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ANALYSIS OF THE MOBILITY OF HEAVY METALS IN SLUDGE FOR THE SEWAGE TREATMENT PLANT IN DALESZYCE

ANALIZA MOBILNOŚCI METALI CIĘŻKICH W OSADACH ŚCIEKOWYCH DLA OCZYSZCZALNI ŚCIEKÓW W DALESZYCACH

Abstract

Sewage sludge is a by-product of wastewater treatment processes. However, it has high fertilising and soil-forming properties, but it cannot always be used for this purpose. The two main criteria limiting their natural use are heavy metals and parasite eggs. Sewage sludge taken from the Daleszyce wastewater treatment plant has been analysed for heavy metals. For this purpose a space analysis was performed to divide the total metal content into four mobility fractions. The mobility issue determines the ability of an element, or one of its forms, to move in the environment. The studies were performed using a four-stage BCR procedure. The results were analyzed and compared to the limits applicable in Poland for sewage sludge intended for environmental use.

Keywords: sewage sludge, speciation analysis, BCR, environmental use of sewage sludge, mobility of heavy metals

Streszczenie

Osady ściekowe są produktem ubocznym procesów oczyszczania ścieków. Wykazują jednak wysokie właściwości nawozowe oraz glebotwórcze, jednak nie zawsze mogą być one wykorzystane w tym celu. Dwa główne kryteria ograniczające ich przyrodnicze wykorzystanie to zawartość metali ciężkich oraz jaj pasożytów. Osady ściekowe pobrane z oczyszczalni ścieków w Daleszycach zostały poddane analizie zawartości metali ciężkich. W tym celu wykonano analizę specjacyjną, pozwalającą podzielić całkowitą zawartość metali na cztery frakcje mobilności. Mobilność określa zdolność pierwiastka, lub któregoś z jego form, do przemieszczania się w środowisku. Badania wykonano, stosując czteroetapową procedurę BCR. Wyniki poddano analizie i porównano do limitów obowiązujących w Polsce dla osadów przeznaczonych do wykorzystania przyrodniczego.

Słowa kluczowe: osady ściekowe, analiza specjacyjna, BCR, przyrodnicze wykorzystanie osadów, mobilność metali ciężkich

1. INTRODUCTION

Sewage sludge generated in sewage treatment plants has high soil-forming and fertilizing properties. They can be used in agriculture as a valuable organic fertilizer provided that they are hygienised and the content of organic and inorganic micro-pollutants (heavy metals) does not cause negative effects in the soil environment [1]. Limits of heavy metals in the aspect of sewage sludge utilisation in Poland and worldwide are presented in Table 1.

Table 1. Normative limit values for heavy metals in sewage sludge for agricultural use

Region	Poland Regulation [2]	EU Directive 86/278/EEC [3]	Chinese Regulation GB 18918-2002 [4]		USA Regulation 40 CFR Part 503, 503.13 [5]	South African Guideline (Pollutant Class a) [6]
			pH < 6.5	pH > 6.5		
Cd	20	20-40	5	20	39	40
Ni	300	300-400	100	200	420	420
Zn	2500	2500-4000	500	1000	2800	2800
Cu	1000	1000-1750	250	500	1500	1500
Cr	500	–	600	1000	–	1200
Pb	750	750-1200	300	1000	300	300

Heavy metals in sewage are in suspension and dissolved form. Sewage treatment processes, including the process of simultaneous precipitation of phosphorus and chemical precipitation with lime, cause adsorption and co-precipitation of heavy metals in the separated sludge, which results in their removal from sewage [7]. Moreover, the processes of mass bioaccumulation by microorganisms in the activated sludge chambers and methane fermentation process (formation of immobile heavy metal sulphides) promote the transfer of heavy metals from sewage to sludge [8]. The above transformations affect the differentiation of chemical forms of heavy metals accumulated in the sewage sludge, only some of which (mobile forms) can penetrate from the sludge to the ground environment [9]. The term „mobility of elements" describes the ability of an element, or one of its chemical forms, to move in the environment [10]. The determination of mobility is decisive in the assessment of the risk associated with the introduction into the environment of substances containing hazardous components, e.g. heavy metals. The metals present in water-soluble compounds and those associated with carbonates are considered to be the most mobile (Table 2). Metals bound to iron and manganese oxides are released to the environment much more slowly. The metals which are temporarily immobile are those which form permanent links with organic matter or occur in the form of sulphides [11]. The unavailable metals are those associated with aluminosilicates. The specialist literature contains numerous studies on the sequential extraction of heavy metals from soils, sewage and river (marine) sludge and compost [12]. The most important factors influencing the assimilability of heavy metals by plants include: total metal content in soil, metal type, soil reaction, organic matter content and clay fraction [13]. Bioaccumulation of heavy metals in plants growing on soils contaminated with metals depends on the plant species and the content of mobile metal fractions in the soil. In soil analysis, multistage extraction of heavy metals should be used [14].

As a result of laboratory tests to compare different sequential extraction procedures, it was found that the optimal way to identify the bioavailable metal fractions for certified soil samples is to use EDTA or acetic acid [15].

Table 2. Mobility of heavy metals depending on the form of occurrence [1]

Type of connection	Degree of extraction	Form of metal presence in the ground
Mobility	0	Remaining in pore water
	1	Occurring in ion exchange complexes which are retained or eluted depending on the ionic composition of the pore water
	2	Carbonate related
Permanently	3	Related to manganese oxides and amorphous iron oxides
	4	Related to amorphous and weakly crystalline iron oxides
	5	Sulphides and organometallic compounds
	6	Bound to silicates and forming part of crystalline structures

2. THE USE OF SPECULATIVE ANALYSIS METHODS TO ASSESS THE MOBILITY OF HEAVY METALS

In the case of sewage sludge samples, the best results were obtained using a four-stage procedure developed by the European Community Bureau of Refe-rence, abbreviated to BCR [1]:

Stage I: extraction of CH_3COOH – to determine the content of assimilable and carbonate-bound metals (FI fraction – interchangeable).

Stage II: extraction of $NH_2OH \cdot HCl$ – for the determination of the content of metals associated with amorphous iron and manganese oxides (FII fraction – reductive).

Stage III: H_2O_2/CH_3COONH_4 extraction – for the determination of the content of the organometallic and sulphide fractions (FIII fraction – oxidation).
Stage IV: mineralization of the residual fraction with a mixture of concentrated acids (HCl, HF, HNO_3) – for the determination of the content of metals bound to silicates (fraction FIV – residual).

By means of X-ray microanalysis the validity of sequential BCR extraction can be confirmed. Adsorbents are present in the matrix, which allow to bind metals in FI to FIV fractions. In the sample sewage sludge from the sewage treatment plant in Daleszyce, heavy metals are combined with organic matter, iron oxides, sulphides and aluminosilicates (Fig. 1).

The results of the study indicate that the migration of heavy metals delivered to the soil with sewage sludge is small, however, it may increase in sandy soils with low pH [16]. Zinc is the most susceptible to metal migration [17]. The profiles obtained from unused limestone soils under study contained trace contents of heavy metals. For this purpose, the columns were filled with the sludge from the local sewage treatment plant mixed with the top 15-centimeter layer of limestone soil [16]. During the study, natural weather conditions were simulated on the columns: constant air temperature and humidity were maintained and samples were irrigated with water in an amount corresponding to the local precipitation. A trace amount of metals which moved from the layer of sediments into the studied profiles was shown. The highest migration capacity was found in the sample with the highest addition of sediments. Nickel proved to be the most mobile metal. Nickel was also the best assimilable to plants and its concentration was highest in leachate from columns. The study clearly shows that the mobility of metals contained in sewage sludge is so low that it does not significantly affect the groundwater quality [16].

A simplified BCR sequential extraction method was used to plan a soil phytemediation treatment in one of the Spanish mining regions: Cartagena - La
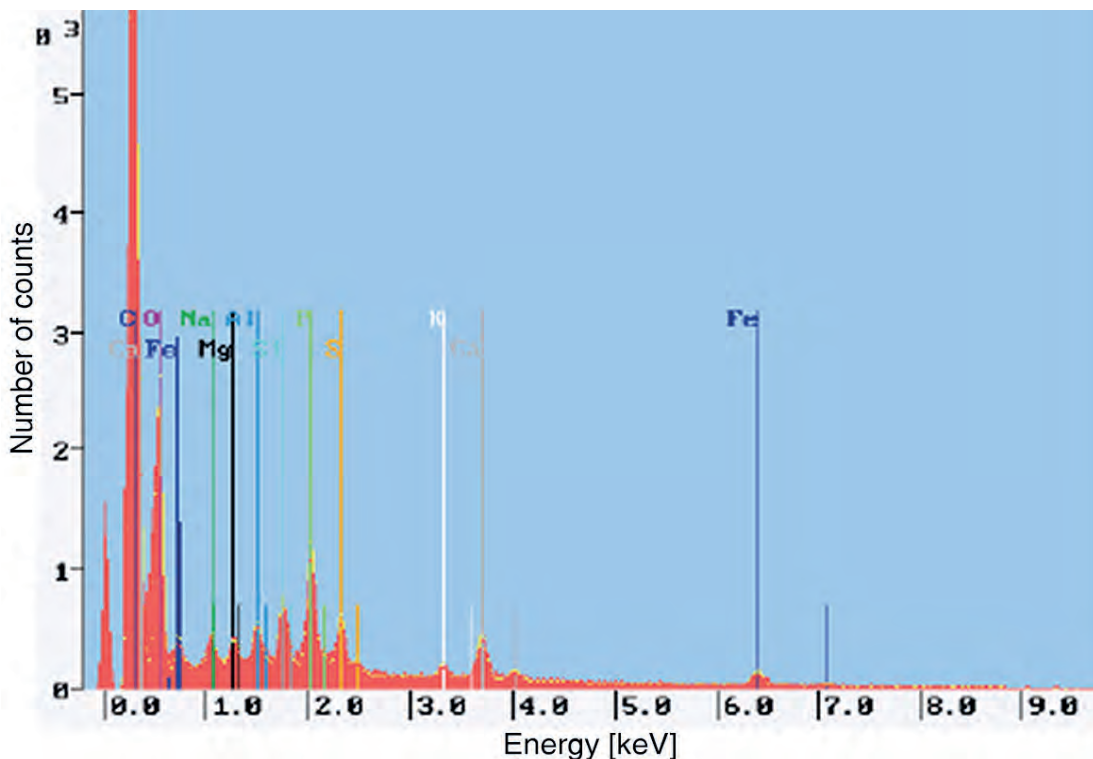

Fig. 1. XRF spectrum of sewage sludge sample from sewage treatment plant O7 [1]

Union [159]. This method was used to assess the degree of bioavailability of heavy metals to plants during the phytremediation process. One of the first observations made was that only a small amount of heavy metals contained in the soil occurred in mobile forms, easily assimilated by plants. However, after extraction, some heavy metals changed their forms to more mobile ones. This indicates the possibility of increased mobility of heavy metals. The conducted studies have shown that some lead, cadmium and zinc have changed into easily assimilable forms, thus posing a potential threat to the environment [18]. However, in the soil, the process of strong binding of these metals in the crystalline mineral networks took place. The formation of such complexes practically limits further migration of heavy metals to zero. Some of the metals were bound in oxidized forms, which due to low solubility also became immobile. However, a change in soil reaction and its oxidative potential may cause the mobilization of oxidized forms. It can therefore be concluded that the release of heavy metals and their possible assimilation by plants is a long-term process that requires appropriate conditions, but is highly likely to occur.

Studies on the mobility of heavy metals were also conducted for samples taken from marshy areas [16]. The conditions in the marshy environment are considered conducive to the immobilization of metals, which has been applied, e.g. in the treatment of contaminated waters. The situation is complicated by the presence of plants in the system. The greatest differences were observed in the rhizosphere. An increase in the amount of oxygen supplied through the root system can be observed here. However, the uptake of nutrients by plants leads to changes in the amount and structure of organic matter. These changes are encouraged by the appearance of new species of microorganisms accompanying the plants. Fungi and bacteria are mainly able to bind heavy metals. During the immobilization of metals, various mechanisms are used, such as precipitation, complexation, sorption or transport to the cell [19]. Moreover, the presence of plants affects the redox potential and soil pH [20].

Under these conditions, processes that immobilise and mobilise heavy metals may occur at the same time. For example, the release of metals may be facilitated by an additional amount of oxygen causing the oxidation of structures that have hitherto been „traps" for heavy metals, such as iron sulphides (FeS). At the same time – the same forms of metals –

can be bound into structures of newly formed organic compounds due to plant metabolism. An additional difficulty in the analysis of this phenomenon is the seasonality of processes. It looks different in the phase of intensive plant growth, and different in the time of their dying. The features of the native soil cannot be omitted, which may significantly affect the course of the processes [16].

Despite many factors that can show that the presence of plants can increase the mobility of metals, the presence of swamp vegetation does not cause their mass mobilization. Therefore, it is clear that the use of plants for immobilization of heavy metals or for purification of contaminated areas is most advisable provided that the existing conditions are recognized [16].

A group of Australian researchers proved that the addition of comminuted clay or bauxite clay to the sediment limits the mobility of heavy metals [21]. This clay is an effective sorption „trap" for metals released due to oxidation of organic compounds washed out by water, activated by the metabolism of plants and microorganisms and by the processes of sediment processing (e.g. drying). The effectiveness of this treatment depends to a large extent on the form in which the element occurs in the sediment. In general, however, it is an excellent solution for limiting the mobility of heavy metals. The majority of metals, after the addition of clay, move from organic forms into the residual phase - i.e. the residue in which the metals are immobilized [21]. Even in laboratory conditions, the separation of metals from the residual phase requires the use of strongly oxidizing mixtures, e.g. royal water. Among the elements studied: chromium, lead, zinc, cadmium, nickel and copper, only copper, which occurs mainly in stable organic forms in the sediment, did not show a tendency to move to the residual phase [21].

An effective method of temporary immobilization of heavy metals is liming of sewage sludge. Although the liming process favours lowering the fertilising value of sludge, it is still used as the best form of prevention of heavy metals uptake by plants [22].

3. STUDY METHODOLOGY

A two-kilogram sample of sewage sludge taken before the hygienization process from all objects was used to study metal mobility. Determinations were performed using Perkin-Elmer 3100 F-AAS atomic absorption spectrometer with ball valve option. The

tests were carried out by BCR sequential extraction. Mineralization of the residual fraction was carried out with royal water. The sample taken was reduced to 8 g and dried (air-dry conditions) at 20ºC for 48 hours. Next, 0.5 g of sewage sludge with 80% hydration was weighed and transferred to a 100 cm^3 centrifuge tube. After addition of 40 cm^3 of 0.11 mol acetic acid solution, the test was shaken for 16 hours at room temperature. The extract obtained was separated from the sediment by centrifugation (4000 rpm). The content of water soluble metals in the obtained liquid was determined. The sewage sludge was washed 20 cm^3 of distilled water by shaking and centrifugation. Then 40 cm^3 of 0.1 mol hydroxylamine hydrochloride solution of pH = 2 was added to the sewage sludge. Nitric acid was used for pH correction. It was proceeded as in the previous stage (shaking and centrifuging). In the liquid the metals of fraction II were determined and the sewage sludge was rinsed. The sewage sludge was quantitatively transferred to quartz steamers and 10 cm^3 30% hydrogen peroxide was added. The content of the evaporator was heated in a water bath at 85ºC for one hour. The operation was repeated by adding to the sewage sludge 10 cm^3 of 8.8 mol hydrogen peroxide solution. After cooling to room temperature the sewage sludge samples were transferred to rotor tubes and 50 cm^3 of ammonium acetate solution was added (1 mol/dm^3, pH = 2 after HNO$_3$ correction). The sample was shaken for 16 hours and then the sludge was separated from the extract. In the solution the metals of fraction III were determined. Sewage sludge was washed and dried to constant mass. Mineralization of the residual fraction was carried out with royal water. To a 300 cm^3 conical flask containing 0.5 g of sewage sludge, 30 cm^3 HCl concentration and 10 cm^3 HNO$_3$ concentration were added. The content of the flask was heated for 30 minutes, then evaporated to dry. After cooling down, 25 cm^3 HCl (1+5) was added to dissolve the sewage sludge and transferred to a volumetric flask

and supplemented with distilled water to 50 cm^3, then the contents of the flask were stirred and seeped into a dry container. In the filtrate, fraction IV metals were determined. The content of heavy metals in the extracts obtained was determined according to ISO 9001:2000 on Perkin-Elmer 3100 F-AAS atomic absorption spectrophotometer, in four independent samples of sewage sludge. A recovery check was carried out based on certified reference material BCR CRM 143R. The results were statistically analysed to exclude coarse errors. Dixon and Grubbs tests were used for this purpose.

4. STUDY RESULTS

Table 3 shows the average heavy metal content in sludge dry matter in the four mobility fractions. The content of the mobile fraction (FI, FII) and the conditionally immobile fraction (FIII) compared to the residual fraction (FIV) was very low (Fig. 2). In the case of heavy metals obtained from FI fractions, water-soluble and carbonate-bound, a significant, 18.4% share was recorded for zinc. No copper was detected in this fraction and lead content was trace (0.6%). In the fraction bound with amorphous iron oxides (FII) zinc and cadmium dominate. The share of both these heavy metals exceeds 16%. A significant percentage of heavy metals was determined in the form of sulfides and in organometallic bonds (FIII). The highest percentage was found in copper (69.2%). The remaining metals also show significant content in FIII: Zn – 40.4%, Cd – 39.4% and Ni – 36.5%. The exception is lead, whose content in the FIII fraction is only 3.8%. Almost all lead content equal to 408,4 mg/kg d.m. is concentrated in the immobile FIV fraction. The relative lead content in the residual FIV fraction is 95.6%. Chromium – 55.9%, nickel – 46.1% and cadmium – 31.9%, respectively, occurred in the lower percentage share. The content of the residual FIV fraction for copper is 30.8%, but for zinc this value drops already to 25.0%.

Table 3. Average content of heavy metals in dry mass of sludge from the sewage treatment plant in Daleszyce in four stability fractions obtained by BCR sequential extraction method

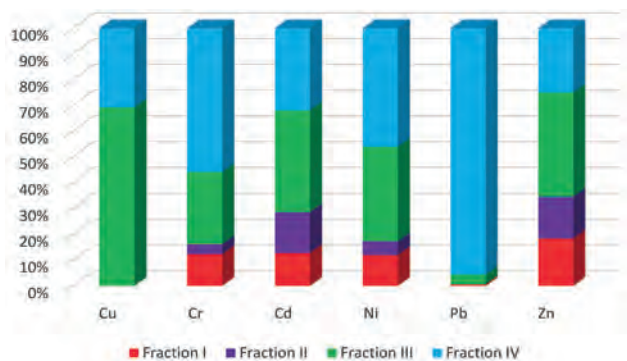| Speciacion	Cu, mg d.m./kg	Cr, mg d.m./kg	Cd, mg d.m./kg	Ni, mg d.m./kg	Pb, mg d.m./kg	Zn, mg d.m./kg
Fraction I	0	13	1.2	2	2.5	509.9
Fraction II	0	4.2	1.5	0.9	0	447.3
Fraction III	14.6	29.4	3.7	6.1	16.2	1119
Fraction IV	6.5	59.1	3	7.7	408.4	693.2

Fig. 2. Average percentage of heavy metals in sludge from the Daleszyce wastewater treatment plant depending on the fraction

The average percentage of heavy metals in the separated fractions in the analysed sewage sludge from the treatment plant in Daleszyce was presented in the following decreasing series of contents:

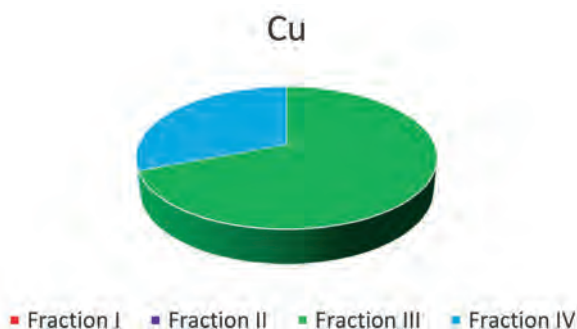– for Cu: FIII(69.2%) > FIV(30.8%) > FII(0.0%) > FI(0.0%) (Fig. 3)

Fig. 3. Average percentage of copper in sewage sludge from the Daleszyce sewage treatment plant depending on the fraction

– for Cr: FIV(55.9%) > FIII(27.8%) > FI(12.3%) > FII(4.0%) (Fig. 4)
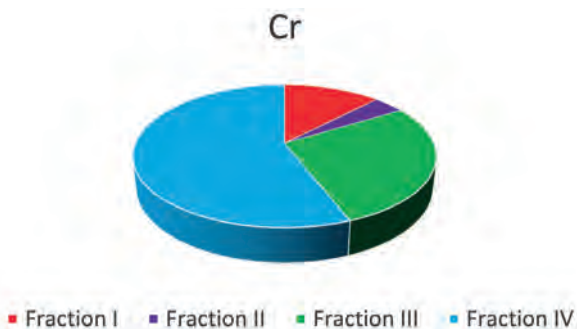
Fig. 4. Average percentage of chromium in sewage sludge from the Daleszyce sewage treatment plant, depending on the fraction

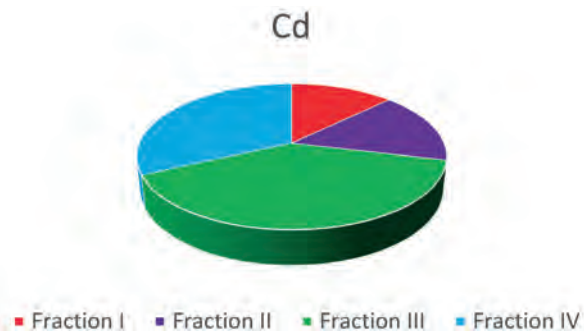– for Cd: FIII(39.4%) > FIV(31.9%) > FII(16.0%) > FI(12.8%) (Fig. 5)

Fig. 5. Average percentage of cadmium in sewage sludge from the Daleszyce WWTP depending on the fraction

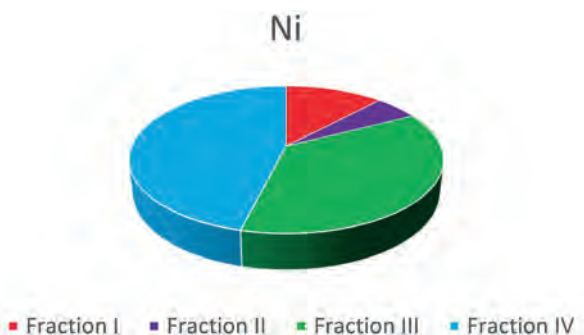– for Ni: FIV(46.1%) > FIII(36.5%) > FII(12.0%) > FII(5.4%) (Fig. 6)

Fig. 6. Average percentage of nickel in sludge from the Daleszyce WWTP depending on the fraction

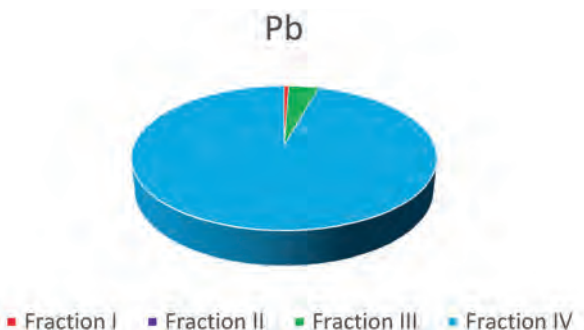– for Pb: FIV(95.6%) > FIII(3.8%) > FI(0.6%) > FII(0.0%) (Fig. 7)

Fig. 7. Average percentage of lead in sewage sludge from the Daleszyce WWTP depending on the fraction

– for Zn: FIII(40.4%) > FIV(25.0%) > FI(18.4%) > FII(16.1%) (Fig. 8)

Fig. 8. Average percentage share of zinc in sludge from the Daleszyce sewage treatment plant depending on the fraction

5. RESULTS

The results obtained allow us to conclude that the content of heavy metals in the tested sediments did not exceed the permissible limits applicable in Poland for sediments intended for natural use, with the exception of zinc, whose maximum permissible content is 2500 mg/kg d.m. In most cases, heavy metals were found in non-mobile fractions, from which they will not get into the soil. The analysis of the mobility of heavy metals is of great importance in assessing the environmental risk of heavy metals. Therefore, it can be concluded that, in terms of the content of heavy metal mobility fractions, sediments are eligible for their natural use. This is one of the three basic criteria to be met by sediments for natural use, in addition to the content of Salmonella bacteria and zero parasite eggs per kg of dry matter. However, it should be considered whether the immobilisation of heavy metals is sufficient and guarantees that there will be no later transfer of metals to mobile forms under the influence of physico-chemical factors such as temperature or electromagnetic radiation. The problem seems to be important, and research on the mobility of heavy metals will continue in further publications.

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