



Monosilicic acid potential in phytoremediation of the contaminated areas



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HIGHLIGHTS

- Monosilicic acid concentration controls heavy metals mobility in soil matrix.
- Monosilicic acid at low concentration increases heavy metals adsorption by barley.
- The negative influence of heavy metals on barley is alleviated by monosilicic acid.
- Monosilicic acid at high concentration reduces heavy metals adsorption by barley.

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ABSTRACT

The contamination of agricultural areas by heavy metals has a negative influence on food quality and human health. Various remediation techniques have been developed for the removal and/or immobilization of heavy metals (HM) in contaminated soils. Phytoremediation is innovative technology, which has advantages (low cost, easy monitoring, high selectivity) and limitations, including long time for procedure and negative impact of contaminants on used plants. Greenhouse investigations have shown that monosilicic acid can be used for regulation of the HM (Cd, Cr, Pb and Zn) mobility in the soil-plant system. If the concentration of monosilicic acid in soil was increased from 0 to 20 mg L⁻¹ of Si in soil solution, the HM bioavailability was increased by 30–150%. However, the negative influence on the barley by HM was reduced under monosilicic acid application. If the concentration of monosilicic acid was increased more than 20 mg L⁻¹, the HM mobility in the soil was decreased by 40–300% and heavy metal uptake by plants was reduced 2–3 times. The using of the monosilicic acid may increase the phytoremediation efficiency. However the technique adaptation will be necessary for phytoremediation on certain areas.

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1. Introduction

Human activities such as industrial production, mining, agriculture and transportation are the major sources of soil contamination with heavy metals (HM), and an increased its uptake by food crops grow on polluted soils is often detected (Azevedo et al., 2012; Keller et al., 2005; Wuana and Okieimen, 2011). Toxic metals can enter the human body by consumption of contaminated food crops, water or inhalation of dust (Cambra et al., 1999). For example more

than 70% of dietary intake of cadmium is contributed via food chain (Wagner, 1993). HM are non-biodegradable and can remain almost indefinitely in the soil environment. The decontamination of the polluted soil ecosystem is actual problem in many regions.

The following soil remediation techniques are available: (i) ex-situ (excavation) or in-situ (on-site) soil washing/leaching/flushing with chemical agents, (ii) chemical immobilization/stabilization method to reduce the solubility of heavy metals by adding some non-toxic materials into the soils, (iii) electrokinetics (electromigration), (iv) covering the original polluted soil surface with clean soils, (v) dilution method (mixing polluted soils with surface and subsurface clean soils to reduce the concentration of heavy metals), (vi) phytoremediation by plants (G.O.C., 2003; Fawzy, 2008; Kord et al., 2010; Nouri et al., 2009; Stupin, 2009).

Abbreviations: HM, heavy metals.

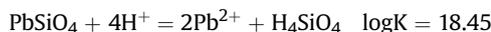
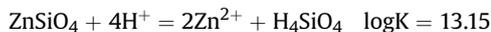
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Phytoremediation is one of the prospective technique, where various types of plants are used for removing, transferring, stabilization, and/or destroy contaminants in the soil (Liang et al., 2012). This procedure has both advantages and limitation. Phytoremediation has been suggested as environment friendly and cost-effective alternative for purification of the HM contaminated lands (Evangelou et al., 2015). Two main problems are related with phytoremediation. First, the total solubility of the HM in the soil is low, but this process is continuous (Tan, 2011). As a result, phytoremediation requires long term operation. Second, HM in contaminated soil negatively affect plant growth and consequently the phytoremediation efficiency (Manara, 2012). Among fields, current research in advanced phytoremediation on, are increasing plant tolerance to the HM toxicity and enhancing HM mobility to increase the availability to a plant.

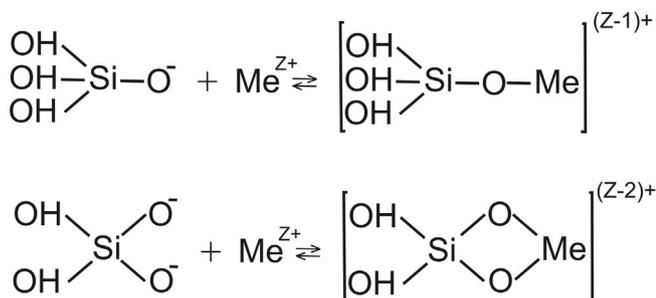
The important role of silicon (Si) in mitigating abiotic stresses in higher plants has attracted the attention of many researchers. The optimization of plant Si nutrition increased the plant tolerance to HM toxicity (Cunha and Nascimento, 2009; Liang et al., 2005; Matichenkov et al., 2013). The mechanism of this process is not clear, but probably related with chemical property of the monosilicic acid. As any acid monosilicic acid can react with metals and forms slightly soluble silicates (Iler, 1979). Secondly, Si-rich substances can adsorb HM in soil matrix and reduce their mobility (Matichenkov et al., 2013). Thirdly, soluble Si can react with HM in the plant roots (Liang et al., 2005).

Monosilicic acid or ortho-silicic acid (H_4SiO_4), $\text{pK} = -9.85$ and its anion (H_3SiO_4^-) are the most widely distributed varieties of silicic acid in natural waters, including soil solution. Monosilicic acid can differently impact the HM mobility related with its chemical properties (Matichenkov et al., 2013). Monosilicic acid reacts with HM and forms sparingly soluble silicates:



The constants of these reactions are available in handbooks (Lindsay, 1979). Our investigations have shown that such reactions are possible only when the concentration of monosilicic acid in soil solution is high (Bocharnikova et al., 1995). However monosilicic acid at low concentrations can form soluble complexes with HM (Schindler et al., 1976). This reaction results in increasing the mobility of HM (Bocharnikova et al., 1995; Schindler et al., 1976) (Fig. 1).

By this means, original monosilicic acid or silicic acid from dissolving of Si-rich minerals has the potential to regulate the



Where Me is any heavy metal

Fig. 1. Formation of the metal complexes with monosilicic acid (Schindler et al., 1976).

mobility of HM in the soil-plant system. The using of this process can reinforce the phytoremediation technique. However the mechanisms of monosilicic acid HM interactions in both soil solution and plant sap are investigated very poor.

The aim of this study was investigation of the heavy metals (Cd, Cr, Pb and Zn) mobility in the soil-barley system under different monosilicic acid concentrations in soil solution.

2. Materials and methods

The upper horizon of soil (0–10 cm), classified as Soddy Podzolic Soil (Moscow region, Russia) was used in this investigation as soil matrix. This soil had the following properties: 45% sand, $\text{pH}_{\text{H}_2\text{O}} = 5.8\text{--}5.9$, organic matter ($\text{C}_{\text{org}} = 1.21\text{--}1.23\%$; cation exchange capacity (CEC) = $8.3\text{--}8.5 \text{ cmol}^+/\text{kg}$. The total contents of the HM were determined as $\text{Cd} = 1.141\text{--}1.147 \text{ mg kg}^{-1}$, $\text{Cr} = 0.84\text{--}0.86 \text{ mg kg}^{-1}$, $\text{Pb} = 2.21\text{--}2.27 \text{ mg kg}^{-1}$ and $\text{Zn} = 0.95\text{--}0.97 \text{ mg kg}^{-1}$.

The interaction between soil and HM is a complex time-consuming process where the equilibrium between soluble, potentially soluble and insoluble forms of metals will be established (Tan, 2011). Therefore the simulation of the soil contamination was realized before greenhouse test. Dry soil was placed in a barrel and polluted with 500 mg kg^{-1} of Cd as CdCl_2 ; 500 mg kg^{-1} of Cr as $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$; 500 mg kg^{-1} of Pb as $\text{Pb}(\text{NO}_3)_2$ and 500 mg kg^{-1} of Zn as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. All HM-contained salts were separately dissolved in the distilled water, which then was mixed with soil in the barrel. During 4 weeks soil was agitated every week, moisture level was kept around 25% and temperature regime was $+20^\circ\text{C} - +24^\circ\text{C}$. Every week the soil was shuffled.

One kg of dried at 65°C , ground and sieved through 3 mm contaminated and original soils were placed into 1 L plastic pots. Then 10 seeds of barley (*Hordeum vulgare* L.) were planted in each pot. Barley is one of the most common plant species, which used for phytoremediation and for study of HM mobility in the soil plant system (Qi et al., 2015; Rathod et al., 2015; Rezvani et al., 2015). All pots were irrigated daily by 50 mL of distilled water or water solution with monosilicic acid at the following concentrations: 5, 10, 20, 50, and 100 mg L^{-1} . The solutions of MS were prepared from metasilicic acid (Fisher Scientific, CAS-No 7699-41-4) by dilution with deionized water. The air temperature in the greenhouse was kept at $24 \pm 2^\circ\text{C}$ during the day and $20 \pm 2^\circ\text{C}$ during the night. The light period was 12 h; at intensity of $950 \text{ mmol photons m}^{-2} \text{ s}^{-1}$. The relative air humidity was $45 \pm 5\%$ during the day and $70 \pm 5\%$ during the night.

One-month-old barley plants were harvested. The biomass of roots and above-ground organs of barley was dried at 65°C and weighted. The total Si, Cd, Cr, Zn, and Pb were analyzed in roots and shoots of barley. The Elliot (1991) method was used for Si testing in solution after $\text{NaOH-H}_2\text{O}_2$ digestion technique in autoclave. The total HM content in plant tissue was determined by using microwave digestion in $\text{HNO}_3\text{-H}_2\text{O}_2$ media (Liu et al., 2013). The contents of Si, Cd, Cr, Zn, and Pb were measured by ICP-OES Perkin Elmer Optima 5300 DV.

The content of monosilicic acid in soil was determined by using water extraction from fresh soil, which gives possibility to test monosilicic acid directly (Matichenkov and Snyder, 1996). Monosilicic acid in the purified water extraction was determined by using molybdenum blue technique (Mullin and Riley, 1955). The mobile forms of HM were tested by using MgCl_2 -extracts (Jena et al., 2013). The potentially mobile forms of Cd, Cr, Pb and Zn were tested by using 0.1 n HCl extracts (McLaughlin et al., 2000; Sabiené et al., 2004). ICP-OES Perkin Elmer Optima 5300 DV was used for HM in extracts.

Each treatment and each analysis had 5 replications. All

obtained data was subjected to a statistical analysis based on comparative methods using Duncan's multiple range tests for mean separation at the 5% level of significance (Duncan, 1957).

3. Results

Dry biomass of roots and shoots of barley is shown in Table 1. The application of monosilicic acid with irrigation significantly increased the mass of barley from 0.43 ± 0.03 to 0.67 ± 0.03 (on 48.8%) and from 0.51 ± 0.03 to 0.84 ± 0.03 g/plant (on 67.7%), respectively for roots and shoots. Higher increase in biomass was observed under the highest monosilicic acid concentration. HM significantly reduced root (from 0.43 ± 0.03 to 0.23 ± 0.03 g/plant) and shoot (from 0.51 ± 0.03 to 0.25 ± 0.02 g/plant) biomass. The irrigation of polluted soil by monosilicic acid resulted in increased plant biomass up to 134% for roots and 156% for shoots.

It should be noted that the total Si in roots and shoots in HM-exposed plants was increased even under the irrigation with distilled water. In the Si-irrigated plants, this increase was more remarkable, up to 35.7% in roots and 68.2% in shoots.

The total Si in the roots and shoots under application of the monosilicic acid was amplified with increasing silicic acid concentration up to 26.6% in roots and 54.8% in shoots. The soil contamination reinforced the Si absorption by barley and total Si in roots were increased up to 36.1% and for shoots up to 68.2%.

The content of Cd, Zn, Cr, and Pb in the roots and shoots of barley grown on unpolluted soil was very low. The application of highest concentration of monosilicic acid significantly reduced the Cr, Zn and Pb in roots and Cd, Cr and Pb in the shoots. In the HM-contaminated soils, the content of all HM in plant tissue increased several times with higher values in the roots than those in the shoots. The influence of monosilicic acid had dual character. Increasing the monosilicic acid concentration from 5 to 20 mg L⁻¹ led to increase in the total HM in roots and shoots of barley. Maximum increases in the Cd, Zn, Cr, and Pb were observed in the

roots of barley in polluted soil – 235.3 ± 5.1 to 397.3 ± 8.2 ; 283.4 ± 10.5 to 422.9 ± 20.5 ; 222.5 ± 10.3 to 315.4 ± 15.3 ; and 268.3 ± 12.5 to 374.3 ± 14.5 mg/kg, respectively. Under monosilicic acid concentrations from 50 to 100 mg L⁻¹, the total HM in the roots and shoots of barley were reduced.

The original soil was characterized by low content of soluble Si (4.2 mg kg⁻¹ of Si), which is typically for sandy soils (Matichenkov and Snyder, 1996) (Table 2). The irrigation of the soil by solution with monosilicic acid concentration more 5 mg L⁻¹ of Si resulted in significant increase of the monosilicic acid content in the soil solution after pot test. Increasing the monosilicic acid concentration in the irrigation solution positively correlated with content of soluble Si in the soil. The maximum content of Si in water extract was 48.9 ± 0.5 and 43.6 ± 0.5 mg kg⁻¹ of Si respectively for unpolluted and contaminated soils irrigated by solution with 100 mg L⁻¹ of Si. The presence of the HM in the contaminated soil significantly reduced the monosilicic acid content in the tested soil samples.

The original unpolluted soil is characterized by low content of mobile and potentially mobile forms of Cd, Cr, Pb and Zn (Tables 2 and 3). The soil pollution by soluble salts of HM remarkably increased the content of mobile and potentially mobile HM in the soil. As a result, the content of HM in the plant tissue was increased several times with their dominating accumulation in the barley roots (Table 1). The monosilicic acid application at low rates (5, 10, and 20 mg L⁻¹ of Si) promoted a slight increase in both mobile and potentially mobile forms of HM in the unpolluted soil and high increase of their mobility in the polluted soil. The increase in the HM mobility caused a slight increase in the root and shoot HM in uncontaminated soil and their significant increase in plants grown in HM-polluted soil.

Monosilicic acid at the rates 50 and 100 mg L⁻¹ of Si reduced the mobility of HM in both polluted and unpolluted soils. The reduction effect was more pronounced with increasing the silicic acid concentration in the irrigation solution from 50 to 100 mg L⁻¹ of Si.

Table 1
Effect of monosilicic acid (MS) on dry biomass and total content of Si, Cd, Zn, Cr, and Pb in roots and shoots of barley plants in unpolluted and HM-polluted soils.

Treatment monosilicic acid, mg L ⁻¹	Biomass of 1 plant, g	Si	Cd	Cr	Pb	Zn
		mg kg ⁻¹				
Roots						
Control (unpolluted soil)	0.43 c	11,356 a	0.73 b	0.45 b	0.29 ab	0.38 ab
MS 5	0.44 c	11,370 a	0.74 b	0.48 b	0.32 b	0.42 b
MS 10	0.47 d	11,382 a	0.82 b	0.55 c	0.33 b	0.53 c
MS 20	0.53 e	13,960 b	0.83 b	0.59 c	0.33 b	0.55 c
MS 50	0.63 f	14,200 c	0.54 a	0.36 a	0.21 a	0.32 a
MS 100	0.67 f	14,380 d	0.64 a	0.32 a	0.16 a	0.29 a
HM (polluted soil)	0.23 a	11,348 a	235.3 e	222.5 g	268.3 e	283.4 f
HM + MS 5	0.28 ab	11,352 a	234.7 e	256.7 f	284.3 f	312.3 g
HM + MS 10	0.32 b	11,380 a	357.3 f	286.5 h	315.6 g	344.5 h
HM + MS 20	0.38 c	14,280 c	397.3 g	315.4 i	374.3 h	422.9 i
HM + MS 50	0.45 d	15,290 e	103.4 d	202.3 e	252.2 d	214.3 e
HM + MS 100	0.54 e	15,448 f	83.4 c	143.5 d	141.0 c	198.3 d
Shoots						
Control (unpolluted soil)	0.51 d	12,550 ab	0.35 b	0.53 c	0.06 b	0.48 ab
MS 5	0.52 d	12,490 a	0.34 b	0.55 c	0.06 b	0.52 b
MS 10	0.58 e	12,790 b	0.42 c	0.63 d	0.07 b	0.55 b
MS 20	0.65 e	14,335 d	0.34 b	0.63 d	0.08 b	0.58 b
MS 50	0.74 g	18,254 e	0.32 b	0.48 b	0.04 a	0.41 a
MS 100	0.84 h	19,430 g	0.23 a	0.32 a	0.03 a	0.40 a
HM (polluted soil)	0.25 a	12,630 b	92.3 g	94.3 h	83.4 e	89.6 c
HM + MS 5	0.32 b	13,025 c	98.2 h	103.2 i	84.5 e	108.3 d
HM + MS 10	0.42 c	13,228 c	123.8 i	122.4 j	135.4 g	122.5 e
HM + MS 20	0.53 d	15,350 d	173.6 j	155.6 k	188.6 h	189.6 f
HM + MS 50	0.59 e	18,570 e	54.6 e	84.5 g	64.3 d	112.4 d
HM + MS 100	0.64 e	21,240 h	17.4 d	66.3 e	42.3 c	89.5 c

†Value within a column followed by the same letter are not different using Duncan's Multiple Range test ($P < 0.05$), ($n = 5$).

Table 2Effect of monosilicic acid (MS) on content of water-extractable Si and mobile forms of Cd, Cr, Pb Zn in unpolluted and HM-polluted soils, mg kg⁻¹.

Treatment monosilicic acid, mg L ⁻¹ of Si	Water extractable	Cd	Cr	Pb	Zn
	Si mg kg ⁻¹				
Control (unpolluted soil)	4.2 a	0.25 bc	0.05 a	0.08 b	0.12 ab
MS 5 ppm	4.8 a	0.27 c	0.05 a	0.09 b	0.15 b
MS 10 ppm	8.5 b	0.31 c	0.05 a	0.09 b	0.16 b
MS 20 ppm	14.3 c	0.34 d	0.04 a	0.14 c	0.15 b
MS 50 ppm	25.6 d	0.21 b	0.04 a	0.07 b	0.08 a
MS 100 ppm	48.9 f	0.12 a	0.04 a	0.04 a	0.07 a
HM (polluted soil)	4.1 a	12.3 g	9.6 c	5.8 f	18.4 e
HM + MS 5 ppm	4.7 a	18.4 h	12.4 d	6.1 f	23.4 g
HM + MS 10 ppm	8.5 b	20.5 i	15.7 e	7.9 g	32.3 h
HM + MS 20 ppm	14.2 c	22.5 i	17.6 g	9.4 h	37.6 h
HM + MS 50 ppm	23.6 d	8.4 f	8.3 c	4.3 e	13.5 d
HM + MS 100 ppm	43.6 e	5.6 e	5.4 b	2.2 d	9.5 c

†Value within a column followed by the same letter are not different using Duncan's Multiple Range test ($P < 0.05$), ($n = 5$).**Table 3**Effect of monosilicic acid (MS) on potentially mobile Cd, Cr, Pb and Zn in unpolluted and HM-polluted soils, mg kg⁻¹.

Treatment monosilicic acid, mg L ⁻¹ of Si	Cd	Cr	Pb	Zn
	Mobile/potentially mobile, mg kg ⁻¹			
Control (unpolluted soil)	0.49 c	0.25 b	0.29 c	0.39 bc
MS 5 ppm	0.52 c	0.23 ab	0.31 c	0.42 c
MS 10 ppm	0.58 d	0.38 c	0.39 d	0.46 c
MS 20 ppm	0.89 e	0.47 d	0.45 d	0.47 c
MS 50 ppm	0.31 b	0.21 a	0.23 b	0.34 b
MS 100 ppm	0.22 a	0.17 a	0.15 a	0.28 a
HM (polluted soil)	128.4 h	108.4 g	155.6 g	155.6 g
HM + MS 5 ppm	139.6 i	112.7 g	167.8 h	162.3 h
HM + MS 10 ppm	159.5 j	136.8 h	184.5 i	233.6 i
HM + MS 20 ppm	193.4 k	155.9 i	199.3 j	255.4 j
HM + MS 50 ppm	85.4 g	87.9 f	122.3 f	118.4 e
HM + MS 100 ppm	65.4 f	65.9 e	104.2 e	84.5 d

†Value within a column followed by the same letter are not different using Duncan's Multiple Range test ($P < 0.05$), ($n = 5$).

4. Discussion

The data obtained showed that using different monosilicic acid concentrations for soil irrigation gives possibility to change HM mobility in the soil-plant system. A raise in the soil HM mobility was observed with increasing the soluble Si concentration from 5 to 20 mg L⁻¹ of Si. An increase in the HM mobility in soil resulted in increasing HM contents in plant tissues with highest values in barley roots. At the same time improved plant supply with Si at the low rate increased the barley biomass, thus enhancing the total HM extraction by plants. The formation of the soluble Si-HM complexes in the soil matrix was explained by Schindler with co-authors (1976) and confirmed by our previous investigations (Bocharnikova et al., 1995). The Si-HM complexes are soluble and this form of HM probably can be absorbed by plants. In the result, more HM will be absorbed by plants and they will be protected against HM toxicity. These processes are important for increasing the phytoremediation efficiency and for reduction of the time-period for soil cleaning. However the mechanism of plant protection against HM toxicity is investigated very poor (Balakhnina et al., 2015; Cunha and Nascimento, 2009; Liang et al., 2005). It is available hypothesis, that optimization of plant Si nutrition can reduce the HM transport via activation of the plant signal system, precipitation of the HM in plant sap and/or reinforcement of the plant gate-bearing transport in apoplast (Balakhnina et al., 2015; Biel et al., 2014; Vaculik et al., 2009).

In the opposite, the high concentrations of monosilicic acid in the soil solution provide the reduction of HM mobility by 40–300%

and significantly decrease the HM uptake by plants. This mechanism is related with formation of the slightly soluble silicates of HM (Brannvall, 2006; Cunha and Nascimento, 2009; Liang et al., 2005). Practically phytoremediation usually does not provide complete removal of pollutants from contaminated soil. Therefore after phytoremediation it is necessary to protect natural surface and underground water and cultivated plants against HM remains. The high rate of monosilicic acid application or using of solid Si-rich substances can be recommended for finalization of phytoremediation technology procedure.

There is no question that content and behavior of the monosilicic acid in different soils is varied. Secondly the interactions between various HM and monosilicic acid can be different. Therefore special adaptation for phytoremediation will be required.

5. Conclusions

The greenhouse tests with unpolluted and contaminated soils have shown that the concentration of the monosilicic acid in the soil matrix can change HM mobility in the soil-plant system. Monosilicic acid added at low concentrations from 5 to 20 mg kg⁻¹ of Si can increase the HM mobility in soil, thus enhancing HM uptake by roots. Monosilicic acid at high concentrations (50 and more mg kg⁻¹ of Si) can reduce the HM mobility and increase plant resistance against HM toxicity. These findings allow improving plant-based remediation technologies. Considering different soil-climatic conditions, type and level of pollution, variety of plant species and Si-rich substances, the technology must be adapted.

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