Heavy metal speciation in municipal sewage sludge depending on treatment method

Józefa Wiater[a,*], Maria Sulewska[b]

[a]*Department of Agri-Food Engineering and Environmental Management, Faculty of Civil Engineering and Environmental Sciences, Bialystok University of Technology, Wiejska 45E Street, 15-351 Białystok, Poland, email: j.wiater@pb.edu.pl*
[b]*Department of Geotechnics and Structural Mechanics, Faculty of Civil Engineering and Environmental Sciences, Bialystok University of Technology, Wiejska 45E Street, 15-351 Białystok, Poland*

ABSTRACT

Heavy metal content of sludge is one of the most important factors determining their final usage. However, total metal content of sludge is not a suitable indicator for assessing its bioavailability. A more substantial assessment is to determine the occurrence of metals bound by sludge components, which means fractions. Three types of sludge (excess sludge, post-fermentation sludge and dried sludge, which were taken in four quarters of 2019/2020 from one sewage treatment plant, were studied in this paper. Determinations of total Zn, Cu, Cr, Ni, Pb, Cd and their fractions were determined using Tessier method. Zinc was the most abundant in sludge, followed by copper, then chromium, nickel, lead, and the least cadmium. Total content of determined metals depended on how sludge was processed and, to some extent, on the sampling date. All analysed sludge types, due to their total content, can be used in agriculture. It was found that the distribution of metal fractions varied more with sludge type than sampling date. In the analysed sludges, irrespective of sampling date and sludge type, the distribution of metals in the fractions was as follows: Zn: reducible > exchangeable > residual > carbonate > oxidisable > soluble, Cu: oxidisable > exchangeable > residual > soluble > carbonate > reducible, Cr: reducible > residual > exchangeable > carbonate > oxidisable > soluble, Ni: reducible > carbonate > exchangeable > residual > soluble > oxidisable, Pb: residual > exchangeable > reducible > oxidisable > carbonate > soluble >, Cd: residual > reducible > exchangeable > carbonate > oxidisable > soluble. The shift of the mobile to non-mobile metal fraction was influenced by the sludge treatment method. These shifts were the most influenced by fermentation, and slightly less by sludge drying.

Keywords: Sewage sludge; Heavy metals; Speciation

1. Introduction

In the European Union countries, including Poland, there is a dynamic development of water supply and sewerage networks, leading to the generation of significant amounts of municipal wastewater. The capacity of municipal wastewater treatment plants has been increased accompanied with construction of new plants or modernisation of existing ones. It leads to rise of the amount of sewage sludge generated in treatment plants. Sludge is formed from the suspended solids contained in wastewater at various stages of wastewater treatment. The quantity and quality of wastewater and thus the quantity and quality of generated sludge depends on the type, condition of sewage system, city industrialisation, amount of water used, standard of inhabitants living. The quality of sludge varies on a daily basis or over a longer period of time. Sludge acquires the status of waste after appropriate treatment in the treatment

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plant. Depending on the classification adopted by the waste producer, the sludge can be sent for treatment by recovery or disposal. These wastes may also undergo intermediate treatment processes to change their properties and obtain waste with other codes. The final usage of municipal sewage sludge, understood as waste treatment, is the last stage of sludge usage, often posing huge problems for treatment plant operators. In order to avoid problems with sludge usage, the direction of final sludge usage should be defined already at the construction or modernisation stage, and appropriate installations for the treatment of municipal sewage sludge should be designed in order to achieve the desired properties, allowing for environmentally safe sludge usage. In order to use it properly, it must be characterised by certain parameters, especially as there is no possibility of storing them [1].

The most important law of European Union on sludge management is Council Directive 86/278/EEC of 12 June 1986 on environmental protection, in particular soil, when sewage sludge is used in agriculture, the so-called Sludge Directive [2]. It provides guidelines for the natural, including agricultural, use of sludge. The Directive allows to use the sludge in agriculture, emphasising that it must meet certain conditions in order to avoid harmful effects on humans and environment. It contains requirements for sludge quality used in agriculture, soil quality on which it is to be applied and restrictions on sludge use for certain crops and at certain times. One of the most important characteristics of sludge used agriculturally is its heavy metal content and the potential for soil contamination with these metals. The Directive defines limit values for heavy metals in soil to which sludge is applied and maximum annual quantities of heavy metals that may be introduced into soil through the application of sludge in agriculture.

In Poland, legal regulations for the sludge classification as waste are contained in the Regulation of the Minister of Environment, 9 December 2014 on the waste catalogue [3]. The waste producer (first waste holder), classifies waste taking into account, among other, the source of its generation, the specificity of the production process in which it is generated, as well as the chemical composition of waste. Article 96 in Waste Act [4] specifies the principles and conditions for the recovery of municipal sewage sludge consisting in its application on the ground or its introduction into the soil for the following purposes: (1) in agriculture, understood as the cultivation of all agricultural crops marketed, including crops intended for the fodder production, (2) for the cultivation of plants intended for the compost production, (3) for the cultivation of plants not intended for consumption and for the production of fodder, (4) for the reclamation of land, including land for agricultural purposes, (5) when adapting land to specific needs resulting from waste management plans, spatial development plans or decisions on the conditions of development and land use. The use of sludge on land is possible provided that the requirements of Article 96 of the Waste Act and the Regulation of the Minister of Environment, 6 February 2015 on municipal sewage sludge [5] are met. In Poland, the amount of municipal sewage sludge has been gradually increasing, with 370 thousand tonnes of d.m. produced in 2000 and 570 thousand tonnes of d.m. in 2020. In agriculture, the use of sludge has increased from 60 thousand tonnes of d.m. in 2000 to 140 thousand tonnes of d.m. in 2020 [6]. A prerequisite for the use of municipal sewage sludge in nature, including agriculture, is in compliance with the permissible content of heavy metals in sludge as well as Salmonella bacteria and live eggs of intestinal parasites. The regulation also stipulates permissible heavy metal contents in the topsoil on which municipal sewage sludge is to be applied. The significant content of organic matter and nutrients such as nitrogen, phosphorus, sulphur, magnesium and micronutrients essential for plants is in favour of agricultural use of sludge [7]. However, the incorporation of these nutrients into the soil with sludge should be in line with the generally applicable principles of fertilisation, while respecting the principles of environmental protection, including, among others, soil and water protection. Determining the application rate and carrying out tests to determine the sludge quality is crucial to fulfil and maintain the purpose of applying municipal sewage sludge into soil. An essential factor to apply the sludge into land is to find willing recipients – the landowners. The landowner should declare the cultivation of crops on which the application of municipal sewage sludge is allowed, having suitable equipment to spread and mix the sludge into soil, but also should base their actions on the code of good agricultural practice. However, sludge can contain toxic and harmful compounds including heavy metals, most of which are unnecessary for plants [8,9].

Metals, once released into the environment, do not disappear and have a very long environmental lifetime and can accumulate in plants and thus become incorporated into the biological cycle. Some metals such as copper and zinc are essential for living organisms, but an excess of them can cause negative effects. Negative symptoms of metal excess become apparent for 13 metals, but in case of lead and cadmium, the effects are the most harmful [8,10,11]. Metals are mainly concentrated in sewage sludge, with industrial wastewater and surface runoff being the source of metals. The total heavy metal content ranges from 0.5 to 2% d.m. of sludge [12]. Shrivastava and Banerjee [13] rank the heavy metal content as follows $Zn > Cu > Cr > Ni > Pb > Cd$. Inorganic matter and organic matter are responsible for the binding of heavy metals in sludge [14,15]. Inorganic matter of sludge consists of carbonates, phosphates, sulphides, and to a large extent non-crystalline oxides and hydroxides of Fe, Al and Mn. The organic matter in sewage sludge consists mainly of living organisms, dead organic debris (detritus) and a layer on mineral particles and has a high affinity for heavy metals [16].

Heavy metal ions are retained by solid sludge phase through a variety of mechanisms. These include: (1) ion exchange, (2) adsorption on internal and external mineral surfaces, (3) precipitation and co-precipitation. Many years of research in various countries have identified a downward trend in the content of heavy metals in sludge, however, some amounts can still be found. The level of heavy metals in sewage sludge can fluctuate considerably and, therefore, sewage sludge should be regularly examined for the dynamics of changes in chemical composition and biological parameters [17]. The overall content of metals in sludge is not a suitable indicator for assessing their bioavailability. A more authoritative assessment is to determine the occurrence

of bound metals by sludge components, or fractions. Many researchers usually use the BCR method proposed by the European Community Bureau of Reference, which includes the exchangeable fraction (ion-exchangeable and carbonate fractions), the reducible fraction and the hydroxide fraction, the oxidisable fraction (organic and sulphide) and the residual fraction [1,9,17,18]. A more accurate method is sequential analysis according to Tessier et al. [19], which separates the soluble, exchangeable, carbonate, reducible, oxidisable (associated with organic matter) and residual fractions. Therefore, the aim of the study undertaken was to determine the total content of the six heavy metals and the proportion of their respective fractions in municipal wastewater sludge at different treatment stages.

2. Study area and methodology

2.1. Description of the wastewater treatment plant

The treatment plant from which the sludge material was taken is located in Bialystok in north-eastern Poland. Its construction began in the 1970s and it was commissioned in the early 1990s. Activated sludge treatment technology is used there with a capacity of 100,000 m^3/d. At the beginning of the 21st century, the treatment plant was modernised to increase the removal of nutrients from wastewater. Wastewater from the city of Bialystok and the surrounding municipalities flows into the plant. The entire treatment process consists of three technological parts: mechanical, biological and sludge. Treated wastewater flows through a control and measurement station and is discharged to a receiver, which is the Biala river.

The sludge sequence begins when the activated sludge is separated in the secondary settling tank and then is returned by the activated sludge return and surplus sludge pumping station to the beginning of the treatment system as activated sludge. Some part of sludge is discharged from the system as surplus sludge and is directed to the mechanical thickening station and then to the II° pumping station. It is equipped with two sludge pumps with a capacity of 20–100 m^3/h each. The raw sludge separated in the primary settling tanks is cycled out and stored in the I° sludge pumping station, which has three pumps with a capacity of 100 m^3/h each. It is then directed to thickeners, which are designed to reduce the volume of primary sludge by separating and discharging the water from the surplus sludge and, in addition, they act as generators of volatile fatty acids to improve the efficiency of biological deforestation. The plant has 2 Bellmer Turbodrein thickeners with a capacity up to 100 m^3/h. The amount of thickened sludge varies between 1,000–1,600 m^3/d. After adequate thickening, the sludge is pumped via a raw thickened sludge pumping station to four fermentation chambers. Each chamber has a capacity of 7,700 m^3 and the capacity of the sludge section is 7,300 m^3. The chambers are cylindrical in shape and have three functions: thickening in the lower part, digestion in the cylindrical part and gas release from the small upper surface. 600–800 m^3 of sludge per day is directed to the chambers. Sludge fermentation in the chambers is carried out for 25–30 d at a temperature of 35°C–37°C. Sludge mixing is carried out using HALBERG-type mechanical tube mixers with a capacity of 3,000 m^3/h, V_{rot} – 490 rpm, with a

motor power of 22 kW. The digested sludge from the separate digesters is transported to two retention tanks with a capacity of 600 m^3 each. The digested sludge undergoes a drying process for further use as fertiliser or fuel.

2.2. Research methodology

The study was carried out on sludge samples collected from the wastewater treatment plant in Bialystok. Samples were taken in four study periods: T I – autumn (November), T II – winter (February), T III – spring (April) and T IV – August (summer) in 2019/2020. Samples were taken in the middle month of a given quarter. Three sludge samples were analysed in each cycle. The average sample consisted of six individual samples of excess, digested and dried sludge.

To determine the total heavy metal content, the sludge samples were dried at 105°C to determine their dry weight and then mineralised in a BUTCHI Speed Digester K-425 using the reagents: 8 cm^3 of nitric acid – 65% HNO_3 and 10 cm^3 of perhydrol – 30% H_2O_2. The process involved thermal decomposition of samples and the transition of complex organic compounds to simple inorganic compounds. In this way, samples were prepared for quantitative analysis of total metal content.

Metal fractions were then determined in the sludge using the method of Tessier et al. [19]. Metals in sludge are bound by the individual constituents present in this waste. This process depends largely on sludge properties and its processing at the treatment stage in the plant. Tessier [19], Wilk and Gworek [20] describe six fractions of metals found in sewage sludge:

- F1 – soluble fraction metals that are present in solution and dissolve in water. It is the ionic form and metals in complex combinations with mineral and organic ligands. The fraction is extracted with redistilled water.
- F2 – exchangeable fraction include the bound metals in an exchangeable manner to the solid components of the sludge by electrostatic interaction. The metal ions released in ionic form and their amount depends on sorption and desorption processes. The amount of metals present in this fraction oscillates around 2% and is easily released once the sludge is introduced into soil. Extraction is caused by CH_3COONH_4 at a concentration of 1 M and 3 pH.
- F3 – carbonate fraction comprises metals associated with carbonates, phosphates and sulfates. It is a fraction that is very susceptible to changes in the natural environment, most notably an increase in acidification, causing a decrease in carbonates, and thus changes in Zn, Cd, Ni, Mn, Ca bound to carbonates can occur. This process depends on the amount of metals in sludge and its type. The extractant was CH_3COONa at a concentration of 1 M and 5 pH.
- F4 – reducible fraction consists of metals bound to oxides of Mn, Fe and Al. This fraction is sorbed or co-precipitated with iron and manganese oxides and hydroxides. They form concretions and interlayer binders covering the mineral particles. They form strong coordination bonds with functional groups of hydrated Fe and Al oxides and silicates, they can be occluded on Fe, Mn

oxides. This fraction is not very stable under low oxidation–reduction potential (Eh) conditions and is present in low amounts in sludge due to thermodynamic instability, anaerobic conditions in sludge and microbial activity. Under anaerobic conditions, reduction of Mn, Fe oxides can occur, resulting in unblocking of heavy metal adsorption. The fraction was extracted with 0.04 M NH_2 + HCl in 5% (v/v) CH_3COOH.

- F5 – oxidisable fraction includes metals bound to organic matter and sulphides and can be released by mineralisation under oxidising conditions. Organic matter binds heavy metals mainly by adsorption, formation of chelate and complex linkages, and heterocyclic bonds. In sludge, organic matter occurs mainly in macromolecular compounds from which metals are released into the environment in small amounts. They form strong metal–organic complexes with metals, which significantly limits their mobility. Extraction with 0.02 M HNO_3 + 30% CH_3COONH_4 in 20% (v/v) HNO_3.
- F6 – residual fraction is the amount of metals incorporated into the crystal lattice of primary and secondary minerals. The metals in this fraction are unavailable to plants. They vary widely and depend mainly on the source of sludge. It has been determined in royal water.

Total content of metals and their fractions were measured by ICP-AES. Prior to analysis, optimisation of the instrument conditions was performed with a mixture of Ce, Co, Li, Tl, Y, Mg standards (Inorganic Ventures) at a concentration of 1 ppb in a 2% HNO_3 solution. During the analysis, the addition of an internal standard (mixtures of Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Ti, W, Zr) of 100 ppb was used to control the stability of the analytical process. The instrument operating parameters are shown in the table. Certified reference materials were used during the analytical procedure: BCR-145R sewage sludge (Institute for Reference Materials and Measurements) and NCS DC 73023 soil (National Analysis Center For Iron & Steel). Recoveries of the analytes tested were obtained in the range of 91%–103%.

2.3. Statistical analysis of research results

Statistical analysis was performed using the computer programme STATISTICA version 12. An analysis of variance – one-way classification ANOVA (analysis of variance) was used to compare several populations. This is a technique for examining outcomes (dependent or explanatory variables) that depend on a single acting factor (grouping or classification factor). It was tested whether the analysed factors effected the observed results. The aim was to test the significance of differences in population means. Using analysis of variance, the significance of differences between multiple averages from multiple groups (populations) is tested. When the averages differ significantly between each other, it can be concluded that the analysed factor influences the dependent variable. When the averages belonging to different groups differ significantly, and those belonging to one group are statistically equal (homogeneous) – based on the tests, it was concluded that: when $p > 0.05$, the differences are insignificant, when $p < 0.05$ the differences are statistically significant, at the assumed significance level of $p = 0.05$. The assumptions of one-factor analysis of variance were checked (based on Bartlett's test and Levene's test, as well as on the graphs of normality of the variables and Shapiro–Wilk's normality test, and it was found that the assumptions of variance analysis were not met: although the variable analysed within k comparison groups is measurable and the samples were drawn randomly, most of the groups do not have normal distributions and mostly the distributions do not have equal variances. In result, Kruskal–Wallis non-parametric tests were used to assess the significance of differences between groups as the non-parametric equivalent of one-way variance analysis. Subsequently, multiple comparison procedures – posthoc tests were used to check which of the means differed and which were equal. These procedures are based on comparing the differences between pairs of sample means with the size of least significant difference (LSD). Among many tests, the Tukey HSD (Honestly Significant Difference Test) was selected as the most popular and recommended test for comparing pairs of means.

The following issues were analysed: (1) Analysis if the percentages of individual metals in sludge differ significantly from each other depending on: metal fraction, test date and sludge type (analysis of the differences significance in the content of metals in different sludge depending on their fractions). (2) Analysis of the differences significance in the total content of different metals in sludge depending on their fraction and test date.

3. Results

Total content of heavy metals in tested sludge was low and did not exceed the content for sludge intended to use in agriculture and land reclamation for agricultural

Table 1
Total zinc, copper, chromium, nickel, lead and cadmium mg/kg sludge d.m.

Date/metal	Excess sludge				Mean	Post-fermentation sludge				Mean	Dried sludge				Mean
	I	II	III	IV		I	II	III	IV		I	II	III	IV	
Zinc	437	678	1,211	761	772	846	545	799	769	740	546	574	458	473	513
Copper	92	116	193	59	115	91	70	140	106	102	56	80	57	81	69
Chromium	21	26	58	16	30	35	38	35	33	35	26	27	26	21	25
Nickel	27	15	29	10	20	29	14	19	25	22	18	13	11	14	14
Lead	9	10	14	11	11	23	7	9	14	13	11	8	7	10	9
Cadmium	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.1	0.1

purposes according to the Regulation of the Minister of the Environment of 6 February 2015. Sludge included the highest content of zinc, followed by copper, then chromium, nickel, lead and the least amount of cadmium. The zinc content differed significantly than the other metals content. Nickel and lead contents was at similar level during the study period. Regardless the sampling date, the average total metal content of Zn, Cu. Cr, Pb, Ni, Cd was similar in excess sludge and post-fermentation sludge. The fermentation process did not reduce the total zinc content, but increased it in case of other metals. In contrast, there were significantly fewer metals in sludge after drying with respect to the surplus and post-fermentation sludge. The variability in metal content on sampling dates was the highest for surplus and fermented sludge. For dried sludge, the sampling date was not significant for total metal content.

The distribution of zinc fractions in total content depended on the type of sludge and the date of collection (Figs. 1 and 2). The highest proportion of zinc was observed in each sludge in the fourth reducible fraction, that is, zinc bound to Mn, Fe and Al oxides, which was significantly higher compared to the other fractions. The average proportion in the study period was similar in all sludge types and was over 50%. The timing of sampling influenced the zinc proportion in this fraction and was different for each sludge type. The soluble fraction of zinc in analysed sludge was low and did not exceed its share of 2% and varied little with sampling date and sludge type. In contrast, the exchangeable fraction accounted for more than 20% in excess sludge and fermented sludge and nearly 20% in dried sludge. It varied due to the sampling date or external conditions such as temperature. The tertiary fraction associated with carbonates varied widely from 1.5% to 10.4% in the excess sludge

depending on the sampling date, and the proportion of this fraction varied less in other sludge along with the sampling dates. The highest proportion of zinc in this fraction occurred in dried sludge compared to more hydrated sludge. Little zinc was associated with organic matter and the proportion of this fraction did not exceed 1.5%. To a small extent, the proportion of this fraction varied according to the type of sludge and sampling date. The share of the residual fraction increased sequentially in analysed sludges. The fermentation process caused an increase in the share of this fraction by nearly twice as much for excess sludge and, successively, the drying process caused further 4% points increase of post-fermentation sludge. The proportion of zinc fraction varied significantly depending on sampling date and sludge type.

The share of copper in soluble fraction was the highest in excess sludge reaching 15.4% on average (Fig. 3). In post-fermentation sludge, it halved in excess sludge, but there was a slight increase of its content in soluble fraction in dried sludge. The content of copper was significantly changeable in this fraction depending on sampling date in more hydrated sludge, and less in dried sludge (Fig. 4). Copper in sludge was mainly accumulated in fraction V associated with organic matter which was dominant and significantly higher compared to most of other fractions. A slightly lower proportion of copper was recorded in second fraction of analysed sludge. In the excess and post-fermentation sludge, both fractions were predominant in comparison to dried sludge. The distribution of copper in second fraction varied according to the date of sludge sampling, while in fifth fraction this relation was not noted and the proportion was similar in individual sludge sampled at different dates. A small amount of copper was associated with Mn, Fe, Al oxides and it reached the level of 3.5%–4.3%. The proportion of copper
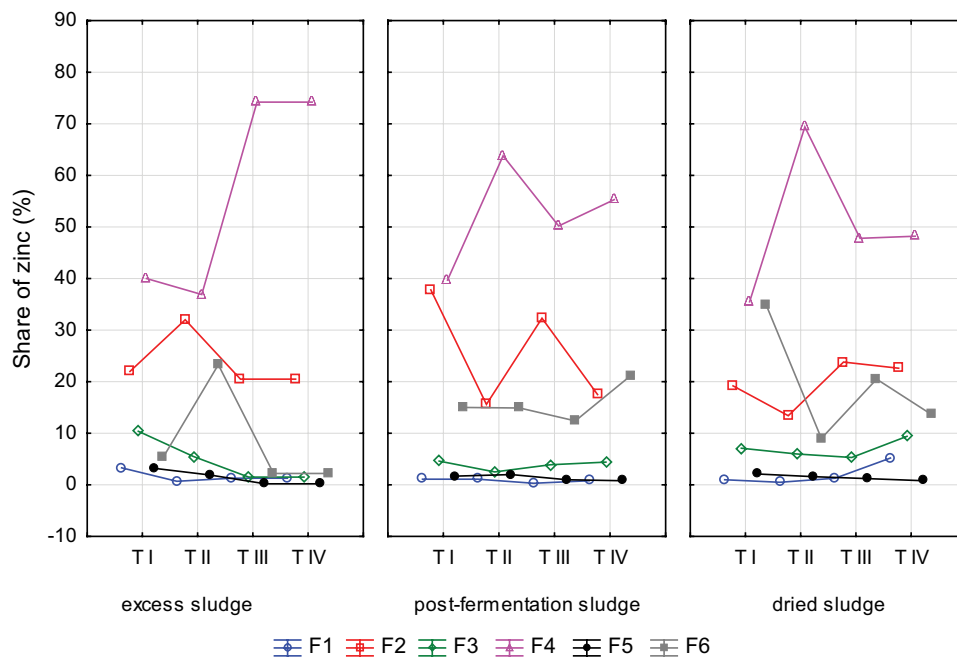

Fig. 1. Share of zinc fractions in particular sludge according to sampling date (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).
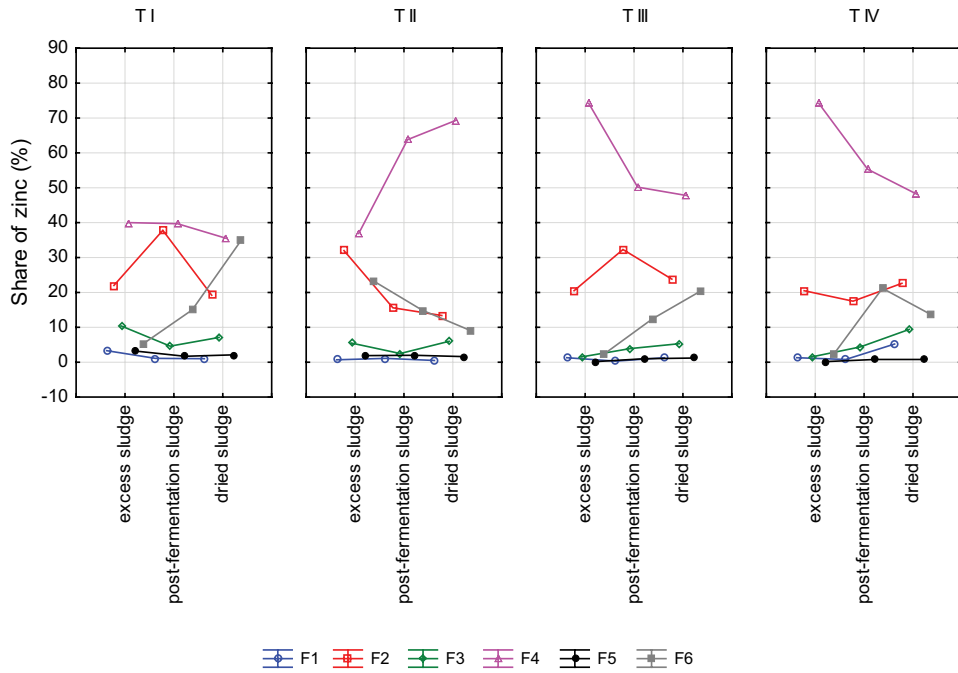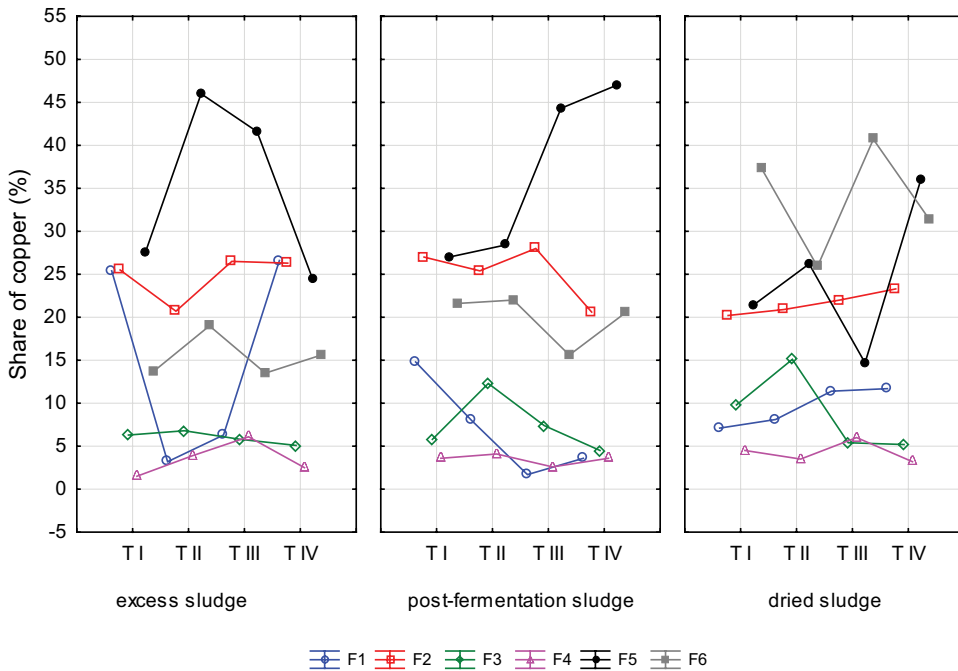
Fig. 2. Share of zinc fraction in sludge according to sampling date and sludge type (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6– residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).

Fig. 3. Share of copper fractions in particular sludge according to sampling date (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).

in fourth fraction varied little between sludge types. It varied more according to sampling date of three sludge types. Little copper was associated with carbonates (fraction III) and this proportion increased with sludge type and was the highest in dried sludge. Copper content in residual fraction was at its lowest level in excess sludge, increased slightly in post-fermentation sludge more than twice in dried sludge compared to the other two sludge types. The sampling dates had little effect on the proportion of copper in residual fraction.
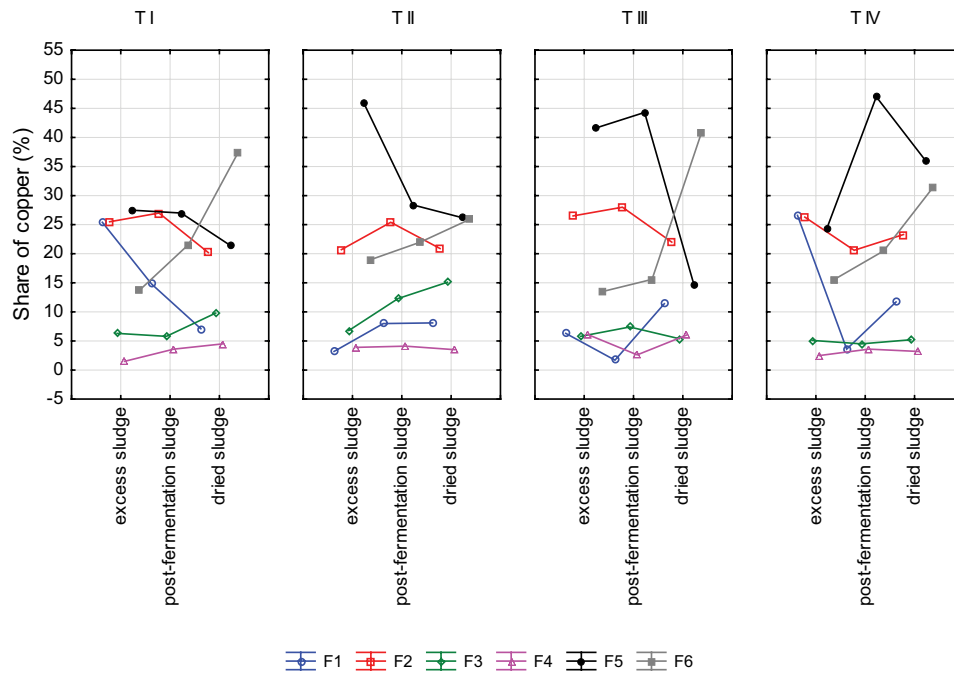
Fig. 4. Share of copper fraction in sludge according to sampling date and sludge type (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).
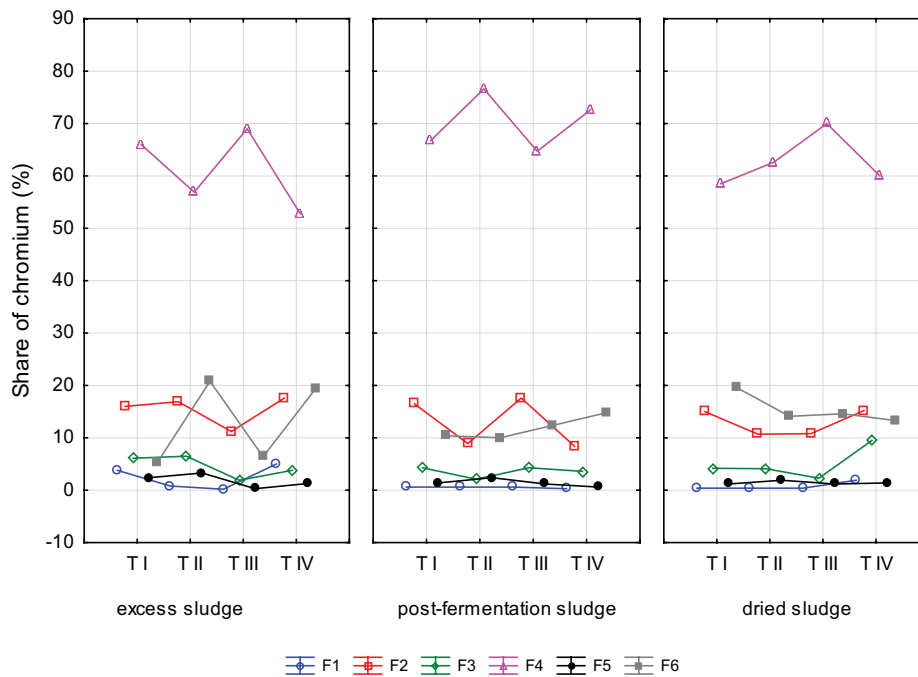

Fig. 5. Share of chromium fractions in particular sludge according to sampling date (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).

Chromium slightly occurred in soluble fraction and reached 2.5% in surplus sludge and less than 1% in the other sludge (Fig. 5). In excess sludge, the proportion of chromium fraction varied in samples taken at different dates (Fig. 6).

This relationship was not observed in fermented and dried sludge. The proportion of chromium in exchangeable fraction amounted to several per cent, it was significantly higher in excess sludge, while in case of other sludge types, it was
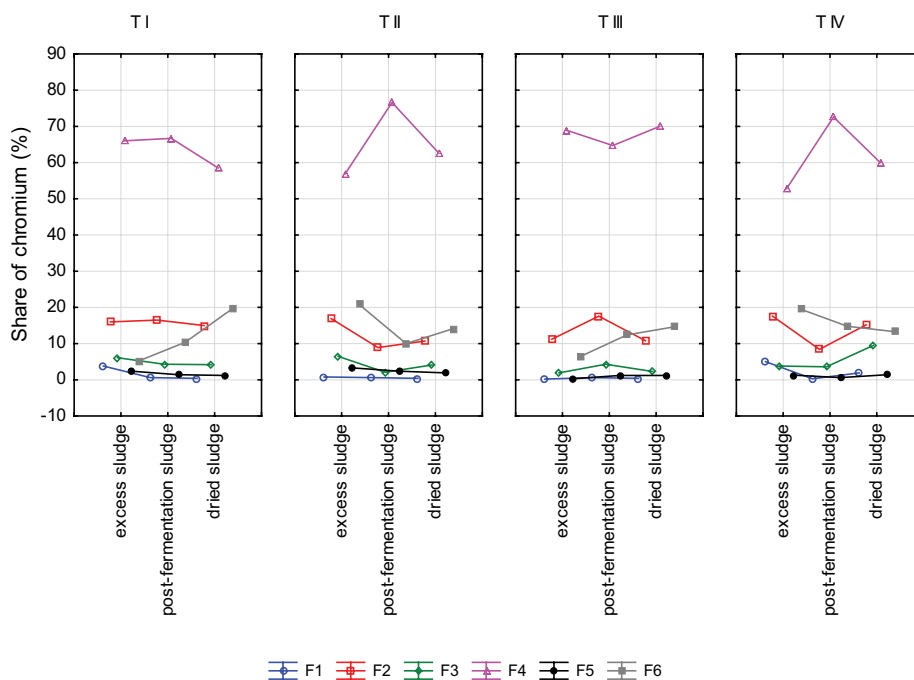
Fig. 6. Share of chromium fraction in sludge on each sampling date according to sludge type (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn term, T II – winter term, T III – spring term, T IV – summer term).

lower and similar to each other. Sampling date more effected the variation of chromium proportion in fermented and dried sludge relatively to excess sludge. Chromium was slightly associated with carbonates (fraction III) and the proportion in this fraction was ranging between 3.4% and 5.0% and varied little between sludge types. Proportion of this fraction between sludge was influenced by sampling date. The dominant fraction for this metal was fraction IV, a combination with Mn, Fe, Al oxides, and this fraction proportion was over 60% for all sludge and this fraction was significantly higher than the other fractions. The highest proportion of this fraction was in the post-fermentation sludge and was significantly different from the other sludge. The sampling date did not significantly affect the proportion of chromium in this fraction. The proportion of chromium in the oxidisable (V) fraction was low and similar in the analysed sludge. In the samples of excess and post-fermentation sludge taken at different dates, the proportion of chromium was diversified in this fraction. In the dried sludge, this relationship was not observed. The proportion of chromium in the residual fraction amounted to several percent on average in the analysed sludge and varied little between sludge types. It diversified significantly in excess sludge taken at different dates. In the other sludge types, the sampling date had no significant effect on the proportion of chromium in this fraction.

Nickel was almost equally distributed in three fractions: II, III and IV of sludge studied (Fig. 7). The proportion varied according to sludge type and their sampling date (Fig. 8). The second (exchangeable) fraction of nickel in excess sludge increased with sampling date, in the fermented and dried sludge such relationship was not found, although some relation of nickel concentration in analysed sludges with sampling date can be observed. The proportion of carbonate

fraction in excess and dried sludge was significantly lower than in the fermented sludge. In excess and fermented sludge, the proportion of nickel fraction varied significantly between sampling dates, while in dried sludge it was similar over the study course. F4 nickel fraction was dominant in all analysed sludge and varied most on sampling dates in excess sludge, and to lesser extent in other sludge. Soluble nickel (F1) amounted to 7.5%–10.4% on average in studied sludge. It was lowest in excess sludge and highest in dried sludge, but the differences between sludge types were not significant. In contrast, date of sludge sampling clearly differentiated the proportion of nickel in the fraction for excess and post-fermentation sludge, and to a lesser extent in dried sludge. There was a low proportion of nickel in the fraction bound to organic matter and it was evenly distributed in analysed sludges and little affected by sampling date. The residual fraction of nickel in studied sludge was more variable. In excess sludge, there were substantial changes in nickel proportion in this fraction depending on sampling date. In post-fermentation sludge, this fraction included less nickel and it was at the similar level over the study period. In dried sludge, there was the highest amount of nickel in this fraction and it was significantly variable over the study period.

lead was significantly most abundant in residual fraction of tested sludges (Fig. 9). In excess sludge, there was significantly less lead in this fraction than in the post-fermentation and dried sludge, in which lead share was comparable. The share of lead in this fraction varied across the sampling dates of *t* post-fermentation sludge, and to a lesser extent in dried sludge (Fig. 10). Soluble fraction of lead reached very low level of 2.4% on average in excess sludge over the study period, while in other sludge it oscillated around 1%. The dates of study were not significant in the variation of
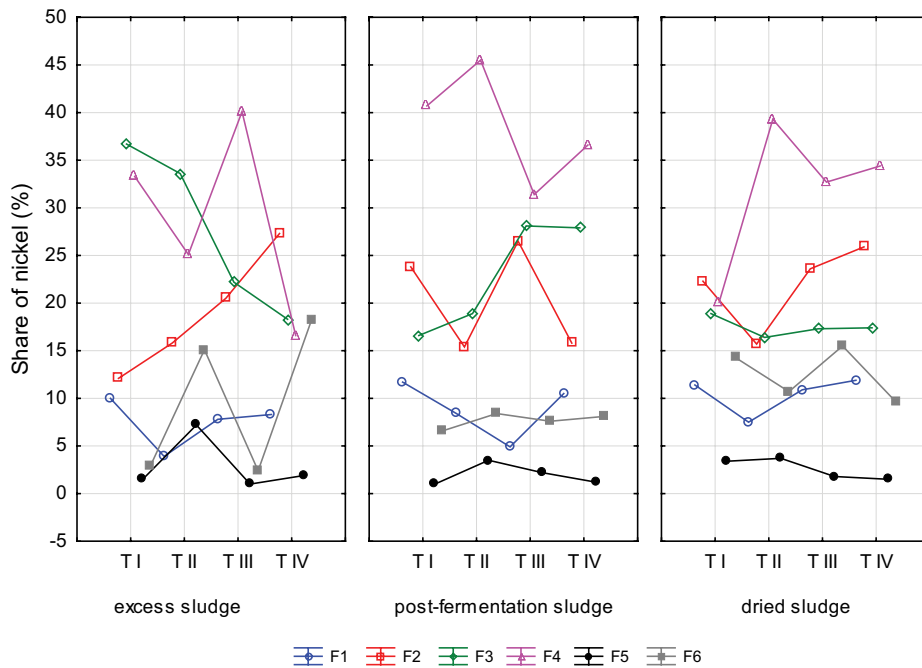
Fig. 7. Share of nickel fractions in particular sludge according to sampling date (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).
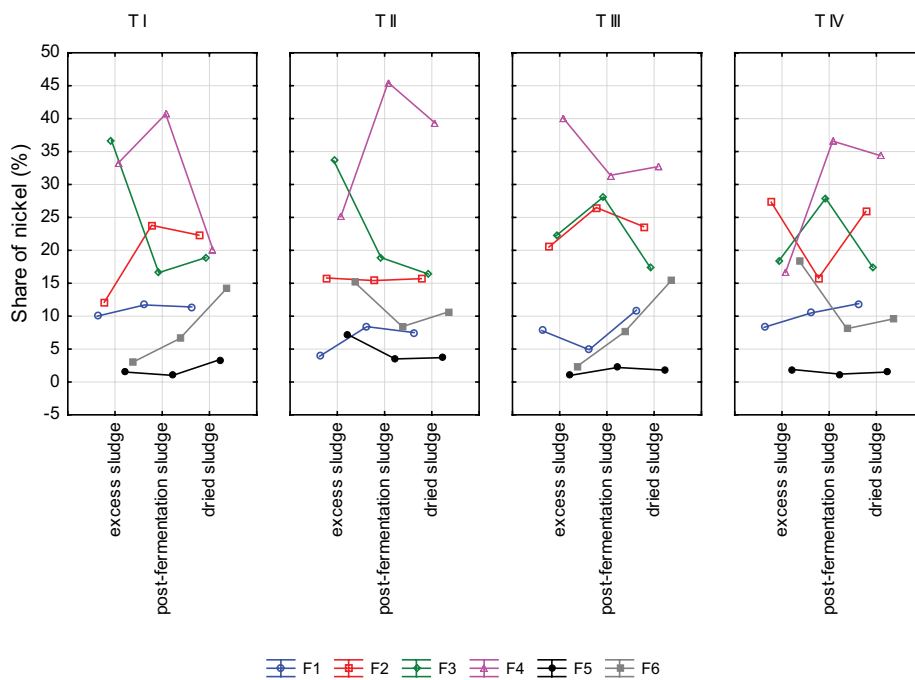

Fig. 8. Share of nickel fraction in sludge on sampling dates according to sludge type (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).

this fraction for all sludge types. The exchangeable fraction of lead in excess and dried sludge was similar, and it was lower by nearly 5% in fermented sludge. The proportion of lead in this fraction of tested sludge varied the most on most dates (I, II, IV), and it was similar on third date. The

fraction with carbonates reached low level, while it was significantly higher in excess sludge compared to fermented and dried sludge. On first date, the share of lead fraction III was significantly different between sludge types, and on other dates it was similar. The average share of fraction IV
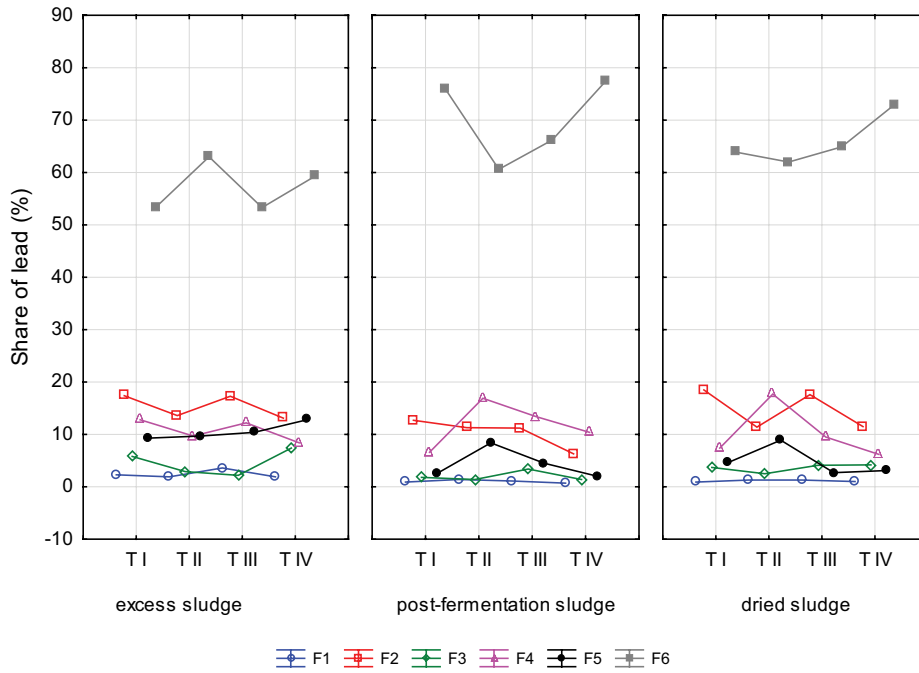
Fig. 9. Share of lead fractions in particular sludge according to sampling date (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).=
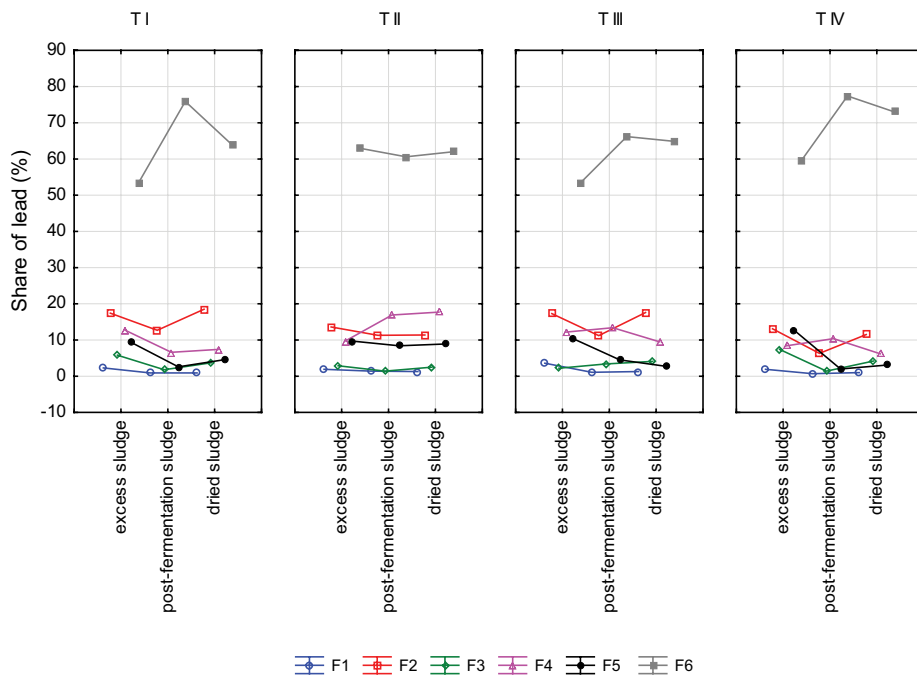

Fig. 10. Share of lead fraction in sludge on sampling dates according to sludge types (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).

during the study period was similar in the analysed sludge types and it reached about 11%. Lead content was ranging at similar level in this fraction due to the sampling date of excess sludge, but it was more diversified in post-fermentation and dried sludge. Lead share in the fraction associated with organic matter was the highest in excess sludge, and much lower in other sludge types. The sampling date had the greatest effect on the distribution of lead in this fraction in the post-fermentation and dried sludge, and it was similar in excess sludge over the study period.

The highest and statistically proven share of cadmium in tested sludges was in fraction VI (residual) (Fig. 11). The proportion in this fraction was significantly lower in excess sludge with respect to the other two sludge. Over the study period, this fraction varied the most in excess sludge, and was similar in the fermented and dried sludge (Fig. 12). The soluble fraction was low and varied between sludge types. It was the highest in excess sludge and the lowest, (only 1%) in
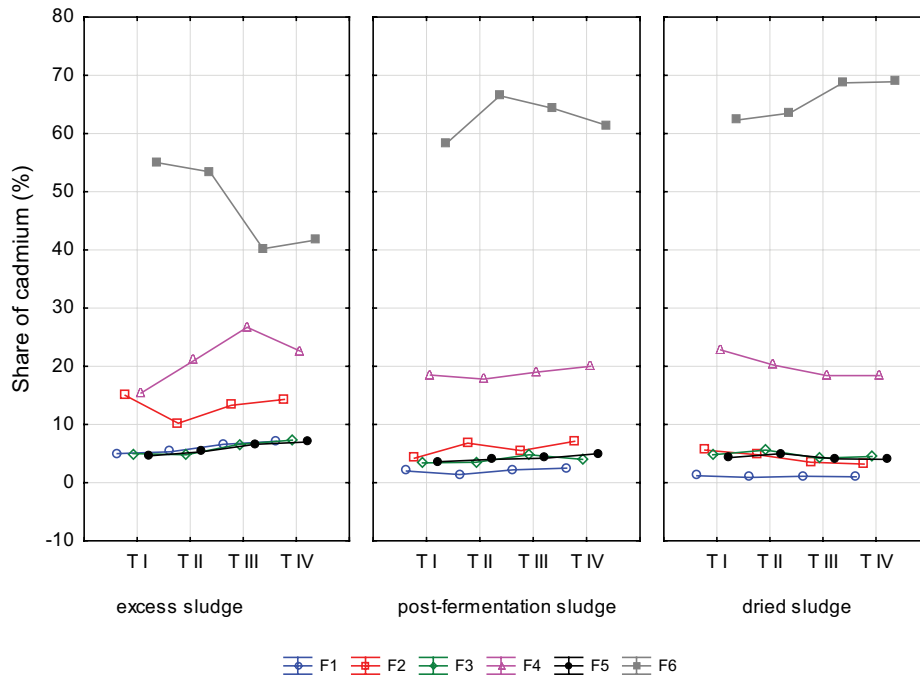

Fig. 11. Share of cadmium fractions in particular sludge according to sampling date (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).
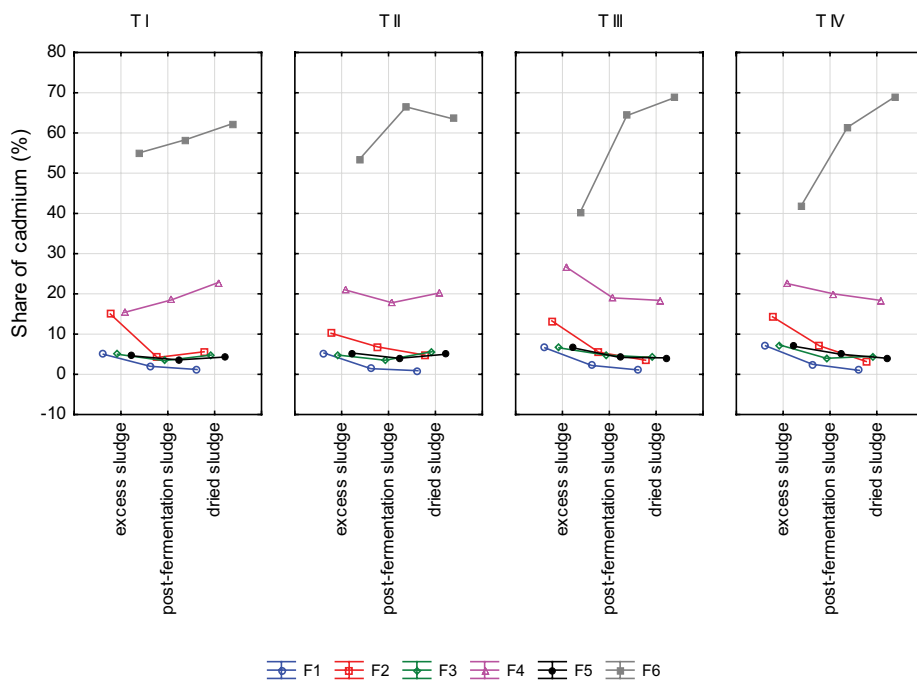

Fig. 12. Share of cadmium fractions in sludge on sampling date according to sludge type (F1 – soluble fraction, F2 – exchangeable fraction, F3 – carbonate fraction, F4 – reducible fraction, F5 – oxidisable fraction, F6 – residual fraction; T I – autumn date, T II – winter date, T III – spring date, T IV – summer date).

dried sludge. The sampling dates did not significantly effect the contribution of this fraction in total cadmium. Similar relationships were found in case of exchangeable fraction II, and its share ranged from 4.3% on average in dried sludge to 13.2% in excess sludge. The fraction with carbonates (III) amounted to a few percent and was similar in all sludge types and sampling dates of particular sludge did not differ it significantly. Fraction V included only a few per cent of cadmium and these values were similar in all sludge types. The sampling date effected slightly the proportion of this fraction of cadmium in studied sludge. The share of cadmium in fraction IV (reducible) was higher compared to fractions I, II, III and V reaching about 20% on average in all sludge types and it was similar over the study period in post-fermentation and dried sludge, while in excess sludge it varied more over the study period.

3. Discussion of results

The total content of heavy metals in sewage sludge does not fully reflect the risk they may pose to the ecosystem. Their mobility and availability to living organisms is important. As occurred in case of analysed sludge, heavy metals can pose a potential threat even at low total content and move through the trophic chain. Zinc was the most abundant in sludge, followed by copper, then chromium, nickel, lead, and the least of cadmium. A similar range of total metal content in sludge was reported by Wang et al. [9], Shrivastava and Banerjee [13] and Tytła et al. [21]. The content of metals in sludge from the analysed treatment plant has decreased significantly compared to the contents reported by the authors, who had previously studied sludge from this treatment plant [7,22,23]. It is caused by much smaller content of industrial wastewater discharged to Bialystok treatment plant. The analysed sludge, irrespective of its processing stage, contains small amounts of metals and it is suitable for natural use including agricultural, as it does not exceed the limits specified in the Regulation of the Minister of Environment for Polish conditions [5]. Speciation analysis of heavy metals contained in sludge aimed at assessing the possibility of their migration to soils and water under agricultural conditions. In examined sludge, irrespectively of sampling date and sludge type, the distribution of metals in fractions was as follows: Zn: reducible > exchangeable > residual > carbonate > oxidisable > soluble, Cu: oxidisable > exchangeable > residual > soluble > carbonate > reducible, Cr: reducible > residual > exchangeable > carbonate > oxidisable > soluble, Ni: reducible > carbonate > exchangeable > residual > soluble > oxidisable, Pb: residual > exchangeable > reducible > oxidisable > carbonate > soluble >, Cd: residual > reducible > exchangeable > carbonate > oxidisable > soluble. Shrivastava and Banerjee [13], based on their own research, report a slightly different ranking of the different metal fractions in sludge: (1) Cu: residual > carbonate > oxidisable > reducible > exchangeable; (2) Zn: residual > reducible > carbonate > oxidisable > exchangeable; (3) Pb: residual > reducible > oxidisable > carbonate > exchangeable; (4) Ni: residual > oxidisable > reducible > carbonate > exchangeable; (5) Cr: residual > oxidisable > carbonate > reducible > exchangeable; (6) Cd: residual > carbonate > reducible > oxidisable > exchangeable. When

sludge is introduced into soil, the soluble forms (F1) and those bound interchangeably with solid sludge particles (F2) are the fastest to pass into soil solution. The mobile fractions also include the fraction bound to carbonates (F3). In studied sludge, the predominance of mobile fractions over non-mobile ones occurred only in case of nickel. Jamali et al. [24] and Zhao et al. [25] state, based on their own studies, that in sludge subjected to treatment, heavy metals are predominantly found in the non-mobile fractions.

Non-mobile fractions occurred in more than 60% of remaining metals. As a result of the processing of analysed sludge, such as fermentation and drying processes, the proportion of non-mobile fractions increased in most metals. Among the non-mobile fractions, the residual fraction, in which mainly lead and cadmium occurred, is considered as inaccessible to plants. The group of non-mobile fractions also includes reducible fraction, that is, metal-oxide combinations of Mn, Fe and Al, with which zinc, chromium and nickel were most associated. Zinc in studied sludge was mainly associated with F4 reducible fraction (iron and manganese oxides), which is sensitive to changes in redox potential. This metal occurrence in reducible fraction is caused by the amount of iron sulphate added to precipitate hardly soluble iron sulphate phosphates from the wastewater, on which its sorption may occur [26]. Zinc was present in about 20% of the exchangeable fraction, and it was present in small amounts in other fractions compared to reducible and exchangeable fractions. Exchangeable fraction can become mobile once the sludge is brought into soil and is dependent on sorption and desorption processes [16,27]. The study showed that copper had a significant affinity for organic compounds. The mobility of these compounds depended on the molecular mass, and they may undergo some mobility during decomposition of organic matter. An increase in ion-exchangeable forms of copper was observed in tested sludge. According to other authors, it may be caused by the formation of mobile anionic forms $[Cu(OH)_3]^-$, $[Cu(OH)_4]^{2-}$ and $[Cu(CO_3)_2]^{2-}$ [26,28]. The distribution of chromium in sewage sludge was mainly associated with the reducible and residual fractions and about 13% with exchangeable fraction. The share of chromium differed from that reported by other authors [29–31], who indicated oxidisable fraction associated with organic matter as the predominant fraction. In other fractions, Cr accounted to a small share. The main factors influencing the fraction and sorption of chromium are redox potential and pH. As acidity increases, Cr^{3+} sorption increases and Cr^{6+} sorption decreases. In tested sludge, the reaction was slightly alkaline and Cr^{6+} sorption predominated. Nickel in sewage sludge was particularly easily bound by Fe/Mn oxides, carbonate fraction and reducible fraction. In sewage sludge, this element formed several percent of ion-exchange fraction. Hanay et al. [17] reported that soluble and exchangeable fraction of nickel and oxidisable fraction predominated. Lead in sludge was mainly associated with the F4 residual fraction, reaching more than 60% of total content. The distribution of this metal in fractions depends on the inflow of industrial, rainwater effluents and the properties of sludge including hydration status and pH. In acidic environments, mobile forms of lead occur mainly as Pb^{2+} and − $PbHCO_3$ cations and organic complexes [30]. Cadmium was more associated with F6 and F4 fractions

than with other fractions. This share of cadmium is mainly determined by the reaction of sludge. As alkalinity increases, the sorption of this metal decreases, probably caused by its displacement from the sorption complex by alkaline metal cations Ca^{2+} and Mg^{2+}. Precipitation of phosphorus from effluent after the addition of coagulants caused cadmium to move to oxide-bound (reducible) fraction [9,26,28]. When sludge is applied to soil and mixed, heavy metal fractions are transformed, resulting in their bioavailability changes. These changes are caused by the changes of equilibrium and kinetic reactions in soil. Some of metals are absorbed by organic matter, clay minerals, oxidised forms of iron and manganese, calcium carbonate contained in soil. This process results in a reduction in proportion of metals in dissolved form. Most of soluble copper and a part of zinc, cadmium and nickel are complexed with organic matter of soil.

The distribution of metals in examined sludge varied according to the treatment method. The highest number of metals in mobile fractions occurred in excess sludge, which was probably caused by assimilation of these elements by activated sludge microorganisms. Metals may have been released in ionic form from the sludge flocs into aqueous solutions [21,32,33]. The proportion of immobile fractions of most metals increased after sludge fermentation process. An increase in content of these fractions was observed in the following order: chromium (15.9%), cadmium (12.3%), nickel and lead (7% each), followed by copper (6.2%) and zinc (3.9%). Fermentation process effect the reduction of mobility of heavy metals in the tested sludge, and thus may increase the chances of natural utilisation of sludge after this process. Gawdzik and Długosz [34] in their study obtained significant reduction in mobility of chromium, zinc and copper in sludge after fermentation process. Fermentation is a biological anaerobic process that results in the decomposition of high molecular weight organic compounds. This process leads to the stabilisation of sludge properties. It is determined by a number of factors such as chemical composition of sludge (including change in total metal content and distribution of metals in particular fractions), duration of fermentation process, pH, VFA content, mixing intensity, total nitrogen and phosphorus content. The following results are observed: reduction in sludge volume, reduction in specific resistance, deprivation of sludge ability to rot and reduction in content of pathogenic organisms in sludge. The increase in immobile fractions in sludge after fermentation may be related to the increase in sludge pH. Other authors report that the fermentation process raises pH, which was observed in examined sludge [21,34]. Slight shift of mobile to non-mobile fractions was obtained in dried sludge, compared to after-fermentation sludge. These fractions increased in copper more than by 7%, cadmium by nearly 3%, zinc by 2%, While a slight reduction in content of non-mobile fractions was observed in case of lead by 5%, chromium – 4%, and nickel by 1.6%. The drying process did not significantly affect the distribution of zinc in fractions. Reducible fraction was dominant. In dried sludge, some amount of this metal was moved from oxidisable fraction to residual one. Heavy metals present in the oxidisable fraction in sludge are mainly combined with organic matter of large particles. A part of organic matter in sludge has low-molecular-weight form (organic acids, polysaccharides, amino acids and polyphenols), which can be degraded during sludge drying. Zinc bound to this fraction may have shifted to the residual fraction and, as a result of the sorption process, may have been retained by hardly soluble iron phosphates present in this fraction [16]. Chromium remained almost at the same level, with an increase in residual fraction at the expense of reducible fraction. Similar relationship was observed for nickel. After sludge drying, the proportion of exchangeable fraction increased and the connections to carbonates decreased slightly. The share of lead in exchangeable fraction increased and residual fraction lowered slightly. In case of cadmium, an increase in residual fraction was observed, while the others remained almost unchanged. Such condition is beneficial for aquatic environment when such sludge is used for fertilisation. Different results were presented by Dąbrowska [35], metals were concentrated mainly in the residual fraction in dry sludge, followed by organic and carbonate fractions.

Sampling dates of sludge influenced the increase in total metal content. It also effected their distribution in particular fractions to some extent. The greatest increase in metal content was observed in samples taken on third date (spring). It was caused by the inflow of rainwater and snowmelt. The increase occurred in all metals except cadmium in all sludge types [1,36].

5. Summary

Examined sludge, irrespective of sampling date and processing method, contained small amount of heavy metals, meeting the requirements for their use for agricultural purposes contained in the European Union Directive and the Regulation of the Minister of Environment in Poland. Zinc was the most abundant in sludge, followed by copper, chromium, nickel, lead and negligible amount of cadmium. The share of fractions of analysed metals was element specific. The metals were mainly found in non-mobile fractions (F4, F5, F6), with the exception of nickel, which was predominantly found in mobile fractions (F1, F2, F3). Zinc was mostly determined in reducible fraction, followed by exchangeable fraction. In case of copper, oxidisable fraction (F5) was dominant and largely exchangeable. Chromium was most abundant in reducible and residual fraction. Nickel was mainly distributed in reducible, carbonate and exchangeable fractions. Lead and cadmium, on the other hand, dominated in residual fraction. Sludge treatment processes, especially fermentation process, reduced the mobility of metals by transferring some of them from mobile to immobile fractions. The increase in heavy metal content of examined sludge was influenced by the inflow of rainwater and snowmelt in the first quarter of 2020 (T III). Sampling dates determined less the distribution of metals in the individual fractions.

References

[1] A. Wojciula, D. Boruszko, A. Kacprzak, Distribution of heavy metal fractions in sewage sludge from a selected municipal sewage treatment plant, Rocznik Ochrona Środowska, 23 (2021) 369–383.

[2] Council Directive of 12th June 1986 on the Protection of the Environment, and in Particular of the Soil, When Sewage Sludge is Used in Agriculture (86/278/EEC).

[3] Regulation of the Minister of Environment of December 9, 2014 on the Catalog of Waste (Dz. U. z 2014 r., poz. 1923).

[4] Act of Waste of 14 December 2012 (Ustawa o odpadach z dnia 14 grudnia 2012) (Dz.U.2022.0.699) (in Polish).

[5] Regulation of the Minister of the Environment of February 6, 2015 on Municipal Sewage Sludge (Rozporządzenie Ministra Środowiska z dnia 6 lutego 2015 r. w sprawie komunalnych osadów ściekowych) (Dz. U. z 2015 r., poz. 257) (in Polish).

[6] Yearbook of Environmental Protection 2021, Central Statistical Office.

[7] J. Wiater, A. Butarewicz, Ways of using sludge from the Bialystok Wastewater Treatment Plant (Sposoby wykorzystania osadów z Oczyszczalni Ścieków w Białymstoku), Inżynieria i Ochrona Środowiska, 17 (2014) 281–291 (in Polish).

[8] J.P. Hillman, J. Hill, J.E. Morgan, J.M. Wilkinson, Recycling of sewage sludge to grassland: a review of the legislation to control of the localization and accumulation of potential toxic metals in grazing systems, Grass Forage Sci., 58 (2003) 101–111.

[9] C. Wang, X. Hu, M.-L. Chen, Y.-H. Wu, Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants, J. Hazard. Mater., 119 (2005) 245–249.

[10] A. Kabata-Pendias, M. Piotrowska, T. Witek, Assessment of the Quality and Potential for Agricultural Use of Heavy Metal Contaminated Soils. Information From the Bulletin on Assessment of Heavy Metal and Sulphur Contamination of Soils and Plants. Framework Guidelines for Agriculture (Ocena jakości i możliwości rolniczego użytkowania gleb zanieczyszczonych metalami ciężkimi. Informacje z biuletynu nt. Ocena stopnia zanieczyszczenia gleb i roślin metalami ciężkimi i siarką. Ramowe wytyczne dla rolnictwa), IUNG Puławy, 1993, pp. 5–14 (in Polish).

[11] H.G. Snyman, Characterisation of sewage sludge metals for classification purposes using the potentially leachable metal fraction, Water Sci. Technol., 44 (2001) 107–114.

[12] S. Babel, D. del Mundo Dacera, Heavy metal removal from contaminated sludge for land application: a review, Waste Manage., 26 (2006) 988–1004.

[13] S.K. Shrivastava, D.K. Banerjee, Speciation of metals in sewage sludge and sludge-amended soils, Water Air Soil Pollut., 152 (2004) 219–232.

[14] J. Bernacka, L. Pawłowska, Potentially Toxic Substances in Sludge From Municipal Wastewater Treatment Plants (Substancje potencjalnie toksyczne w osadach z komunalnych oczyszczalni ścieków), Instytut Ochrony Środowiska. Monografia., Warszawa, 2000 (in Polish).

[15] G. Merrington, I. Oliver, R.J. Smernik, M.J. McLaughlin, The influence of sewage sludge properties on sludge-borne metal availability, Adv. Environ. Res., 8 (2003) 21–36.

[16] C.R.M. Rao, A. Sahuquillo, J.F. Lopez Sanchez, A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials, Water Air Soil Pollut., 189 (2008) 291–333.

[17] Ö. Hanay, H. Hasar, N.N. Kocer, S. Aslan, Evaluation for agricultural usage with speciation of heavy metals in a municipal sewage sludge, Bull. Environ. Contam. Toxicol., 81 (2008) 42–46.

[18] M. Szumska, B. Gworek, Methods of searching heavy metals in sewage sludge components, Ochrona Środowiska i Zasobów Naturalnych, 41 (2009) 42–63.

[19] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem., 51 (1979) 844–851.

[20] M. Wilk, B. Gworek, Heavy metals in sewage sludge (Metale ciężkie w osadach ściekowych), Ochrona Środowiska i Zasobów Naturalnych, 39 (2009) 40–59 (in Polish).

[21] M. Tytła, K. Widziewicz, E. Zielewicz, Heavy metals and its chemical speciation in sewage sludge at different stages of processing, Environ. Technol., 37 (2016) 899–908.

[22] D. Boruszko, A. Butarewicz, W. Dąbrowski, L. Magrel, Research on the End Use of Dewatered Sludge for Non-industrial Use (Badania nad ostatecznym wykorzystaniem odwodnionych osadów ściekowych do nieprzemysłowego wykorzystania), Politechnika Białostocka, Białystok, 2005 (in Polish).

[23] J. Wiater, D. Łapiński, In: M. Pawłowska, L. Pawłowski, Eds., Advances in Environmental Engineering Research in Poland, Routledge, London, 2021, pp. 55–65.

[24] M.K. Jamali, T.G. Kazi, H.I. Afridi, M.B. Arain, N. Jalbani, A.R. Memon, Speciation of heavy metals in untreated domestic wastewater sludge by time saving BCR sequential extraction method, J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng., 42 (2007) 649–659.

[25] J. Zhao, C. Qiu, X. Fan, J. Zheng, N. Liu, C. Wang, D. Wang, S. Wang, Chemical speciation and risk assessment of heavy metals in biochars derived from sewage sludge and anaerobically digested sludge, Water Sci. Technol., 84 (2021) 1079–1089.

[26] A. Kabata-Pendias, Heavy Metals in Silos – Issues in Central and Eastern Europe, Heavy Metals in Environment, Hamburg, 1996.

[27] R.P. Singh, M. Agrawal, Potential benefits and risks of land application of sewage sludge, Waste Manage., 28 (2008) 347–358.

[28] A. Czechowska-Kosacka, Solidification of liquid sludge with mineral waste materials and metal speciation forms (Solidifikacja osadów ciekowych mineralnymi surowcami odpadowymi a formy specjacyjne metali), II Kongres Inżynierii Środowiska – materiały. Monografie Komitetu Inżynierii środowiska PAN, tom 1, 32 (2008) 1071–1079 (in Polish).

[29] M.J. Sánchez-Martín, M. García-Delgado, L.F. Lorenzo, M.S. Rodríguez-Cruz, M. Arienzo, Heavy metals in sewage sludge amended soils determined by sequential extractions as a function of incubation time of soils, Geoderma, 142 (2007) 262–273.

[30] S. Nomeda, P. Valdas, S.-Y. Chen, J.-G. Lin, Variations of metal distribution in sewage sludge composting, Waste Manage., 28 (2008) 1637–1644.

[31] Y. Liu, L. Ma, Y. Li, L. Zheng, Evolution of heavy metal speciation during the aerobic composting process of sewage sludge, Chemosphere, 67 (2007) 1025–1032.

[32] E. Alonso Alvarez, M. Callejón Mochón, J.C. Jiménez Sánchez, M. Ternero Rodríguez, Heavy metal extractable forms in sludge from wastewater treatment plants, Chemosphere, 47 (2002) 765–775.

[33] C. Wang, X.-C. Li, H.-T. Ma, J. Qian, J.-B. Zhai, Distribution of extractable fractions of heavy metals in sludge during the wastewater treatment process, J. Hazard. Mater., 137 (2006) 1277–1283.

[34] J. Gawdzik, J. Długosz, Influence of sewage sludge fermentation for heavy metals mobility in wastewater treatment plant in Skarżysko-Kamienna, Arch. Waste Manage. Environ. Prot., 15 (2013) 13–20.

[35] L. Dąbrowska, Speciation of heavy metals in non-volatile solids of sewage sludge, Desal. Water Treat., 52 (2014) 3761–3766.

[36] K. Górska, M. Sikorski, Occurrence of heavy metals in rain wastewater on example of catchment in Kielce, Proc. ECOpole, 7 (2013) 333–341.