

Article

Transformation of Pb, Cd, and Zn Minerals Using Phosphates

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Abstract: Heavy metal contamination in soils has become one of the most critical environmental issues. The most efficient in-situ remediation technique is chemical immobilization that uses cost-effective soil amendments such as phosphate compounds to decrease Pb, Cd and Zn accessibility in the contaminated soils. The present study examined the effectiveness of KH_2PO_4 in immobilizing Pb, Cd and Zn in three samples of contaminated soils collected from ZGH “Bolesław” (Mining and Smelting Plant “Bolesław”). Effectiveness was evaluated using the following methods: a toxicity characteristic leaching procedure (TCLP)-based experiment, sequential extraction, X-ray diffraction analyses (XRD), and scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS). The most efficient percentage reduction of total leachable metal concentration assessed by TCLP was observed for lead (50%–80%), and the least reduction was observed for zinc (1%–17%). The most effective immobilization of stable compounds assessed by sequential extraction was noted for lead, while the weakest immobilization was noted for cadmium. New insoluble mineral phases were identified by SEM-EDS analysis. Cd, Zn, and Pb formed new stable mineral substances with phosphates. The predominant crystal forms were dripstones and groups of needles, which were easily formed by dissolved carbon rock surfaces containing zinc ions. The alkaline nature of the soil and a large number of carbonates mainly influenced the formation of new structures.

Keywords: immobilization; heavy metal-contaminated soil; soil remediation; TCLP

1. Introduction

Anthropogenic activities have polluted soils with heavy metals and metalloids in many places worldwide [1]. The leading causes of soil pollution by heavy metals are fossil fuel consumption, agrochemical use, military training and the discharge of waste and wastewater from industrial, mining and smelting activities. The accumulation of Cd, Pb and Zn may result in decreasing soil fertility, soil microbial activities, and biodiversity [2,3]. Soils that have a high concentration of Cd, Pb and Zn pose a potential threat to human health if directly ingested or transferred through foods [4]. Chronic cadmium exposure can cause emphysema, hypertension, diabetes mellitus, and skeletal malformation; it is challenging to eliminate Cd from the body, and it can remain in the body even for decades [5,6]. Lead even at low concentration may damage the kidney, liver, and the central nervous system and can cause many dangerous diseases [7]. At the low level, zinc is an essential element for living organisms; however, exposure to high concentrations of Zn can cause depression, lethargy, increased thirst, and some neurologic symptoms [8].

Several treatment methods have been developed and applied to treat metal-polluted soils. The remediation of contaminated soils can be divided into two types according to the location: in-situ and ex-situ remediation.

Ex-situ remediation techniques include soil washing [9], solidification [10], and vitrification [11]. In-situ remediation techniques include biological technologies such as phytoremediation [12], microbial remediation [13,14], and genetic engineering remediation [15] as well as encapsulation [16], electrokinetic extraction [17], soil flushing [18], and chemical immobilization. Most of these remediation technologies are expensive and time-consuming. Therefore, the choice of suitable technologies is often difficult but extremely important.

Chemical immobilization is a method where relatively cheap materials are added to contaminated soil to decrease mobility, bioavailability and bioaccessibility of heavy metals [19]. A broad range of materials has been used, including fly ash, red mud, goethite, zeolite, silica gel, vermiculite, chitosan, compost, and biochar [13,15,20–24]. Recently, much research has proved that using phosphate in the form of phosphate salt or relatively stable rock decreases aqueous metal concentration in metal-contaminated soil solutions because of rapid and exclusive formation of metal phosphates such as pyromorphite [25–27]. The use of phosphate compounds is a cost-effective and environmentally positive remediation method [28].

Phosphate compounds can immobilize metals in soils by decreasing their bioavailability [29]. Numerous studies have proven that P-induced metal immobilization significantly lowers the bioavailability of heavy metals [19,27,30–35]. Phosphates have been shown to be sufficient in immobilizing lead, zinc, and cadmium in contaminated soils by the formation of stable minerals. The addition of various phosphate compounds such as phosphate rocks, synthetic hydroxyapatite, or commercial phosphate fertilizers to contaminated soils effectively decreases Pb concentration and forms lead phosphate—pyromorphite, fluoropyromorphite or apatite [26,36–40]. Phosphate ions react with Zn and form hopeite, while cadmium phosphate is precipitated by the reaction of phosphate ions with Cd [41]. The effectiveness of Pb, Cd, and Zn immobilization depends on the solubility of P amendments [42]. Readily soluble phosphates such as KH_2PO_4 or H_3PO_4 can be used as available sources of phosphates [43,44].

Recently, a high volume of publications about immobilization of heavy metals in contaminated soils has been published. As the effectiveness of raw phosphate rocks is usually low, researchers tried to modify them to release more soluble P. The oxalic acid-activated rock is much more efficient in immobilization of Pb or Cd [38,45]. Studies have been conducted over both a short and a long period [46–49]. Another kind of phosphoric material is bone meal, created from animal bones and slaughter-house waste products, that also significantly decreased the bioavailability of Pb in soils [50–52]. While most research pointed to the potential influence of P compounds in the immobilization of individual metals in soils, such as Pb, only a few studies describing the simultaneous immobilization of Zn, Cd and Pb from natural soils have been published [27]. There is still a lack of definitive studies involving the formation of Zn, Cd and Pb phosphates. Information about the methodology of the process, as well as condition in which the newly formed phases remain in a stable insoluble form, are also insufficient.

There were two primary objectives of these studies: (1) To examine the effectiveness of immobilization of Zn, Cd and Pb by potassium phosphate additions to natural soil, and (2) To identify and characterize the newly formed metal phosphate precipitates.

2. Materials and Methods

2.1. Materials

Samples of soils rich in Pb, Zn, and Cd used in this study were collected from nearby areas of ZGH “Bolesław” (Mining and Smelting Plant “Bolesław”) and storage places for post-flotation materials. ZGH “Bolesław” is located in the Upper Silesia region in southern Poland. It has long been an area of large-scale mining and processing of Pb–Zn ores [53]. The nature of this geological structure, as well as mining and smelter operations and the presence of heaps, led to significant soil and water pollution in this area.

Samples were taken from three different points (BI, BII, and BIII) from outcrops with dimensions of 0.5 m × 1.0 m × 0.3 m. BII and BIII sampling points were close to the flotation waste tanks, and BI sampling point was located approximately 100 m from smelters. Soil profiles were divided into two parts—the first part was a surface layer consisting of an organic level and/or a humus level, and the

second part was a subsurface layer covering the level of enrichment. For samples, BI and BII, the borderline between those two parts were determined based on an apparent change in soil colour (depth: approx. 14–18 cm for BI; 20 cm for BII). In the case of sample BIII, where there is no clear differentiation of the soil profile, the borderline between the layers was determined at a depth of 16 cm. This depth corresponded to the depth at which the boundary between the surface and subsurface layers was found at point BII. The material was taken from the surface layer, which was characterized by a higher concentration of Zn, Cd and Pb [53]. The collected samples were air-dried, gently disaggregated, passed through a 2-mm sieve and homogenized by mixing before use. The selected properties and concentrations of Cd, Zn and Pb in the soil samples collected from BI, BII and BIII points have been previously characterized by Szrek et al., [53] (Table 1). Chemical composition of these samples was determined by X-ray fluorescence and is presented in Table 2.

Table 1. Selected properties and concentrations of Cd, Zn, and Pb in the soils from BI, BII and BIII points [53].

Sample	Particle Size Analysis (%) ¹			OM (%) ²	LOI (%) ³	Total Content (mg/kg) ⁴		
	Sand	Silt	Clay			Cd	Zn	Pb
BI	69	12	19	2.51	0.23	34 ± 1.7	3078 ± 137	699 ± 6
BII	63	17	20	6.75	0.35	78 ± 1.4	8103 ± 78	2479 ± 83
BIII	71	18	11	4.17	0.38	53 ± 0.4	19173 ± 4	910 ± 15

¹ Sand (0.053–2.0 mm), silt (0.002–0.053 mm), clay (<0.002 mm). ² Organic matter content. ³ Loss on ignition. ⁴ Mean ± standard deviation (*n* = 2).

Table 2. Chemical composition of the samples BI, BII and BIII.

Element	BI (%)	BII (%)	BIII (%)
Na ₂ O	0.28	0.40	0.36
MgO	2.15	1.91	2.48
Al ₂ O ₃	3.87	4.99	4.59
SiO ₂	79.46	68.52	63.07
P ₂ O ₅	0.14	0.22	0.97
SO ₃	0.21	1.63	1.13
K ₂ O	0.83	0.89	0.59
CaO	2.98	3.18	5.98
TiO ₂	0.25	0.31	0.27
Cr ₂ O ₃	0.01	0.10	0.05
MnO	0.18	0.37	0.05
Fe ₂ O ₃	2.06	4.18	2.95
NiO	0.01	0.01	0.01
CuO	0.01	0.01	0.01
ZnO	0.54	1.14	0.54
Rb ₂ O	0.00	0.01	0.00
SrO	0.00	0.01	0.01
ZrO ₂	0.82	0.08	0.05
PbO	0.10	0.27	0.09
As ₂ O ₃	<0.01	0.02	0.01
CdO	<0.01	0.01	0.01
BaO	<0.01	0.04	0.03
V ₂ O ₅	0.01	0.01	<0.01
SnO ₂	<0.01	<0.01	0.04
Cl	<0.01	<0.01	0.01
Co ₂ O ₃	<0.01	<0.01	0.01

2.2. Hydrolytic Acidity

The hydrolytic acidity was determined by measuring the pH value of a suspension of a soil sample and water in a 1:1 ratio. The samples were shaken for 6 h at room temperature and then centrifuged for 10 min at 14,000 rpm.

2.3. Immobilization of Heavy Metals with Phosphorus Compounds

A 150 g mass of each sample and the appropriate amount of phosphate were placed in the polythene bottles, mixed, and kept in darkness at room temperature (20 °C) for 30 days. The experiment was conducted in triplicate. On day 30, the samples were dried to an air-dry state and crushed. As a source of phosphate, an aqueous solution of KH_2PO_4 was used. The experiment of immobilization was divided into two parts:

1. The experimental system (ES)—the amount of potassium phosphate (KH_2PO_4) was calculated according to the expected reaction product, metal phosphate ($\text{Me}_3(\text{PO}_4)_2$). Thus, the molar ratio of metal to phosphate ($\text{Me}:\text{PO}_4$) was 3:2. The content of Zn, Cd, and Pb determined by Szrek et al., (2011) was used as the amount of metal [53]. Total concentrations of Zn, Pb and Cd were obtained by digesting the solid samples using aqua regia (a mixture of 38% hydrochloric acid and 65% nitric acid in ratio 3:1 of HCl to HNO_3 , by volume). The digestion lasted for 16 h at 25 °C and 2 h at 120 °C. The digests were analyzed for metals using atomic absorption spectrometer. Throughout the experiment, the moisture level was kept at 25% (by adding a volume of water equivalent to the loss of evaporated water).
2. A control system (CS)—The soil samples were allowed to react with double-distilled water. The moisture level was kept at 25%.

The TCLP-based experiment (Toxicity Characteristic Leaching Procedure) was used to determine the leaching of Zn, Cd and Pb elements from soil samples [54]. The test was carried out on soil samples from ES and CS. Samples were then treated with acetate buffer (0.1 M CH_3COONa + 0.1 M CH_3COOH) with pH of 5. The suspensions of soil samples and acetate buffer were shaken for 24 h at room temperature and centrifuged for 10 min at 4500 rpm. The supernatant was filtered and analyzed by atomic absorption spectroscopy.

Geochemical modelling was conducted with the aid of the computer program PHREEQC [55] with the modified MINTEQA4 thermodynamic database [56]. Thermodynamic data used for calculations are listed in Table S1 [56–59].

2.4. Solid-Association of Zn, Cd and Pb

To determine the forms of occurrence of Zn, Cd, and Pb in soil samples, a seven-step extraction method was used [60–63]. The test was conducted on soil samples from ES and CS. The extraction method was applied according to the following steps:

Step I: ion exchange positions—1 M $\text{CH}_3\text{COONH}_4$ (ammonium buffer), pH 7, the ratio of the solid phase to the solution: 1:20, and shaking time 2 h.

Step II: carbonates—1 M CH_3COONa (sodium acetate) + 27 mL concentrated CH_3COOH (acetic acid), pH 5, the ratio of the solid phase to the solution: 1:50, and shaking time 5 h.

Step III: manganese oxides—0.1 M NH_2OH (hydroxylamine), pH 2 (controlled with 1M HCl (hydrochloric acid)), the ratio of the solid phase to the solution: 1:50, and shaking time 0.5 h.

Step IV: amorphous oxides and iron oxyhydroxides—0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (ammonium oxalate) + 0.2M $\text{C}_2\text{H}_2\text{O}_4$ (oxalic acid), pH 3, the ratio of the solid phase to the solution: 1:50, and shaking time 4 h (in dark).

Step V: crystalline iron oxides—DCB (dithionite-citrate-bicarbonate) method, the extraction was carried out at 85 °C in a water bath; 40 mL 0.3 M $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ (sodium citrate dihydrate), 5 mL 1 M NaHCO_3 (sodium bicarbonate), and 0.5 g solid $\text{Na}_2\text{S}_2\text{O}_4$ (sodium dithionite), pH 8.5, the ratio of the solid phase to the solution: 1:50, and reaction time 15 min.

Step VI: organic substance and sulfides—30% H₂O₂ (hydrogen peroxide), pH 2 (controlled with 1 M HNO₃ (nitric acid)), the ratio of the solid phase to the solution: 1:50, temperature 85 °C, time = until the reaction with H₂O₂ ceases. The residue was extracted with 1 M CH₃COONH₄ (as in Step I).

Step VII: residuum—HF (hydrofluoric acid) + HClO₄ (perchloric acid), the residue after evaporation was dissolved in concentrated HCl (hydrochloric acid), and the ratio of the solid phase to the solution: 1:100.

2.5. Methods of Analysis

The concentrations of Zn, Cd and Pb in solutions were analyzed by atomic absorption spectrometry (Savant AA GBC Scientific Equipment, Braeside, Australia). The analyses were conducted at the following wavelengths: Zn: 213.9 nm; Cd: 228.8 nm; Pb: 217.0 nm (accuracy: 0.5%–2%; precision: 0.5%; limit of detection: 0.01 ppm for all analyzed elements). Air-dried uncoated samples were analyzed by electron microscopy using a variable pressure field-emission scanning electron microscope (FEI QUANTA 200, Graz, Austria) equipped with an energy dispersive spectrometer (EDS, Graz, Austria) for elemental microanalysis. The chemical composition of the samples was determined by X-ray fluorescence (WD-XRF ZSX Primus II Rigaku, RIGAKU, Tokyo, Japan) on powder pellets (accuracy: 0.1%; precision: 0.1%; limit of detection: from 0.00018% to 0.01470% depending on the element and the sample). Qualitative XRD were conducted with Philips APD X'pert PW 3020 (Philips, Eindhoven, Holland) to investigate the mineral composition of soil samples (limit of detection: 2%–5% depending on the mineral phase).

3. Results and Discussion

3.1. Mineral Composition of Soil

The X-ray diffraction patterns presented in Figure 1 indicate that the main components of the samples BI, BII and BIII are quartz, dolomite and feldspar. In addition to dolomite, other carbonates are also present in the tested samples; however, due to the overlapping of diffraction peaks, it was not possible to determine them. The analysis did not reveal any presence of new mineral phases because of the reaction of Zn, Cd and Pb with phosphates. The reason might be a small number of developed phases as well as insufficient sensitivity and detectability of the method used [38].

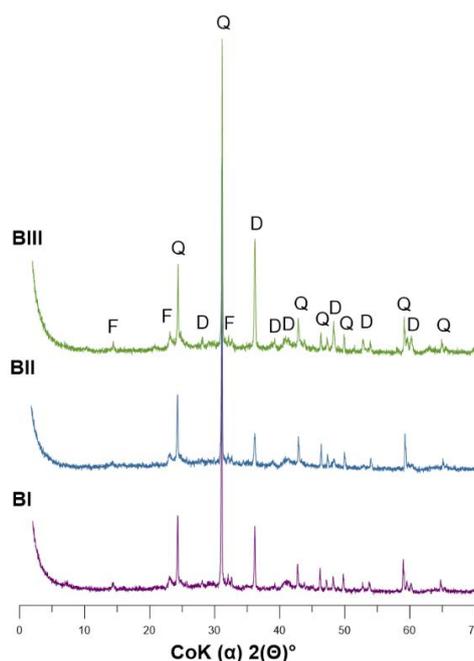


Figure 1. X-ray diffraction patterns for BI, BII, and BIII samples. Q—Quartz, D—Dolomite, F—Feldspar.

3.2. Hydrolytic Acidity Parameters for Soil Samples

Figure 2 presents the results of pH values for samples from ES and CS. The pH values for samples from CS ranged from 7.11 (BII) to 7.93 (BIII). Lower pH of samples from ES was due to the addition of monopotassium phosphate. The solution of KH_2PO_4 is acidic (pH 4.4–4.7); therefore, it reduces the pH of samples from the ES. Despite the slight decrease in pH, it might suggest that the addition of KH_2PO_4 will cause a reduction in soil pH.

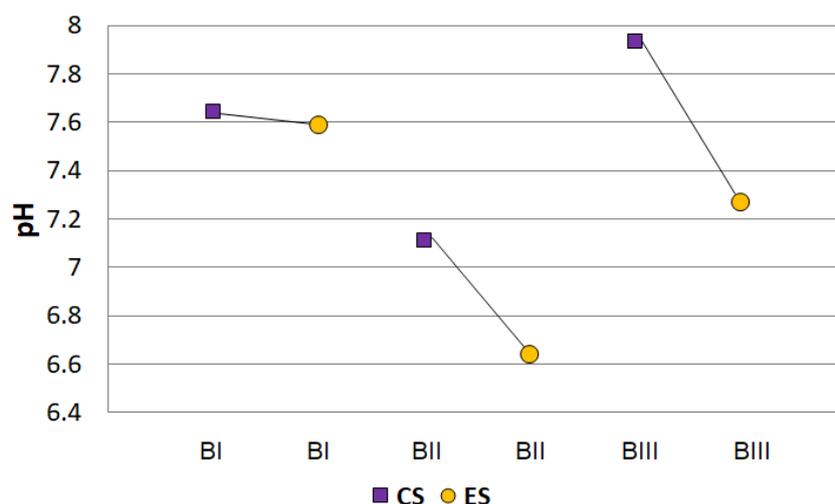


Figure 2. The changes in pH values for samples from the experimental system (ES) and the control system (CS).

3.3. Immobilization of Heavy Metals with Phosphorus Compounds

The leaching of Zn, Cd, and Pb elements from soils was examined by the experiment based on the TCLP developed and used by the US EPA in 1992 [54]. The use of acetate buffer causes mobilization of metals from ion-exchange positions and metals associated with carbonates. Furthermore, the addition of acetate buffer simulates the conditions of reducing the pH of the soil environment, which may lead to an increase in the mobility of heavy metals [64]. The effect of phosphates on the immobilization of heavy metals was analyzed in soil samples from ES and CS. The results compared with U.S. EPA regulatory limits are as follows: Zn: 250 mg L^{-1} , Cd: 1 mg L^{-1} , Pb: 5 mg L^{-1} [54].

The highest concentration of leachable lead was observed in BII (control system)— 9.42 mg L^{-1} , which significantly exceeded the EPA's regulatory limit value for Pb (Figure 3a). The use of potassium phosphate enabled a decrease of leachable lead in sample BII from 9.42 mg L^{-1} to 1.86 mg L^{-1} . The EPA's regulatory limit for Cd was exceeded for all soil samples (BI, BII, and BIII); however, only in sample BI (1.07 mg L^{-1}) did the use of potassium phosphate enable a decrease in content of leachable Cd below the limit value (1 mg L^{-1}). The highest value (2.01 mg L^{-1}) was observed in sample BII (Figure 3b). The content of leachable Zn in the control soil samples varied from 84.3 mg L^{-1} for sample BI to 260.4 mg L^{-1} for sample BIII (Figure 3c). The EPA's regulatory limit was exceeded only for BIII. Exposure of Zn to K_2HPO_4 influenced its mobility; however, the limit value was still slightly exceeded for experimental sample BIII (250.8 mg L^{-1}).

The percentage reduction of the concentration of zinc, cadmium, and lead ions was calculated according to the following formula:

$$R_p = 100\% - \frac{C_{ES}}{C_{CS}} \times 100\% \quad (1)$$

R_p —percentage reduction of the concentration. C_{ES} —the average concentration of metal in the experimental system. C_{CS} —the average concentration of metal in the control system.

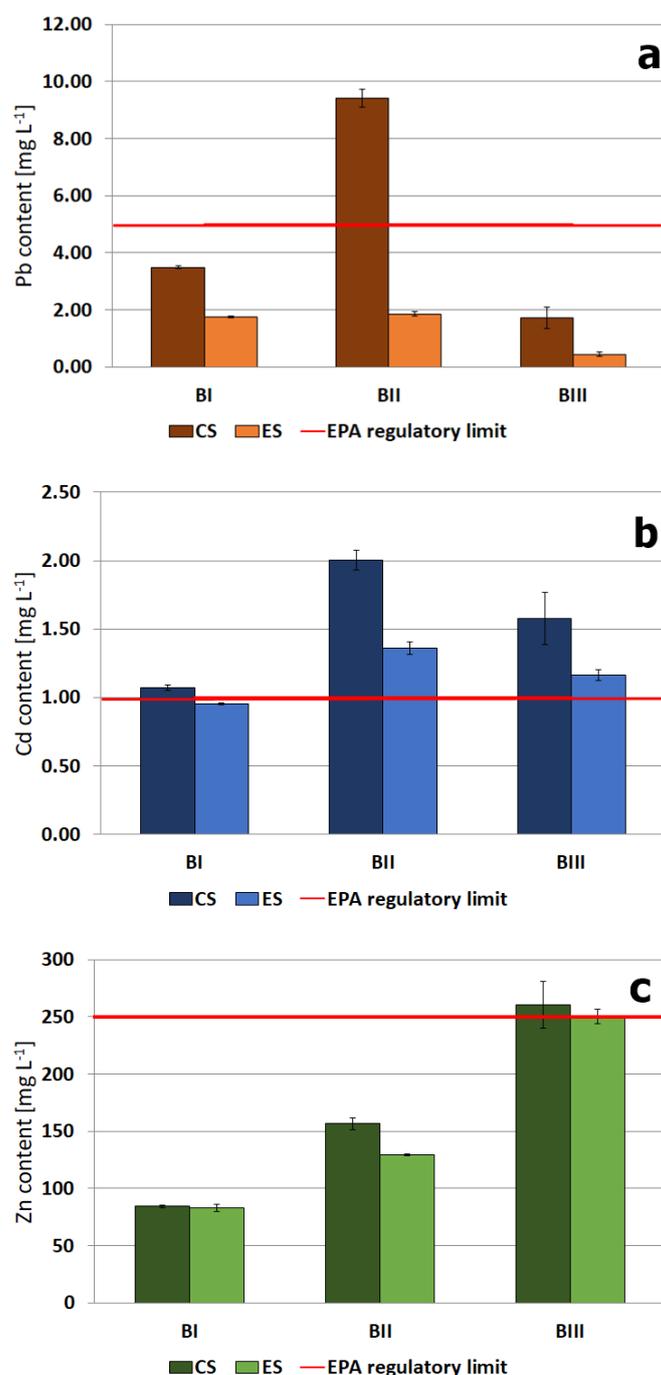


Figure 3. Content of Pb (a), Cd (b) and Zn (c) in soil samples (ES—results for the experimental system, CS—results for the control system). Data based on TCLP.

A higher percentage decrease in leachable concentration was achieved for Pb (49%–80%), and then for Cd (11%–32%), and the lowest percentage reduction was observed for Zn (1%–17%) (Figure 4); this finding suggests that lead forms bonds with phosphates more quickly than with other metals [26,30,65]. Based on the modelling results (Table S2), it can be stated that for each sample, not all the amount of phosphates added were consumed for the formation of Pb, Zn, Cd phosphates, despite the reduction of metal concentration to $<0.1 \mu\text{g L}^{-1}$. The results of the experimental studies obtained in this paper clearly show that the concentration of leaching amounts of metals has not been reduced by 100%. This means that there are other leachable metals (e.g., Ca, Fe and Al) in the soil samples that can be combined with phosphates, reducing PO_4 concentration. However, analysis of the constant solubility of potential

metal phosphates (Table S1) indicates that lead, zinc and cadmium phosphates will preferentially be formed. Besides, it is known that phosphates readily adsorb onto soil components [61,66], which is an additional reason for the PO_4 immobilization and reduction of phosphate availability for connections with Pb, Zn, Cd. Experiments conducted by Ren et al. [65] prove that there are competitive reactions of Pb, Zn and Cd with phosphates when those heavy metals coexist in the soil. The percentage entrapping of Zn and Cd from single-metal-contaminated soil was higher than for competitive stabilization. However, immobilization of Pb did not change, which proves that entrapping of lead is more favourable. An experiment conducted by Ruby et al. [30] indicated that lead immobilization by phosphates reduced Pb concentration very rapidly, in less than 10 min. Based on geochemical modelling, in the presence of Na_2HPO_4 and a sample containing 10 g of Pb per 1 kg of soil, new stable minerals were formed, and Pb concentration was decreased to approximately 0.1 $\mu\text{g/L}$ [30]. This resulted in the formation of stable, sparingly soluble mineral forms, among which chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), hydroxypyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$), and fluoropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{F}$) were most commonly formed, depending on the anions available in the soil [26,30,34,35]. These newly formed compounds are not available for plants [30]. Immobilization of cadmium and zinc was significantly lower, which may suggest that cadmium and zinc hardly form stable mineral forms with phosphates. The mechanisms involved in P-induced Pb immobilization include ionic exchange and chemical precipitation [26,42,67,68]; however, the formation of pyromorphite-like minerals is considered to be the primary mechanism of reducing Pb mobility in soils [28,42].

In contrast, the immobilization of Zn and Cd is usually attributed to various processes, including ion exchange [27,33], surface complexation [68,69], sorption on the surface of phosphate minerals [27,70], etc. The formation of pyromorphite-like minerals upon addition of P has been proved by several previous studies [26,30,31,42,71–73]. However, the formation of pyromorphite-like minerals was not determined by our XRD results and is only partially confirmed by SEM results (discussed in Section 3.5. SEM-EDS Analysis), where new formations resembling phosphate-hopeite are present. This result may be caused by reaction time—the complete formation may take more time than previously estimated.

Moreover, except for metal-phosphates, the formation of phosphate anion precipitates with other cations (like Ca) is also possible. Potassium ions (derived from KH_2PO_4) exchange for Ca, Mg and other cations, bringing them into solution [19,74–78]. It is too complicated to indicate the main mechanisms of heavy metal immobilization using phosphate—they can be only predicted based on literature-derived data. More detailed studies are required to confirm the occurrence of these mechanisms and phrases unambiguously.

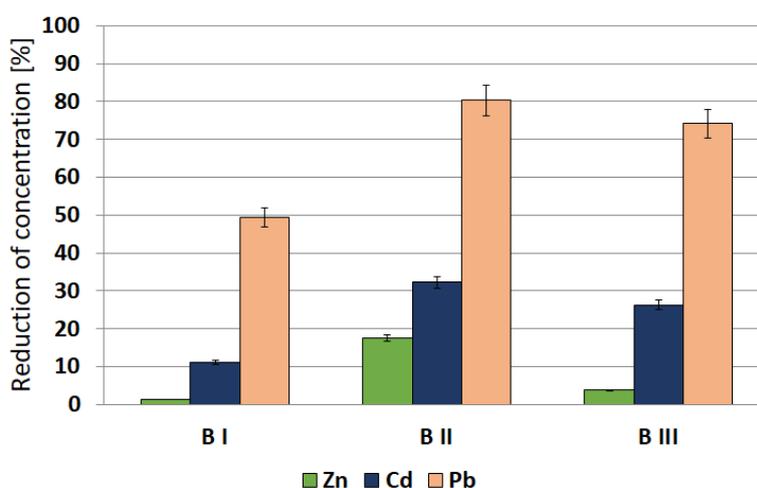


Figure 4. Reduction of concentration of Pb, Cd and Zn in soil samples treated with KH_2PO_4 .

The highest percentage reduction of concentration was obtained for sample BII (Figure 4). The lower pH can explain this result in sample BII (pH = 6.64) compared to that of BI (pH = 7.59) and BIII (pH = 7.27). The lower pH significantly increases the formation of new, stable, and sparingly soluble phosphates of metals in the soil [79].

3.4. Solid-Association of Zn, Cd and Pb

The method of selective extraction was used to determine the binding forms of the metals in the soil. This method consists of the gradual dissolution of subsequent mineral forms in the soil. The selective extraction allows estimation of metal ions associated with successive dissolved mineral phases. Although the phases in sequential extraction schemes are defined by the reagents used for dissolution processes, it is generally accepted that the water-soluble, exchangeable, carbonate-bound, Fe–Mn oxides and organic-bound phases are more bioavailable than the residual phase [26,42,68,80]. The analysis was conducted for soil samples from ES and CS to examine whether the addition of potassium phosphate affected the stability of Zn, Cu, and Pb. The results are shown in Figure 5.

Lead, zinc, and cadmium are usually associated with ion exchange positions and carbonates (30%–50% of total metal content in soil samples). This is related to the occurrence of zinc-lead mineralization in the research area, including dolomitic middle-silicon limestones [81]. An exchangeable fraction consists of weakly adsorbed metals bound by weak electrostatic interactions. These metals can be released by ion exchange processes and coprecipitated with carbonates [64]. Metals bound with carbonates occur at metastable positions; thus, metals can be relatively quickly released as a result of changes in the geochemical conditions in the soil [64,68]. The lower content of metals in metastable positions for soil samples treated with potassium phosphate (ES), than for soil samples from the CS, indicates increasing immobilization of heavy metals by phosphates. This implicates an increased resistance of newly formed metal phosphates to dissolution. The influence of phosphate salts on the immobilization of toxic metals is also apparent in step VII. In this step, the most durable minerals are dissolved. An evident increase in the number of metals that form hardly soluble bounds, especially for zinc and lead (Figure 5a,c), indicates the effective immobilization and formation of new, durable mineral substances associated with the heavy metals.

The addition of KH_2PO_4 significantly reduced exchangeable Pb and simultaneously increased residual Pb fractions (Figure 5a). These changes reflect a conversion of Pb from bioavailable to less bioavailable forms [33]. This was also noted in previous investigations, which indicated a significant reduction of soil Pb in the exchangeable fraction and an increase in the residual fraction upon P addition [25,33,65,68,82].

The phosphates also influenced Cd fractionation (Figure 5b). Decrease in exchangeable Cd and increase in carbonate-bound and Fe–Mn-oxide-bound Cd was observed. The dissolution of the carbonate matrix probably causes an increase in carbonate-bound Cd under more acidic conditions in the presence of phosphate. Carbonate anions compete with phosphates for available metals. The mechanism underlying the decrease in Cd at exchangeable positions is not known, mainly because the decline in soil pH produced by KH_2PO_4 is expected to increase exchangeable Cd [33]. For Pb, the newly formed pyromorphite-like minerals could be the reason for the decrease in nonresidual fractions, but there is no comparable insoluble Cd phosphate mineral [33]. Thus, besides the precipitation of Cd-phosphates, sorption of Cd onto Fe and Mn-oxides is also possible [83–85].

The decline in the bioavailability of Zn depends strongly on the sample (Figure 5c). The presence of KH_2PO_4 influences the content of carbonate-bound and Fe–Mn-oxide-bound Zn, which was also observed by Zwonitzer et al. [33]. In all samples, there was a significant increase in residuum content, which implies the occurrence of new, stable forms. The increase in exchangeable Zn was most probably due to the slight acidification caused by phosphate salt [33].

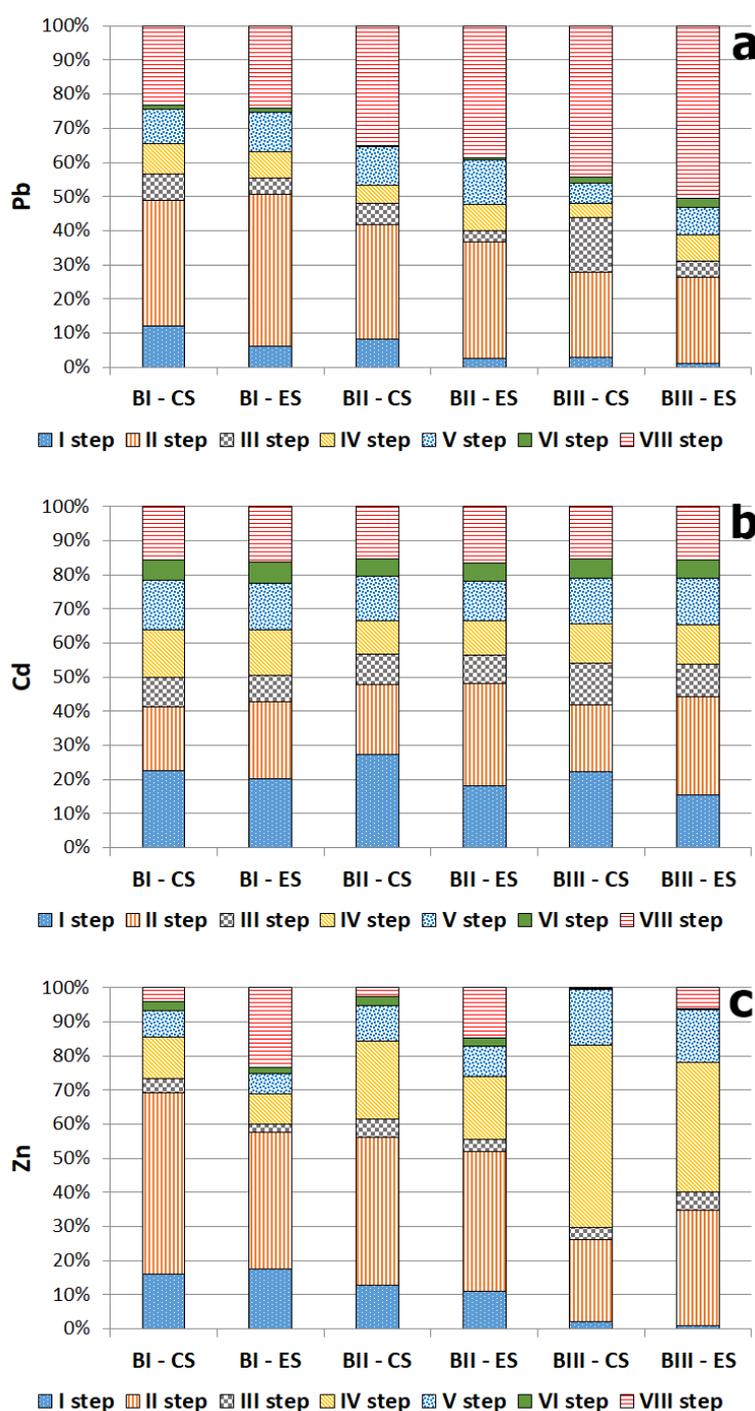


Figure 5. Contents of Pb (a), Cd (b) and Zn (c) in individual stages of selective extraction in soil samples (ES—results for the experimental system, CS—results for the control system). Step I: ion exchange positions—1 M $\text{CH}_3\text{COONH}_4$; Step II: carbonates—1 M CH_3COONa ; Step III: manganese oxides—0.1 M NH_2OH , pH 2 (controlled with 1M HCl); Step IV: amorphous oxides and iron oxyhydroxides—0.2 M $((\text{NH}_4)_2\text{C}_2\text{O}_4)$ + 0.2M $\text{C}_2\text{H}_2\text{O}_4$, pH 3; Step V: crystalline iron oxides—DCB method; Step VI: organic substance and sulfides—30% H_2O_2 , pH 2 (controlled with 1 M HNO_3), the residue was extracted with 1 M $\text{CH}_3\text{COONH}_4$ (as in Step I); Step VII: residuum— $\text{HF} + \text{HClO}_4$.

Similar to the previous studies, the higher increase of insoluble phases for Pb ions probably occurred because Pb-phosphate precipitates (pyromorphite-like minerals) were easier to form because of their extremely low solubility ($\log K_{\text{sp}} = -71.63$ to -83.7 , compared to -35.3 for $\text{Zn}_3(\text{PO}_4)_2$ and -38.1 for Cd_3

(PO_4)₂) [66,67]. Moreover, the formation of metal-phosphates is more favourable than the formation of metal-carbonates. Values of $\log K_{sp}$ for PbCO_3 , ZnCO_3 and CdCO_3 are much lower than for phosphate analogues (around -13.13 , -10.85 and -11.28 respectively). The competitive effect that occurs between Pb, Zn and Cd ions may also explain the more effective conversion of Pb to the residual fraction than for Zn and Cd. As was mentioned before, experiments conducted by Ren et al. [65] indicate that in the case of the ternary metal mixture in the soil immobilization of Pb ions is more favourable than Zn and Cd ions.

Utilization of phosphate for in-situ remediation of soil may potentially lead to release of mobile phosphates into the environment. Phosphate retention and concentration in the soils is mostly controlled by hydrous metal oxides of Fe, Al, and Mn. The equilibrium between phosphates adsorbed on solid surfaces and those in soil solution may be altered, for example, by changing the concentration of phosphate species, pH, ionic strength, and temperature, which may be an effect of in-situ soil remediation [33,86,87]. Moreover, previous research concerning stability of the phosphate compounds in soils indicates that bacteria naturally occurring in the soils are one of the greatest threats to the stability of metal phosphates. Some bacteria are able to actively capture P from insoluble phosphate compounds like apatites which results in remobilization of heavy metals in the environment. It is generally accepted that the action of organic acids synthesized by soil microorganisms is the major mechanism of mineral phosphate solubilization [88–92]. Nevertheless, despite many studies concerning in-situ immobilization of heavy metals using phosphates, more detailed study regarding assessment of the mobility and leachability of phosphate from treated samples needs to be performed.

3.5. SEM-EDS Analysis

The elemental composition obtained from the EDS spectrum shows that the samples contain many admixtures of metal compounds such as Pt, Ti, Fe, As, Al, V, Co and rare earth elements. The presence of these compounds is a result of precious mineralization of carbonates and activity of metallurgical industry.

Stable mineral forms, especially zinc phosphates, were primarily created on carbonates, which contain abundant admixtures of zinc and lead. During the dissolution of clasts, zinc reacted with phosphates, and acicular forms were created on carbonates, which resemble hydrated zinc phosphate—hopeite (Figure 6a,b) [93]. A few lamellar forms on easily dissolved silicates were also formed. Insoluble zinc compounds also occurred in agglomerations, thus creating typical “brushes” made of parallel cone-shaped crystals (Figure 6c). The chemical analyses of the grains visible in Figure 6d indicate that lead and phosphorus created stable mineral phases, probably lead phosphates co-occurring with clay minerals in the form of compact agglomerates about 2 μm in size.

Studies on the chemical composition of individual carbonate grains using the scanning electron microscope with the EDS attachment showed a significant number of zinc ions present in the form of admixtures. On the surface of these forms, some pits and cavities indicate an intensive dissolution process. Chemically unstable limestones released zinc into the solution during the grain digestion process. The released zinc reacted quickly with phosphate anions (added as KH_2PO_4 salts), thus creating zinc phosphate on the dissolved surface. New mineral substances usually created various types of infiltration that partially covered the carbonate grain. In addition to the dripstone formations, very fine, chaotically arranged spherical needles crystallized on the carbonate crumbs (Figure 6b). They formed small, irregular structures, which indicates very rapid and intense crystallization. Zinc phosphates are formed only on structures containing zinc in their composition, which is released as a result of dissolution. Figure 6e shows that carbonates with crystallized phosphate structures (Zn) are surrounded by quartz grains (Q) on which no new mineral forms have been formed.

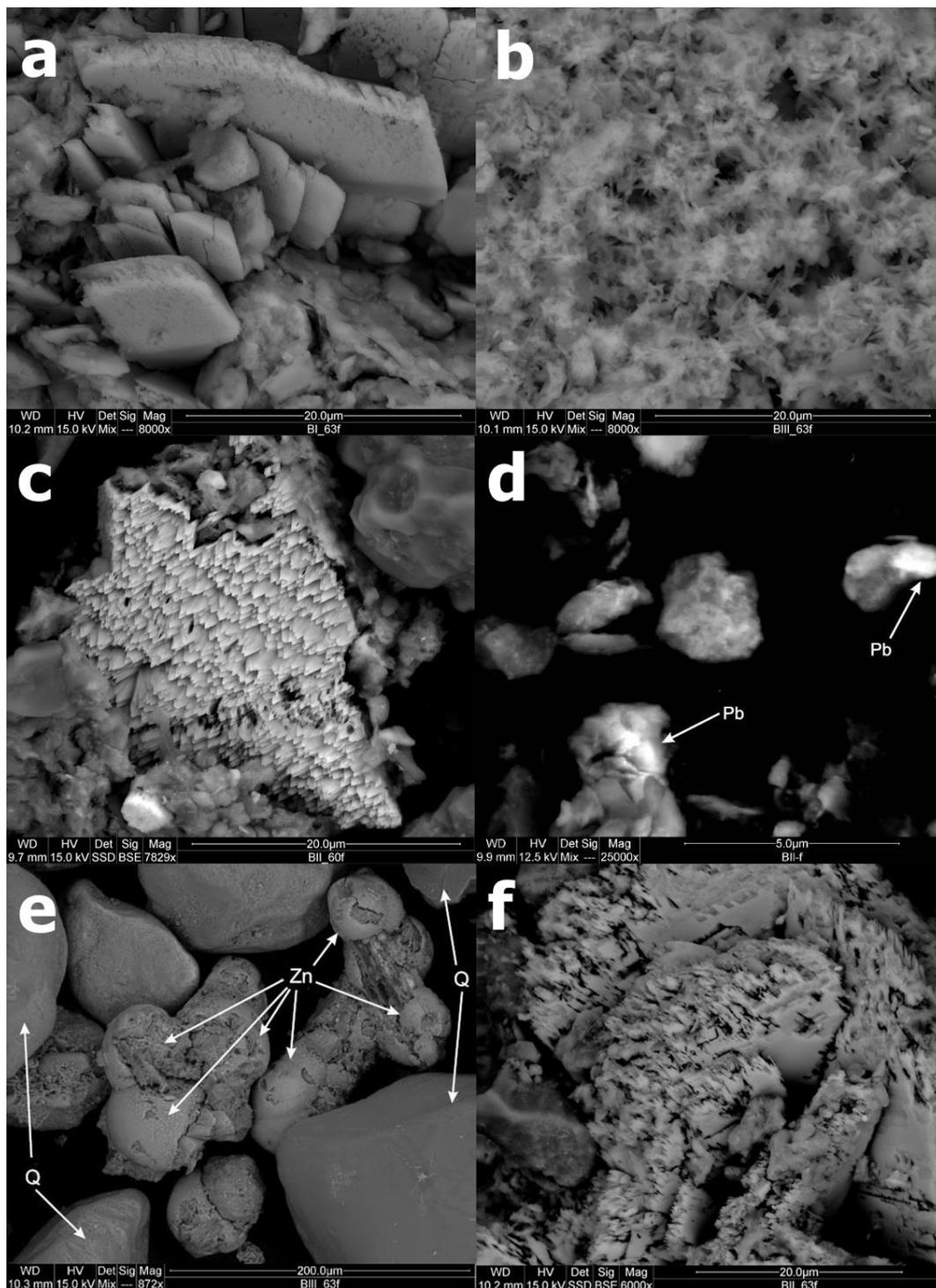


Figure 6. SEM images: (a) lamellar forms of zinc phosphate (BI-ES), (b) needle forms of lead phosphate (BII-ES), (c) brush made of parallel conical crystals—zinc silicates (BII-ES), (d) lead phosphate structures (BII-ES), (e) spherical forms of zinc phosphate on carbonates (BIII-ES), (f) lamellar forms of zinc phosphate (BII-ES).

Along with carbonates, there are also soluble silicates containing zinc admixtures. Figure 6f shows zinc phosphate plates crystallized on the silicate grains. These plates are jagged on their edges, which indicates the dissolution process of these structures. The Zn ions released from their structure react with phosphates and form plaques on the surface of rock crumbs; these plaques are not parallel to

each other and have a size up to 50 μm [94]. These plaques morphologically resemble hydrated zinc phosphate—hopeite $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, as also observed by Chen et al. [93] and Zwonitzer et al. [33]. In addition, zinc forms sparingly soluble forms of zinc sulfide as individual grains and a characteristic brush made of parallel conical crystals of zinc silicates (Figure 6c). These structures are similar to the willemite [33,95].

Lead ions also reacted with phosphates to form stable and sparingly soluble compounds as reported by Letcher [96]. This is also confirmed by the results of the analysis of the chemical composition of grains of soil samples in which the presence of fine, needle forms of lead phosphate was detected (Figure 6b). The percentage content of lead in the residuum ranged from 25% to 50%. The most common, stable minerals of lead are lead silicates found in the form of small, jagged plaques as well as spherical grains. The crystalline lead in the form of infiltrations is also present. The presence of infiltrations is probably caused by the metallurgical activity of the ZGH “Boleslaw” plant [94]. The concentration of lead and zinc potentially available for living organisms were 10 and 260 mg L^{-1} , respectively. With such a low lead concentration, detecting the products of Pb reaction with phosphate ions by XRD and SEM was impossible. The effectiveness of lead immobilization in the soil can be evaluated using the results from the TCLP-based procedure, as well as selective extraction methods. Tests of chemical composition and phase composition did not show the formation of stable forms of cadmium phosphates. This may be related to the limitations of the methods used together with the small amount of Cd released to the solution.

4. Conclusions

There are different and complex interactions among phosphates, heavy metal, and soil, especially the direct reaction between phosphate anions and heavy metals, which leads to different immobilization efficiencies. Our results indicated that phosphate amendments could effectively decrease Zn, Pb, and Cd leachability from soils. The easily soluble phosphate salts (KH_2PO_4) used in the experiment contributed to the partial immobilization of Zn, Cd, and Pb. The highest percentage decrease in leachable metal concentration was obtained for Pb (49%–80%), and then for Cd (11%–32%), and the lowest was observed for Zn (1%–17%). The results of experiments on immobilization of heavy metals using KH_2PO_4 indicate a high efficiency in the decrease of mobile content, especially of Pb and Zn. In all samples, there was a significant increase in residuum content, which implies the occurrence of new, stable forms. SEM images revealed that the dominant, newly formed phases occur as infiltrates and needles on soluble carbonate rock fragments. The alkaline nature of the soil and the high amount of carbonate has a fundamental influence on the formation of new structures.

The experiments were conducted on natural samples, where heavy metals coexist with each other. Our results shed light on the possibility and effectiveness of simultaneous immobilization of Zn, Cd and Pb using KH_2PO_4 . Despite the competitive effect that occurs between analyzed heavy metals, it was possible to reach U.S. EPA regulatory limits in almost all samples. However, new, more detailed studies are required to determine concentrations of phosphates needed for the most effective immobilization of heavy metals. Furthermore, the formation of stable minerals combined with a lower content of mobile phases has a significant impact on the bioavailability of heavy metals—sparingly soluble minerals are not available for plants. Thus, immobilization of heavy metals with phosphorous compounds could be a practical approach for the reduction of soil pollution in industrial areas.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/4/342/s1>, Table S1. Theoretical solubility of phosphate phases used in geochemical modelling (calculations for $T = 298.15 \text{ K}$; $\log K$ —equilibrium constant). Table S2. Modelling of metal concentration after phosphate treatment.

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References

1. Xiao, R.; Wang, S.; Li, R.H.; Wang, J.J.; Zhang, Z.Q. Soil heavy metal contamination and health risks associated with artisanal gold mining in Tongguan, Shaanxi, China. *Ecotoxicol. Environ. Saf.* **2017**, *141*, 17–24. [[CrossRef](#)]
2. Perez-Esteban, J.; Escolastico, C.; Masaguer, A.; Vargas, C.; Moliner, A. Soluble organic carbon and pH of organic amendments affect metal mobility and chemical speciation in mine soils. *Chemosphere* **2014**, *103*, 164–171. [[CrossRef](#)] [[PubMed](#)]
3. Forjan, R.; Asensio, V.; Rodriguez-Vila, A.; Covelo, E.F. Contribution of waste and biochar amendment to the sorption of metals in a copper mine tailing. *Catena* **2016**, *137*, 120–125. [[CrossRef](#)]
4. Liu, J.W.; Mwamulima, T.; Wang, Y.M.; Fang, Y.; Song, S.X.; Peng, C.S. Removal of Pb(II) and Cr(VI) from aqueous solutions using the fly ash-based adsorbent material-supported zero-valent iron. *J. Mol. Liq.* **2017**, *243*, 205–211. [[CrossRef](#)]
5. Hasani, T.; Eisazadeh, H. Removal of Cd (II) by using polypyrrole and its nanocomposites. *Synth. Met.* **2013**, *175*, 15–20. [[CrossRef](#)]
6. Saif, M.M.S.; Kumar, N.S.; Prasad, M.N.V. Binding of cadmium to *Strychnos potatorum* seed proteins in aqueous solution: Adsorption kinetics and relevance to water purification. *Colloids Surf. B Biointerfaces* **2012**, *94*, 73–79. [[CrossRef](#)]
7. Padmavathiamma, P.K.; Li, L.Y. Phytoremediation technology: Hyper-accumulation metals in plants. *Water Air Soil Pollut.* **2007**, *184*, 105–126. [[CrossRef](#)]
8. Omraei, M.; Esfandian, H.; Katal, R.; Ghorbani, M. Study of the removal of Zn(II) from aqueous solution using polypyrrole nanocomposite. *Desalination* **2011**, *271*, 248–256. [[CrossRef](#)]
9. Sanderson, P.; Thangavadivel, K.; Ranganathan, S.; Chadalavada, S.; Naidu, R.; Bowmanc, M. Effectiveness of gravity based particle separation and soil washing for reduction of Pb in a clay loam shooting range soil. *Environ. Technol. Innov.* **2019**, *16*, 7. [[CrossRef](#)]
10. Xia, W.Y.; Feng, Y.S.; Jin, F.; Zhang, L.M.; Du, Y.J. Stabilization and solidification of a heavy metal contaminated site soil using a hydroxyapatite based binder. *Constr. Build. Mater.* **2017**, *156*, 199–207. [[CrossRef](#)]
11. Ballesteros, S.; Rincon, J.M.; Rincon-Mora, B.; Jordan, M.M. Vitrication of urban soil contamination by hexavalent chromium. *J. Geochem. Explor.* **2017**, *174*, 132–139. [[CrossRef](#)]
12. Marques, A.; Rangel, A.; Castro, P.M.L. Remediation of heavy metal contaminated soils: Phytoremediation as a potentially promising clean-up technology. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39*, 622–654. [[CrossRef](#)]
13. Wu, H.P.; Lai, C.; Zeng, G.M.; Liang, J.; Chen, J.; Xu, J.J.; Dai, J.; Li, X.D.; Liu, J.F.; Chen, M.; et al. The interactions of composting and biochar and their implications for soil amendment and pollution remediation: A review. *Crit. Rev. Biotechnol.* **2017**, *37*, 754–764. [[CrossRef](#)]
14. Sprocati, A.R.; Alisi, C.; Tasso, F.; Marconi, P.; Sciallo, A.; Pinto, V.; Chiavarini, S.; Ubaldi, C.; Cremisini, C. Effectiveness of a microbial formula, as a bioaugmentation agent, tailored for bioremediation of diesel oil and heavy metal co-contaminated soil. *Process. Biochem.* **2012**, *47*, 1649–1655. [[CrossRef](#)]
15. Ye, S.J.; Zeng, G.M.; Wu, H.P.; Zhang, C.; Dai, J.; Liang, J.; Yu, J.F.; Ren, X.Y.; Yi, H.; Cheng, M. Biological technologies for the remediation of co-contaminated soil. *Crit. Rev. Biotechnol.* **2017**, *37*, 1062–1076. [[CrossRef](#)] [[PubMed](#)]
16. Ucaroglu, S.; Talinli, I. Recovery and safer disposal of phosphate coating sludge by solidification/stabilization. *J. Environ. Manag.* **2012**, *105*, 131–137. [[CrossRef](#)] [[PubMed](#)]
17. Rosestolato, D.; Bagatin, R.; Ferro, S. Electrokinetic remediation of soils polluted by heavy metals (mercury in particular). *Chem. Eng. J.* **2015**, *264*, 16–23. [[CrossRef](#)]
18. Yun, S.M.; Kang, C.S.; Kim, J.; Kim, H.S. Evaluation of soil flushing of complex contaminated soil: An experimental and modeling simulation study. *J. Hazard. Mater.* **2015**, *287*, 429–437. [[CrossRef](#)]
19. Basta, N.T.; Gradwohl, R.; Sneten, K.L.; Schroder, J.L. Chemical immobilization of lead, zinc, and cadmium in smelter-contaminated soils using biosolids and rock phosphate. *J. Environ. Qual.* **2001**, *30*, 1222–1230. [[CrossRef](#)]

20. Gray, C.W.; Dunham, S.J.; Dennis, P.G.; Zhao, F.J.; McGrath, S.P. Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud. *Environ. Pollut.* **2006**, *142*, 530–539. [[CrossRef](#)]
21. Belviso, C.; Cavalcante, F.; Ragone, P.; Fiore, S. Immobilization of Ni by synthesising zeolite at low temperatures in a polluted soil. *Chemosphere* **2010**, *78*, 1172–1176. [[CrossRef](#)] [[PubMed](#)]
22. Farrell, M.; Jones, D.L. Use of composts in the remediation of heavy metal contaminated soil. *J. Hazard. Mater.* **2010**, *175*, 575–582. [[CrossRef](#)] [[PubMed](#)]
23. Chen, Y.S.; Xu, J.H.; Lv, Z.Y.; Xie, R.J.; Huang, L.M.; Jiang, J.P. Impacts of biochar and oyster shells waste on the immobilization of arsenic in highly contaminated soils. *J. Environ. Manag.* **2018**, *217*, 646–653. [[CrossRef](#)] [[PubMed](#)]
24. Kumpiene, J.; Lagerkvist, A.; Maurice, C. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—A review. *Waste Manag.* **2008**, *28*, 215–225. [[CrossRef](#)]
25. Ryan, J.A.; Zhang, P.C.; Hesterberg, D.; Chou, J.; Sayers, D.E. Formation of chloropyromorphite in a lead-contaminated soil amended with hydroxyapatite. *Environ. Sci. Technol.* **2001**, *35*, 3798–3803. [[CrossRef](#)]
26. Cao, X. Immobilization of heavy metals in contaminated soils amended by phosphate-, carbonate-, and silicate-based materials: From lab to field. In *Twenty Years of Research and Development on Soil Pollution and Remediation in China*; Luo, Y., Tu, C., Eds.; Springer: Singapore, 2018; pp. 535–543.
27. Seshadri, B.; Bolan, N.S.; Choppala, G.; Kunhikrishnan, A.; Sanderson, P.; Wang, H.; Currie, L.D.; Tsang, D.C.W.; Ok, Y.S.; Kim, G. Potential value of phosphate compounds in enhancing immobilization and reducing bioavailability of mixed heavy metal contaminants in shooting range soil. *Chemosphere* **2017**, *184*, 197–206. [[CrossRef](#)]
28. Cao, X.D.; Wahbi, A.; Ma, L.N.; Li, B.; Yang, Y.L. Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid. *J. Hazard. Mater.* **2009**, *164*, 555–564. [[CrossRef](#)]
29. Bolan, N.S.; Adriano, D.C.; Duraisamy, P.; Mani, A. Immobilization and phytoavailability of cadmium in variable charge soils. III. Effect of biosolid compost addition. *Plant. Soil* **2003**, *256*, 231–241. [[CrossRef](#)]
30. Ruby, M.V.; Davis, A.; Nicholson, A. In-situ formation of lead phosphates in soils as a method to immobilize lead. *Environ. Sci. Technol.* **1994**, *28*, 646–654. [[CrossRef](#)]
31. Hettiarachchi, G.M.; Pierzynski, G.M.; Ransom, M.D. In situ stabilization of soil lead using phosphorus and manganese oxide. *Environ. Sci. Technol.* **2000**, *34*, 4614–4619. [[CrossRef](#)]
32. Cao, X.D.; Ma, L.Q.; Chen, M.; Singh, S.P.; Harris, W.G. Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environ. Sci. Technol.* **2002**, *36*, 5296–5304. [[CrossRef](#)] [[PubMed](#)]
33. Zwonitzer, J.C.; Pierzynski, G.M.; Hettiarachchi, G.M. Effects of phosphorus additions on lead, cadmium, and zinc bioavailabilities in a metal-contaminated soil. *Water Air Soil Pollut.* **2003**, *143*, 193–209. [[CrossRef](#)]
34. Mahar, A.; Wang, P.; Li, R.; Zhang, Z. Immobilization of lead and cadmium in contaminated soil using amendments: A review. *Pedosphere* **2015**, *25*, 555–568. [[CrossRef](#)]
35. Maenpaa, K.A.; Kukkonen, J.V.K.; Lydy, M.J. Remediation of heavy metal-contaminated soils using phosphorus: Evaluation of bioavailability using an earthworm bioassay. *Arch. Environ. Contam. Toxicol.* **2002**, *43*, 389–398. [[CrossRef](#)] [[PubMed](#)]
36. Yang, J.; Mosby, D.E.; Casteel, S.W.; Blanchar, R.W. Lead immobilization using phosphoric acid in a smelter-contaminated urban soil. *Environ. Sci. Technol.* **2001**, *35*, 3553–3559. [[CrossRef](#)]
37. Tang, X.Y.; Zhu, Y.G.; Chen, S.B.; Tang, L.L.; Chen, X.P. Assessment of the effectiveness of different phosphorus fertilizers to remediate Pb-contaminated soil using in vitro test. *Environ. Int.* **2004**, *30*, 531–537. [[CrossRef](#)]
38. Huang, G.Y.; Su, X.J.; Rizwan, M.S.; Zhu, Y.F.; Hu, H.Q. Chemical immobilization of Pb, Cu, and Cd by phosphate materials and calcium carbonate in contaminated soils. *Environ. Sci. Pollut. Res.* **2016**, *23*, 16845–16856. [[CrossRef](#)]
39. Falamaki, A.; Tavallali, H.; Eskandari, M.; Farahmand, S.R. Immobilizing some heavy metals by mixing contaminated soils with phosphate admixtures. *Int. J. Civ. Eng.* **2016**, *14*, 75–81. [[CrossRef](#)]
40. Abbaspour, A.; Golchin, A. Immobilization of heavy metals in a contaminated soil in Iran using di-ammonium phosphate, vermicompost and zeolite. *Environ. Earth Sci.* **2011**, *63*, 935–943. [[CrossRef](#)]
41. Basta, N.T.; McGowen, S.L. Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil. *Environ. Pollut.* **2004**, *127*, 73–82. [[CrossRef](#)]
42. Melamed, R.; Cao, X.D.; Chen, M.; Ma, L.Q. Field assessment of lead immobilization in a contaminated soil after phosphate application. *Sci. Total Environ.* **2003**, *305*, 117–127. [[CrossRef](#)]

43. Austruy, A.; Shahid, M.; Xiong, T.T.; Castrec, M.; Payre, V.; Niazi, N.K.; Sabir, M.; Dumat, C. Mechanisms of metal-phosphates formation in the rhizosphere soils of pea and tomato: Environmental and sanitary consequences. *J. Soils Sediments* **2014**, *14*, 666–678. [[CrossRef](#)]
44. Cao, X.D.; Liang, Y.; Zhao, L.; Le, H.Y. Mobility of Pb, Cu, and Zn in the phosphorus-amended contaminated soils under simulated landfill and rainfall conditions. *Environ. Sci. Pollut. Res.* **2013**, *20*, 5913–5921. [[CrossRef](#)]
45. Su, X.J.; Zhu, J.; Fu, Q.L.; Zuo, J.C.; Liu, Y.H.; Hu, H.Q. Immobilization of lead in anthropogenic contaminated soils using phosphates with/without oxalic acid. *J. Environ. Sci.* **2015**, *28*, 64–73. [[CrossRef](#)] [[PubMed](#)]
46. Almaroai, Y.A.; Usman, A.R.A.; Ahmad, M.; Moon, D.H.; Cho, J.S.; Joo, Y.K.; Jeon, C.; Lee, S.S.; Ok, Y. Effects of biochar, cow bone, and eggshell on Pb availability to maize in contaminated soil irrigated with saline water. *Environ. Earth Sci.* **2014**, *71*, 1289–1296. [[CrossRef](#)]
47. Guo, F.Y.; Ding, C.F.; Zhou, Z.G.; Huang, G.X.; Wang, X.X. Stability of immobilization remediation of several amendments on cadmium contaminated soils as affected by simulated soil acidification. *Ecotoxicol. Environ. Saf.* **2018**, *161*, 164–172. [[CrossRef](#)]
48. Hashimoto, Y.; Takaoka, M.; Oshita, K.; Tanida, H. Incomplete transformations of Pb to pyromorphite by phosphate-induced immobilization investigated by X-ray absorption fine structure (XAFS) spectroscopy. *Chemosphere* **2009**, *76*, 616–622. [[CrossRef](#)]
49. Huang, G.Y.; Gao, R.L.; You, J.W.; Zhu, J.; Fu, Q.L.; Hu, H.Q. Oxalic acid activated phosphate rock and bone meal to immobilize Cu and Pb in mine soils. *Ecotoxicol. Environ. Saf.* **2019**, *174*, 401–407. [[CrossRef](#)]
50. Ahmad, M.; Lee, S.S.; Yang, J.E.; Ro, H.M.; Lee, Y.H.; Ok, Y.S. Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. *Ecotoxicol. Environ. Saf.* **2012**, *79*, 225–231. [[CrossRef](#)]
51. Darwish, M.; Aris, A.; Puteh, M.H.; Jusoh, M.N.H.; Kadir, A.A. Waste bones ash as an alternative source of P for struvite precipitation. *J. Environ. Manag.* **2017**, *203*, 861–866. [[CrossRef](#)]
52. Chen, L.; Kivela, J.; Helenius, J.; Kangas, A. Meat bone meal as fertiliser for barley and oat. *Agric. Food Sci.* **2011**, *20*, 235–244. [[CrossRef](#)]
53. Szrek, D.; Bajda, T.; Manecki, M. A comparative study of the most effective amendment for Pb, Zn and Cd immobilization in contaminated soils. *J. Environ. Sci. Health Part A Toxic Hazard. Subst. Environ. Eng.* **2011**, *46*, 1491–1502. [[CrossRef](#)] [[PubMed](#)]
54. United States Environmental Protection Agency EPA. *Method 1311: Toxicity Characteristic Leaching Procedure; Waste, O.O.S., Ed.*; EPA: Washington, DC, USA, 1992.
55. Parkhurst, D. *User's Guide to PHREEQC, A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations*; Water-Resources Investigations Report 95-4227; U.S. Geological Survey: Reston, VA, USA, 1995; p. 143.
56. Allison, J.D.; Brown, D.S.; Novo-Gradac, K.J. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual EPA/600/3-91/021*; US Environmental Protection Agency, Environmental Research Laboratory: Athens, GA, USA, 1991.
57. Ayati, M.; Madsen, H.E.L. Solubility product of the cadmium phosphate $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ at 37 degrees C. *J. Chem. Eng. Data* **2001**, *46*, 113–116. [[CrossRef](#)]
58. Zhu, Y.N.; Zhu, Z.Q.; Zhao, X.; Liang, Y.P.; Dai, L.Q.; Huang, Y.H. Characterization, dissolution and solubility of synthetic cadmium hydroxylapatite $Cd_5(PO_4)_3OH$ at 25–45 degrees C. *Geochem. Trans.* **2015**, *16*, 11. [[CrossRef](#)]
59. Nriagu, J.O. Formation and Stability of Base Metal Phosphates in Soils and Sediments. In *Phosphate Minerals*; Nriagu, J.O., Moore, P.B., Eds.; Springer: Berlin/Heidelberg, Germany, 1984.
60. Calmano, W.; Forstner, U. Chemical-extraction of heavy-metals in polluted river sediments in central-Europe. *Sci. Total Environ.* **1983**, *28*, 77–90. [[CrossRef](#)]
61. Tessier, A.; Campbell, P.G.C.; Bisson, M. Sequential extraction procedure for the speciation of particulate trace-metals. *Anal. Chem.* **1979**, *51*, 844–851. [[CrossRef](#)]
62. Shuman, L.M. Separating soil iron-oxide and manganese-oxide fractions for micro-element analysis. *Soil Sci. Soc. Am. J.* **1982**, *46*, 1099–1102. [[CrossRef](#)]
63. Mehra, O.P.; Jackson, M.L. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* **1958**, *7*, 317–327. [[CrossRef](#)]
64. Filgueiras, A.V.; Lavilla, I.; Bendicho, C. Chemical sequential extraction for metal partitioning in environmental solid samples. *J. Environ. Monit.* **2002**, *4*, 823–857. [[CrossRef](#)]

65. Ren, J.; Zhang, Z.; Wang, M.; Guo, G.L.; Du, P.; Li, F.S. Phosphate-induced differences in stabilization efficiency for soils contaminated with lead, zinc, and cadmium. *Front. Environ. Sci. Eng.* **2018**, *12*, 9. [[CrossRef](#)]
66. Edwards, A.C. Phosphate in soils: Interactions with Micronutrients, Radionuclides and heavy metals. *Eur. J. Soil Sci.* **2015**, *66*, 962. [[CrossRef](#)]
67. Zeng, G.M.; Wan, J.; Huang, D.L.; Hu, L.; Huang, C.; Cheng, M.; Xue, W.J.; Gong, X.M.; Wang, R.Z.; Jiang, D.N. Precipitation, adsorption and rhizosphere effect: The mechanisms for Phosphate-induced Pb immobilization in soils—A review. *J. Hazard. Mater.* **2017**, *339*, 354–367. [[CrossRef](#)] [[PubMed](#)]
68. Xu, M.; Zhou, S.; Chen, S. Remediation of Heavy Metal-Contaminated Soils by Phosphate Fertilizers. In *Twenty Years of Research and Development on Soil Pollution and Remediation in China*; Luo, Y., Tu, C., Eds.; Springer: Singapore, 2018.
69. Xu, S.H.; Boyd, S.A. Cation-Exchange Chemistry of Hexadecyltrimethylammonium in a Subsoil Containing Vermiculite. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1382–1391. [[CrossRef](#)]
70. Sun, L.; Chen, S.; Chao, L.; Sun, T.H. Effects of flooding on changes in Eh, pH and speciation of cadmium and lead in contaminated soil. *Bull. Environ. Contam. Toxicol.* **2007**, *79*, 514–518. [[CrossRef](#)]
71. Ma, Q.Y.; Logan, T.J.; Traina, S.J. Lead immobilization from aqueous-solutions and contaminated soils using phosphate rocks. *Environ. Sci. Technol.* **1995**, *29*, 1118–1126. [[CrossRef](#)]
72. Cotter-Howells, J.; Caporn, S. Remediation of contaminated land by formation of heavy metal phosphates. *Appl. Geochem.* **1996**, *11*, 335–342. [[CrossRef](#)]
73. Laperche, V.; Logan, T.J.; Gaddam, P.; Traina, S.J. Effect of apatite amendments on plant uptake of lead from contaminated soil. *Environ. Sci. Technol.* **1997**, *31*, 2745–2753. [[CrossRef](#)]
74. Cao, X.D.; Harris, W. Carbonate and magnesium interactive effect on calcium phosphate precipitation. *Environ. Sci. Technol.* **2008**, *42*, 436–442. [[CrossRef](#)]
75. Cao, X.; Harris, W.G.; Josan, M.S.; Nair, V.D. Inhibition of calcium phosphate precipitation under environmentally-relevant conditions. *Sci. Total Environ.* **2007**, *383*, 205–215. [[CrossRef](#)]
76. Hu, C.; Zhang, T.C.; Huang, Y.H.; Dahab, M.F.; Surampalli, R. Effects of long-term wastewater application on chemical properties and phosphorus adsorption capacity in soils of a wastewater land treatment system. *Environ. Sci. Technol.* **2005**, *39*, 7240–7245. [[CrossRef](#)]
77. Chen, S.B.; Zhu, Y.G.; Ma, Y.B. The effect of grain size of rock phosphate amendment on metal immobilization in contaminated soils. *J. Hazard. Mater.* **2006**, *134*, 74–79. [[CrossRef](#)] [[PubMed](#)]
78. Theodoratos, P.; Papassiopi, N.; Xenidis, A. Evaluation of monobasic calcium phosphate for the immobilization of heavy metals in contaminated soils from Lavrion. *J. Hazard. Mater.* **2002**, *94*, 135–146. [[CrossRef](#)]
79. Brown, S.; Christensen, B.; Lombi, E.; McLaughlin, M.; McGrath, S.; Colpaert, J.; Vangronsveld, J. An inter-laboratory study to test the ability of amendments to reduce the availability of Cd, Pb, and Zn in situ. *Environ. Pollut.* **2005**, *138*, 34–45. [[CrossRef](#)] [[PubMed](#)]
80. Ma, L.Q.; Rao, G.N. Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. *J. Environ. Qual.* **1997**, *26*, 788–794. [[CrossRef](#)]
81. Wójcik, A.J.; Chmura, J. Deposits of natural resources and changes in the environment caused by mining in the area of Bukowno (Upper Silesia Region, Poland). *Górnictwo I Geoinżynieria* **2005**, *29*, 219–236.
82. Berti, W.R.; Cunningham, S.D. In-place inactivation of Pb in Pb contaminated soils. *Environ. Sci. Technol.* **1997**, *31*, 1359–1364. [[CrossRef](#)]
83. McKenzie, R.M. Adsorption of Lead and Other Heavy-Metals on Oxides of Manganese and Iron. *Aust. J. Soil Res.* **1980**, *18*, 61–73. [[CrossRef](#)]
84. Trivedi, P.; Axe, L. Modeling Cd and Zn sorption to hydrous metal oxides. *Environ. Sci. Technol.* **2000**, *34*, 2215–2223. [[CrossRef](#)]
85. Dong, D.M.; Nelson, Y.M.; Lion, L.W.; Shuler, M.L.; Ghiorse, W.C. Adsorption of Pb and Cd onto metal oxides and organic material in natural surface coatings as determined by selective extractions: New evidence for the importance of Mn and Fe oxides. *Water Res.* **2000**, *34*, 427–436. [[CrossRef](#)]
86. Manecki, M.; Bogucka, A.; Bajda, T.; Borkiewicz, O. Decrease of Pb bioavailability in soils by addition of phosphate ions. *Environ. Chem. Lett.* **2006**, *3*, 178–181. [[CrossRef](#)]
87. Cabrera, F.; Dearambarri, P.; Madrid, L.; Toca, C.G. Desorption of phosphate from iron-oxides in relation to equilibrium pH and porosity. *Geoderma* **1981**, *26*, 203–216. [[CrossRef](#)]

88. Beveridge, T.J.; Meloche, J.D.; Fyfe, W.S.; Murray, R.G.E. Diagenesis of metals chemically complexed to bacteria—Laboratory formation of metal phosphates, sulfides, and organic condensates in artificial sediments. *Appl. Environ. Microbiol.* **1983**, *45*, 1094–1108. [[CrossRef](#)] [[PubMed](#)]
89. Park, J.H.; Bolan, N.; Megharaj, M.; Naidu, R. Isolation of phosphate solubilizing bacteria and their potential for lead immobilization in soil. *J. Hazard. Mater.* **2011**, *185*, 829–836. [[CrossRef](#)] [[PubMed](#)]
90. Topolska, J.; Latowski, D.; Kaschabek, S.; Manecki, M.; Merkel, B.J.; Rakovan, J. Pb remobilization by bacterially mediated dissolution of pyromorphite $Pb_5(PO_4)_3Cl$ in presence of phosphate-solubilizing *Pseudomonas putida*. *Environ. Sci. Pollut. Res.* **2014**, *21*, 1079–1089. [[CrossRef](#)]
91. Drewniak, L.; Sklodowska, A.; Manecki, M.; Bajda, T. Solubilization of Pb-bearing apatite $Pb_5(PO_4)_3Cl$ by bacteria isolated from polluted environment. *Chemosphere* **2017**, *171*, 302–307. [[CrossRef](#)]
92. Rodriguez, H.; Fraga, R. Phosphate solubilizing bacteria and their role in plant growth promotion. *Biotechnol. Adv.* **1999**, *17*, 319–339. [[CrossRef](#)]
93. Chen, X.B.; Wright, J.V.; Conca, J.L.; Peurrung, L.M. Effects of pH on heavy metal sorption on mineral apatite. *Environ. Sci. Technol.* **1997**, *31*, 624–631. [[CrossRef](#)]
94. Cabala, J.; Krupa, P.; Misz-Kennan, M. Heavy Metals in Mycorrhizal Rhizospheres Contaminated By Zn–Pb Mining and Smelting Around Olkusz in Southern Poland. *Water Air Soil Pollut.* **2008**, *199*, 139–149. [[CrossRef](#)]
95. Bolewski, A. *Mineralogia Szczegółowa*; Wydawnictwa Geologiczne: Warszawa, Poland, 1975; p. 528.
96. Letcher, T. *Thermodynamics, Solubility and Environmental Issues*; Letcher, T., Ed.; Elsevier Science: Amsterdam, The Netherlands, 2007.



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