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Experimental immobilization of Zn, Pb and Cd by additives to highly contaminated soils

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Abstract

The immobilization effect of soil amendments on leaching and bioavailability of Pb, Zn and Cd in highly contaminated soils under industrial impact was studied by collecting the soils in the surroundings of Zn-Pb Smelter "Miasteczko Śląskie" in southern Poland as an example. Various amounts of four additives (phosphate fertilizer, limestone powder, bentonite rock and bog iron ore) were tested in laboratory experiments to compare the effectiveness of three dominant mechanisms of immobilization: precipitation of phosphates, pH increase, and sorption. The contents of metals before immobilization were determined by extraction in $CaCl_2$, EDTA and *aqua regia*. Cadmium and zinc are mainly represented by soluble, bioavailable forms extractable in $CaCl_2$, while lead by potentially bioavailable speciations extractable by EDTA. Most effective in the immobilization of these metals were the amendments increasing soil pH: limestone powder and phosphate fertilizer. Bog iron ore and bentonite were less effective because the soil pH was too low for efficient cation adsorption.

Keywords: trace elements, soil amendments, soil extraction, industrial pollution, Miasteczko Śląskie

1. Introduction

Migration of trace elements in the environment depends largely on their speciation and, in particular, on the solubility of the phases containing these elements. Therefore, the occurrence of relatively highly soluble, bioavailable forms of metals and metalloids is currently one of the biggest environmental concerns. This provides the basis of the technology for the neutralization of toxic components in soils or sediments by their in situ immobilization. In general, it involves the induction of precipitation of hardly soluble forms by chemical transformations triggered by appropriate additives. This results in the formation of new forms (speciations) of toxic constituents that are less mobile and much less bioavailable (Ma et al. 1993; Khalid et al. 2017). In this way, the total metal content in the soil is not altered, while its negative impact on the environment becomes minimized (Lee et al. 2009). The method is considered cost-effective and sustainable for the remediation of contaminated soils and sediments (Nejad et al. 2018). The processes responsible for a decrease of mobility de-

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pend on the particular metal involved and include e.g. crystallization of new phases, which may be accompanied by sorption and formation of stable complexes with organic ligands (Vitková et al. 2016; Khalid et al. 2017). The most commonly used additives are iron, manganese, and aluminum oxyhydroxides, zeolites, clay minerals, fly ash, blast furnace slags, lime and limestone, various organic compounds and wastes, biochar, zero valent iron (ZVI), and phosphate carriers such as fertilizers or bone meal (e.g. Ma et al. 1993; Basta, McGowen 2004; Hettiarachchi, Pierzynski 2004; Brown et al. 2005; Gray et al. 2006; Kumpiene et al. 2008; Lee et al. 2009; Szrek et al. 2011; Vítková et al. 2016; Lahori et al. 2017a,b, 2020; Sun et al. 2018; Wang et al. 2018; Zhang et al. 2019, 2021; Mitzia et al. 2020). The amendments are often combined with phytoremediation for the removal of constituents that are not fully immobilized (Mendez, Meier 2008; Uchimiya et al. 2012; Grobelak et al. 2013; Břendová et al. 2015; Sun et al. 2018).

In situ immobilization of toxic metal(loid)s through the formation of virtually insoluble phosphates and arsenates is a widely discussed and applied method for the remediation of contaminated soils and sediments (Ma et al. 1993; Raicevic et al. 2005; Bajda et al. 2011). Phosphate compounds can form secondary, poorly soluble forms that bind trace metals (Ma et al. 1993; Manecki et al. 2006; Miretzky, Fernandez-Cirelli 2008; Zhang et al. 2019). Experimentally calculated solubility constants of selected trace metal phosphates and arsenates are relatively low and range from 9.0×10^{-33} for zinc phosphate (Zai et al. 2020), $10^{-65.58}$ for cadmium chlorapatite (Wołowiec et al. 2019), $10^{-76.11}$ for lead arsenate, to $10^{-79.6}$ for lead chlorapatite (pyromorphite) (Flis et al. 2011). Furthermore, these phases can be highly stable over a wide range of pH and Eh conditions (Matusik et al. 2012). It is noted that the efficiency of treatment is affected by various parameters including initial pH and ion concentration, and the products vary in crystallite size and morphology (Zhang et al. 1997; Manecki et al. 2006; Matusik et al. 2008; Zhu et al. 2016; Shi et al. 2020). The use of phosphate fertilizers can make this method cheap (680 EUR/t) with promising performance. However, in situ immobilization of trace elements in the presence of phosphates can be associated with an increase in phosphorus concentration in soils and water, which can lead to eutrophication, another serious environmental problem (Hong et al. 2008; Cui et al. 2022).

Bentonites are considered an excellent sorbent of hazardous ions. They are composed mainly of smectite, a phyllosilicate possessing a large specific surface area and cation exchange capacity. It is an inexpensive material which makes its large-scale application cost-effective (200-320 EUR/t). The sorption efficiency using bentonite depends on the degree of contamination, initial pH of the solutions, exposure time, adsorbent dose and temperature (Naseem, Tahir 2001; Talaat et al. 2011; Mohammed-Azizi et al. 2013; Du et al. 2022).

Bog ores are Holocene iron accumulations formed in marshy, swampy areas. They consist mainly of iron oxyhydroxides and a relatively high proportion of organic matter (Rzepa et al. 2016). Therefore, they have a highly developed specific surface area and complex surface chemistry, which qualifies them as cheap, fast and effective mineral sorbents. The sorption efficiency by bog ores is influenced by the content of iron oxyhydroxides, the presence of organic matter and other components (silicates or manganese oxides), as well as by interactions with bacteria (Rzepa et al. 2016; Dębiec et al. 2017).

Among the materials used in this paper, limestone is the most abundant in nature. Although its specific surface area is lower than that of the sorbents mentioned above, it is considered a promising low-cost (50-60 EUR/t) adsorbent. Moreover, it is non-toxic and does not pose environmental problems. Pristine limestone shows satisfactory sorption efficiency (Nkutha et al. 2021). The surface properties can be easily modified under laboratory conditions. The presence of limestone in the contaminated environment significantly raises the pH, which is beneficial for reducing the mobility of metals (Iakovleva et al. 2015).

For the purpose of this study, samples of soils were collected in close proximity to a Zn-Pb smelter in Miasteczko Śląskie, southern Poland. The smelter started its operation in the 1960s and its location was chosen due to the proximity to zinc-lead deposits, good transport links and proximity to water sources (Gerold-Śmietańska 2007). The plant was designed as a metallurgical mill producing zinc, raw and refined lead, and sulfuric acid. As a result of its operation there was a huge increase in the emission of dust into the atmosphere, reaching several dozen tons of Zn and Pb per year. In the 1980s, the plant was among the largest sources of pollution in Europe (Kicińska 2019). Over the years, the quality of soils around the smelter has degraded dramatically. Before the start of the operation, the concentrations of trace metals in soils corresponded to the natural background. Currently, very high contamination of soils is observed, mainly with cadmium, lead and zinc (Sierka et al. 2001, 2002; Bielińska, Mocek-Płóciniak 2010; Kicińska 2020) as well as arsenic and thallium (Kicińska 2019). In the surface layer of soils sampled near the plant (50-500 m), 0.2-2.8% Zn, 0.06-0.6% Pb, and 9-188 mg/kg Cd were found, and contents clearly correlate with distance from the emitter (Baran, Faber 1976; Widera 1980; Diatta et al. 2010; Kicińska 2011; Grobelak et al. 2013; Nadgórska-Socha et al. 2013; Rozpondek et al. 2017). Based on metal analyses in the moss *Pleurozium*

schreberi, it has been proven that wind direction is an important factor influencing the spread of pollutants in the area (Kaczmarek et al. 2017). The harmful impact on the environment has been reduced in recent years and in many places regenerative changes in the biosphere and a clear decrease of metal content in pine wood are observed (Gerold-Śmietańska 2007). The sampled area is a highly degraded peat bog located in the immediate vicinity of the smelter. Apart from the organic matter content, the soil mainly consists of quartz, accompanied by aluminosilicates, carbonates and clay minerals (Kicińska 2019). The poor vegetation is dominated by sedges (Smieja-Król et al. 2017). Surface waters are acidic and strongly enriched in sulfates and trace metals which results in, among others, the appearance of secondary mineralization of Zn and Pb sulfides during wet periods (waterlogged conditions) and sulfates (barite, gypsum, anglesite) during dry periods (Smieja-Król et al. 2017).

The aim of this study was the experimental determination of the effect of soil amendments on leaching and bioavailability of Pb, Zn and Cd present in highly contaminated soils in the vicinity of the smelter. This will allow the future development of in situ remediation strategies at such sites using appropriate, cost-effective additives. Various amounts of four additives were tested in laboratory experiments: phosphate fertilizer, limestone powder, bentonite rock and bog iron ore. The reaction products were also characterized and the effectiveness of three dominant mechanisms of immobilization were compared: precipitation of phosphates, pH increase, and sorption. Previous studies have shown the beneficial effect of various amendments (Usman et al. 2006; Xu et al. 2016; Lahori et al. 2017b; Zhang et al. 2021; Zhang et al. 2021) and their combinations (Grobelak, Napora 2015; Lahori et al. 2017a, 2020, Kicińska, Wikar 2021) on the immobilization of trace elements in the soil. However, little is known about the impact of different additives on the same soil, especially in terms of directly comparing the effectiveness of competing mechanisms governing the immobilization processes. Moreover, even existing research comparing different additives and mechanisms of metal immobilization (Szrek et al. 2011) provides little mineralogical evidence, focusing mainly on chemical evidence. The results of ex situ experiments are universal and allow optimization of remediation strategies in other similarly polluted sites. In situ field experiment at a specific application site may be necessary to further fine-tune the procedures and to consider the combined use of fertilizer and additive mixtures.

2. Samples and methods

2.1. Soil sampling, preparation and extraction

Soil was sampled at ten different sites within the degraded peat bog located approximately 0.5 km southeast of the zinc smelter, east of road 912 (Fig. 1). Samples (0.5 kg of topsoil, 0-30 cm) were collected with a sampling stick in the corners and at the intersection of 2.5–4 m square diagonals, placed in separate bags and transported to the laboratory. Air-dried soil samples were crushed and sieved through a 2 mm sieve. Soil pH was measured in distilled water and KCl with a solid phase to solution ratio equal to 1:10 with a standard potentiometer electrode in order to determine exchange acidity and active acidity, respectively. Three leaching procedures were applied to determine the content of selected metals (Zn, Pb, Cd) in sampled soils: extraction with neutral salt, extraction with complexing agent and extraction with *aqua regia*.

Extraction with a neutral salt solution (0.01 M $CaCl_2$) is commonly used to determine the current phytoavailability of the metals in the soil (Houba et al. 1996, 2000; Pueyo et al. 2004). For extraction, dry soil was weighed

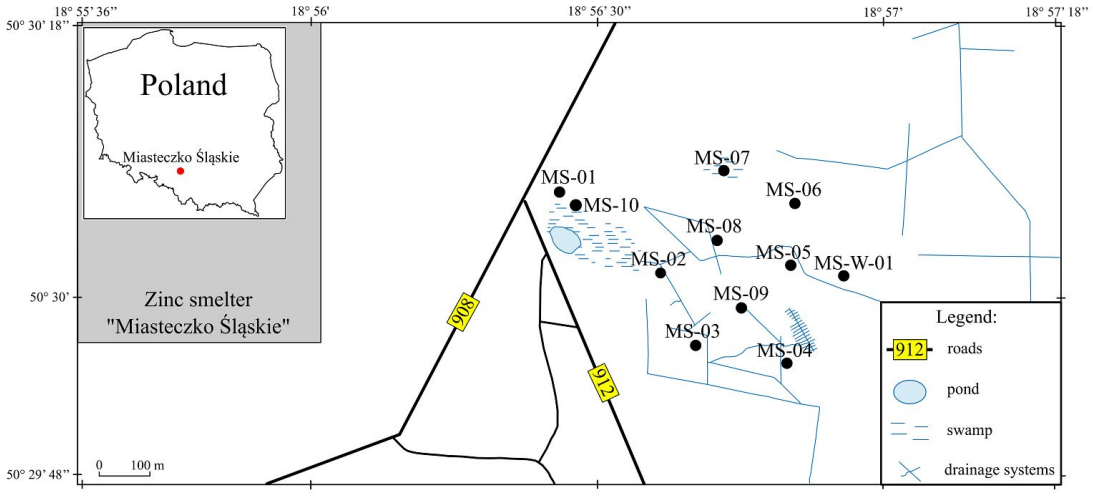


Figure 1. Study area and sample site location near the Zinc smelter "Miasteczko Śląskie". Top left corner – location of the area in Poland.

into plastic centrifuge tubes and 0.01 M $CaCl_2$ solution was added in a 1:10 solid-liquid ratio (3 g of soil and 30 cm^3 of solution). The suspension was stirred for 2 hours on a rotary shaker and then filtered through Whatman® filter papers.

Extraction with a complexing solution is used to determine the content of toxic, i.e. potentially bioavailable forms of metals (Manouchehri et al. 2006; Manouchehri, Bermond 2009). The extraction was carried out using ethylenediaminetetraacetic acid (EDTA). A solution of 0.02 M EDTA in acetate buffer at pH 4.65 and at the ratio 1:5 solid to solution (5 g of soil to 25 cm^3 of solution) was applied. The suspension was stirred for 30 minutes on a rotary shaker and then centrifuged.

Extraction in *aqua regia* was used to determine pseudo-total metal content of soils (Chen, Ma 2001; Santoro et al. 2017). For the preparation of *aqua regia* solution analytical grade 38% hydrochloric acid (HCl) and 65% nitric acid (HNO_3) were used at the ratio of 3:1, respectively. The weight of the sample was equal to 1 g. Extraction was carried out on the heating plate for 2 hours with the temperature gradually increasing from 120°C to 200°C.

Losses of ignition were determined by putting 2 g of the air-dried sample in ceramic crucibles and roasting them at 550°C and 950°C in a muffle furnace for 24 hours (Heiri et al. 2001). Based on the extraction results, samples with the highest extractable contents of Zn, Pb Cd were selected for immobilization experiments.

2.2. Analytical methods

Concentrations of metals in the solutions were determined using atomic absorption spectrometry (AAS) (GBC SavantAA). Scanning electron microscope (SEM) analyses of solids were carried out in low vacuum mode using an FEI 200 Quanta FEG microscope equipped with an EDS/EDAX spectrometer. The acceleration voltage was 15-20 kV, and the pressure was 60 Pa. The samples were not coated with any conductive layer. The mineral composition of soil additives was determined with powder X-ray diffraction (XRD). The patterns were collected using a Rigaku SmartLab instrument equipped with a graphite monochromator, rotation Cu anode, 45 kV and 200 mA generator settings, 2–75° 2Θ recording range, 0.05° step size, and counting time of 1 second per step.

2.3. Characteristics of soil additives

The samples selected for the experiments (MS-01, MS-02 and MS-08) were treated with phosphate fertilizer, limestone and bentonite. Additionally, bog iron was also used with sample MS-02 due to the insufficient amounts of other samples left over from other experiments. These additives were selected to induce transformations from mobile to immobile forms of Zn, Pb and Cd through sorption and precipitation of new phases resulting from the reaction with the added components or/and alteration of soil pH. The phase composition of all additives determined by XRD is presented in Figure 2.

POLIDAP was an ammonium phosphate fertilizer. Phase composition determined with XRD included various ammonium and magnesium phosphates: $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, $(NH_4)H_2PO_4$ and $Mg_3(PO_4)_2 \cdot 22H_2O$. Using SEM it was found that this fertilizer consisted of aggregates of different sizes and shapes, composed of grains of <25 µm. EDS analyses showed that apart from phosphorus, nitrogen and sulphur, there are also admixtures of other elements such as silicon, magnesium, sodium and iron.

Limestone powder (fraction <0.08 mm) made of natural limestone from Czatkowice (Poland) consisted of calcite with accessory quartz and dolomite. SEM imaging has shown that calcite occurs in the form of strongly aggregated fragments composed of crystallites a few micrometers in size.

The bentonite used in experiments comes from Kopernica (Slovakia). XRD analysis revealed the presence of dioctahedral smectite and opal-CT with traces of mica and quartz.

The so-called fine (loose) bog ore from the Kolechowice deposit (Poland) was used in the experiments with sample MS-02. Its chemical composition was dominated by Fe_2O_3, while SiO_2, P_2O_5 and CaO were present in minor quantities, and the contents of the other components did not exceed tenths of a percent. Relatively high values of ignition losses (LOI) resulted from the presence of both iron oxyhydroxides and organic matter. The presence of fine crystalline goethite as well as quartz and trace amounts of feldspar were determined by XRD analysis. Significant amounts of ferrihydrite were evidenced on the XRD pattern as elevated background in the range 30-45° and 55-65° 2Θ (Rzepa et al. 2016).

Mineral additives used in the experiment were also analyzed as blanks for metal concentrations extracted in $CaCl_2$. The results showed that the analyzed metals are present but in relatively low amounts (Table 1). The highest content of extractable metals was found in phosphate fertilizer which is consistent with previous studies (e.g. Szrek et al. 2011).

Table 1. The concentration of available forms of trace metals (extracted in 0.01 M $CaCl_2$) in the mineral additives.

	Cd [mg/kg]	Pb [mg/kg]	Zn [mg/kg]
phosphate fertilizer	1.50	6.70	4.30
limestone	0.97	5.09	1.53
bentonite	0.96	5.13	1.44
bog iron ore	1.06	5.34	1.66

Table 2. The concentrations of zinc, cadmium and lead extracted in $CaCl_2$, EDTA and *aqua regia* (values in mg/kg) and comparison of losses of ignition (in wt%). Values in bold are for samples chosen for the immobilization experiment. LOD – limits of detection, LOI 550 – loss of ignition at 550°C, LOI 950 – loss of ignition at 950°C.

Sample	$CaCl_2$ extraction			EDTA extraction			Aqua regia extraction			LOI 550 [wt%]	LOI 950 [wt%]
	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn		
MS-01	**8.13**	**4.4**	**289**	**31.28**	**1343**	**593**	**34.17**	**1422**	**1014**	**5.35**	**0.31**
MS-02	**5.25**	**15.6**	**97**	**6.93**	**498**	**132**	**17.97**	**828**	**411**	**4.18**	**0.21**
MS-03	3.97	0.9	176	6.60	188	208	9.31	215	342	5.23	0.16
MS-04	4.53	7.4	182	7.60	356	251	11.13	365	393	16.32	0.18
MS-05	5.42	6.0	137	5.64	258	160	8.23	289	247	1.72	0.14
MS-06	3.03	9.6	43	3.49	183	56	4.87	215	90	1.80	0.26
MS-07	3.66	9.2	126	4.29	179	162	5.93	191	242	1.62	0.28
MS-08	**9.96**	**14.6**	**333**	**24.41**	**974**	**493**	**32.41**	**1092**	**817**	**26.49**	**0.29**
MS-09	1.29	6.7	20	1.61	163	30	4.91	361	197	1.43	0.20
MS-10	12.55	43.0	181	20.68	1214	199	26.59	1399	607	4.95	0.17
MS-W-01	6.50	10.4	388	9.54	481	276	10.99	515	361	21.60	0.24
LOD	0.1	1.0	0.5	0.05	0.5	0.25	0.5	5.0	2.5		

2.4. Immobilization experiment setup

The experiment was designed to determine the effect of additives on reducing the mobility of trace metals. The experimental setup was based on Szrek et al. (2011). Each set consisted of 15 g of soil, a mineral additive (in the amount of 2 wt% or 10 wt%) and redistilled water, which was used to maintain a constant water content of 25 wt%. Control experiments were carried out on soil samples without any amendments. The experimental kits consisted of a plastic container with a cap equipped with a plastic baguette to mix the sample. Samples were stirred 1-2 times a week and water was refilled as needed to maintain 25% humidity. All experiments were duplicated. After four months of reaction, the final pH of soil solutions was measured, and the experimental mixtures and the control samples were extracted with 0.01 M $CaCl_2$ solution to evaluate the amount of currently mobile speciations. Metal concentrations in the extraction solutions were determined using AAS. The centrifuged and dried solids were analyzed with the use of XRD and electron microscopy.

3. Results

3.1. Evaluation of trace metal speciations in soils

The results of extraction before the immobilization experiment showed the extent of contamination of soils caused by metallurgical activities of the smelter. The concentrations determined after different extraction procedures ($CaCl_2$, EDTA, and *aqua regia*) also allowed comparison of the relative proportions of readily leachable and bioavailable speciations with a total content of Cd, Pb, and Zn in the soils (Table 2). The pseudo-total concentrations approximated by *aqua regia* extraction ranged from 4.87 to 34.17 mg/kg for Cd, 191 to 1422 mg/kg for Pb and 90 to 1014 mg/kg for Zn. No clear trend was observed, but the highest metal content was related to the distance from the pollution source and probably to the vicinity of the flowing water: it was higher near the smelter and in locations adjacent to the watercourses (Fig. 1). The concentrations of Cd and Pb were close to each other and were clustered relatively close

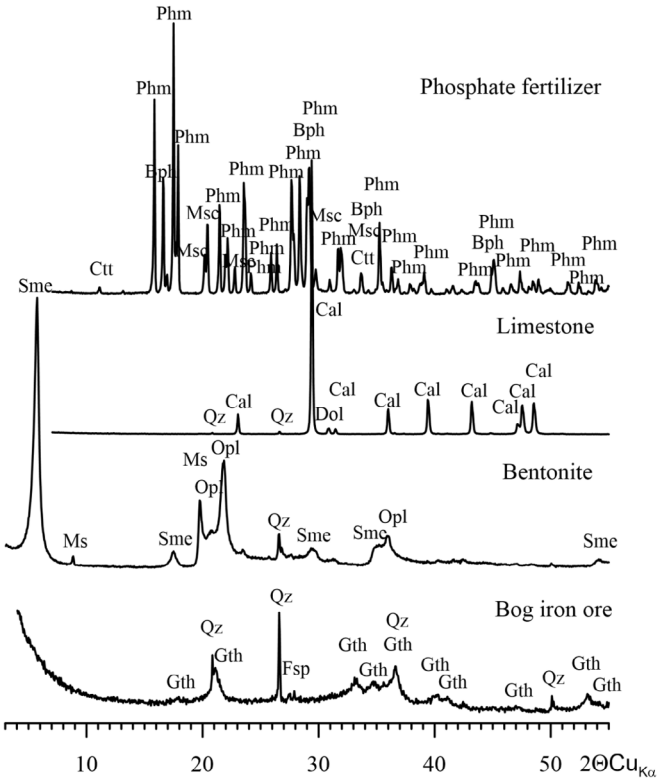


Figure 2. XRD patterns of mineral additives used in the experiments. Phm – phosphammite ($(NH_4)_2HPO_4$), Pbh – biphosphammite ($(NH_4)H_2PO_4$), Msc – mascagnite ($(NH_4)_2SO_4$), Ctt – cattiite ($Mg_3(PO_4)_2 \cdot 22H_2O$), Cal – calcite, Dol – dolomite, Qz – quartz, Sme – smectite, Ms – muscovite, Opl – opal, Gth – goethite, Fsp – feldspar.

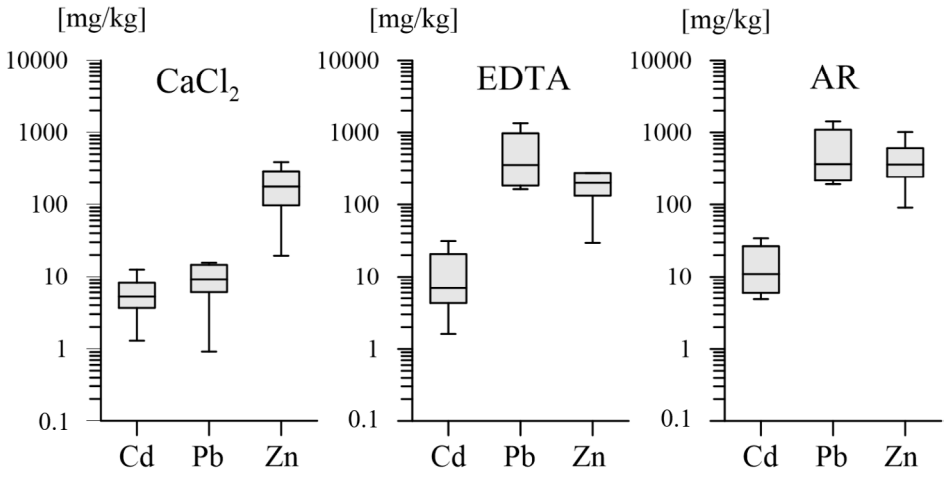


Figure 3. Box-whisker plots of Zn, Pb and Cd concentrations [mg/kg] extracted using $CaCl_2$, EDTA and *aqua regia* (before any amendments).

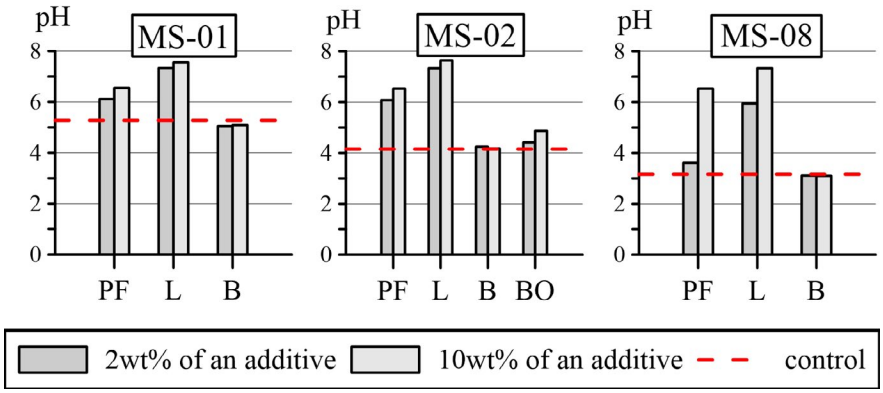


Figure 4. Effect of the amount of mineral additives on soil pH in comparison with the control sample (no additives). PF = phosphate fertilizer, L = limestone, B = bentonite, BO = bog ore.

to the median value, about 10 mg/kg and 400 mg/kg, respectively. In contrast, Zn concentration values were significantly more scattered, particularly in lower ranges (Fig. 3).

The concentrations of bioavailable metal speciations were lower compared to the total amount. The contents of easily leachable, currently bioavailable forms of trace elements extracted in $CaCl_2$ were the lowest, not exceeding 9.96 mg/kg for Cd, 43 mg/kg for Pb, and 388 mg/kg for Zn. They were also the most widely dispersed, especially for the lower values. A comparison of the contents within individual soil samples showed that for Cd and Zn these forms represent between 20 and 65% of the total content and their percentages are higher in soils with lower total contents. In contrast, the leachability of Pb determined by extraction in $CaCl_2$ was much lower and did not exceed 5% of its total amount.

Thus, it was observed that Cd and Zn were mainly represented by highly soluble, currently bioavailable forms extractable in $CaCl_2$, while Pb was mainly represented by potentially bioavailable speciations extractable by EDTA. Considering all the listed observations, the samples with the highest contents of metals: MS-01, MS-02 and MS-08 were selected for immobilization experiments.

3.2. Effects of amendments on soil pH

Soils in the examined area in the Miasteczko Śląskie peatland were acidic. The potential acidity measured in KCl before the experiments (control in Table 3) ranged from 3.16 to 5.28 and was close to the active acidity (i.e. that measured in H_2O). The application of limestone and phosphate fertilizer resulted in an increase in the pH of the soils (Fig. 4). At 10% addition of limestone, the soil is neutralized (pH values are mainly >7.0). Other mineral additives increased pH less effectively. There were no clear pH changes in experiments with bentonite, and very limited (from 4.42 and 4.87 to 5.01 and 5.41, respectively) increase for bog ore (Table 3). Increasing concentrations of soil additives slightly affected the pH of the samples, which was generally a little higher (not more than 25%) for higher concentrations.

3.3. Effects of amendments on the mobility of Cd, Pb and Zn

Evaluation of trace metals immobilization with different mineral additives was carried out by extraction in $CaCl_2$. A comparison of Zn, Pb, and Cd concentrations before and after amendments showed that the use of an ad-

Table 3. Values of pH for samples with and without additives. Hyphen stands for “no data”.

Sample	Proportion of additive	MS-01		MS-02		MS-08	
		pH-KCl	pH-H_2O	pH-KCl	pH-H_2O	pH-KCl	pH-H_2O
Soil (control)	-	5.28	5.39	4.15	4.48	3.16	4.20
Soil with phosphate fertilizer	2%	6.11	7.11	6.08	6.82	3.61	5.16
	10%	6.55	6.94	6.53	6.92	5.49	6.15
Soil with limestone	2%	7.33	7.50	7.33	7.61	5.95	6.50
	10%	7.55	7.79	7.64	7.75	7.33	7.65
Soil with bentonite	2%	5.05	5.38	4.24	4.68	3.11	4.21
	10%	5.09	5.93	4.17	4.77	3.10	4.24
Soil with bog iron	2%	-	-	4.42	5.01	-	-
	10%	-	-	4.87	5.41	-	-

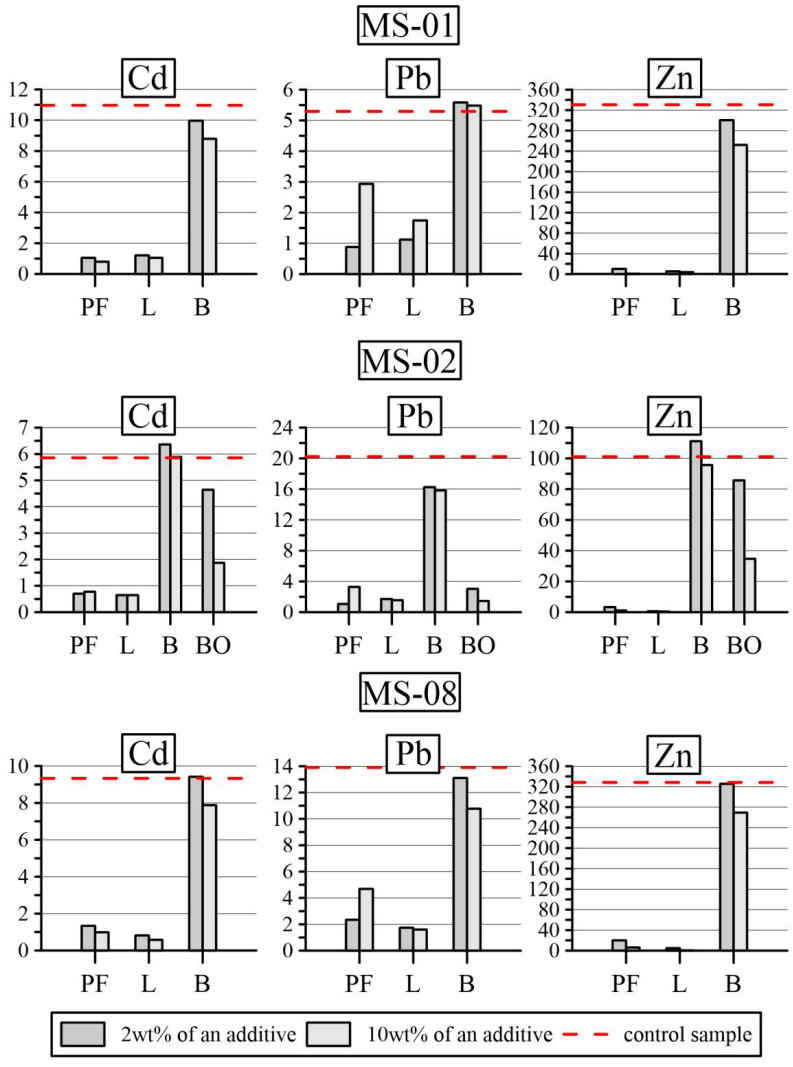


Figure 5. Concentrations of trace metals leachable in $CaCl_2$ after immobilization experiment compared to control sample (no amendments). Vertical axis – values in mg/kg. Horizontal axis – used additives: PF – phosphate fertilizer, L – limestone, B – bentonite, BO – bog ore.

ditive reduced the leaching yield of bioavailable metal forms (Fig. 5).

The degree of immobilization varied depending on the type of additive. The most effective in immobilization were phosphate fertilizer and limestone powder. The addition of the former reduced bioavailable Zn by two-three orders of magnitude, Cd by order of magnitude, and Pb by several times (Fig. 5). This corresponded to immobilization of 94-99% Zn, 85-93% Cd, and 45-95% Pb (Table 4). Limestone showed similar effectiveness: 98.5-99.5% for Zn, 89-94% for Cd and 67-92% for Pb. Bentonite was the least effective: immobilization efficiency rarely exceeds several percent, and in a few cases may even result in an increase in the concentration of

Table 4. Percentage effectiveness of immobilization. Negative values denote an increase in the available speciation concentration. Hyphen stands for "no data".

		MS-01			MS-02			MS-08		
		Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn
Phosphate fertilizer	2%	90.40	83.37	96.93	88.09	94.72	96.74	85.67	83.15	93.86
	10%	92.72	44.52	99.76	86.83	83.77	98.92	89.38	66.28	98.11
Limestone	2%	88.98	78.82	98.37	88.97	91.53	99.46	91.26	87.51	98.50
	10%	90.44	66.99	98.83	89.04	92.33	99.57	93.79	88.46	99.84
Bentonite	2%	9.09	-5.46	9.11	-8.32	19.67	-9.98	-0.92	5.71	0.83
	10%	19.83	-3.55	23.74	-0.22	21.74	5.33	15.60	22.49	17.95
Bog iron	2%	-	-	-	20.94	85.06	15.20	-	-	-
	10%	-	-	-	68.14	92.86	65.64	-	-	-

the bioavailable form of an element (Pb in sample MS-01 and Zn and Cd in sample MS-02). Bog ore used as an additive in sample MS-02 showed an immobilization efficiency comparable to fertilizer and limestone for Pb (85-93%), but significantly poorer for Zn and Cd (Fig. 5). Typically, a higher amount of additive (10% versus 2%) resulted in better immobilization efficiency. This difference was most pronounced in the case of bog ore, increasing the immobilization of Zn and Cd from a dozen to almost 70% (Table 4). The higher addition rate was also beneficial for bentonite (Fig. 5). The smallest effect was observed for limestone. The opposite phenomenon, a slightly reduced immobilization efficiency with a higher amount of addition, was observed for Pb in the case of phosphate fertilizer (Fig. 5).

4. Discussion

Soils in the studied area have low pH. The measurements carried out in this study are consistent with those previously described by other authors for this area (Diatta et al. 2010; Pająk, Jasik 2010; Grobelak et al. 2013; Smieja-Król et al. 2017). The potential acidity of the studied soils (in KCl) is generally lower than the active acidity measured in H_2O. Therefore, a high contribution of exchangeable hydrogen is observed in the soil system compared to the total content of acid and acidic factors (Kicińska et al. 2021).

Soil pH has been mostly raised by used additives. The mechanism of pH increase depends on the additive. Limestone is likely to dissolve at lower pH, releasing calcium cations that are known to form bases. Moreover, lime reacts with CO_2 and water present in the soil to form HCO_3^- ions, which have a high potential to trap acid-forming ions such as H^+ and Al^{3+} and thus increase soil pH (McCauley et al. 2009). Even higher pH values can be achieved in soils using quicklime (Vondráčková et al. 2013). The increase in pH after phosphorus fertilizer application is likely due to generating an ammonium buffer, as the fertilizer used in the experiment was rich in ammonium ions. However, the application of ammonium-based fertilizer with different phase compositions can also cause a decrease in pH due to the release of hydrogen ions (Szrek et al. 2011). The effect of bentonite additives on pH is minor. Sodium-rich bentonites can cause alkaline reactions that raise soil pH (Vrînceanu et al. 2019). However, under the conditions of this experiment, the addition of bentonite did little to change soil pH. The same was true for bog iron. Bog iron itself typically has a pH in the range of 3.7 to 6.4, which can be higher in response to some soil components (Kaczorek et al. 2009; Dębiec et al. 2017).

The increase in soil pH caused by the additives correlates with their higher immobilization efficiency (Tables 3 and 4). Phosphate fertilizers and limestone powder, which are most effective in immobilizing metals, clearly neutralize soil pH. Results presented in previous research reported the effectiveness of phosphate additives ranging from 84 to 99% (Mignardi et al. 2012) and a decrease of metal content 57-98.5% (Houben et al. 2012). However, the tested soils had higher initial pH or the influence of pH was not considered. Bentonite, on the other hand, has almost no effect on pH values and has the weakest sorption efficiency. Bog iron shows a varying degree of immobilization depending on the element and a minor effect on soil pH.

Zinc, lead and cadmium are present in the investigated soils (Kicińska et al. 2019, 2020) in amounts significantly exceeding the content allowed by legal regulations in Poland and in other countries (see for example Tóth et al. 2016 and the literature cited therein). Additionally, the acidity of these soils (pH around 4) favors the mobility of most metals (Vítková et al. 2016). Trace elements in the soils were represented both by distinct phases and occurred as impurities in other minerals. The most common metal carriers were sulfides, oxides, and sulfates (Fig. 6a-c). Admixtures of trace metals were also present in iron (oxyhydr)oxides (Fig. 6d). Cadmium does not form its own mineral phases or distinct secondary precipitates here. It occurs as substitutions in other min-

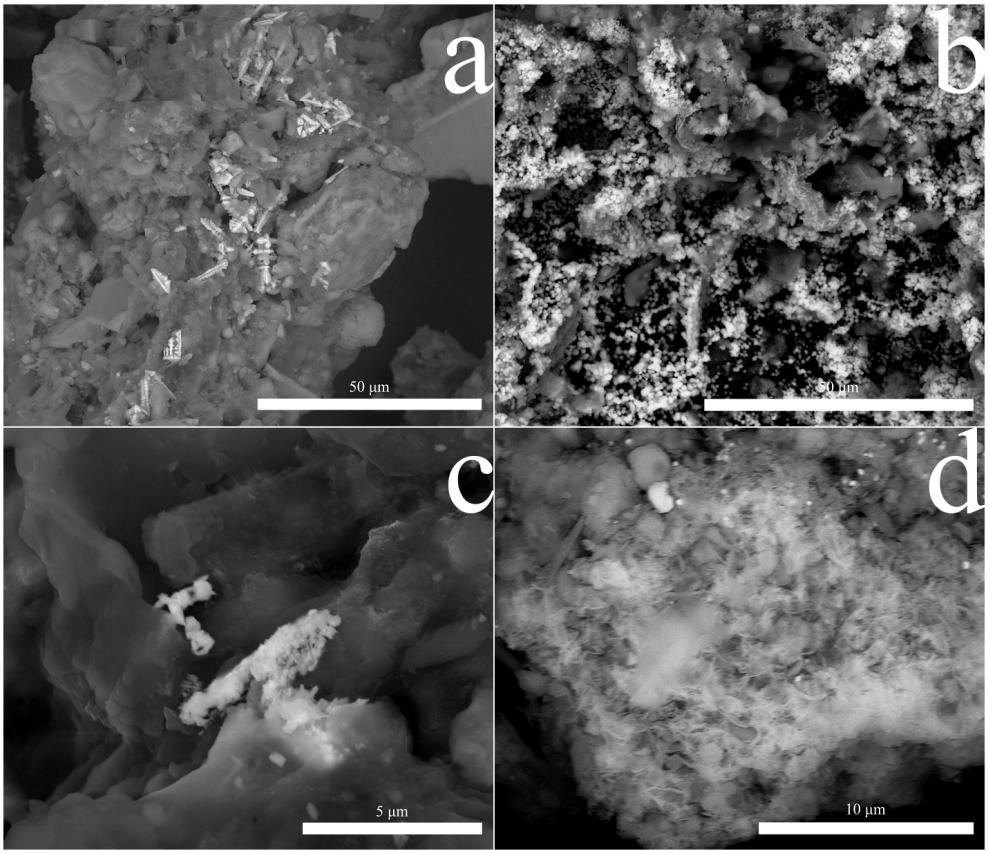


Figure 6. Representative SEM–BSE images of heavy metal carriers in the soils. (a) Fe-Zn oxides (franklinite), sample MS-01; (b) Zn sulphides, sample MS-07; (c) Pb sulphates, sample MS-02; (d) Fe (oxyhydr)oxides with Pb admixture, sample MS-09.

erals, mainly zinc sulfide. Due to geochemical similarity, cadmium often accompanies zinc in its minerals, both primary and secondary (Kabata-Pendias, Pendias 2001; Kabata-Pendias, Mukherjee 2007).

Analyzed soils revealed various losses on ignition at 550°C and generally low losses on ignition at 950°C, depending on the sample location (Fig. 1, Table 2). The samples collected in closer vicinity to sources of water represent higher values (over 20 wt%) of loss of ignition at 550°C than other samples. This is related to organic matter content since 550°C is the temperature where organic matter and hydrates (e.g. gypsum) decompose, however, analyzed samples contain a small amount of the hydrates. Slightly lower values of organic matter content in analyzed area were reported before (Nadgórska-Socha et al. 2013). The low values of loss on ignition at 950°C are a result of the low amount of clay minerals and carbonates in the soils. These observations were in agreement with the mineral composition of soils in this area reported previously (Kicińska 2019).

Examination of pH values before and after amendments, comparison of sorption efficiencies and SEM images indicate different immobilization mechanisms depending on soil additives. An important immobilization mechanism of the most effective additives is the formation of sparingly soluble phases (phosphates, hydroxides, carbonates and possibly secondary metal sulfides) and sorption.

In the case of phosphate fertilizer, the mechanism of immobilization is coupled dissolution-precipitation: dissolution of primary phases and precipitation of secondary phosphates (Kumpiene et al. 2019; Xu et al. 2021). The primary phases in the soils may have dissolved under acidic conditions, which is enhanced by the addition of ammonium-rich fertilizer. The dominant secondary forms are double phosphates, containing trace metal elements and other metals present in the system (Fig. 7a,b). Since it is hardly possible to precipitate secondary phosphates under alkaline conditions, the low pH of the reaction is responsible for the process (Grobelak et al. 2013; Vondráčková et al. 2017). The degree of metal immobilization is high. The secondary phases obtained after the addition of phosphate fertilizer are stable and therefore hardly soluble. However, the use of phosphate fertilizer can increase the amount of available forms of other metals, such as copper and iron, as well as arsenic, due to the geochemical similarity of phosphate to arsenate (Basta, McGowen 2004; Mains et al. 2006; Mendez, Meier 2008). In contrast to other contaminated sites (see e.g. Vondráčková et al. 2017), secondary cadmium phases were not observed here. This is probably due to the relatively low concentration of cadmium.

Immobilization of trace metals by limestone is associated with a distinct increase in soil pH. The resulting secondary phases are mainly hydroxides and carbonates containing those metals and calcium (Fig. 7c,d). Sulfides

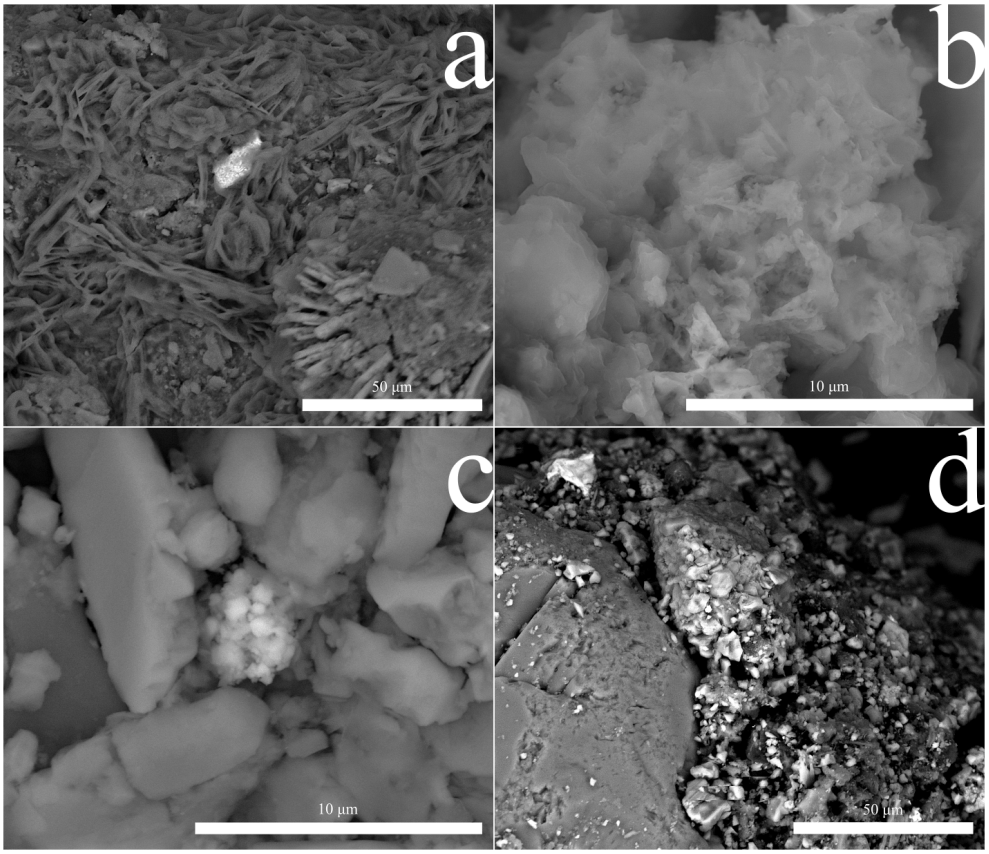


Figure 7. Examples of SEM–BSE images of metal carriers after the immobilization experiment. (a) Zn-Pb phosphates, sample MS-01, phosphate amendment; (b) Ca-Zn phosphates, sample MS-08, phosphate amendment; (c) Zn-Pb carbonate/hydroxide, sample MS-02, limestone amendment; (d) Pb hydroxide, quartz and calcite, sample MS-02, limestone amendment.

were also observed. The mobility of metals is significantly reduced. The effect of liming depends on the initial pH of the soil. In acidic soils, carbonates can increase the pH and thus reduce the mobility of trace elements (cf. e.g. Simon 2005; Houben et al. 2012; Xu et al. 2021), whereas in alkaline soils there is no effect of carbonate application on the soil pH and on the mobility of cadmium, zinc and lead (Vondráčková et al. 2013).

Bentonite had a weak effect on immobilization. The primary phases (zinc and lead sulfides) observed in the SEM images of the soils before the experiment are not transformed by this amendment. A slight increase in metal content in other phases was observed. The main immobilization mechanism occurring in this system is sorption (Mohammed-Azizi et al. 2013; Yu et al. 2017; Xu et al. 2021). Since sorption efficiency is lower at lower pH and bentonite had little effect on raising pH, the immobilization efficiency was also poor. At acidic pH, the negatively charged sorption sites of metal cations are reduced, by which the sorption efficiency at lower pH is usually lower (see e.g. Vítková et al. 2016; Liu et al. 2016).

Bog iron immobilized trace metals also mainly by sorption. This process is related to the presence of ferrihydrite and poorly-ordered goethite. These oxyhydroxides effectively bond metals through chemisorption (Pieczara, Rzepa 2016; Xiu et al. 2019; Song et al. 2021). No formation of secondary phases was observed for this additive. The sorption efficiency of bog iron is higher for Pb and lower for Zn and Cd (Rzepa et al. 2009). This is likely due to similar geochemical properties of Zn to Cd and slightly different properties of Pb. Lead in soils occurs in different forms than other trace metals. Bog iron is often recommended as a good immobilizer due to their low negative environmental impact (Dębiec et al. 2017).

Additives leading to the formation of new phases (limestone powder and phosphate fertilizers) were the most effective in immobilizing trace metals in the studied soils. However, in some cases, there may be some drawbacks to using these two most effective materials. Limestone powder is effective primarily in acidic soils but not necessarily in neutral and alkaline. On the other hand, the application of phosphate fertilizer requires simultaneous control of the mobility of other metals and arsenate. There is also a risk of overdosing this fertilizer and excess phosphorus and ammonium compounds getting into surface waters causing eutrophication.

In this paper, experiments were conducted with single additives. In this way, the effect of individual substances on the immobilization of trace metals was investigated. The next step should be to combine several potentially immobilizing additives to identify potential synergistic effects resulting in further efficiency improvements. For

example, it was found that the combination of sewage sludge, phosphate and lime in a certain proportion can result in a significant reduction of Zn, Pb and Cd leachability by $CaCl_2$ (Grobelak, Napora 2015).

5. Conclusions

Our study has shown that the immobilization of toxic trace elements in highly contaminated acidic soils using mineral additives might be effective but apparently depends on the properties of the applied additive. Four additives used in the study included limestone powder, phosphate fertilizer, bentonite and bog iron ore. They differed distinctly in both mineral and chemical composition as well as in the expected mechanism of metal immobilization. Limestone, composed chiefly of calcite, raises soil pH and favors the precipitation of metal hydroxides and/or carbonates. Application of phosphate fertilizer, containing mainly ammonium phosphate, results in the precipitation of hardly soluble metal phosphates. The dominant bentonite mineral composition is smectite, and therefore adsorption and ion exchange are the prominent processes of metal immobilization. Bog iron ore mineralogy is more complex, with dominant cryptocrystalline ferrihydrite and goethite, hence chemisorption onto iron oxyhydroxides is the major expected metal bonding mechanism.

The amendments which increased soil pH, i.e. limestone powder and phosphate fertilizer, have been proved to immobilize all the metals the most effectively. On the other hand, the application of bog iron and, especially, bentonite did not result in significant changes of initial soil pH and therefore was less effective, because of unfavorable conditions for cation adsorption.

These results were acquired in ex situ experiments in a laboratory. In order to fully evaluate the effectiveness of the proposed treatments it is necessary to perform field experiments in situ. The combined use of phosphate fertilizer and limestone powder should also be considered to prolong the action and slow down the leaching of possible excess phosphate to surface waters.

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Conflicts of interest

The authors have no conflicts of interest to declare.

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