Effect of sludge sample drying before the determination of mobility of metals by sequential extraction method

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ABSTRACT

Identification of chemical forms of metals is performed by numerous sequential extraction methods e.g. three-stage extraction procedure BCR. However, many modifications of this method, which were supposed to accelerate the extraction process, made it difficult to compare the results obtained by different researchers. Differences are also found at the stage of preliminary sample preparation for extraction. Sometimes, samples are dried to dry weight before extraction and in other cases they are not dried. So, the results obtained by the same sequential extraction procedure can differ from each other, since the sample structure and type of element bonding with the individual fractions can change during drying. Therefore, the impact of preliminary preparation of sewage sludge samples, consisting in drying the samples to dry weight at 105 °C, on the manner of element binding with the individual fractions was studied. It was found that drying of sludge samples prior to sequential extraction caused immobilization of the elements. Drying of the samples had the greatest impact on Cr, Co, Pb and Ni. It was found that concentration of these elements increased in fraction associated with organic matter in comparison to undried samples.

*Keywords***:** sequential extraction, mobility of elements, sewage sludge

1. INTRODUCTION

Methods of speciation analysis are commonly used in studies on mobility and bioavailability of metals in the environment. For this purpose sequential extraction is used, among others. It consists in carrying out the extraction in several steps using in each next step the extractant and extraction conditions with growing power of metal leaching. Many different methods to study the mobility of metals were developed, from simple one-step methods to the complex ones consisting of many sequences [1-4]. They differ from each other in the number of extraction stages, the type and concentration of reagents used for extraction, time and temperature in the various stages of extraction. Depending on the speciation form to be isolated, the different extractants are used. The most frequently isolated fractions are: ion-exchange fraction, carbonate fraction, fraction associated with the iron and manganese oxides, fraction associated with organic matter and residual fraction [5-9]. The most common method of sequential extraction applied for of the samples of soil and sewage sludge is the method proposed by Tessier, Campbell and Bisson in 1979 for fractionation of Cd, Co, Cu, Ni, Pb, Zn, Fe and Mn [10].

This method has found numerous applications in the original version [11, 12] as well as with many modifications [13-15]. One of the problems encountered when analysing the results of sequential extraction is the fact that there are numerous modifications of the extraction procedure, which makes it difficult to interpret and compare the results obtained by different procedures. Therefore, an attempt was taken in order to standardize the sequential extraction procedures and to develop an universal method. These actions caused development of a three-step extraction procedure proposed by Community Bureau of Reference of Commission of the European Community, called BCR method [16]. The procedure allows to separate three fractions: the first is ion-exchange of metals and associated with carbonates, the second associated with iron and manganese oxides and the third associated with the organic matter.

Similarly to Tessier's method, the BCR method has also numerous modifications. An example can be the application of ultrasounds in order to shorten the extraction time, increasing the extraction temperature or change in concentration of extractants [17-19]. Differences are also found at the stage of sample preparation for extraction. Some authors in studies on the mobility of elements apply drying the sample to constant weight at 105 °C or to air-dry weight, while other use for extraction the samples without drying stage [20,21]. This fact is very important, since the studies on thermal disintegration of sludge showed that, due to the action of high temperature on sludge (in the range from 90 to 180 °C), an increase in the solubility of organic compounds occurs [22-24]. Seeing that under the influence of high temperature the organic bonds are degraded, so also bonds of metals with organic matter of soil or sewage sludge can disintegrate during drying. This in turn can cause the release of metals from stable bonds with organic matter.

In this work, the effect of drying of the sewage sludge samples on mobility of chromium, cobalt, nickel, copper and lead was studied. A sequential extraction was carried out simultaneously for fresh sludge (not dried prior to sequential extraction) and sewage dried to constant weight at 105 °C. A three-stage sequential extraction procedure BCR was used for the extraction. The content of metals in the extracts obtained was determined by ICP-AES method.

2. EXPERIMENTAL

2. 1. Sample description

The sewage sludge for testing were sampled from the sewage treatment plant in Bydgoszcz (Poland) whose planned throughputs were: 43.000 m³ of municipal wastewater per day and 29.000 m^3 of industrial sewage per day. Samples of sludge were collected into the polyethylene containers. To prevent the biochemical changes in the material, the determinations were carried out immediately after delivery of samples to laboratory. The raw sewage sludge and sewage sludge after thermal disintegration were used in our studies.

2. 2. Three-stage sequential extraction procedure, BCR

The mobility of Co, Ni, Pb, Cr and Cu in sewage sludge was determined by the use of three-stage sequential extraction procedure proposed by Community Bureau of Reference, now Standards, Measurements and Testing Programme of the European Community, called BCR method [16]. The method allows to obtain three metal fractions: F1 - ion-exchange fraction associated with carbonates after the first stage of extraction, F2 - fraction associated with oxides of iron and manganese after the second stage of extraction and F3 - fraction associated with organic matter after the third stage of extraction.

The 1st stage: ion-exchange fraction associated with carbonates. 2.000 g of sewage sludge was weighted to PTFE vessel, 40 ml of acetic acid solution was added (CH$_3$COOH, 0.11 mole L^{-1}) and it was shaken on laboratory shaker (Elpin+, water bath shaker, type 357) at room temperature for 16 h. The extract was separated from solids by centrifugation at 4000 rpm for 20 min. A clear extract was decanted into volumetric flasks of 50 ml, 1 ml of concentrated nitric acid was added and flasks were filled up to the mark. So prepared extract was stored until analysis at 4 °C. Residual sludge was washed with 20 ml of water by shaking for 15 min., after centrifugation solution above the sludge was decanted and discarded.

The 2nd stage: fraction associated with iron and manganese oxides. 40 ml of hydroxylamine hydrochloride solution ((NH$_2$OH·HCl), 0.1 mole L^{-1}, pH = 2) was added to the vessel with sludge after the first stage. A solution was prepared on the day when the second stage of extraction was conducted. Extraction was carried out for 16 h at room temperature. Further operations were performed as in stage 1.

The 3rd stage: fraction associated with organic matter. 10 ml of hydrogen peroxide solution (H$_2$O$_2$, 8.8 mole L^{-1}, pH = 2) was added to the vessel with sludge remaining after the second stage. Solution was added in small portions to avoid losses during the rapid reaction of sludge with hydrogen peroxide. The content was digested at room temperature for 1 h with stirring from time to time. Extraction was continued in a water bath at 85 °C for 1 h in the closed vessels. Then, the volume was reduced to a few millilitres, a further 10 ml of hydrogen peroxide solution was added and extraction was performed in a water bath at 85 °C for 1 h in the closed vessels. The volume was again reduced to several millilitres. Then, 50 ml of ammonium acetate solution (CH$_3$COONH$_4$, 1.0 mole L^{-1}, pH = 2) was added to the cold precipitate and shaken for 16 h at room temperature. The extract was separated by centrifugation as in the previous steps. Simultaneously, a control sample was prepared for each extraction stage.

2. 3. Total content of metals in sewage sludge

The samples were mineralized in microwave mineralizer Speedwave MWS-2 (Products + Instruments GmbH Lab Technik, BERGHOF). 250 mg of sludge samples, dried earlier to dry weight at 105 °C, were weighed and introduced into mineralization vessels. 10 ml of nitric acid was used to dissolve (Suprapur®, Merck).

In the solutions obtained by sequential extraction and the solutions after mineralization, the content of Cr, Co, Ni, Cu and Pb was determined by atomic emission spectrometry with inductively induced plasma (ICP-AES, Inductively Coupled Plasma Atomic Emission Spectroscopy). An ICP-AES Jobin Yvon JY 38S HORIBA spectrometer equipped with a glass nebulizer and a cyclone nebulization chamber was used. The analytical wavelengths (nm) used were: Cr 283.563, Co 238.892, Ni 221.647, Cu 324.754, Pb 220.353 nm.

3. RESULTS AND DISCUSSION

3. 1. Total content of metals in the raw sewage sludge and sludge after thermal disintegration

The content of investigated elements in sewage sludge can be arranged in the following series: Cr > Cu > Ni > Pb > Co. The content of the individual elements in raw sludge (Tab. 1) and in sludge after thermal disintegration (Tab. 2) did not differ significantly.

Table. 1. Total content of elements in raw sewage sludge, n = 22

indicator	Content of element [mg·kg^{-1} DW]				
	Cr	Co	Cu	Ni	Pb
mean value	241.7	9.87	125.3	116.4	21.1
median	217.9	10.68	121.3	107.8	18.0
max.	395.8	19.50	238.9	70.81	40.7
min.	90.61	4.07	92.80	103.8	7.12

n – number of samples studied

Table 2. Total content of elements in sewage sludge after thermal disintegration, n=22

indicator	Content of element [mg·kg^{-1} DW]				
	Cr	Co	Cu	Ni	Pb
mean value	246.1	10.19	113.8	111.99	21.14
median	217.0	11.46	117.8	106.25	19.90
max.	427.4	15.15	158.2	186.75	38.35
min.	151.9	3.595	60.40	73.82	9.112

n – number of samples studied

3. 2. Impact of sewage sludge drying on mobility of metals

The paper presents an effect of drying of sewage sludge samples on the form of Cr, Co, Ni, Cu and Pb binding with solid phase of sewage sludge. Mobility studies were carried out by using a three-stage BCR extraction method, on fresh samples immediately after delivery to the laboratory and on samples dried to dry weight at 105 °C. It results from the studies that drying of raw sludge samples causes immobilization of elements in various degrees. It was observed that the drying process of the samples had the greatest effect on Co (Fig. 1). In the case of raw sludge, this element is evenly distributed between three fractions. However, analysis of mobility in the sample after drying showed that the percentage of cobalt in fraction associated with organic matter increased to 73.1% (fraction F3).

Furthermore, it was observed that this increase was primarily due to the loss of cobalt content in the ion exchange fraction (F1). In sludge after thermal disintegration, Co occurred mainly in exchange fraction (48.1%), whereas after drying content of the metal in this fraction was reduced to 16.9%. Simultaneously, Co concentration in fraction F3 increased to 63.7%. Chromium occurs mainly in the fraction associated with organic matter (oxidizable fraction) (Fig. 2). Its content in the raw sludge was 75.4%, and in sludge after thermal disintegration 72.4%. This trend has also been demonstrated by Alvarez et al. [25]. In raw sludge and sludge after thermal disintegration, chromium content in fractions: ion-exchange and associated with carbonates is similar i.e. about 4% in fraction F1 and 20% in fraction F2, respectively. In the raw sludge after drying, concentration of Cr increased in fraction F3 by 23.7%. Such a dependence was observed also in sludge after thermal disintegration. In the raw sludge, nickel - as the only one from the elements studied – was associated mainly in ion-exchange fraction (61.3%) (Fig. 3).

In the natural environment Ni occurs in a variety of forms, which range from very mobile to those that have low reactivity. It depends largely on environmental conditions such as organic matter content, pH, or carbonate content [26]. It was observed that in soils fertilized with organic waste, Ni was readily adsorbed by humic substances [27]. Nickel also easily change the form of occurrence during composting of sewage sludge [28]. Studies have shown that the action of high temperature is a factor that easily changes the kind of Ni bonds. During the drying process, nickel was associated in oxidizable fraction (F3). It was observed that Ni concentration in this fraction increased by 50.4%. Drying the sample before sequential extraction have no effect on Ni mobility in sludge after thermal disintegration. However, in this case it should be noted that the thermal disintegration process itself caused immobilization of this element by incorporating it into the fraction associated with organic matter (F3).

The results of sequential extraction have shown that lead was agglomerated mainly in the fraction associated with organic matter (Fig. 4). It represents 62.4% of the total amount of this element in the raw sludge and 57.0% in the sludge after thermal disintegration. This is consistent with investigations conducted in soils. In the soil environment, lead accumulates in top layer, what is related to the presence of organic matter being a decisive factor in adsorption of lead [15]. Mobilization of Pb is usually slow but some soil parameters, such as increased acidity can increase the solubility of lead [26,29]. A strong tendency to bind lead with organic matter is apparent in samples that were dried prior to sequential extraction. Both in the raw sludge and in the sludge after thermal disintegration, lead was completely concentrated in combinations with organic matter (F3). Such a tendency creates a danger that drying the sample prior to sequential extraction will lead to wrong findings that lead does not

occur in the most mobile fractions (ion-exchange and associated with Fe and Mn oxides). This is especially important for elements that have a toxic effect on organisms. Copper was characterized by the least sensitivity to thermal treatment before sequential extraction (Fig. 5). This element occurs mainly in fraction F3. Its content is 84.8% in raw sludge and 96.8% in sludge after thermal disintegration, respectively. Concentration of copper in the oxidizable fraction is characteristic for this element. It was also described by Alvarez et al. [25] who studied the forms of elements in raw sludge and after composting. Also the studies carried out with application of sequential extraction with ultrasounds showed that 88% of copper occurs in oxidisable fraction [30]. Only in raw sludge, the percentage of copper increased by 6% in F3 fraction as a result of drying. In the sludge after disintegration, a slight reduction in the content of this element after drying (2.2%) in fraction F3 was observed.

It results unequivocally from the studies that drying the sludge samples prior to mobility analysis by sequential extraction causes changes in the manner of binding the elements with a solid phase of sludge. This impact is different depending on the element analysed, and type of sludge. Drying of the sample has a less impact on sludge after the thermal disintegration compared to the raw sludge because thermal disintegration modifies the sludge structure leading to chemical and physical changes. As the concentration of metals in the fraction associated with organic matter during drying of samples increases, the participation of these elements in the mobile fractions: ion-exchange (F1) and associated with Fe and Mn (F2) is reduced. Consequently, this leads to the wrong conclusions that heavy metals that are toxic to living organisms are concentrated in low mobile combinations in the environment. And this in turn could indicate that they do not pose a threat to plant or animal organisms. Reduction in percentages of these elements in fractions F1 and F2, which are considered as mobile fractions and binding them in F3 fraction, i.e. associated with organic matter, means the decrease in mobility of these elements as a result of higher temperature during drying of samples.
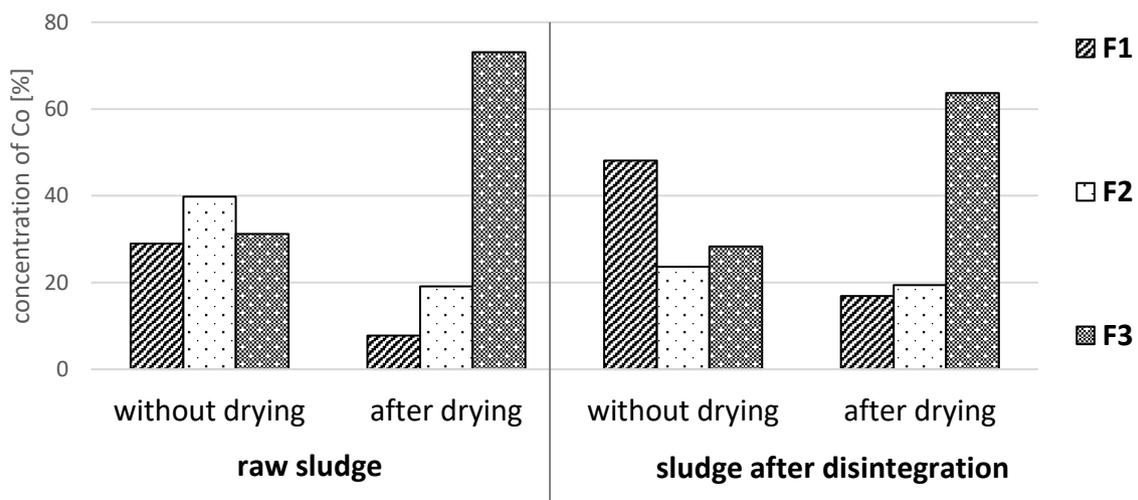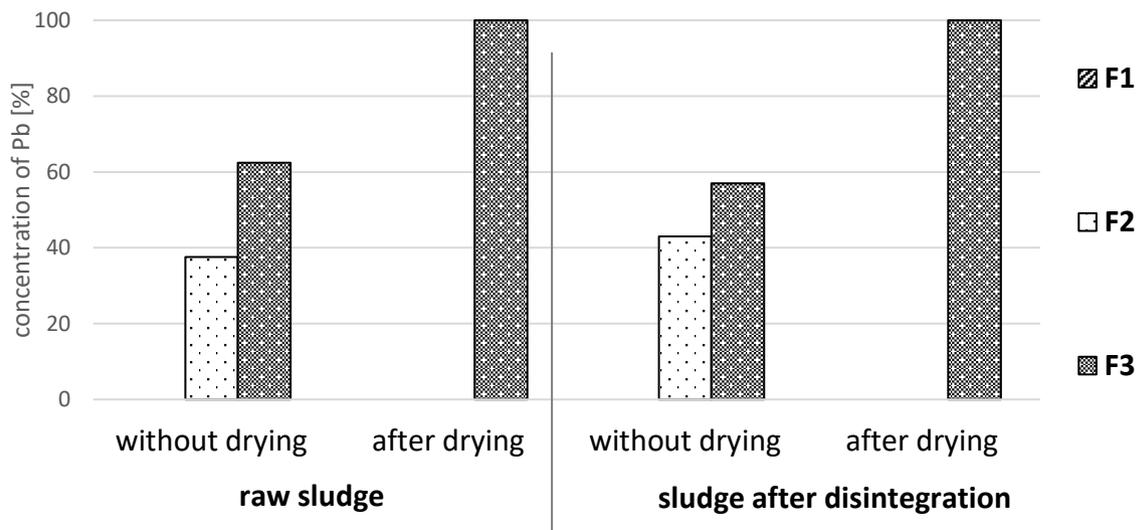

Figure 1. Concentration of Co in the individual fractions in sludge without drying in samples dried prior to sequential extraction, F1 – ion-exchange fraction associated with carbonates, F2 – fraction associated with iron and manganese oxides, F3 – fraction associated with organic matter, n = 10
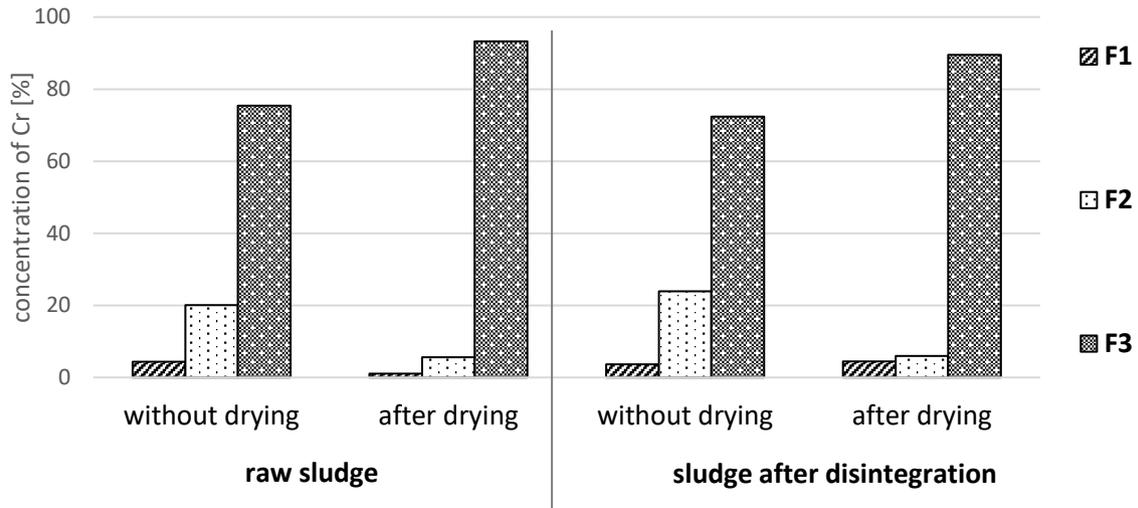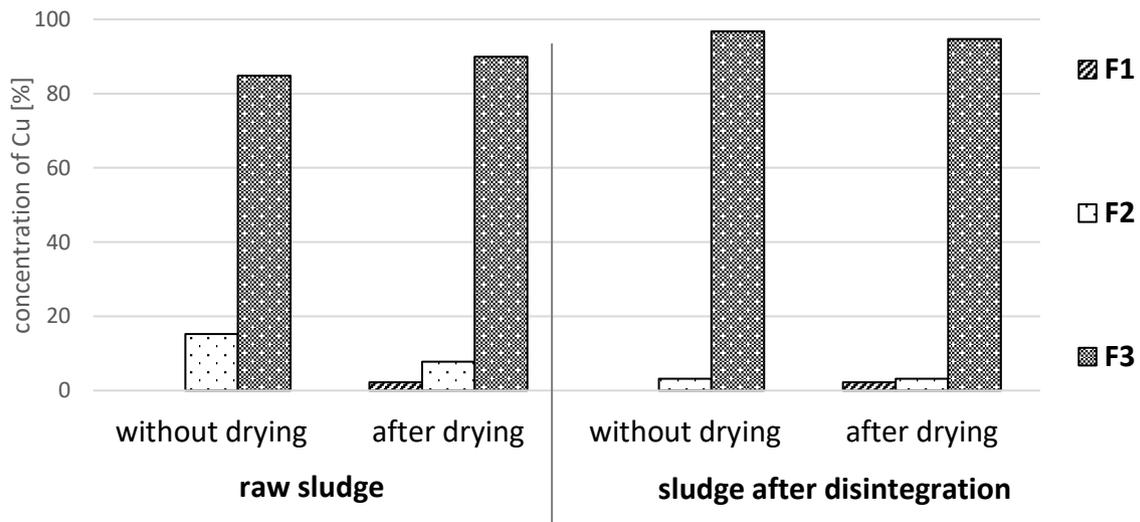
Figure 2. Concentration of Cr in the individual fractions in sludge without drying in samples dried prior to sequential extraction, F1 – ion-exchange fraction associated with carbonates, F2 – fraction associated with iron and manganese oxides, F3 – fraction associated with organic matter, n = 10
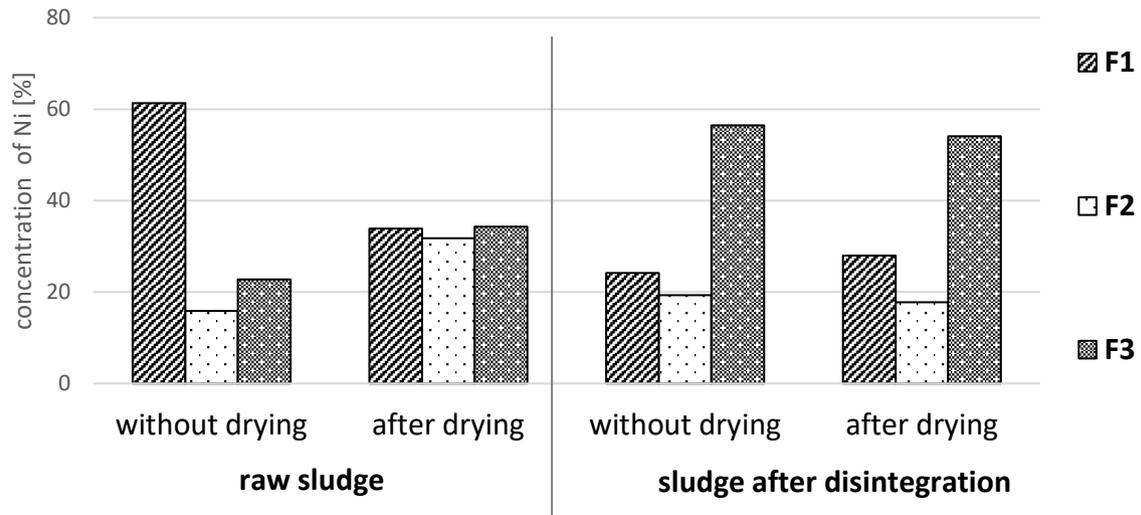
Figure 3. Concentration of Ni in the individual fractions in sludge without drying in samples dried prior to sequential extraction, F1 – ion-exchange fraction associated with carbonates, F2 – fraction associated with iron and manganese oxides, F3 – fraction associated with organic matter, n = 10

Figure 4. Concentration of Pb in the individual fractions in sludge without drying in samples dried prior to sequential extraction, F1 – ion-exchange fraction associated with carbonates, F2 – fraction associated with iron and manganese oxides, F3 – fraction associated with organic matter, n = 10

Figure 5. Concentration of Cu in the individual fractions in sludge without drying in samples dried prior to sequential extraction, F1 – ion-exchange fraction associated with carbonates, F2 – fraction associated with iron and manganese oxides, F3 – fraction associated with organic matter, n = 10

4. CONCLUSIONS

Knowledge of the form in which the element occurs allows for predicting its migration, determination of the element availability for plants and potential toxicity to plant and animal

organisms. Occurrence of elements, including heavy metals in mobile form, increases the possibility of their penetration into groundwater, which poses a potential threat to the environment and danger to human. A common analytical method used to identify the type of element bonding with a solid phase in the environment is sequential extraction. Application of different parameters in the extraction procedure as well as different methods of sample preparation for extraction causes that the results obtained by the same procedure are different for the same sample. It was found that drying of the sludge samples before sequential extraction changed the form in which the element occurred. In most the cases studied, the immobilization of elements occurred. Consequently, the elements showed stronger bindings with organic matter in sludge samples dried prior to sequential extraction compared to the undried samples.

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