

Effectiveness of Oxide-Amendments in the Stabilization Process of Cu, Pb and Zn in Artificially Contaminated Soil

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Abstract

Three oxide-bearing amendments – steel shots, spodic horizon and Portland cement – were evaluated by sequential extraction procedure and leaching test to determine their ability to reduce heavy metal mobility in metal-spiked soil. The incubation experiment was conducted on surface soil horizon that was contaminated with Cu, Pb and Zn as $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Each metal was introduced at the rate of $5,000 \text{ mg} \cdot \text{kg}^{-1}$. As soil pH strongly influences heavy metal mobility, especially Zn, in this experiment two levels of soil reaction were tested – pH 4 and pH 6. The rise of pH up to pH 6 was undertaken by the addition of calcium carbonate to contaminated soil after 4 weeks of pre-incubation. Next, oxide-bearing amendments were added at the rate: 0, 1 and 3% (on dry weight basis) and the incubation proceeded further for 12 weeks. When the incubation process was finished leaching test was started. During leaching test, additional pH of leachate was analyzed. Result from leaching test showed that metal mobility changed with soil reaction. When reaction of soil solution was below pH 4.6, metal leaching decreased for $\text{Zn} < \text{Cu} < \text{Pb}$, but between pH 4.6 and the 8.2 the sequence was $\text{Zn} < \text{Pb} < \text{Cu}$. Above pH 8.2 of soil solution metals showed completely different mobility pattern, the quantity of metals washed out in the order $\text{Cu} < \text{Pb} < \text{Zn}$. Among tested amendments, the highest efficiency of stabilization process was obtained with cement, independently of soil pH and the dose of the stabilizer. In the case of steel shot, immobilization of trace elements depended on pH and the dose of amendment, higher reduction of metal mobility was obtained in the soil with 3% of stabilizer dose in CaCO_3 -treated soils.

Keywords: heavy metals, chemical stabilization, sequential extraction, leaching test, oxide-amendments

Introduction

Soils contaminated with heavy metals create potential risk for ground water quality and biota, and might be a source of spreading these metals into other areas. These heavy metals may adversely affect soil ecology, water quality and agriculture production. Remediation techniques

available for contaminated soils with heavy metals are numerous. Nowadays, stabilization is one of the more widely suggested techniques, as it is seen to be cost-effective and promising remediation technology [1-3]. In this technique, concentration of the mobile fractions of heavy metals are reduced by introducing into contaminated soil different amendments (stabilizers) that could bind, adsorb or co-precipitate them. The main objective of this technique is to change trace metals speciation, which increases

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the content of low soluble fractions, forcing reduction of the mobile fractions. However, it is important to emphasize that stabilization techniques do not reduce the total concentration of heavy metals, which is why effectiveness of stabilization should be monitored over long periods [4, 5].

Identification and quantification of heavy metals pool in the soil can be achieved by sequential extraction. This analytical method divides metals on the basis of their solubility, which changes with pH, redox condition or during complexation reactions [6, 7]. Usually, the considered fractions are: exchangeable, carbonated bound, hydrous-oxide bound, organic bound and strongly attached to the lattice material (referred as residual). Water-soluble and exchangeable fractions are regarded as a mobile pool of trace elements, others with the exception of residual are treated as potentially mobile if specific conditions in the soil environment have appeared.

The pool of metals that could be potentially transferred to ground water was analyzed by leaching tests. This test more accurately reproduces conditions occurring in a natural soil environment than sequential extraction, which uses strong extractants and may overestimate metal mobility.

Different chemical properties of heavy metals and specific site conditions of contaminated soils mean that there is no one perfect stabilizer, and new effective and cheaper amendments are still sought. In this study three oxide-bearing stabilizers were selected, as they could potentially stabilize trace elements by the adsorption process [8] and occlusion reaction, or by formation of insoluble secondary oxidation minerals [5]. For the stabilization process the following sources of oxides were selected: steel shots, spodic horizon and Portland cement. Steel shot, an industrial by-product, contains mainly iron that corrodes and oxidizes to produce iron oxides [9]. Spodic is a subsurface horizon that contains illuvial amorphous substances that consist of organic matter, sesquioxides of aluminium and iron. The third stabilizer tested in this work was Portland cement, a common material in the construction industry. The chemical composition of Portland cement, especially the appearance of silica, aluminium, and iron oxides, indicates that this material has the potential ability to immobilize heavy metals by adsorption, precipitation surface complexation and isomorphous substitution [10].

As soil reaction strongly influences heavy metal mobility, in this experiment two levels of soil reaction were tested. Cu, Pb and Zn show higher mobility in acid conditions, so in this study heavy metals behaviour was tested in a strongly acid environment \approx pH 4 and a slightly acid environment \approx pH 6. According to McBride et al. [11], Basta and McGowen [12] increasing soil pH may result in stronger immobilization of trace elements as a consequence of higher soil binding capacity and changes in chemical forms of metals.

The aim of our work was to evaluate the efficiency of Portland cement (CE), steel shot (SS) and spodic horizon (SH) for copper, lead and zinc stabilization in metal-spiked soil, in two variants of soil pH (pH 4 and pH 6), under condition of incubation. The sequential extraction and leaching test were used to evaluate and compare the effects of soil

treatments. The specific aim was to pinpoint chemical changes after incorporation of these amendments in strongly acidic (pH \approx 4) and a slightly acidic condition (pH \approx 6).

Experimental Procedures

Soil Preparation and Treatment Processes

This work was conducted on a surface soil horizon (0-10 cm) of Stagnic Albeluvisol [13] sampled from Rudnica (52° 20.736 N; 16° 23.381 E) that was artificially contaminated with lead, copper and zinc. All three elements were incorporated at a dose of 5,000 mg·kg⁻¹, as nitrate salt to get extremely high concentration of mobile metals. Prior to contamination, soil was sieved, pieces larger than 4.0 mm were thrown away and afterwards the soil was uniformly mixed with salts: Pb(NO₃)₂, Cu(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O.

Metal-spiked soil was pre-incubated for 4 weeks under 18-21°C and soil moisture content close to field capacity (step I). Then soil was divided into two parts. To the first one calcium carbonate was introduced to raise soil pH up to 6, to the second one no additional amendments were added (step II). After the following 4 weeks, the stabilizer steel shot (SS), spodic horizon (SH) and Portland cement (CE) were added at the rates: 0, 1 and 3% on dry weight basis (step III). From this point the experiment was conducted in two directions. Soil for sequential extraction analysis was further incubated in the boxes from which soil samples for chemical analysis were taken every 4 weeks (step IV a). In this research data for the 112th day of stabilization process are presented. In the second part of this experiment, after adding amendments (stabilizers) soil was packed into soil columns and further incubated for the next 12 weeks. Then the leaching process was started (step IV b). Each treatment (soil with amendments) was incubated in duplicate. Soil preparation and treatment are shown in Table 2. Additionally, after the leaching process was finished, soil samples were taken and sequential analyses were done to evaluate which fraction of metals were washed out by water.

Physical and Chemical Analyses

Prior to analysis, soil samples were air-dried and ground to pass through a 1.0 mm mesh sieve. Particle size distribution was determined according to Polish guidelines [14, 15]. Organic carbon was determined with the dichromate wet oxidative of the Walkley-Black method [16]. Soil pH was potentiometrically measured in redistilled water, 0.01M CaCl₂ and 1M KCl. The cation exchange capacity (CEC) of uncontaminated soil was done by the method of Mehlich modified by Kociałkowski and Ratajczak [17]. The total metal content was determined by the Lim and Jackson method modified by Komisarek [18]. The characterization of soil and stabilizers used in the current study are listed in Tables 1 and 3, respectively.

Table 1. Select physical and chemical properties of uncontaminated soil.

Soil properties	Unit	Uncontaminated soil
pH (1:1 H ₂ O)	-	6.00
pH (1:2 CaCl ₂)	-	5.95
pH (1:1 KCl)	-	5.52
Organic carbon	%	1.68
Cation exchange capacity	cmol ₍₊₎ ·kg ⁻¹	7.28
Texture – loamy sand	%	
Sand	%	75
Silt	%	21
Clay	%	4
Total concentration	mg·kg ⁻¹	
Cu	mg·kg ⁻¹	16.53
Pb	mg·kg ⁻¹	16.92
Zn	mg·kg ⁻¹	37.46

Table 2. Soil sampling and treatment preparation.

1	Excavation of surface soil horizon.
2	Removal of large substances and plant remains.
3	a) Soil contamination with Cu, Pb and Zn (step I). b) 4 weeks of pre-incubation.
4	a) Dividing contaminated soil into two parts and incorporation CaCO ₃ into one part of soil – increasing soil pH up to 6 (step II). b) Incubation of soil for another 4 weeks.
5	a) Application of stabilizer at the rate of 0, 1 and 3% of dry weight basis (step III). b) 12 weeks of incubation contaminated of soil with stabilizer.
6	Leaching process (step IV b).

Sequential Extraction Procedure

The metals distribution were evaluated by a modified Tessier's method [19]. This scheme is a six-step sequential extraction procedure:

- F1 water soluble;
- F2 exchangeable;
- F3 bound to carbonates or specifically adsorbed;
- F4 bound to Fe-Mn oxides;
- F5 bound to organic matter and sulphides and
- F6 residual.

The steps and the operationally defined metal fractions are summarized in Table 4. Each analysis was done in duplicate. The sequential analysis was carried out in samples before and after the leaching process to assess which form of metals was washed out by water. All extracts and digests were stored in glass tubes at 4°C for analysis, and metal concentrations were determined by AAS method.

Leaching Process

The leaching process was conducted in polyethylene columns, 250 mm in length, 105 mm in internal diameter that were filled with contaminated soil to a height of 150 mm, and the soil was compacted to obtain soil density equal to 1.4 g·cm⁻³. The soil columns were washed with 105 mm of redistilled water, which was divided into seven equal doses. This amount of water is estimated to be an equivalent to the annual mean of water percolated through the unsaturated zone to ground water in the Wielkopolska region. As a leaching solution, redistilled water was chosen, as water is a common solvent in the environment. The effluents (leachates) were collected and analyzed two days after adding water, and another dose of water was added three days later. The leachates prior to metals concentration analysis were stored at 4°C. Additionally, pH and electrical conductivity in effluents were measured immediately after collecting.

Statistical Methods

To assess the degree of association among washed out from soil columns amounts of the heavy metals, Ca, K and pH and EC of leachates (effluents) principal component analysis (PCA) was used. Principal component analysis

Table 3. Chemical composition of amendments.

Amendments properties	Unit	Cement	Steel shot	Spodic horizon
pH (1:1 H ₂ O)	-	13.08	7.88	4.78
pH (1:2 CaCl ₂)	-	ND*	6.88	4.57
pH (1:1 KCl)	-	13.25	8.54	4.03
Organic carbon	%	ND	ND	0.51
Cation exchange capacity	cmol ₍₊₎ ·kg ⁻¹	ND	0.57	11.00
Total concentration	mg·kg ⁻¹			
Cu	mg·kg ⁻¹	33.95	701	2.13
Pb	mg·kg ⁻¹	114	37.85	110
Zn	mg·kg ⁻¹	118	29.00	2.12
Mn	mg·kg ⁻¹	426	2417	53.05
Fe ₂ O ₃	%	4.75	80.79	0.41
Al ₂ O ₃	%	11.6	0.89	4.15

* ND – not determined

Table 4. Sequential extraction procedure used in present study.

Step	Fraction	Reagent	Shaking time and temperature
1	Water soluble	15 ml of redistilled water	5 h at ambient temperature
2	Exchangeable	15 ml of 1mol·dm ⁻³ NH ₄ Cl (pH 5.8)	5 h at ambient temperature
3	Bound to carbonates or specifically adsorbed	15 ml of 1mol·dm ⁻³ NH ₄ OAc/OHAc (pH 5)	5 h at ambient temperature
4	Bound to Fe-Mn oxides	20 ml of 0.04 mol·dm ⁻³ NH ₂ OH×HCl in 25% OHAc (pH 2)	5 h at 96°C
5	Bound to organic matter and sulphides	0.02 mol·dm ⁻³ HNO ₃ in 30% H ₂ O ₂ (pH 2); 3.2 mol·dm ⁻³ NH ₄ Ac in 20% HNO ₃	4 h at 85°C
6	Residual	aqua regia	24 h at ambient temperature and 2 h at 85°C

Table 5. Changes of treatments pH(H₂O) after 112th day of incubation.

pH 4		pH 6	
3% of cement (CE3)	8.39	3% of cement (CE3)	8.74
1% of cement (CE1)	5.84	1% of cement (CE1)	7.53
3 % of spodic horizon (SH3)	3.78	3% of spodic horizon (SH3)	5.42
1% of spodic horizon (SH1)	3.80	1% of spodic horizon (SH1)	5.56
3% of steel shot (SS3)	3.97	3% of steel shot (SS3)	6.72
1% of steel shot (SS1)	3.86	1% of steel shot (SS1)	5.99
control sample	3.80	control sample	5.85
Original soil pH _{H₂O} 6.0			

(PCA) is a multivariate statistical technique for data reduction and for deciphering patterns within large sets of data [20, 21]. The PCA was carried out using Statistica version 8.0.

Result and Discussion

The main target of the stabilization process is to reduce heavy metal mobility and bioavailability, which is obtained by creating suitable conditions for this transformation by introducing amendments to contaminated soil [1, 22]. Stabilizers exert an influence on physical and chemical properties of soil and metal by changing the conditions of soil environment to those more favourable for metal retention or precipitation. In this study, the effectiveness of the stabilization process was estimated on the basis of sequential extraction. The reduction of metals concentration in the water soluble fraction was the main target. The results obtained showed that metals concentration in fraction F1- (water soluble), the most mobile, depended on soil reaction, type of metal and properties of amendments.

The simultaneous incorporation of Cu, Pb and Zn has led to a decrease in soil reaction from pH 6.0 to a value below pH 4. This reaction was a result of heavy metal hydrolysis which in turn led to the production of nitric acid.

Introduced stabilization materials had a different influence on soil pH in respect to the nature of amendment and soil reaction (Table 5). The amendments behaved differently in soil treatments with and without CaCO₃. Among stabilizer materials, Portland cement had a stronger impact on soil pH than steel shot and spodic horizon. Only the application of spodic horizon to CaCO₃-treatments decreased soil pH by 0.43 and 0.29 respectively, at doses of 3% and 1%. Furthermore it should be stressed that for all stabilizers tested, the higher the rate of amendment the stronger the pH change.

Sequential Extraction

In this study, the efficiency of the stabilization process was estimated on the basis of sequential extraction. Results showed that metal concentration in fraction F1 (water soluble), the most mobile one, depended on soil pH, type of metal incorporated and properties of amendments. Metal distribution revealed that in CaCO₃-untreated soils Cu, Zn, Pb occurred in large amounts in fraction F1 (Fig. 1), except treatments with cement. The observed process could have been related to artificial contamination and relatively short periods of incubation. Similar results were reported by Martínez and Motto [23]. Furthermore, in this study metals

were introduced in the form of nitrate salts, which are characterized by high solubility. Additionally, contaminated soil was incubated for 24 weeks (step I, Table 2), while treatments with amendments were incubated for only 16 weeks (step III, Table 2). According to Zhou et al. [24], an aging process, where easily extractable fractions of Cu gradually transforms into less extractable forms, is a slow process (over one year). These factors influenced the higher share of heavy metals in the first fraction F1. From all elements studied, Pb had the lowest concentration in water-soluble fraction in CaCO₃-untreated soils. In the control sample, the share of metals in the first fraction, F1, were: Pb (42%), Cu

(71%) and Zn (91%) (Fig. 1, Table 6). The strong sorption of lead was related to its high electronegativity and softness (according to Pearson acid-base theory) [11, 25].

After liming, the sorption sequence changed. The strongest sorption was observed for copper, in the control sample, at pH 5.85, the share of Cu and Pb in the fraction F1 were 3.9% and 5.5% respectively (Table 6). Weaker retention of lead might be related to strong competition among Ca²⁺ and Pb²⁺, Cu²⁺, Zn²⁺ for sorption sites. In the control sample at pH 3.80, Pb concentration in the exchangeable fraction (F2) was 1,160 mg·kg⁻¹ and increased only up to 1,372 mg·kg⁻¹ (18.7%) after liming.

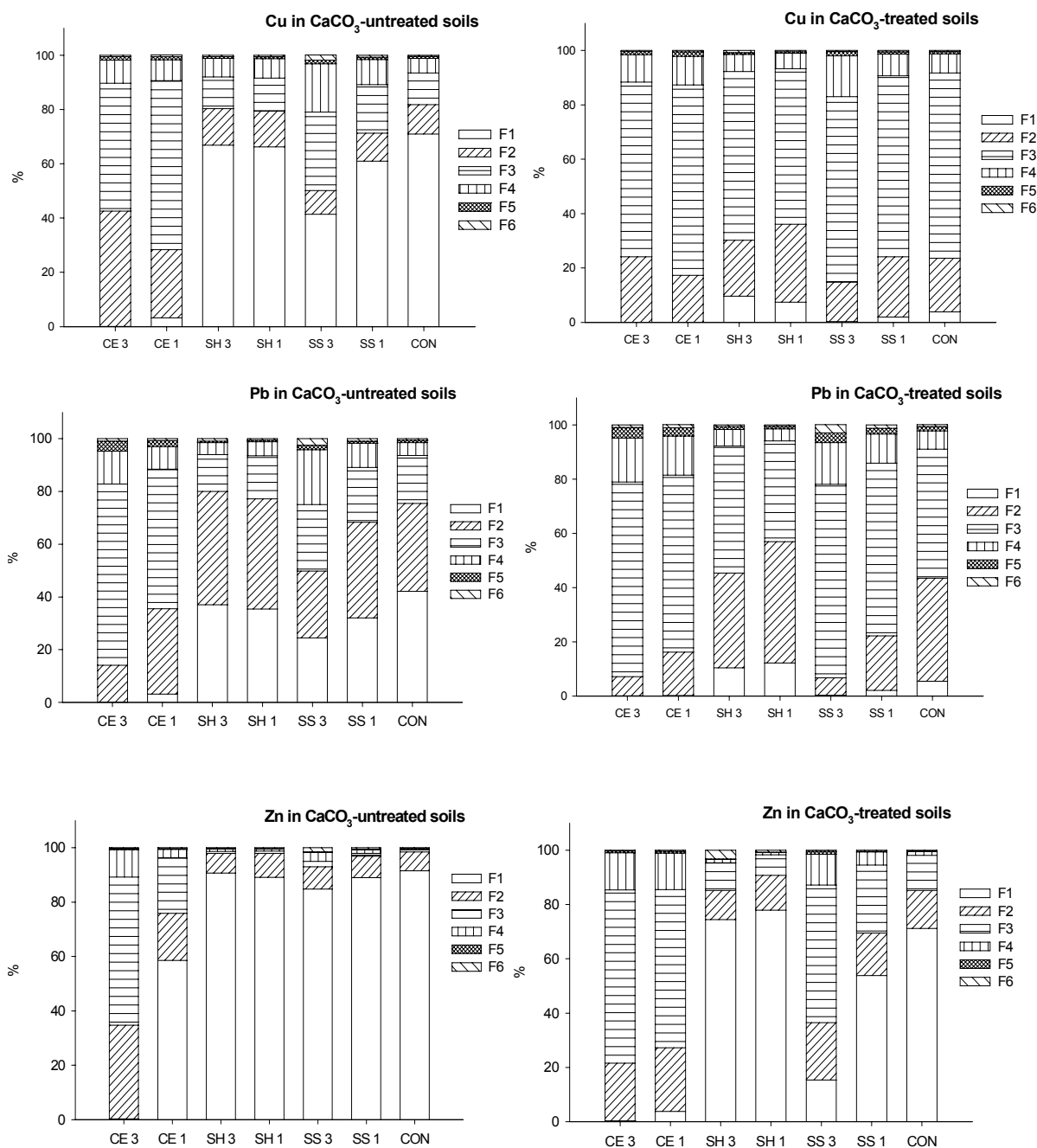


Fig. 1. Metal speciation in particular treatments studied. Fractions: F1 = water soluble, F2 = exchangeable, F3 = bound to carbonates, F4 = bound to Fe-Mn oxides, F5 = bound to organic matter and F6 residual. Contaminated soil with: 3% of cement (CE3), 1% of cement (CE1), 3% of spodic horizon (SH3), 1% of spodic horizon (SH1), 3% of steel shots (SS3), 1% of steel shots (SS1); contaminated soil without stabilizer = control sample (CON).

Table 6. Metal concentration in water-soluble fraction F1 extracted from soil treatments (112th day of incubation)^a.

Soil treatment	CaCO ₃ -untreated soils			CaCO ₃ -treated soils		
	Cu	Pb	Zn	Cu	Pb	Zn
	mg·kg ⁻¹					
CE3	5.00	3.90	12.6	2.70	4.95	10.65
CE1	127.0	116.7	2,279	1.20	7.80	160.5
SH3	2,335	1,122	3,167	450	405	3,715
SH1	2,302	1,017	3,039	347	484	3,944
SS3	1,270	682	2,914	12.75	9.00	480
SS1	1,949	929	3,136	84.0	72.3	2,239
CON	2,749	1,468	3,874	170	211	2,991

^a The data are the average of duplicate sample.

Contaminated soil with: 3% of cement (CE3), 1% of cement (CE1), 3% of spodic horizon (SH3), 1% of spodic horizon (SH1), 3% of steel shot (SS3), 1% of steel shot (SS1); contaminated soil without stabilizer = control sample (CON).

In the case of Ca, at pH 5.85, the share of this metal in fraction F2 increased about 148% in comparison to pH 3.80. Contrary to Pb, the share of Cu and Zn in fraction F2 increased about 130% and 140%, respectively, after introducing CaCO₃. Diatta [26] showed that a high concentration of calcium in soil solution led to desorption of PbOH⁺, as they have similar ionic radius. The comparison of results from sequential extraction for treatments without CaCO₃ (pH ≈4) and with CaCO₃ (pH≈6), revealed that amounts of all metals decrease by 93% (Cu), 86% (Pb) and 23% (Zn) (Table 6), in water-soluble fraction after incorporation of calcium carbonate, and at the same time an increase in metals content in second (F2) and third (F3) fractions was observed. Lower mobility of Cu, Pb and to a lesser extent of Zn were a consequence of precipitation of hardly soluble carbonates and hydroxides, and increasing soil cation exchange capacity.

Soil amendments differently influence metal mobility and furthermore the efficiency of the stabilization process depended both on amendments and metal properties. The most pronounced reduction was observed in treatments with cement, which significantly decreases metal content in the water-soluble fraction, irrespective of initial soil pH, while other amendments showed a notably lower degree of stabilization, especially in CaCO₃-untreated soils. Increasing soil reaction throughout CaCO₃ application increased the sorption ability of steel shot. This amendment was more efficient in metal immobilization at pH ~6.3 than pH ~3.90 by 42% and 29% for Pb, 39% and 22% for Cu, 59% and 6% for Zn, respectively, at the rates of 3% and 1% (Fig. 2). A contradictory effect after liming (pH 5.50) was observed for spodic horizon for all studied metals (Table 6). In comparison to the control sample, the incorporation of the spodic horizon to CaCO₃-treatment enhance metal mobilization, due to its strongly acid pH. A high concentration of exchangeable hydrogen and aluminium, in the spodic horizon, led to dissolution of newly precipitated hydroxides of heavy metals and also transformation of heavy met-

als carbonates into easily soluble bicarbonate forms. Moreover, in these treatments weaker retention of trace elements could be related to competition among H⁺ and Pb²⁺, Cu²⁺, and Zn²⁺ for sorption sites (Fig. 1). Higher reduction of metal mobility in treatments with steel shot at pH ~6.3, was probably connected with a deprotonation of functional groups on Fe, Al and Mn oxides and hydroxide surface. Moreover, pH condition in CaCO₃-treated soil was more suitable for precipitation of Fe²⁺, released from steel shots, as a sparingly soluble Fe(OH)₂ (pH 5.5) and its transformation into Fe(OH)₃ [9, 26]. These results confirm the effectiveness of Portland cement and steel shots in stabilizing trace elements in contaminated soils, as previously reported by Mench, et al. [2] and Diatta, et al. [28].

Leaching Process

Metal concentrations in the leachates has gradually decreased throughout the leaching experiment. A similar trend was observed for electrical conductivity (EC) values. Data analysis revealed that concentrations of Cu, Pb and Zn in effluents collected from particular columns depended on three factors: soil pH, properties of amendments and metal type. A higher level of metal leaching was observed for CaCO₃-untreated soils as compared to CaCO₃-treated soils. This may be related to the increased solubility of metal compounds under an acid environment. Copper and lead ions are generally less mobile elements in soils since they are strongly bound to the colloid surface. This explains the facts of their lower concentrations in leachates with respect to Zn [29, 30]. Such regularity was specifically noticeable in the case of strongly acid treatments (pH 3.80). Similar results were obtained by Jang, et al. [31] who reported metal mobility to be altered after applying a more acidic leaching solution. At the end of the leaching test, 5.5 g Zn (60.5% of total added) had leached on average from the control sample with pH 3.80. Total leaching of Zn in

CaCO₃-untreated soils was reduced by 99.9%, 44.2%, 37.0%, 26.0%, 30.8%, and 44.8%, in the CE3, CE1, SH3, SH1, SS3 and SS1 treatments, respectively (Table 7). In comparison with Zn, leaching of Cu and Pb in pH 3.80 from the control sample and treatments were significantly lower, except combination CE3. The application of 3% cement created more suitable conditions for Zn hydrolysis and precipitation in carbonate and hydroxide forms that consequently led to a sharp decrease of its mobility. In the current study the addition of CaCO₃ reduced the amounts of Cu and Pb removed from soil columns by over 80%. In the case of Zn, its leachability after CaCO₃ application was still high, and decreased about 30%. The weaker reaction of zinc to increasing soil pH compared with Cu and Pb was attributed to the solubility of newly formed carbonates and hydroxides of these metals. The better solubility of the zinc compound caused its high mobility and in consequence a higher concentration of zinc was measured in leachates than Pb and Cu in all tested combinations. Only in the treatment with Portland cement, particularly at the rate of 3% (CE3), Zn concentration in effluents significantly decreased and was similar to the level recorded for Pb. A contradictory effect was observed for Cu. The application of Portland cement at the dose of 3% to limed soil (pH 8.74) led to increasing Cu leachability from 8.62 mg (pH 8.39) to 15.97 mg (pH 8.74). The increase in copper mobility could be attributed to the appearance of soluble copper anions, as in this treatment soil pH was over value pH 8.7. Lindsay [32] and Kabata-Pendias [29] have reported that near pH 8 the concentration of Cu(OH)₃⁻, Cu(OH)₄²⁻ and Cu(CO₃)₂²⁻ species increase (their being a basis of Cu remobilisation). Among the amendments tested in soil under CaCO₃ treatments, the application of spodic horizon increased metal mobility as this material decreases pH of soil solution (Table 7).

The amounts of metals (Pb, Cu, Zn) (in mg) leached from the particular treatments are illustrated in Fig. 2 (logarithmic scale), as a function of leachates pH. These amounts were obtained by multiplying the metal concentration in percolate (mg·cm⁻³) by percolate volume (cm³) at each sampling moment. For graphic presentation purposes

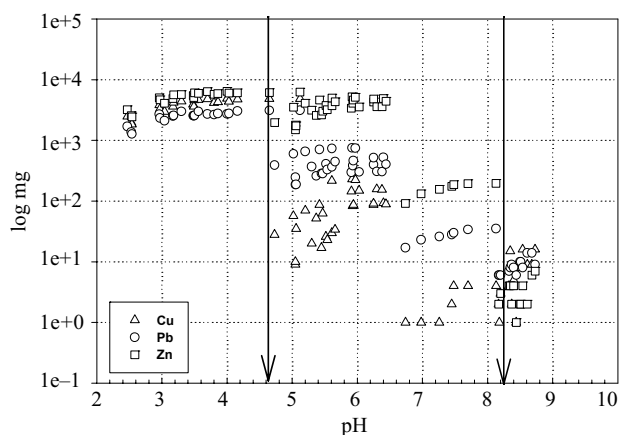


Fig. 2. Amounts of metals in leachates as a function of soil solution pH.

Table 7. Reduction of metal leaching from soil columns^a.

Soil treatment	Total reduction in metal leaching (%)					
	CaCO ₃ -untreated soils			CaCO ₃ -treated soils		
	Cu	Pb	Zn	Cu	Pb	Zn
CE3	99.8	99.5	99.9	91.5	98.4	99.8
CE1	96.3	88.5	44.2	98.0	93.3	95.4
SH3	54.7	54.8	37.0	-5.7	-20.0 ^b	-9.8
SH1	48.2	48.1	26.0	-48.8	-44.0	-8.3
SS3	31.3	35.5	30.8	93.3	94.7	79.4
SS1	20.2	17.8	44.8	83.8	77.2	38.4

^a The data are the average of duplicate sample.

^b Increase of metal leaching was observed.

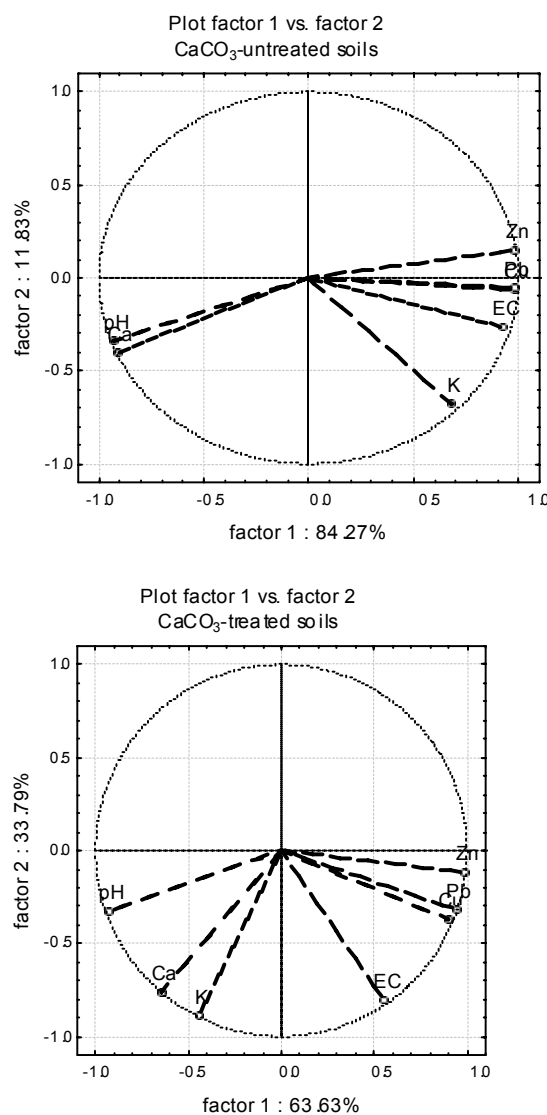


Fig. 3. Principal component analysis for the leaching test.

the amounts of metals washed from soil columns were logarithmic. Data obtained in this study showed that metal affinity to sorption sites changed with pH. Lead ions were preferentially sorbed when the pH of the soil solution was below value 4.6, whereas above this value copper ions were sorbed more strongly (Fig. 2). Zinc ions were generally more mobile than Pb^{2+} and Cu^{2+} . Only when soil solution pH was over 8.2 Zn mobility rapidly diminished. Such a sharp decrease in Zn mobility was probably attributed to its precipitation, mostly as $Zn(OH)_2$.

In order to obtain the degree of association among leached heavy metals, Ca, K and the pH and EC of soil solution, the PCA method was applied. The results of the principal component analysis are given as diagrams (Fig. 3). During PCA analysis two factors were extracted, which explained 96.1% and 97.42% of total variance in $CaCO_3$ -untreated soils and in $CaCO_3$ -treated soils, respectively. In $CaCO_3$ -untreated soils the first factor was responsible for 84.27% of total variance and was positively connected with amounts of leached heavy metals

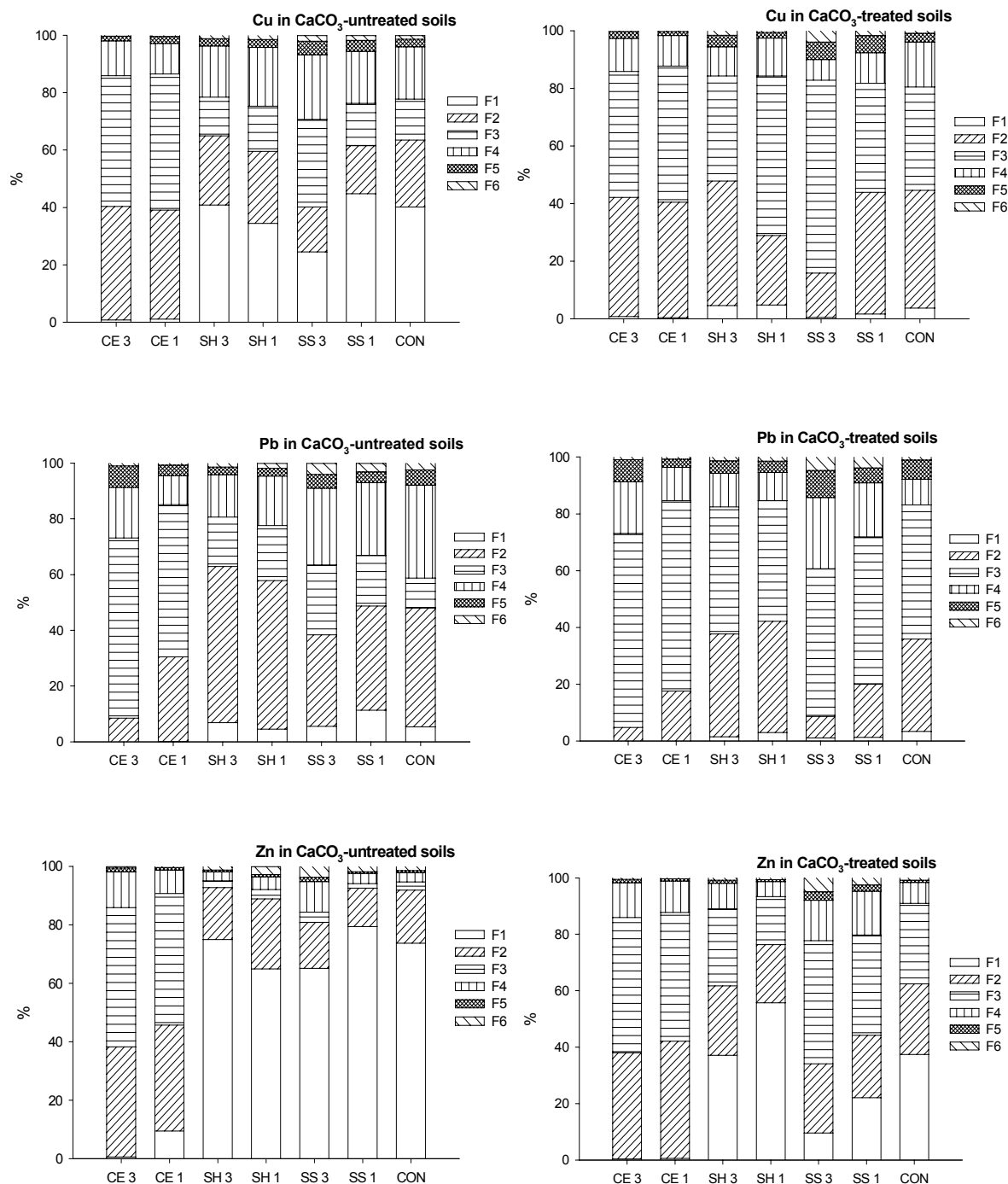


Fig. 4. Metal speciation in particular treatments studied after leaching test. Fractions: F1 = water soluble, F2 = exchangeable, F3 = bound to carbonates, F4 = bound to Fe-Mn oxides, F5 = bound to organic matter and F6 residual. Contaminated soil with: 3% of cement (CE3), 1% of cement (CE1), 3% of spodic horizon (SH3), 1% of spodic horizon (SH1), 3% of steel shot (SS3), 1% of steel shot (SS1); contaminated soil without stabilizer = control sample (CON).

and electrical conductivity of soil solution and negatively with Ca and pH. The second factor explained 11.83% of total variance and was mainly caused by K and to a lesser extent by Ca and pH. In the case of CaCO₃-treatments, the first factor explained 63.63% of total variance and Cu, Pb, Zn and pH gave the most contribution. The second factor was responsible for 33.79% of total variance and was represented by EC, K and to a lesser extent by Ca. The PCA analysis showed that amounts of leached Cu, Pb and Zn were negatively correlated with pH and to a lesser extent with Ca. In both treatment variants (with and without CaCO₃) Zn leachability, among the trace elements studied, exhibits the strongest reaction on pH changes of soil solution.

Metal Distribution After the Leaching Process

When the leaching process was finished the soil columns were allowed to dry at ambient temperature. Then soil samples were collected for sequential extraction in order to assess the fractions of the metals being leached out. As expected, metals were removed mainly in their water soluble forms (fraction F1). To a lesser extent the content of the fraction F2 (exchangeable) decreased. Surprisingly, the metal concentration in the fraction F3 (bound to carbonates) also decreased, even though the pH of soil solution increased during the leaching process. Probably carbonate salts of Cu, Pb and Zn, which normally are barely soluble, were dissolved by water as these salts were newly formed and more prone to a dissolution process. The content of metals in other fractions decreased minutely, as a result of physical transport of soil particles by water. Data obtained have shown that, irrespective of soil pH, Cu, Pb and Zn were removed from F1, F2 and F3 fractions. The metal distribution analysis carried out after the leaching test has shown that all metals studied still occurred mainly in mobile (F1) and easy mobilisable fractions (F2) (Fig. 4) that could be explained by a short period of incubation. As aging of heavy metals added to soil is a slow process, even after 112 days of incubation most metals existed in easily extractable species.

Conclusions

1. The introduction of stabilizers to contaminated soil induced changes in metal speciation accordingly to the properties of the amendments. The highest metal immobilization was observed with Portland Cement. Also, steel shot showed a high potential to immobilize heavy metals, but in contrast to cement, its efficiency depended on pH. Steel shot were more efficient in metal immobilization at pH ~6.3 than pH ~3.90 by 42% and 29% for Pb, 39% and 22% for Cu, 59% and 6% for Zn respectively, at the rate 1 and 3%.
2. Results obtained indicate that spodic horizon was not able to immobilize Cu, Pb and Zn in soil with pH ~5.5.

A strong acid reaction of this material (pH_{H₂O} 4.78) led to dissolution of newly precipitated carbonate and hydroxide forms of heavy metals.

3. The soil presented a special affinity to adsorb certain metals in elevated amounts. This affinity changed with soil reaction. When soil pH was below the 4.6 sorption sequence runs in order Pb < Cu < Zn. Above this value until pH 8.2, sorption affinity runs in the order Cu < Pb < Zn, and above pH 8.2 Zn < Pb < Cu.
4. Soil reaction exerted a significant effect on metal mobility, efficiency of immobilization process and metals concentration in leachates. Higher efficiency of heavy metals immobilization for the control sample and treatments was obtained in CaCO₃-treated soils, except in combination with spodic horizon.

References

1. VANGRONSVELD J., CUNNINGHAM S.D. Introduction to the Concepts. Metal-contaminated soils: In situ inactivation and phytoremediation. Springer-Verlag and R.G. Landes Company, **1998**.
2. MENCH M., VANGRONSVELD J., LEPP N.W., EDWARDS R. Physico-chemical aspects and efficiency of trace element immobilization by soil amendments. Metal-contaminated soils: In situ inactivation and phytoremediation. Springer-Verlag and R.G. Landes Company, **1998**.
3. WANG Y.M., CHEN T.C., YEH K.J., SHUE M.F. Stabilization of elevated heavy metal contaminated site. Journal of hazardous Materials, **B88**, 63, **2001**.
4. HARTLEY W., EDWARDS R., LEPP N.W. Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests. Environmental Pollution, **131**, 495, **2004**.
5. KUMPIENE J., ORE S., RENELLA G., MENCH M., LAGERKVIST A., MAURICE C. Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. Environmental Pollution, **144**, 62, **2006**.
6. LEŠTAN D., GRČMAN H., ZUPAN M., BAČAC N. Relationship of soil properties to fraction of Pb and Zn in soil and their uptake into *Plantago lanceolata*. Soil and Sediment Contamination, **12**, 507, **2003**.
7. SIEBIELEC G., STUCZYŃSKI T., KORZENIOWSKA-PUCULEK R. Metal bioavailability in long-term contaminated Tarnowskie Gory soils. Polish Journal of Environmental Studies, **15**, (1), 121, **2006**.
8. DĄBKOWSKA-NASKRĘT H. Free iron oxides and their impact on the specific surface area of alluvial soils. Soil science annual, **XLVII**, (3-4), 23, **1996** [In Polish].
9. RUTTENS A., MENCH M., COLPAERT J.V., BOISSON J., CARLEER R., VANGRONSVELD J. Phytostabilization of a metal contaminated sandy soil. I: Influence of compost and/or inorganic metal immobilizing soil amendments on phytotoxicity and plant availability of metals. Environmental Pollution, **144**, 524, **2006**.
10. BERARDI R., CIOFFI R., SANTORO L. Matrix stability and leaching behaviour in ettringite- based stabilization systems moped with heavy metals. Waste Management, **17** (18), 535, **1997**.
11. MCBRIDE M. B. Reactions controlling heavy metal solubility in soils. Advances in Soil Science, **10**, 1, **1989**.

12. BASTA N.T., MCGOWEN S.L. Evaluation of chemical immobilization treatment for reducing heavy metal transport in a smelter-contaminated soil. *Environmental Pollution*, **127**, 73, **2004**.
13. World reference base for soil resources. A framework for international classification, correlation and communication. World soil resources reports No. 103, **2006**.
14. Polish Standard: Polish Standardisation Committee, ref. PN-R-04032: Soil and mineral material. Sampling and determination of particle size distribution. **1998** [In Polish].
15. Polish Standard: Polish Standardisation Committee, ref. PN-R-04033. Soil and mineral material. Division into fractions and textural groups. **1998** [In Polish].
16. NELSON D.W., SOMMERS L.E. Total carbon and organic matter. Methods of soil analysis. P.2. Chemical and microbiological properties. Ed. A.L. Page. Agronomy Monograph **9**. ASA-SSSA, Madison: 539-580, **1982**.
17. KOCIAŁKOWSKI W. Z., RATAJCZAK M. J. Simplified Mehlich's method for the determination of soil cation exchange capacity. *Annual of Agriculture University of Poznań*, **CXLVI**, 105, **1984** [In Polish].
18. KOMISAREK J. Formation of soil properties and chemistry of groundwater of udalfs and aquolls in the catena of undulating ground moraine of the Poznań Lakeland. *Annual of Agriculture University of Poznań*, **307**, 19, **2000** [In Polish].
19. TESSIER A., CAMPBELL P.G.C., BISSON M. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, **51**, 844, **1979**.
20. FARNHAM I.M., JOHANNESSON K.H., SINGH A.K., HODGE V.F., STETZENBACH K.J. Factor analytical approaches for evaluating groundwater trace element chemistry data. *Analytica Chimica Acta*, **490**, 123, **2003**.
21. CHEN K., JIAO J.J., HUANG J., HUANG R. Multivariate statistical evaluation of trace elements in groundwater in a coastal area in Shenzhen, China. *Environmental Pollution*, **147**, 771, **2007**.
22. RUTTENS A., COLPAERT J.V., MENCH M., BOISSON J., CARLEER R., VANGRONSVELD J. Phytostabilization of a metal contaminated sandy soil. II: Influence of compost and/or inorganic metal immobilizing soil amendments on metal leaching. *Environmental Pollution*, **144**, 553, **2006**.
23. MARTÍNEZ C.E., MOTTO H.L. Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution*, **107**, 153, **2000**.
24. ZHOU S.-W., XU M.-G., MA Y.-B., CHEN S.-B., WEI D.-P. Aging mechanism of copper added to bentonite. *Geoderma*, **147**, 86, **2008**.
25. LI Z., SHUMAN L.M. Mobility of Zn, Cd and Pb in soil affected by poultry litter extract – II. Redistribution among soil fraction. *Environmental Pollution*, **95**, 227, **1997**.
26. DIATTA J.B. The impact of additional Pb input on the dynamics of Pb-enriched agricultural soils. *Polish Journal of Environmental Study*, **15**, (2), 219, **2006**.
27. DOBRZAŃSKI L. Metal science with fundamental of materials technology. WNT Press, **1999** [in Polish].
28. DIATTA J.B., GRZEBISZ W., WIATROWSKA K. Assessment of copper and zinc stabilization process in soils after the application of brown coal, sugar beet leaves and cement. *Ecological Chemistry and Engineering*, **14**, (2), 181, **2007**.
29. KABATA-PENDIAS A., PENDIAS H. Biogeochemistry of trace element. PWN Press, **1999** [In Polish].
30. TACK F.M.G., SINGH S.P., VERLOO M.G. Leaching behavior of Cd, Cu, Pb and Zn in surface soils derived from dredged sediments. *Environmental Pollution*, **106**, 107, **1999**.
31. JANG A., CHOI Y.S., KIM S. Batch and column tests for the development of an immobilization technology for toxic heavy metals in contaminated soil of closed mines. *Water Science Technology*, **37**, (8), 81, **1998**.
32. LINDSAY W.L. Chemical equilibria in soils. The Blackburn Press, **1979**.