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NEW INDICES DETERMINING HEAVY METALS MIGRATION IN A SEWAGE SLUDGE

NOWY WSKAŹNIK OKREŚLAJĄCY STABILNOŚĆ METALI CIĘŻKICH W OSADACH ŚCIEKOWYCH

Abstract: The four step procedure developed by the European Community Bureau of Reference (BCR) is the optimum means of identifying heavy metal fractions in sewage sludge samples. Using the BCR procedure enables to get the date basing on which one can calculate metal stability index which supplies information on the strength of metal bonds with mineral organic soil components. Unfortunately, very popular formulae describing this index do not possess any theoretical justification and do not generate all values in the range of [0; 1]. Hence, in this paper one has presented new formulae describing not only the stability index but also a strictly connected with it the mobility index. In addition, one has suggested that these new formulae depend on the Equivalent Population (EP) indicator.

Keywords: sewage sludge, the BCR procedure, extraction, stability index, mobility index

Introduction

Determining heavy metals migration in a sewage sludge seems of primary importance when the sludge is used in agriculture. Sewage sludge from sewage treatment plants has both soil- forming and fertilising properties. It contains organic substances, nitrogen, phosphorus, magnesium, calcium and potassium forms that are available to plants. The constraints on sewage sludge use as an organic fertiliser result mainly from inappropriate microbiological composition and high heavy metals content.

The major factors that affect the heavy metal bioavailability to plants include the following: the total metals content in the soil, sort of metals, the pH of the soil, the content of an organic matter and a clay fraction. Bioaccumulation of heavy metals in plants growing on soils contaminated with heavy metals depends on the plant kind and the content of metal

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mobile fractions in the soil. Recent analytical techniques make possible to assess the actual hazard posed by the soil exposition to sewage sludge containing heavy metals when their direct transfer to the soil involves only their mobile forms.

The sludge under consideration ought to be subjected to speciation analysis. Basically, the speciation analysis with the Kersten and Forstner method involves chemical extraction of heavy metals contained in the sewage sludge. As a result of the process, extracts containing metals in the mobile, organic, oxidized, reduced and immobile forms are obtained [1, 2].

Theoretical

It was found out that the four-step procedure developed by the European Community Bureau of Reference (BCR) is the optimum means of identifying metal fractions in sewage sludge samples [3-5]:

- Step I: CH_3COOH extraction - to determine the content of metals that are accessible and bound to carbonates (F1 - exchangeable fraction).
- Step II: $NH_2OH \cdot HCl$ extraction - to determine the content of metals bound to amorphous iron and manganese oxides (F2 - reducible fraction).
- Step III: H_2O_2/CH_3COONH_4 extraction - to determine the content of metal-organic and sulphide fractions (F3 - oxidizable fraction).
- Step IV: mineralisation of the residual fraction in a mixture of concentrated acids (HCl, HF, HNO_3) - to determine the content of metals bound to silicates (F4 - residual fraction).

The BCE procedure described above is additionally presented in Figure 1.

The heavy metals in the obtained extracts were determined in accordance with ISO 9001:2000 using a Perkin-Elmer 3100 FAAS-BG atomic absorption spectrophotometer (with impact bead). Each test was repeated four times.

Mathematical description

Metal stability index I_R provides information on the strength of metal bonds with mineral-organic soil components over the time that elapsed from the moment of contamination. It can take on the values in the range $0 \leq I_R \leq 1$. If a metal occurs in the easily soluble and exchangeable form, the value of I_R is close to zero, whereas when $I_R \approx 1$, the metal predominantly occurs in stable, mainly residual forms. Intermediate values indicate the metal occurrence in both mobile and stable forms. A very popular formula describing this index has the following form [3]:

$$I_R = \sum_{i=1}^{k} \frac{i^2 \cdot C_i}{k^2} \tag{1}$$

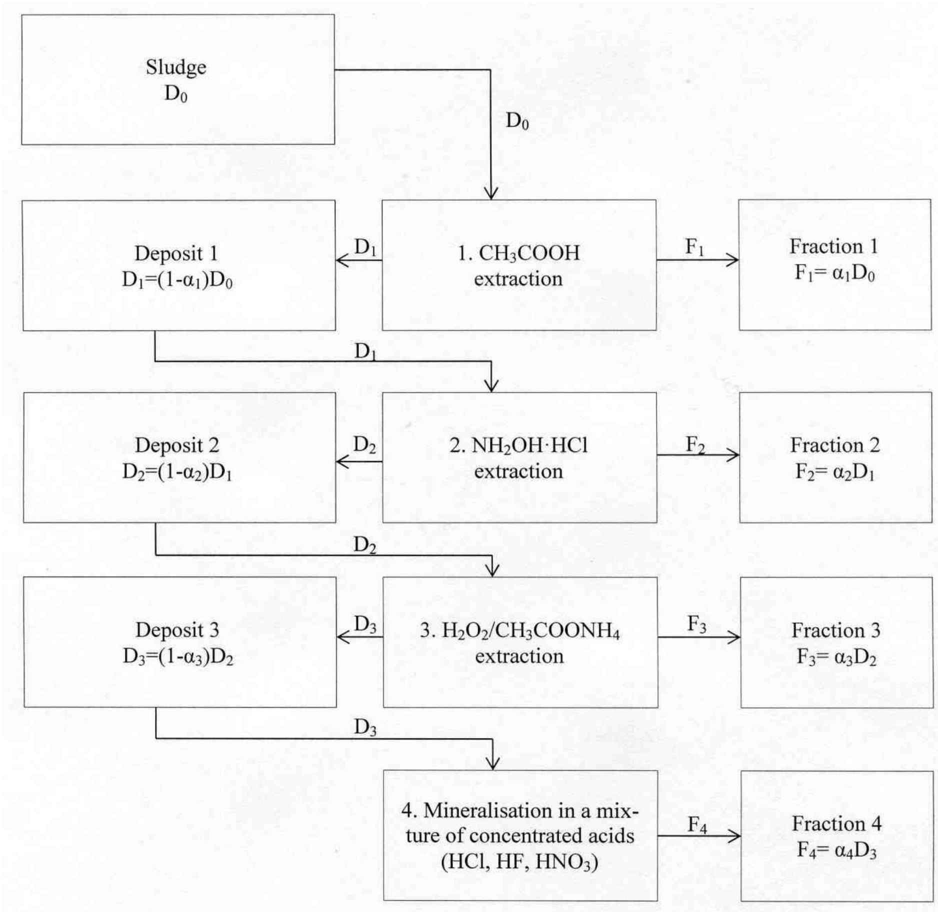
where:

i - denotes a subsequent step of the sequential extraction,

k - maximum number of extractions (in the BCR procedure $k = 4$),

C_i - relative metal content in the i^{th} chemical form.

Unfortunately equation (1) does not possess any theoretical justification and does not generate all values in the range of [0; 1]. So, the main goal of this paper is to present a new formula describing the stability index (*IS*).



where D_i determines the contents of heavy metals in the deposit i (i = 0, 1, 2, 3)

Fig. 1. Sequential analysis for separating sewage sludge samples

Let α_i be an efficiency in the i^{th} step of the sequential extraction defined as follows:

$$\alpha_i = \frac{F_i}{D_{i-1}} \tag{2}$$

(i = 1, 2,…, k; in the BCR procedure k = 4), hence

$$F_i = \alpha_i D_{i-1} \quad (i = 1, 2, 3, 4) \tag{3}$$

where:

$$\alpha_4 = 1 \tag{4}$$

So, each extraction step may be described both by equation (3) and the mass balance equation of the form:

$$D_{i-1} = F_i + D_i \quad (i = 1, 2, 3, 4) \tag{5}$$

Combining equations (3) and (5) we get the following equations:

$$D_i = D_{i-1}(1-\alpha_i) \quad (i = 1, 2, 3, 4) \tag{6}$$

Equations (3) and (6) create the following sequences:

$$\begin{aligned} &D_0 \\ D_1 &= (1-\alpha_1)D_0 \quad F_1 = \alpha_1 D_0 \\ D_2 &= (1-\alpha_2)D_1 \quad F_2 = \alpha_2 D_1 \\ D_3 &= (1-\alpha_3)D_2 \quad F_3 = \alpha_3 D_2 \\ D_4 &= (1-\alpha_4)D_3 \quad F_4 = \alpha_4 D_3 \end{aligned} \tag{7}$$

The above sequences can be easy presented as the functions of the heavy metals contents in the sludge D_0:

$$\begin{aligned} D_1 &= (1-\alpha_1)D_0 \quad F_1 = \alpha_1 D_0 \\ D_2 &= (1-\alpha_2)(1-\alpha_1)D_0 \quad F_2 = \alpha_2(1-\alpha_1)D_0 \\ D_3 &= (1-\alpha_3)(1-\alpha_2)(1-\alpha_1)D_0 \quad F_3 = \alpha_3(1-\alpha_2)(1-\alpha_1)D_0 \\ D_4 &= (1-\alpha_4)(1-\alpha_3)(1-\alpha_2)(1-\alpha_1)D_0 \quad F_4 = \alpha_4(1-\alpha_3)(1-\alpha_2)(1-\alpha_1)D_0 \end{aligned} \tag{8}$$

Remembering that $\alpha_4 = 1$ (equation (4)) it is easy to prove the following:

$$F_1 + F_2 + F_3 + F_4 = D_0 \tag{9}$$

Assuming, that the fractions F1, F2 and F3 are not stable it is possible to define the stability index *IS* by the following equation:

$$IS = 1 - \frac{F_1}{D_0} - \frac{F_2}{D_0} - \frac{F_3}{D_0} \tag{10}$$

and hence, using the results of equation (8) we obtain as follows:

$$IS = 1 - \alpha_1 - \alpha_2(1-\alpha_1) - \alpha_3(1-\alpha_2)(1-\alpha_1) \tag{11}$$

The above equation can be easy expressed in the form:

$$IS = \prod_{j=1}^{3}(1-\alpha_j) \tag{12}$$

Under strictly defined conditions the fraction being considered is stable or unstable (mobile). So, in this case the metal mobility index (*IM*) should be defined by the following expression:

$$IM = \frac{F_1}{D_0} + \frac{F_2}{D_0} + \frac{F_3}{D_0} \tag{13}$$

which can be presented in the form:

$$IM = \alpha_1 + \alpha_2(1-\alpha_1) + \alpha_3(1-\alpha_2)(1-\alpha_1) \tag{14}$$

Combining equations (8) and (11) one has obtained the following relationship:

$$IM = 1 - IS \tag{15}$$

On the other hand, making an assumption that only the fractions F1 and F2 are not stable leads to the following expression determining both indices:

$$IS = 1 - \sum_{i=1}^{2} \frac{F_i}{D_0} = (1-\alpha_1)(1-\alpha_2) = \prod_{j=1}^{2}(1-\alpha_j) \tag{16}$$

and

$$IM = \alpha_1 + \alpha_2(1-\alpha_1) \tag{17}$$

The carried out observations show that probably there exists a relation between the indicator EP and the mobility index *IM* of heavy metals. For the large sewage treatment plants participation of the mobile fractions are usually distinctly lower than in the case of the large sewage treatment plants, working in the anaerobic conditions, one has proposed to calculate the stability and mobility indices using respectively the equations (16) and (17). But for the smaller sewage treatment plant, working in the oxidative condition, one has proposed using respectively the equations (12) and (14) for calculation the stability and mobility indices.

Experimental

Values of the metal mobility and stability indices have been determined in sewage sludges coming from the three of sewage treatment plants located in central Poland.

1. A sewage treatment plant located in Sandomierz is the mechanical-biological one with a nominal capacity of 7500 m^3/d, a real capacity of 3132 m^3/d and EP of 29550 g BOD/d.
   The biological part of this plant bases on the activated sludge method fitted with increased removal of the biogenes.

Table 1

Heavy metals mean contents in 0.5 g of the dry mass of the stabilized sewage sludges coming from the sewage treatment plant in Sandomierz

Speciation*	**Metal [μg]**						**Fraction**
	Cu	**Cr**	**Cd**	**Ni**	**Pb**	**Zn**	
Sewage sludge							
Fraction 1	23.9 ± 0.2	4.9 ± 0.1	2.3 ± 0.2	8.1 ± 0.2	51.7 ± 4.0	349.5 ± 3.5	440.37
Fraction 2	43.5 ± 0.4	27.1 ± 0.4	1.3 ± 0.1	11.2 ± 0.3	88.7 ± 4.3	140.0 ± 1.6	311.68
Fraction 3	41.7 ± 0.2	19.3 ± 0.3	0.7 ± 0.1	5.5 ± 0.2	36.6 ± 0.7	45.5 ± 0.4	149.17
Fraction 4	3.1 ± 0.1	11.8 ± 0.2	0.8 ± 0.1	4.9 ± 0.1	22.7 ± 0.3	15.5 ± 0.3	58.82
ΣF1…4	112.1	63.08	4.95	29.7	199.7	550.5	960.02

*F1, F2 - mobile fraction, F3 - conditionally immobile fraction, F4 - immobile fraction, ΣF1…F4 - total content

This part consists of two clutched (each other) reactors built on the centrally located sedimentation tank and the circumferentially located sedimentation chambers. The stabilized sewage sludges coming from this plant are used as the fertilizers for energy forestry (*Salix viminalis*) cultivation. The heavy metals contents in the sewage sludges coming from the plant obtained by the use of the BCR method are presented in Table 1.

2. A sewage treatment plant located in Jedrzejow is the mechanical-biological one with increased removal of the biogenes, a capacity of 8622 m^3/d and EP of 48272 g BOD/d. Sewage from the plant are supplied to the Brzeznica river. Sewage sludges coming from this plant are utilized in agricultural fields. The heavy metals contents in the sewage sludges coming from the plant are presented in Table 2.

Table 2

Heavy metals mean contents in 0.5 g of the dry mass of the stabilized sewage sludges coming from the sewage treatment plant in Jedrzejow

Speciation*	**Metal [μg]**						**Fractions**
	Cu	**Cr**	**Cd**	**Ni**	**Pb**	**Zn**	
Sewage sludge							
Fraction 1	8.2 ± 0.2	0.7 ± 0.1	0.6 ± 0.1	0.9 ± 0.1	2.5 ± 0.4	2.0 ± 0.1	14.88
Fraction 2	0.7 ± 0.1	0.1 ± 0.1	0.5 ± 0.2	0.6 ± 0.1	1.8 ± 0.3	1.9 ± 0.1	5.68
Fraction 3	7.6 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	0.9 ± 0.2	0.2 ± 0.3	10.3 ± 0.2	18.98
Fraction 4	36.8 ± 0.3	41.4 ± 0.5	1.8 ± 0.1	2.4 ± 0.3	45.3 ± 0.5	604.1 ± 7.1	731.66
ΣF1…F4	53.18	42.28	2.88	4.87	49.72	618.25	771.18

*As in Table 1

3. A sewage treatment plant located in Mniow is the modified structure using the activated sludge method COMA-TEC in which sewage are purified in the hypoxic or anaerobic conditions and then aerated in order to get entire oxygen stabilization of the sewage sludges. The plant has a capacity of 140 m^3/h and EP of 9550 g BOD/d. Sewage from this plant are supplied to the Czarna Taraska river. The heavy metals contents in the sewage sludges coming from the sewage treatment plant in Mniow are presented in Table 3.

Table 3

Heavy metals mean contents in 0.5 g of the dry mass of the stabilized sewage sludges coming from the sewage treatment plant in Mniow

Speciation*	**Metal [μg]**						Fractions
	Cu	**Cr**	**Cd**	**Ni**	**Pb**	**Zn**	
Sewage sludge							
Fraction 1	1.6 ± 0.1	0.8 ± 0.1	0.2 ± 0.1	1.3 ± 0.1	4.7 ± 0.5	49.6 ± 1.1	58.26
Fraction 2	0.80 ± 0.1	0.7 ± 0.1	0.1 ± 0.1	3.1 ± 0.2	5.6 ± 0.6	61.6 ± 1.6	71.89
Fraction 3	18.1 ± 0.3	7.2 ± 0.1	0.8 ± 0.1	4.6 ± 0.2	4.9 ± 0.5	249.9 ± 4.1	285.48
Fraction 4	11.1 ± 0.2	9.5 ± 0.2	0.7 ± 0.1	2.2 ± 0.2	49.3 ± 4.1	162.3 ± 3.9	234.98
ΣF1…F4	31.55	18.25	1.90	11.05	64.45	523.40	650.60

*As in Table 1

Values of the stability and mobility indices calculated using respectively both equations (12) and (14) proposed for the smaller treatment plants and equations (16) and (17) proposed for the large sewage treatment plants are presented in Table 4. Additionally, in this Table for comparison one has presented the stability index I_R calculated from the empirical equation (1).

The values IM_h and IS_h obtained for the sewage treatment plant in Mniow should not be used because is a small plant (with the low value of the *EP*), for which the indices IM_i and

IS_i are proposed. The above mentioned indices IM_h and IS_h are given in Table 4 for illustration.

Table 4

Stability and mobility indices obtained for the random chosen sewage treatment plants located in central Poland

Index	Name of wastewater treatment plant		
	Sandomierz STP	**Jedrzejow STP**	**Mniow STP**
IS_h	0.060	0.949	0.363
IS_l	0.217	0.974	0.802
IM_h	0.099	0.051	0.637
IM_l	0.783	0.026	0.198
I_R	0.258	0.966	0.641

IS_h - stability index calculated for high values of the *EP* (eq. (16)), IS_l - stability index calculated for low values of the *EP* (eq. (12)), IM_h - mobility index calculated for high values of the *EP* (eq. (17)), IM_l - mobility index calculated for low values of the *EP* (eq. (14)), I_R - stability index calculated using (eq. (1))

Conclusions

- The new methods of determining the stability and mobility indices basing on the fraction definition (equation (3)) have been presented.
- In the case of sewage treatment plants the stability and mobility indices can be calculated using respectively the equations (16) and (17), respectively.
- One has proposed that for the smaller sewage treatment plants both the *IS* and *IM* indices are better calculated from the equations (12) and (14).
- Under strictly defined conditions the fraction of concern is stable or mobile (unstable). In such case the relationship (15) is true.

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NOWY WSKAŹNIK OKREŚLAJĄCY STABILNOŚĆ METALI CIĘŻKICH W OSADACH ŚCIEKOWYCH

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Abstrakt: Czterostopniowa procedura proponowana przez European Community Bureau of Reference (BCR) jest optymalnym sposobem identyfikacji frakcji metali ciężkich w osadach ściekowych. Zastosowanie procedury BCR umożliwia uzyskanie informacji o sile wiązań tych metali z materią organiczną gleby, określonej przez wskaźnik stabilności. Niestety istniejące w literaturze formuły określające ten wskaźnik nie mają teoretycznego uzasadnienia i nie generują wszystkich wartości z przedziału [0; 1]. W niniejszej pracy wyprowadzono nowe wzory umożliwiające nie tylko wyznaczenie wskaźnika stabilności, ale również ściśle z nim związanego wskaźnika mobilności. Z przeprowadzonych obserwacji wynika, że postacie wyprowadzonych wskaźników zależą od wielkości oczyszczalni ścieków określonej wartością wskaźnika RLM.

Słowa kluczowe: osady ściekowe, procedura BCR, ekstrakcja, wskaźnik stabilności, wskaźnik mobilności