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Distribution of Heavy Metal Fractions in Sewage Sludge from a Selected Municipal Sewage Treatment Plant

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Abstract: Sewage sludge used for reclamation of egraded areas or in agriculture must have a certain total heavy metal content, as required by law. In practice, however, it is important to carry out a fractional analysis of the elements contained in the sludge. This activity allows to determine the chemical form of a given metal, thanks to which it is possible to assess the assimilability of elements by plants. The study proved that the fraction of certain metals in sewage sludge can vary depending on the period studied. The combination of elements with other compounds in sludge from one treatment plant can vary from month to month. Once analysis has been carried out, it should not be the basis for assessing the bioavailability of metals if sludge from a given treatment plant were to be sampled several times a year.

Keywords: sewage sludge, heavy metals, heavy metal fractions

1. Introduction

The number of municipal wastewater treatment plants in Poland is steadily increasing. In the period 2000-2019, their number has increased from 2417 to 3278. The need to serve an increasing population through WWTPs makes it necessary to build more facilities or modernise existing ones in order to increase their capacity and adapt them to new legal conditions (Skorbiłowicz & Ofman, 2015). In Poland, in 2000, the number of cities served by WWTPs was 801, and

19 years later, the number had increased to 938 (Statistical Office, 2020). These aspects determine the inflow of more and more wastewater to municipal treatment plants, and this has an impact on the increase in the amount of generated sludge. In 2010, 895,100 tonnes of sewage sludge were generated and in 2019, 17% more was produced (www.bdl.stat.gov.pl).

Figure 1 shows the quantities of sewage sludge used in agriculture in selected years. Clearly presented statistical data indicate that since 2004 an increasing amount of sludge has been used as a fertiliser for agricultural crops. However, it should be noted that sewage sludge contains heavy metals (Bauman-Kaszubska & Sikorski 2011), as well as other toxic compounds (Ofman & Skoczko 2018, Ofman & Struk-Sokołowska 2019, Struk-Sokołowska et al. 2020). The amount of organic and inorganic pollutants in sewage sludge depends on the chemical characteristics of the wastewater flowing into the facility (WIOŚ 2018). The composition of wastewater is also seasonally variable (Skoczko et al. 2017), so the content of pollutants in sewage sludge may vary depending on the sampling period.

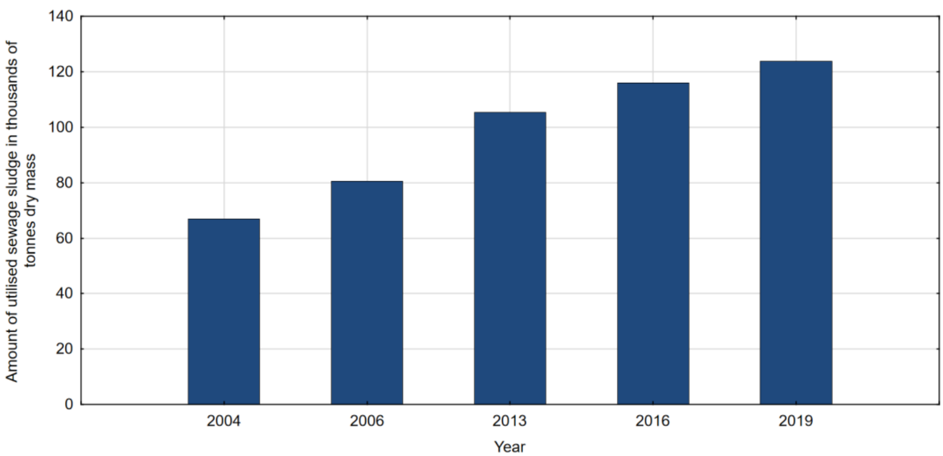

Fig. 1. Use of sewage sludge in agriculture in Poland
Source: Statistical Office: www.bdl.stat.gov.pl

Polish regulations set a limit for the content of heavy metals in sewage sludge used in agriculture and for land reclamation for agricultural purposes (Journal of Laws of 2015, item 257). However, the standards define a general acceptable content of these elements in sludge. Appropriate agricultural practice should include knowing the amount of metals in sludge by fraction (Wikarek-Paluch et al. 2016). Thanks to this, it is possible to determine the mobility of elements. This is important knowledge because mobile metals migrate in the environment, easily find their way into plants and then, when plant consumption takes place, they can enter living organisms, i.e. animals and humans (Boruszko 2013, Amir et al. 2005). Above all, however, performing speciation analysis makes it possible to reduce the occurrence of toxic effects that are caused by an excess of particular metals in the soil (Bozkurt et al. 2006; Dąbrowska & Nowak 2014).

The excess fraction of mobile heavy metals in soil is associated with their penetration through the biological membranes of plants (Matejczyk et al. 2020). Metals are able to completely restrict plant growth and development, as they limit the uptake of important micro- and macroelements by the roots (Wolak et al. 1999, Gruca-Królikowska & Wacławek 2006). Besides, they disrupt photosynthesis, contribute to abnormal transpiration, reduce turgor in leaves, and cause oxidative stress in plants (Kaczyńska et al. 2015, Wolak et al. 1999).

The sequential extraction process of heavy metals was carried out according to the modified BCR method, which gives the same results as the classical four-step BCR extraction method (Leśniewska et al. 2016). Therefore, 4 fractions of heavy metals were distinguished. Fraction I, the exchangeable-carbonate fraction, is the most available to plants. For this reason it is also referred to as the mobile fraction. It is a combination of elements with carbonates. Solubility in acids is a characteristic feature of this form. In an acidified soil environment, metals from this fraction are easily released and then migrate and reach plants (Boruszko 2013). The next fraction, termed reducible, is less mobile. It represents combinations of elements with manganese and iron oxides. The release of metals is determined by changes in the oxidation-reduction potential. Dismutation occurs under anaerobic conditions (Gawdzik 2010; Boruszko 2013). There is also a meta-stable fraction, otherwise known as oxidisable fraction. In this form, elements are bound to sulphides and/or organic matter. Metals are temporarily immobilised but can be released by microorganisms that decompose organic matter, regardless of the degree of oxidation of the environment (Dąbrowska & Nowak 2014). Fraction IV, the residual fraction, consists of metal-silicate combinations. Under natural conditions, elements in this form are completely immobilised (Żelezik & Gawdzik 2015, Wasilkowski & Mrozik 2016).

The aim of this study was to determine the variability of heavy metal fractions (Cu, Zn, Ni, Cd, Pb) in sewage sludge. Sludge was collected for analysis every month for half a year from a sewage treatment plant of 2500 PE. Until now, no research has been conducted in Poland and probably in Europe to determine the variability of heavy metal fractions in sewage sludge from a single plant.

2. Materials and methods

Sludge samples were collected from one wastewater treatment plant with a population equivalent (p.e.) of 2,500, located in the Podlaskie Voivodeship. Wastewater composition is seasonally variable, therefore sludge was sampled monthly for half a year, from October to March. The tested sludge samples were after the dewatering process, but before further treatment, i.e. stabilisation. The finished samples were tested for total heavy metal content and their fractions. The measurement for each sewage sludge sample was performed 3 times and the results were averaged. Figure 2 shows the technological scheme of the sewage treatment plant in Stawiski. The existing treatment plant consists of the following devices: radial sand trap, sludge stabilization chamber, expansion chamber, anaerobic chamber, and two aeration chambers. In addition, there is a catchment point and sludge plots. Sediment samples were collected from the sediment plots.

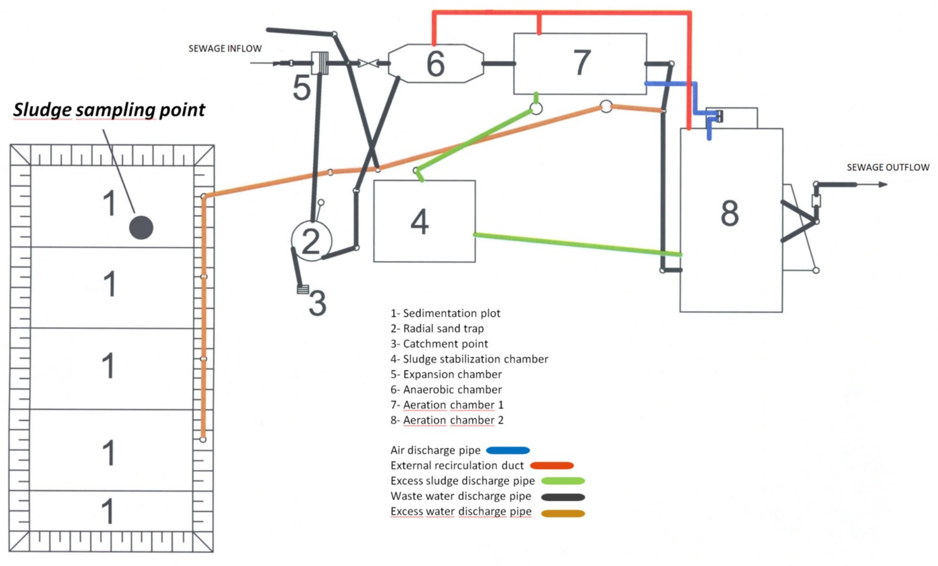

Fig. 2. Technological scheme of the sewage treatment plant in Stawiski

Source: Water permit for wastewater discharge from Stawiski WWTP to Dzierzbia river

Samples were prepared for analysis by drying them at 105°C to constant weight. This was followed by analysis of Cu, Ni, Pb, Cd and Zn using a modified BCR method. Unlike the classical BCR method, this technique uses a sonifier that generates ultrasound to allow mixing of the samples (Łapinski et al.

2019). This is done much faster than with the classical method. According to literature reports (Leśniewska et al. 2016), the modified BCR method, based on the use of ultrasonic waves for the heavy metal extraction process allows to obtain identical results in comparison with the classical four-step BCR extraction method. During the analysis, the probe was immersed to a depth of 4 cm, the amplitude of the probe operation was 70%, and the power was 16W. A 15-second pause after 15 seconds of operation of the device was also established. A sonifier from MIRIS was used for the study.

For BCR extraction, 1 g of dried sample was taken. For the extraction of the first fraction, a 0.11 mol·dm^{-3} solution of CH_3COOH at 40 ml was used. The sample was extracted for 7 minutes. The second fraction was extracted for 10 minutes with 40 ml of 0.5 mol·dm^{-3} $NH_2OH \cdot HCl$ solution. The third fraction was extracted using 50 ml of a 1.0 mol·dm^{-3} solution of CH_3COONH_4, and this took 4 minutes. However, before extracting the heavy metals from the third fraction, the organic matter had to be oxidised. For this purpose, H_2O_2 of 30% concentration was used in an amount of 10 ml, and the operation was performed on a water bath at 80°C. For the determination of the fourth fraction, the sample was incinerated at 470°C and then mineralised in a microwave mineraliser in a mixture of 9 cm^3 HCl and 3 cm^3 HNO_3. The total heavy metal content of the sludge was also determined after mineralisation. The first step was to burn the sample at 470°C, followed by mineralisation in a mixture of 9 cm^3 HNO_3 and 1 cm^3 H_2O_2 (Wojciula et al. 2021). The extracts prepared according to the described methodology were subjected to quantitative analysis on an ICE-3500 Thermo atomic absorption spectrometer using a flame technique operating on an air-acetylene gas mixture. The quantification threshold (LOD) for Cu and Cd was 0.02 mg/L, for Zn and Ni 0.01 mg/L, and for Pb the LOD value was 0.03 mg/L.

In order to indicate significant differences between the contents of all forms of the studied metals in sewage sludge, the results were statistically processed. This was possible by carrying out an analysis of variance, ANOVA using Tukey's test for equal samples (Ofman et al. 2020, Dobrowolska 2016). The total heavy metal content as well as the content of individual elements in the fractions were the dependent variables. In turn, the quality factor was the period (month) of sampling. Saphiro-Wilk's test and Bartlett's test were also performed. This confirmed that the results were characterised by a normal distribution and homogeneity of variance. The level of statistical significance was assumed to be 0.05. Statistical analyses were performed in the Statistica 13.1 software package.

3. Results and disscusion

The examined sewage sludge was characterized by a hydration level of 50% and an organic matter content of 80±5%. These data did not change in the analyzed months. Because of the seasonal variation of the sewage sludge composition, sludge samples were taken monthly for half a year.

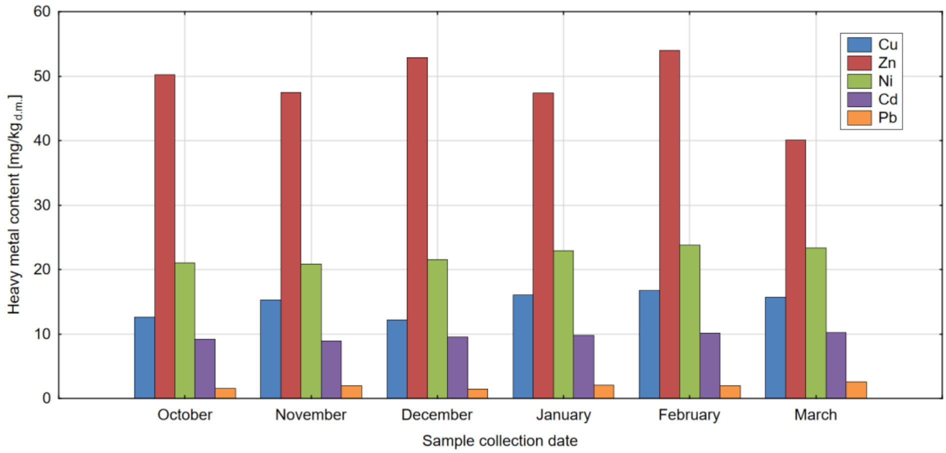

Fig. 3. Total content of heavy metals in sewage sludge according to the study period

Each of the sewage sludge samples, during the 6 months of the study, met the requirements established in the Regulation of the Minister of the Environment of 6 February 2015 on municipal sewage sludge. Sewage sludge from the selected treatment plant can be used for land reclamation for agricultural purposes, as well as in agriculture, but it must meet one condition. It must not be applied to the topsoil (0-25 cm). Figure 3 shows the total content of copper, zinc, nickel, cadmium and lead in the sewage sludge samples taken each month, from October to March. Copper, zinc and nickel occurred in the highest amounts in the sludge collected in February. Cadmium and lead, on the other hand, showed the highest content in the sludge collected in March. Figure 3 clearly shows that the overall metal contents of the samples were, however, very similar to each other, regardless of the season. The only exception was zinc. In February the element was 14 mg/kg d.m. more than in March. The reason for the high amount of zinc in February may have been increased thawing. Górska and Sikorski (2013) proved that zinc and lead are present in the highest concentration in rainwater sewage. In March, with heavy snowfall, zinc concentrations in wastewater were up to 7 times higher than nickel and cadmium concentrations. Lead concentration in that period was twice as high as chromium concentration. This is related to the occurrence of these elements in transport, automotive industry (Górska & Sikorski 2013, Struk-Sokołowska et al. 2020). So far, in Poland and probably in Europe, there have been no studies on periodic changes of heavy metals in dewatered sewage sludge ready for use. Controlled so far are, among others, changes in metal fractions during the composting process, i.e. stabilization of sewage sludge (Ingelmo et al. 2012), as well as differences in metal concentrations in sludge from different locations (Tytła 2019).

Statistically significant differences in Cu and Cd contents between individual periods of environmental sampling were observed over the study period. This phenomenon may indicate variation in the inflow of these elements with raw sewage. On the other hand, the contents of Ni, Zn and Pb did not show statistically significant differences over the study period, which may indicate similar concentrations of these elements in the wastewater flowing into the treatment plant over the study period.

Studies describing changes of heavy metal fractions in sewage sludge depending on the season of sludge intake are very rare. Authors mainly present transformations of metal fractions in sewage sludge during sludge stabilisation, or describe changes in metal forms depending on the size of the treatment plant or the type of sewage inflow. However, it is worth noting that in the same facility, sewage sludge can be characterised by different contents of heavy metal fractions, depending on the time of sludge intake.

According to Figure 4, the distribution of the Cu fraction in the sewage sludge samples varied. In January, the exchange-carbonate fraction, i.e. the fraction most available to plants, occurred at a level of 1.8%, while in November, this fraction occupied almost 12% of the total Cu content. Fraction II, which depends on the oxidation-reduction potential in the environment, occurred in similar amounts in each month (from 29% to 35%). There were more non-mobile fractions than mobile fractions in all samples studied. The highest number of non-mobile Cu fractions (III and IV) occurred in the sludge from January (68%) and the least from December (58%), but this was a 10% difference. Jamali et al (2009) report that Cu is an element very often associated with organic matter. The study carried out also confirmed this. The transformation of Cu fractions can take place under the influence of high temperature. Dąbrowska and Nowak (2014) proved that the incineration of sewage sludge at a temperature of 800°C results in the release of Cu from combinations with organic compounds. In their study, transformations of Cu fractions occurred to a small extent and may have depended on the composition of the influent wastewater.

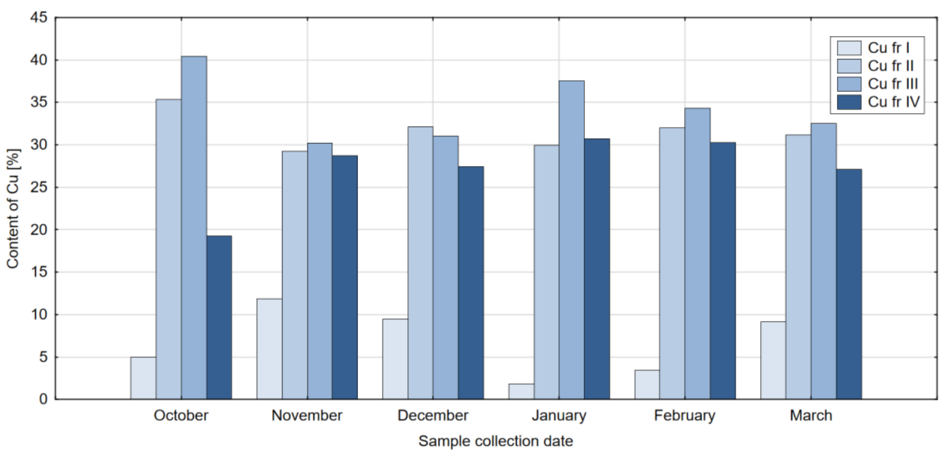

Fig. 4. Average fraction of Cu in sewage sludge samples collected in study period

In the case of Cu statistically significant differences at α = 0.05 level between individual periods of sampling sludge for the study were observed in case of I and IV fraction. On the other hand, the content of this element in the II and III fractions did not show statistically significant differences between individual times of environmental sampling. This observation confirms the observation that the content of Cu in the individual fractions may have been to a larger extent dictated by the form of this element present in the sewage compared to the transformations that may take place in the sludge.

Figures 5 and 6 show the average percentage contribution of Ni and Cd fractions in sewage sludge samples. For both elements, the summed value of the immobile fractions prevailed from October to March. In each month, the contents of individual fractions of both elements were very similar. Changes in the combinations of these metals with other compounds can occur when industrial wastewater is discharged to the treatment plant, or when corrosion of pipes or other elements of the sewage system occurs (Gawdzik 2012, Ilba et al. 2014, Surowska 2002).

In the case of Ni and Cd, no statistically significant differences were observed between the contents of these elements in individual fractions over the study period. This observation may indicate that the chemical forms in which these elements occur in wastewater are not subject to seasonal changes, and the sheer amount of Ni and Cd entering the wastewater treatment plant was equal during the study period.

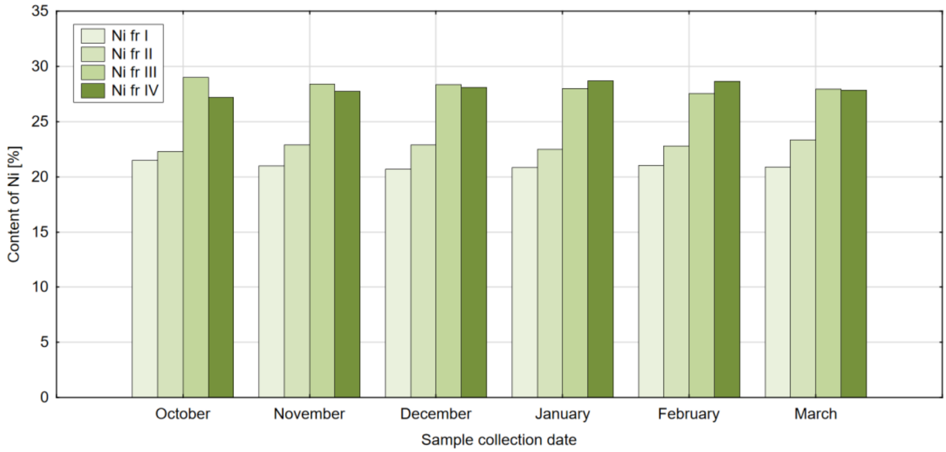

Fig. 5. Average proportion of Ni fractions in sewage sludge samples collected in study period

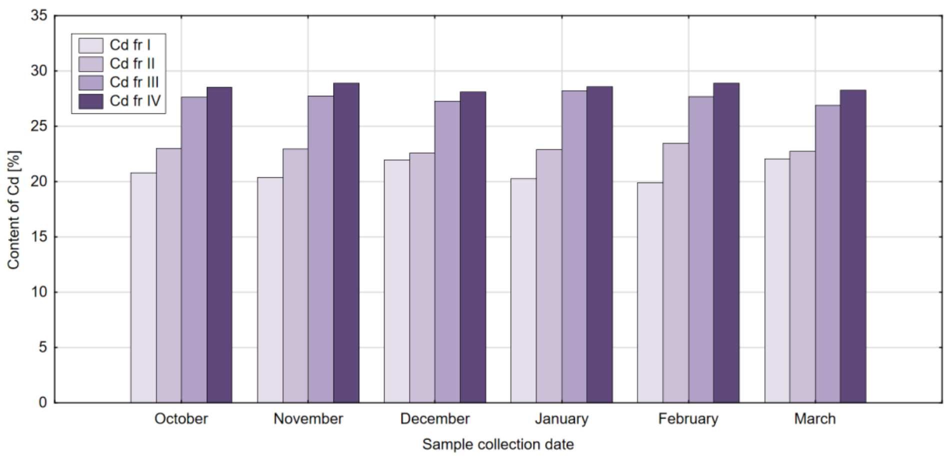

Fig. 6. Average fraction of Cd in sewage sludge samples collected in study period

Associations of Zn with other compounds in the studied sewage sludge differed considerably depending on the period of sludge sampling. It is also worth noting that of all the analysed elements, only Zn was predominantly present in the sludge in the most plant available form. Sludge collected from wastewater treatment plant from the Świętokrzyskie Voivodeship had the highest content of residual zinc fraction (460 mg/kg), but the content of exchangeable fraction (152 mg/kg) was higher than the content of reducible and metastable fraction (Gawdzik 2010). In turn, Gondek (2010) identified zinc as a highly mobile metal in waste materials. Other authors deduced that zinc was mainly bound to iron and manganese oxides, i.e. it occurred in a form where the release of the element is determined by changes in the oxidation-reduction potential (Piotrowska & Dudka 1987).

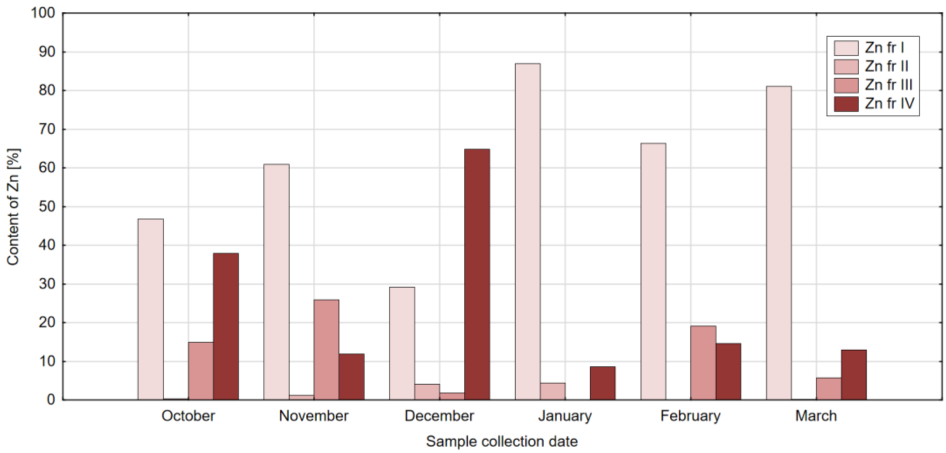

Fig. 7. Average proportion of Zn fraction in sewage sludge samples collected in study period

In almost every month fraction I had the highest share in the total Zn content, as shown in Figure 7. The exception was the sludge collected in December. It contained almost 70% of the immobile fraction. On the other hand, the sludge taken in January showed already less than 10% of these fractions. That is why sequential analysis is so important. Zn is an essential element for plant life, while an excess of it may limit photosynthesis or cause chlorosis and necrosis of leaves (Asati et. al. 2016, Ociepa-Kubicka & Ociepa 2012). The variability of heavy metal forms in sewage sludge largely depends on the composition of the wastewater. In turn, the composition of wastewater can be variable if rainwater enters the combined sewer system. Zn and Pb are the largest contributors to rainwater effluent (Górska & Sikorski 2013). Different rainfall intensity or variable snowmelt frequency can affect the content of zinc forms in the wastewater and, consequently, in the sewage sludge.

In the case of Zn, statistically significant differences were observed between all fractions in individual periods of environmental sampling. This may be due to a change in the chemical form of Zn entering the sewage treatment plant or, in the case of transformations observed in fractions I and III, to the transformation of this element by microorganisms in the sewage sludge.

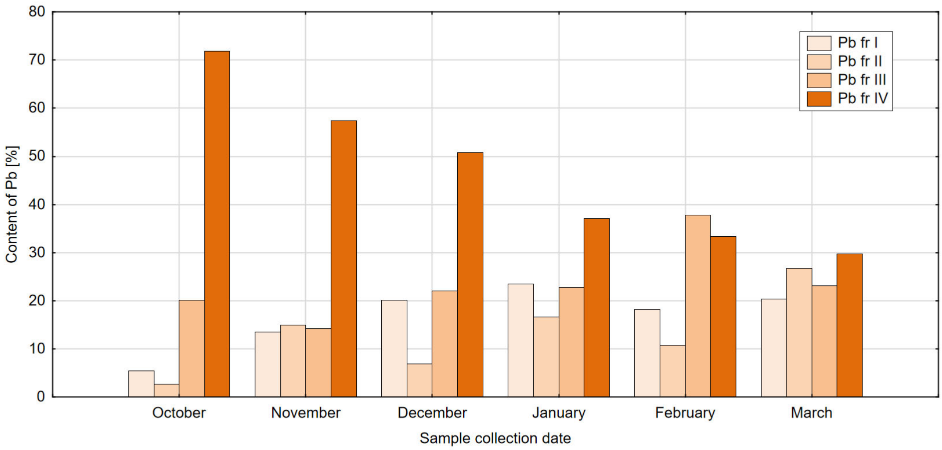

Fig. 8. Average share of Pb fraction in sewage sludge samples collected in study period

The distribution of Pb fractions also varied considerably. Figure 8 clearly shows that from October onwards, Pb was present in increasingly smaller amounts month by month in the form of combinations with silicates. The mobile fractions are also worth noting, as their amount was much higher in March than in October. Variable amounts of Pb fractions may be caused by higher or lower inflow of industrial wastewater, but also by snowmelt or heavy rainfall. Rainwater entering sewerage systems, flushes pollutants from street areas or from green areas (Górska & Sikorski 2013). Depending on the location of the runoff, Pb can form combinations with other compounds. The transformation of Pb fractions in sewage sludge can be influenced by the composting process. Ingelmo et al. (2011) demonstrated that composting contributed to the formation of more immobile fractions. Dąbrowska and Nowak (2014), on the other hand, proved that incineration at 800°C resulted in an almost complete loss of Pb fractions I, II and III, in favour of fraction IV. Sludge stabilisation processes can also have a significant impact on the transformation of heavy metal fractions in sewage sludge (Obarska-Pempkowiak & Gajewska 2008).

The Pb content in fractions I, II and III showed statistically significant differences at the $\alpha = 0.05$ level over the study period, between individual dates of sludge sampling, while for fraction IV statistically significant differences were observed only in the months of October to January. In the rest of the study period no statistically significant differences in Pb content were observed in fraction IV. Taking into account the chemical specificity of Pb and its potentially toxic effect on living organisms, the observed changes in the content of this element in individual fractions may be caused by changes in the form of its occurrence in raw sewage or by additional inflow of rainwater associated with seasonality. On the other hand, to a lesser extent, this element could be subject to transformations connected with the activity of microorganisms present in the sludge.

The total content of heavy metals determined after digestion of the studied sewage sludge was consistent with the total content of metals in particular fractions. The scientific aspect of the study was to determine whether seasonal variation of heavy metal fractions in sewage sludge occurs on the same object. The study confirmed that such changes do occur. In polish and foreign literature there were no references on the subject.

4. Conclusions

1. The proportion of lead, zinc and copper fractions in the sewage sludge varied according to the period studied.
2. The greatest differences in the contents of fractions in the half-year period were found for zinc and lead. These are the elements which have the largest share in rainwater effluents.
3. The distribution of nickel fractions in sewage sludge was very similar in every sample, irrespective of the period of sampling. A similar relationship was observed for cadmium.
4. In almost every analysed sludge sample the highest amount of fraction I of zinc was found. This means that in each month the sediment contained a considerable amount of this element in the form most available, assimilable for plants.
5. In the absence of industrial wastewater inflow to the treatment plant, rainwater, or more precisely the amount of precipitation or frequency of snowmelt, has a decisive influence on the transformation of the fraction.
6. The sum of immobile fractions of all metals (except zinc) was predominant in the studied samples.

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