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Original Research

Effect of Quick Lime and Dolomite Application on Mobility of Elements (Cd, Zn, Pb, As, Fe, and Mn) in Contaminated Soils

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Abstract

Weakly acidic Litavka and alkaline Malín soils are good examples of multi-contaminated soils in the Czech Republic. The aim of this study was to investigate the effects of different application rates of quick lime (lime) and dolomite on the mobility of cadmium, zinc, lead, arsenic, iron and manganese.

Additives were applied to soil samples at three rates and incubated for 7, 14, 28, and 42 days. Plant-available (extracted by $CaCl_2$) and acid-extractable (extracted by CH_3COOH) concentrations of elements were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). In alkaline soil, there was no effect of lime and dolomite application on concentrations of elements. In acid soil, there was a decrease in plant-available concentrations of Cd and Zn, no effect on plant-available Fe and Mn concentrations, and a slight increase in plant-available Pb and As concentrations after lime application. With the exception of a decrease in Pb and Mn concentrations, the same trends were observed for acid-extractable concentrations of elements. Dolomite application was less effective than lime application. The effect of dolomite on the immobilization of elements increased with increasing application rates. There was a weak effect of time during incubation on changes in concentrations of elements.

We concluded that high immobilization efficiency of alkaline additives on Cd and Zn can be recorded only on acid soils. Application of lime and dolomite is an ineffective measure to immobilize Pb and As in both acid or alkaline soils.

Keywords: alkaline additives, arsenic, cadmium, lead, plant-available and acid-extractable concentrations, zinc

Introduction

Excessive concentrations of trace elements in soils pose a significant health risk to humans, animals, and plants, as has been documented by many authors [1-3]. Unlike organic compounds, trace elements cannot be degraded, and the cleaning of soils usually requires their complete removal, or at least immobilization [4].

Many additives have been screened for their potential to immobilize heavy metals in soils [5]. Each of these additives has a different effect on the bioavailability of metals, micronutrient availability, soil pH, and soil microstructure [6]. Liming is the most widely used treatment, and can lead to the precipitation of metals as metal-carbonates and sig-

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nificantly decrease the exchangeable fraction of metals in contaminated soils [7]. Alkaline additives reduce heavy metal solubility in the soil by increasing soil pH and concomitantly increasing metal sorption to soil particles [3, 8]. Soil pH is one of the main parameters controlling the solubility and mobility of heavy metals in soils [9]. The available range of liming materials includes limestone ($CaCO_3$), quick lime (CaO), slaked lime [$Ca(OH)_2$], dolomite [$CaMg(CO_3)_2$], and slag ($CaSiO_3$), which vary in capacity for acid-neutralizing of a liming material [10]. The most effective is quick lime because of its high solubility and reactivity and its large effect on soil pH [11]. One of the possible mechanisms for the immobilization of heavy metals by soil additives such as limestone is enhanced metal adsorption through surface charge [10].

Bioavailability is a key factor for remediation technologies, and immobilization may be a preferred option [10]. The plant-available fraction represents the mobile portion of the trace elements that can easily be taken up by plants from the soil solution [12]. Extraction by $CaCl_2$ gives a fraction that is highly mobile in natural conditions [13]. The easily mobilizable fraction extracted by organic acids or chelates represents the portion of elements in soil that are bound on the surface of oxides and in organic matter [14]. The exchangeable and acid-extractable fractions (elements bound to carbonates) comprise elements adsorbed onto the surface of soil particles. The decrease in soil pH leads these to migrate from the solid phase to water and into plants [15].

The aim of this paper was to investigate the effect of quick lime and dolomite application on the immobilization of Cd, Zn, Pb, As, Fe, and Mn in weakly acidic and alkaline soils with regard to application rates and incubation days.

Experimental Procedures

Soil Samples Collection

Two heavily contaminated soils differing in physicochemical parameters were selected for the incubation experiment (Table 1). Weakly acidic soil, called "Litavka," was collected from the alluvium of the Litavka River in the village of Trhové Dušníky (60 km south of Prague). Litavka soil has been contaminated by Cd, Zn, and Pb due to waste from smelter settling pits [16]. Alkaline soil, called "Malín," was collected from a bank of Beránka stream near Malín village (close to the town of Kutná Hora, 82 km east of Prague). Malín soil is contaminated by As, Cd, and Zn due to the tailings of silver mining in the 13-16th centuries [17]. Soil samples were collected in March 2010 from topsoil in the layer at 0-20 cm depth, and were then air-dried at 20ºC, ground in a mortar, and passed through a 2 mm plastic sieve before establishment of the incubation experiment.

Table 1. Basic characteristics of soil collection sites and chemical properties of investigated soils. Mean values calculated from three replications (n=3) together with standard error of the mean (SE) are provided for each measured property. Cation exchange capacity (CEC) was analyzed only in mixed soil samples without any replication.

Soil property	Soil	
	Litavka (49º43'N, 14º0'E)	Malín (49º58'N, 15º17'E)
Altitude (m a.s.l.)	450	230
Mean annual temperature (ºC)	7.3	8.5
Mean annual precipitation (mm)	623	575
Soil texture	Clay loamy sand	Loam
Soil type	Fluvisol	Luvisol
pH_{CaCl_2}**	6.5±0.02	7.3±0.02
CEC ($mmol \cdot kg^{-1}$)	55	346
C_{org} (%)	3.6±0.1	2.7±0.1
Ca^a ($mg \cdot kg^{-1}$)**	1856±31	8914±98
Mg^a ($mg \cdot kg^{-1}$)**	160±5	354±5
K^a ($mg \cdot kg^{-1}$)*	192±8	234±4
P^a ($mg \cdot kg^{-1}$)**	9±0.3	56±3
Cd_{total} ($mg \cdot kg^{-1}$)**	53.8±0.9	11.3±0.2
Zn_{total} ($mg \cdot kg^{-1}$)**	6172±42	1022±18
Pb_{total} ($mg \cdot kg^{-1}$)**	3305±85	98±31
As_{total} ($mg \cdot kg^{-1}$)**	354±2	688±26
Fe_{total} ($mg \cdot kg^{-1}$)**	21193±146	17379±224
Mn_{total} ($mg \cdot kg^{-1}$)**	2688±16	371±4

^{a} – plant-available concentrations of nutrients determined by Mehlich III extraction procedure [20].

$_{total}$ – total concentrations of elements extracted by *Aqua Regia*. Legislation limits for total concentrations of elements in light-textured/other soils ($mg \cdot kg^{-1}$): Cd 0.4/1.0, Zn 130/200, Pb 100/140, As 30/30 [46]. Calculated by one-way ANOVA, differences between locations were either not statistically significant (n.s.), significant on the 0.05(*) probability level, or were significant on the 0.01 (**) probability level.

Design of the Incubation Experiment

The incubation experiment was established in the laboratory of the Department of Agroenvironmental Chemistry and Plant Nutrition in Prague in April 2010. The experiment comprised seven treatments for each soil, giving 14 treatments for both soils in total (C, control without any additive; L1, L2, and L3 treatments with application of quick lime; D1, D2, D3 treatments with the application of dolomite). Each treatment was replicated ten times and soils were incubated for 7, 14, 28, and 42 days; the experiment was therefore composed of 140 bottles for each incubation time and therefore a total of 560 bottles. We applied 50 g of dry soil to each acid-clean polyethylene 250 ml plastic bottle. In the L1, L2, L3, D1, D2, and D3 treatments, the soils were mixed with a specific amount

Table 2. Basic chemical characteristics of applied alkaline additives. Mean values together with standard error of the mean (SE) are provided in the case of the chemical properties of additives. Concentrations of Ca and Mg were provided by distributors of additives and therefore they were not analyzed. All analyzed concentrations and values of pH were performed in three replications (n=3).

Property	Quick lime [a] (L)	Dolomite [b] (D)
pH_{CaCl_2}**	12.0±0.01	8.3±0.02
Ca ($g\cdot kg^{-1}$)	686	220
Mg ($g\cdot kg^{-1}$)	0	100
Cd ($mg\cdot kg^{-1}$)	0	0.02±0.01
Zn ($mg\cdot kg^{-1}$)	0	0.7±0.2
Pb ($mg\cdot kg^{-1}$)	0	0.29±0.01
As ($mg\cdot kg^{-1}$)	0	1.2±0.3
Fe ($mg\cdot kg^{-1}$)	0	516±6
Mn ($mg\cdot kg^{-1}$)	0	69.4±0.5

[a] – analytical grade purity, distributor Lach-Ner Ltd., Czech Republic

[b] – distributor Agro CS SpA., Czech Republic

Legislation limits for total concentrations of elements in mineral calcareous and magnesium-calcareous fertilizers ($mg\cdot kg^{-1}$): Cd 1.5, Pb 30, As 20 [47]. Calculated by one-way ANOVA, differences between additives were either not statistically significant (n.s.), were significant on the 0.05(*) probability level, or were significant on the 0.01 (**) probability level.

of additive (see Table 2 for chemical properties of used additives and Table 3 for the quantity of elements applied by three rates for each additive). Deionized water at a volume equivalent to 60% of the maximum water holding capacity was then added to each bottle (18 ml for Litavka soil and 17 ml for Malín soil). The incubation was performed at a constant temperature of 25ºC. Bottles were opened and aerated by fresh air every week.

Chemical Analyses

The total element concentrations in investigated soils were determined using a microwave assisted wet digestion system: for details see [18]. A certified reference material RM 7004 Loam (Analytika, CZ) containing 1.52±0.15 mg $Cd\cdot kg^{-1}$, 227±7 mg $Zn\cdot kg^{-1}$, 93.4±3.4 mg $Pb\cdot kg^{-1}$, 49.6±2.9 mg $As\cdot kg^{-1}$, and 869±34 mg $Mn\cdot kg^{-1}$ was used for quality assurance of the analytical data used for determining total elements, and 1.45 mg $Cd\cdot kg^{-1}$, 232 mg $Zn\cdot kg^{-1}$, 96.1 mg $Pb\cdot kg^{-1}$, 51.2 mg $As\cdot kg^{-1}$, and 852 mg $Mn\cdot kg^{-1}$ were determined for this sample. The total content of element in the dolomite was determined using *Aqua Regia*. At days 7, 14, 28, and 42, plant-available and acid-extractable concentrations of elements in soils were determined. Soil samples were extracted using a 0.01 $mol\cdot L^{-1}$ $CaCl_2$ aqueous solution (plant-available concentrations) at a solid/liquid ratio of 1/2.4 (50 g+120 ml) for six hours, and with a 0.11 $mol\cdot L^{-1}$ aqueous solution of CH_3COOH (acid-extractable concentrations) at a solid/liquid ratio of 1/2.4 (50 g+120 ml) overnight. Hettich Universal 30 RF (Germany) equipment was used for centrifugation of the reaction mixtures at 3,000 rpm for 10 min. Supernatants were kept at laboratory temperature until measurement. Blank extracts representing 5% of the total number of extracts were prepared using the same batch of reagents and the same apparatus. Blank extracts were prepared and analyzed in the same way as soil extracts. All extracts were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) (VARIAN Vista Pro, Varian, Australia) and a standard edition procedure was used for evaluating the data. The concentration of organic carbon in soil was determined colorimetrically, according to Sims and Haby [19]. Available concentrations of nutrients were determined by the Mehlich III soil extraction procedure [20], using flame atomic absorption spectroscopy (FAAS, VARIAN SpectrAA-280, Australia) (for Ca, K, and Mg) and ICP-OES (for P). Soil and dolomite pH was measured in 1/5 (10 g+50 ml) and quick lime pH in 1/20 (10 g+200 ml) 0.01 $mol\cdot L^{-1}$ $CaCl_2$ at 20±1ºC. Cation exchange capacity (CEC)

Table 3. Amount of applied elements placed into experimental pots by three levels of applied quick lime (treatment abbreviations L1, L2, and L3) and dolomite (treatment abbreviations D1, D2, and D3).

Amount of applied elements	Treatment abbreviation (TA)					
	L1	L2	L3	D1	D2	D3
Ca ($g\cdot kg^{-1}$ soil)	15	30	60	15	30	60
Mg ($g\cdot kg^{-1}$ soil)	0	0	0	6.8	13.6	27.2
Cd ($mg\cdot kg^{-1}$ soil)	0	0	0	0.001	0.003	0.006
Zn ($mg\cdot kg^{-1}$ soil)	0	0	0	0.05	0.1	0.2
Pb ($mg\cdot kg^{-1}$ soil)	0	0	0	0.02	0.04	0.08
As ($mg\cdot kg^{-1}$ soil)	0	0	0	0.1	0.2	0.3
Fe ($mg\cdot kg^{-1}$ soil)	0	0	0	35.2	70.4	140.7
Mn ($mg\cdot kg^{-1}$ soil)	0	0	0	4.7	9.5	18.9

was calculated as the sum of Ca, Mg, K, Na, and Al extractables in 0.1 mol·L^{-1} $BaCl_2$ (w/v=1:20 for 2 hours) [21]. All used reagents were of electronic grade purity (Analytika, Ltd., CZ).

Data Analyses

All univariate analyses were performed using STATISTICA 9.0 software (StatSoft, Tulsa, OK, USA). A repeated measures ANOVA was applied to identify the effect of treatments, time, and their interactions. A one-way ANOVA followed by a post-hoc comparison Tukey test was used to identify significant differences between treatments for incubation time. We used ANOVA because data were sufficiently homogeneous within groups and with sufficient normality.

Results

As calculated by repeated measures ANOVA, plant-available Cd, Zn, As, and Mn and acid-extractable Cd, Zn, As, Fe, and Mn concentrations were significantly affected by treatment ($p<0.002$), time ($p<0.001$), and by treatment × time interaction ($p<0.004$) in both soils. Plant-available Pb concentrations were significantly affected by treatment ($p<0.001$) and treatment × time interaction ($p<0.001$) only in Litavka soil, and plant-available Fe concentrations by treatment × time interaction ($p<0.001$). Acid-extractable Pb concentrations were only significantly affected by treatment ($p<0.001$) in Litavka soil.

Concentrations of Elements in Used Soils

Total concentrations of Cd, Zn and As in soils considerably exceeded the Czech legislation limits (Table 1). Total Pb concentrations were close to the legislative limit in Malín soil and exceeded the limit by thirty-three times in Litavka soil. Total concentrations of Cd, Pb, and As in dolomite did not exceed the Czech legislative limits for fertilizers (Table 2).

Soil pH

Individual soil additives resulted in varying changes in soil pH (Fig. 1a and b). Dolomite did not affect the soil pH, which was 6.9 and 7.3 in Litavka and Malín soils, respectively. Application of lime rapidly and considerably increased the pH values to 12.3 and 12.0 in Litavka and Malín soils, respectively. The pH values were stable during the incubation period, with no effect resulting from different application rates of the additives.

Cadmium

In comparison to the control, lime application substantially and permanently decreased mobility of Cd in Litavka soil (Fig. 2a) but only slightly in Malín soil (Fig. 2b). In Malín soil, there was a substantial decrease in plant-available Cd concentrations in the control at the end of the experiment.

The effect of dolomite on plant-available Cd concentrations was not as marked as in the case of lime. In Litavka soil, a slightly significant decrease in concentrations of plant-available Cd was recorded after dolomite application (Fig. 2a) in comparison to the control, and the concentrations were only slightly affected by the application rate of dolomite. In Malín soil, the decrease in plant-available concentrations of Cd in dolomite treatments (Fig. 2b) was the same as that in the control.

In comparison to the control, lime application substantially and permanently decreased concentrations of acid-extractable Cd in Litavka soil (Fig. 2c). In Malín soil, lime application also permanently decreased concentrations of acid-extractable Cd (Fig. 2d) but, in the control, there was a decrease in acid-extractable Cd concentrations as measured on the 28th day of the experiment, though later the Cd concentrations again increased.

The effect of dolomite application on concentrations of acid-extractable Cd was not as marked as in the case of lime. In Litavka soil, there was only found to be a minimal effect of dolomite on concentrations of acid-extractable Cd (Fig. 2c). In Malín soil, there was no decrease in acid-extractable Cd concentrations in dolomite treatments

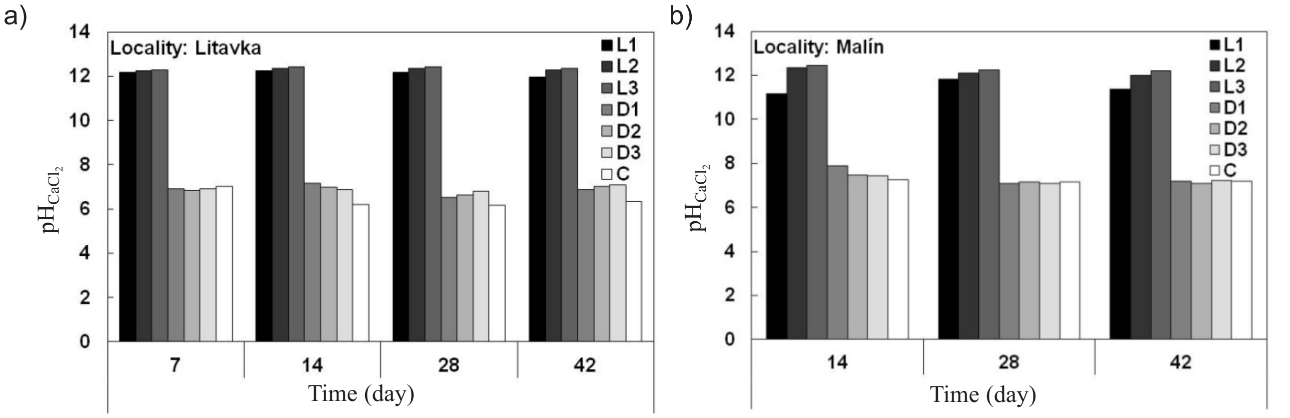

Fig. 1. Effect of treatment on pH_{CaCl_2} in (a) Litavka and (b) Malín soils. Treatment abbreviations are given in Table 3. Values of pH were analyzed only in mixed soil samples without any replication.

(Fig. 2d) up to the 14th day of the experiment. Later, as measured on the 28th day, there was a decrease in Cd concentrations in the D3 treatment and in the control. On the 42nd (last) day of the experiment, an increase in Cd concentrations was recorded in the control, but there were very low concentrations in all dolomite treatments.

Zinc

In comparison to the control, lime application substantially and permanently decreased mobility of Zn in Litavka soil (Fig. 3a). In Malín soil, a decrease in plant-available Zn concentrations after lime application (Fig. 3b) was recorded on the 7th and 14th days of the experiment, but later there was found to be no effect of lime application on plant-available Zn concentrations, which were not significantly different from the control.

The effect of dolomite on concentrations of plant-available Zn was not as marked as was the case for lime. In Litavka soil, a slightly significant decrease in concentrations of plant-available Zn was recorded after dolomite application (Fig. 3a), and the Zn concentration was significantly though slightly affected by the application rate of dolomite. In Malín soil, changes in plant-available concentrations of Zn in dolomite treatments (Fig. 3b) were the same as changes in the control, and therefore there was no effect from dolomite applications on plant-available Zn concentrations.

In comparison to the control, lime application substantially and permanently decreased concentrations of acid-extractable Zn in Litavka and Malín soils (Figs. 3c and d). In Malín soil, on the 28th day a decrease in acid-extractable concentrations of Zn was recorded, as well as in the control. There were therefore no significant differences in Zn concentrations between lime treatments and control.

The effect of dolomite application on concentrations of acid-extractable Zn (Figs. 3c and d) was very similar to the case for Cd.

Lead

In comparison to the control, lime application substantially and permanently increased plant-available concentrations of Pb in Litavka soil (Fig. 4a), and Pb concentrations were only slightly affected by the lime application rate. In Malín soil, concentrations of plant-available Pb were the same in lime treatments (Fig. 4b) as they were in the control, and slightly decreased during the experiment.

There was no effect of dolomite application on plant-available concentrations of Pb in Litavka and Malín soils (Figs. 4a and b), as plant-available concentrations of Pb were found to be the same as in the control.

In comparison to the control, lime application substantially and permanently decreased concentrations of acid-extractable Pb in Litavka soil (Fig. 4c). With the exception of the 14th day of the L1 treatment for Malín soil, concen-

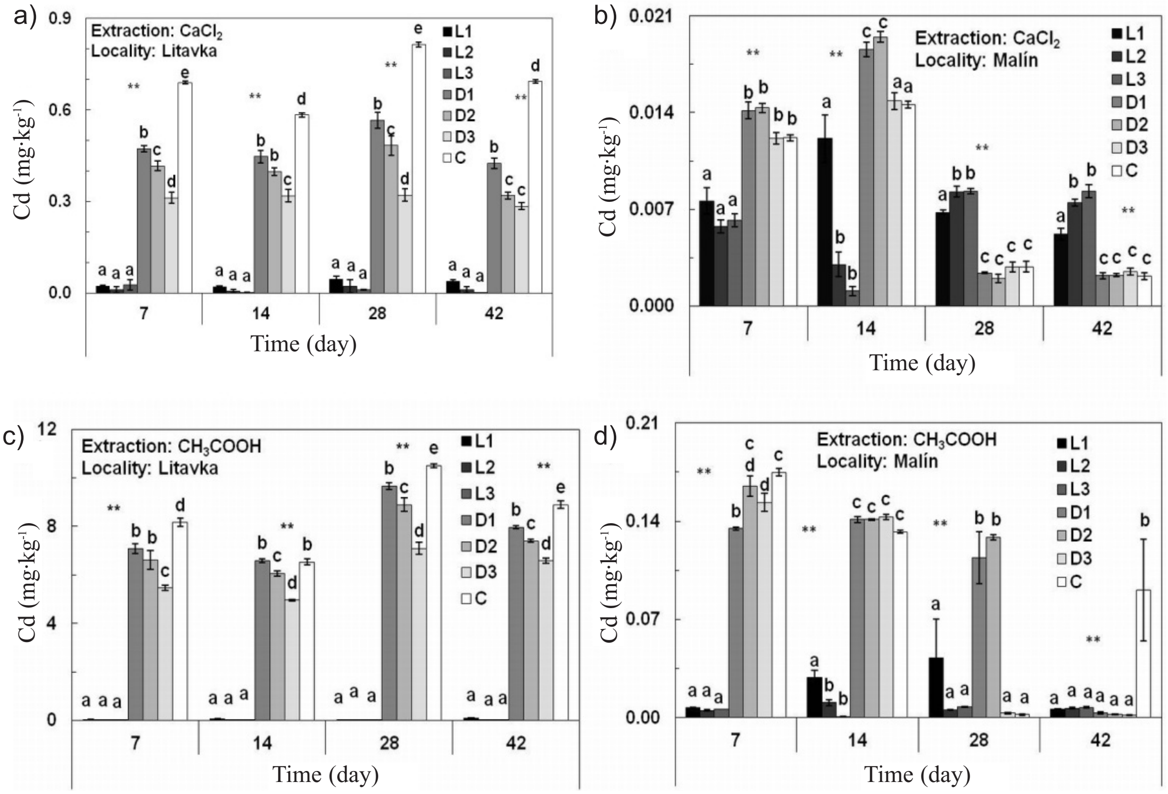

Fig. 2. Effect of treatment on mean concentrations of plant-available Cd (a, b) and acid-extractable Cd (c, d) in Litavka and Malín soils. Treatment abbreviations are given in Table 3. Error lines represent standard error of the mean (SE). Calculated by one-way ANOVA, differences between treatments either were not statistically significant (n.s.), were significant on the 0.05(*) probability level, or were significant on the 0.01 (**) probability level.

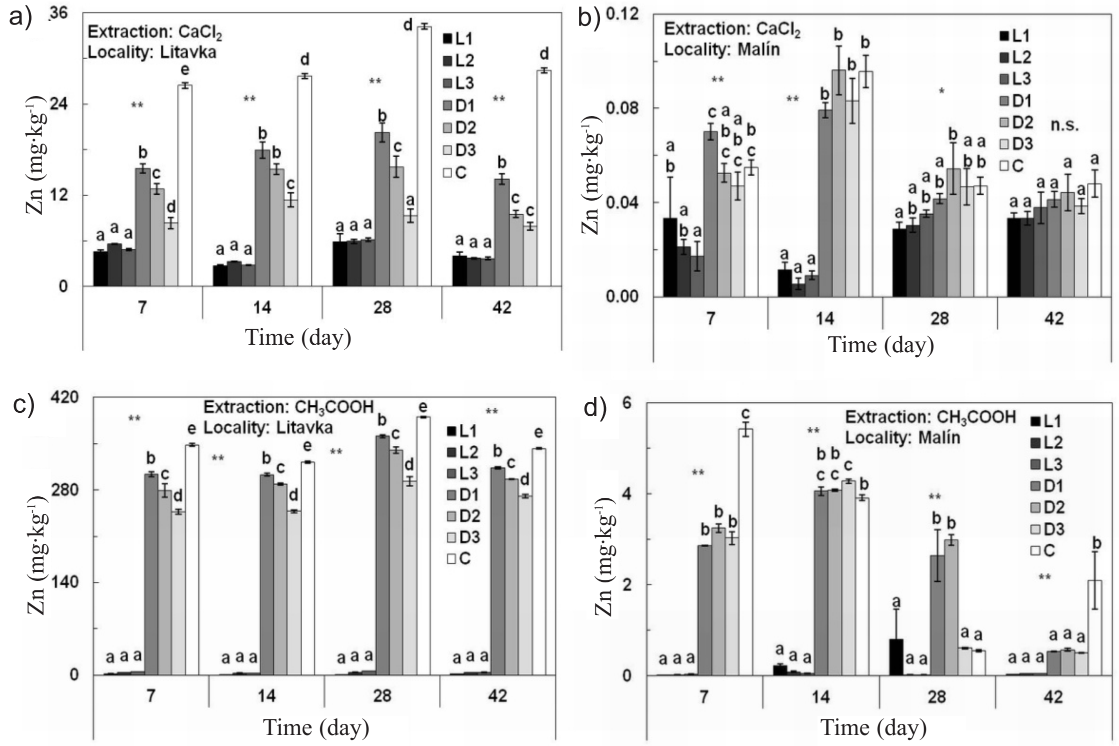

Fig. 3. Effect of treatment on mean concentrations of plant-available Zn (a, b) and acid-extractable Zn (c, d) in Litavka and Malín soils. Treatment abbreviations are given in Table 3. Error lines represent standard error of the mean (SE). Calculated by one-way ANOVA, differences between treatments were either not statistically significant (n.s.), were significant on the 0.05(*) probability level, or were significant on the 0.01 (**) probability level.

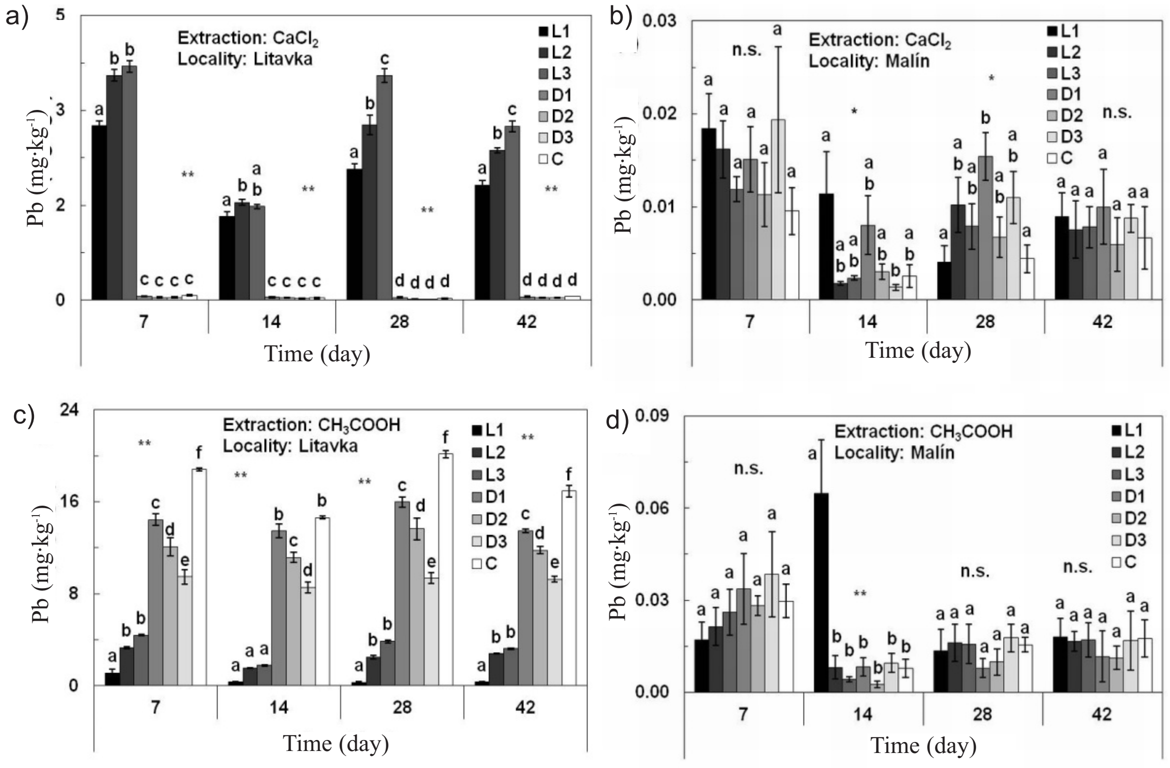

Fig. 4. Effect of treatment on mean concentrations of plant-available Pb (a, b) and acid-extractable Pb (c, d) in Litavka and Malín soils. Treatment abbreviations are given in Table 3. Error lines represent standard error of the mean (SE). Calculated by one-way ANOVA, differences between treatments were either not statistically significant (n.s.), were significant on the 0.05(*) probability level, or were significant on the 0.01 (**) probability level.

trations of acid-extractable Pb in lime treatments (Fig. 4d) were the same as in the control.

The effect of dolomite on acid-extractable Pb concentrations was recorded only in Litavka soil, where a slight decrease in Pb concentrations was recorded (Fig. 4c), dependent on the application rate of dolomite. In Malín soil, the decrease in acid-extractable concentrations of Pb in dolomite treatments (Fig. 4d) was the same as that for the control, and therefore there was no effect of dolomite application on acid-extractable Pb concentrations.

Arsenic

In comparison to the control, lime application increased concentrations of plant-available As in Litavka soil (Fig. 5a), and As concentrations were affected by the application rate of lime. In Malín soil, the concentration of plant-available As in lime treatments (Fig. 5b) was the same as in the control, with the exception of a high increase for the L1 treatment on the 14th and 42nd days of the experiment.

There was no effect of dolomite application on plant-available concentrations of As in either soil (Figs. 5a and b).

In both soils, there were minimal differences between concentrations of plant-available and acid-extractable As in comparison to other elements.

In comparison to the control, lime application permanently increased acid-extractable concentrations of As in Litavka soil (Fig. 5c), and As concentrations were only slightly affected by the lime application rate. In Malín soil, the decrease in acid-extractable concentrations of As in lime treatments (Fig. 5d) was similar to the decrease found in the control.

There was no effect of dolomite application on acid-extractable concentrations of As in Litavka soil (Fig. 5c), and only a slight effect in the Malín soil (Fig. 5d). In Malín soil, the effect of dolomite application on concentrations of acid-extractable As was similar to that for Cd and Zn.

Iron

In Litavka soil, a decrease in plant-available concentrations of Fe in lime treatments (Fig. 6a) was the same as the decrease in the control, with the exception of an increase in all L1 treatments. In Malín soil, the increase in plant-available concentrations of Fe in lime treatments (Fig. 6b) was the same as that for the control.

In Litavka and Malín soils, concentrations of plant-available Fe in dolomite treatments (Fig. 6a and b) was the same as in the control; therefore there was no effect of dolomite application on plant-available Fe concentrations.

In Litavka soil, the concentration of acid-extractable Fe in lime treatments (Fig. 6c) was the same as that for the control, with the exception of a high increase in the L1 treatment in Litavka soil on the 14th, 28th, and 42nd days. In Malín soil, concentrations of acid-extractable Fe in lime treatments (Fig. 6d) were the same as in the control, in that they increased on the 14th day and then substantially decreased.

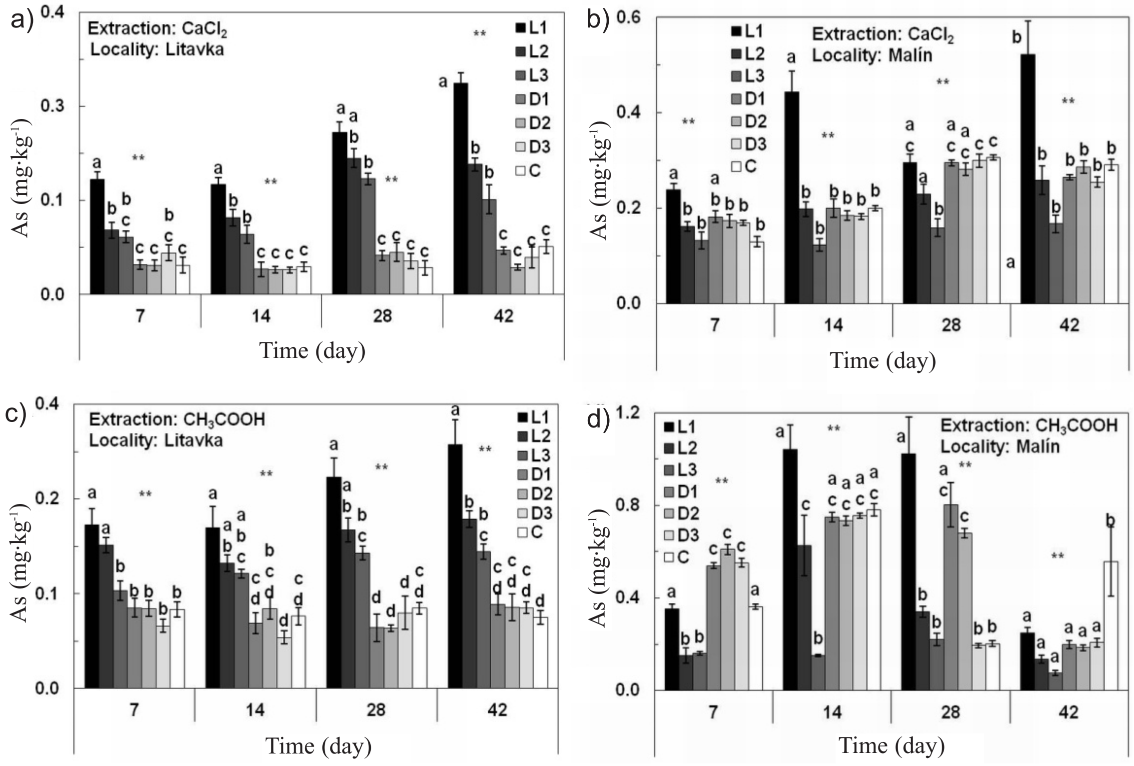

Fig. 5. Effect of treatment on mean concentrations of plant-available As (a, b) and acid-extractable As (c, d) in Litavka and Malín soils. Treatment abbreviations are given in Table 3. Error lines represent standard error of the mean (SE). Calculated by one-way ANOVA, differences between treatments were either not statistically significant (n.s.), were significant on the 0.05(*) probability level, or were significant on the 0.01 (**) probability level.

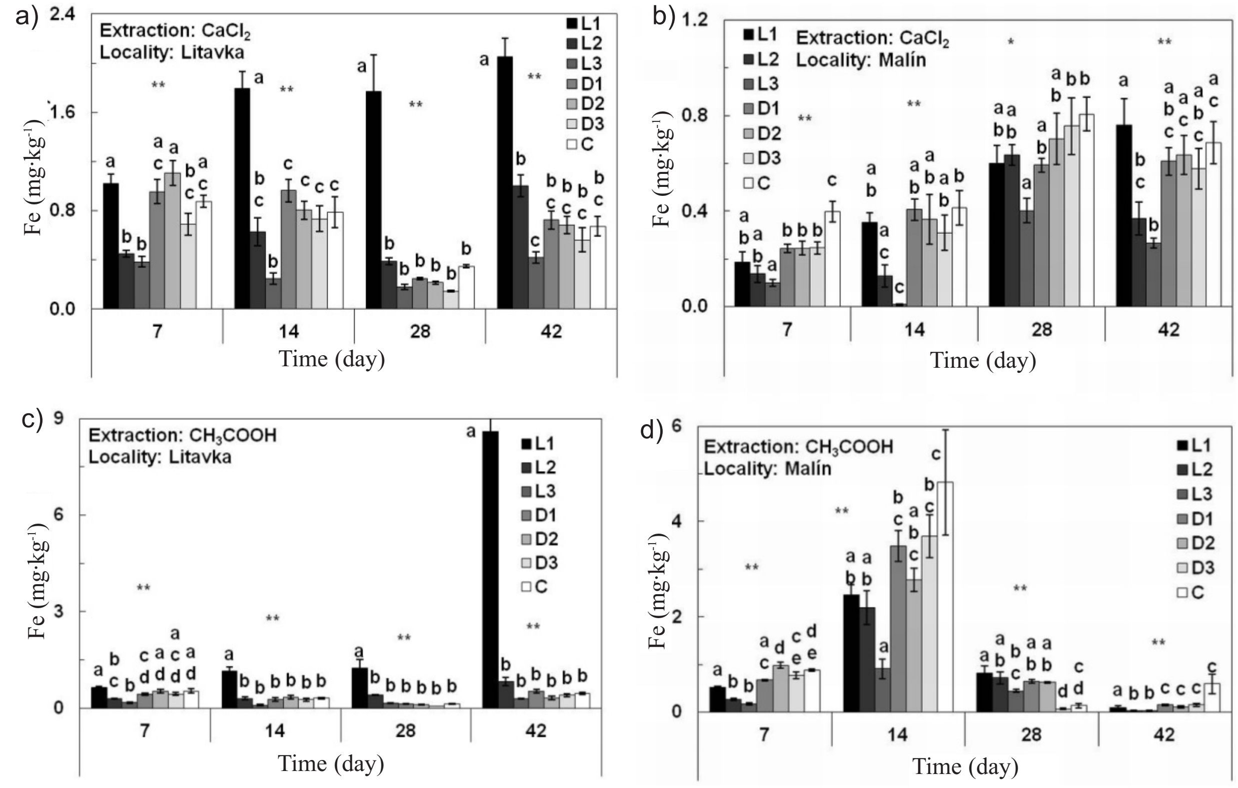

Fig. 6. Effect of treatment on mean concentrations of plant-available Fe (a, b) and acid-extractable Fe (c, d) in Litavka and Malín soils. Treatment abbreviations are given in Table 3. Error lines represent standard error of the mean (SE). Calculated by one-way ANOVA, differences between treatments were either not statistically significant (n.s.), were significant on the 0.05(*) probability level, or were significant on the 0.01 (**) probability level.

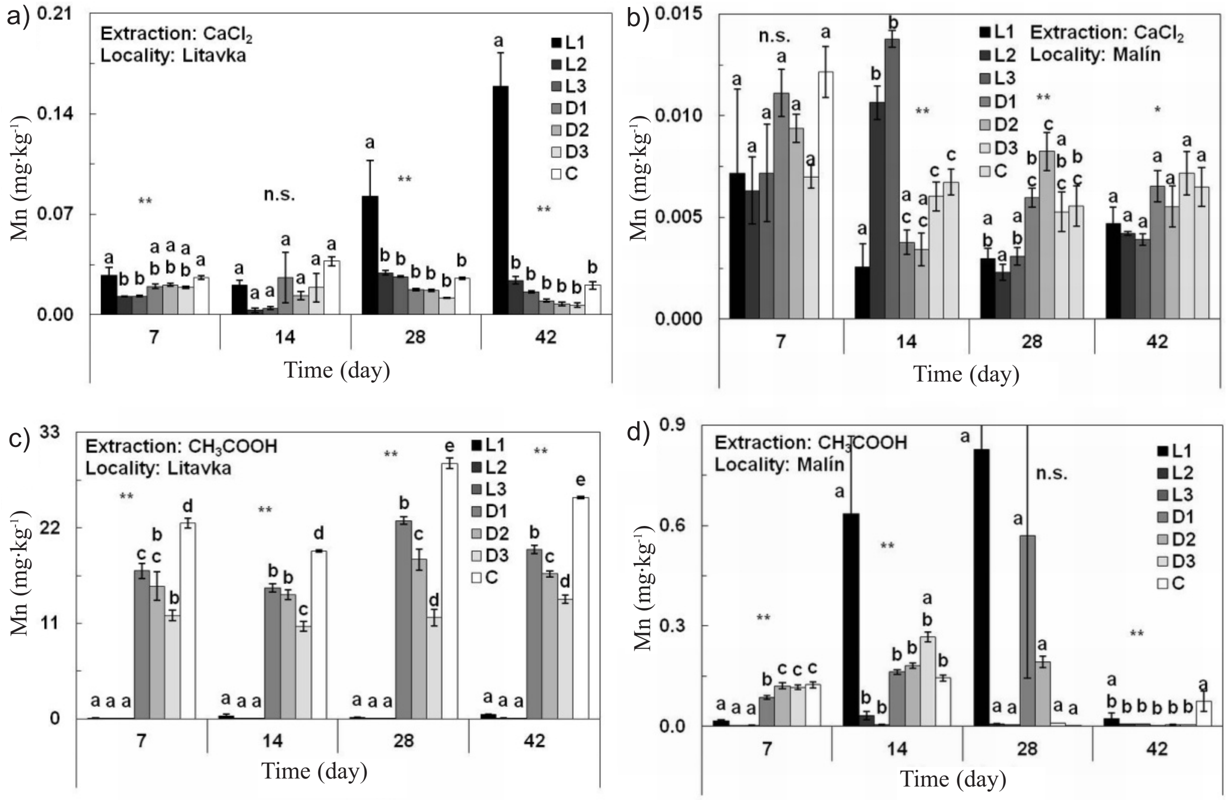

Fig. 7. Effect of treatment on mean concentrations of plant-available Mn (a, b) and acid-extractable Mn (c, d) in Litavka and Malín soils. Treatment abbreviations are given in Table 3. Error lines represent standard error of the mean (SE). Calculated by one-way ANOVA, differences between treatments were either not statistically significant (n.s.), were significant on the 0.05(*) probability level, or were significant on the 0.01 (**) probability level.

In both soils, concentrations of acid-extractable Fe in dolomite treatments (Fig. 6c and d) were the same as in the control.

Manganese

In Litavka soil, with the exception of an increase for the L1 treatment on the 28th and 42nd days, concentrations of plant-available Mn in lime treatments (Fig. 7a) and in the control remained stable during the experiment. In Malín soil, with the exception of an increase in the L2 and L3 treatments recorded on the 14th day, concentrations of plant-available Mn in lime treatments (Fig. 7b) and in the control remained stable.

There was no effect of dolomite application on plant-available concentrations of Mn in either soil (Fig. 7a and b).

In comparison to the control, lime application substantially and permanently decreased concentrations of acid-extractable Mn in Litavka soil (Fig. 7c). In Malín soil, with the exception of an increase for the L1 treatment on the 14th and the 28th days, the decrease in acid-extractable concentrations of Mn in lime treatments (Fig. 7d) was the same as the decrease in the control.

There was only a slight effect of dolomite application on concentrations of acid-extractable Mn. In Litavka soil, a slight decrease in Mn concentrations was recorded after dolomite application (Fig. 7c). In Malín soil, the recorded decrease in acid-extractable concentrations of Mn in dolomite treatments (Fig. 7d) was the same as that for the control. No effect of dolomite application on acid-extractable Mn concentrations was therefore found.

Discussion of Results

Soil pH

There was a high and immediate effect of lime but no effect of dolomite application on the pH value of the soils, although the amount of Ca supplied by both additives was the same. This result was because of the different anion form found in each of the additives. Calcium in lime is bound in an oxide form, whereas in dolomite it is in a carbonate form [22]. Anion form plays an important role in additive solubility. The carbonate form is characterized by poor solubility, while the oxide form is highly soluble [22, 23]. The addition of lime to moist soil created strongly alkaline slaked lime, which highly increased soil pH. The addition of dolomite does not usually increase soil pH above 7 [24]. Soil pH also was connected with the different buffering capacities of the soils. Buffering capacity is positively related to cation exchange capacity. In the Malín soil, there was a value of cation exchange capacity that was six times higher than for the Litavka soil, and a similar content of organic C. Therefore, Malín soil is characterized by a higher buffering capacity than Litavka soil. This is clear from the different pH value of the L1 treatment in both soils. The amount of applied Ca was very high in L2 and L3 treatments, and therefore the differences in buffering capacity between soils were not sufficiently high to affect soil pH, which was 12 in both soils.

Cadmium

In Litavka soil, the mean plant-available Cd concentration in the control was 0.7 mg·kg^{-1}, but in Malín soil, plant-available Cd concentrations were about one order lower. In Europe, plant-available Cd concentrations in common agricultural soils with low total Cd concentrations are up to 0.05 mg·kg^{-1} [25, 26]. Therefore, in Litavka soil, plant-available Cd concentrations without any additive were about one order higher than in common agricultural soils.

Plant-available Cd concentrations were about one order lower than acid-extractable Cd concentrations, in both soils. This was driven by the different leaching capacity of the used extractants. Calcium chloride is a mild extractant and behaves like an enhanced soil solution [27]. Weak acetic acid is a stronger extractant and is able to release a proportion of the elements bound onto a soil sorption complex [28] and carbonate-bound fractions. Another driver is the low pH of acetic acid, as the mobility of Cd is especially high under conditions of low soil pH [11, 27]. In Malín soil, plant-available Cd concentrations were very low, approaching the detection limit. This was probably because of the low mobility of Cd, due to the high pH value and high carbonate content of the soil [17].

Lime application decreased plant-available Cd concentrations substantially and constantly in Litavka soil. This was connected with a high increase in soil pH after lime application, as has also been recorded by other authors [22, 29-31]. The lack of any effect of lime application rates suggests that a decrease in Cd mobility can also be recorded under lower lime application rates than were tested in this study. Therefore, to detect minimal effective lime application rates, any future study must be designed with substantially lower lime application rates.

In Malín soil, there were minimal changes in plant-available Cd concentrations after lime application. This was because of an initially high pH value and the high Ca status of the control soil. At the end of the experiment, there was a slight increase in plant-available Cd concentrations in all treatments to which lime was applied. This was probably because of the presence of dissolved organic C that could minimize adsorption of Cd onto solid phases [32]. Although there was a minimal effect of lime application on Cd mobility, initial concentrations of plant-available Cd were very low and it was not necessary to decrease them further. We can therefore conclude that lime application decreases Cd mobility considerably, especially on acid soils, as has been recorded by other authors [11, 33, 34].

Dolomite application slightly decreased plant-available Cd concentrations in Litavka soil. This was probably because carbonates created with Cd^{2+} precipitate $CdCO_3$ [32]. There was a decrease of plant-available Cd concentrations with the application rate of dolomite, and therefore a future study must be designed with higher dolomite application rates so as to detect a maximal possible decrease of plant-available Cd concentrations after dolomite application.

In Malín soil, there was no effect of dolomite application on plant-available Cd concentrations. This was because of an initially high pH value in the control soil, and there was no increase in soil pH after dolomite application. Therefore, we can recommend dolomite application only on acidic soils, especially at higher application rates. This conclusion is in agreement with other authors [11, 33, 34].

Zinc

In Litavka soil, the mean plant-available Zn concentration in the control was 29 mg·kg^{-1}, but in Malín soil plant-available Zn concentrations were about three orders lower. In Europe, plant-available Zn concentrations in common agricultural soils with low total Zn concentrations are up to 0.2 mg·kg^{-1} [25, 26]. Therefore, in Litavka soil, plant-available Zn concentrations were, without any additive, about two orders higher than in common agricultural soils.

Plant-available Zn concentrations were about one order lower than acid-extractable Zn concentrations in Litavka soil and about two orders lower than acid-extractable Zn concentrations in Malín soil, as was also recorded by Száková et al. [11].

The effect of lime and dolomite applications to decrease plant-available Zn concentrations in both soils was the same as found for plant-available Cd concentrations. This was due to the similar chemical properties of Cd and Zn [35]. We can therefore conclude that the practical use of lime and dolomite applications follows the same rules as for Cd and Zn.

Lead

In Litavka soil, the mean plant-available Pb concentration in the control was 0.05 mg·kg^{-1}, but in Malín soil, plant-available Pb concentrations were about three orders lower. In Europe, plant-available Pb concentrations in common agricultural soils with low total Pb concentrations are up to 0.2 mg·kg^{-1} [25, 26]. Therefore, in Litavka soil, plant-available Pb concentrations were, without any additive, about one order lower than in common agricultural soils.

Plant-available Pb concentrations were about one order lower than acid-extractable Pb concentrations in Litavka soil. In Malín soil, plant-available and acid-extractable Pb concentrations were similar.

Lime application increased plant-available Pb concentrations in Litavka soil. This was connected to the release of Pb from soil organic matter after lime application, because Pb is bound especially to organic matter [13, 36]. Dissolved organic matter after lime application released Pb, which then formed complexes with hydroxides. These soluble hydroxide complexes are formed in highly alkaline conditions at pH > 12, as has also been recorded by other authors [32].

In Malín soil, lime application had no effect on plant-available Pb concentrations. This was connected to an initial high soil pH and the generally low mobility of Pb. Therefore, we can conclude that lime application is not suitable for decreasing the mobility of Pb on acid soils.

In both soils, dolomite application had no effect on plant-available Pb concentrations. We can therefore conclude that the application of dolomite is not a suitable measure to impact the mobility of Pb on soils with different pH values.

Lime application decreased acid-extractable Pb concentrations in Litavka soil. This was probably because of the occurrence of Pb in insoluble forms in alkaline soil conditions [37]. Therefore, we can conclude that lime application is effective in decreasing acid-extractable Pb concentrations in acid soils with weak soil sorption. This conclusion is in agreement with Friesl-Hanl et al. [38].

The lack of any effect of lime application on acid-extractable Pb concentrations in Malín soil was the same as was the case for plant-available Pb concentrations.

In Litavka soil, there was a significant decrease in acid-extractable Pb concentrations after dolomite application. This was probably because of $PbCO_3$ formation [39]. The slight effect of dolomite application rates indicates that the decrease in Pb mobility is connected to the higher adsorption capacity for Pb in $CaCO_3$-rich soils [39]. Therefore, a future study must be designed with substantially higher dolomite application rates in order to detect the most effective dolomite application rates. We can therefore conclude that dolomite application is suitable for decreasing acid-extractable Pb concentrations in acid soils at higher application rates.

The lack of any effect of dolomite application on acid-extractable Pb concentrations in Malín soil was the same as was the case for plant-available Pb concentrations. Therefore, we concluded that dolomite and lime application is not a suitable method to immobilize Pb in alkaline soil.

Arsenic

In Litavka soil, the mean plant-available As concentrations in the control was 0.05 mg·kg^{-1} and plant-available As concentrations were similar in Malín soil. In Europe, plant-available As concentrations in common agricultural soils with low total As concentrations are up to 0.3 mg·kg^{-1} [25, 26]. Therefore, in Litavka soil, plant-available As concentrations were, without any additive, similar or approximately one order lower than in common agricultural soils.

Plant-available As concentrations were similar to acid-extractable As concentrations in both soils.

Lime application slightly increased plant-available As concentrations in Litavka soil. This was probably connected with the formation of mobile arsenite, which is typical for alkaline soils, as has been recorded by other authors [11, 25, 40].

There were minimal changes in plant-available As concentrations after lime application in Malín soil. A similar trend was recorded by Hartley et al. [41]. This was probably because of the initially high pH value of the control soil. Mobile arsenite was therefore already dominant in the soil before lime application. In both soils, lime application rate slightly affected plant-available As concentrations. The high amount of applied Ca in the soil was probably precipitated as As-Ca complexes, $CaHAsO_4$ and $Ca_3(AsO_4)_2$, as has been recorded by other authors [42, 43].

In both soils, there was no effect of dolomite application on plant-available As concentrations and this is in accordance with the results of Hartley et al. [41]. This was probably because dolomite had no effect on soil pH and therefore no effect on the change of As species in the soil.

We can conclude that lime and dolomite applications are not a suitable measure to immobilize As, either in acid or in alkaline soils. This conclusion is in agreement with Száková et al. [11].

Iron

In Litavka soil, the mean plant-available Fe concentration in the control was 0.4 mg·kg^{-1} and, in Malín soil, plant-available Fe concentrations were similar. In Europe, plant-available Fe concentrations in common agricultural soils are up to 6 mg·kg^{-1} [25]. Therefore, in Litavka soil, plant-available Fe concentrations were, without any additive, approximately one order lower than in common agricultural soils.

Plant-available Fe concentrations were approximately one order lower than acid-extractable Fe concentrations in both soils.

In Litavka soil, there was a minimal effect of lime application on plant-available Fe concentrations. The reason for discrepancies in plant-available Fe concentrations in L1 treatment requires further research.

In Malín soil, there was no effect of lime application on plant-available Fe concentrations.

In both soils, there was no effect of dolomite application on plant-available Fe concentrations. This was because of the high soil pH in which metals are generally, with few exceptions, less soluble than in acid soil [44].

Manganese

In Litavka soil, the mean plant-available Mn concentration in the control was 0.03 mg·kg^{-1} but, in Malín soil, plant-available Mn concentrations were approximately one order lower. In Europe, plant-available Mn concentrations in common agricultural soils are up to 5 mg·kg^{-1} [25, 26], and therefore in Litavka soil, plant-available Mn concentrations were, without any additive, approximately two orders lower than in common agricultural soils.

Plant-available Mn concentrations were approximately three orders lower than acid-extractable Mn concentrations in both soils.

In both soils, there was in most cases no effect of lime and dolomite application on plant-available Mn concentrations. This was because of high soil pH under which the mobility of Mn is generally low [44].

Lime application substantially and permanently decreased acid-extractable Mn concentrations in Litavka soil. In Malín soil, there was no clear effect of lime application on acid-extractable Mn concentrations.

We can conclude that lime application is suitable as a method for decreasing acid-extractable Mn concentrations in acid soils.

Dolomite application slightly decreased acid-extractable Mn concentrations in Litavka soil. This can be explained by Mn chemisorptions on $CaCO_3$ and following the precipitation of $MnCO_3$, as has been recorded by other authors [32, 45]. There was a slight effect of dolomite application rates, indicating that the decrease in Mn mobility is probably connected with the amount of carbonate in soils.

In Malín soil, there was no effect of dolomite application on acid-extractable Mn concentrations. We can therefore conclude that dolomite application slightly immobilized the Mn in acid soil, but that there was no effect in alkaline soils.

Conclusions

The incubation experiment provides clear evidence of the different efficiency of lime and dolomite application on immobilization of elements in contaminated soils with different soil pH and sorption properties. Lime application is an effective measure to immobilize Cd and Zn only in acid soils. On the other hand, lime application is an ineffective measure for immobilizing Pb and As, either in acid or in neutral soils. Dolomite application is a suitable measure to immobilize Cd and Zn in acid soils, but with higher application rates than lime. Dolomite application is an ineffective measure for immobilizing Pb and As, either in acid or in neutral soils. It can be concluded that application rate plays a significant role, especially in the case of the less effective dolomite. During incubation, there was a weak effect of time on immobilization of the various elements.

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References

1. ALKORTA I., BECERRIL J.M., GARBISU C. Phytostabilization of metal contaminated soils. Rev. Environ. Health. **25**, 135, **2010**.
2. DO NASCIMENTO C.W.A., XING B. Phytoextraction: a review on enhanced metal availability and plant accumulation. Sci. Agric. **63**, 299, **2006**.
3. PUSCHENREITER M., HORAK O., FRIESL W., HARTL W. Low-cost agricultural measures to reduce heavy metal transfer into the food chain – a review. Plant Soil Environ. **51**, 1, **2005**.
4. KUMPIENE J., LAGERKVIST A., MAURICE C. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments - A review. Waste Manage. **28**, 215, **2008**.
5. MISRA V., TIWARI A., SHUKLA B., SETH C.S. Effects of soil amendments on the bioavailability of heavy metals from zinc mine tailings. Environ. Monit. Assess. **155**, 467, **2009**.

6. LOMBI E., HAMON R.E., MCGRATH S.P., MCLAUGHLIN M.J. Lability of Cd, Cu and Zn in polluted soils treated with lime, beringite, and red mud and identification of a non-labile colloidal fraction of metals using isotopic techniques. Environ. Sci. Technol. **37**, 979, **2003**.
7. LEE T.-M., LAI H.-Y., CHEN Z.-S. Effect of chemical amendments on the concentration of cadmium and lead in long-term contaminated soils. Chemosphere **57**, 1459, **2004**.
8. MCBRIDE M., SAUVÉ S., HENDERSHOT W. Solubility control of Cu, Zn, Cd, and Pb in contaminated soils. Eur. J. Soil Sci. **48**, 337, **1997**.
9. BURGOS P., MADEJÓN E., PÉREZ-DE-MORA A., CABRERA F. Spatial variability of the chemical characteristics of a trace-element-contaminated soil before and after remediation. Geoderma **130**, 157, **2006**.
10. BOLAN N.S., DURAISAMY V.P. Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies. Aust. J. Soil Res. **41**, 533, **2003**.
11. SZÁKOVÁ J., TLUSTOŠ P., PAVLÍKOVÁ D., HANČ A., BATYSTA M. Effect of addition of ameliorative materials on the distribution of As, Cd, Pb, and Zn in extractable soil fractions. Chem. Pap. **61**, 276, **2007**.
12. MORAL R., GILKES R.J., MORENO-CASELLES J. A comparison of extractants for heavy metals in contaminated soils from Spain. Comm. Soil Sci. Plant Anal. **33**, 2781, **2002**.
13. YOBOUET Y.A., ADOUBY K., TROKOUREY A., YAO B. Cadmium, copper, lead and zinc speciation in contaminated soils. Inter. J. Eng. Sci. Tech. **2**, 802, **2010**.
14. HICKEY M.G., KITTRICK J.A. Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. J. Environ. Qual. **13**, 372, **1984**.
15. ZERBE J., SOBCZYŃSKI T., ELBANOWSKA H., SIEPAK J. Speciation of heavy metals in bottom sediments of lakes. Pol. J. Environ. Stud. **8**, 331, **1999**.
16. BORŮVKA L., HUAN-WEI C., KOZÁK J., KRIŠTOUFKOVÁ S. Heavy contamination of soil with cadmium, lead and zinc in the alluvium of the Litavka River. Rostl. Výr. **42**, 543, **1996**.
17. KRÁLOVÁ L., SZÁKOVÁ J., KUBÍK Š., TLUSTOŠ P., BALÍK J. The variability of arsenic and other risk element uptake by individual plant species growing on contaminated soil. Soil Sediment Contam. **19**, 617, **2010**.
18. SZÁKOVÁ J., MIHOLOVÁ D., TLUSTOŠ P., ŠESTÁKOVÁ I., FRKOVÁ Z. Effect of soil properties and sample preparation on extractable and soluble Pb and Cd fractions in soils. Agric. Sci. **3**, 119, **2010** (doi:10.4236/as.2010.13015).
19. SIMS J.R., HABY V.A. Simplified colorimetric determination of soil organic matter. Soil Sci. **112**, 137, **1971**.
20. MEHLICH A. Mehlich 3 Soil Test Extractant: a modification of Mehlich 2 Extractant. Commun. Soil Sci. Plant Anal. **15**, 1409, **1984**.
21. ISO 11260. Soil quality – determination of effective cation exchange capacity and base saturation level using barium chloride solution; International Organization for Standardization, **1994**.
22. MAYFIELD J.L., OZANNE L., MITCHELL C.C., SIMONNE E.H., SIBLEY J.L. Laboratory and greenhouse evaluation of quicklime sources for suitability as agricultural liming materials. Comm. Soil Sci. Plant Anal. **35**, 1167, **2004**.
23. BUTORAC A., MESIĆ M., FILIPAN T., BUTORAC J., BAŠIĆ F., KISIĆ I. The influence of special natural amendments based on zeolite tuff and different lime materials on some soil chemical properties. Rostl. Výr. **48**, 133, **2002**.
24. MEDA A.R., PAVAN M.A., CASSIOLATO M.E., MIYAZAWA M. Dolomite lime´s reaction applied on the surface of a sandy soil of the Northwest Paraná, Brazil. Braz. Arch. Biol. Technol. **45**, 219, **2002**.
25. HEJCMAN M., SZÁKOVÁ J., SCHELLBERG J., ŠREK P., TLUSTOŠ P. The Rengen Grassland Experiment: soil contamination by trace elements after 65 years of Ca, N, P and K fertiliser application. Nutr. Cycl. Agroecosyst. **83**, 39, **2009**.
26. UPRETY D., HEJCMAN M., SZÁKOVÁ J., KUNZOVÁ E., TLUSTOŠ P. Concentration of trace elements in arable soil after long-term application of organic and inorganic fertilizers. Nutr. Cycling Agroecosyst. **85**, 241, **2009**.
27. SAHUQUILLO A., RIGOL A., RAURET G. Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. Trends Anal. Chem. **22**, 152, **2003**.
28. SZÁKOVÁ J., TLUSTOŠ P., BALÍK J., PAVLÍKOVÁ D., VANĚK V. The sequential analytical procedure as a tool for evaluation of As, Cd and Zn mobility in soil. Fresen. J. Anal. Chem. **363**, 594, **1999**.
29. DONG J., MAO W.H., ZHANG G.P., WU F.B., CAI Y. Root excretion and plant tolerance to cadmium toxicity – a review. Plant Soil Environ. **53**, 193, **2007**.
30. MÜHLBACHOVÁ G., TLUSTOŠ P. Effects of liming on the microbial biomass and its activities in soils long-term contaminated by toxic elements. Plant Soil Environ. **52**, 345, **2006**.
31. TRAKAL L., NEUBERG M., TLUSTOŠ P., SZÁKOVÁ J., TEJNECKÝ V., DRÁBEK O. Dolomite limestone application as a chemical immobilization of metal-contaminated soil. Plant Soil Environ. **57**, 173, **2011**.
32. BRADL H.B. Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interface Sci. **277**, 1, **2004**.
33. TLUSTOŠ P., SZÁKOVÁ J., KOŘÍNEK K., PAVLÍKOVÁ D., HANČ A., BALÍK J. The effect of liming on cadmium, lead and zinc uptake reduction by spring wheat grown in contaminated soil. Plant Soil Environ. **52**, 16, **2006**.
34. VÁCHA R., PODLEŠÁKOVÁ E., NĚMEČEK J., POLÁČEK O. Immobilisation of As, Cd, Pb and Zn in agricultural soils by the use of organic and inorganic additives. Rostl. Výr. **48**, 335, **2002**.
35. HERREN T., FELLER U. Transport of cadmium via xylem and phloem in maturing wheat shoots: comparison with the translocation of zinc, strontium and rubidium. Ann. Bot. **80**, 623, **1997**.
36. TLUSTOŠ P., SZÁKOVÁ J., STÁRKOVÁ A., PAVLÍKOVÁ D. A comparison of sequential extraction procedures for fractionation of arsenic, cadmium, lead, and zinc in soil. Cent. Eur. J. Chem. **3**, 830, **2005**.
37. GHARAIE H.A. Lead adsorption characteristics of selected calcareous soils of Iran and their relationship with soil properties. American-Eurasian J. Agric. Environ. Sci. **6**, 637, **2009**.
38. FRIESL-HANL W., PLATZER K., HORAK O., GERZABEK M.H. Immobilising of Cd, Pb, and Zn contaminated arable soils close to a former Pb/Zn smelter: a field study in Austria over 5 years. Environ. Geochem. Health. **31**, 581, **2009**.
39. ELKHATIB E.A., ELSHEBINY G.M., BALBA A.M. Lead sorption in calcareous soils. Environ. Pollut. **69**, 269, **1991**.

40. WILSON S.C., LOCKWOOD P.V., ASHLEY P.M., TIGHE M. The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: a critical review. Environ. Pollut. **158**, 1169, **2010**.
41. HUANG B., KUO S., BEMBENEK R. Availability to lettuce of arsenic and lead from trace element fertilizers in soil. Water Air Soil Pollut. **164**, 223, **2005**.
42. HARTLEY W., EDWARDS R., LEPP N.W. Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests. Environ. Pollut. **131**, 495, **2004**.
43. PORTER S.K., SCHECKEL K.G., IMPELLITTERI C.A., RYAN J.A. Toxic metals in the environment: thermodynamic considerations for possible immobilization strategies for Pb, Cd, As, and Hg. Crit. Rev. Env. Sci. Technol. **34**, 495, **2004**.
44. ADRIANO D.C. Trace elements in terrestrial environments – biogeochemistry, bioavailability, and risk of metals, 2nd ed.; Springer: New York, pp. 866, **2001**.
45. OTERO X.L., FERREIRA T.O., HUERTA-DÍAZ M.A., PARTITI C.S.M., SOUZA JR. V., VIDAL-TORRADO P., MACÍAS F. Geochemistry of iron and manganese in soils and sediments of a mangrove system, Island of Pai Matos (Cananeia – SP, Brazil). Geoderma **148**, 318, **2009**.
46. ANONYMOUS. Public notice No. 13/1994 for the management of soil protection. Czech Ministry of the Environment, Prague, **1994** [In Czech].
47. ANONYMOUS. Public notice No. 271/2009, which changes Public notice No. 474/2000 about determination requirements for fertilizers. Czech Ministry of Agriculture, Prague, **2009** [In Czech].