Phosphorous and lime-induced zinc fractions transformations in Zn deficit tropical paddy soils

CrossMark

Shahram Mahmoud Soltani^{1*} , Mohamed Musa Hanafi^{2, 3} , Abdul Wahid Samsuri³ , Sharifah Kharidah⁴

Article Info

ABSTRACT

Accepted:
29 May 2020

Keywords:

Highly weathered
soils, Organic zinc,
Residual fraction,
Sequential analysis

The soil geochemical Zn controlling factors in soil solid- solution equilibrium influence the phyto-available forms of Zn in soil Zinc fraction pools. A laboratory incubation experiment was conducted on two highly weathered tropical soil orders (Ultisols and Entisols) to investigate the effects of some of the most important of these factors (various levels of Phosphorus (P), lime, and Zn) on Zn fractions in six tropical paddy soils. The sequential fractionation procedure was used to determine soils Zn fractions after 30 days of submerged incubation threaten by the aforementioned factors. The non-residual and available fractions (water-soluble plus exchangeable (WE) and organic complexes (Org)) increased by Zn treatments about 1.29 to 2.65 times, and 1.7 to 4 times, respectively and decreased with increasing lime application levels about 9 to 30%, and 3 to 37%, respectively, whereas the non-residual and non-available (amorphous (Amor) and manganese oxides (MN)) and the residual fractions increased with the increasing level of applied P and lime. The effects of P, lime, and Zn applications on Zn fractions were similar for all soils. The application of P plus lime was more effective in reducing available Zn fractions and increasing non-available fractions than the separate application of P or lime between 30 to 70%. It can be concluded that at the studied soil conditions and to avoid Zn deficiency in rice paddy fields due to P and lime application, Zn fertilizer should be applied more than rice nutrition requirements to overcome converted Zn to the unavailable fractions.

INTRODUCTION

The capacity of Zinc (Zn) fractions to supply available Zn for optimum growth of crops varies widely among soil types. Zinc deficit soils are developing seriously across tropical paddy soils which are heavily weathered and leached (Alloway, 2008). Soil zinc presents in a number of chemical fractions with varying solubility (Almendros et al. 2008). The phyto-available Zn in soils depends greatly on its specific fractions rather than its total concentrations (Fan et al. 2009). The

availability of Zn in soils depends on the equilibrium among different Zn fractions (Lee et al. 2012; Cao et al. 2013).

The main controlling factors that affect the equilibrium between plant-available and other Zn fractions of soils are the total amount of soil Zn content, soil pH, reduction and oxidation conditions, calcium carbonate (CaCO₃) content (liming), organic matter (OM) percentage, and the concentrations of micro- and macro-elements especially phosphorus (P) (Alloway 2009). In tropical paddy soils, liming and P content are the most crucial factors controlling plant available Zn. (Alloway 2009).

Excess amount of P application have been reported to induce Zn deficiency in rice (Ranjha et al. 2001; Nawaz et al. 2012) due to the interactions between P and Zn (Gao et al. 2012). High available P in paddy soils causes a change in soil surface charges and a change in soil pH due to P adsorption by the soil colloids (Mandal and Mandal 1986; Shuman 1985, 1998). Rupa et al. (2003)

¹ Assistant Professor of Rice Research Institute of Iran, Agricultural Research, Education and Extension Organization, Rasht, Iran.

² Laboratory of Plantation Crops, Institute of Tropical Agriculture, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia.

³ Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia.

⁴ Department of Food Science, Faculty of Food science and technology, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia.

* E-mail: shmsoltani@gmail.com

reported that the different soil Zn fractions indicated various response to the added P levels. Application of more than 40 mg kg⁻¹ P decreased the concentration of plant-available Zn fractions (water soluble plus exchangeable (WE) and organo-complexes (Org)), whereas the concentration of non-soluble forms (crystalline (Cry), manganese oxide (MN)) and residual fractions increased in soils. Also, in spite of high reduction in the residual fraction due to P application, the only lower transformation of added Zn to WE and Org fractions negatively affected Zn uptake by crops (Rieuwerts 2007).

Application of lime increases the pH and the amount of basic cations (Ca²⁺ and Mg²⁺) in tropical paddy soils (Chen et al. 2000) and reduced the Al³⁺ and Fe²⁺ toxicity (Alloway 2008). However, the bioavailability of soil Zn within a short-term use of lime sharply decreased due to the increase in soil pH which causes Zn precipitation (Adhikari and Rattan 2007; Wang et al. 2001; Zhang et al. 2010b). Wang (2001) showed that the concentrations of extractable Zn were significantly reduced by 96% after 30 days of CaCO₃ application. Lime often can stabilize the Zn exchangeable fractions due to precipitating of this fraction to insoluble compounds (Cakmak et al. 2010) and increasing the cation exchange capacity of soil (Hong et al. 2002). In the rare situations, high soil pH can promote the dissolution of soil organic matter (Laor et al. 1998; Zhang et al. 2010a), and increase in the availability of soil Zn (Wang et al. 2001). Keeping the above facts in view, management of Zn tropical paddy soil is very important in order to avoid Zn deficiency. Therefore, this study was conducted to determine the interactive effects of Zn, lime and P applications on Zn fractions in tropical paddy soils.

MATERIALS AND METHODS

The incubation experiment was conducted on two highly weathered tropical soil orders (Ultisols and Entisols) that divided into six soil series. Available zinc concentrations in the all selected soils were below critical zinc level (double acid method) and soils are Zn deficit.

The soils from the surface layer (0-30 cm) of the rice paddy fields of Kelantan and Kedah states- two largest rice production areas in Malaysia- were sampled. The soil samples were air-dried, ground to pass through a 2-mm metal sieve and stored for the current experiment. The physical and chemical properties of the selected soil samples, such as: texture, organic carbon, pH (1:2.5), cation exchange capacity (CEC) (C mole kg⁻¹), available Zn, Phosphorus, Fe+2 and Mn+2 were determined. A pipette method was used to analyse soil particle-size (Gee et al., 1986). Soil pH and electrical conductivity were measured in a 1:2 ratio (w: v)

soil to water suspension. Cation-exchange capacity was measured by leaching and replacing procedure (Bower et al., 1952). Phosphorus was measured by Bary and Krutz (1945) method. Oxidizable organic matter was measured using the Walkley-Black (Jackson 1964) and available zinc by double acid method (Amacher 1996).

10 grams portions of the stored soil samples were placed in 294 of 100 mL plastic vials and treated with: (i) three levels of P (0, 50, and 100 mg kg⁻¹) as KH₂PO₄, (ii) three levels of Zn (0, 2.5 and 5 mg kg⁻¹) as zinc sulphate, and two levels of liming requirement (LR) (0 and LR to reach pH to 5.5), all in the form of solutions, which are mixed uniformly with the soils. The flooded moisture regimes were maintained for all of the treatments. a randomized complete design with four factors factorial triplicate experiment and 3 levels of P, 6 types of soil series, 3 levels of Zn and 2 levels of LR were carried out. The containers were incubated at room temperature (25°C ± 0.5) in the laboratory of agricultural faculty in University of Putra Malaysia. The soil samples were sequentially extracted after 30 days (reproductive stages initiation). Zinc fractions (fertility fractions), water soluble plus exchangeable, organically complexes, amorphous sesquioxides bound and crystalline sesquioxides bound fractions were determined by modified Mandal and Mandal (1986) procedure and residual (Res) and total Zn with aqua regia method. Data analyses were done using the IBM SPSS 21 and SAS 9.2 software.

RESULTS AND DISCUSSION

Classification and general properties of soils

According to USDA soil taxonomy, selected soils, Telemong, Lubok Itek and Kundur soil series belong to Entisols orders and Chengai, Tok Yang, and Tepus soil series classified in Ultisols orders, whereas parent material of all soils almost were recent alluvial. Available Zn ranged from 0.56 mg Z/kg soil in Tepus soil series of acid sulphate soils, to 1.185 mg Zn/kg in Telemong soil series as a neutral soils, which all Zn contents of soils series were less than the critical limit in paddy soils (2 mg kg⁻¹) (Dobermann 2000).

Concentration and distribution of Zinc fractions in soil

According to the soil native Zn sequential fractionation total Zn were low to medium level (10.136 to 52.018 mg kg⁻¹), with highest content of residual fractions ranged from 5.167-38.700 mg kg⁻¹ (54 to 82% of total Zn), whereas WE form varied from 0.273 to 0.517 mg kg⁻¹ (0.5-3.4%, an average of 2.13% of total Zn) which indicated low bioavailability of Zn for rice uptake in all soils. These data emphasized that studied paddy soils were Zn deficit. Between these two extreme

Table 1. Concentrations of water soluble and exchangeable Zn in six tropical soil series in incubation experiment receiving various Zn, P and lime levels

Treatment		Tropical Soil Orders and Series					
		-----Entisols-----		-----Ultisols-----		Entisols	
		Lubok Iték	Kundur	Tok Yong	Chengai	Tupus	Telemong
		mg Zn kg ⁻¹ soil					
P(0)	Zn0 L0	0.52	0.52	0.27	0.42	0.34	0.35
	Zn0 L1	0.42	0.33	0.18	0.34	0.31	
	Zn5 L0	1.17	0.94	0.50	0.63	0.45	0.35
	Zn5 L1	0.68	0.61	0.43	0.41	0.19	
	Zn10 L0	1.31	1.67	0.64	0.60	0.82	0.45
	Zn10 L1	1.01	1.49	0.47	0.60	0.14	
P(50)	Zn0 L0	0.33	0.34	0.13	0.34	0.26	0.08
	Zn0 L1	0.27	0.33	0.10	0.21	0.14	
	Zn5 L0	0.66	0.77	0.30	0.44	0.30	0.32
	Zn5 L1	0.40	0.73	0.31	0.36	0.27	
	Zn10 L0	0.93	1.47	0.46	0.60	0.52	0.51
	Zn10 L1	0.80	1.44	0.34	0.46	0.19	
P(100)	Zn0 L0	0.17	0.17	0.08	0.23	0.21	0.07
	Zn0 L1	0.16	0.29	0.24	0.24	0.22	
	Zn5 L0	0.45	0.54	0.20	0.20	0.16	0.38
	Zn5 L1	0.28	0.47	0.35	0.36	0.11	
	Zn10 L0	0.70	1.04	0.36	0.59	0.43	0.54
	Zn10 L1	0.48	1.10	0.34	0.33	0.19	

ranges, Mn (0.243-1.193 mg kg⁻¹), Org (0.584-3.04 mg kg⁻¹), Amor (0.875-6.280 mg kg⁻¹) and crystalline bound zinc fractions (0.259-3 mg kg⁻¹) were located. Therefore, the fractionation distributions were in the following order: WE< MN< Org< Amor< Cry< RES. Thus, Zn in these soils seems to have predominantly been fixed with mineral crystalline lattices.

Zn fractions transformations

Water soluble plus exchangeable zinc fraction

Analysis of variance showed that the concentration of WE fraction were significantly affected by soil type ($P \leq 0.01$), Zn levels ($P \leq 0.01$), lime application ($P \leq 0.01$), P ($P \leq 0.01$) and also by treatments combination interactions ($p \leq 0.01$) (Table 7). By increasing the Zn level from 0 to 2.5 mgkg⁻¹, the concentrations of WE fractions in all soils were elevated from 1.29 times in Tepus and Telemong (low total Zn soil series) to 2.65 times in Tok Yong with the highest amount of total Zn; nevertheless, compared to the 2.5 mgkg⁻¹, more Zn concentration was observed in 5 mg kg⁻¹ treatments but the slope of increasing did not follow any regular pattern (Table 1). Also, the results of Table 1 showed a distinct decrease of native NH₄OAc-extractable fraction (WE) due to P and lime application under submerged soil condition either separately or in combination, the reduction in WE concentration being more accelerated in combination conditions. Although, applied Zn treatments would increase WE availability, particularly by increasing Zn values from 0 to 5 mg kg⁻¹ in comparison with non-treated soils, but the

most decreasing percentage in concentration of WE fraction vs P and lime application were observed in the highest level of Zn. It meant that the excess amount of Zn would accelerate the immobilization of Zn in the soils. The effect of treatments on reduction of WE fractions are in the following order: P + lime> P> lime in all incubated soils.

In addition, applied P and lime also caused a drop in the transformation of applied Zn into WE fraction. As mentioned before about native soil Zn (untreated soils), the depressing effect was more pronounced under P plus lime treatments than these two alone. The change in applied Zn in WE vs P and lime followed the same trend as native Zn fractionation. Soil solution thermodynamic findings for Zn behaviour in flooded soils showed soluble P was the most effective in Zn immobilization through lower soluble Zn products formation (Mandal and Mandal 1990; Rupa et al. 2003). Integrated amendment of soluble P materials followed by the excessive P immobilized with carbonaceous materials, for example, CaCO₃ or (Ca Mg) CO₃, could promote excessive Zn reduction. Furthermore, the native soil P solubility increased by the submerged condition due to the reduction and/or hydrolysis of Fe and Al phosphate. The final product diffusion combination with Zn caused the depression of WE Zn fraction (Cao et al. 2013). Liming of previous acid soils by relatively increase pH values and a high content of strongly adsorptive CaCO₃, can retain Zn through chemisorption (Alloway 2009; Kiekens 1995; Singh et al. 2005; Vondráčková et al. 2013). In line with the original calcareous soils,

Table 2. Concentrations of organic complexes Zn in six tropical soil series in incubation experiment receiving various Zn, P and lime levels

Treatment		Tropical soil Orders and Series					
		----Entisols----		-----Ultisols-----		Entisols	
		Lubok Itek	Kundur	Tok Yong	Chengai	Tupus	Telemong
		mg Zn kg ⁻¹ soil					
P(0)	Zn0 L0	3.04	1.48	0.66	1.15	0.58	1.38
	Zn0 L1	1.89	1.24	0.64	0.86	0.41	
	Zn5 L0	5.30	3.05	1.98	2.61	2.23	3.69
	Zn5 L1	3.98	2.83	1.84	2.41	2.04	
	Zn10 L0	6.44	6.11	3.30	3.75	2.77	5.77
	Zn10 L1	5.61	5.38	2.91	3.50	2.55	
P(50)	Zn0 L0	2.46	1.52	0.76	1.10	0.52	1.27
	Zn0 L1	2.18	1.38	0.73	0.83	0.40	
	Zn5 L0	5.50	3.77	1.94	2.56	1.69	3.38
	Zn5 L1	4.44	3.47	1.62	2.37	1.05	
	Zn10 L0	6.50	5.78	2.88	3.60	2.68	5.66
	Zn10 L1	5.81	5.20	2.48	2.88	2.57	
P(100)	Zn0 L0	2.54	1.42	0.67	1.04	0.28	1.14
	Zn0 L1	2.18	1.40	0.63	0.97	0.25	
	Zn5 L0	4.365	3.63	1.71	2.55	1.52	3.32
	Zn5 L1	3.92	3.88	1.60	2.33	1.30	
	Zn10 L0	5.57	6.26	2.80	3.46	2.48	4.73
	Zn10 L1	5.04	4.32	2.30	3.25	2.29	

heavily lime application of loamy or sandy texture of different soil orders could still cause Zn deficiency, where the total Zn content is relatively low (Alloway 2009), especially in in tropical soils which need liming material to grow high yielding varieties of cereal crops (Fageria and Stone 2008). Decreasing of available Zn (WE fraction) due to pH changes and the formation of insoluble Zn compounds will be accelerated by submerging soil condition (Johnson-Beebout et al. 2009; Nascimento et al. 2007). On the other hand, formation of Fe²⁺ and Mn²⁺ in soil under the flooded condition, compete with Zn²⁺ for exchange sites and thus restricts the entry of applied Zn into the exchange complexes sites. The increase in soluble Fe²⁺ and Mn²⁺ may also displace some of the Zn that already present in the exchange complex leading to its reaction with P in the solution phase with formation of compounds with lower solubility (Mandal and Mandal 1990; Shuman 1985; Shuman 1998).

Organic complexes Zn fraction

The mean value of Org fraction in selected paddy soils and its variations across applied treatments was shown in Table 2. The organically bound zinc was considerably increased by increasing organic carbon content in non-treated soils except in Tepus acid sulphate soil which it had the lowest value. Org elevated by increasing the Zn levels, around 1.7 to 4, and 2 to 5 times in comparison with control at 2.5 and 5 mg kg⁻¹, respectively. Surprisingly, two times increasing in

applied Zn levels have not caused two times increases in Org concentration, and also, the highest increase percentage (4 and 5 times) observed at the lowest organic matter (0.68% OC) background (Tepus acid sulphate soil series). The first might be as a consequence of several soil factors involve in Zn chemistry, and the second might be due to strongly acidic nature of acid sulphate soil (pH=4) compared to others.

Lime application permanently decreased the Org concentration in all soils and all levels of added Zn treatments, nevertheless, compared to 0 Zn level, the Org concentration reduction in 2.5 and 5 mg kg⁻¹ were not significant. Similar to lime, P application decreased the Org Zn concentration for both 50 and 100 mgkg⁻¹ levels, but two times increasing in applied P levels have not caused two times reduction in Org concentration. As expected from lime and P separate effects, combination of P and lime vs Zn levels reduced Org fractions in all treated soils, too. Among all treatments, single lime had the greatest and significant effect on decreases of Org concentration than P, while P plus lime effect was not significant. As reported in the previous studies, the phosphates could also reduce the Zn mobility, likely through surface precipitation or co-precipitation of apatite or tertiary metal phosphates (Ownby et al. 2005). These newly formed precipitates compound have a lower solubility and bioavailability and they cannot be extracted in the second step of the sequential extraction by the 0.05 M Cu (OAc)₂. Additionally, the formed alkaline environment also favours

Table 3. Concentrations of amorphous sesquioxide Zn in six tropical soil series in incubation experiment receiving various Zn, P and lime levels

Treatments		Tropical Soil Orders and Series					
		-----Entisols-----		-----Ultisols-----			Entisols
		Lubok Iték	Kundur	Tok Yong	Chengai	Tupus	Telemong
		mg Zn kg ⁻¹ soil					
P(0)	Zn0 L0	2.53	1.67	6.28	2.20	0.88	1.9
	Zn0 L1	2.63	1.62	2.10	2.17	2.70	
	Zn5 L0	4.55	3.90	2.23	4.30	2.39	3.627
	Zn5 L1	4.24	3.53	4.63	4.05	3.85	
	Zn10 L0	6.11	5.92	4.48	6.880	3.74	6.075
	Zn10 L1	5.62	5.64	7.13	6.32	6.20	
P(50)	Zn0 L0	2.64	1.75	6.55	2.08	1.04	2.05
	Zn0 L1	2.58	1.61	1.90	2.03	1.34	
	Zn5 L0	4.72	4.06	2.13	4.59	2.22	4.43
	Zn5 L1	4.29	3.12	4.56	3.50	3.99	
	Zn10 L0	6.04	6.31	4.77	6.27	4.01	5.46
	Zn10 L1	5.66	5.67	6.74	6.13	6.70	
P(100)	Zn0 L0	2.70	1.84	7.17	2.36	1.07	2.55
	Zn0 L1	2.57	1.68	2.34	2.30	1.03	
	Zn5 L0	4.90	4.25	4.63	3.65	2.44	4.99
	Zn5 L1	4.31	3.88	4.64	4.61	5.11	
	Zn10 L0	6.62	6.63	5.39	6.13	3.99	6.77
	Zn10 L1	6.00	5.64	7.18	5.60	6.64	

transforming the Org fractions into those bound to oxy-hydroxides, therefore, this Zn fractions are clearly decreased (Zhang et al. 2010). Also, lime is often conducive to stabilizing the Zn phyto-available fractions as well as those bound to ferric oxides, hydroxides and inner sphere surface complex on the soil minerals, and by facilitating of the dissolution of more soil organic matter (Laor et al. 1998; Wang et al. 2001; Zhang et al. 2010). Therefore, the high pH condition facilitates the dissolution of soil organic matter, and under this condition, more Zn to be adsorbed or co-precipitated with Fe oxy-hydroxides (Miretzky and Fernandez-Cirelli 2008).

Amorphous sesquioxide bound Zn fractions

Concentrations of Amorphous sesquioxide Zn in six tropical soil series in incubation experiment receiving various Zn, P and lime and the treatment interactions listed in Tables 3 and 7, respectively. Similar to the WE and Org fractions, Amor Zn concentration, increased more in the Zn treated environments in much larger absolute value. As shown in Table 2, in contrast with the two more previous soluble fractions, the concentration values increased significantly by increasing the added Zn from 2.5 to 5 mg kg⁻¹ and it is more linear than the former ones. The soil pH seemed to be more effective in the elevation of this fraction, because the highest increase was observed in Tepus soil series with the lowest pH(six times) compared to the other neutral or near to neutral soils(two times).

As illustrated in Table 3, although added P increased the Amor Zn fractions concentration and

the increment also positively related to the P levels, but was not significant (Tables 9 and 10). It can be explained by Zn adsorption with hydrous oxides due to low or moderate enrichment of the oxides with phosphate (Benjamin and Bloom 1981; Mandal and Mandal 1990). Phosphorus sorption can increase the surface negative charge or potential (or reduced surface positive charge), or precipitation a new adsorbing plane of Fe phosphate on the surface of the oxides. Sorption process was more active under flooded compare to non-flooded moisture regimes through changing of the crystalline forms of sesquioxides to the amorphous sesquioxides (Hazara et al. 1987), and by increasing of crystalline oxide surface area could facilitated greater P enhanced Zn adsorption (Logeragan et al. 1982).

Similar to P, the added lime also increases the Amor fractions in all soils and the greater increase belongs to Tepus acid sulphate soil. Zhang et al. (2010) indicate that by using lime as an amendment material in soils Zn bound to Fe/ Mn oxides of low crystallinity fraction concentration increased around 2 times. The results of Tables 9 and 10 illustrated the combined effect of phosphate and lime on Amor Zn fraction was not significant. The findings were in line with Nascimento et al. (2007) that showed addition of lime significantly increased this fraction in Ultisols.

Manganese oxide Zn faction

As listed in Table 4 and similar with pervious fractions, the Mn oxide fraction increased by increasing applied Zn levels. In contrary to 2.5 mg

Table 4. Concentrations of manganese oxide Zn in six tropical soil series in incubation experiment receiving various Zn, P and lime levels

Treatments		Tropical Soil Orders and Series					
		-----Entisols-----		-----Ultisols-----		Entisols	
		Lubok Itek	Kundur	Tok Yong	Chengai	Tupus	Telemong
		mgZn kg ⁻¹ soil					
P(0)	Zn0 L0	0.94	0.42	1.19	0.95	0.24	0.38
	Zn0 L1	1.42	0.71	0.41	1.02	0.80	
	Zn5 L0	1.40	1.14	1.57	1.35	0.72	1.09
	Zn5 L1	1.42	1.17	0.75	1.49	1.15	
	Zn10 L0	2.78	1.04	1.35	2.04	1.49	1.03
	Zn10 L1	2.63	1.73	1.42	1.69	1.62	
P(50)	Zn0 L0	1.39	0.67	0.53	1.53	1.03	0.48
	Zn0 L1	1.17	0.37	0.62	0.48	0.80	
	Zn5 L0	1.82	1.24	1.03	1.71	0.43	1.18
	Zn5 L1	1.56	1.56	1.41	1.90	1.45	
	Zn10 L0	1.96	1.65	1.92	2.07	1.14	1.35
	Zn10 L1	2.50	1.51	1.28	2.23	1.54	
P(100)	Zn0 L0	1.06	0.71	0.59	0.85	0.57	0.44
	Zn0 L1	1.50	1.07	0.75	1.75	0.55	
	Zn5 L0	1.70	0.99	1.63	1.71	0.81	1.34
	Zn5 L1	1.84	0.99	0.90	1.50	0.93	
	Zn10 L0	2.33	1.20	1.63	1.65	0.48	1.09
	Zn10 L1	2.15	1.18	1.11	1.56	1.79	

Zn kg⁻¹, the 5 mg kg⁻¹ Zn treatment showed higher increases in the overall concentration of MN, although, two times increasing in applied Zn levels have not caused two times increases in its concentration. The slightly acidic soils (pH 5-5.5)-Lubok Itek, Kundur and Tok Yong soil series - showed the lesser increase in MN fraction concentration under Zn levels in comparison with the Tepus acid sulphate soil series (pH 3.8) due to lower acidic condition of former soil. A sequential extraction procedure findings in major soils (Entisols order) of Indian paddy fields indicated that all applied Zn treatments increased the Mn oxide Zn fraction in all soils studied (Adhikari and Rattan 2007). Almost all of treatments, separately or in combination, significantly increased Mn fraction concentration o, but in a few samples decreasing of MN fraction were recorded. The 100 mg kg⁻¹ added P by dropping down the soil pH inversed the increasing of MN concentration (Cao et al. 2013).

Crystalline sesquioxide Zn fraction

In contrast to Amor fractions, crystalline sesquioxide Zn fraction strongly affected by all three treatments (alone or in combinations) ($p \leq 0.01$) (Table 7). As listed in Table 5 by increasing Zn, lime and P, the Cry concentration increased significantly. Zinc, lime and P treatments were very effective to increase the concentration of Cry, respectively. The acidic soil (pH 3.8)- Tepus soil series comparing with slightly acidic soil (pH, 5-5.5), Lubok Itek, Kunbur and Tok Yong soil series and neutral Telemong soil series showed the highest increase in Cry fraction

(around 2 times) under either Zn level application or P and lime treatments. As noted before, the increase in Cry-Zn content was related to the greater adsorption of Zn by the higher negative charges developed on the surfaces of Fe and Al oxides as a result of P adsorption (Mandal and Mandal 1990).

Residual Zinc fraction

As illustrated in Zn fractions and distribution of the original soils (Non-treated soils) section, around 54 to 82% portion of Zn belonged to residual forms. Furthermore, as presented in WE and Org fractions sections, their concentrations decreased due to P and lime application. Thus, the redistribution of decreased fractions to Res pool and elevation of Res was acceptable. In comparison to the control treatment, lime application as well as P application (singly and in combination) increases the concentration of Res, but the rising rate was not significant at any treatments (Tables 6, and 7). Also, applied Zn treatments had significant effect on Res content at 5% confidence level. Thus, the more added Zn was retained very less in residual fraction (Tables 1 to 8). These findings were in line with the pervious works that suggested the short term Zn application to soils increased more proportions of Zn in the most available forms (We and Org) in comparison with residual and non-residual non- mobile Zn fraction (Ma and Uren 1997; Nascimento et al. 2007; Nyamangara and Mzezewa 1999). It can be concluded that, incubation time or duration after application are an important factors on the Zn availability in the soil and, longer reaction times

Table 5. Concentrations of crystalline sesquioxide Zn in six tropical soil series in incubation experiment receiving various Zn, P and lime levels

Tropical Soil Orders and Series							
		-----Entisols-----		-----Ultisols-----		Entisols	
Treatments		Lubok Itek	Kundur	Tok Yong	Chengai	Tupus	Telemong
mgZn kg ⁻¹ soil							
P(0)	Zn0 L0	3.08	2.58	4.21	4.66	1.10	0.97
	Zn0 L1	3.53	3.86	4.65	5.38	2.52	
	Zn5 L0	3.61	3.90	4.73	5.83	2.517	2.02
	Zn5 L1	3.89	4.49	5.38	6.49	3.277	
	Zn10 L0	4.90	5.09	5.67	6.18	3.443	
	Zn10 L1	5.22	5.51	6.00	6.50	4.387	3.57
P(50)	Zn0 L0	3.28	3.08	5.05	5.250	3.21	1.65
	Zn0 L1	4.06	3.49	5.15	5.75	3.50	
	Zn5 L0	4.08	4.29	5.25	6.58	3.81	3.68
	Zn5 L1	4.49	5.51	5.55	7.13	3.88	
	Zn10 L0	5.38	5.63	6.14	6.58	4.34	4.97
	Zn10 L1	5.69	6.00	6.46	7.83	6.16	
P(100)	Zn0 L0	4.08	3.70	6.14	6.51	3.48	2.38
	Zn0 L1	4.53	4.28	6.46	7.68	4.27	
	Zn5 L0	4.67	5.07	6.64	8.47	5.74	4.89
	Zn5 L1	5.37	6.36	6.93	8.82	6.40	
	Zn10 L0	8.10	5.92	7.00	7.43	5.66	5.43
	Zn10 L1	10.62	6.48	8.03	9.67	6.99	

Table 6. Concentrations of residual Zn in six tropical soil series in incubation experiment receiving various Zn, P and lime levels

Tropical Soil Orders and Series							
		-----Entisols-----		-----Ultisols-----		Entisols	
Treatments		Lubok Itek	Kundur	Tok Yong	Chengai	Tupus	Telemong
mg Zn kg ⁻¹ soil							
P(0)	Zn0 L0	31.30	10.70	38.70	9.03	7.37	5.17
	Zn0 L1	31.63	11.70	40.43	14.23	12.33	
	Zn5 L0	31.43	11.90	39.50	17.77	6.83	5.47
	Zn5 L1	32.63	12.40	36.60	17.97	10.40	
	Zn10 L0	31.90	12.00	39.70	19.60	7.73	6.34
	Zn10 L1	31.00	13.90	41.73	14.27	7.57	
P(50)	Zn0 L0	28.43	11.20	39.83	16.43	13.03	6.40
	Zn0 L1	32.47	12.50	37.93	15.13	10.77	
	Zn5 L0	30.27	13.20	42.93	16.67	23.73	6.10
	Zn5 L1	31.97	13.80	45.97	14.13	8.73	
	Zn10 L0	29.80	14.30	40.80	16.80	11.87	6.60
	Zn10 L1	34.20	15.00	45.27	17.03	7.37	
P(100)	Zn0 L0	26.47	12.60	41.17	18.53	8.97	5.50
	Zn0 L1	31.97	13.30	45.20	16.80	13.10	
	Zn5 L0	28.87	13.50	42.17	16.60	11.80	5.13
	Zn5 L1	31.37	13.90	45.07	19.67	12.30	
	Zn10 L0	30.37	14.40	42.43	20.67	12.77	7.67
	Zn10 L1	31.20	15.34	43.73	22.03	12.53	

transformed more Zn into stable fractions (Barrow 1993; Nascimento et al. 2007).

Total and Summation (SUMF) of Zinc fractions

As listed in Tables 7, these fractions showed the same reactions as pervious fractions for various amounts of added Zn. They increased 4-6% for 2.5 mg kg⁻¹ and 8-14% for 5 mg kg⁻¹ added Zn treatment, averagely. The total Zn concentration increased through Zn application in submerged soils and elevation amount is close to but is not

equal to the summation of untreated and applied Zn concentration at 30 days data collection, while by increasing the incubation time makes it more close to summation (Wijebandara 2007). Phosphorus and lime treatments showed different effects on total and SUMF, when the total Zn significantly ($p \leq 0.01$) (Table 7) affected by P treatments, the SUMF did not affect significantly. Also, the combination of treatments showed no significant effects in almost of the condition.

Table 7. Summary of analysis of variances of zinc fractions in 6 soils series

Sources	df	Mean squares							
		WE	ORG	AMOR	MN	CRY	RES	SUMF	Total
*Combination (Com)	10	1.19**	32.27**	11.08**	3.39**	4.80**	5134.92**	6016.83**	6393.93**
P	2	1.37**	2.209**	3.60**	0.32**	5.05**	46.86*	252.91**	133.44**
Zn	2	5.02**	253.67**	334.98**	17.72**	22.10**	56.12**	3470.19**	4011.60**
Com*P	20	0.09**	0.28 ^{NS}	0.87**	0.10**	0.08*	33.27**	38.58**	36.09**
Com*Zn	20	0.30**	2.30**	10.04**	0.25**	0.92**	16.23 ^{NS}	41.87**	42.66**
P*Zn	4	0.02*	0.57 ^{NS}	0.37 ^{NS}	0.41**	0.75**	3.03 ^{NS}	4.72 ^{NS}	5.88 ^{NS}
Com*P*Zn	40	0.02**	0.22 ^{NS}	0.45*	0.31**	0.06**	15.61*	17.02*	33.17*

Note: Com=combination of soil and lime levels as an one level in ANOVA analysis

CONCLUSIONS

Overall, not only the phyto- available fractions (WE and Org) but also the concentration of the non-residual and non-available fractions such as, Amor, MN and the residual and residual fraction greatly increased by applying Zn sulphate in all soils studied. Moreover, the phyto- available fractions decreased with increasing the P levels and lime application, whereas, the non-residual and non-available fractions increased with the increase of applied P and lime treatments and this trend accelerated by increase of Zn levels. The changes in Zn concentrations vs P and lime levels was similar in all soils, further supporting that the effect of P and lime was responsible for Zn immobilization in all soils. In addition, sequential fractionation of Zn vs Zn, P and lime application showed that a substantial portion of the applied Zn had reverted to plant-unavailable fractions. Thus, our study helped to confirm the knowledge concerning the controlling mechanisms of Zn availability under high rates of P and lime application in agricultural fields. It also showed that Org fractions play the most important role in adding Zn to the plant-available pool. However, the attention should be paid to the relation of the results of this study with plant morphology, growth stages and Zn uptake in future works.

ACKNOWLEDGMENTS

This research was financially supported by Long-term Research Grant Scheme (LRGS 5525001), Food Security Project, under the Ministry of Higher Education Malaysia (MOHE) and to Universiti Putra Malaysia for providing laboratory and other research facilities.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

ORCID

Shahram Mahmoud Soltani: <https://orcid.org/0000-0002-1300-9536>

Mohamed Musa Hanafi: <https://orcid.org/0000-0003-1898-6819>

Abdul Wahid Samsuri: <https://orcid.org/0000-0002-5450-0604>

Sharifah Kharidah: <https://orcid.org/0000-0002-9908-1503>

REFERENCES

- Adhikari T. Rattan R.K. (2007) Distribution of Zn fractions in some major soils of India and impact on nutrition of rice. *Communication in soil science and plant analysis*, 38:2779–2798.
- Alloway B.J. (2009) Soil factors associated with zinc deficiency in crops and humans. *Environmental geochemistry and health*, 31(5):537-48.
- Barrow N.J. (1993) Mechanisms of reaction of zinc with soil and soil components. In *Zinc in Soils and Plants*; Robson, A.D. (ed.) Kluwer Academic Publishers, Dordrecht, Netherlands.
- Cao X. Liang Y. Zhao L. Le H. (2013) Mobility of Pb, Cu, and Zn in the phosphorus-amended contaminated soils under simulated landfill and rainfall conditions. *Environmental Science and Pollution Research*, 20:5913-5921.
- Dobermann A. Fairhurst T. H. (2000) Nutrient disorders and nutrient management Potash and Phosphate Institute of Canada and International Rice Research Institute, Singapore.
- Fageria N.K. Stone L.F. (2008) Micronutrient deficiency problems in South America. In *Micronutrient deficiencies in global crop production*, ed. B. J. Alloway, 247-268 Springer, New York.
- Hazara G.C. Mandal B. Mandal L.N. (1987) Distribution of zinc fractions and their transformation in submerged rice soils. *Plant and Soil* 104 175-181.
- Johnson-Beebout S.E. Sarah E. Lauren J. Duxbury J. (2009) Immobilization of Zinc Fertilizer in Flooded Soils Monitored by Adapted DTPA Soil Test. *Communication in soil science and plant analysis*, 40:1842-1861.
- Kiekens L. (1995) Zink. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils*, 2nd ed. Blackie Academic & Professional, Glasgow, UK.
- Laor Y. Farmer W.J. Aochi Y. Strom P.F. (1998) Phenanthrene binding and adsorption to

- dissolved and to mineral-associated humic acid. *Water Research*, 32(6):1923-1931.
- Logeragan J.K. Grunes D.L. Welch R.M. et al. (1982) Phosphorus accumulation and toxicity in leaves in relation to zinc supply. *Soil Science Society of America Journal*, 46:345-352.
- Ma Y.B. Uren N.C. (1997) The effects of temperature, time, and cycles of drying and rewetting on the extractability of zinc added to a calcareous soil. *Geoderma*, 75:89 - 97.
- Mandal B. Mandal L.N. (1990) Effect of phosphorus application on transformation of zinc fractions in soil and on the zinc nutrition of low land rice. *Plant Soil*, 121:115-123.
- Miretzky P. Fernandez-Cirelli A. (2008) Phosphates for Pb immobilization in soils: a review. *Environmental Chemistry Letters*, 6:121- 133.
- Nascimento C.W.A.D. de Melo E.E.C., Nascimento R.S.D.M.P., Leite P.V.V. (2007) Effect of Liming on the Plant Availability and Distribution of Zinc and Copper among Soil Fractions. *Communications in Soil Science and Plant Analysis*, 38:545-560.
- Nyamangara J. Mzezewa J. (1999) The effect of long-term sewage sludge application on Zn, Cu, Ni and Pb levels in a clay loam soil under pasture grass in Zimbabwe. *Agriculture, Ecosystems & Environment*, 73:199 -204.
- Ownby D.R. Galvan K.A. Lydy M.J. (2005) Lead and zinc bioavailability to *Eisenia fetida* after phosphorus amendment to repository soils. *Environmental Pollution*, 136:315-321.
- Rupa T.R. Srinivasa Rao C. Subba Rao A. Singh M. (2003) Effects of farmyard manure and phosphorus on zinc transformations and phyto-availability in two alfisols of India. *Bioresource Technology*, 87:279-288.
- Shuman L.M. (1985) Fractionation method for soil micronutrients. *Soil Sci*, 140:11-22.
- Shuman L.M. (1998) Micronutrient fertilizers. *Journal of Crop Production*, 2:165-195.
- Singh B. Natesan S.K.A. Singh B.K. Usha K. (2005) Improving zinc efficiency of cereals under zinc deficiency. *Curr Science*, 88(36-44).
- Vondráčková S. Hejzman M. Tlustos P. Szakova J. (2013) Effect of quick lime and dolomite application on mobility of elements (Cd, Pb, As, Fe, and Mn) in contaminated soils. *Polish Journal of Environmental Studies*, 22(2):577-589.
- Wang Y.M. Chen T.C. Yeh K.J. Shue M.F. (2001) Stabilization of an elevated heavy metal contaminated site. *Journal of Hazardous Materials*, 88(1):63-74.
- Wijebandara D.M.D.I. (2007) Studies on distribution and transformation of soil zinc and response of rice to nutrients in traditional and system of rice intensification (SRI) methods of cultivation. DHARWAD University of agricultural sciences.
- Zhang W.H. Huang H. Tan F.F. Wang H. Qiu R.L. (2010) Influence of EDTA-washing on the species and mobility of heavy metals residual in soils. *Journal of Hazardous Materials*, 173(1-3):369-376.