

Mobility of Heavy Metals in Municipal Sewage Sludge from Different Throughput Sewage Treatment Plants

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Abstract

Sewage sludge heavy metals can be dissolved, precipitated, co-precipitated with metal oxides, and adsorbed or associated on the particles in biological debris. Heavy metals are found in the form of oxides, hydroxides, sulphides, sulphates, phosphates, silicates, organic bindings forming complexes with humic compounds, and complex sugars.

Polish regulations specifying the maximum levels of heavy metals in municipal sewage sludge used for agricultural purposes refer to the total content of lead, cadmium, mercury, nickel, zinc, copper, and chromium.

The aim of our study was to evaluate the mobility of heavy metals in sewage sludge from wastewater treatment plants in Świętokrzyskie Province. Stabilized sewage sludge from wastewater treatment was analyzed in accordance with the extraction method proposed by the Community Bureau of Reference (BCR).

Zinc, cadmium, lead, and nickel were determined by means of the standard addition with the use of a Perkin-Elmer 3100-BG FAAS atomic absorption spectrophotometer. Chromium and copper were tested using the FAAS technique.

The sequence analysis revealed the presence of heavy metals in all fractions (F-I, F-II, F-III, F-IV). It should be strongly emphasized that organometallics and aluminosilicates constitute the most prevalent forms of metals under consideration. Those, according to BCR, make fraction III and fraction IV, respectively. The results for stabilized sewage sludge confirmed a trend being observed in heavy metals concentrations in the immobile fractions, here in combination with aluminosilicates. On the basis of the investigations, it can be concluded that the dominant forms of heavy metals are immobile. It was shown that the total content of heavy metals in the sewage sludge does not provide an objective criterion for environmental risk evaluation. Bearing that in mind, however, it should be noted that heavy metals immobilized in the fraction F-III, may pose a potential hazard to soil in the aeration zone.

Keywords: heavy metals, BCR, sewage sludge, metal speciation

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Introduction

Heavy metals (HMs) are elements that have density greater than 4.5 g/cm^3 and which in chemical reactions tend to give away electrons, forming simple cations. In the solid and liquid states they are characterized by good thermal and electrical conductivity; they are shiny and opaque. They have high melting and boiling points. They are malleable and ductile, their vapors are most frequently monatomic. They have reduction properties [1].

HMs comprise the following: Cu, Co, Cr, Cd, Fe, Zn, Pb, Sn, Hg, Mn, Ni, Mo, V, and W, plus non-metal Se. The group includes both the elements that are indispensable for living organisms and those whose role in the physiology of plants, animals, and humans is still unexplained [2].

HMs constitute very important components of the earth's crust and are considered to be non-renewable natural resources. Also, HMs play an important role in microorganism metabolic processes, e.g. those in bacteria, by taking part in the control of biochemical process, in cell structure stabilization, or in enzyme reaction catalysis [3]. HM pollution constitutes a major problem in all water-related environmental issues. The environmental problem HMs pose is complex in character. On one hand their ores get depleted, on the other, heavy metal concentration both in living organisms (plants, animals, humans) and also in the habitats of those organisms tends to increase continuously [1].

Dynamically developing industries and transport unreasonably apply crop protection chemicals in agriculture, sewage sludge, and wastes used to deacidify soils. All contribute to the excessive accumulation of trace elements in plant soils, which poses a health hazard for animals and humans [4]. One of the effects produced by the growth of urbanization and industrialization involves a constant increase in HM content in the natural environment, which continues to adversely affect the operation of ecosystems. The accumulation of HMs in soil is particularly dangerous due to the fact that soil constitutes the most crucial link in the element cycle in nature. HMs migrating to the environment produce an impact on all components of the food chain. They affect micro-organisms, plants, animals and, finally, humans. Plants that people and animals eat are a natural source of heavy metals, therefore the latter constitute a substantial health risk due to the dietary quality of food crops. Those elements accumulate both in soft and hard tissues in animals and people. On the basis of their toxicity, two groups of HMs are differentiated. The first one includes cadmium, mercury, and lead, which are highly toxic for humans and animals and less harmful for plants. The other group comprises copper, zinc, and nickel, which when present at excessive levels, are more damaging to plants than to animal and human organisms [5].

Increased content of HMs can lead to ground water contamination, produce an adverse effect for soil biological properties, be toxic for plants, and also alter the food chain. Above the admissible level, toxic metals significantly reduce soil fertility. They also inhibit enzyme activity in the soil and alter soil acidity.

Plants, animals, and humans differ in their reactions to various HMs [1]. The mechanisms of the harmful action of HMs are diversified. They can inactivate enzyme systems, thus leading to physiological changes which, in the most extreme cases, can cause tissue and cell necrosis. For instance, inhibited nitrate reductase can result in the accumulation of nitrates in plants, which is particularly dangerous for humans and animals. The natural content of HMs in soils generally does not pose a hazard to plants, animals, or people [4]. Due to the results of investigations, however, alarming voices of research can be heard that industrialization and heightened standards of living makes the acreage of soils having the natural HM concentrations shrink constantly. The lack of information on the natural content of HMs in the environment leads to a gross simplification in the evaluation and interpretation of the causes of HM pollution.

The total content of HMs in sewage sludge does not provide information on what amount is accessible to plants, thus on what amount will enter the biological cycle. It is only the sequence analysis that makes it possible to estimate the percentages of metals in their mobile form that are accessible to plants. In the hydrosphere, heavy metals are found in the form of suspensions or they are dissolved. The analysis of metals in a complex environmental matrix requires mineralization. This stage decides on metals being converted into their ionic forms [1]. In accordance with the guidelines for the regulation [6], it is recommended to use the analytical method, applied after sample mineralization with aqua regia (or with concentrated acids), in which an AAS spectrophotometer is employed.

Many wet and dry mineralization methods with different oxidation agents are known [4].

Occurrence of HMs in Sewage and Sewage Sludge

Industrial sewage, which through the municipal sewage system is brought to sewage treatment plants, provides a relevant source of HMs in the environment. Surface flows constitute an additional source of HMs in sewage [7-8].

Although HMs found in sewage cannot disturb biological purification processes, they accumulate in sludge, which affects its treatment and determines its final composition. Sewage sludge can be used for remediation of degraded areas, provided that the requirements specified in the regulations are satisfied [6, 9-14].

Forms of HM Occurrence in Sewage and Sewage Sludge

The level of pollution with HMs is determined by the amount of metal ions dissolved in sewage and sludge liquid phase, floating in suspension and precipitated with the sludge. Ions of HMs can be naturally bound in them through [15]:

- Cation exchange and adsorption binding on the surface of fine particles (e.g. clayey particles, iron and manganese oxides and hydroxides, and organic substances).

- Organic binding – especially with humic acids, which are insoluble in water and which are characterized by a high ability to exchange cations. They cause the formation of chelates, from which HM ions do not return to the solution.
- Inorganic binding, which is a main means of binding HM ions.
- co-precipitation with oxides or hydroxides of iron and manganese, which allows HM ions binding with the sludge.

In the presence of ammonia, some HMs in sewage and sludge form soluble complex compounds [7].

HM Mobility in Sewage Sludge

In sewage sludge, HMs can occur in mobile forms that migrate from the sludge to the fertilized soil, and also in immobile forms that do not produce any toxicological effect under given environmental conditions.

Mobile metals are considered to be those that occur in ion-exchange complexes, and which are either stopped or eluted, depending on the ionic composition of pore waters.

Metals bound to carbonates, which can be released at lowered soil reaction, also are easily accessible to plants.

Metals bound to manganese oxides, amorphous iron oxides and silicates, and also metals in the crystalline structures of minerals, have stable forms [16].

In sewage sludge processing and neutralizing, the forms of metal occurrence can change.

Speciation of HMs

Speciation involves the occurrence of different physical and chemical forms and chemical individuals of a given element in the examined material [17, 18].

Metals removed from sewage accumulate in sludge, which can affect further processing and finally make it impossible to apply sewage sludge to the environment. The total content of HMs in the sludge does not illustrate a potential hazard they pose. The accessibility of HMs to living organisms is conditioned by the mobility of the former [19, 20].

Due to the diversity of natural systems, the following types of speciation can be differentiated [21, 22]:

- physical speciation distinguishes a dissolved and a suspended form of a given element
- chemical speciation deals with different chemical forms of an element in the sample
- group speciation is a type of chemical speciation that refers to compounds of a given element in different oxidation states
- operational speciation describes forms of the sample that earlier underwent analytical operations
- functional speciation distinguishes element forms that demonstrate chemical or physical activity of a certain type
- kinetic speciation distinguishes metal complexes that occur in the environment on the basis of the ligand exchange rate

Metals that occur in bindings that are water-soluble and metals bound to carbonates are considered to be the most mobile ones. Metals bound to iron and manganese oxides and to organic matter also are dangerous, yet their disengagement usually proceeds slowly. Metals bound to aluminosilicates are thought to be inaccessible. In order to determine bindings, in which heavy metals occur, thus their bioaccessibility, so-called speciation analysis is performed [20, 23, 24].

The speciation analysis determines forms, defined in a different manner, of a given element in a sample [22, 25].

Speciation analysis employs analytical techniques and sample preparation for tests that do not affect the original balance of the sample.

Every change in environmental conditions, such as acidity, redox potential, inorganic and organic ligand concentrations results in mobility changes, and thereby in metal bioaccessibility [26]. Therefore, identifying changes in the soil and in the sludge helps understand geochemical processes and estimate the re-mobility potential and the environmental risk, including the toxicological hazard. Speciation analysis is used to identify the above-mentioned changes. For soils and sludge, speciation analysis does not identify separate chemical forms. The basic type of speciation for soils and sludge is fractionation, i.e. analyte classification in accordance with selected physical properties, e.g. with respect to different solubility or chemical properties, e.g. reactivity [22, 27].

For fractionation, single-stage extraction and more often, sequential extraction are used [17, 22].

- Single-stage extraction – isolating a single fraction that has required parameters, which is done with appropriately selected extraction solvent (leaching agent). The method is most often used for soil speciation analysis. It makes it possible to determine the content of phyto-accessible forms. It is also possible to determine amounts of metals that were taken up by the plant root systems.
- Sequential extraction – performed with solutions that have increasing leaching powers. In this method, fractions, examined as an entity, are identified instead of specific chemical individuals. Then, in each separated fraction that contains given speciation forms, the content of metals is determined, applying arbitrarily chosen methods of trace analysis. In this examination, a suitable extraction solvent is chosen, which is capable of extracting groups of metal bindings of known properties.

Sequential extraction is a widely known method of soil [28], waste or sludge fractionation. It has some shortcomings, however, because it is time-consuming and uses low-specificity reagents. Other disadvantages involve the possibility of readsorption of metals released in analyses and the lack of standardized procedures for sample preparation [22, 25].

The analytical techniques that are applied make it possible to determine the concentration of mobile forms of heavy metals. Depending on the type of extracted matrix,

the speciation of heavy metals can be carried out in accordance with different procedures. For sewage sludge examination, a four-stage procedure is frequently used, which is recommended by the Community Bureau of Reference (EC/BCR) [23, 29, 30]:

- Stage I: CH_3COOH extraction – in order to identify and measure the content of accessible metals and those bound to carbonates (fraction I).
- Stage II: $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction – in order to identify and measure the content of metals bound to iron and manganese oxides (fraction II).
- Stage III: $\text{H}_2\text{O}_2/\text{CH}_3\text{COONH}_4$ extraction – in order to identify and measure the content of metal-organic fraction and sulphide fraction (fraction III).
- Stage IV: mineralization of the residual fraction with a mixture of concentrated acids (HCl , HF , HNO_3) – in order to identify and measure the content of metals bound to silicates (fraction IV).

Speciation Analysis Application

The results of the determination of the total content of metals for sludge and soil samples may provide information on the natural concentrations of an element (hydrogeochemical background), or they can show the impact of anthropogenic pressure. The total content of an element, however, does not indicate the environmental processes in which the element takes part. Neither does it provide information on element migration, real toxicity, bioaccessibility, or accumulation. Therefore, it is important to differentiate the forms of elements that occur in sludge and soil samples (speciation) by identifying chemical compounds or groups of compounds, which is possible due to speciation analysis.

The determination of the forms of elements broadens knowledge of the natural environment and often provides a reference point for defining the trends that develop in ecosystems and their dynamics. It also forms a basis for further actions geared toward the protection of the natural environment [31].

In hydrogeology, such investigations may provide a point of reference while identifying the conditions of subterranean water circulation and inform on pollution inflow. In addition, the results of determinations complement the knowledge of the element behavior and the role it plays in the environment. In hydrogeochemical investigations the results can become a point of reference for the analysis of element migration.

Speciation analysis is primarily applied to define toxic and eco-toxic effects produced by individual elements. It can be used to study full bio-cycles of elements and to check the quality of food products and pharmaceuticals.

In the natural environment pollutants and chemical compounds undergo chemical, biochemical, and physico-chemical changes. Different forms of those have various biological, medical, and toxic properties. Identifying chemical forms and toxic forms of elements is often more important than finding out about their total content. Therefore, environmental metal speciation is performed for various reasons, which include the following [22, 32]:

- conducting research aimed at finding out about metal balances and changes in the environment; experimental results are applied to the modelling of pollution transport in the environment
- monitoring biological and biochemical processes; for living organisms, the metal chemical and physical forms that are taken up are decisive for the effect they produce
- industries and technological processes, where the course and efficiency of a process depends on the presence of a given metal form

Materials and Methods

Sample Collection and Pre-Treatment

The tests were conducted on municipal sewage sludge collected (in accordance with [33]) from nine municipal sewage treatment plants located in central Poland (Table 1).

The Sequence Extraction

The tests were conducted in accordance with the four-step BCR sequential extraction procedure [23, 29], introducing a change in the method of residual fraction mineralization (i.e. aqua regia was used in the process of mineralization [34]).

Step one: acid soluble/exchangeable fraction (F-I)

A 2 g sample of sewage sludge was placed in a 100 cm³ test-tube for centrifuging. Then 40 cm³ of 0.11-molar acetic acid solution was added. The sample was shaken for 16 hours at room temperature. The extract was separated from the sewage sludge by centrifuge (4,000 rpm). The content of the soluble metals in the water was marked in the liquid.

Step two: reducible fraction (F-II)

Sewage sludge was washed in 20 cm³ of distilled water (shaken and centrifuged). Subsequently, 40 cm³ of 0.1-molar hydroxylamine hydrochloride solution (pH=2) was added to the sewage sludge. Nitric acid was used for the correction of the pH value. The procedure was the same as in step one: the mixture was shaken and centrifuged. Fraction II metals were marked in the liquid.

Step three: oxidation fraction (F-III)

The sewage sludge was carried over quantitatively to a quartz evaporating dish and 10 cm³ of 30% hydrogen peroxide was added. The contents of the evaporating dish were heated in a water bath at 85°C for one hour. The process was repeated with the addition of 10 cm³ of 8.8-molar hydrogen peroxide solution to the sewage sludge. After drying, the sewage sludge sample was transferred to test-tubes to be centrifuged and then 50 cm³ of ammonium acetate solution (1 mol/dm³, pH=2; nitric acid was used to

Table 1. Sewage sludge from eight different throughput water treatment plants.

Sample notation	Location	Type of water treatment plant	EP	Sludge stabilization method	Sludge use
S1	Kostomłoty-Laskowa	Mechanical-biological SBR	3,000	Aerobic mesophilic sludge stabilization	Land reclamation
S2	Daleszyce	Mechanical-biological SBR	5,000	Aerobic mesophilic sludge stabilization	Soilless land reclamation
S3	Strawczyn	Mechanical-biological	6,800	Aerobic sludge stabilization	Land reclamation
S4	Małogoszcz Zakurcze	Mechanical-biological	8,000	Aerobic sludge stabilization	Land reclamation
S5	Cedzyna	Mechanical-biological	9,500	Aerobic sludge stabilization	Soilless land reclamation
S6	Busko-Siesławice	Mechanical-biological	30,500	Aerobic sludge stabilization	Land reclamation
S7	Skarżysko-Kamienna	Mechanical-biological	50,000	Fermentation in closed fermentation chambers	Insulating layers at the landfill
S8	Jędrzejów	Mechanical-biological	57,480	Aerobic sludge stabilization	Land reclamation
S9	Sitkówka-Nowiny	Mechanical-biological	275,000	Fermentation in closed fermentation chambers	Soilless land reclamation

correct the pH value) was added. The sample was shaken for 16 hours and afterward the sewage sludge was separated from the extract. Fraction III metals were marked in the solution.

Step four: residual fraction (F-IV)

The sludge was washed and dried to a solid state. The mineralization of the residual fraction was conducted with aqua regia; 30 cm³ of concentrated hydrochloric acid and 10 cm³ of concentrated nitric acid were added carefully to a 300 cm³ conical flask together with 0.5 g of sludge. The conical flask was heated for 30 min and subsequently evaporated to dryness. After cooling, 25 cm³ of 5% hydrochloric acid were added. The sewage sludge was dissolved, carried over to a metal measuring flask, and topped off with 50 cm³ distilled water. Then the sample was mixed and strained to a dry dish. In the filtrate, the metal forms, Fraction IV, were marked.

The HMs in the extracts obtained were determined in accordance with ISO 9001:2000 using a Perkin-Elmer 3100 FAAS-BG atomic absorption spectrophotometer (impact bead). Each determination was repeated four times.

Results and Discussion

Fig. 1 shows the relative content of a selected HM (% mass.) determined in extracts in relation to its total content in F-I to F-IV fractions. The sequence analysis demonstrates that various forms of metals are present in the sewage sludge.

For metals examined in the experiment, the percentage participation of individual HM fractions in sewage sludge does not depend on the method of sludge stabilization.

Sequential extraction makes it possible to state the mobility level of HMs in sewage sludge. Fraction I metals,

which are in water-soluble bindings, and fraction II metals, which are bound to carbonates, are considered to be the most mobile ones. Immobile metals are those bound to iron and manganese oxides (fraction III), and also metals bound to aluminosilicates (fraction IV).

The analysis shows that the majority of trace elements under consideration are found in the fraction bound to iron and manganese oxides (fraction III) and in the fraction bound to aluminosilicates (fraction IV). In those fractions, copper and lead were determined to have the highest content, and nickel the lowest.

In fractions I and II low content of HMs was found when compared with immobile fractions. Only for the Kostomłoty-Laskowa sewage water treatment plant (S1) was the content of metal mobile forms raised in comparison with the sewage sludge from other wastewater treatment facilities (S2-S9). The fractions were characterized by the highest content of zinc and nickel.

A relationship between the throughput of the sewage treatment plant and the relative content of mobile HM fractions (F-I + F-II) was observed. The significance of the correlation was checked with F test for $\alpha=0.15$ $R^2=0.34$ (Fig. 11).

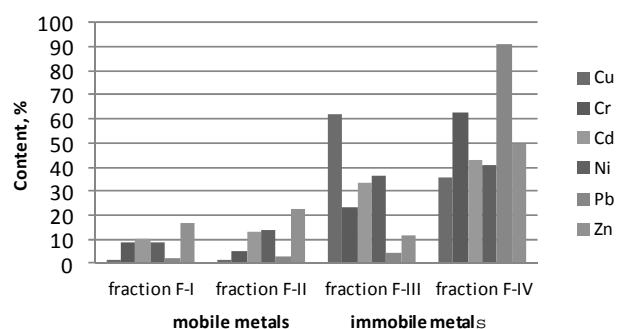


Fig. 1. Speciation of heavy metals in sewage sludge from the wastewater treatment plant in Cedzyna (S5).

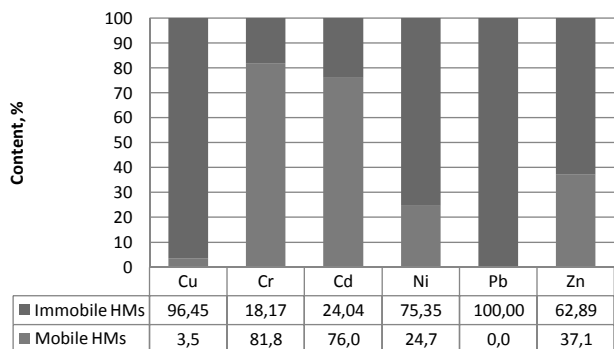


Fig. 2. Analysis of heavy metal mobility based on metal speciation in sewage sludge from the Kostomłoty-Laskowa wastewater treatment plant (S1).

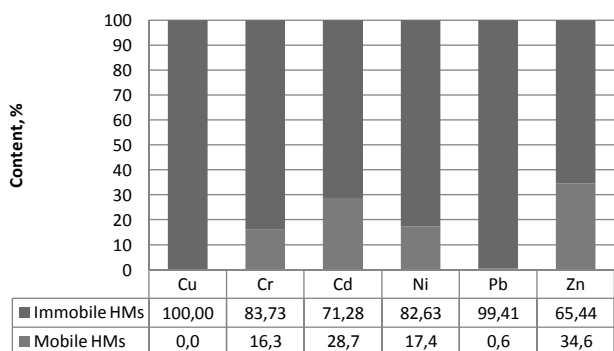


Fig. 3. Heavy metal mobility analysis based on metal speciation in sewage sludge from the Daleszyce wastewater treatment plant (S2).

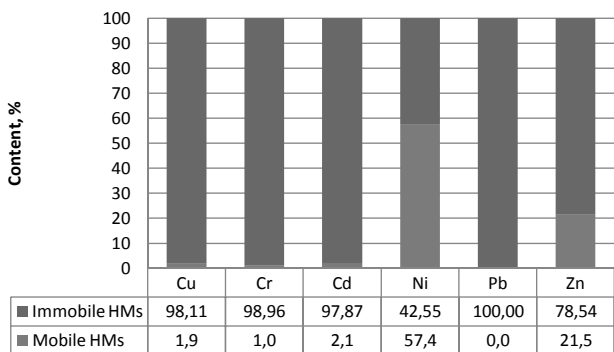


Fig. 4. Analysis of heavy metal mobility based on metal speciation in sewage sludge from the Strawczyn wastewater treatment plant (S3).

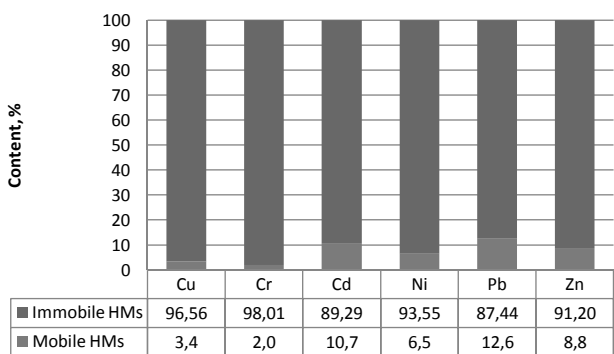


Fig. 5. Analysis of heavy metal mobility based on metal speciation in sewage sludge from the Małogoszcz-Zakurcze wastewater treatment plant (S4).

In addition, item remainder analysis was performed to obtain additional information on the prediction model adopted for investigations (Fig. 12).

The point distribution in Fig. 12 is homogeneous, which confirms that the adopted prediction method is correct.

In Fig. 13 the histogram of copper fraction contained in metal-organic and/or sulphide fraction (F-III) is presented. It was proved statistically that the mean value of copper concentration in fraction F-III does not significantly differ from 61.8% for $\alpha=0.05$. It is probable that the distribution of copper content in the analyzed sewage sludge is characteristic. Over 60% of the total content of this metal in sewage sludge is usually concentrated in the immobile sulphide fraction (F-III). This interesting property of copper was confirmed by Chen et al. [27].

Conclusions

The negative impact of sewage on the environment should be reduced by purification in waste water treatment plants. At each treatment facility, sewage should be purified to such an extent so that it would not detrimentally affect the aquatic environment. Therefore, constantly analyzing and checking the effectiveness of sewage treatment, in accordance with standards and regulations in force, provides an important criterion for the assessment of sewage treatment plant operation.

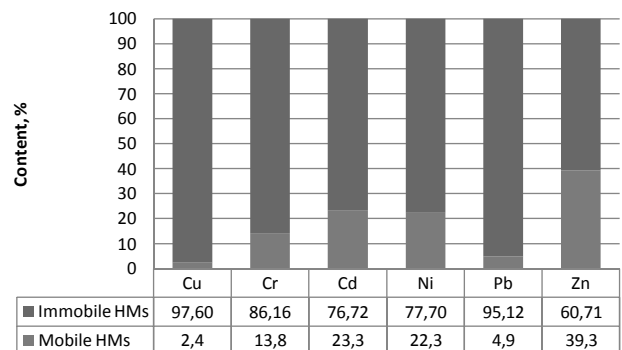


Fig. 6. Analysis of heavy metal mobility based on metal speciation in sewage sludge from the Cedzyna wastewater treatment plant (S5).

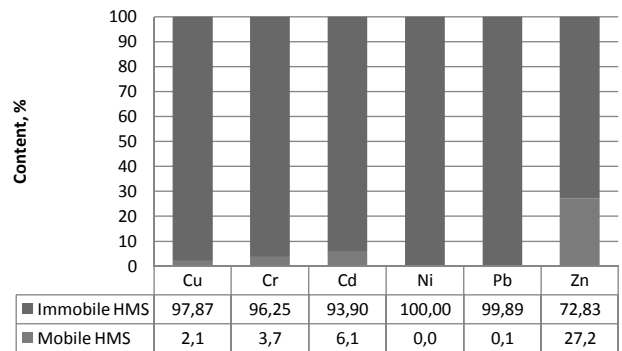


Fig. 7. Analysis of heavy metal mobility based on metal speciation in sewage sludge from the Busko-Siesławice wastewater treatment plant (S6).

Sewage sludge is apparently abundant in nutrients. However, heavy metals found in it restrict or even make it impossible to use sludge for biological purposes. Metals occur in various physical and chemical forms, which to a large extent determines their toxicity.

In sewage sludge, heavy metals are found in mobile forms that migrate to the soil, and in immobile forms that do not significantly affect ground and water environments.

Speciation analysis is based on the sequential extraction carried out in accordance with BCR methodology. Stabilized sewage sludge from wastewater treatment plants underwent extraction. In extracts, zinc, cadmium, lead, and nickel were determined using the standard addition method.

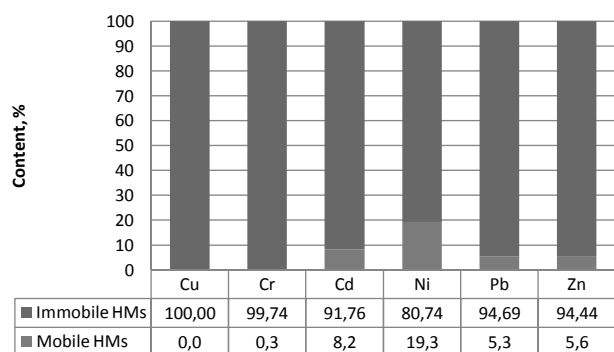


Fig. 8. Analysis of heavy metal mobility based on metal speciation in sewage sludge from the Skarżysko-Kamienna wastewater treatment plant (S7).

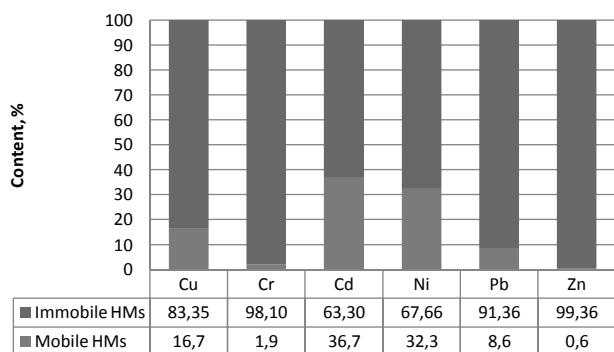


Fig. 9. Analysis of heavy metal mobility based on metal speciation in sewage sludge from the Jędrzejów wastewater treatment plant (S8).

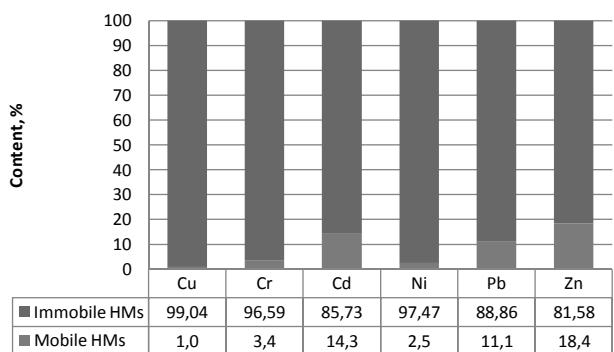


Fig. 10. Analysis of heavy metal mobility based on metal speciation in sewage sludge from the Sitkówka-Nowiny wastewater treatment plant (S9).

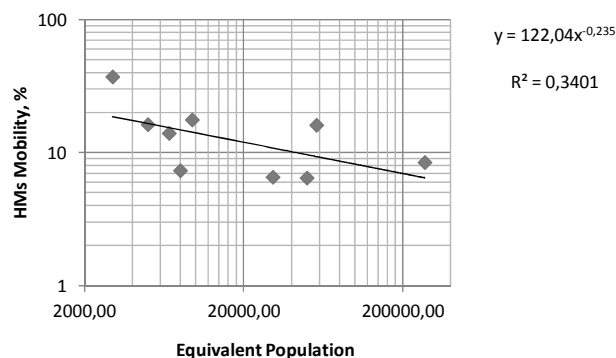


Fig. 11. Correlation between Equivalent Population for sewage treatment plant throughput S1-S9 and relative content of heavy metals in mobile fractions of BCR.

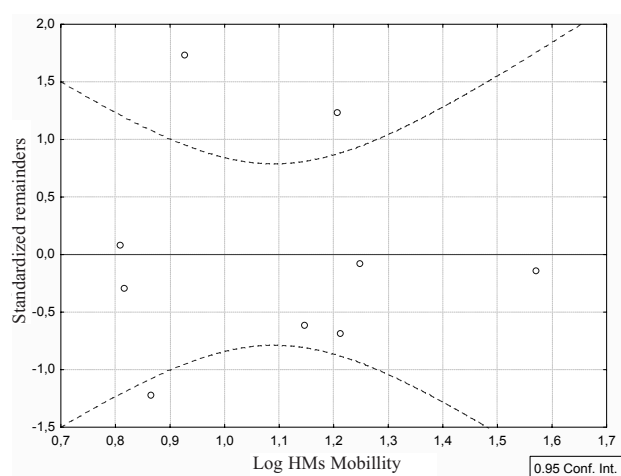


Fig. 12. Item remainder analysis in the model of correlation between sewage treatment plant throughput S1-S9 and the relative content of heavy metals in mobile fractions of BCR.

A Perkin-Elmer 3100-BG FAAS atomic absorption spectrophotometer (with the background correction function turned on) was employed. Chromium and copper were tested using the FAAS technique.

The sequence analysis showed the presence of HMs in all fractions (F-I, F-II, F-III, F-IV). It must be stressed that organometallics and aluminosilicates are the most prevailing forms of metals under consideration. Those, according to BCR, constitute fraction III and fraction IV, respectively. On the basis of the investigations, it can be concluded that the dominant forms of HMs are immobile. It was demonstrated that the total content of heavy metals in the sewage sludge does not provide an objective criterion to assess the environmental hazard. Nevertheless, it should be noted that heavy metals immobilized in fraction F-III may pose a potential risk to soil in the aeration zone.

A statistical correlation method made it possible to check whether a relationship holds between the capacity of the sewage treatment plant (EP) and mean mobility of heavy metals in selected stabilized sewage sludge from treatment facilities in the Świętokrzyskie Province.

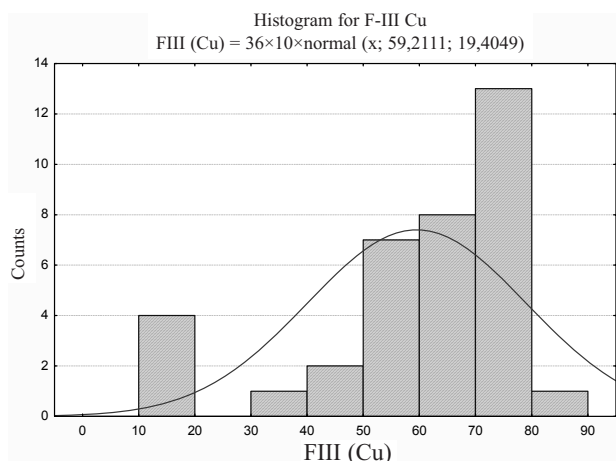


Fig. 13. Histogram of copper in sulphide fraction FIII-BCR.

In statistical investigations, the significance of the correlation between mean mobility of heavy metals and capacity of the sewage treatment plant (EP) was observed. Relatively large sewage treatment plants were demonstrated to generate sewage sludge in which heavy metals are found mainly in immobile bindings, which are not relevant from the toxicological standpoint.

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