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CHANGES OF HEAVY METAL CONTENTS IN SLUDGE FROM SELECTED TREATMENT PLANTS IN THE WESTERN MALOPOLSKA REGION IN 1995–2009

ZMIANY ZAWARTOŚCI METALI CIĘŻKICH W OSADACH Z WYBRANYCH OCZYSZCZALNI ŚCIEKÓW ZACHODNIEJ MAŁOPOLSKI W LATACH 1995–2009

Abstract: In presented research were analyzed changes in the contents of cadmium, chromium and lead for the period 15 subsequent years (1995–2009) in sludge originating from 9 major treatment plants in western Malopolska Region, where usually municipal sewage is being treated. The analyses were conducted using methods which are recommended as referential in Poland.

Chromium accumulation in the analyzed sewage sludge was most diversified (14–6000 mg · kg^{-1} d.m.), its content in many samples from Myslenice, Krakow-Plaszow, Proszowice, Slomniki and Dobczyce exceeded the level of 5000 mg · kg^{-1} d.m., which conditions the agricultural use of these materials. The highest chromium concentration – 6000 mg · kg^{-1} d.m. was assessed in the sludge from Myslenice in 1997. In 2009 this content was even 150-fold lower. A 11-fold decrease in the average chromium accumulation in sludge samples from all analyzed treatment plants was noted during the investigated period. Diversification of lead and cadmium contents in the studied sewage sludge was much lower than chromium. The greatest amounts of these metals were usually assessed in the sludge from Krzeszowice (on average 126.5 mgPb and 3.79 mgCd · kg^{-1} d.m.), whereas the lowest contents of cadmium were noted in Proszowice and lead in Dobczyce. The average lead content in sludge from all studied treatment plants diminished 3.5-fold and cadmium amount by 2.4-fold over the 15-year period of investigations.

Keywords: cadmium, chromium, lead, sewage sludge, pollution reducing

The amount of sewage sludge produced in treatment plants has been growing proportionately to the amount of annually treated sewage. 567.3 thousand Mg (tons) of sludge were produced in Poland in 2008, of which 44.9 thousand d.m. in the area of the Malopolska province [1]. As a rule it contains considerable amounts of nitrogen, phosphorus and organic substance, which suggests its environmental or agricultural application (as fertilizer). It is also the most economical way of sludge management [2].

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In the initial period of the presented investigations, about 50 % of sewage sludge was used in agriculture and for reclamation [3], whereas currently the amount decreased to 38 % [1]. In practice this application is often impossible due to an excessive accumulation of heavy metals in the sludge and its sanitary pollution with eggs of digestive tract parasites (*Ascaris* sp., *Trichuris* sp., *Toxocara* sp.) and pathogenic bacteria, particularly *Samonella* sp. [4]. Even if the sanitary condition may be improved by composting or intensive liming, yet reduction of heavy metal concentrations on a major scale is practically impossible [5–7]. For this reason a considerable part of produced sludge is stored at treatment plants. By the end of 2008 as much as 599 thousand Mg (tons) d.m. of sludge was deposited in the areas of sewage treatment plants in Poland [1]. Sludge analyses conducted for many years in Poland and worldwide [3, 8, 9] indicate a downward trend for heavy metal content in sludge from municipal sewage, however simultaneously there are cases when these metals permissible contents in sludge are exceeded.

According to the Decree of the Minister of the Environment on municipal sewage sludge [4], analyses of the sludge are conducted in treatment plants depending on the number of inhabitants they serve: up to 10 thousand of inhabitants – once in 6 months, 10–100 thousand once in 4 months and over 100 thousand – once in two months. It results from a considerable diversification of the chemical composition of the sludge produced in various treatment plants and changes of the composition over time.

Research was undertaken to analyze the changes of heavy metal contents in sludge originating from 9 major treatment plants in western Malopolska region, *ie* from Dobczyce, Krakow-Plaszow, Krzeszowice, Myslenice, Niepolomice, Proszowice, Skala, Skawina and Slomniki during successive 15 years of investigations (1995–2009). These treatment plants usually treat municipal sewage, whereas municipal-industrial sewage flows only into Krakow-Plaszow treatment plant.

Materials and methods

Between 2 and 8 representative sludge samples, with some exceptions, were collected in the investigated treatment plants each year in May and November, since 1995. Because of extension and modernization of the treatment plant in Proszowice, sludge sampling in this treatment plant started in May 1996. Analyzed treatment plants are situated at the distance no longer than 35 km from Krakow and daily each treats mechanically and biologically between 800 and 5000 m^3 of municipal sewage which flows in by urban drainage or is supplied by septic tankers. Standing out among the analyzed treatment plants is the plant in Krakow-Plaszow, where usually over 100 000 m^3 of municipal sewage polluted with industrial pollutants flows in daily. Mostly it is only mechanically treated before reaching the sewerage system.

After stabilized and dehydrated sewage samples were supplied to the laboratory, they were homogenized and then stored fresh until analysis in closed glass vessels, at the temperature of 2–5 ^{o}C. The analyses were conducted using the methods which in Poland have been accepted as referential methods of research on sewage sludge [4]. After drying at 105 ^{o}C and determining dry mass content, the samples were digested in a

mixture of concentrated nitric(V) and perchloric(VII) acids (3 : 2, v/v) and heavy metal concentrations in the obtained mineralizates were assessed by means of *atomic absorption spectrophotometer* (AAS) or by *emission absorption spectrometer with inductively coupled plasma* (ICP-AES). The analysis were conducted in 2 replications and they were repeated if the relative error was higher than 5 %.

Results

The paper presents only changes in accumulation of cadmium, chromium and lead in the analyzed sewage sludge. These are metals, whose presence in sewage from the researched treatment plants and changes during the time of the investigations were most strongly diversified. Presented results are mean values for the individual years of the investigations and were converted into the metal content in the sludge dry mass.

The highest diversification of heavy metal content in the analyzed sewage sludge was noted for chromium, whose contents in the samples from Proszowice, Slomniki, Dobczyce and Myslenice were described by the relative standard deviation approximate to 100 % (Table 1). The highest chromium concentration (on average 6000 mg · kg^{-1} d.m.) was assessed in 1997 in the sludge from Myslenice. However, this content was reduced 150-fold (Fig. 1) in 2009. The unnatural origin of chromium in the analyzed sludge from some treatment plants has been indicated by the values of geometric mean content of this metal in the studied sludge, much closer to median than arithmetic means. Exceedance the level of 500 mg · kg^{-1} d.m. which conditions agricultural utilization of the sludge was registered in the samples collected in the above-mentioned treatment plants and in the plant in Plaszow, where municipal-industrial sewage is being treated (Fig. 1).

The exceedance was noted only during one year of the investigations in Dobczyce, for 2 years in Slomniki, for 3 years in Proszowice, for 6 years in Plaszow and for 10 years (until 2004) in Myslenice. If we assume geometric mean, which better than arithmetic mean describes chromium content in all analyzed sludge samples, from Myslenice as 100, then its content in the analogous sludge from Krakow-Plaszow will be 58, from Slomniki 16, from Proszowice 11, whereas in the sludge from Skawina only 5.8, from Krzeszowice 3.6 and from Skala 3.4. All analyzed sludge samples from Skala and Krzeszowice and most samples from Skawina contained less than 100 mgCr · kg^{-1} d.m. In 1997 a considerable increase was noted in chromium assessed in sewage sludge from three treatment plants in: Krakow-Plaszow, Proszowice and particularly from Myslenice to which sewage from the local tannery was inflowing. Over the whole 15-year period of the investigations chromium content in the sewage from treatment plants receiving sewage polluted with this metal (Myslenice, Slomniki, Proszowice and Plaszow) diminished several dozen times (in Myslenice even 15-fold) and several fold in the other treatment plants.

Diversification of lead and cadmium contents in the analyzed sewage sludge was considerably smaller than chromium (Table 1, Fig. 1).The greatest amounts of lead occurred usually in the sludge from Krzeszowice (on average 126.5 mg), whereas elevated quantities of cadmium, respectively: 3.79 and 3.65 were noted in Krzeszowice

Table 1

Heavy metals contents in sewage sludge from 9 selected sewage treatment plants in western Malopolska Region [mg · kg^{-1}] in 1995–2009

Value	Niepolomice	Dobczyce	Plaszow	Krzeszowice	Myslenice	Skala	Skawina	Slomniki	Proszowice
Cadmium									
Minimum	1.48	1.37	1.79	2.21	1.12	2.33	1.32	1.03	1.32
Maximum	4.11	4.04	5.44	5.59	4.05	8.07	4.12	4.64	3.14
Average	2.71	2.39	3.95	3.63	2.40	4.17	2.48	2.33	1.90
Median	2.50	1.96	4.15	4.00	2.24	3.50	2.10	2.10	1.75
RSD* [%]	28.0	35.3	30.7	30.3	33.7	38.5	36.0	40.2	26.5
Chromium									
Minimum	22.1	50.4	171.1	15.9	258.9	20.0	14.2	57.5	27.2
Maximum	400.3	750.4	1750.0	49.8	6000.0	90.2	99.7	1280.0	1180.0
Average	143.4	155.3	702.0	35.2	1953.6	37.8	63.0	275.8	312.8
Median	66.9	80.0	490.0	33.7	1245.0	26.0	60.0	100.0	94.0
RSD [%]	82.0	131.8	61.2	26.6	81.3	65.7	42.1	129.2	126.8
Lead									
Minimum	29.1	28.4	43.4	54.0	47.6	40.6	11.1	14.1	25.5
Maximum	90.2	90.4	230.2	220.3	180.2	170.2	136.4	185.2	112.2
Average	59.7	56.7	122.3	141.5	97.2	99.2	82.9	78.2	63.7
Median	54.0	45,.0	96.5	125.0	73.8	67.5	70.0	55.0	52.0
RSD [%]	27.3	35.0	47.2	38.4	43.9	42.4	42.1	62.6	41.6

* Relative standard deviation.

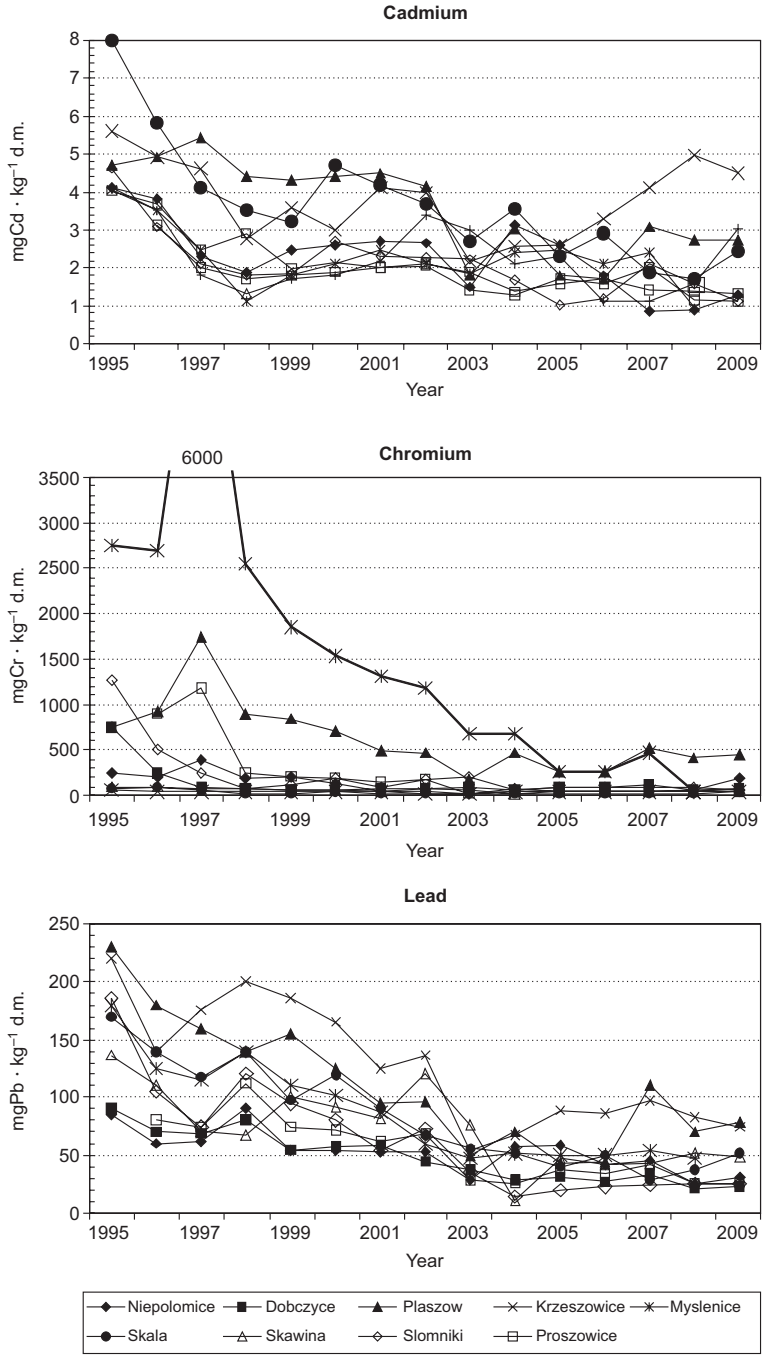

Fig. 1. Contents of heavy metals in sewage sludge from treatment plants of western Malopolska Region in 1995–2009

and Skala. These cities are situated in the area under the influence of the Olkusz region of lead and zinc ores extraction and within the range of pollution emitted by the Upper Silesia Region. Relatively big quantities of lead and cadmium were found also in the sludge from Krakow-Plaszow polluted with the industrial sewage and dust washed off the Krakow agglomeration streets. The lowest contents of lead were assessed in the sludge from Dobczyce and cadmium from Proszowice; these were respectively 2.6 and 2.1 times lower than the highest contents. Mean lead content in sludge from all investigated treatment plants diminished 3.5-fold and cadmium content 2.4-fold over the 15-year period of the investigations. It should be also emphasized that in the three first years of the research a markedly higher content of cadmium and lead was assessed in the sludge from a majority of the investigated treatment plants. In the subsequent years these metals content in sewage sludge was decreasing much more slowly, or as in the case of cadmium, remained on a similar level.

Discussion

Sludge forming at municipal sewage treatment as a rule is abundant in biogenic substances, mainly nitrogen and phosphorus. It is also a good source of organic substance, which when applied to the soil may improve soil humus balance, at the same time improving the soil physical properties and its sorption capacities [10–12]. However, at these beneficial properties the sludge may be also a source of sanitary contamination, contamination with organic toxins, *eg polycyclic aromatic hydrocarbons* (PAHs) which move easily in the soil profile [13], or with heavy metals strongly bound in the top soil layer [2, 14].

The main source of heavy metals contained in municipal sewage sludge is their occurrence in various household waste materials discharged into the sewer system and the roadway runoff from vehicles and emitted by industries [8, 15]. Because of considerable biological harmfulness of these elements, metal contents must be checked both in the sludge and in the soil at each of its agricultural or environmental application. Limit contents of metals conditioning agricultural or reclamation use of municipal sewage sludge in Poland are as follows: 10 mg of cadmium and 500 mg of chromium and lead per 1 kg d.m. of sludge [4]. Sludge polluted with industrial sewage from Krakow-Plaszow cannot be used for the purposes mentioned above.

Among municipal sewage sludge monitored in the presented investigations, all analyzed samples contained smaller quantities of cadmium and lead than limit values stated for these metals. Only chromium content in the sludge from Dobczyce, Slomniki and Proszowice was higher, whereas in the case of sludge from Myslenice it was many times higher than assumed threshold value. Such high accumulation of chromium in sewage sludge from these treatment plants in previous years was mainly caused by the sludge contamination with technological solutions from the process of chromium hide tanning (in Myslenice, Proszowice and Dobczyce) or with galvanizing solutions (Krakow-Plaszow and Slomniki). Once the sources of chromium in the sludge were identified, its excessive content was reduced in the sludge from Dobczyce, Proszowice and Slomniki already after 2–3 years of the investigations. On the other hand

considering the treatment plant in Myslenice, only in the samples collected there in 2005 less than 500 mgCr was assessed whereas some samples from 1997 contained even 8000 mgCr · kg^{-1} of sludge d.m.

Changes in cadmium and lead concentrations in the sludge from monitored treatment plants were progressing more slowly than in case of chromium, but in all treatment plants a notable reduction in these metals contents was observed over the 15-year period of research. Relative standard deviations describing the diversification in these metals contents in sludge from individual treatment plants range from 26.5 % (Cd content in sludge from Proszowice) to 62.6 % (Pb in Slomniki). A decrease in the cadmium and lead contents in the sludge during the investigated period most probably is the result of limiting metal bearing dust emission into the atmosphere and general improvement of the environment quality in the Malopolska Region. Many sources of emission and points of heavy metal pollution, mainly with cadmium, lead and zinc were once documented in this region; these processes were especially intensified in the seventies and eighties of the previous century [15, 16].

Similar trends were observed in the countries of Western Europe. For example, average cadmium content in sewage sludge in Switzerland in 1975–1999 declined from 25.2 to 1.7 mg, in Germany in 1982–2000 it decreased from 4.0 to 1.3 mg, whereas in the same years (1982–2000) lead content diminished from 190 to 60 mg · kg^{-1} d.m. [8].

Despite the fact that reduction of cadmium content in the studied sewage sludge was the lowest among all analyzed metals (on average 2.4-fold in all treatment plants) it should be assessed as most beneficent from the perspective of diminishing the risk of the environment pollution with this metal. This metal has very strong toxic effect on living organisms (particularly people and animals) but at the same time labile, forming relatively readily soluble bonds, easily entering the food chain [2–7].

Conclusions

1. The contents of cadmium and lead assessed in 1995–2009 in all sludge samples originating from municipal sewage treatment in the treatment plants of the western Malopolska Region do not limit their agricultural or reclamation application. The condition was not fulfilled for chromium content in many sludge samples originating from municipal sewage with tannery (Myslenice, Proszowice and Dobczyce) or galvanizing sewage (Slomniki) supplement.

2. During the 15-year period of the investigations mean cadmium content in the sludge from all 9 monitored sewage treatment plant diminished on average 2.1-times, lead concentrations 3.5-times and chromium even 11-times.

3. Diminished accumulation of heavy metals in sewage sludge should increase the potential of fertilizer applications of these materials abundant in biogenic components and organic substance.

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Abstrakt: W prezentowanych badaniach analizowano zmiany zawartości kadmu, chromu i ołowiu w okresie 15 kolejnych lat (1995–2009) w osadach pochodzących z 9 większych oczyszczalni ścieków zachodniej Małopolski, w których na ogół oczyszczane są ścieki komunalne. Analizy przeprowadzono metodami zalecanymi w Polsce jako metody referencyjne.

Nagromadzenie chromu w badanych osadach ściekowych było najbardziej zróżnicowane (14–6000 mg · kg^{-1} s.m.), a jego zawartość w wielu próbkach, pochodzących z Myślenic, Krakowa-Płaszowa, Proszowic, Słomnik i Dobczyc, przekraczała poziom 500 mg · kg^{-1} s.m., warunkujący rolnicze wykorzystanie tych materiałów. Największą zawartość chromu – 6000 mg · kg^{-1} s.m., oznaczono w osadzie z Myślenic w 1997 r. W 2009 r. zawartość ta była aż 150-krotnie mniejsza. Zmniejszenie średniego nagromadzenia chromu w próbkach osadów z wszystkich badanych oczyszczalni w badanym okresie było 11-krotne. Zróżnicowanie zawartości ołowiu i kadmu w badanych osadach ściekowych było znacznie mniejsze niż chromu. Największe ilości tych metali notowano zwykle w osadach z Krzeszowic (średnio 126,5 mg Pb i 3,79 mg Cd · kg^{-1} s.m.), a najmniejsze kadmu w Proszowicach i ołowiu w Dobczycach. Średnia zawartość ołowiu w osadach z wszystkich badanych oczyszczalni zmniejszyła się w 15-letnim okresie prowadzenia badań 3,5-krotnie, a kadmu 2,4-krotnie.

Słowa kluczowe: kadm, chrom, ołów, osady ściekowe, zmniejszenie zanieczyszczenia