Heavy metals contamination of sediments from chosen dam reservoirs in terms of their usage in earthworks

KAROLINA KOŚ, EUGENIUSZ ZAWISZA
Department of Water Engineering and Geotechnics
Agricultural University in Cracow
21 Mickiewicza Street, 30-059 Cracow
POLAND
karolinasudyka@wp.pl

Abstract: Evaluation of heavy metals contamination of the bottom sediments from chosen dam reservoirs was presented in the paper. A Ph reaction and the content of thirteen heavy metals were determined. Obtained values were compared with the ones given by numerous regulations and classifications. A possibility of using bottom sediments for earthworks purposes was also discussed in legal terms. It was stated that the bottom sediments from Czorsztyński and Rzeszowski Lakes are not a threat to the environment and they can be used as a construction material in earthworks.

Key-Words: dam reservoirs, bottom sediments, heavy metals

1 Introduction

Chemical constitution of sediments in water reservoirs depend primarily on the lithology of the drainage area, the morphology and the climate, which influences the weathering process, the elements mobilization and their accumulation in the environment [14]. Increased heavy metals contents can occur in the bottom sediments of rivers and reservoirs, it is the result of human activity – sewage discharges, agricultural use of land etc. Most of the potentially harmful metals and organic compounds that reach surface waters are retained by the bottom sediments – they accumulate elements like zinc, cooper, chromium, cadmium, lead, nickel, mercury as well as organic pollutants, such as polycyclic aromatic hydrocarbon (PAHs), polychlorinated biphenyl (PCB) and organochlorine pesticides [14]. Because of the possibility of contamination, when dredging works are planned on a river or reservoir, the sediments should be tested and heavy metals content should be determined.

2 Problem Formulation

Dredged material is usually treated like waste and put on a heap, but it can be a valuable material, for example in earthworks. Usability evaluation of the bottom sediments for earthworks purposes should be done based on their geotechnical parameters as well as their influence on the environment. Issues concerning the geotechnical aspect of using bottom sediments in road or hydrotechnical engineering were presented by few authors [5,6]. This paper concerns the problems connected with the ecological aspect of using sediments as a construction material in earthworks. The purpose of this paper was to evaluate heavy metals contamination of the bottom sediments from water reservoirs and consider the possibility of their beneficial use in earthworks.

2.1 Materials and methods

Bottom sediments from two different water reservoirs were tested, the first reservoir (Rzeszowski Lake) is quite small, shallow and located in the city center. The siltation process has a great influence on its functioning (after fourteen years of functioning over 60% of the initial capacity has been filled with sediments). The other one is Czorsztyński Lake, which is one of the biggest dam reservoirs in Poland and it is located between Pieniny and Gorce Mountains, so there are not many sources of contamination within the basin. It was built in 1997 and so far the effects of the siltation process can be noticed only in the backwater area.

The range of tests included determining of the pH reaction and the content of thirteen heavy metals. In order to determine pH 10 g of the air dry material was put in glass beaker and poured with 25 cm^3 of distilled water and 25 cm^3 of KCL solution of 1 mole/dm^3. The content of the beakers was mixed using glass rod and left for 24 hours. After that time it was mixed again and electrodes were immersed; the pH reaction was read from the pH-meter scale.
Determination of the heavy metals content was carried out in the Laboratory of Department of Agricultural and Environmental Chemistry

(University of Agriculture in Cracow). The heavy metals content was determined using microwave method. In order to change the soil material into solution about 0.5 g of soil was weight and mixed with 9 cm^3 of HNO_3 and 6 cm^3 of HCl. Then it was put in the 16HF100 solution, closed and put in a MULTIWAVE 3000 microwave oven. After mineralization samples were filtered into 25 cm^3 flasks using distilled water. The solution obtained in this process was used to determine contents of individual elements. The tests were carried out using ICP OES Optima 7300DV apparatus produced by Perkin Elmer.

Determination of heavy metals contents was also carried out using one more method – by changing soil material into the solution of the mixture of nitric and perchloric acids after previous incineration of the organic substance. 2 g of soil was weight and burnt in 450°C for 12 hours. Then samples were poured with the mixture of nitric and perchloric acids and left for 12 hours. After that samples were evaporated, poured with the solution of hydrochloric acid 1:1 and 1% hydrochloric acid and left for 2 hours. Then the content was transferred to flasks using 1% hydrochloric acid. The determination of heavy metals contents was carried out using the same apparatus as in the previous method.

Determination of the mercury content was carried out using AMA 254 mercury analyzer, without a previous preparation (mineralization) of the soil sample, a mercury vapor technique was used. After thermal decomposition in the atmosphere of pure oxygen, the obtained products went to the catalyst, where the oxidation ended. Then in the amalgamator the mercury was released in the form of vapor and moved to the measuring cuvette. The test was carried out in the range of 0.05 – 600 ng of mercury at a single measurement.

3 Problem Solution

The bottom sediments of Czorsztyńskie Lake in geotechnical terms are silty sands, their organic matter content allows to classify them as mineral soil. They are characterized by relatively high values of shearing strength and bearing ratio [9]. The bottom sediments of Rzeszowski Lake are silts in a liquid state, they have a low hydraulic conductivity, a high specific surface area, an increased organic matter content and relatively high values of the angle of internal friction and cohesion [10].

The heavy metals contents in the bottom sediments and their pH reaction are presented in Table 1. It can be stated that the heavy metals content in the sediments of Rzeszowski Lake is higher than in the sediments of Czorsztyńskie Lake. Apart from the outside factors (sources of pollution) it is the result of a higher fine fraction content, which plays the main role in the accumulation of pollutants. Fine-grained fractions have an active surface where, as a result of sorption and precipitation, metal ions and their complex combinations are cumulated [7].

Table 1. Heavy metals content in the bottom sediments and their pH reaction

Parameter		Content in the bottom sediments from	
		Czorsztyński Lake	Rzeszowski Lake
Metal [$mg \cdot kg^{-1}$]	arsenic	2,303	2,925
	chromium	26,130	34,489
	zinc	43,211	75,881
	cadmium	0,745	0,522
	copper	11,047	20,941
	nickel	17,360	24,661
	lead	11,141	15,288
	manganese	300,778	476,260
	iron	13305,42	18058,77
	mercury	0,1088	0,1702
	barium	48,046	67,339
	cobalt	0,260	2,445
	molybdenum	0,461	0,424
pH reaction		7,67	7,30

Heavy metals contents in the tested bottom sediments should firstly be compared with the values given by the Regulation of the Minister of Environment [12]. According to types and concentrations of substances presented there it can be stated whether the slime is contaminated or not. Mentioned regulation was repealed in January 2013, nonetheless by comparing the obtained values with the allowable ones given by this regulation a degree of contamination can be preliminarily determined. The regulation determines the allowable maximum values of pollutants concentration like heavy metals content in the slime dredged from sea, reservoirs, ponds, rivers, canals or ditches. When the concentration of at least one substance exceeds the allowable value the slime is considered to be contaminated. In case of the bottom sediments form both Rzeszowski and Czorsztyński Lakes it can be stated that the content of every tested heavy metal was much lower than the allowable concentration (Table 2), so according to the regulation the tested sediments are not contaminated.

Table 2. Heavy metals content in relation to the allowable values in a dredged material [12]

Metal	Allowable value	Content in the bottom sediments from	
		Czorsztyński Lake	Rzeszowski Lake
	[mg·kg^{-1}]		
arsenic	30	2,303	2,925
chromium	200	26,130	34,489
zinc	1000	43,211	75,881
cadmium	7,5	0,745	0,522
copper	150	11,047	20,941
nickel	75	17,360	24,661
lead	200	11,141	15,288
mercury	1	0,1088	0,1702

According to Regulation of the Minister of Environment on soil quality standards [13] the soil should be considered contaminated when the concentration of at least one substance exceeds the allowable value. Soil or dredged material that is used in earthworks has to fulfill the criteria set for their location. There are three groups of soils, depending on their current or planned function: A – soils of protected areas, B – soils of agricultural, forest, built-up, urbanized areas or wastelands, C – soils of industrial, transport or mining areas. Allowable concentrations of heavy metals for each group of soil are resented in Table 3. While comparing them with the obtained values it can be stated that the sediments from both lakes can be allowed for using in earthworks. Heavy metals contents in the tested sediments did not exceed the threshold values in any case even for the A group – the most restricted one, because of its function (protected areas).

Presented allowable values must be fulfilled when the material is supposed to be used in earthworks but there are many other soil classifications which are based on the heavy metals contamination that can be used to determine the purity class of the soil. One of them are geochemical classes of purity complied for water sediments by Bojakowska and Sokołowska [3]. The authors determined threshold values of heavy metals contents for the geochemical background and purity classes (Table 4). While comparing these values with the obtained results it can be noticed that the sediments from Rzeszowski Lake are more contaminated, although for both reservoirs the values were relatively low. In case of Czorsztyński Lake the heavy metals contents did not exceed the geochemical background or they were within the range for the 1st class of purity. Only in case of chromium and mercury the sediments were classified to the 2nd class – sediments contaminated to a small extend, although in case of the mercury the value was very close to the threshold value for the 1st class (< 0,1 mg·kg^{-1}). In case of chromium a higher content was expected in the sediments from Czorsztyński Lake. The main source of chromium in contaminated alluvia is sewage from the tanneries, where chrome tanning processes are used [3]. The drainage basin of Czorsztyński Lake is an area where tanning industry is highly developed, there about 150 tanneries [4].

The bottom sediments of Rzeszowski Lake were classified as the 2nd class of purity, which was the result of chromium, copper and mercury contents. Apart from the mentioned tanning industry, sewage from the metallurgical plants where metallic products are chromed can also have an influence on the chromium content [3]. Probably the WSK Rzeszów Metallurgical Plant, which is located next to the reservoir, is the reason for the heighten chromium content in the sediments. The copper content was close to the threshold value for the 1st class, whereas the increased mercury content might be caused by sewage from treatment plants, industrial factories producing chlorine or fibers and pulp mills [3]. In case of other metals, their content did not exceed the threshold values for the backgrounds or the 1st classes of purity (Table 4).

Another commonly used classification is the one prepared by the Institute of Soil Science and Plant Cultivation in Puławy [8] for agricultural areas, which accounts not only the heavy metals content, but also the factors that influence their mobility – fine-grained fraction content and reaction. There are different limit values for three soil groups, which are distinguished by the content of fine fraction (< 0,02 mm) and reaction (Table 5). In case of the sediments of Czorsztyński Lake it is 15.0% and pH = 7.67, so they are in the group B. The sediments from Rzeszowski Lake are in group CG, because the fine fraction content is higher (48%, pH = 7,30).

While comparing the obtained results with the threshold values presented in the mentioned classification (Table 6) it can be stated that almost all the values fulfill the requirements set for the "zero pollution degree". The ISSPC defines "0" pollution degree as unpolluted soil with natural contents, which are suitable for any gardening or agriculture. The sediments were classified so high in this classification because the value of pH was taken into consideration, which – in this case is neutral – works to their advantage.

Table 5. Groups of soils [8]

Parameter		pH reaction			
		< 4,5	4,5 – 5,5	5,5 – 6,5	> 6,5
Fine fractions content [%]	< 10	AG	AG	AG	AG
	10 – 20	AG	AG	AG	BG
	20 – 35	BG	BG	CG	CG
	35 – 55	BG	BG	CG	CG

In conclusion it can be stated that the heavy metals contents in the bottom sediments of both reservoirs were relatively low. According to different purity classification they are classified as unpolluted material. Only in case of chromium and mercury an increased contents were noticed (but still lower than the allowable values), which did not exclude the possibility of using this material. It should be emphasized that the concentrations of the analyzed metals in the sediments of both reservoirs are lower than the allowable values set by the Regulation of the Minister of the Environment [13] which allows using sediments in earthworks.

Apart from the possibility of heavy metals contamination there is also a legal issue that has to be considered while using dredged sediments. In Poland for a while there was an Act stating that the material dredged from a water reservoir or a river is a waste and it should be deposited on a landfill [1]. Using this material for earthworks or agricultural purposes was practically impossible. The currently effective Act [2] states that it shall not apply to the sediments which were dredged as a result of the waterways maintaining, water management or flood protection unless they are dangerous. Therefore if it does not apply, these sediments are not a waste. The tested sediments they are not dangerous and they do not pose a threat to the environment, so (assuming that their dredging will be carried out in order to maintain waterways or to deepen reservoirs) these sediments, according to Polish law, are not a waste and they can be used for earthworks purposes. When we look at the European Union law there is a problem at the very begging, there is no clear answer to the question is the dredged material a waste or not. There are several EU documents that influence the dredging process: Water Framework Directive, Waste Framework Directive, Habitats and Birds Directives and Marine Strategy. It should be remembered that there is a distinction between dredging in marine and fresh water and in this last case mainly Waste Framework Directive applies. In terms of the decision logic the following "disposal" modes were considered [11]:

- Beneficial use: as fill material, as construction material, for soil improvement of agricultural land;
- Relocation: placing dredged material at specific locations in the environmental compartment so that it fulfills its role in the sediment balance;
- Placement: the disposal of dredged material at suitable disposal location;
- Processing: separation of sand and silt, manufacturing bricks and basalt, biological treatment to reduce contaminant level, dewatering, ripening, land farming and more.

It should be noticed that according to the EU directives there are no specific limit values of contaminants, as they should be set by the member states.

4 Conclusions

1. Heavy metals contents in the tested sediments were relatively low, so according to various classifications in most cases they were classified as unpolluted. The reaction of the sediments was neutral and it is also not harmful to the water and soil environment.
2. Sediments from the mentioned reservoirs do not pose a threat to the environment and they can be used as a construction material for earthworks purposes. As was shown in the paper, despite the popular opinion, not all of the sediments are heavily contaminated with heavy metals and they fulfill all the requirements set by Polish regulations for materials used in earthworks.
3. As long as the dredged material is not contaminated (according to national threshold values) there are no legal issues preventing its use in earthworks, in both Polish and European legislature.
4. Disposal of dredged material concerns mainly marine water dredging – harbors and canals. Although it should be remembered that it is also a problem of dam reservoirs, where siltation can cause operating problems and dredging is often the only solution.

.

References:

[1] Act on Waste/27.6.1997. Journal of Laws 1997 item 97.96.592

[2] Act on Waste/14.12.2012. Journal of Laws 2013 no 0 item 21.

[3] Bojakowska I., Sokołowska G. 1998. Geochemical purity classes of water sediments. *Przegląd geologiczny*, 46, 1, 49-54. [in Polish, summary in English]

[4] Czaplicka-Kotas A., Szalińska E., Wachałowicz M. 2008. Distribution of chrome concentration in Czorsztyn reservoir bottom deposits. *Gospodarka Wodna* nr 11. 457-462 [in Polish, summary in English]

[5] Gruchot A., Sudyka K. 2011. Usability evaluation of bottom sediments from backwater of Czorsztyn – Niedzica reservoir in geotechnical engineering. Geologija. Versita Publisher. 53, No.2 (74), 20-27

[6] Gwóźdź R. 2007. Properties of cohesive sediments from Rożnowskie Lake in the aspect of their geotechnical usage. Doctoral Thesis. PK Cracow [in Polish]

[7] Helios-Rybacka E., Sikora W. S., Wójcik R., Wardas M., Strzebońska M., Adamiec E., Łagan Ł. 2000. Evaluation of heavy metal contamination of bottom sediments of the Upper and Middle Odra River. *Gospodarka Wodna*, r. 60, nr 8, s. 300–304 [in Polish, summary in English]

[8] ISSPC Puławy 1993. Basis of the evaluation of chemical contamination of soil. Team manager Kabata – Pendias A. Biblioteka Monitoringu Środowiska. Warsaw [in Polish]

[9] Koś K. 2013. Geotechnical characteristics of bottom sediments from Czorsztyn Reservoir in the aspect of their usage in earthworks. *Inżynieria Morska i Geotechnika*, nr 2/2013 [in Polish]

[10] Koś K., Zawisza E. 2012. Usability evaluation of bottom sediments from Rzeszowski Reservoir for soil liners in municipal waste disposal sites. *Acta Sci. Pol., Formatio Circumiectus*, 11 (4), 49-60 [in Polish, summary in English]

[11] Mink F., Dirks W., Van Raalte G., De Vlieger H., Russel M. 2006. Impact of European Union environmental law on dredging. Terra et Aqua. Number 104

[12] Regulation of the Minister of the Environment/16. 04. 2002 on types and concentrations of substances that classify the material as contaminated. *Journal of Laws* 2002 no 55 item 498.

[13] Regulation of the Minister of the Environment/9. 9. 2002 on the standards of soil quality. *Journal of Laws* 2002 no 165 item 1359

[14] The impact of climate change on the environment, economy and society. 2011. Task 8: Preventing the degradation of Polish reservoirs. 2010 report. IMGW. Team manager: E.Sieinski. Available Online: www.klimat.imgw.pl

APPENDIXES:

Table 3. Heavy metals content in relation to the allowable values in soil [13]

Metal	Allowable value									Content in the bottom sediments from	
	Group A	Group B					Group C			Czorsztyński Lake	Rzeszowski Lake
		Głębokość [m p.p.t.]									
		0-0,3 m	0,3 – 15,0 m		>15 m		0-2 m	2-15 m			
			Hydraulic conductivity [m/s]					Hydraulic conductivity [m/s]			
			to	below	to	below		to	below		
			$1 \cdot 10^{-7}$		$1 \cdot 10^{-7}$			$1 \cdot 10^{-7}$			
	$[mg \cdot kg^{-1}]$										
arsenic	20	20	20	25	25	55	60	25	100	2,303	2,925
barium	200	200	250	320	300	650	1000	300	3000	48,046	67,339
chromium	50	150	150	190	150	380	500	150	800	26,130	34,489
tin	20	20	30	50	40	300	350	40	300	-	-
zinc	100	300	350	300	300	720	1000	300	3000	43,211	75,881
cadmium	1	4	5	6	4	10	15	6	20	0,745	0,522
cobalt	20	20	30	60	50	120	200	50	300	0,260	2,445
copper	30	150	100	100	100	200	600	200	1000	11,047	20,941
molibden	10	10	10	40	30	210	250	30	200	0,461	0,424
nickel	35	100	50	100	70	210	300	70	500	17,360	24,661
lead	50	100	100	200	100	200	600	200	1000	11,141	15,288
mercury	0.5	2	3	5	4	10	30	4	50	0,1088	0,1702

Table 4. Heavy metals contents in the bottom sediments in relation to the threshold values set for the geochemical background and purity classes of water sediments [3]

Metal	Threshold values of the geotechnical background and purity classes				Content in the bottom sediments from			
					Czorsztyński Lake		Rzeszowski Lake	
	Back-ground	I	II	III	Mean value	Class	Mean value	Class
	ppm				ppm		ppm	
arsenic	<5	<10	<20	<50	2,303	x	2,925	x
barium	<51	<100	<300	<500	48,046	x	67,339	I
chromium	5	<20	<100	<500	26,130	II	34,489	II
zinc	48	<200	<1000	<2000	43,211	x	75,881	I
cadmium	<0,5	<1	<5	<20	0,745	I	0,522	I
cobalt	2	<10	<20	<50	0,260	x	2,445	I
copper	6	<20	<100	<200	11,047	I	20,941	II
nickel	5	<30	<50	<100	17,360	I	24,661	I
lead	10	<50	<200	<500	11,141	I	15,288	I
mercury	<0,05	<0,1	<0,5	<1,0	0,1088	II	0,1702	II

x – the value did not exceed the limit value of the geochemical background

Table 6. Heavy metals contents in the bottom sediments in relation to the threshold values given for the pollution degrees [8]

Metal	Group of soil	Threshold values of the pollution degrees						Content in the bottom sediments from			
								Czorsztyński Lake		Rzeszowski Lake	
		0	I	II	III	IV	V	Mean value	Pollution degree	Mean value	Pollution degree
		[mg · kg^{-1}]						[mg · kg^{-1}]	-	[mg · kg^{-1}]	-
cadmium	AG BG CG	0,3 0,5 1,0	1,0 1,5 3,0	2 3 5	3 5 10	5 10 20	>5 >10 >20	0,745	I	0,522	0
cooper	AG BG CG	10 20 25	30 50 70	50 80 100	80 100 150	300 500 750	>300 >500 >750	11,047	0	20,941	0
chromium	AG BG CG	20 30 50	40 60 80	80 150 200	150 300 500	300 500 1000	>300 >500 >1000	26,130	0	34,489	0
nickel	AG BG CG	10 25 50	30 50 75	50 75 100	100 150 300	400 600 1000	>400 >600 >1000	17,360	0	24,661	0
lead	AG BG CG	30 50 70	70 100 150	100 250 500	500 1000 2000	2500 5000 7000	>2500 >5000 >7000	11,141	0	15,288	0
zinc	AG BG CG	50 70 100	100 200 300	200 300 500	700 1000 2000	1500 3000 5000	>1500 >3000 >5000	43,211	0	75,881	0