu, Ni, Cr