https://doi.org/10.56093/ijas.v90i11.108582

Indian Journal of Agricultural Sciences **90** (11): 2156–60, November 2020/Article

Zinc sorption characteristics and release kinetics from soils with long-term zinc and phosphorus application

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Received: 28 January 2020; Accepted: 12 March 2020

ABSTRACT

We investigated the effect of long-term phosphorus (P) and zinc (Zn) application in three soils (Soil-I, Soil-II and Soil-III) with differential P content on Zn sorption and release kinetics to understand the underlying mechanism controlling Zn sorption-desorption reactions. Zn sorption was highest in soil-III (54.4-96.4% of added Zn), and was the lowest in soil-I (44.1-94.3% of added Zn) in no-P applied soils. In soil-III, 60.6-97.6% of applied Zn gets sorbed on soil colloidal complex with P application at 100 mg P kg^{-1}, which was 1.2-11.4% higher at differential levels of Zn application. Results showed that Langmuir sorption maxima (b) and Freundlich's adsorptive capacity (Y) were lowest for soil-I without P application and was the highest in soil-III with P application. These results suggests that soil-III with P application at 100 mg P kg^{-1} with highest Zn sorption had the lowest Zn release capacity. Further, these results showed that Elovich equation best described the kinetics of Zn release from three soils with highest value of coefficient of determination (R^2=0.93-0.98*, p<0.05) and lowest standard error (S.E.= 0.172-0.256).

Key words: Elovich's equation, Freundlich adsorption isotherm, Langmuir adsorption isotherm, Parabolic diffusion equation, Power function equation

Phosphorus (P) and zinc (Zn) are essential nutrients and their deficiency has been ascribed to their mutual antagonism occurring in plant-soil system (Soltanpour 1979). Zinc sorption increased due to the presence of phosphate ions that could be ascribed to the formation of P–Zn complex on organic and inorganic colloid surfaces. Zinc sorption increased with fertilizer P application (Saeed and Fox 1979), due to increased negative charges on the surface of iron (Fe) and aluminium (Al)-oxides due to P sorption on their surfaces (Bolland *et al.* 1977). Zn solubility is decreased by the presence of phosphate ions in soil solution (Thakur *et al.* 2006). Perej-Novo *et al.* (2011) showed that phosphates, mainly at high concentrations can reduce solubility and availability of Zn, and prevent its mobility to water bodies. The P-Zn complex formation on soil colloidal surface has been due to strong chemical bond and electrical attraction at outer surface sites inducing non-specific Zn sorption (Jurinak and Bauer 1956). Replacement of O^{2-} and OH^- by Zn^{2+} in the interlayer crystal structure of different oxides as well as hydroxides causes its specific sorption (Kalbasi *et al.* 1978). Various factors like soil pH, amount of clay, soil organic matter, carbonate and bicarbonate content and amount of applied Zn controlled Zn–sorption (Arias *et al.* 2005; Perez-Novo *et al.* 2008). The negative correlation between extractable Zn and cation exchange capacity (CEC), calcium carbonate ($CaCO_3$) and soluble Ca and Mg has been reported (Al-Hadethi *et al.* 2003). Adsorption and precipitation of minerals on oxides of Fe and Mn also influenced the solubility of Zn and also their interactions (Wang and Harrell 2005). Zinc sorption-desorption reactions on soil colloid complex controls Zn concentration in soil solution and availability to crop. Phosphorus sorption on Fe and Al-oxides surface enhanced negative charge and increases Zn sorption (Bolland *et al.* 1977). The adsorption-desorption reactions at various pH and Zn contents mainly determined Zn concentration in equilibrium solution with clay fractions of soils (Singh *et al.* 2008). The studies on Zn sorption in soils with differential P content and P and Zn application are scarce. The present study was therefore, conducted to investigate the effect of P and Zn application in soils with differential P content on Zn sorption and release kinetics, so as to understand the underlying mechanism controlling Zn sorption-desorption reactions.

MATERIALS AND METHODS

Collection of soil samples and analysis: The collection

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of soil samples were done from the ongoing long-term field experiment on maize-wheat cropping sequence in progress since 1971 at research farm of Department of Soil Science, Punjab Agricultural University, Ludhiana (30°56'N, 75°52'E and 274 m above the sea level). Surface (0-15 cm) soil samples were collected using core sampler (inner diameter 7.2 cm). The soil samples were air dried, ground in wooden pastel and mortar, sieved through 2.0 mm stainless steel sieves and then stored in plastic containers with tight lids until analysis. Soil reaction (pH) was measured in 1:2 soil: water suspension using a pH meter fitted with a calomel glass electrode, followed by determination of concentration of soluble salts measured as electrical conductivity (EC) in the same extract, once the supernatant solution is clear with help of conductivity bridge. Soil organic carbon was determined using wet digestion method using diphenylamine indicator (Walkley and Black 1934). Available-N in soil samples was determined using distillation method. Available-P concentration was determined using 0.5 M $NaHCO_3$ (pH=8.5) (Olsen and Watanabe 1957) and available-K by flame photometer (Jackson 1965). The concentration of micro-nutrients (Zn, Cu, Fe and Mn) was extracted by DTPA method (Lindsay and Norwell 1978). Important soil physical and chemical properties of selected soils are presented in Table 1.

Zn sorption study: A 2 g soil sample was equilibrated with 20 ml 0.01M, $NaNO_3$ solution containing 5, 10, 20, 40, 60, 80, 100 and 200 mg Zn L^{-1} (added through zinc nitrate) and 0 and 100 mg L^{-1} P (di-hydrogen sodium mono phosphate) in 50 ml centrifuge tubes for 24 h, followed by centrifugation for 10 minutes at 4000 rpm. After filtration through Whatman No. 1 filter paper, concentration of Zn was determined on atomic absorption spectrophotometer. Amount of Zn sorbed was calculated by difference in Zn added and in equilibrium solution using Eq. 1.

Table 1 Important soil physical and chemical characteristics of the selected soils

Characteristics	Soil-I	Soil-II	Soil-III
pH (1:2)	7.28	7.21	7.25
EC (1:2, dS m^{-1})	0.15	0.14	0.15
Organic Carbon (%)	0.30	0.42	0.38
Available N (mg kg^{-1})	50.4	56.5	48.4
Available P (mg kg^{-1})	14.6	25.8	9.2
Available K (mg kg^{-1})	41.1	63.3	39.6
Fe (mg kg^{-1})	12.3	6.57	12.3
Cu (mg kg^{-1})	1.64	2.27	1.33
Zn (mg kg^{-1})	0.97	1.00	1.27
Mn (mg kg^{-1})	7.4	7.6	9.6
Sand (%)	76.5	76.4	76.5
Silt (%)	15.4	15.5	15.5
Clay (%)	8.1	8.1	8.0
Soil texture	Sandy loam	Sandy loam	Sandy loam

$$x/m = v/g\ (Ci-Ce) \quad \text{(Eq. 1)}$$

where, 'x/m'=amount of Zn sorbed (mg Zn kg^{-1} soil), 'v'=equilibrium solution, 'g'=weight of soil (g), 'Ci'=Zn concentration in added solution (mg L^{-1}) and 'Ce'=Zn concentration in equilibrium solution. The sorption data were analyzed using Langmuir (Eq. 2), Freundlich (Eq. 3) and Dubinin Raduhkevitch (D-R) adsorption isotherms (Eq. 4).

$$C/x/m = 1/Kb + C/b \quad \text{(Eq. 2)}$$

where, 'C'=equilibrium Zn concentration (mg Zn L^{-1}), 'x/m'=quantity of Zn adsorbed per unit weight of soil (mg kg^{-1} soil), 'K'=a constant which tells about bonding energy (L mg^{-1}) and 'b'=adsorption maxima (mg kg^{-1} soil).

$$x/m = YC^n \quad \text{(Eq. 3)}$$

where, 'x/m'=amount of Zn adsorbed per unit weight of soil (mg kg^{-1} soil), 'C'=equilibrium Zn concentration (mg L^{-1}) and 'Y' and 'n' are constants. A linear plot of 'log x/m' versus 'log C' leads to 'Y' and 'n' from the intercept and slope, respectively.

$$lnq_e = lnq_m - \beta\varepsilon^2 \quad \text{(Eq. 4)}$$

where, 'q_e'=amount of adsorbate adsorbed per unit weight of adsorbent (mg kg^{-1}), 'q_m'=maximum adsorption capacity (mg kg^{-1}), 'β'=constant related to adsorption energy and 'ε'=Polanyi potential (kJ^2 mol^{-2}).

Kinetic of Zn release: Zn release from soil surfaces was explained by different models. Least square regression technique was applied to test the predictive performance of different models for explaining the Zn release phenomenon and its kinetics (Singh and Singh 2016). The amount of Zn release was estimated for different time (t) periods and Zn release data were interpreted using four kinetics models viz. first order (Eq. 5), power function (Eq. 6), parabolic diffusion function (Eq. 7) and Elovich's equation (Eq. 8).

$$ln\ (q_o-q) = a - b\ t \quad \text{(Eq. 5)}$$

$$lnq = ln\ a + b\ ln\ t \quad \text{(Eq. 6)}$$

$$q = a + b\ t^{1/2} \quad \text{(Eq. 7)}$$

$$q = a + b\ ln\ t \quad \text{(Eq. 8)}$$

where, 'q'=amount of released Zn^{2+}, 't'=time of release, 'q_o'=maximum Zn^{2+} released, 'a' and 'b'=constants.

Statistical analysis: Statistical analysis was performed with SPSS for windows 22.0 (SPSS Inc. Chicago, USA). Least square regression technique was applied to test the predictive performance of different kinetics models for describing the Zn release from soils. The coefficients of determination (R^2) and standard error of estimate (SE) were calculated for different models.

RESULTS AND DISCUSSION

Effect of P and Zn application on Zn sorption: Table 2 illustrates the Zn sorption pattern of three soils. The results showed that Zn sorption was highest in soil-III (54.4-96.4% of added Zn) and was the lowest in soil-I (44.1-94.3% of added Zn) in no-P applied soils (Table 2). Soil application

Table 2 Amount of Zn sorbed (mg kg^{-1} soil) in different soils treated with different concentrations of Zn and P at 25°C

Zn added (mg kg^{-1})	Equilibrium concentration (mg L^{-1})	Amount of Zn adsorbed (mg kg^{-1} soil)	% Zn adsorbed	Equilibrium concentration (mg L^{-1})	Amount of Zn adsorbed (mg kg^{-1} soil)	% Zn adsorbed
	0 mg kg^{-1} P			100 mg kg^{-1} P		
Soil-I						
2.5	0.14	23.6	94.3	0.12	23.8	95.2
5.0	0.28	47.2	94.5	0.23	47.7	95.4
10.0	1.12	88.8	88.8	0.97	90.3	90.3
20.0	3.87	161.3	80.7	3.14	168.6	84.3
40.0	13.4	265.7	66.4	11.4	285.7	71.4
80.0	36.3	436.8	54.6	31.6	483.6	60.5
160.0	89.4	705.8	44.1	76.5	834.7	52.2
Soil-II						
2.5	0.10	24.0	95.9	0.07	24.3	97.2
5.0	0.21	47.9	95.7	0.20	48.0	96.0
10.0	0.91	90.9	90.9	0.82	91.8	91.8
20.0	3.18	168.2	84.1	2.76	172.4	86.2
40.0	9.31	306.8	76.7	7.43	325.7	81.4
80.0	32.1	479.2	59.9	28.0	519.7	65.0
160.0	78.0	819.8	51.2	69.4	905.7	56.6
Soil-III						
2.5	0.09	24.1	96.4	0.06	24.4	97.6
5.0	0.20	48.0	95.9	0.17	48.3	96.5
10.0	0.87	91.3	91.3	0.64	93.6	93.6
20.0	2.88	171.2	85.6	2.47	175.4	87.7
40.0	8.11	318.9	79.7	7.04	329.6	82.4
80.0	29.0	509.6	63.7	24.6	554.4	69.3
160.0	73.0	869.8	54.4	63.1	969.1	60.6

of 100 mg P kg^{-1} resulted in considerable increase in Zn sorption in all three soils. In soil-III, 60.6-97.6% of applied Zn gets sorbed on soil colloidal complex with P application at 100 mg P kg^{-1}, which was 1.2-11.4% higher at differential levels of Zn application. Zn sorption pattern of three soils was similar, but with lower magnitude in soil-I and soil-II. The highest Zn sorption in soil-III with P application at 100 mg L^{-1} was due to higher P content and increased negative sites for Zn sorption. Increased P concentration leads to increased Zn sorption in soils (Saeed and Fox 1979; Rupa and Tomar 1999).

Langmuir adsorption isotherms: Langmuir's sorption maxima (b=1000 mg kg^{-1}) was highest for soil-III with P application and lowest for soil-II without P application (769 mg kg^{-1}) (Table 3). Results showed that Langmuir sorption maxima increased with P application, compared with no-P application. The magnitude of this increase was however higher for soil-III, compared with other two soils. The bonding energy (k) ranged from 0.079 and 0.112 l kg^{-1}, and was higher for soil-III with P application. Bonding energy of Zn in the three soils increased by an average of ~2.7% with P application, compared with no-P application in soil. The Freundlich's adsorptive capacity (Y) was lowest in soil-I without P application and was the highest in soil-III with P application. Freundlich's adsorptive capacity increased by 12.8-16.1% in three soils with P application, compared with no-P application. The D-R isotherms showed that all soils had 'E' value less than 8 kJ mol^{-1}, indicating occurrence of physical sorption of Zn. Soil-III with P application had the highest 'E' (2.88 kJ mol^{-1}), while soil-I had the lowest 'E' value (2.23 kJ mol^{-1}). The coefficient of determination (R^2) for D-R isotherm ranged between 0.69 and 0.74. The soil-III with P application had the highest adsorption capacity 'q_m' (319.6 mg kg^{-1}), while the soil-I had the lowest value (272.1 mg kg^{-1}). The results were consistent with (Kurdi and Doner 1983; Bolland *et al.* 1977) who observed that increased negative charge sites resulted in more adsorption of zinc.

Kinetics of Zn release: Zn release was higher from soil-I without P application and was the lowest from the soil having high Zn sorption capacity. These results suggests that soil-III with P application at 100 mg P kg^{-1} with highest Zn sorption had the lowest Zn release capacity. Four different kinetics models viz. first order (Fig 1a), power function (Fig 1b), Elovich's equations (Fig 1c) and parabolic diffusion function (Fig 1d) were used to study the Zn release rate

Table 3 Estimated D-R parameters for Zn sorption and values of extent of sorption (n), adsorptive capacity (Y), sorption maxima (b), bonding energy (K) and co-efficient of determination (R^2) of two different sorption isotherms for three soils with and without P application

Treatment	D-R parameters for Zn sorption (at 298 K)				Freundlich Isotherm			Langmuir Isotherm		
	q_m (mg kg^{-1})	$\beta \times 10^{-6}$ ($mol^2k^{-1}J^{-2}$)	E (KJ mol^{-1})	R^2	n (mg kg^{-1})	Y (L mg^{-1})	R^2	b (mg kg^{-1})	K (L mg^{-1})	R^2
Soil-I	272.1	1×10^{-7}	2.23	0.74	0.50	76.7	0.99	769	0.079	0.93
Soil-I +P	298.6	9×10^{-8}	2.35	0.74	0.52	86.5	0.99	909	0.081	0.90
Soil-II	298. 6	8×10^{-8}	2.50	0.75	0.51	91.0	0.99	893	0.104	0.92
Soil-II +P	301.9	6×10^{-8}	2.88	0.69	0.51	102.8	0.99	1000	0.107	0.92
Soil-III	307.0	7×10^{-8}	2.67	0.72	0.52	97.1	0.99	909	0.109	0.93
Soil-III +P	319.6	6×10^{-8}	2.88	0.70	0.52	112.5	0.99	1000	0.112	0.92

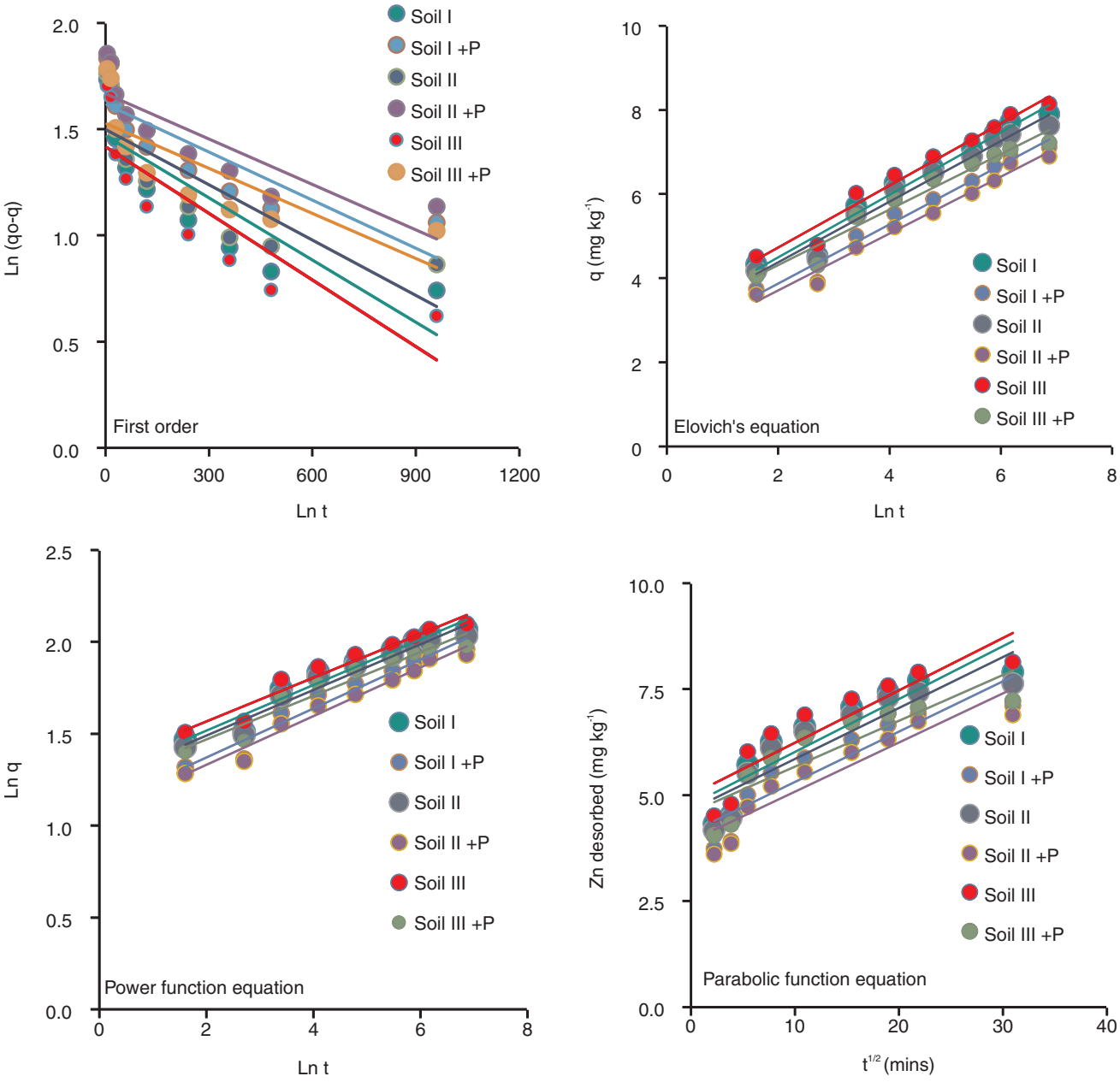

Fig 1 Time dependent Zn release from different soils with and without long-term P application illustrated through different empirical models.

Table 4 Parameters of different kinetics equations used to describe Zn release kinetics from three soils with and without P application

Treatments	First order equation		Power function equation		Parabolic diffusion equation		Elovich equation	
	a ($\mu g\ g^{-1}$)	b ($\mu g\ g^{-1}$)	a ($\mu g\ g^{-1}$)	b ($\mu g\ ml^{-1}$)	a ($\mu g\ g^{-1}\ h^{-1/2}$)	b ($\mu g\ ml^{-1}$)	a ($\mu g\ g^{-1}\ h^{-1}$)	b ($\mu g\ g^{-1}$)
Soil-I	1.41	0.001	3.77	0.119	5.00	0.123	3.26	0.73
Soil-I +P	1.53	0.001	3.42	0.118	4.59	0.108	2.99	0.66
Soil-II	1.47	0.001	3.55	0.124	4.76	0.125	3.01	0.74
Soil-II +P	1.62	0.001	3.02	0.133	4.12	0.118	2.46	0.70
Soil-III	1.50	0.001	3.47	0.124	4.65	0.120	2.93	0.72
Soil-III +P	1.67	0.001	2.91	0.132	3.92	0.116	2.35	0.67

kinetics (Table 4). Results showed that Elovich equation best described the kinetics of Zn release from three soils with highest value of coefficient of determination (R^2=0.93-0.98*, *p<0.05*) and lowest standard error (SE = 0.172-0.256). These results are in conformity to those reported earlier showing the superiority of Elovich equation over others (Singh and Singh 2011; Singh and Singh 2016). Rupa and Tomar (1999) also reported that Elovich equation was best in explaining Zn release kinetics data affected by P application. The power function constant 'a' that varied between 2.91 and 3.77 $\mu g\ g^{-1}$, and was the highest in soil-I without P application and decreased by 22.8% in soil-III with P application. Elovich's constant 'a' and 'b; also exhibited a decrease with increased Zn sorption in the soils.

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