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# The study of cobalt leaching from soils, sewage sludges and composts using a one-step extraction

Badanie wymywalności kobaltu z gleb, osadów ściekowych i kompostów przy wykorzystaniu ekstrakcji jednostopniowej

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#### Abstract

The study evaluated the leaching of cobalt (Co) in soils fertilised with sewage sludge (SS) and composts depending on the extractant used. SS came from rural, mechanical-biological treatment plant in Dobrzeń, Lower Silesia region. In addition, those SS were processed by composting. Sludges and composts were used to fertilise the energy plants during lysimeter experiment conducted during 2008-2013. The overall, as well as extracted by H2O, 0.1M HCl and 1M HCl, 0.05M Na2EDTA and 0.1M Na<sub>a</sub>EDTA, content of Co in samples were analysed. Additionally, the impact of pH and organic matter (OM) content on the leachability of Co were researched. It was found that the soil samples were rich in Co. Its share slightly depended on fertilisation with SS and compost. Co leaching depends on the type and concentration of extractant. The highest content of Co were leched with 0.1 M Na<sub>2</sub>EDTA, and the lowest content with 0.1M HCI. Co concentration in H<sub>2</sub>O extracts was not determined as its content was below the limit of quantification. Leachability of Co in the analysed samples was influenced by the overall Co content as well as pH and OM content.

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## Streszczenie

W pracy dokonano oceny wymywalności kobaltu w glebach nawożonych osadami ściekowymi i kompostami osadowymi w zależności od wykorzystanego ekstrahentu. Osady ściekowe pochodziły z wiejskiej, mechaniczno-biologicznej oczyszczalni ścieków w Dobrzeniu, województwo dolnośląskie. Dodatkowo osady poddawano kompostowaniu. Osady i komposty stosowano nawożenia roślin energetycznych w doświadczeniu lizymetrycznym prowadzonym w latach 2008-2013. W próbkach zbadano zawartość ogólną kobaltu oraz po ekstrakcji H<sub>2</sub>O, 0,1M HCl i 1M HCl, 0,05M Na<sub>2</sub>EDTA i 0,1M Na<sub>2</sub>EDTA. Dodatkowo oceniono wpływ pH i zawartości substancji organicznej na wymywalność kobaltu. Stwierdzono, że badane gleby były zasobne w kobalt. Jego udział w niewielkim stopniu zależał od nawożenia osadem ściekowym i kompostem. Wymywalność kobaltu zależała od rodzaju i stężenia ekstrahentu. Najwięcej kobaltu wymyto przy roztworu 0,1M Na<sub>2</sub>EDTA, natomiast najmniej 0,1M HCl. W wyciągach wodnych nie oznaczono zawartości kobaltu, jego udział znajdował się poniżej granicy oznaczalności. Na wymywalność Co z badanych próbek wpłynęła zawartość ogólna tego metalu, odczyn pH i zawartość substancji organicznej.

## 1. INTRODUCTION

Heavy metal mobility and bioavailability in sediments depend strongly on the mineralogical and chemical forms in which they occur. Extraction techniques are used to evaluate the mobility of heavy metals in environmental samples. The analysis allows determining the content of different forms of metals relative to their total concentration. This is useful, for example, for assessing the migration of metal ions from the sewage sludge (SS) and soils to plants [5, 26]. Different extraction reagents to leaching metals are used to assess their bioavailability in solid samples. Many methods are prepared to determine the mobility of the metals in different parts of the environment (sediments, soils, SS, waste et al.). Methods for chemical leaching of metals can be divided into single- (one-step) or multi-stage (sequential) extraction. One-step extraction tests are commonly used to study the ecotoxicity and mobility of metals in environmental samples. This method allows an assessment of bioavailability of metals and environmentally accessible trace metals upon disposal of wastes on a soil, thus assessing contamination of ground waters [1]. The method is most often used for soil speciation analysis. It makes it possible to determine the content of phytoavailable forms that were taken up by the plant. The advantage of one-step extraction is primarily a short time of analysis. In the sequential extraction (speciation), separation techniques in different forms of the matrix metal are used. Sequential extraction procedures are commonly applied, because they provide information on the fractionation of metals in the different lattices of the solid sample and to give information on environmental contamination risk. The advantages of these methods are more accurate estimation of the chemical forms of metals and easier prediction of their bioavailability. The disadvantage is the time and the need to use several extractants. For this reason, in 1987, the European

Community Standards, Measurement and Testing Programme (SM&T, preciously BCR) was started during which several research projects were implemented in which many laboratories throughout Europe took part. The result of the programme was to standardise the techniques of separation of metals in soils and sediments and the development of a three-step extraction method [24]. A large number of different reagents, that can extract almost all or part of the metals commonly found in soils (H2O, salts as NaNO2, NH4NO2, KNO2, CaCl2, CH2COONH4, chelating agents as EDTA, DTPA and acids CH<sub>3</sub>COOH, HNO3, HCI) have been used. In many European countries, it is recommended to use different extractant to exchangeable metal determination in soils. For example, in Germany 1M NH, NO,, in Switzerland 0.1M NaNO, in the Netherlands 0.01 M CaCl<sub>a</sub>, in France DTPA (NFX 31-121) and 1M NH<sub>4</sub>OAc (French standard NF X 31-108) are used. In Poland, 1M HCl are used in the assessment of potential bioavailability of micronutrients in soils [16]

Single extractants can be considered for their role of releasing elements from particular solid samples phases with which they are bound or associated [17]. However, single extraction is seldom used, because they are not sufficiently specific [9]. Leaching of metals depends on the type of eluent. Water-soluble metal ions can easily be mobilised, and may be considered as highly available [18, 26]. This extractants contain the watersoluble species made up of free ions and ions complexed with soluble organic matter (OM). Usually the concentration of trace metals in the soil solution is very low [17]. Higher degree of elution characterised by inorganic acids (HNO2, HCI), followed by complex (chelates) (Ethylenediaminetetraacetic acid - EDTA or Diethylenetriaminepentaacetic acid DTPA) and salt solutions [21]. Complex extraction solutions have been developed to ascertain bioavailability of heavy metals. Complexation by EDTA and other chelates are thought to simulate complexing behaviour of root exudates. Extractions using EDTA solution are widely used in ecochemical evaluations and more particularly those involving plant uptake. Complexing extractants such as EDTA or DTPA solutions can displace metals from insoluble organic or organometallic complexes in addition to those sorbed on inorganic components of solid phase. Those solutions attack the aluminosilicate structure, or Fe-bearing silicates minimally [11, 21, 23]. The elution ratio of metals by chelating agents such as EDTA, is influenced by the concentration, temperature and extraction time. The metal content of these extracts is strongly correlated with participation in plants. Therefore, the chelating agent is most often used to evaluate the bioavailability of metals in the soil [1, 17, 25]. EDTA is a stronger extractant than other chelating agents such as DTPA, hydroxyethyenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA) or ethylene glycol tetraacetic acid (EGTA) [4]. It was also shown that EDTA can release more metals from soils than inorganic acids [3]. Extractable metals by inorganic acids (HNO<sub>3</sub>, HCI) have been suggested as a measure for geochemically active metals presented in solid samples. Hydrochloric acid (HCI) dissolves large amounts of trace elements, far in excess of the nutritional needs of plants. Therefore, it is often criticised [14]. In Poland, the method with 1M HCl is used to assess the potential bioavailability of metals in soils. Some authors suggest that the use of HCl at such a high concentration allows only to determine the 'pseudo-total' metal content in solid samples. For this reason, it is proposed to replace the 1M HCl solution having a lower concentration of this acid (0.1 M HCl) [3, 12, 13].

Cobalt (Co) belongs to the important micronutrients necessary for plant life [10]. In Polish SS the content of Co contains within 2-40 mg kg<sup>-1</sup> d.m. However, rarely exceeds content 25 mg kg<sup>-1</sup> d.m. For comparison, typically contains manure: 0.22-0.78 mg kg<sup>-1</sup> d.m. [6]. The UK and Switzerland set a limit of Co in the sludge used for agricultural uses at 100 mg kg<sup>-1</sup> d.m. France allowed for agricultural use of SS containing not more than 20 mg kg<sup>-1</sup> d.m. [19]. Siuta i Wasiak [19] proposed Polish limit values for Co in SS on 50 mgCo/kg d.m. The authors suggest that the sludge contain a higher content of cobalt could be used for purposes other than agricultural uses, and even cobalt fertilisation of agricultural land. The content range in the tissues of plants is in the range of 0.02-1 mg kg<sup>-1</sup> d.m. The phytotoxic effect depends on the plant species. Toxic effects of Co in plants revealed drooping leaves, growth inhibition, chlorosis, leaf curling and a reduction in the weight of shoots [7, 10].

The aim of the study was to evaluate the leaching of Co in soils fertilised with SS and composts depending on the type of extractant.

#### 2. MATERIAL AND METHODS

Research material consisted of soil fertilised with SS and the composts. SS came from rural, mechanical-biological treatment plant with a capacity of 160 m<sup>3</sup>·d<sup>-1</sup>. Sewage is located in Dobrzeń, Lower Silesia region. SS were treated (composted) with the addition of structural materials (grass and sawdust). Composting process of SS was performed within Lower Silesia Research Centre in Wroclaw. Composting was carried out in heaps, on a specially prepared compost area. The proportion of fertiliser was calculated in each case, taking into account the ratio of carbon to nitrogen (C:N). Sludges and composts were used to fertilise the energy plants in lysimeter experiment conducted during 2008-2013. Samples of soils, sludges and composts were collected once a year, before fertilisation of soils. After drying and grinding, the samples were analysed. The pH of the samples was determined in KCI and OM content by gravimetric method at 550°C. The samples were digested in a Microwave Digestion System Millestone Start D in closed teflon bombs. For determination of 'pseudo-total' Co concentrations in soil, SS and compost samples were digested in agua regia (1:3 HNO<sub>2</sub>/HCI). The name 'pseudo-total' concentration of metals in environmental samples was proposed by Rao et al. [17] and Meers et al. [13]; it means of the total metals content in solid samples, except metals associated in silicates crystal structures. 'Pseudo-total' content gives an assessment of the maximum potential hazard that could occur in long term or in extreme environmental regimes.

In addition, mobile forms of Co was also researched. The availability of Co was measured using  $\rm H_2O$ , 0.1M HCl i 1M HCl, 0.05M  $\rm Na_2EDTA$  i 0.1M  $\rm Na_2EDTA$ , The extraction with deionised water was performed within 24 hours at room temperature, the mass ratio of 1:10, in accordance with PN–EN 12457–2:2006

[15]. The extraction with HCI (0.1M i 1M) and chelating solution  $Na_2$ EDTA (0.05M i 0.1M), was performed within 1 hour at room temperature, the mass ratio of 1:10 [8, 11, 16].

All analyses were performed in triplicate. Obtained results were statistically verified by Statistica 10 programme for significance level P<0.05. Correlation coefficients (r) were calculated for the relation between concentration of Co in extract solutions and 'pseudo-total', pH, OM contents in samples (linear and multivariate regression). For quality control of total metal content determination in the samples, certified reference materials (CRM) were also analysed using the method for analysing 'pseudo-total' content as described above. Two CRM were analysed: 'SS amended soil' CRM005–050 and 'Metals in soil' CRM028–050 (Tusnovics). The recovery of Co content in CRM were 96% and 91%, respectively.

#### 3. DISCUSSION

The pH $_{\rm KCl}$  of the SS (7.0–7.9) was slightly higher than the compost sedimentary (6.1–7.1). The soils were characterised by a slightly acidic pH $_{\rm KCl}$  level (6.0–6.6). Fertilisation did not affect significantly change of soil pH $_{\rm KCl}$ . The content of OM in SS ranged from 64% to 76%, while composts from 53% to 66%. The content of OM (OM) in the non-fertilised soil (S1) ranged from 1.43% to 1.8%. In fertilised soils, OM content ranged from 1.6% to 3.1% (S2) and 1.6% to 2.7% (S3). Over the years, the experiment found a gradual increase in the content of OM in fertilised soils.

Table 1 shows the averaged results (2008–2013) of Co content in SS and composts. Contents in SS (SS) and composts (Ct) differed depending on the date of sampling (SS 4.58–15.09 mg kg $^{-1}$  d.m. and Ct 4.79–8.25 mg kg $^{-1}$  d.m.) (Table 1). Symanowicz and Kalembasa (2010) [20] have determined the amount of Co in SS at the level of 5.1 mg kg $^{-1}$  d.m. and 8.2 mg kg $^{-1}$  d.m., while Środa *et al.* (2013) [22] has determined a higher content of that metal in SS (10.9–13.9 mg kg $^{-1}$  d.m.).

The Co content in the soil was at the same level regardless of the method of fertilisation (2.23-2.31 mg kg<sup>-1</sup> d.m.). In

Table 1. Average  $(\bar{x})$ , SD and range of Co 'pseudo-total' content in samples: soils (S1–3), SS and composts (Ct) [mg kg<sup>-1</sup> d.m.]

Type of sample	'Pseudo-total' content of Co			
	$\frac{-}{x} \pm SD$	Range		
SS	6.65 ± 4.14	4.58–15.09		
Ct	5.99 ± 1.57	4.79–8.25		
Soil 1 (S1)	2.23 ± 0.35	1.67–2.96		
Soil 2 (S2)	2.26 ± 0.34	1.90–3.05		
Soil 3 (S3)	2.31 ± 0.27	1.64-2.93		

SD: Standard deviation; SS: Sewage sludges

S1 – soils without fertilisation

S2 – soils fertilised with compost

S3 - soils fertilised with sewage sludge

Canada, regulations for the concentration of Co in soils depend on the background considered: 0.01 mgCo kg $^{-1}$  d.m. for natural content, 0.04 mg kg $^{-1}$  d.m. for agricultural purposes;, 0.05 mgCo kg $^{-1}$  for residential purposes;, 0.3 mg kg $^{-1}$  d.m. for industrial purposes. The European Union is working to standardise the chemical status of the soil in order to assess the environmental risk by anthropopression [7]. According to Kabata–Pendias i Pendias (1999) [10] Co content in Polish soils ranged: 0.5–10 mgkg $^{-1}$ d.minsandysoils,5–25 mgkg $^{-1}$ d.m.inheavysoilsand 0.2–30 mg kg $^{-1}$ d.m. in organic soils. Comparing the results with literature data, it can be concluded that the analysed soils were rich in Co.

In order to evaluate the mobility of Co, the samples were leached using five different aggressive extractants. Water extracted the smallest amounts of metals compared with the other extraction media The content of Co in the water extracts in all samples was below the limit of quantification (<0.2 mg kg $^{-1}$  d.m.). HCl extracts low cobalt content (4–5% for 0.1M HCl and 5–6% for 1M HCl of the 'pseudo-total' were determined in SS and compost samples. Higher concentration of Co was determined in EDTA solutions. Whereas, in SS and compost samples, chelating agent (Na $_2$ EDTA) leached higher amounts of Co than HCl. Co showed the quantities extracted with 0.1M Na $_2$ EDTA highest (55% SS and 31% Ct of the 'pseudo-total') than 0.05M Na $_2$ EDTA highest (37% SS and 23% Ct of the 'pseudo-total') (Fig. 1).

The degree of leaching of Co from soil was similar regardless of the method of fertilisation. The higher percentage of the total metal content was found in the extracts: 0.1Na<sub>2</sub>EDTA (61–63%), followed 0.05Na<sub>2</sub>EDTA (34–36%), 1M HCI (17–21%) and 0.1M HCI (11–12%). Chelates, extractants such as EDTA, aim to remove metals chelated by OM and Fe–Mn oxides, associated with Co [7, 8]. Greinert (2011) [7] presents a higher level of soil leaching of Co extracted by HCI: 18–25% for 0.1M HCI and 52–66% for 1M HCI. The author said that the level of eluted Co from the soil affects the type of extractant.

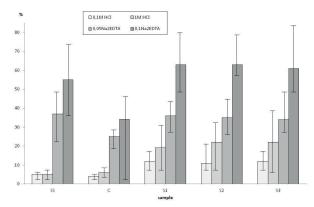


Fig. 1. Percentage of mobile form of cobalt extracted by different solutions

In order to determine the influence of selected parameters on the leaching of Co, statistical analysis of the results was carried out. The correlation coefficient (r) between the 'pseudo-total' content, pH and OM on leached forms of Co in soils, SS and composts (linear correlation) was calculated. In addition, multivariate

regression analysis was performed, where the dependent variable was the content of leachable form of Co, whereas the independent variables were: Co 'pseudo-total' content, pH, and the content of OM in the samples. The results of the statistical analysis are shown in Tables 2 and 3.

In conjunction of obtaining the results below the limit of determination in the aqueous extracts in SS, composts and soils, statistical analysis were not calculated for those samples. Co in EDTA and HCI extractants were correlated positively and significantly with total metal content in analysed samples (Table 2). After taking into account additional factors, such as pH and OM content, the value of the r was increased. This testifies

to the influence of both factors on the mobility of Co. Higher r was calculated for SS than for compost, whereas soils were characterised by low values of r. According to Greinert (2011) [7], the bioavailability of Co affects soil pH and redox conditions. Co in acidic solution may be found in dissolved forms, but in a neutral solution, as a part of a sorption complex. The solubility of Co in soils depends on the pH, water content, redox potential, OM and granulometric composition, the content of manganese oxides, type of fertiliser and temperature. The elution of Co is increased by increasing acidity, hydration and iron content; while manganese reduces the mobility of cobalt [7].

Table 2. Correlation coefficients (r) of linear and multivariate regression (r, P<0.05) calculated for the relation between concentration of Co in extract solutions ( $Co_{(extract)}$ ) and 'pseudo-total' ( $Co_{(p-total)}$ ), pH, OM contents in samples

	Type of extractant						
	H <sub>2</sub> O	0.1M HCI	1M HCI	0.05M Na <sub>2</sub> EDTA	0.1M Na <sub>2</sub> EDTA		
Sewage sludge							
Co(extract) = (Co <sub>p-total</sub> )	-	0.937	0.932	0.987	0.989		
Co(extract) = (pH)	-	0.358	0.439	0.443	0.457		
Co(extract) = (OM)	-	0.316	0.499	0.605	0.586		
$Co(extract) = (Co_{p-total}) + (pH)$	-	0.937	0.935	0.989	0.992		
$Co(extract) = (Co_{p-total}) + (OM)$	-	0.957	0.932	0.993	0.993		
$Co(extract) = (Co_{p-total}) + (pH) + (OM)$	-	0.958	0.936	0.995	0.996		
Compost							
Co(extract) = (Co p-total)	-	0.681	0.851	0.912	0.648		
Co(extract) = (pH)	-	0.532	0.763	0.967	0.725		
Co(extract) = (OM)	-	-0.600	0.129	0.196	0.632		
Co(extract) = (Co p-total) + (pH)	-	0.750	0.857	0.967	0.732		
Co(extract) = (Co p-total) + (OM)	-	0.927	0.857	0.927	0.891		
Co(extract) = (Co p-total) + (pH) + (OM)	-	0.923	0.874	0.967	0.894		
Soil 1							
Co(extract) = (Co p-total)	_	0.123	-0.484	0.365	0.351		
Co(extract) = (pH)	-	0.166	0.138	0.284	0.208		
Co(extract) = (OM)	-	0.186	0.618	0.442	0.420		
Co(extract) = (Co p-total) + (pH)	-	0.188	0.545	0.420	0.420		
Co(extract) = (Co p-total) + (OM)	-	0.257	0.703	0.665	0.634		
Co(extract) = (Co p-total) + (pH) + (OM)	-	0.262	0.704	0.666	0.641		
Soil 2							
Co(extract) = (Co p-total)	_	-0.367	-0.573	0.025	-0.095		
Co(extract) = (pH)	-	0.052	0.208	0.210	0.252		
Co(extract) = (OM)	-	0.086	0.682	0.675	0.732		
Co(extract) = (Co p-total) + (pH)	-	0.376	0.573	0.234	0.252		
Co(extract) = (Co p-total) + (OM)	-	0.373	0.757	0.746	0.762		
Co(extract) = (Co p-total) + (pH) + (OM)	-	0.380	0.759	0.758	0.774		
Soil 3							
Co(extract) = (Co p-total)	-	0.003	-0.480	0.058	0.078		
Co(extract) = (pH)	-	0.136	-0.448	-0.311	-0.317		
Co(extract) = (OM)	-	0.039	0.412	0.417	0.413		
Co(extract) = (Co p-total) + (pH)	-	0.142	0.575	0.351	0.367		
Co(extract) = (Co p-total) + (OM)	-	0.044	0.531	0.494	0.501		
Co(extract) = (Co p-total) + (pH) + (OM)	-	0.262	0.622	0.614	0.627		

Table 3. Correlation coefficients (r) of linear regression (r, P<0.05) between Co contents in extractants

Extractant	1M HCI	0.05M Na <sub>2</sub> EDTA	0.1M Na <sub>2</sub> EDTA
0.1M HCl	SS r = 0.778 C r = 0.683 S1 r = -0.211 S2 r = 0.139 S3 r = 0.070	SS r = 0.875 C r = 0.605 S1 r = -0.121 S2 r = 0.148 S3 r = 0.186	SS r = 0.883 C r = 0.230 S1 r = -0.124 S2 r = 0.162 S3 r = 0.123
1M HCI	-	SS r = 0.959 C r = 0.856 S1 r = 0.241 S2 r = 0.634 S3 r = 0.634	SS r = 0.962 C r = 0.800 S1 r = 0.271 S2 r = 0.331 S3 r = 0.628
0.05M EDTA	-	-	SS r = 0.999 C r = 0.827 S1 r = 0.984 S2 r = 0.980 S3 r = 0.991

In addition, among others, the r value was analysed (Table 3). Significant correlations were found between Co–HCl and Co–Na $_2$  EDTA concentrations in SS and compost samples (r = 0.800 – 0.962). The contents of Co extracted with 0.05M Na $_2$ EDTA were highly correlated with the 0.1M Na $_2$ EDTA (r = 0.827(Ct) – 0.999(SS)). In the case of soil in the majority of cases, the relationship between the extracts was not statistically significant. Statistically significant correlation between the extracts of 0.05M and 0.1M Na $_2$ EDTA in the soils samples were only determined. The lower r were calculated between 1M HCl and 0.05M or 0.1M Na $_2$ EDTA in fertilised soils.

## 4. CONCLUSIONS

The studied soils were rich in Co. Co content in soils slightly depends on fertilisation with SS and compost. Cobalt leaching

from soils, sludges and composts depends on the type and concentration of the extractant. More of the metals were eluted using a chelating agent (Na,EDTA) than the HCl.

Pseudo-total' content, pH and OM level also affects leachability of Co. Co in soil is mainly bound with organic fraction and oxides of Fe–Mn. Therefore, it is gradually leached out of the soil. In Poland, there is a standardised content of this metal in sludge used for agricultural purposes. The Co content in the SS is usually several times higher than in typical organic fertilisers. Although the metal is part of the trace elements necessary for the growth of plants, the excess in the soil may affect toxicity. Therefore, when SS is used as fertiliser, it should be taken into account not only the overall metal content limited by law, but also other metals and the percentage of mobile forms.

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