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# Fractions of heavy metals in the soil after the application of municipal sewage sludge, peat and furnace ash

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## Abstract

The aim of the study was to evaluate the effect of the addition of various materials, i.e. municipal sewage sludge, furnace ash and peat, as well as various doses of ash-sludge and ash-peat mixtures, on some physico-chemical properties of the soil: pH, hydrolytic acidity, sorption complex capacity, organic C content, the content of P, K and Mg available forms, total content of heavy metals and their forms soluble in 1 mol · dm-3 HCl solution, and their speciation as well. Municipal sewage sludge and of ash-sludge and ash-peat mixtures use in the experiment caused the greatest increase in sorption capacity, in content of phosphorus, potassium and magnesium and resulted in a gradual increase in the content of studied heavy metals. The addition of ash and applied mixtures to the soil caused a change in soil reaction (the pH increase). The ash was characterized by a low content of heavy metals. After peat and its mixtures with ash application decreased content of heavy metals was observed, and when the peat was used alone could be seen the greatest increase in the organic C content in the substrate. Distribution of heavy metals in the fractions separated in different combinations show large variations, depending on the tested metal and the studied variant. Chromium, zinc, lead and cadmium have been stored mainly in the residual fraction (FV), and most of the copper and nickel have been specifically bound with organic matter (FIV). It has been found that the alkaline materials application to the soil decreased the solubility of most heavy metals, which results in a limitation of their uptake by plants. Chromium and copper were an exception, which solubility increased with the alkalinity of the substrate. An exception was chromium and copper, which solubility increased with the alkalinity of the substrate.

**Key Words:** Municipal sewage sludge, peat, furnace ash, soil, heavy metals, speciation.

## INTRODUCTION

Application of ash-sludge and ash-peat mixtures to the soil not only improves the physicochemical properties of the substrate, but also enriches it in digestible macronutrients and micronutrients (Samaras et al., 2008). Incineration waste can be used as material improving the physical properties of reclaimed land and sustainably managed soils (Antonkiewicz 2011), as well as a material deacidifying and providing valuable components to plants (Wojcieszczuk et al., 2009). The use of municipal sewage sludge improves soil physicochemical properties. Municipal sewage sludge is a source of organic matter, macronutrients and micronutrients that can be used by plants (Sienkiewicz, Czarnecka 2012). Incineration ash and municipal sewage sludge can be a source of heavy metals and other organic pollutants (Dabrowska et al. 2011). Peat as a natural material is a rich source of organic matter. Application of peat to the soil improves the sorption properties and increases the buffering capacity of the substrate (Antonkiewicz 2008).

The main limitation in the application of sewage sludge and bottom ash can be a high content of heavy metals. Hence, the necessity of control of the soil and substrate to which the waste is used (Papadimitriou 2008). Moreover, one should assess whether the use of waste helps to improve the physicochemical properties of the soil or substrate, for example reclaimed landfill.

The aim of the experiment was to evaluate the effect of the addition of various materials, i.e. municipal sewage sludge, incineration ash and peat, as well as various doses of ash-sewage sludge and ash-peat mixtures on some physicochemical properties of the soil, the total content of heavy metals and their fractions.

## MATERIAL AND METHODS

Research on the impact of municipal sewage sludge, incineration ash, peat and their mixtures on the physicochemical properties of soil was carried out after completion of the 3-year pot experiment. The study was conducted on very acid soil with a particle size of clay dust (Table 1). It contained 18% sand, 8% of coarse dust, 36% of fine dust, 24% coarse silty clay, 9% of fine clay and 5% colloidal clay. The furnace ash used in the pot experiment, in the terms of agronomic soil category corresponded to medium soil, and in terms of grain composition of sandy silty clay (Systematics of Polish Soils. PTG. 1989).

**Table 1.** Characteristic of physicochemical materials used in experiment

| Parameter | Unit | Soil | Sewage slugge | Ash | Peat |
|---|---|---|---|---|---|
| Texture | | Clayey silt | - | Sandy silty loam | - |
| pH$_{(KCl)}$ | pH | 3.60 | 6.67 | 9.85 | 4.82 |
| pH$_{(H_2O)}$ | pH | 4.73 | 6.82 | 10.06 | 5.26 |
| Hydrolytic acidity | mmol(+)/kg$^{-1}$ | 70.68 | 161.96 | 3.63 | 831.94 |
| BEC Base exchange capacity | mmol(+)/kg$^{-1}$ | 42.45 | 887.03 | 260.25 | 317.09 |
| C - Organic | g · kg$^{-1}$ | 18.48 | 219.16 | 23.69 | 370.50 |
| N - Total | g · kg$^{-1}$ | 1.92 | 35.25 | 0.53 | 11.49 |
| P – Available | mg · kg$^{-1}$ | 57.43 | 611.40 | 41.18 | 269.75 |
| K – Available | mg · kg$^{-1}$ | 72.42 | 247.60 | 140.33 | 117.97 |
| Mg – Available | mg · kg$^{-1}$ | 109.75 | 885.49 | 989.86 | 999.86 |
| Cr | mg · kg$^{-1}$ | 39.33 | 48.95 | 33.85 | 11.55 |
| Pb | mg · kg$^{-1}$ | 40.40 | 59.25 | 18.65 | 2.75 |
| Cu | mg · kg$^{-1}$ | 8.28 | 272.25 | 74.50 | 1.18 |
| Zn | mg · kg$^{-1}$ | 70.25 | 1182.50 | 93.75 | 9.28 |
| Cd | mg · kg$^{-1}$ | 0.43 | 5.10 | 0.28 | 0.05 |
| Ni | mg · kg$^{-1}$ | 30.08 | 23.03 | 39.98 | 7.30 |

The experiment was conducted in quadruplicate in polyethylene pots with a capacity of 6 kg, filled with ash-sludge and ash-peat mixtures in the amount of 1-30% relative to the total weight of soil. The experimental design comprised also objects containing only single components of the mixtures (Table 2). Usual NPK fertilization in an amount of 0.3 g of N, 0.08 g P, 0.2 g K . kg$^{-1}$ of soil, in the form of $NH_4NO_3$, $KH_2PO_4$, KCl was used annually for all pots. Mineral fertilizers were applied in the form of solutions in the first two weeks before the sowing of the plants and thoroughly mixed with the substratum. In the second and third year of the experiment fertilizers were applied in early spring before the start of plant mixture vegetation. The mixture included: *Festuca rubra* L. - 47%, *Festuca arundinacea* Schreb. - 17.5%, *Poa pratensis* L. - 23.5%, *Lotus corniculatus* L. - 12%. During the growing season the plants were watered with redistilled water, and the soil moisture was maintained at 60% of maximum water capacity. The yield and content of heavy metals in the mixture of plants were stated in paper of Antonkiewicz (2007).

In the soil after the experiment pH was assessed in $H_2O$ and 1 mol of KCl . dm$^{-3}$, hydrolytic acidity by Kappen's method, the base exchange capacity (BEC) in 1 mol . dm$^{-3}$ $CH_3COONH_4$, organic carbon content by Tiurin's method, nitrogen – by Kieldahl's method, the content of available phosphorus and potassium – by Egner-Riehm's method, and magnesium by Schatschabel's method. Total content of heavy metals was determined in the soil after dissolving the samples in a mixture of nitric and perchloric acids (3:2).

### Fractionation of heavy metals

The determinations of the various fractions of metals in the tested substrates sequential fractionation schema version metals proposed by Tessier et al. (1979) was used. Five fractions were isolated heavy metals (Cr, Zn, Pb, Cu, Cd, Ni):

1. Metals superstructure (FI) - air-dry and homogenized material was extracted with 8 $cm^3$ of 1.0 M $MgCl_2$ at pH 7, with shaking for 1 hour at $25^{O}C$.

2. Associated with the second metal carbonates (FII) - the form of a replaceable residue was extracted with 8 ml of 1.0 M $CH_3COONa$, pH 5, still shaking for 5 hours at $25^{O}C$.

3. Associated with the metals iron and manganese oxides (FIII) - carbonates residue was extracted by five hours 20 $cm^3$ of 0.04 M $NH_2OH$ . HCl dissolved in 25% $CH_3COOH$ (vol/vol) at $96^{O}C$ stirring from time to time.

4. Metals associated with organic matter (FIV) - residue form of Fe-Mn oxides was extracted 3 $cm^3$ 0.02 M $HNO^3$ + 5 $cm^3$ of 30% $H_2O_2$ (v/v) for 2 hours at 85° C, stirring occasionally, then add 3 $cm^3$ of 30% $H_2O_2$ at 85° C while stirring from time to time. And shaken with 5 ml of 3.2 M $CH_3COONH_4$ in 20% $HNO_3$ (vol/vol) for 0.5 hour at $25^{O}C$.

5. Metal residue associated with silicates, residual fraction (FV) - the remains of decomposed organic form hot with 10 $cm^3$ of 40% HF and 2 $cm^3$ of 70% $HClO_4$, the drying of 1 $cm^3$ $HClO_4$ was added and heated to the appearance of white fumes. The residue was dissolved in HCl (1:1) and diluted to 100 $cm^3$.

Extraction of one gram of the substrate samples was carried out in 50 $cm^3$ polyethylene centrifuge cartridge case. After each extraction the samples were centrifuged for 30 min 3000xg. The residue was washed with 8 $cm^3$ extraction $H_2O$, centrifuged again as above and the supernatant was removed. The filtrates from each replicate (vase), determine the content of Cr, Zn, Pb, Cu, Cd, Ni present in the individual fractions by ICP-AES (Indicatively coupled plasma).

For statistical calculations used Microsoft Excel spreadsheet 7.0 and Statistica v. 7.0 Statistical evaluation of the different sources of variation were made using analysis of variance procedure. The significance of differences between the compared averages of survey characteristics (performance indicators) found on the basis of Tukey's T-test at the significance level for the pot experiments $\alpha = 0.01$.

## RESULTS AND DISCUSSION

The basic properties of physicochemical soil after application of municipal sewage sludge, peat, mixtures of ash-sludge and ash-peat was published in an earlier paper (Antonkiewicz, 2008). The research shows that the use of the experience of municipal sewage sludge, peat, ash, and mixtures of ash and sediment and peat ash was the cause of increasing the sorption capacity, content of available phosphorus, potassium and magnesium. The addition of soil and ash, and mixtures of ash and sediment and peat ash resulted in a change of pH (pH increase). As a result of the use of peat and its mixtures of ash-peat was increased organic carbon content in the soil.

### The content of heavy metals in soil and wastes

The soil used in the experiment was characterized by the natural content of Pb, Cu and Cd, and the raised Cr, Ni and Zn (Table 1), (Kabata-Pendias, et al. 1995]. Reported heavy metal content was below the acceptable amounts of these elements in soils classified as municipal sewage sludge fertilization (Regulation, 2010). Assessing the content of heavy metals in the ash grate according to the number of boundary proposed by IUNG (Kabata-Pendias et al. 1995) found a natural content of these elements with the exception of copper. The content of heavy metals in the ash, as compared to the soil, there was large, and was not environmental hazard from incineration ash. Applied municipal sludge contained higher amounts of heavy metals in the ash compared to incineration ash, however, marked the content of these metals did not exceed the limit values determining nature of their use of (Regulation, 2010).

As used only municipal sludge (object II) content of Cr, Zn and Cd were respectively more than: 0.28, 20, 12-fold greater than that of the soil. As used in the experiment only peat (object IV) was characterized in comparison to the soil, ash-sludge, and mixtures there of containing metals studied the best. The contents of Cr, Zn, Pb, Cu, Cd and Ni in peat was by more than 72%, 85%, 93%, 85%, 89,47%, 72% lower compared to the soil. In the case of using only the ash-sludge mixture (object V), registered a significant increase of Zn, Cd and Cu in the substrate, respectively, the increase was more than 10, 5.5, 22-fold higher than in controls. In contrast, in a mixture of ash-peat (object VI) had a significantly lower content of Cr, Zn, Pb and Cd in the soil compared to the control, except Cu, where there were more than four times the content of this element in comparison to the control. After three years of growing a mixture of crops was recorded that under the influence of increase in the percentage shares of mixtures of ash-sludge (objects VII-XII), a systematic increase in Cr, Zn, Cd in the soil, and recorded a reduction of Pb and Ni in soil (Table 2-4). The increase in the content of Cr, Zn and Cd in soil fertilized with mixtures of ash-sludge explains the high content of these elements in municipal sewage sludge. Under the influence of increase in the percentage shares of mixtures of ash-peat in soil (objects XIII-XVIII) there was recorded decrease of Cr, Zn, Pb, Cd and Ni in soil (Table 2-4). Lowering the content of Cr, Zn, Pb, Cd and Ni in soil explained by a low content of these elements in peat and ash. Applying to the soil mixtures of ash and sewage sludge and ash-peat (objects VII-XVIII) resulted in a systematic, albeit insignificant, increase in the content of Cu in the media. The source of these objects Cu was municipal sewage sludge and incineration ash, in which the content of the trace element was suitably more than 35-fold and 9-fold higher compared to the contents in the soil.

### The fractions of heavy metals in soil and wastes

Percentage distribution of individual metals between the separated fractions varied depending on the element in question, the object (type and dose of waste). Percentage distribution of heavy metals in the individual fractions are shown in Tables 2-4.

The study was taken as most mobile i.e. readily available to the plant the first two fractions (FI-FII). From the literature (Rosik-Dulewska 2000, Gworek et al. 2006) is known that very active i.e. easily penetrating into the soil solution and collected by plants believed to form water-soluble metal - interchangeable and related carbonates (FI-FII). Fractions strongly associated trace metals from the soil solid phase (waste), mainly iron and manganese oxides and organic matter (FIII-FIV) are also a potential source of heavy metals to plants, but their release from the soil (waste) generally occurs more slowly. Metals "forming" connections aluminosilicate (residue FV) are dissolved only in concentrated mineral acids and is believed to be unavailable to plants (Tessier et al. 1979, Rosik-Dulewska, 2000, Gworek et al. 2006).

In the control soil, after 3 years of cultivation of mixed plants there was showed the greatest share of Cr, Zn, Pb in the residual fraction (FV), while Cu and Ni in the fraction bound to organic matter (FIV), and Cd from the exchangeable fraction (FI), (Table 2-4). In the control soil, among the metals studied, the smallest share in the most mobile fractions i.e. plant available (fractions FI-FII) was found in the case of Cr, which did not exceed 0.26% Cr general.

After a 3-year cultivation mixed plants on municipal sludge (object II) also there was found a small amount of Cr in the fractions of mobile and the sum of the first two fractions did not exceed 0.35% of the total content. The sludge applied only found the greatest amount of Cr, Zn and Pb in the residual fraction (FV) and organic (FIV). Cu and Ni were most strongly bound by organic matter in the sludge located and most Cd determined in the residual fraction (over 43%) and the exchangeable fraction (over 21%). A similar distribution of heavy metals in the fractions in sewage sludge reported by other authors (Dąbrowska et al. 2011, Gawdzik, 2012).

The ash used only (object III) metals such as Cr, Zn, Pb and Cd were mainly distributed in the residue fraction, and Cu and Ni were mainly distributed in the organic fraction (FIV). The greatest availability of heavy metals from the ash incineration (occurrence of mobile fractions, FI-FII total) was found in the case of Cd and Cr, and 12, respectively, and exceeded 10% of the total content. Other metals tested such as Zn, Pb, Cu and Ni in the fractions were the most mobile, and in small quantities. The contents of Zn, Pb, Cu and Ni in fractions FI-FII accounted for more than a mixture of plants, respectively: 2.88%, 1.04%, 0.34%, 0.18% of the total content. With own research and literature that ash in the slightest accumulating Ni and Cu in fractions of mobile (Kalembkiewicz and Soco 2004). A significant part in the binding of Pb, Cu, Cd and Ni was occurring organic fraction in the form of ash, unburned carbon residue and to the mixture were respectively over the plants: 28%, 57%, 29%, 68% of the total content.

In the applied only peat (object IV) there was recorded that Cr, Pb and Cd occurred mainly in the residual fraction (FV), and Zn, Cu and Ni were mainly in the organic fraction (FIV). The peat showed the greatest share of Cd in the most mobile fractions (FI-FII). Cd content in these fractions exceeded more than 41% of the total content.

**Table 2.** Content of Cr and Zn in soil after experiment [mg ˙kg$^{-1}$d.m.], and percentage of heavy metal fractions

| Objects* | | Cr | | | | | | Zn | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number | Name | Total | Fraction | | | | | Total | Fraction | | | | |
| | | mg/kg | FI | FII | FIII | FIV | FV | mg/kg | FI | FII | FIII | FIV | FV |
| I | Control | 35.20 | 0.09 | 0.15 | 0.56 | 17.78 | 81.42 | 53.38 | 6.98 | 11.32 | 19.76 | 26.25 | 35.69 |
| II | Sludge | 45.26 | 0.13 | 0.22 | 0.94 | 43.42 | 55.29 | 1089.50 | 6.07 | 8.95 | 13.64 | 35.32 | 36.02 |
| III | Ash | 31.18 | 0.05 | 12.73 | 13.62 | 10.74 | 62.87 | 82.25 | 0.22 | 2.65 | 6.69 | 18.72 | 71.71 |
| IV | Peat | 9.60 | 0.22 | 0.08 | 0.98 | 13.14 | 85.58 | 7.86 | 2.75 | 7.41 | 14.15 | 61.11 | 14.57 |
| V | AS | 35.29 | 0.12 | 0.68 | 5.69 | 23.66 | 69.85 | 583.63 | 1.47 | 3.45 | 4.17 | 14.71 | 76.19 |
| VI | AP | 23.19 | 0.07 | 0.59 | 4.57 | 29.17 | 65.60 | 45.25 | 0.53 | 1.04 | 2.08 | 40.02 | 56.33 |
| VII | AS 1% | 35.13 | 0.08 | 0.18 | 0.78 | 17.96 | 81.00 | 57.38 | 6.85 | 10.35 | 18.87 | 23.23 | 40.70 |
| VIII | AS 2% | 36.36 | 0.11 | 0.18 | 0.94 | 22.25 | 76.53 | 59.33 | 5.42 | 8.25 | 15.85 | 24.78 | 45.70 |
| IX | AS 5% | 37.38 | 0.10 | 0.20 | 0.94 | 22.81 | 75.95 | 65.00 | 4.80 | 4.98 | 12.00 | 27.72 | 50.50 |
| X | AS 10% | 37.90 | 0.12 | 0.19 | 0.97 | 26.36 | 72.36 | 77.88 | 2.63 | 4.19 | 9.26 | 27.08 | 56.84 |
| XI | AS 20% | 38.85 | 0.14 | 0.21 | 1.00 | 28.36 | 70.30 | 85.25 | 0.53 | 2.55 | 6.77 | 28.14 | 62.01 |
| XII | AS 30% | 39.16 | 0.15 | 0.23 | 1.12 | 30.65 | 67.84 | 101.88 | 0.29 | 1.09 | 4.65 | 25.58 | 68.39 |
| XIII | AP 1% | 34.78 | 0.10 | 0.14 | 0.64 | 19.08 | 80.04 | 54.13 | 7.05 | 10.04 | 18.55 | 26.26 | 38.10 |
| XIV | AP 2% | 33.16 | 0.10 | 0.14 | 0.69 | 20.19 | 78.88 | 53.50 | 6.16 | 9.25 | 17.61 | 29.60 | 37.38 |
| XV | AP 5% | 32.15 | 0.11 | 0.18 | 0.82 | 23.35 | 75.54 | 50.38 | 5.91 | 5.88 | 15.29 | 37.54 | 35.38 |
| XVI | AP 10% | 32.09 | 0.09 | 0.19 | 0.90 | 23.29 | 75.53 | 45.00 | 0.72 | 6.13 | 14.12 | 47.23 | 31.80 |
| XVII | AP 20% | 30.48 | 0.13 | 0.22 | 1.01 | 26.93 | 71.72 | 44.75 | 0.55 | 4.91 | 11.23 | 57.25 | 26.06 |
| XVIII | AP 30% | 30.68 | 0.14 | 0.25 | 1.10 | 29.49 | 69.02 | 42.16 | 0.37 | 2.42 | 8.66 | 66.70 | 21.85 |
| V%** | | 22.56 | 32.66 | 316.41 | 154.46 | 30.96 | 10.20 | 185.05 | 84.07 | 56.77 | 46.09 | 43.06 | 39.10 |
| LSD$_{(\alpha=0.01)}$ | | 7.72 | | | | | | 52.50 | | | | | |

*Object: I-Control; II- Sewage sludge; III-Ash; IV-Peat; V-AS Ash-Sludge 1:1; VI-AP Ash-Peat 1:1; VII-AS Ash-Sludge 1%; VIII-AS Ash-Sludge 2%; IX-AS Ash-Sludge 5%; X-AS Ash-Sludge 10%; XII-AS Ash-Sludge 20%; XII-AS Ash-Sludge 30%; XIII-AP Ash-Peat 1%; XIV-AP Ash-Peat 2%; XV-AP Ash-Peat 5%; XVI-AP Ash-Peat 10%; XVII-AP Ash-Peat 20%; XVIII-AP Ash-Peat 30%.

**Variability coefficent

**Table 3.** Content of Pb and Cu in soil after experiment [mg ˙kg$^{-1}$d.m.], and percentage of heavy metal fractions

| Objects* | | Pb | | | | | | Cu | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number | Name | Total | Fraction | | | | | Total | Fraction | | | | |
| | | mg/kg | FI | FII | FIII | FIV | FV | mg/kg | FI | FII | FIII | FIV | FV |
| I | Control | 32.10 | 5.66 | 8.19 | 16.94 | 27.17 | 42.03 | 7.10 | 1.90 | 5.46 | 11.81 | 43.23 | 37.59 |
| II | Sludge | 54.25 | 7.26 | 11.38 | 13.47 | 28.28 | 39.60 | 253.13 | 2.34 | 1.07 | 3.31 | 80.51 | 12.76 |
| III | Ash | 13.68 | 0.42 | 0.62 | 11.46 | 28.81 | 58.70 | 65.75 | 0.26 | 0.07 | 4.04 | 57.66 | 37.97 |
| IV | Peat | 2.10 | 2.06 | 2.37 | 8.50 | 32.32 | 54.75 | 1.01 | 8.70 | 1.49 | 9.55 | 61.03 | 19.23 |
| V | AS | 32.75 | 0.28 | 0.45 | 7.63 | 18.23 | 73.41 | 156.75 | 3.99 | 0.68 | 3.31 | 60.11 | 31.91 |
| VI | AP | 9.71 | 0.35 | 1.02 | 11.28 | 14.59 | 72.75 | 33.00 | 0.54 | 0.44 | 4.04 | 73.91 | 21.07 |
| VII | AS 1% | 35.24 | 5.33 | 7.37 | 15.19 | 25.90 | 46.21 | 7.98 | 1.36 | 4.72 | 9.85 | 41.49 | 42.58 |
| VIII | AS 2% | 34.86 | 4.40 | 7.65 | 15.31 | 25.45 | 47.18 | 9.48 | 0.99 | 3.77 | 7.51 | 40.56 | 47.16 |
| IX | AS 5% | 33.58 | 4.07 | 7.53 | 12.54 | 19.19 | 56.67 | 9.65 | 0.93 | 2.51 | 6.71 | 38.70 | 51.15 |
| X | AS 10% | 33.30 | 2.20 | 3.94 | 6.76 | 19.25 | 67.86 | 12.75 | 0.55 | 1.74 | 4.23 | 32.57 | 60.90 |
| XI | AS 20% | 33.06 | 0.74 | 3.19 | 5.92 | 13.61 | 76.54 | 15.43 | 0.26 | 1.18 | 2.46 | 38.64 | 57.47 |
| XII | AS 30% | 30.89 | 0.63 | 1.67 | 3.97 | 11.97 | 81.76 | 22.01 | 0.20 | 0.81 | 1.50 | 36.42 | 61.08 |
| XIII | AP 1% | 35.33 | 5.20 | 7.14 | 14.85 | 19.87 | 52.94 | 7.00 | 1.42 | 4.87 | 9.68 | 48.67 | 35.36 |
| XIV | AP 2% | 34.58 | 4.23 | 6.39 | 14.18 | 20.13 | 55.07 | 7.58 | 1.06 | 4.49 | 8.27 | 55.62 | 30.56 |
| XV | AP 5% | 35.23 | 3.70 | 5.81 | 9.91 | 15.85 | 64.73 | 8.13 | 0.92 | 2.46 | 6.29 | 54.50 | 35.84 |
| XVI | AP 10% | 34.86 | 1.07 | 2.15 | 5.93 | 12.33 | 78.51 | 8.36 | 0.73 | 1.96 | 4.71 | 52.21 | 40.40 |
| XVII | AP 20% | 33.74 | 0.62 | 1.45 | 3.76 | 10.49 | 83.68 | 10.50 | 0.30 | 1.45 | 2.63 | 62.01 | 33.60 |
| XVIII | AP 30% | 31.73 | 0.50 | 1.03 | 2.49 | 7.38 | 88.60 | 11.25 | 0.30 | 1.29 | 2.45 | 85.18 | 10.79 |
| V%** | | 37.60 | 84.06 | 74.90 | 45.34 | 36.79 | 23.88 | 181.69 | 136.58 | 75.01 | 54.75 | 28.52 | 40.56 |
| LSD$_{(\alpha=0.01)}$ | | 9.49 | | | | | | 23.83 | | | | | |

*Object: I-Control; II- Sewage sludge; III-Ash; IV-Peat; V-AS Ash-Sludge 1:1; VI-AP Ash-Peat 1:1; VII-AS Ash-Sludge 1%; VIII-AS Ash-Sludge 2%; IX-AS Ash-Sludge 5%; X-AS Ash-Sludge 10%; XI-AS Ash-Sludge 20%; XII-AS Ash-Sludge 30% XIII-AP Ash-Peat 1%; XIV-AP Ash-Peat 2%; XV-AP Ash-Peat 5%; XVI-AP Ash-Peat 10%; XVII-AP Ash-Peat 20%; XVIII-AP Ash-Peat 30%.

**Variability coefficent

**Table 4.** Content of Cd and Ni in soil after experiment [mg ˙kg$^{-1}$d.m.], and percentage of heavy metal fractions

| Objects* | | Cd | | | | | | Ni | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number | Name | Total mg/kg | Fraction FI | FII | FIII | FIV | FV | Total mg/kg | Fraction FI | FII | FIII | FIV | FV |
| I | Control | 0.38 | 58.71 | 7.68 | 10.97 | 8.92 | 13.72 | 23.36 | 3.13 | 0.24 | 11.08 | 66.21 | 19.34 |
| II | Sludge | 4.75 | 21.92 | 11.67 | 12.06 | 10.83 | 43.51 | 21.81 | 6.44 | 1.91 | 7.40 | 71.47 | 12.78 |
| III | Ash | 0.26 | 3.32 | 7.46 | 20.73 | 29.64 | 38.86 | 32.88 | 0.12 | 0.06 | 9.11 | 68.09 | 22.62 |
| IV | Peat | 0.04 | 26.14 | 15.69 | 0.00 | 25.49 | 32.68 | 6.54 | 3.47 | 0.59 | 12.87 | 59.82 | 23.25 |
| V | AS | 2.10 | 1.25 | 0.31 | 10.67 | 7.44 | 80.33 | 30.11 | 0.44 | 0.16 | 7.41 | 67.51 | 24.48 |
| VI | AP | 0.09 | 7.21 | 12.01 | 12.01 | 31.23 | 37.54 | 21.14 | 0.23 | 0.22 | 11.47 | 63.56 | 24.53 |
| VII | AS 1% | 0.34 | 57.54 | 10.01 | 12.51 | 10.16 | 9.77 | 22.30 | 3.01 | 0.28 | 11.25 | 71.15 | 14.31 |
| VIII | AS 2% | 0.40 | 45.37 | 7.75 | 11.07 | 9.89 | 25.93 | 21.66 | 2.72 | 0.26 | 11.00 | 76.84 | 9.18 |
| IX | AS 5% | 0.41 | 41.97 | 5.31 | 13.28 | 11.22 | 28.22 | 21.35 | 2.39 | 0.23 | 9.27 | 81.41 | 6.70 |
| X | AS 10% | 0.44 | 35.15 | 4.52 | 15.07 | 13.87 | 31.39 | 20.84 | 1.96 | 0.21 | 6.64 | 78.76 | 12.43 |
| XI | AS 20% | 0.56 | 25.02 | 2.27 | 12.32 | 14.17 | 46.21 | 20.73 | 0.77 | 0.17 | 5.67 | 80.75 | 12.64 |
| XII | AS 30% | 0.63 | 16.89 | 1.76 | 15.83 | 17.15 | 48.37 | 20.45 | 0.58 | 0.10 | 3.89 | 86.63 | 8.79 |
| XIII | AP 1% | 0.33 | 55.70 | 12.75 | 10.07 | 13.09 | 8.39 | 22.34 | 3.12 | 0.23 | 11.41 | 71.01 | 14.23 |
| XIV | AP 2% | 0.31 | 52.53 | 10.65 | 10.65 | 17.30 | 8.87 | 22.06 | 3.20 | 0.24 | 7.82 | 71.36 | 17.37 |
| XV | AP 5% | 0.31 | 48.85 | 8.14 | 13.57 | 20.95 | 8.48 | 21.93 | 3.09 | 0.18 | 7.63 | 73.92 | 15.18 |
| XVI | AP 10% | 0.30 | 35.54 | 4.35 | 18.13 | 30.64 | 11.33 | 21.38 | 0.82 | 0.19 | 5.77 | 77.00 | 16.22 |
| XVII | AP 20% | 0.30 | 32.53 | 2.77 | 19.03 | 34.86 | 10.81 | 21.05 | 0.75 | 0.18 | 4.12 | 78.30 | 16.66 |
| XVIII | AP 30% | 0.29 | 25.31 | 2.98 | 26.06 | 43.56 | 2.09 | 20.14 | 0.20 | 0.07 | 2.98 | 82.43 | 14.32 |
| V%** | | 162.87 | 56.08 | 61.42 | 39.96 | 54.44 | 74.36 | 23.25 | 82.60 | 135.73 | 36.31 | 9.69 | 33.66 |
| LSD$_{(\alpha=0.01)}$ | | 0.57 | | | | | | 7.36 | | | | | |

*Object: I-Control; II- Sewage sludge; III-Ash; IV-Peat; V-AS Ash-Sludge 1:1; VI-AP Ash-Peat 1:1; VII-AS Ash-Sludge 1%;
VIII-AS Ash-Sludge 2%; IX-AS Ash-Sludge 5%; X-AS Ash -Sludge 10%; XI-AS Ash-Sludge 20%;XII AS Ash-Sludge 30%
XIII-AP Ash-Peat 1%; XIV-AP Ash-Peat 2%; XV-AP Ash-Peat 5%; XVI-AP Ash-Peat 10%; XVII-AP Ash-Peat 20%; XVIII-Ap Ash-Peat 30%.
**Variability coefficent

Mixture of ash-sludge (object V) and a mixture of ash-peat (object VI) the greatest amount of Cr, Zn, Pb and Cd accumulate in the residual fraction (FV), and the Cu and Ni in the organic fraction (FIV). Furthermore, the mixture of ash-peat (object VI) was the source of Cd for a mixture of plants, because the sum of the most mobile fraction (FI-FII) was more than 19% of the total content. Research Rosik-Dulewski and others (2008) found confirmation that the mixture of ash and sedimentary heavy metals accumulate mainly in the fraction of residues and organic.

When applied to the soil mixture of ash and sewage sludge (VII-XII objects) and a mixture of ash-peat (objects XIII-XVIII) contained Cr, Zn, Pb, mainly in the residual fraction (FV), Cu and Ni in the organic fraction (FIV), Cd in exchangeable fraction (FI), the most available to plants. In mixtures of ash-sludge (objects VII-XII) and mixtures of ash-peat (XIII-XVIII) also found a significant share of Cr, Zn, Pb in the organic fraction (FIV). In these studies found lower levels of heavy metals in a mixture of ash-peat (objects XIII-XVIII), in comparison to the amount of heavy metals in the ash-sludge mixtures (objects VII-XII).

Mobility of heavy metals, the sum of the first two fractions (FI+FII) in the tested mixtures of ash-sludge and ash-peat applied to the soil (objects VII-XVIII), was variable and depending on the object ranged: 0.24-0.39% Cr, 1.38-17.19% Zn, Pb 1.53-12.70% Pb, 1.01-6.29 Cu, 18.65-68.46% Cd, 0.27-3.44 % Ni total content. The presented research shows that the greatest availability for plants characterized by Cd, then Zn, Pb, Cu, Ni, and Cr smallest. In the experiment, it was found that the main role in the storage of Cr, Zn, Pb played a residual fraction (FV), the Cu and Ni fraction bound to organic matter (FIV), and Cd exchangeable fraction (FI) and residual (FV).

## CONCLUSION

1.Municipal sewage sludge was the largest source of heavy metals present in the fractions most available to plants (FI-FII), while the incineration ash contained the smallest amount of heavy metals present in the fractions available to plants.

2.As a result of the mixing of ash-sludge found decreased amounts of heavy metals present in the fractions most accessible to plants. The greater part of ash in the ash-sludge mixtures, the smaller the share of metals in plant available forms.

3.Addition to the soil increasing shares of mixtures of ash-peat was the cause of the gradual reduction of the share of Cr, Zn, Pb, Cd and Ni in soil, which can be explained by a low content of these elements in the peat.

4.When applied to the soil mixture of ash-sludge and mixtures of ash-peat contained Cr, Zn, Pb, 5.Management of sewage sludge and incineration ash for reclamation of industry land sites (including landfills) in addition to reducing the amount of landfill will allow the use of nutrients by the plants present in this waste. The condition of the natural use should be conducting monitoring studies of heavy metals in sewage sludge and ash content, and control their environment.

6.It was found that the materials used in the experiment limited the mobility of heavy metals, as evidenced by the small share of interchangeable forms. Thus, these materials reduce the availability of these elements to plants

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