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# HEAVY METALS IN SEDIMENTS OF WATER AND WASTEWATER SYSTEM IN CRACOW

Pollution of the air and the surface of Earth and also sewage sediments with heavy metals results in a heavy contamination of the storm run-off water. The use of retention–sedimentation basins (separators) is a novel approach to limitation of water pollution by urban run-off, preventing environmental water from degradation by drainage systems in receiving waters. Research was carried out in small, urban catchments in the south distinct of Cracow. Concentrations of heavy metals have been measured with the AAS in sediment samples from separators and water-courses above and below the outlets of the drainage systems. Estimation of the quantity of metals in samples was done based on sediment samples also from "Rudawa", "Dłubnia" and "Raba" drinking water plants and "Płaszów" and "Kujawy" sewage treatment plants.

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The problem of sediments in water and the problem of wastewater management also in the city of Cracow have been only recently considered in terms of their influence on environment (GAMBUŚ et al. [10]). Such problems are considered as serious because of an increasing volume of that type of environmental material or because it is necessary to recover or at least to minimize the area occupied by the settlement lagoons. However, in the case of economic usage or utilization of sediments, the permissible concentrations of various substances, including heavy metals, must not be exceeded (M.P. 2000. 43.851 (Official Journal of the Republic of Poland [13])). In Polish legislation, particularly in view of joining the European Union (GROMIEC [11]), a number of directives for sewage sediments were laid down (Dz.U. 1997. 96.592 [4], Dz.U. 1999. 50.501 (Journal of Law) [5]).

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In water and wastewater management, the sediments formed during a sewage treatment are of special importance, but the same problem also appears if we deal with rainwater drainage system. The law established recently obliges economic entities managing wastewater system to protect surface waters receiving waters from overflows and rainwater drains. It shall be implemented by fitting storage-sediment reservoirs – separators before the sediments enter final receptors (Dz.U. 1999. 43.430 [6]).

The separators operate as receptors of solid particles present in rain sewage, mainly as suspended matter, and during torrential rains as a floating matter or even as particles of larger size. These particles are captured mainly due the decrease in the flow velocity and fallout of the suspension. Thus the separators protect, to a large extent, watercourses from pollutant load bound on surface or within the structure of solid particles of sediments. The solid particles build deposits of considerable thickness.

Contaminants cumulated in sediments, especially heavy metals, pose problem, particularly during emptying the separators. Any economic usage of such sediments is possible, provided that the concentrations of toxic components do not exceed permissible standards (Dz.U. 1999. 72.813 [7]). Procedures for that type of deposits, which are classified as waste, adhere to the Act on Fees for Economic Use of the Environment (Dz.U. 1996. 154.747 [3], Dz.U. 1993. 133.638 [2]). Selection of the method for processing sediment from separators should be preceded by evaluation of their impact on the environment, and also economic calculation of costs and expenditures, with a general reservation that the sediments in question should be fit for economic utilization (Dz.U. 1999. 50.501 [5], Dz.U. 2000. 122.1326 [9]).

Urban agglomerations constitute a substantial source of heavy metals which except for mineral formations are the elements that diffuse through natural environment, whereas in cities, they are subjected to the secondary *anthropogenic* accumulation. Heavy metals find their way to surface watercourses together with the dust, which settles on road surfaces, on soil particles and on plants. They are washed out, particularly during rainfalls, in diluted forms or in forms, which more or less permanently are bound with solid bodies (OSMÓLSKA-MRÓZ [15]). Similarly as in natural water systems, suspended matter and bottom sediments in the sewage system are sensitive indicators of the degree of pollution of discharged wastewaters, hence they may be useful in assessing the actual impact of companies and industrial plants on the environment. Control measurements show that regulations that should be applied to the level of heavy metals in the wastewaters discharged into the watercourses are usually obeyed, while examination of the sediments settled at the bottom of sewage systems and catch basins reveals considerable concentrations of heavy metals. Solid particles capture and accumulate heavy metals, "recording" even their most minute traces whose concentration in wastewaters varies in time.

In order to protect urban watercourses in the vicinity of Cracow, the Cracow Municipal Department installed separators, among others for solid substances, before

discharging the wastewaters from storm drainage network. At present, such separators operate only in the southern district of the city, in the neighbourhood of the main transit routes, along the Zakopiańska, Skotnicka, and Zawiła Streets, and quite recently, in the vicinity of the newly completed southern by-pass.

The material for the present study consists of the samples of sediments taken from separators, as well as from such watercourses as the Wilga river, the Sidzinka stream, and the watercourse of Urwisko (Rzewny) to which suprasediment wastewaters were pumped. The samples of sediments from separators, which were tested in December 2000, had been collected for nearly a year.

The samples of bottom sediments taken from separators before and below the outlet of suprasediment waters, likewise the samples from separators themselves, for individual habitats (environments), have not proved representative enough in time and space. In subsequent studies, the entire profiles of sediment from separators, up to the very bottom of the reservoir, will be examined, which at this stage of research has proved to be impracticable due to considerable hydration and refinement of structure, as well as relatively sparse structure of sediments.

For a better control of test quality, assessment and elimination of gross errors, as well as in order to take into account the possibility of making analytical errors, the research has also been carried out on two randomly selected "parallel" samples, as well as on certified material. At the present stage of the research, the considerations have been based both on mean and extreme values; the latter are of a particular interest if an environmental aspect of the study is taken into account. In analyses, the following methods have been applied: optical microscopy, electronic microscopy with a chemical analyzer SEM/EDX and AAS. The heavy metals were extracted from the samples of raw sediment by means of concentrated nitric acid.

Apart from the practical aspect of establishing mineral and chemical (geochemical) structures of the sediments, which allows us to adopt suitable procedures to deal with the sediments from separators, their disposal or possible utilization, the research also has a significant cognitive aspect. Heavy metals in the bottom sediments of separators reflect geochemical structure of the individual components of the environment, thus create an image of the actual pollution of the environment in the individual regions. The results obtained together with standard values and the values recorded by other researchers for similar types of environmental samples are presented in table 1.

The collation presented clearly shows that the sediments from separators, except sediment No. 1, are less or comparably contaminated than the sediments of surface watercourses receiving the storm drain discharges. High level of cadmium (even for sewage sediments) in the separator No. 1 would make their agriculture usage impossible.

Table 1

Physicochemical characteristics of river and bottom sediments from separator

| No. | pH* | PEW*, mS | Cd | Co | Ni | Cr | Cu | Pb | Zn | Mn | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | mg/kg | | | | | | | | % |
| The Wilga River catchment | | | | | | | | | | | |
| B.2 – before | 7.05 | 0.956 | 1 | 6 | 11 | nd | 3 | 10 | 1 | 108 | 0.39 |
| Sep. 1 – B.1 | 7.27 | 0.184 | 16 | 40 | 21 | nd | 201 | 266 | 589 | 1249 | 2.43 |
| B.3 – below | 7.01 | 1.180 | 2 | 12 | 24 | nd | 18 | 12 | 69 | 878 | 1.19 |
| The Sidzinka stream catchment | | | | | | | | | | | |
| B.5 – before | 6.85 | 2.790 | 3 | 15 | 41 | 21 | 62 | 150 | 415 | 420 | 2.71 |
| Sep. 2a – B.4 | 7.06 | 0.695 | 3 | 11 | 18 | 3 | 16 | 9 | 58 | 997 | 1.24 |
| Sep. 2b – B.7 | 7.32 | 0.258 | 2 | 6 | 9 | 5 | 10 | 4 | 6 | 322 | 1.16 |
| B.6 – below | 6.81 | 2.020 | 4 | 13 | 42 | 5 | 73 | 64 | 571 | 370 | 2.84 |
| The Rzewna watercourse catchment | | | | | | | | | | | |
| B.10 – before | 6.76 | 2.001 | 4 | 13 | 33 | 31 | 120 | 111 | 912 | 373 | 1.93 |
| Sep. 3a – B.8 | 6.93 | 0.659 | 3 | 7 | 17 | nd | 51 | 94 | 203 | 475 | 0.94 |
| Sep. 3b – B.9 | 7.08 | 0.705 | 3 | 15 | 39 | 2 | 102 | 139 | 437 | 947 | 2.26 |
| B.11 – below | 7.08 | 2.050 | 5 | 13 | 31 | 43 | 113 | 110 | 1200 | 421 | 1.92 |
| Water sediments in that area** | | | 8 | 16 | 25 | 12 | 40 | 150 | 800 | 2500 | 7.00 |
| Standard values for sediments | | | | | | | | | | | |
| Sewage sediments [1] | | | 10 | | 100 | 500 | 800 | 500 | 2500 | | |
| Harbour sediments [2] | | | 30 | | 100 | 600 | 400 | 700 | 2500 | | |
| Sediments from sewage treatment plant [3] | | | 5 | | 200 | 900 | 800 | 900 | 2000 | | |
| $I_{geo}$ classes[4] | | | 0.40 | 28 | 102 | 135 | 67 | 30 | 142 | 1275 | 7.15 |
| Geochemical background[5] | | | 0.3 | 19 | 68 | 90 | 45 | 20 | 95 | 850 | 4.7 |

nd – not detected.

B.1, B.4, B.7, B.8, B.9 denote sediments from separators.

* 10% water suspensions.

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[1] Classification of sewage sediments used in agriculture.

[2] Classification of harbour sediments taken from the bottom of harbours in Italy for class >III when their deposition requires controlled conditions.

[3] Of sewage from treatment plant.

[4] German $I_{geo}$ classification of super-fine grain sediments (fr. <0.002 mm), taking account of the background value – class 0 unpolluted.

[5] Background value according to TUREKIAN and WEDEPOHL [16].

Other classifications do not indicate sediments from the examined separators for special treatment during their utilisation. According to "class O" in the classification $I_{geo}$, which gives the boundary values for uncontaminated sediments close to the background values, the sediment in separator No. 1 is contaminated by cadmium (class V),

cobalt (class I), copper (class II), lead (class IV) and zinc (class III). According to this classification the sediments in separators No. 2a and No. 2b being installed before the outlet to the Sidzinka stream show Cd level of class III and no contamination by other heavy metals (class O). The sediments separators No. 4 and No. 5 located before the outlet to the Rzewna stream show various pollution by Cd(III), Cu(O,I), Pb(II,III) and Zn(I,II); however, the highest pollutant load is found in separator No. 5 These differences may result from a greater free surface flow (unbuilt area) and from different basal complex (loess containing carbonates which increase the capacity of sediments for absorbing heavy metals).

Heavy metals also occur in the sediments formed in technological processes of water conditioning and sewage treatment in the Cracow water supply and sewage disposal systems. Maximum values of metal concentrations determined in these sediments are given in table 2. Analogous methods of sampling (autumn 2000) and analysis were applied.

Table 2

Heavy metals (mg/kg) in sediments of water supply and sewage disposal system of Cracow

| Max values | Water conditionong plant | | | Sewage treatment unit | |
|---|---|---|---|---|---|
| | Raba | Rudawa | Dłubnia | Płaszów | Kujawy |
| Cd | 3 | 7 | 3 | 8 | 6 |
| Co | 29 | 21 | 46 | 17 | 13 |
| Ni | 81 | 25 | 48 | 79 | 27 |
| Cr | 62 | 7 | 37 | 1433 | 375 |
| Cu | 150 | 34 | 503 | 484 | 257 |
| Pb | 17 | 124 | 824 | 4183 | 91 |
| Zn | 247 | 665 | 469 | 4183 | 1921 |

In sediment management, the above results should be taken into consideration. Preliminary research does not allow a proper estimation of the metal load adjusted to the volume of sediments in particular separators, settlement ponds of water treatment plant or lagoons on the premises of sewage treatment unit.

The directive of European Council 86/278/EEC being in force in the EU recommends first agricultural usage of sediments, but with no deterioration of environmental quality, otherwise they should be used as energy sources, secondary materials or should be incinerated.

In the case of rain drainage, the results obtained clearly indicate that the separators installed in storm drainage network considerably decrease the amounts of heavy metals, which usually find their way directly to surface watercourses, together with rainfall. What seems necessary at the present stage is to inspect the storm overflows in the other districts of the city of Cracow, and particularly those that are characterized by a considerable degree of pollution of the environment, including contamination with

heavy metals. In those districts of the city, separators have not been yet installed and most likely, large amounts of heavy metals find their way to surface watercourses, together with rainfall. The studies, aiming at obtaining a solution of this problem, could lead to an installation of subsequent separators in locations most heavily contaminated with heavy metals. Additionally, our knowledge about the distribution of heavy metals, their transport routes, and concentrations in the sediments drained by means of storm drainage systems would be considerably developed, constituting an interesting supplement to all types of geochemical maps of the city of Cracow and its neighbourhood. Making an inventory of the conditions of soil and water environment in areas with the outflows of rain waters, both those with and without separators, seems to be an absolute necessity. In the cases, where anthropogenic solid phases or increased concentration of heavy metals in sediments are observed, the source of supply could be established by means of pollution mapping. Besides the linear sources – transport routes – quite frequently the cause of increased levels of heavy metal contamination may be industrial plants and companies which over entire period do not comply with water supply and sewage effluent disposal regulations. In conditions of decentralized market, identification of those who are responsible for this contamination results, by virtue of the law, in shifting the costs of financing the research into condition of environment (local monitoring) to polluter.

For economic and particularly ecological reasons, this is immensely important. Additionally, the law states "if the forecasted levels of water and soil contamination exceed the permitted levels given in separate regulations one should foresee the implementation of suitable preventive measures eliminating or limiting the consequences of this contamination"; and thus, the law imposes on those managing the rain drainage network an obligation to examine the condition of the environment, particularly in the areas where a separate sewage system operates. Using the existing infrastructure of this system, one should be able to obtain a complete picture of the distribution of individual elements' concentration, their routes of migration, and, first of all, their sources. Until now, this type of research has not been carried out. Maybe in the near future it will be possible to find sponsors who could cover the costs of such research. As a city which has found its entry into the "World Heritage List", Cracow deserves such research in order to enable a restitution of the urbanized, degraded surface watercourses (Dz.U. 1999. 98.1150 [8]).

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## METALE CIĘŻKIE W OSADACH SYSTEMU WODNO-KANALIZACYJNEGO KRAKOWA

Zanieczyszczenie metalami ciężkimi powietrza i powierzchni terenu, a także osadów w kanałach jest wywołane silnym skażeniem wód opadowych. Stosowanie zbiorników retencyjno-sedymentacyjnych (separatorów) stanowi nowoczesną metodę ograniczenia zanieczyszczenia wód ściekami opadowymi, gdyż zapobiega degradacji środowiska wodnego, bo zbiorniki tego typu stają się odbiornikami ścieków z systemów kanalizacyjnych. Badania prowadzono w małych, zurbanizowanych zlewniach w południowym regionie Krakowa. Stężenia metali ciężkich zmierzono, korzystając z metody AAS, w próbkach osadów z separatorów i cieków powyżej i poniżej ujścia systemów kanalizacyjnych. Oceny ilości metali w próbkach dokonano także na podstawie próbek z Zakładów Uzdatniania Wód „Rudawa", „Dłubnia" i „Raba", a także Oczyszczalni Ścieków „Płaszów" i „Kujawy".

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