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CONTENTS OF IRON, MANGANESE AND ZINC IN THE SEDIMENTS OF RAINWATER RESERVOIRS SITUATED ALONG THE NATIONAL ROAD No. 4

ZAWARTOŚĆ ŻELAZA, MANGANU I CYNKU W OSADACH ZE ZBIORNIKÓW WÓD DESZCZOWYCH USYTUOWANYCH WZDŁUŻ DROGI KRAJOWEJ Nr 4

Abstract: The research aimed at identification and assessment of iron, manganese and zinc contents in bottom sediments of retention reservoirs – the receivers of rainwater runoff from the national road No. 4. The samples were collected in 2007 and 2008 from the top layer 0–10 cm of the sediments accumulated on the bottom of the reservoirs situated on both sides of the road along the section of about 10 km between the Sulkow and Suchoraba villages. Heavy metal concentrations were determined with ICP-AES method in solutions after the previous mineralization of the sediments in a muffle furnace and in a mixture of concentrated $HClO_4$ and HNO_3 acids (2:3, v/v).

The contents of individual metals in the analyzed sediments ranged from 7.25 to 18.11 gFe $\cdot$ kg^{-1} d.m., from 283 to 3225 mgMn $\cdot$ kg^{-1} d.m. and from 60.06 to 507.5 mgZn $\cdot$ kg^{-1} d.m. Average contents of Fe, Mn and Zn were: 11.84 g, 761 mg and 187 mg $\cdot$ kg^{-1} d.m., respectively. Iron content in the analyzed sediments depended on the sampling date, but no effect of the reservoirs localization on this metal content in the sediments was registered. Neither unambiguous influence of sampling date nor the reservoir distance from Krakow on manganese content in the analyzed sediments was noted. On the other hand, considerable differences in zinc content in the sediment taken from the individual reservoirs and dependant on sampling date were observed. Successive diminishing of zinc amount in the sediments was noted with increasing distance from Krakow.

Keywords: rainwater reservoirs, sediments, metals content, Fe, Mn, Zn

Vehicle transport is one of major sources of environmental pollution. Diesel engines emit considerable amounts of primary pollutants, such as: nitrogen oxides, sulphur dioxide and dusts, they also cause a formation of a secondary pollution, *eg* ozone. A vast number of pollutants enter the environment also in result of car brakes and both tyres and road surface abrasion. Dusts are carriers of many dangerous pollutants, such

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PAHs or heavy metals. These components emitted to the atmosphere find their way to the ground with precipitations and become a component of rainwater, particularly in sealed areas. Intensive development of vehicle transport which happened in the second half of the 20th century generated a new dispersed source of pollution. Construction of heavily loaded communication routes in the developed countries posed a danger of introducing excessive amounts of pollutants to the ecosystems situated in close vicinity to the roads. Storing of water originating from thoroughfare drainage and high throughput highways allows retain these pollutants, protecting the neighbouring water ecosystems and ground waters against enrichment in toxic substances. *Environmental Protection Agency* (EPA) attaches great importance to this type of pollution, which locally may lead to environment degradation. Pollution linear distribution and dispersion on the terrain make protection of the environment additionally difficult. Many researchers of the problem are convinced that in highly urbanized areas coefficient rainwater pose now the greatest hazard for surface and underground water quality [1–3], therefore the facilities for temporary rainwater retaining and pretreatment must become an inevitable element of high throughput highways in order to efficiently protect the environment. The method of rainfall waste water cleaning, yielding the best results, is the use of retention reservoirs. Creating conditions for suspension sedimentation in them favour immobilization of heavy metals and organic impurities. Rainwater may be also cleaned of heavy metals by means of their infiltration through organic sorbents. Organic matter contained in the sorbents causes heavy metal binding [4]. Exploitation of such retention reservoirs leads to formation of a considerable amount of sediments whose utilization may pose a problem due to excessive quantities of pollutants. Considerable quantities of iron and zinc occur in runoffs from roads because of their common use in vehicle transport. These elements enter the runoffs from car bodies and undercarriage elements corrosion, but are also emitted during fuel burning. Because of that iron and zinc content in the sediments from rainwater reservoirs may be considerable and pose a hazard to the environment.

Presented research aimed at determining iron, manganese and zinc contents in the sediments from reservoirs of rainwater running of the surface of national road No. 4.

Material and methods

Sediments from retention reservoirs which are the receivers of rainwater runoffs from the national road No. 4 were sampled along the *ca* 10 km section, between the Sulkow and Suchoraba villages. Parameters of the reservoirs and the catchment were given in Table 1.

The samples were collected in May 2007 and in April and June 2008. Analyzed were sediments from a total of 11 reservoirs: 3 in Sulkow, 1 in Biskupice, 1 in Przebieczany, 2 in Bodzanow and 4 in Suchoraba. The mean sample was formed from initial samples collected from the whole area of the reservoirs. A laboratory sample was representative for the whole reservoir. The sediments were collected from the surface 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).

Table 1

Characteristic of researched 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 material prepared in this way was dissolved in HCl acid and the concentration of iron, manganese and zinc was assessed using ICP-AES method in JY 238 ULTRACE apparatus (Jobin Yvon Emission). Organic matter content was determined on the basis of weight loss during calcination at 550 ^{o}C. The methods were validated on the basis of internal reference materials.

Results and discussion

Iron contents in the analyzed sediments from rainwater reservoirs ranged from 7.25 $g \cdot kg^{-1}$ to 18.11 $g \cdot kg^{-1}$ with an average of 11.84 g Fe $\cdot kg^{-1}$ (Table 2).

Table 2

Parameters of heavy metals quantity in sediments from stormwater ponds

Element	Following sampling	Minimum	Maximum	Mean	Median	RSD* [%]
		[$mg \cdot kg^{-1}$ d.m.]				
Fe	I	7249	12168	9427	9115	14.63
	II	9206	16000	11945	11687	17.36
	III	9744	18106	14140	12525	21.35
Mn	I	283	701	480	449	26.93
	II	321	1925	725	517	65.78
	III	287	3225	1079	617	88.82
Zn	I	60.1	339	148	117	55.92
	II	82.3	326	193	183	46.12
	III	62.4	507	221	210	58.94

* RSD – *Relative standard deviation.*

The greatest amounts were assessed in the sediments taken at the third sampling time. There was a half more than the quantities found in the sediments from the first sampling date and by about 30 % more than in the sediments taken on the second one. No effect of the reservoirs localization on this metal content in the sediments was registered.

Iron contents determined in the sediment of individual reservoirs differed slightly (Fig. 1).

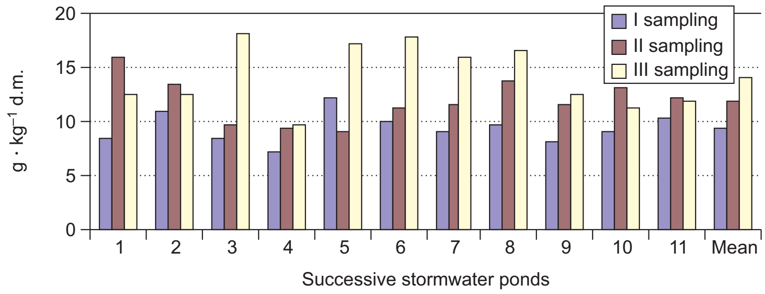

Fig. 1. Iron content in sediment from successive stormwater ponds

Relative standard deviation (RSD) for the sediments from all reservoirs was about 20 %. The amounts of iron in the studied sediments indicate its anthropogenic enrichment. Wisniowska-Kielian and Niemiec [5] assessed iron content between 7 and 25 g · kg^{-1} in bottom sediments of the Dunajec River. These are values comparable with registered in the presented investigations. Mayer et al [6] report iron contents in the sediment of the reservoir receiving stormwaters in Toronto ranging from 23 g · kg^{-1} to 27 g · kg^{-1}. Huert-Diaz et al [7] determined this metal content in the sediments of two ports in Baja, Mexico (Ensenada and Suazal) within narrower range from 54.6 to 89.0 g · kg^{-1}. The studied areas are threatened with strong anthropopressure both from the ships and rainfall runoffs from the port area. The sediments from the Ensenada port contained much greater amounts of iron than those from Suazal port. Suazal port is 26 years older and 10 times bigger. The source of iron from the vehicle movement is in the first place wearing out of engines and vehicle parts. The common use of this metal for car construction suggests that much bigger quantities should be found in this type of sediments than in the sediments from reservoirs under lesser anthropopressure. The data obtained in the presented investigations and the literature data indicate that the amounts of iron in the sediments from urbanized areas are not higher than observed in the natural reservoirs. Iron contents in river and lake sediments of Poland are comparable, even bigger than obtained in the presented research and reported by other authors [8, 9]. The cause may be poor iron binding with sediments and this element removal to the environment with excessive waters from the reservoirs. The literature data point to a slight diversification of iron amounts in runoffs from urbanized areas, from roads and highways.

Manganese content in the investigated sediments ranged widely from 283 mg · kg^{-1} to 3225 mg · kg^{-1}. Average content of this element in the analyzed sediments amounted 761 mg · kg^{-1} (Fig. 2).

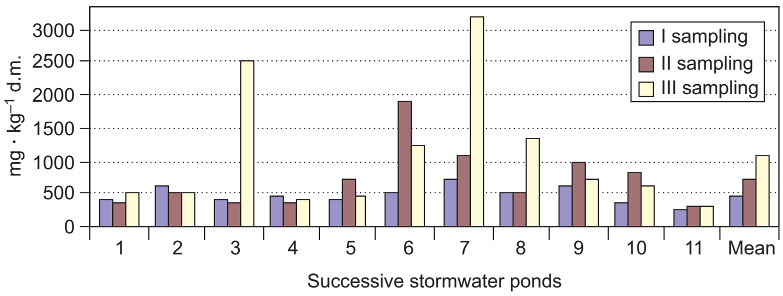

Fig. 2. Manganese content in sediment from successive stormwater ponds

No unequivocal effect of either the sampling date or the reservoir distance from Krakow on manganese content in the sediments was observed. Sediments collected in June 2008 from the reservoirs No. 22 and 36 and the sediments taken in April 2008 from the reservoir No. 36 contained very big quantities of manganese (over 1900 mg Mn · kg^{-1}). The other sediments revealed an approximate content. Manganese is emitted to the environment from communication sources, mainly from wearing of engines [6]. It may occur in considerable amounts in sediments from antropogenically transformed areas, therefore monitoring of this element contents in materials of this type is conducted. Huert-Diaz et al [7] studied the sediments from two ports in Baja, Mexico, stated manganese quantities ranging from 337 mgMn · kg^{-1} to 1090 mgMn · kg^{-1}. However, these authors point to a higher content of this element in Ensenada port than in Suazal port. Rosenkrantz et al [10] reported very low average amounts of this element, fluctuating from 31 mgMn · kg^{-1} to 131 mgMn · kg^{-1}, in the sediments from rainwater reservoirs in Melbourne, Australia. Datry et al [11] in the studies of sediments from infiltration pools of rainfall runoffs in the vicinity of Lyon noted manganese content on reached 429 mg · kg^{-1}.

Sediments from the studied reservoirs revealed a big content of zinc, in the range from 60.1 mg · kg^{-1} d.m. to 507.5 mg · kg^{-1} d.m. and assumed the average value of 187.5 mg · kg^{-1} (Fig. 3). The highest contents of this element were determined in the sediments collected in June 2008 (3rd sampling time), whereas the lowest in the sediments collected in April 2008 (2nd sampling). Considerable differences were

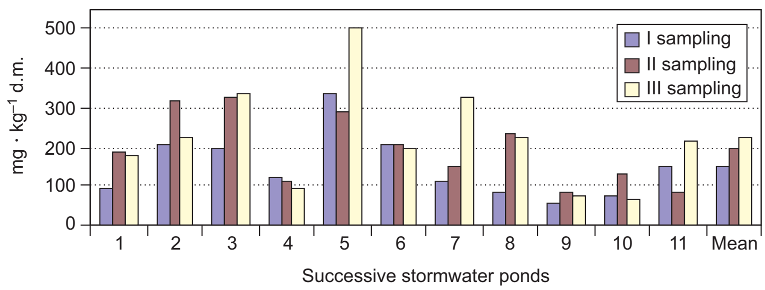

Fig. 3. Zinc content in sediment from successive stormwater ponds

assessed in this metal content in the sediments from individual reservoirs. Relative variability of zinc contents in the sediments from the reservoirs was from 45 to 59 % and was the highest for the third sampling. Successive diminishing of zinc content in the sediments was observed with increase of distance from Krakow. Average content of this metal in sediments from 6 reservoirs situated closest to Krakow was 288.6 mg, whereas in the other reservoirs reached 227.8 mgZn $\cdot$ kg^{-1}.

Zinc is one of major pollutants in runoffs from anthropogenically transformed areas. The main source of zinc from vehicle transport is abrasion of tyres and this element leaching from galvanized steel surfaces [6]. Therefore considerable quantities are found both in the runoffs from highways and from built-up areas. Rosenkrantz et al [10] reported that quantities of this element in the sediments from rainwater reservoirs in Melbourne, Australia, ranged from 508 mgZn $\cdot$ kg^{-1} to 2230 mgZn $\cdot$ kg^{-1}. Duong and Lee [12] stated average content of this element in the sediments from runoffs from the cities in South Korea of between 120 mgZn $\cdot$ kg^{-1} and 160 mgZn $\cdot$ kg^{-1}. Mayer et al [6] investigated the effect of anthropogenic reservoirs collecting rainwater on amphibiotic organisms settling these reservoirs. Even at this element value reaching 80 mg $\cdot$ kg^{-1} the authors reported unfavourable influence on amphibiotic organisms inhabiting these reservoirs. Camponelli et al [13] reported that zinc leached from aged tire debris is bioavailable to developing wood frog (*Rana sylvatica*) and accumulated in sediments may influence its population dynamics. On the other hand Datry et al [11] reported this element quantities in the sediments from infiltration pools of rainwater runoff in the vicinity of Lyon ranging from 329 mg $\cdot$ kg^{-1} to 1542 mg $\cdot$ kg^{-1}. Mayer et al [6] stated that the sediments from the reservoir receiving stormwater in Toronto contain between 262 mgZn $\cdot$ kg^{-1} and 519 mgZn $\cdot$ kg^{-1}. Jartun et al [14] report average zinc contents in the sediments of runoffs in Bergen, Norway, reaching 403 mgZn $\cdot$ kg^{-1}. Birch and McCready [16] tested zinc content in street dust and in sediments originating from reservoirs gathering rainwater in Sydney. Average zinc content in street dust amounted 502 mg $\cdot$ kg^{-1}, whereas in the sediments over 1700 mgZn $\cdot$ kg^{-1}, with maximum amounting 11300 mg $\cdot$ kg^{-1} [16]. Therefore, zinc concentrations in sediments of the analyzed reservoirs were not high and generally lower than reported by other authors. Basing on the data of Lis and Pasieczna [17], zinc contents below 100 mgZn $\cdot$ kg^{-1} may be consider as natural. Assuming these criteria 21 % of samples revealed a natural content of this element whereas 80 % points to anthropogenic enrichment.

Metals contained in runoffs from roads and other sealed areas become a hazard to surface and underground waters. The literature data for similar materials in the world indicate a considerable variability of pollutant concentrations, which is conditioned by many factors, such as: total pollutant quantity emitted per area unit, the weather conditions and kind of surface. Collecting and pretreatment of rainfall waters running off roads in specially adjusted facilities allows to improve their quality through sedimentation of pollutants together with the suspension to the sediments. The analyzed reservoirs collect water from the road of a daily throughput of 34000 cars. Moreover, the catchments of these reservoirs are characterized by a small share of hard surfaced areas in total catchment area. At systems collecting water from catchments with higher proportion of hard surfaced areas one should expect higher contents of the examined metals in sediments. Pretreated water generally meets the standards of sewage disposal to water or to the ground [18]. However, there is a possibility of excessive pollutant concentration in forming sediments. Harmful substances bound in sediments may under some conditions become mobile and carried by rainfall water and may flow into surface hydroecosystems and underground waters. Proper exploitation of rainwater reservoirs requires a periodic removal of sediments. The problem of disposal of sediments formed as a result of purification of road runoffs will aggravate with increasingly larger number of constructed facilities for runoff water pretreatment. As has been mentioned earlier, metal contents in sediments increase during their exploitation, therefore their harmful effect may increase in result of mobilization of metals contained in the sediments. In the studies conducted by Clement et al [19] majority of sediments formed in urban retention ponds as a result of sedimentation of pollutants contained in runoffs from high traffic roads located in various parts of France, had no acute or chronic ecotoxicological effect for aquatic surface ecosystems after 21 days of exposure. On the other hand Camponelli et al [13] found that zinc contained in sediments can result in measurable physiologic outcomes (greater time to metamorphosis and smaller mass) in population dynamics of wood frogs (*Rana sylvatica*).

Conclusions

1. Sediments from the investigated rainwater reservoirs revealed much smaller iron content than analogous sediments collected from reservoirs in various cities of the world.
2. Content of iron was increased in the analyzed sediments taken from most reservoirs in successive sampling date, but in case of manganese and zinc there was no evident dependence with the date of sampling.
3. Zinc content in sediments of the studied reservoirs was diminishing regularly with increasing distance from Krakow agglomeration. Content of iron and manganese did not depend on the reservoir localization.
4. Considering iron, manganese and zinc contents, the analyzed sediments do not pose a hazard to the environment.

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ZAWARTOŚĆ ŻELAZA, MANGANU I CYNKU W OSADACH ZE ZBIORNIKÓW WÓD DESZCZOWYCH USYTUOWANYCH WZDŁUŻ DROGI KRAJOWEJ Nr 4

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Abstrakt: Celem badań było oznaczenie i ocena zawartości żelaza, manganu i cynku w osadach dennych zbiorników wód deszczowych usytuowanych wzdłuż drogi krajowej nr 4. W 2007 i 2008 r. pobrano próbki osadów ze zbiorników będących odbiornikami spływów deszczowych z jezdni i drogi krajowej nr 4 na odcinku 10 km, pomiędzy Sułkowem i Suchorabą. Osady pobrano z ich wierzchniej warstwy (0–10 cm) z każdego zbiornika. Zawartość metali ciężkich w osadach oznaczono po uprzedniej mineralizacji materiału w piecu muflowym oraz w mieszaninie kwasów $HClO_4$ i HNO_3 (2:3, v/v), metodą ICP-AES.

Zawartości poszczególnych metali w analizowanych osadach wahały się od 7,25 do 18,11 gFe $\cdot$ kg^{-1} s.m., od 60,05 do 507,5 mgZn $\cdot$ kg^{-1} s.m. oraz od 283 do 3225 mgMn $\cdot$ kg^{-1} s.m. Średnie zawartości Fe, Zn, Mn wynosiły odpowiednio: 11,84 g, 187,5 mg oraz 761 mg $\cdot$ kg^{-1} s.m. Zawartość żelaza w analizowanych osadach była zależna od terminu pobrania próbek, nie stwierdzono natomiast wpływu usytuowania zbiorników na zawartość tego metalu w osadach. Nie stwierdzono jednoznacznego wpływu terminu pobrania ani oddalenia zbiornika od Krakowa na zawartość manganu w osadach. Stwierdzono znaczne różnice zawartości cynku w osadach z poszczególnych zbiorników oraz w zależności od terminu pobrania próbek. Zaobserwowano sukcesywne zmniejszanie się ilości cynku w osadach w miarę oddalania się od Krakowa.

Słowa kluczowe: zbiorniki wód deszczowych, osady, zawartość metali, Fe, Mn, Zn