

Copper release kinetics: Effect of two extractants and wheat (*Triticum aestivum* L.) rhizosphere

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ABSTRACT

The greenhouse experiment was performed to determine Cu release characteristics in the bulk and the rhizosphere of some calcareous soils using rhizobox. The kinetics of Cu release in the bulk and the rhizosphere soils were determined by successive extraction with diethylenetriaminepentaacetic acid-triethanolamine (DTPA-TEA) and 10 mmol/L citric acid in a period of 1 to 504 h at $25 \pm 1^\circ\text{C}$. The results of kinetics study showed that Cu extracted using DTPA-TEA in the rhizosphere soils was significantly ($P < 0.01$) lower than the bulk soils, while Cu extracted using citric acid in the rhizosphere soils was significantly ($P < 0.01$) higher than the bulk soils. The mean of released Cu after 504 h using DTPA-TEA were 8.59 and 7.46 mg/kg in the bulk and the rhizosphere soils, respectively. The mean release of Cu after 504 h using citric acid was 14.73 and 16.05 mg/kg in the bulk and the rhizosphere soils, respectively. Release kinetics of Cu in two extractants conformed fairly well to parabolic diffusion, power function, and first order equations. The results of correlation analysis illustrated that a significant correlation between Cu desorption after 504 h with citric acid and Cu concentration in wheat was found ($r = 0.96$ and $r = 0.90$ in the rhizosphere and the bulk soils, respectively, $P < 0.01$). Therefore, application of 10 mmol/L citric acid extractant would be recommended in the future study on the kinetics of release of Cu in calcareous soils.

Keywords: citric acid; DTPA-TEA; plant indices; successive extraction

Copper (Cu) in plant was derived from soil matrix; however, the bioavailability and the transfer dynamics of Cu in soil-plant system can be poorly predicted by the total content (Achiba et al. 2010). Bioavailability of Cu in soils is controlled by removal of Cu from the soil solution by sorption onto soil particles, release of the Cu from the soil particles to the soil solution (release), and precipitation-dissolution of the Cu as an independent phase in the soil matrix (Sparks 2003). Singh et al. (1994) stated that release of Cu from exchange complex and its release from organic matter, crystalline minerals and other metastable compounds to the solution phase are processes that determine the relative contribution of soil Cu to plant nutrition. Copper uptake by plants is a continuous process and depends largely on the replenishment of soil solution Cu from relatively non-labile Cu forms. Therefore, a release rate of soil Cu is an important parameter of Cu supplying capacity of soils. Although it is important to study kinetics of Cu release from soils to identify soil Cu buffering capacity, little attention was paid to Cu release rate studies (Elkhatib et al. 2007).

The rhizosphere is a biologically active zone in soil where complex interactions occur among plant roots, soil particles and microbes (Puglisi et al. 2008). Plants have the ability to transform metal fractions for easier uptake through root exudation or pH changes in the rhizosphere (Wang et al. 2002). The soil properties, metal fractions, plant species and especially soil-plant interactions determine the bioavailability of metals in soils. Recent investigations focused on the rhizosphere modification in relation to plant nutrient uptake (Zhang et al. 2004). The anions of low-molecular-weight organic acids can form soluble complexes with metal cation, and modify the fixation of metals by soil organic matter, oxides, clays, and enhance their release (Chen et al. 2003). Little information about the effect of processes of rhizosphere on release of Cu is available. In some researches, kinetics of Cu release in soils was studied using chemical extractants such as diethylenetriaminepentaacetic acid (DTPA) (Reyhanitabar and Karimian 2008) and organic ligands (Elkhatib et al. 2007). Elkhatib et al. (2007) investigated Cu release characteristics from three contaminated soils using organic acids

such as citric acid, malic acid, and succinic acid. They stated that Elovich and parabolic diffusion models were used to describe release of Cu from three studied soils.

Comparison of DTPA and citric acid extractants in Cu release from the rhizosphere soils of calcareous soils has not been studied. In most researches, Cu release kinetics using artificial chelating such as DTPA is studied, whereas plants secrete organic acids such as citric acid. Therefore, the objectives of the present study were (i) to evaluate the Cu release using DTPA and citric acid from bulk and rhizosphere soils; (ii) to evaluate different mathematical models for describing Cu release, and (iii) to examine the relationship of Cu release after 504 h with plant indices.

MATERIAL AND METHODS

Physicochemical properties of soils. Ten soil samples used in this study were collected from the surface soils (0–30 cm) of Chaharmahal-va-Bakhtiari Province, in central Iran. The soil samples were air-dried and ground to pass through a 2 mm sieve for laboratory analysis. Particle size distribution, electrical conductivity (EC), pH, organic carbon (OC), equivalent calcium carbonate and cation exchange capacity were determined. Total and available Cu were determined using 4 mol/L HNO₃ (Sposito et al. 1982) and DTPA-TEA (Lindsay and Norvell 1978), respectively.

Greenhouse experiment. In this study, a home-made rhizobox (Wang et al. 2002) was used to plant wheat. The rhizobox was divided into three sections: a central zone or rhizosphere zone (30 mm in length), which was surrounded by nylon cloth (300 mesh), and left and right non-rhizosphere zones (bulk soils) (50 mm in length). 4.5 kg soils were put in rhizobox. To ensure a sufficient supply of nitrogen, potassium, and iron, 100 mg/kg N as (NH₄)₂CO₃, 100 mg/kg K as K₂SO₄ and 5 mg/kg Fe as Fe-EDDHA were added to soils. A total of 3 seeds were sown per rhizosphere zone. Plants were grown under greenhouse conditions. Plants were harvested 60 days after germination. The rhizobox was then dismantled. The roots were found completely in the central zone. The soils taken from rhizosphere soil zone and bulk soil zones of the left and right were mixed separately for further analysis. Roots and shoots were washed out with tap water to remove soil. Both the roots and shoots were rinsed with deionized water, and then dried at 60°C for 48 h, and the dried sample was finely ground for analysis.

Copper release kinetics. Kinetics of Cu release was studied by successive extraction with DTPA-TEA and 10 mmol/L citric acid solutions. Seven drops of toluene were added to each extractant to inhibit microbial activity. Two grams of the bulk and rhizosphere soils, in triplicate, suspended in 20 mL of each solution were equilibrated at 25 ± 1°C for 1, 8, 24, 48, 72, 96, 120, 144, 168, 336 and 504 h by shaking for 15 min before incubation and 15 min before the suspensions were centrifuged. Cu release with time was fitted by using different equations (Table 1).

Five models were tested by the least-square regression analysis to determine which equation described better the Cu release from the soils. Standard error of the estimate (SE) was calculated by:

$$SE = \left[\frac{\sum (Cu - Cu^*)^2}{(n-2)} \right]^{0.5}$$

Where: Cu and Cu* – the measured and calculated amounts of Cu in soil at time t, respectively; n – the number of data points evaluated.

Statistical analysis. The significant differences of amount of released Cu between the rhizosphere and the bulk soils were determined by using paired-samples *t*-test. Also, the significant differences of amounts of released Cu in DTPA-TEA and citric acid solutions were determined by using independent-samples *t*-test. The Pearson's correlation between Cu release after 504 h and plant indices were determined.

RESULTS AND DISCUSSION

Properties of the soils are presented in Table 2. These results show that there was a wide variation in the selected chemical and physical properties

Table 1. Kinetic models used in this study (Hosseinpur et al. 2012)

Kinetic equation	Expression form ^a
Zero-order reaction	(Cu ₀ – Cu _t) = a – K ₀ t
First-order reaction	ln (Cu ₀ – Cu _t) = a – K ₁ t
Parabolic diffusion	Cu _t = a + R t ^{0.5}
Power function	ln Cu _t = ln a + b lnt
Simplified Elovich	Cu _t = a + 1/β lnt

^aCu₀ – amount of Cu (mg/kg) release at 504 h; Cu_t – amount of Cu (mg/kg) release at time t (h) and a and K₀, K₁, R, b and 1/β are constants

Table 2. Selected properties of soils

Soil No.	Clay	Silt	CaCO ₃ (g/kg)	Organic carbon	pH	EC (dS/m)	CEC (cmol _c /kg)	Available Cu (mg/kg)	Total Cu (mg/kg)
1	550	400	287	7.2	7.8	0.13	20.9	1.18	24
2	530	440	356	3.0	8.1	0.13	19.3	1.50	23
3	490	390	294	5.1	7.9	0.12	22.5	0.86	19
4	460	420	264	7.1	7.8	0.14	21.6	1.12	18
5	410	420	322	5.4	8.1	0.13	16.0	1.07	18
6	370	440	325	8.0	7.6	0.16	15.6	0.85	17
7	250	330	410	4.7	7.7	0.21	11.5	0.54	15
8	380	550	231	11.9	8.1	0.24	17.9	1.30	21
9	480	460	113	11.6	7.8	0.25	18.5	0.89	21
10	490	460	148	9.7	7.9	0.23	17.9	1.41	25

of the studied soils. Clay contents in all studied soils ranged from 250 to 550 g/kg. The soils were alkaline and low in EC and organic matter. The equivalent calcium carbonate contents varied from 113 to 410 g/kg. Available Cu ranged from 0.54 to 1.50 mg/kg. Total Cu ranged from 15 to 25 mg/kg in the studied soils.

The results of comparison of dissolved organic carbon and microbial biomass carbon between the rhizosphere soils and the bulk soils illustrated that dissolve organic carbon (DOC) and microbial biomass carbon in the rhizosphere soils in comparison to the bulk soils were increased significantly (data not shown). DOC stays dissolved in the soil solution under natural conditions and it was found that it might be responsible for the dissolution equilibria of metals in the soil especially at neutral pH values. DOC also has a unique role in the chemistry of heavy metals in soils; it reduces metal adsorption onto soil surfaces by both competing more effectively for the free metal ion and forming soluble organo-metallic complexes or being preferentially adsorbed onto the surfaces instead of the metals it is competing with (Guisquiani et al. 1998).

The pattern of successive extraction of Cu from both the bulk and the rhizosphere soils No. 1 in DTPA-TEA and citric acid solutions are presented in Figure 1. Also, other soils showed the same trend similar to soil No. 1. Amounts of released Cu in DTPA-TEA and citric acid solution from both the bulk and the rhizosphere soils are shown in Table 3. The results of this table showed that Cu extracted using citric acid in the rhizosphere soils were significantly ($P < 0.01$) higher than the bulk soils, while Cu extracted using DTPA-TEA in the rhizosphere soils were significantly ($P < 0.01$) lower than the bulk soils.

Kinetics release of Cu in soils especially in the rhizosphere that is important environmental zone with quite different chemical and biological properties gives information about potential of soils to supplying Cu for plant uptake. The different chemical and biological conditions of the rhizosphere soils with respect to the bulk soils can be changed with Cu fractions and therefore release of Cu (Tao et al. 2003).

The results of Table 3 showed that DTPA-TEA could extract 25 to 47% of total Cu in the rhizosphere soils and 31 to 47% of total Cu in the bulk soils, while citric acid could extract 64 to 93% of total Cu in the rhizosphere soils and 61 to 84% of total Cu in the bulk soils. The results of kinetics study showed that the amount of Cu release using citric acid from both the bulk and the rhizosphere soils increased with respect to the amount of Cu release using DTPA-TEA. On average, citric acid extracted 97% more Cu from the bulk soils and 87% more Cu from the rhizosphere soils than DTPA-

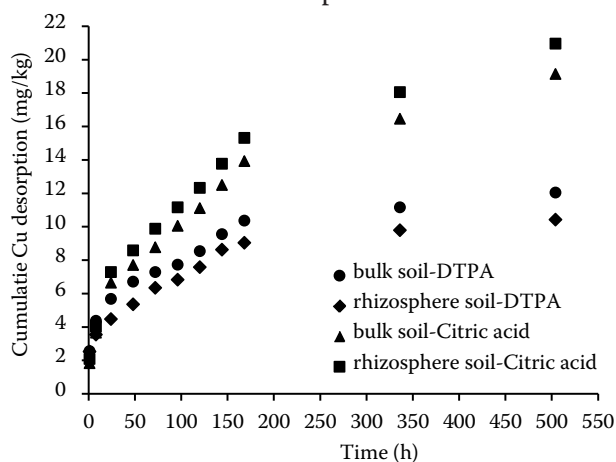


Figure 1. Cumulative amount of Cu release with time in soil No. 1 by successive extractions with diethylenetriaminepentaacetic acid-triethanolamine (DTPA-TEA) and citric acid solutions

Table 3. Concentration of Cu (mg/kg) release in the studied soils

Soil No.	DTPA-TEA		Citric acid	
	rhizosphere	bulk	rhizosphere	bulk
1	8.18(31)	10.44(39)	18.81(71)	16.82(63)
2	7.15(29)	7.77(31)	17.14(70)	15.43(61)
3	4.88(25)	6.42(33)	15.84(83)	14.40(73)
4	7.02(35)	7.45(36)	15.79(79)	15.05(73)
5	5.80(30)	6.38(32)	15.30(79)	13.77(70)
6	5.84(33)	7.74(43)	14.78(83)	14.00(77)
7	6.01(38)	7.08(47)	14.76(93)	12.79(84)
8	9.93(47)	10.32(47)	15.60(74)	14.28(65)
9	9.04(43)	10.26(46)	15.90(76)	14.80(67)
10	10.66(41)	12.08(46)	16.60(64)	15.93(61)
Mean	7.46(35) ^b	8.59(40) ^a	16.05(76) ^a	14.73(68) ^b

Numbers in parenthesis are (amount of Cu desorption/total of Cu) × 100. Means in final row for amounts of Cu release in each extractant from the bulk and the rhizosphere soil followed by the different letters are significantly different ($P < 0.01$); DTPA-TEA – diethylenetriaminepentaacetic acid-triethanolamine

TEA. The ligands of organic acids can form soluble complexes with Cu, and modify the fixation of Cu by soil organic matter, oxides, clays, and enhance its release (Chen et al. 2003). Mineral dissolution by acids is a process to remove Cu from minerals. Hinsinger et al. (1993) reported that dissolution of phlogopite structure occurred in the rhizosphere of rape (*Brassica napus* L.) probably due to proton excretion by roots. Therefore, an increase in the Cu release in citric acid with respect to DTPA-TEA may be due to dissolution minerals, which is much more soluble at pH 2.8 (10 mmol/L citric acid) than at pH 7.3 (DTPA-TEA). The mechanisms

by which citric acid enhances mineral weathering include donating protons to dissolve minerals, forming complexes with metal ions in mineral structures, and reducing iron and manganese to disrupt mineral structures (Kodama et al. 1983).

Different mathematical models (Table 1) were tested for their suitability to describe release of Cu with DTPA-TEA and citric acid from both the bulk and the rhizosphere soils. Comparisons of R^2 and SE values (Table 4) indicated that the power function, parabolic diffusion, and first order equations described the reaction rates fairly well, as evidenced by the high coefficients of determination values and low standard error of the estimate. Similar to our results Khater and Zaghlou (2002) concluded that power function, parabolic diffusion and first order equations were the best fitted equations used to describe Cu release. Elkhatab et al. (2007) stated Elovich and parabolic diffusion models were used to describe release of Cu as affected by the organic ligands.

There was a wide variation in the Cu release characteristics between soils, between the bulk and the rhizosphere soils and between DTPA-TEA and citric acid solutions. Release rate constants and intercept of Cu for four models are given in Table 5. Release rate constants in power function, parabolic diffusion, and first order equations were introduced an index of Cu release rates in the soils. The results of Table 5 showed that Cu release rate in citric acid solution were more than in DTPA-TEA solution. The results of Table 5 showed that the diffusion rate (R constant) in DTPA-TEA solution in the rhizosphere soils was lower than the bulk soils. While the diffusion rate in citric acid solution in the rhizosphere soils was higher than the bulk soils. According to researches of Tao et

Table 4. Coefficient of determination (R^2) and standard error of the estimate (SE, mg/kg) of various kinetic models for Cu release in diethylenetriaminepentaacetic acid-triethanolamine (DTPA-TEA) and citric acid

Extractant	Soils		Zero-order		First-order		Parabolic diffusion		Simplified Elovich		Power function	
			range	mean	range	mean	range	mean	range	mean	range	mean
DTPA-TEA	bulk	R^2	0.79–0.96	0.84	0.91–0.98	0.95	0.95–0.97	0.96	0.78–0.89	0.84	0.91–0.97	0.95
		SE	0.43–1.23	0.88	0.24–0.55	0.38	0.24–0.54	0.40	0.54–1.01	0.77	0.37–0.63	0.52
	rhizosphere	R^2	0.79–0.98	0.84	0.92–0.99	0.95	0.91–0.98	0.95	0.81–0.88	0.84	0.93–0.97	0.95
		SE	0.45–1.36	0.82	0.18–0.51	0.35	0.22–0.51	0.36	0.52–1.18	0.74	0.34–0.65	0.47
Citric acid	bulk	R^2	0.80–0.91	0.83	0.97–0.98	0.98	0.97–0.98	0.97	0.89–0.93	0.90	0.99–0.99	0.99
		SE	1.38–2.63	1.71	0.76–1.20	0.98	0.51–0.70	0.58	0.88–1.74	1.18	0.32–0.48	0.37
	rhizosphere	R^2	0.79–0.93	0.82	0.97–0.98	0.98	0.96–0.98	0.97	0.89–0.92	0.90	0.99–0.99	0.99
		SE	1.57–2.53	1.80	0.38–0.95	0.82	0.50–0.71	0.64	0.96–1.60	1.17	0.35–0.90	0.62

All coefficients of determination (R^2) are significant at the 0.01 level

Table 5. Parameters of models used to describe release kinetics of Cu in the bulk and the rhizosphere of studied soils

Soil No.	First order				Parabolic diffusion				Power function			
	bulk		rhizosphere		bulk		rhizosphere		bulk		rhizosphere	
	<i>a</i>	$K_1 \times 10^{-4}$	<i>a</i>	$K_1 \times 10^{-4}$	<i>a</i>	<i>R</i>	<i>a</i>	<i>R</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
	(mg/kg)h	1/(mg/kg)	(mg/kg)h	1/(mg/kg)	mg/kg	mg/(kg h ^{1/2})	mg/kg	mg/(kg h ^{1/2})	mg/(kg h)	1/(mg/kg)	mg/(kg h)	1/(mg/kg)
DTPA-TEA												
1	1.92	75.97	1.71	75.93	2.77	0.43	1.93	0.35	2.52	0.229	1.83	0.241
2	1.67	62.87	1.66	82.02	1.55	0.33	1.37	0.33	1.58	0.247	1.42	0.260
3	1.54	51.06	1.34	68.63	1.09	0.25	0.71	0.22	1.22	0.238	0.82	0.275
4	1.69	64.76	1.64	67.07	1.51	0.30	1.46	0.29	1.55	0.238	1.51	0.239
5	1.44	52.28	1.29	53.51	1.48	0.24	1.51	0.22	1.47	0.214	1.42	0.217
6	1.75	63.27	1.46	73.86	1.27	0.33	1.18	0.25	1.41	0.260	1.26	0.235
7	1.65	66.49	1.55	78.22	1.34	0.30	0.96	0.27	1.43	0.242	1.08	0.269
8	1.87	67.52	1.83	72.36	2.73	0.42	2.65	0.41	2.55	0.221	2.46	0.223
9	1.94	68.36	1.83	76.97	2.33	0.43	1.96	0.40	2.29	0.234	1.87	0.256
10	2.08	71.50	2.00	72.53	2.93	0.50	2.34	0.45	2.79	0.233	2.34	0.239
Citric acid												
1	2.57	59.42	2.70	58.41	1.74	0.78	1.73	0.87	1.68	0.382	1.88	0.377
2	2.53	57.32	2.61	57.93	1.11	0.72	1.51	0.79	1.32	0.402	1.69	0.378
3	2.45	58.64	2.51	58.88	1.04	0.69	1.68	0.73	1.14	0.425	1.70	0.365
4	2.40	59.45	2.44	58.59	2.25	0.67	2.60	0.68	1.98	0.334	2.43	0.304
5	2.33	59.45	2.41	59.71	1.79	0.62	2.43	0.67	1.62	0.353	2.13	0.324
6	2.35	59.00	2.37	60.13	1.86	0.63	2.28	0.66	1.69	0.347	1.93	0.339
7	2.24	59.61	2.38	59.68	1.95	0.56	2.23	0.65	1.71	0.331	1.93	0.330
8	2.36	59.15	2.43	59.17	2.02	0.64	2.44	0.68	1.88	0.330	2.21	0.318
9	2.37	58.98	2.44	59.44	2.37	0.65	2.45	0.70	2.05	0.324	2.11	0.323
10	2.51	58.24	2.50	58.93	1.74	0.73	2.49	0.73	1.70	0.367	2.22	0.329

al. (2003) and Wang et al. (2002), the different chemical and biological conditions of the rhizosphere soil can change Cu fractions and therefore amounts of release of Cu.

The best supporting evidence for any equation used to describe the kinetics of Cu release is the comparison of the amount of Cu desorption with plant indices on soils with a range of Cu supply. The plant indices including concentration of Cu, yield and uptake were determined (data not shown). The results of correlation studies indicated that significant correlation between Cu desorption after 504 h with DTPA-TEA in the rhizosphere soils and Cu uptake in shoot was found ($r = 0.64$, $P < 0.05$). The results of correlation analysis showed that a significant ($P < 0.01$) correlation between Cu desorption after 504 h with citric acid and Cu concentration in root ($r = 0.92$ and $r = 0.84$ in the

rhizosphere and the bulk soils, respectively) and Cu concentration in shoot ($r = 0.87$ and $r = 0.91$ in the rhizosphere and the bulk soils, respectively) were found.

Chelating agents offer great promise for assessing readily available micronutrient cations in soils. These agents combine with free metal ions in solution forming soluble complexes and thereby reduce the activities of the free metal ions in solution. In response, metal ions desorb from soil surfaces or dissolve from labile solid phases to replenish the free metal ions in solution (Lindsay and Norvell 1978). These synthetic chelating agents are capable of dissolving, e.g., secondary metal oxides etc., releasing thus the metals into the soil solution.

The results of this study illustrated that Cu extracted using DTPA-TEA in the rhizosphere soils were significantly ($P < 0.01$) lower than the

bulk soils, while Cu extracted after 504 h using 10 mmol/L citric acid in the rhizosphere soils were significantly higher than in the bulk soils. It may be attributed to ability of these extractants to release Cu from different Cu fractions. The results of kinetics study showed that amount of Cu release using citric acid from both the bulk and the rhizosphere soils increased than amount of Cu release using DTPA-TEA. It may be attributed to dissolution of minerals by citric acid. The results of correlation studies indicated that a significant correlation between Cu desorption after 504 h with DTPA-TEA in the rhizosphere soils and Cu uptake in shoot was found ($P < 0.05$). Also, a significant correlation between Cu desorption after 504 h with citric acid and Cu concentration in root and shoot were found ($P < 0.01$). Therefore, application of 10 mmol/L citric acid extractant would be recommended in the future study on the kinetics of release of Cu in calcareous soils.

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