ŚRODKOWO-POMORSKIE TOWARZYSTWO NAUKOWE
OCHRONY ŚRODOWISKA
Rocznik Ochrona Środowiska
Tom 13. Rok 2011 ISSN 1506-218X 83-100

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Heavy Metal Compounds in Wastewater and Sewage Sludge

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1. Introduction

Sewage sludge happens to contain heavy metal compounds, including toxic mercury, considerable concentrations of which indicate appearance of new anthropogenic sources of those elements [1, 3, 4, 11]. The sewage sludge is frequently used, due to fertilising components content, in production of compost and the manufactured product (organic fertiliser) is used for soil fertilisation [5, 6]. In the event of excessive concentration of toxic, and even carcinogenic compounds of those metals in natural environment they cause its irreversible pollution. The sludge can also be incinerated, due to considerable presence of organic substance, and such generated waste (slag, ash) is often used in agriculture or applied in production of building materials – then it becomes a valuable raw material [7, 15, 19]. Reclamation of sewage sludge both through composting as well as incineration requires their preliminary treatment. Sewage sludge requires dehydration or drying before it arrives at the compost facility or incineration plant. Therefore, the manufactured product makes a concentrate in which concentration of the heavy metals can be many times (even tenfold) higher than in the sludge subjected to this process [8].

In this study an attempt was made to assess the ways of migration of heavy metals contained in municipal sewage and in sewage sludge generated in one of the seaside wastewater treatment plants. It is suspected that the sewage contains some amount of mercury compounds originating from various sources, including laundry sewage. The research work performed has indicated that following sewage thickening and then dehydration in presses the concentration of those elements in sewage sludge increases causing, consequently, increase of heavy metals concentration from low level in raw sewage up to a considerable level in sewage sludge [13, 14]. Also an assumption can be made that the metals are partly bound with the solid phase contained in tested sewage, therefore, they will occur in the thickened and then dehydrated sewage sludge. It's clear that some amount of those metals remains in the liquid phase after dehydration and depending on the applied wastewater treatment process, it is recycled or discharged to receiving water [16].

2. Materials and research methods applied

Samples of raw sewage were taken for tests from four catchment basins (PI, PIII, PIV i PVI) and one sample of laundry sewage plus a sample of thickened sludge and a sample of dehydrated sludge. The heavy metals (Cu, Cr, Cd, Ni, Pb, Zn, Hg) content analysis was performed in accordance with the applicable methodologies. The samples were mineralised using microwave energy (MILENSTONE 1200 Mega microwave mineraliser). The metal content in particular samples was determined by application of the flame atomic absorption spectroscopy method (FAAS) using PU 9100X Philips spectrometer [12, 18].

To assess the phenomena occurring in the studied sewage and sludge also STATISTICA package has been used [21, 22].

3. Test results

The sewage and sewage sludge test results being averaged for three samples taken at the same time are shown in Figs 1 and 2. Figure 1 comprises the results for sewage taken from various catchment basins

(PI, PIII, PIV, PVI) and laundry sewage. Heavy metals concentrations in raw sewage samples can be arranged in the following way:

Zn > Cu > Pb > Ni > Hg >Cr, Cd.

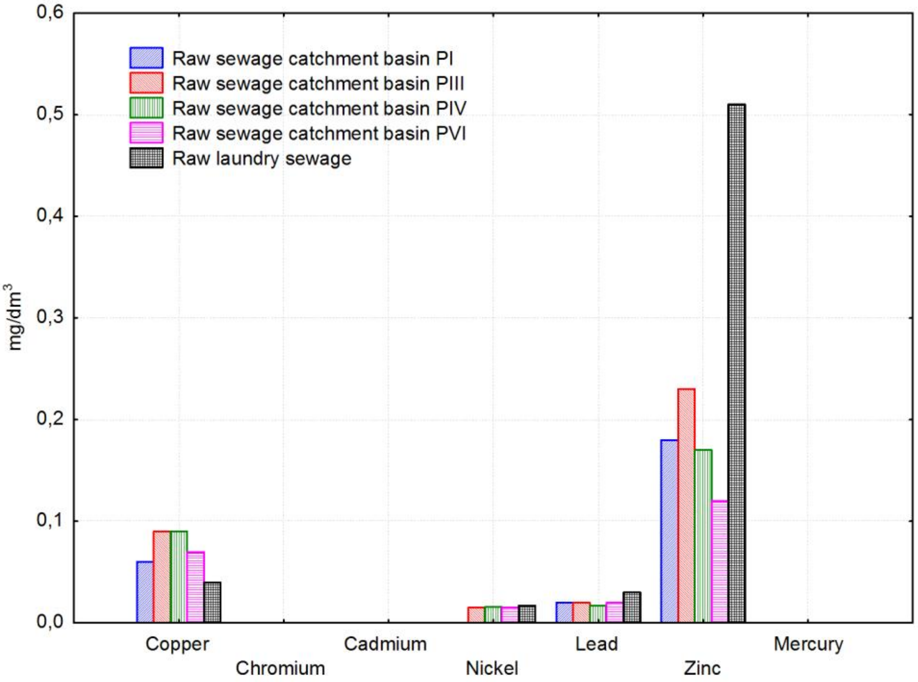

Fig. 1. Concentrations of heavy metals in raw sewage
Rys. 1. Stężenia metali ciężkich w ściekach surowych

The mercury content did not exceed 0.0005 mg/dm^3. The sewage was coming mixed to the wastewater treatment plant where it was subjected to thickening and then dehydration. As a result of this process it has appeared that in several cases (Fig. 2) content analyzed of metals in the thickened sewage sludge was much higher than in the dehydrated sewage sludge [17]. The heavy metal content in the sewage sludge (Fig. 2) looks as follows:

Zn > Cu > Pb > Ni > Cr > Hg > Cd

For example, mercury concentration in the thickened sewage sludge was on average 0.78 mg/kg d.m., whereas in the dehydrated sewage sludge it was 0.61 mg/kg d.m. Only in the case of cadmium and lead content thereof in the thickened sewage sludge was lower than in the dehydrated sewage sludge.

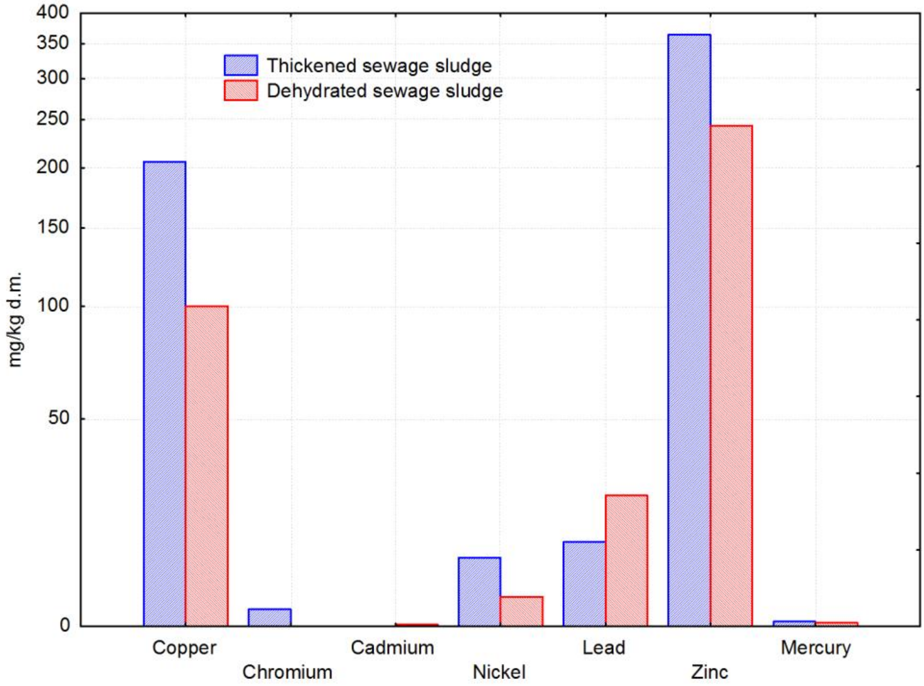

Fig. 2. Heavy metals content in raw sewage test results
Rys. 2. Zawartość metali ciężkich w osadach ściekowych

4. Discussion of results

As one can see from the data presented in graphs in Figures 1 and 2 the sewage samples taken from particular catchment basins indicate similar heavy metals concetrations. The laundry sewage departs slightly from such composition; it shows the highest concentration of zinc and lead compounds. Mercury content in all sewage samples was determined at a level below 0.0005 mg/dm^3. Nevertheless, a distinct concentration of those metals both in the thickened and dehydrated sewage sludge has happened [10]. There is no slightest doubt that some amount of the heavy metals was adsorbed on the sewage sludge particles and some amount remained in the post-treatment waters. Intensity of this process for particular metals varied. Further technological processes (thickening and dehydration) caused a considerable, even tenfold increase of heavy metals concentration in this medium with considerable differences to have occurred in the thickened and dehydrated sewage sludge. Compared with the dehydrated sewage sludge, concentrations of particular metals in the thickened sewage sludge increased by the following values:

Cu – 106%,
Cr – 282%,
Ni – 249%,
Zn – 150%,
Hg – 28%.

At the same time, compared with the dehydrated sewage sludge, the thickened sewage sludge has indicated elimination of particular metals, which can be presented as follows: Cd – down to trace amounts, Pb – 59%.

This means that despite low heavy metals concentration in sewage, their amount increases considerably in the thickened sewage sludge. Unfortunately, after sewage sludge dehydration in presses some amount of those metals is discharged, together with the purified wastewater, to receiving waters. In the analysed case this does not cause any definite threat for purity of waters compared with the applicable regulations and statutes as well as the generated wastewater load. In the case of big waste water treatment plants those phenomena may have similar character, then discharge of heavy metal containing, including mercury, lead, cadmium or chrome compounds, wastewater may pose a threat for purity of the aqueous environment. It seams that the laundry sewage may cause here a particular hazard due to washing of various materials of unknown origin imported from the Far East countries in which occurrence of mercury, lead and chromium compounds was being ascertained many times [20].

Table 1 comprises correlations between particular sewage pollution indicators and average values plus the standard deviation. The majority of the studied constituents has shown negative correlation between each other, including negative correlation of copper with lead and zinc as well as very strong positive correlation of lead with zinc ($r = 0.939028$).

Table 1. Correlations between particular sewage pollution indicators
Tabela 1. Korelacje między poszczególnymi wskaźnikami zanieczyszczenia ścieków

Correlations between particular pollution indicators. The determined correlation coefficients are significant with p < .05000 N = 5						
	Average	**Std. dev.**	**Copper**	**Nickel**	**Lead**	**Zinc**
Copper	0.070	0.021	1.000	0.183	**-0.852**	**-0.693**
Nickel	0.013	0.007	0.183	1.000	0.239	0.317
Lead	0.021	0.005	**-0.851**	0.239	1.000	**0.939**
Zinc	0.242	0.154	**-0.693**	0.317	**0.939**	1.000

The correlations are illustrated in subsequent graphs. Nickel had very weak correlations with the other metals. Due to trace amounts of chromium, cadmium and mercury in the studied sewage it was impossible to find any correlation between those elements and the other metals. The correlations have been illustrated in Figure 3 as a matrical graph of dispersion for selected variables whereas the categorised graphs of dispersion with regression lines for particular metal pairs are shown in Figures 4÷9.

As one can see a strong positive correlation occurs for lead with zinc, weak positive correlation occurs for nickel with lead, nickel with zinc and copper with nickel. Therefore, we can assume that increase of concentration of one of those elements will be accompanied by increase of concentration of the second one, particularly for the lead-zinc pair. A considerable negative correlation occurs for copper with lead and zinc, which means that with increase of concentration of given metal in sewage the second metal should be eliminated. The matrical graph of dispersion of particular metals comprises also frequency of occurrence of given metal and its concentration. As you can see they vary considerably. Nevertheless, the most stable ones pertain to zinc, lead and nickel and, to much lesser extent, copper.

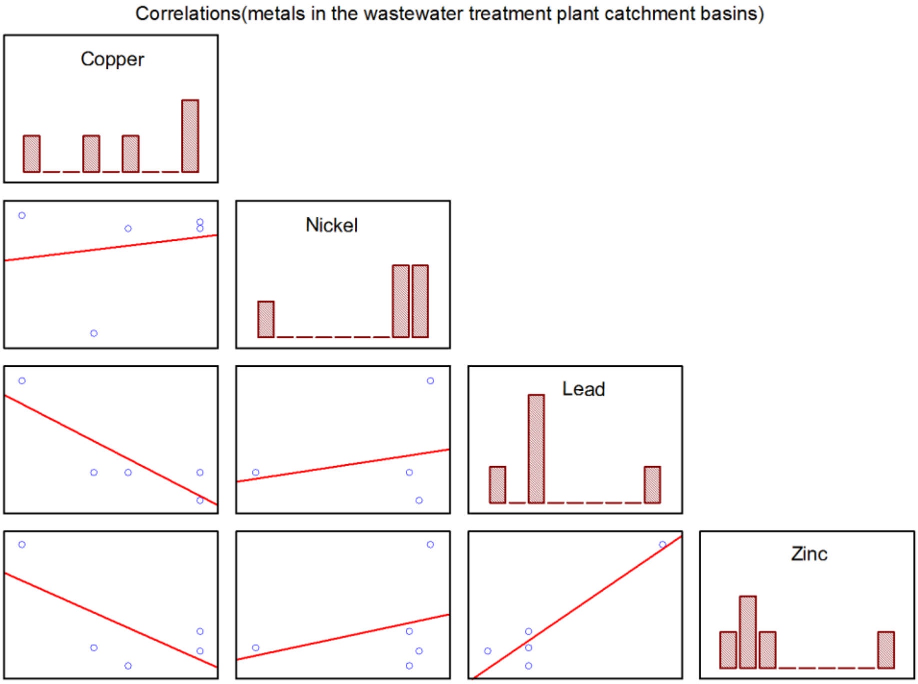

Fig. 3. The matrix graph of metal dispersion for selected variables in sewage
Rys. 3. Macierzowy wykres rozrzutu metali dla wybranych zmiennych w ściekach

Figure 4 shows a categorised graph of dispersion with the regression line for nickel and copper. Also frequency of occurrence of metals depending on the concentration, average values, standard deviation plus minimum and maximum value have been indicated. Furthermore, it comprises also the regression equation having the following form:

$$\text{nickel} = 0.00832 + 0.06 \cdot \text{copper}$$

Unfortunately, interrelationship between those metals is very weak, which is indicated by weak correlation coefficient (r = ca. 0.18). Also values of concentrations of the studied metals, particularly copper, show poor repeatability, which has been proven by frequency of occurrence of this metal graphs shown in Figure 4.

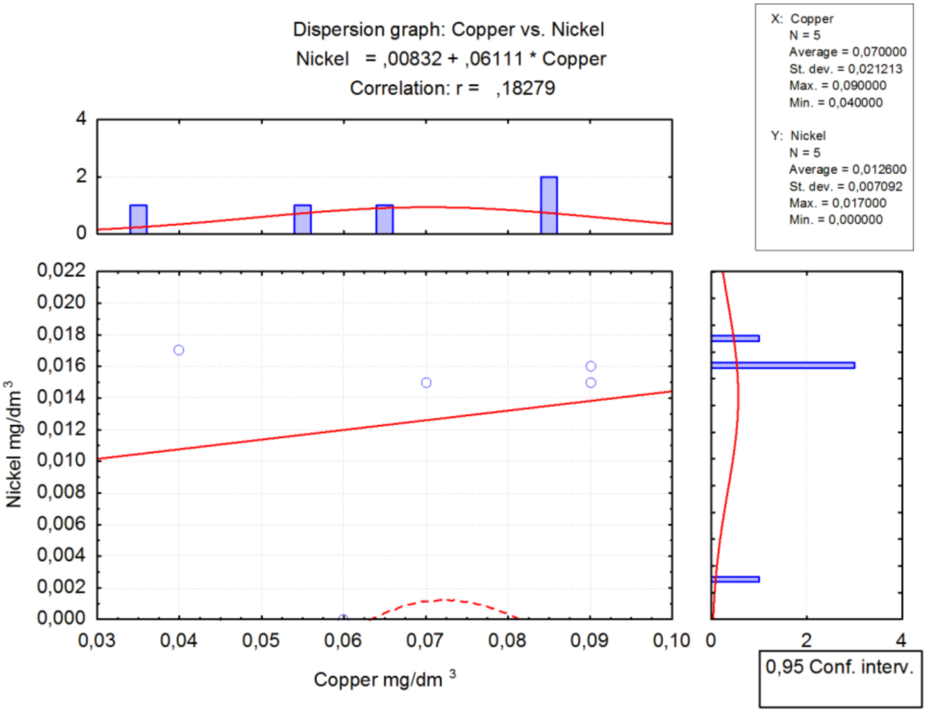

Fig. 4. Categorised graph of dispersion with the regression line for nickel and copper
Rys. 4. Skategoryzowany wykres rozrzutu wraz z linią regresji dla niklu i miedzi

Figure 5 shows a categorised graph of dispersion with the regression line for zinc and copper. Also frequency of occurrence of metals depending on the concentration, average values, standard deviation plus minimum and maximum value have been indicated. Furthermore, it comprises also the regression equation having the following form:

$$\text{zinc} = 0.59589 - 5.056 \cdot \text{copper}$$

There is fairly high negative interrelationship between those metals as indicated by the correlation coefficient (r = ca. -0.69). The concentration values for studied metals, particularly for copper, show high dispersion, which is proven by the graphs of frequency of occurrence of given metal as illustrated in Figure 5.

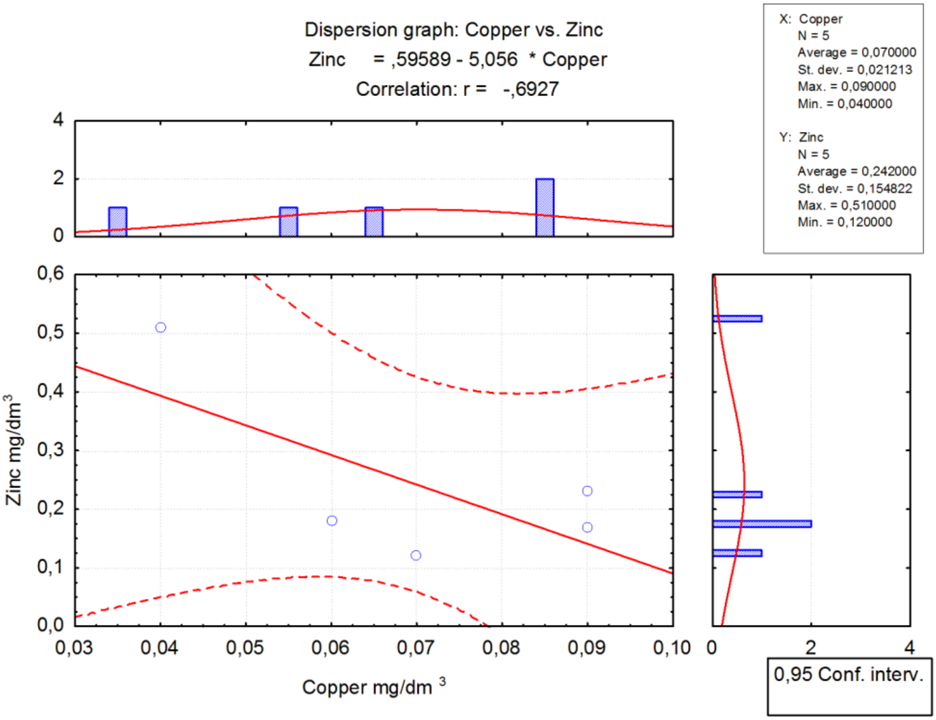

Fig. 5. Categorised graph of dispersion with the regression line for zinc and copper
Rys. 5. Skategoryzowany wykres rozrzutu wraz z linią regresji dla cynku i miedzi

Figure 6 shows a categorised graph of dispersion with the regression line for lead and copper. Also frequency of occurrence of metals depending on the concentration, average values, standard deviation plus minimum and maximum value have been indicated. Furthermore, it comprises also the regression equation having the following form:

$$\text{lead} = 0.03540 - 0.2000 \cdot \text{copper}$$

There is very high negative interrelationship between those metals as indicated by the correlation coefficient (r = ca. -0.85). Also values of concentrations of the studied metals, particularly copper, show poor

repeatability, which has been proven by frequency of occurrence of given metal graphs shown in Figure 6.

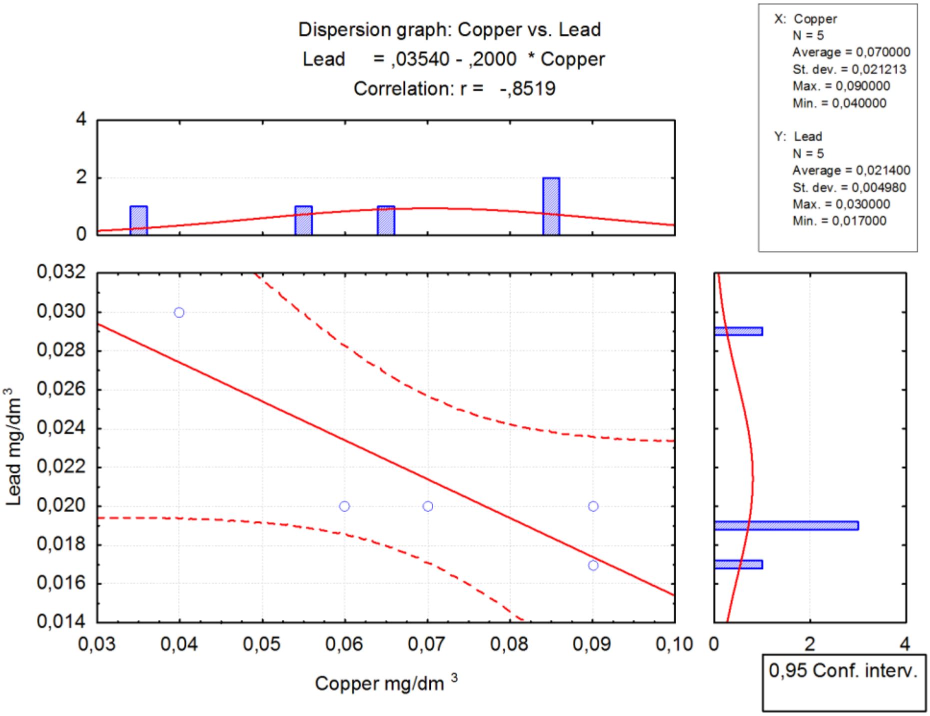

Fig. 6. Categorised graph of dispersion with the regression line for lead and copper
Rys. 6. Skategoryzowany wykres rozrzutu wraz z linią regresji dla ołowiu i miedzi

Figure 7 shows a categorised graph of dispersion with the regression line for zinc and lead. Also frequency of occurrence of metals depending on the concentration, average values, standard deviation plus minimum and maximum value have been indicated. Furthermore, it comprises also the regression equation having the following form:

$$\text{zinc} = 0.3827 + 29.194 \cdot \text{lead}$$

There is very high positive interrelationship between those metals as indicated by the correlation coefficient (r = ca. 0.94). Values of concentrations of the studied metals, particularly lead, show poor

repeatability, which has been proven by frequency of occurrence of given metal graphs shown in Figure 7.

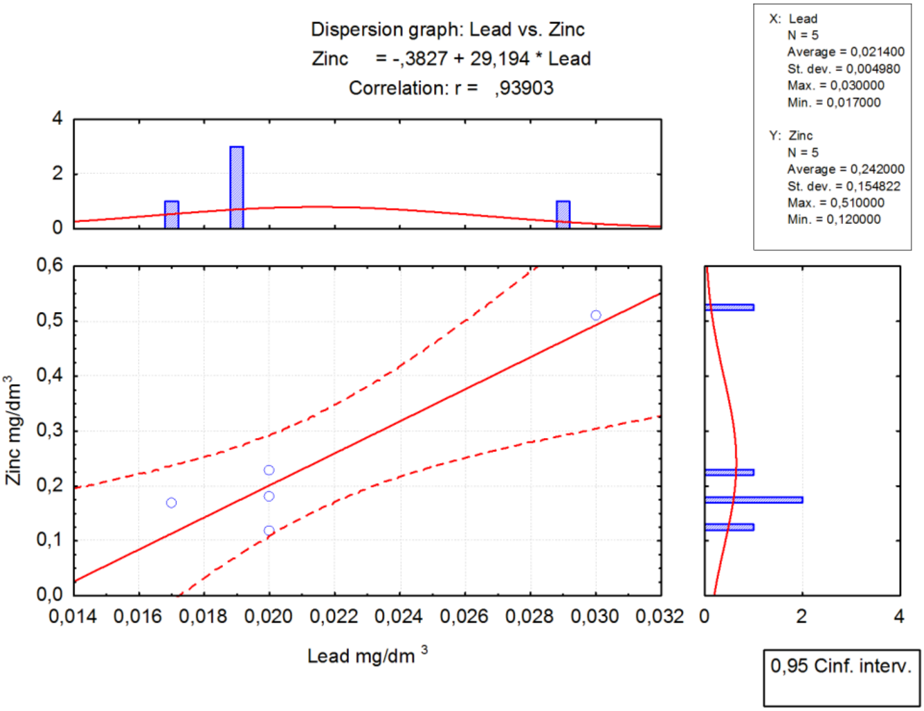

Fig. 7. Categorised graph of dispersion with the regression line for zinc and lead
Rys. 7. Skategoryzowany wykres rozrzutu wraz z linią regresji dla cynku i ołowiu

Figure 8 shows a categorised graph of dispersion with the regression line for nickel and lead. Also frequency of occurrence of metals depending on the concentration, average values, standard deviation plus minimum and maximum value have been indicated. Furthermore, it comprises also the regression equation having the following form:

$$\text{lead} = 0.1928 + 0.16799 \cdot \text{nickel}$$

There is weak positive interrelationship between those metals as indicated by the correlation coefficient (r = ca. 0.24). Values of concentrations of the studied metals, particularly nickel, show poor

repeatability, which has been proven by frequency of occurrence of given metal graphs shown in Figure 8.

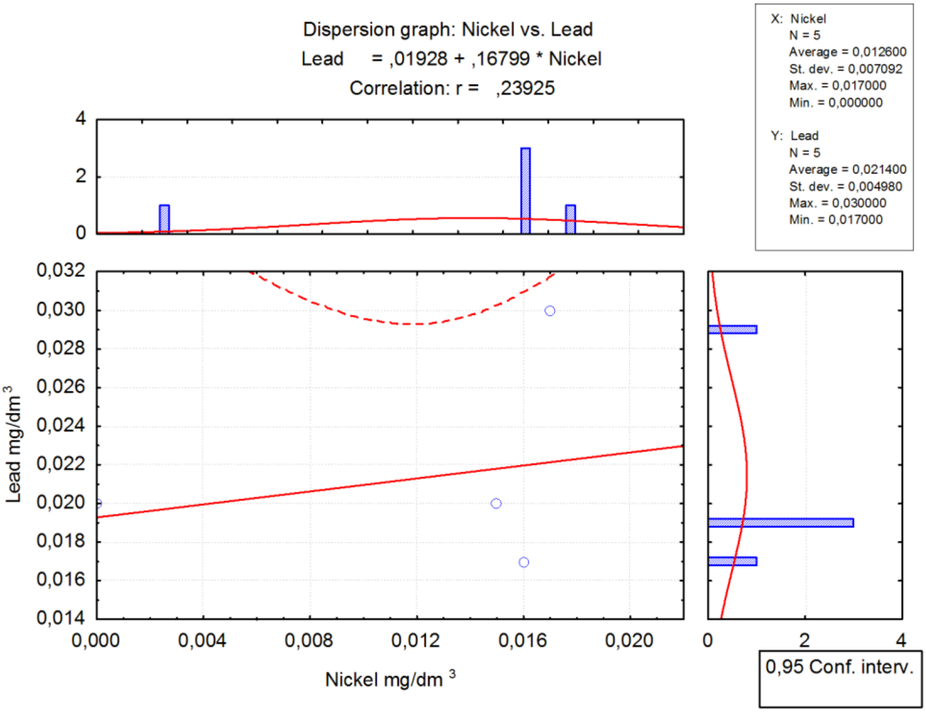

Fig. 8. Categorised graph of dispersion with the regression line for lead and Nikel

Rys. 8. Skategoryzowany wykres rozrzutu wraz z linią regresji dla ołowiu i niklu

Figure 9 shows a categorised graph of dispersion with the regression line for nickel and zinc. Also frequency of occurrence of metals depending on the concentration, average values, standard deviation plus minimum and maximum value have been indicated. Furthermore, it comprises also the regression equation having the following form:

$$\text{zinc} = 0.15470 + 6.9284 \cdot \text{nickel}$$

There is weak positive interrelationship between those metals as indicated by the correlation coefficient (r = ca. 0.32). Values of concentrations of the studied metals, particularly nickel, show poor repeatability, which has been proven by frequency of occurrence of given metal graphs shown in Figure 9.

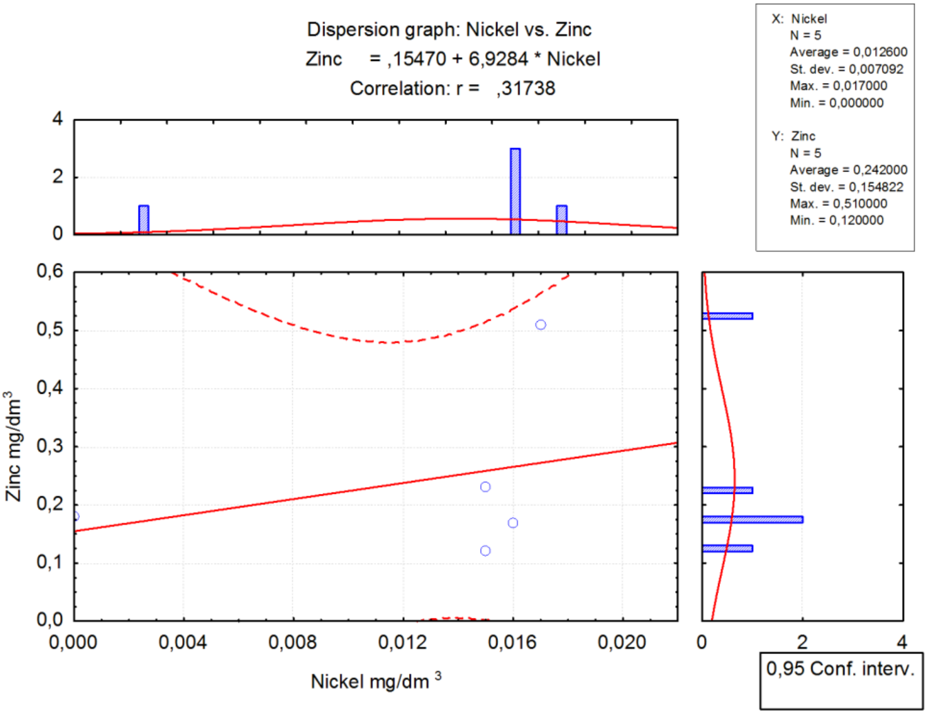

Fig. 9. Categorised graph of dispersion with the regression line for zinc and nickel
Rys. 9. Skategoryzowany wykres rozrzutu wraz z linią regresji dla cynku i niklu

Figure 10 shows an example histogram taking into account the high positive correlation between those metals, particularly between lead and zinc (r = 0.94), and slightly weaker negative, between lead and copper (r = -0.85).

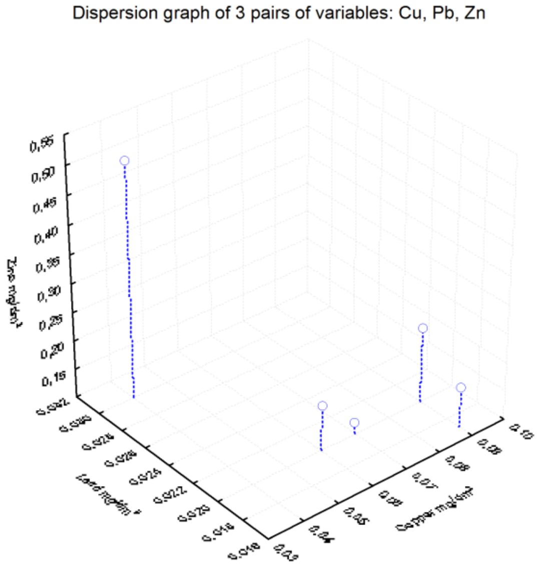

Fig. 10. Three-dimensional histogram for selected pairs of variables: zinc, lead and copper
Rys. 10. Trójwymiarowy histogram dla wybranych par zmiennych: cynku, ołowiu i miedzi

Due to too small number of heavy metals determinations in thickened and dehydrated sewage no attempt has been made to describe the phenomena occurring here through application of the statistical analysis.

5. Final conclusions

It appears from the studies performed that:

- some heavy metals occur in the tested raw sewage samples in small amounts or even at trace level (Hg, Cd and Cr),
- considerable increase of concentrations of all heavy metals in thickened and dehydrated sewage sludge has been observed and those metals, because of their value, can be arranged in the following series:

Zn > Cu > Pb > Ni > Hg > Cr, Cd,

- content of those metals in the thickened and dehydrated sewage was approx. tenfold higher compared with their content in raw sewage,
- the source of mercury in laundry sewage can be carpets of unknown origin, which can contain mercury, lead and chromium compounds,
- to assess the phenomena occurring in the studied sewage and sewage sludge popular numerical packages, which well describe correlations between particular sewage pollution indicators, can be used,
- the metals tested showed negative correlation between each other (copper with lead and zinc), or very strong positive correlation (between copper and zinc).

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Związki metali ciężkich w ściekach komunalnych oraz osadach ściekowych

Streszczenie

W osadach ściekowych zdarzają się przypadki występowania związków metali ciężkich, w tym toksycznej rtęci, których znaczne stężenie wskazuje na pojawienie się nowych antropogenicznych źródeł tych pierwiastków. W przypadku nadmiernej koncentracji toksycznych, a nawet rakotwórczych związków tych metali w środowisku naturalnym, powodują one jego nieodwracalne skażenieZarówno unieszkodliwianie osadów ściekowych poprzez kompostowanie, jak też spalanie, wymaga wstępnej obróbki. Osady ściekowe, zanim trafią do kompostowni lub spalarni odpadów wymagają odwodnienia lub wysuszenia. Tym samym powstały produkt stanowi koncentrat, w którym stężenie tych metali może być wielokrotnie (nawet dziesięciokrotnie) wyższe niż w ściekach poddawanych temu procesowi.

Z przeprowadzonych badań wynika, że w próbkach badanych ścieków surowych niektóre metale ciężkie występują w niewielkich ilościach lub na poziomie śladowym (Hg, Cd i Cr). Obserwuje się znaczący wzrost wszystkich metali ciężkich w osadach ściekowych zagęszczonych i odwodnionych, które można uszeregować następująco:

Zn > Cu > Pb > Ni > Hg >Cr, Cd

W stosunku do zawartości metali ciężkich w ściekach, zawartość tych metali w ściekach zagęszczonych i odwodnionych była około 10-krotnie wyższa. W osadach ściekowych zagęszczonych nastąpiła kumulacja metali ciężkich w stosunku do zawartości tych metali w ściekach surowych jak też odwodnionych. Wzrost ten dotyczy: Cu o 106%, Cr o 282%, Ni o 249%, Zn o 150% i Hg o 28%. Jednocześnie w ściekach zagęszczonych zmalało stężenie kadmu do ilości śladowych oraz ołowiu o 59%. Oznacza to, że kadm i ołów są zdecydowanie słabiej sorbowane przez składniki mineralne i organiczne osadów, a tym samym mogą przenikać wraz z wodami ociekowymi do zbiorników wodnych. Źródłem rtęci w ściekach pralniczych mogą być dywany i wykładziny podłogowe niewiadomego pochodzenia, które mogą zawierać związki rtęci, ołowiu i chromu. Do oceny zjawisk zachodzących w badanych ściekach oraz osadach ściekowych można wykorzystać popularne pakiety numeryczne, które dobrze opisują korelacje między poszczególnymi wskaźnikami zanieczyszczenia ścieków. Większość badanych składników wykazywała ujemną korelację względem siebie, w tym: miedź z ołowiem i cynkiem oraz bardzo silną dodatnią ołowiu z cynkiem.