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Effect of organic substances on iron-release kinetics in a calcareous soil after basil harvesting

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Abstract: Desorption of iron from soil is important for evaluating the availability and toxicity of soil Fe in agriculture. The aim of this investigation was to study the effect of organic substances (cow and sheep manures and vermicompost) on Fe release from a calcareous soil and determine the best models for the description of the Fe desorption kinetics. Organic substances were added to soils at the rate of 3 %. Basil (*Ocimum basilicum* L.) seeds were sown in each pot and pots were kept at 24–25 °C at about field capacity for 90 days. After 90 days, plants were harvested and soil samples were used for Fe desorption analysis. Seven kinetic models were evaluated to describe the rate of Fe desorption in soil extracted with diethylenetriaminepentaacetic acid (DTPA). Results showed that Fe release from soil samples increased with time. Release of Fe was rapid at first and then became slower. Iron release in the organic substances treatments was higher than in the unamended soil and the two-constant rate, parabolic diffusion and simple Elovich models were the best equations for the description of Fe release from soils.

Keywords: desorption; manure; vermicompost; kinetics; calcareous soil.

INTRODUCTION

The environmental impact of heavy metal contaminants depends on the retention capacity of soils, but also on the speciation of heavy metals.[1–4] Bioavailability of metals in soils are controlled by three main processes: a) the removal of metals from the soil solution by sorption onto soil particles, b) the release of the metal from the soil particle to the soil solution (desorption) and c) the precipitation–dissolution of the metal as an independent phase in the soil matrix.[5,6] The uptake of elements by plants leads to consumption of soil solution elements and a consequent net release of elements from soil solid to liquid phase. Therefore, in addition to the quantity of reserved elements in the soil, the amount of

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soluble elements at any time largely depends on the rate of release of elements from the soil particles into the soil solution.[7] In recent years, the application of organic fertilizer (sewage sludge, livestock manures, compost and vermicompost) as a source of organic matter other than traditional fertilizers has become popular and efficient for the improvement of soil organic matter and soil properties. However, the use of organic residues can lead to problems related to their heavy metal content and their successive application, which result in heavy metal accumulation in soil. Land disposal of organic residues may directly or indirectly alter the heavy metal status of the soil by affecting metal solubility or dissociation kinetics.[8] Therefore, the studies on the kinetics of metal release from soil or soil constituents are of importance in evaluating the availability and toxicity of soil metal in agriculture. To understand the dynamic interaction of elements with the soil matrix, and to predict its fate, the knowledge of the reaction kinetics focused primarily on describing the element availability for plants.[9,10] Desorption of iron (Fe) is an important factor in determining Fe availability in calcareous soils. Yu and Klarup[11] reported that the extraction kinetics of Fe, aluminium, copper and zinc can be well described by the two-constant model. Motaghian and Hosseinpur[12] showed that the best model for describing Zn desorption kinetics for rhizosphere and bulk soils was the power function equation. Reyhanitabar and Karimian[13] reported that the best model for describing kinetics of DTPA extraction of Zn from calcareous soils was the exponential rate equation. Jalali and Moharami[14] reported that a power model satisfactorily described Fe and Mn release from contaminated calcareous soils. Motaghian and Hosseinpur[15] stated that desorption of Zn in the rhizosphere soil is the primary factor that affects the bioavailability of Zn and the desorption kinetics of Zn conformed fairly well to first-order, parabolic diffusion and power function equations. The correlation studies showed that the rate constants in the power function equation were significantly correlated with Zn extracted, using DTPA–TEA (diethylenetriaminepentaacetic acid–triethanolamine), AB–DTPA (ammonium bicarbonate–diethylenetriaminepentaacetic acid) in the bean rhizosphere and the bulk soils.

Motaghian and Hosseinpur[16] showed that amount of cumulative of Zn desorbed in soils amended with cow manure (CM) and vermicompost (VC) was significantly higher than in unamended soil. Concentration of Zn desorbed in 0.5 and 1 % of CM and VC compared with unamended soil increased 26, 54, 12 and 46 %, respectively.

Determining Fe desorption characteristics in amended soils with organic substances is very important to understand the ability of this new source to Fe desorption in soil solution and determine Fe availability in calcareous soils. Therefore, the aim of this investigation was to study the influences of organic substances (cow and sheep manures and vermicompost) on Fe release from a cal-

careous soil and to determine the best models to describe the kinetics of Fe desorption in the soil after basil harvesting.

EXPERIMENTAL

Soil sample was collected from the surface horizon 0–30 cm of a calcareous soil (Fine, mixed, mesic, Fluventic Calcixerepts) from agricultural fields located in Bajgah, Bajgah Agricultural Station of Shiraz University, Iran. The soil sample was air-dried, passed through a 2-mm sieve and used for laboratory analyses. Selected properties of the studied soil are given in Table I. These included texture by hydrometer method;[17] pH in saturated paste;[18] electrical conductivity of saturation extract (ECe);[19] calcium carbonate equivalent (CCE) by neutralization with hydrochloric acid and titration with sodium hydroxide;[20] phosphorus was determined according to the Watanabe and Olsen method;[21] and iron, zinc and copper by DTPA extraction[22] and measured using (Shimadzu, AA-670) atomic absorption spectrophotometer.

TABLE I. Selected chemical and physical properties of the studied soil

Property	Value
pH	7.00
Electrical conductivity, dS m^{-1}	0.54
Texture	Sandy clay
Organic matter content, %	0.9
Calcium carbonate equivalent , %	40.67
DTPA-extractable Fe, mg kg^{-1}	6.09
DTPA-extractable Cu, mg kg^{-1}	1.09
DTPA-extractable Zn, mg kg^{-1}	0.95
P content, mg kg^{-1}	9.64

Organic substances characteristics

The organic substances (OS) used in this study were cow manure (CM), sheep manure (SM) and vermicompost (V). The samples were air dried, passed through a 0.25-mm sieve, and stored in a plastic bag for physicochemical analyses (Table II). For the analysis of Fe, Zn and Cu, organic substances were ground and dry-ashed at 550 °C. The ash was dissolved in 2 M hydrochloric acid and, after passing through filter paper, was used to determine P by colorimetric method using spectrophotometer and Fe, Zn, and Cu concentrations by atomic absorption spectrophotometer.[23] Organic substances pH and EC were measured in 1:5 organic materials (OM) to water.

TABLE II. Some properties of the organic substances

Organic substance	pH	EC / dS m^{-1}	Total P, mg kg^{-1}	c_{Fe} / mg kg^{-1}	c_{Cu} / mg kg^{-1}	c_{Zn} / mg kg^{-1}
Cow manure (CM)	8.70	7.40	259.91	1274.90	11.95	73.25
Sheep manure (SM)	9.08	10.31	255.66	882.90	9.35	430.10
Vermicompost (V)	7.88	1.45	469.52	1164.35	10.25	200.80

Pot experiment

Treatments consisted of OM including CM, SM and V (each at 2 % rate), and control sample which receive no organic substances. Experimental samples were 500 g of the studied soil that treated with OM in separate plastic pots. The whole experiment was repeated three

times. Seven basil seeds (*Ocimum basilicum* L.) were sown in each pot. Pots were kept at 24–25 °C and near field capacity for 90 days. After 90 days, plants were harvested and soil samples were dried, ground, and used for studying Fe desorption kinetics.

Desorption kinetics experiments

For Fe release studies, 5 g of the air-dried <2 mm soil sample was extracted with 25 ml of a DTPA[22] on an end-over-end circulatory shaker for 20, 40, 60, 120, 180, 480, 960 and 1,440 min at 25±2 °C, centrifuged at 2500 rpm (≈1000*g*) for 15 min to obtain a clear supernatant; and passed through a Whatman 42 filter paper to ensure the clarity of the equilibrium solution.

The filtrates were analyzed for Fe by atomic absorption spectrophotometer. Seven kinetic models were used to describe Fe release from the soils (Table III).

TABLE III. Equations used to describe Fe release kinetics[26]

Model	Equation	Parameter
Zero order	$q_t = q_0 - k_0 t$	k_0: zero order rate constant, mg Fe kg^{-1} s^{-1}
First order	$\ln q_t = \ln q_0 - k_1 t$	k_1: first-order rate constant, s^{-1}
Second order	$\dfrac{1}{q_t} = \dfrac{1}{q_0} - k_2 t$	k_2: second-order rate constant, mg^{-1} Fe kg s^{-1}
Third order	$\dfrac{1}{q_t{}^2} = \dfrac{1}{q_0{}^2} - k_3 t$	k_3: third-order rate constant, mg^{-2} Fe kg^2 s^{-2}
Parabolic diffusion	$q_t = q_0 - k_p t^{1/2}$	k_p: diffusion rate constant, mg$^{-0.5}$ Fe kg$^{0.5}$
Simple Elovich	$q_t = \dfrac{1}{\beta_s}\ln(\alpha_s \beta_s) + \left(\dfrac{1}{\beta_s}\right)\ln t$	α_s: initial Fe desorption rate, mg Fe kg^{-1}s^{-1}, β_s: Fe desorption constant, mg^{-1} Fe kg
Two-constant rate	$q_t = a t^b$	a: initial Fe desorption rate constant, mg^b Fe kg^{-b} s^{-b}; b: desorption rate coefficient, mg^{-1} Fe kg

To determine the equation that best described Fe release, least square regression analysis was used. Equations showing the greatest coefficient of determination (r^2) and having the least standard error of estimate (*SE*) were chosen.[24] The standard error was calculated as follows:

$$SE = \left(\frac{\sum (q - q')^2}{n - 2} \right)^{0.5} \tag{1}$$

where *q* and *q′* are the measured and calculated amounts of Fe release in soil at time *t*, respectively, and *n* is the number of measurements.[25] Various Fe release rate parameters were subsequently obtained from fitted equations.

Statistical analysis

Statistical analysis was performed using the SPSS 19.0 software and Microsoft Excel 2010 packages. The difference between means was compared by Duncan's multiple range test.

RESULTS AND DISCUSSION

The cumulative Fe desorption by DTPA extractions in soils treated with different OS is presented in Fig. 1. The patterns of Fe desorption were similar in

the soils, but, the amount of Fe release in the control samples at all times was less than in the soils treated with different OS. The order of Fe release in soil samples were: soil + V > soil + CM > soil + SM > control, respectively. In the OS treated soils, Fe release from soil samples increased with time and it was higher than in the control sample. Decomposition of the vermicompost and manures during 3-month incubation in soil might have been responsible for increasing of Fe release in the soil samples. Also, OS might have formed soluble complexes with Fe and enhanced their release. Karaca[27] reported that the DTPA-extractable Zn increased with increasing of organic waste rates added to soil. Shuman[28] found that pH, clay content, and organic matter content, influenced the adsorption of metal by soils. Mandal and Hazra[29] found that the organic matter application and low pH arrested a decreasing trend in metal adsorption, and with increasing soil organic matter levels, the extractability of Zn increased. Ramadan *et al.*[30] reported that the available micronutrients (Cu, Zn and Mn) in soil increased by using poultry manure. Sadegh Kasmaei and Fekri[31] showed that Cu extractability in soil increased with addition of pistachio compost treatment. It might be concluded that low molecular weight organic acids, originated from decomposition of soil organic matter, can form soluble complexes with metal cations,[32] and modify the fixation of metals by soil organic matter, and oxides, clays, as well as enhance their release.[33] Organic matter and pH could have a great effect on the Zn extractability.[34] Arnesen and Singh[35] found that extractable Cu increased with increasing rate of peat, and they suggested that the low pH in the peat-amended soil probably decreased the Cu sorption in the soil. Motaghian and Hosseinpur[16] showed that amount of cumulative Zn desorbed in soils amended with cow manure and vermicompost was significantly higher than in the unamended soil.
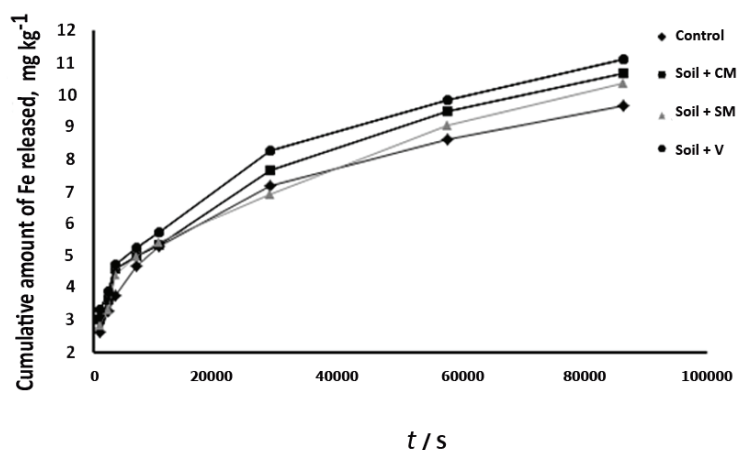

Fig. 1. Cumulative amount of Fe release over time in soil treated with different OS (CM: cow manure, SM: sheep manure, V: vermicompost).

During the reaction periods from 20 to 1440 min, Fe release from soil samples increased with time (Fig. 1). In all samples, Fe release was rapid at first and then became slower, but the equilibrium was not achieved in any of soil samples. Measuring Fe release kinetics for the soil samples indicated that about 50 % of total desorbed Fe was released within initial 180 min (Fig. 1), while the Fe extracted with DTPA after plant harvesting, which is an indicator of soil available Fe, covers about 91 % of this section (Fig. 2). Fe extracted by DTPA was the highest for vermicompost amended samples, compared to other organic materials (Fig. 2); this observation is attributed to higher Fe content of vermicompost (Table II).
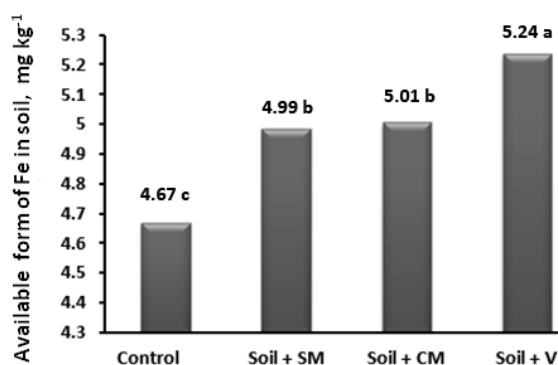

Fig. 2. Amounts of available Fe in soil treated with different OS (CM: cow manure, SM: sheep manure, V: vermicompost) after plant harvesting; mean values followed by the same letters are not significantly different ($p \leq 0.05$) by Duncan's multiple range test.

It is very difficult to identify compounds; those are involved in the Fe extraction with DTPA. Geiger and Loeppert[36] showed that DTPA extractable Fe was highly correlated with the ammonium oxalate extractable Fe (amorphous or poorly crystalline Fe oxide) and clay content as well as with organic carbon parameters in calcareous soils of Texas.

Data fitting to different kinetic equations

The zero-, first-, second-, and third-order equations, the parabolic diffusion equation, the two-constant rate equation, and the simple Elovich equation were used to describe Fe release from OS treated soils. To determine the equation that best described Fe release in soil samples, coefficient determination (r^2) and standard error of estimate (*SE*) was calculated for each equation (Table IV). A relatively high value of r^2 and low *SE* are often used as criteria for the best fitting model(s).[13,24,37] The amount of Fe released from soil samples during 1440 min was poorly described by the zero-, first-, second-,and third-order equations, and with increasing order of reaction from zero to third, r^2 decreased and SE increased in the soils studied (Table IV).

Comparisons of r^2 and *SE* values of different models in the Table IV indicated that the best models for describing Fe desorption, in all studied soil

samples, were two-constant rate, parabolic diffusion and simple Elovich equations (Table IV).

TABLE IV. Coefficient of determination (r^2) and standard error of the estimate (*SE*) of kinetic equations; CM: cow manure, SM: sheep manure, V: vermicompost

Treated soil	Equation												
	Zero order		First order		Second order		Third order		Parabolic diffusion		Simple Elovich		Two-constant rate	
	r^2	*SE*	r^2	*SE*	r^2	*SE*	r^2	*SE*	r^2	*SE*	r^2	*SE*	r^2	*SE*
Control	0.89	0.89	0.78	1.47	0.63	1.61	0.49	2.32	0.98	0.35	0.97	0.39	0.99	0.10
Soil+ CM	0.89	0.86	0.82	1.48	0.67	1.86	0.51	3.59	0.98	0.32	0.96	0.62	0.99	0.25
Soil+ SM	0.89	0.80	0.80	1.40	0.64	1.51	048	2.03	0.98	0.34	0.96	0.59	0.99	0.28
Soil+ V	0.89	0.89	0.82	1.47	0.69	2.91	0.55	4.77	0.98	0.33	0.96	0.61	0.99	0.23

Best fitted models

Two-constant model. Equation $q_t = at^b$ was used to fit the experimental data. According to this equation, there is a linear relationship between ln q_t and ln t, *i.e.*:

$$\ln q_t = \ln a + b\ln t \qquad (2)$$

High values of r^2 with relatively low amounts of *SE* (Table IV) showed that the two-constant rate equation was one of the best kinetic equations that described Fe release in the soil samples (Fig. 3). But the generally appropriate fit equation may be due to the logarithmic transformations that minimizes the sensitive data.[38] On the other hand, it is not so unlikely that the that two-constant equation could describe Fe release from soil samples, because this equation is quite flexible with two empirical coefficients.[11] Jalali and Moharami[14] reported that a power model ($y = at^b$) satisfactorily described Fe and Mn release from contaminated calcareous soils.
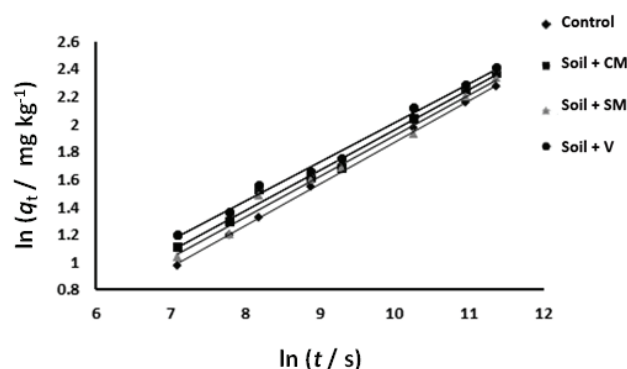

Fig. 3. Measured and predicted Fe release as described by two-constant rate equation in soil treated with different OS (CM: cow manure, SM: sheep manure, V: vermicompost) after plant harvesting.

In this equation, q_t is the quantity of the Fe released in time t, a is the initial Fe release rate constant, mg kg^{-1} and b is the release rate coefficient, mg kg^{-1}. The previous equation can be written as $d_q / d_t = ab$. and ab may be taken as initial release rate of soil nutrient.

Dang et al.[26] proposed that an increase in the value of a, and decrease in the value of b in the two-constant rates equation probably indicate an increase in the rate of desorption from soils. In our studied soil samples treated with OS, the values of a and ab constants increased and the values of b constants decreased significantly than that of control, and the highest values of a and ab constants were observed in the vermicompost treatment (Table V).

TABLE V. Calculated rate constants for the best kinetic models; α_s and β_s: initial Fe desorption rate, mg Fe kg^{-1} s^{-1} and desorption constant, mg^{-1} Fe kg of simple Elovich equation, respectively, a and b: initial Fe desorption rate constant, mg^b Fe kg^{-b} s^{-b} and desorption rate coefficient, mg^{-1} Fe kg of two-constant rate equation, respectively, and k_p: diffusion rate constant of parabolic diffusion model, mg$^{-0.5}$ Fe kg$^{0.5}$; CM: cow manure, SM: sheep manure, V: vermicompost; means in each column followed by the same letters are not significantly different at $p \leq 0.05$ by Duncan's multiple range test

Soil	Simple Elovich		Two-constant rate			Parabolic diffusion
	α_s	β_s	a	b	ab	k_p
Control	0.0050[c]	0.604[a]	0.319[c]	0.305[a]	0.095[d]	0.027[d]
Soil+ CM	0.0061[ab]	0.566[c]	0.393[b]	0.292[c]	0.113[b]	0.029[b]
Soil+ SM	0.0056[b]	0.588[b]	0.367[b]	0.295[b]	0.106[c]	0.028[c]
Soil+ V	0.0065[a]	0.547[d]	0.447[a]	0.284[d]	0.125[a]	0.030[a]

Parabolic diffusion model

The linear form of Fe release in front of $t^{0.5}$ and estimation of r^2 and *SE* values (high r^2 and low *SE*, Table IV) indicated that the parabolic diffusion equation was the best fitted model that describe Fe release process as well as the two-constant rate equation (Table IV, Fig. 4). The parabolic diffusion equation, fitting with data, may suggest that the Fe release process is controlled by diffusion.[39,40] Water soluble ions and easily exchangeable ions are the product of the
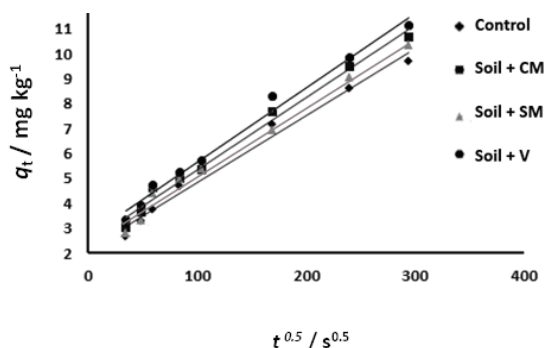

Fig 4. Measured and predicted Fe release as described by parabolic diffusion equation in soil treated with different OS (CM: cow manure, SM: sheep manure, V: vermicompost) after plant harvesting.

fast extraction reaction[41] and strongly adsorbed, chelated ions are the result of the slower reaction. Motaghian and Hosseinpur[15] stated that desorption kinetics of Zn conformed fairly well to parabolic diffusion, and power function equations in the rhizosphere soil.

In the parabolic diffusion equation ($q_t = q_0 - k_p t^{1/2}$), k_p is Fe diffusion rate constant. In soil samples with OS treatment, the values of k_p constants increased significantly compared to the corresponding value in the control soil, and the highest value of k_p constant was observed for the vermicompost treated soil (Table V).

Simple Elovich equation

The Elovich model in the linear form (simple Elovich equation) was tested by plotting the cumulative Fe released as a function of the log of time, where, q_t is the concentration of Fe in the soil, mg kg^{-1} at any given time, t is the time, s and α_s and β_s are the desorption constants, mg kg^{-1}. A linear relationship exists between q_t and ln t for each OS treated soil (Fig. 5). Each curve in Fig. 5 can be converted into two segments. Low,[42] while describing the chemical adsorption of gases on solid surfaces, suggested that the fractures in curves can point to the existence of different mechanisms controlling the speed of the processes. Some researchers explained that fractures or multiple line segments in simple Elovich curve can be considered an indicator of change from one type of banding place to another one.[24,43] The constants of this equation are shown in Table V.
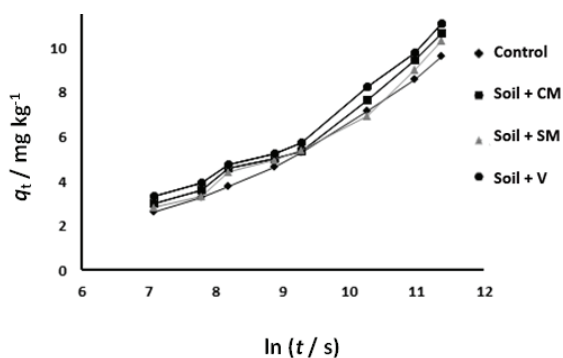

Fig 5. Measured and predicted Fe release as described by simple Elovich equation in soil treated with different OS (CM: cow manure, SM: sheep manure, V: vermicompost) after plant harvesting.

The values of α_s in Elovich equation increased and β_s decreased with the application of OS, in comparison to the corresponding values in the control soil (Table V). An increase in the value of α_s and a decrease in the value of β_s are indicative of an increase in the rate of release.[24] The results obtained from the desorption experiments on our OS treated soil showed that increasing OS leads to an increase in the amount of Fe desorbed.

The highest value of α_s constant and the lowest value of β_s constant were observed in vermicompost treatment. Most Fe deficiency disorders occur in cal-

careous soils with pH 7.4 or higher where the solubility of Fe is decreased due to the increase of pH. Since higher desorption rate usually results in higher availability of metals to plants, OS, especially with vermicompost, may be used in some calcareous soils to increase the uptake of Fe by plants.

CONCLUSION

Results showed that Fe desorption from soil increased with the application of organic substances (*i.e.*, cow manure, sheep manure and vermicompost) as compared to control. Decomposition of the manures and the vermicompost during 3-month in soil might have been increased Fe release in the OS treated soil. Also, organic matters might have formed soluble complexes with Fe and enhanced their release.

Also, Fe release in vermicompost treated soil was greater than in sheep and cow treatments, probably through the enhancement of bioavailability of Fe sorbed by soil colloids. Since higher desorption rate usually results in higher availability of metals to plants, OS especially vermicompost may be used in some calcareous soils to increase the uptake of Fe by plants, but Fe contamination and accumulation in soil must be considered. In all of samples, Fe release was characterized by a rapid initial desorption, followed by a slower release rate. Measuring Fe release kinetics for the soil samples indicated that about 50 % of total Fe desorbed was released within initial 180 min, while soil available Fe covers about 91 % of this section. Among seven kinetic equations fitted to Fe release from soil, two-constant rate, parabolic diffusion and simple Elovich were the best equations for description of Fe release from soils. Furthermore, the constant values of these equations showed that Fe desorption was greater in soil samples treated with OS, than in the control sample.

ИЗВОД

УТИЦАЈ ОРГАНСКИХ СУПСТАНЦИ НА КИНЕТИКУ ОСЛОБАЂАЊА ГВОЖЂА У КРЕЧНОМ ТЛУ НАКОН ЖЕТВЕ БОСИЉКА

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Десорпција гвожђа (Fe) из земљишта је важна за одређивање доступности и токсичности гвожђа из земљишта у пољопривреди. Циљ овог испитивања је био проучавање утицаја органских супстанци (сточно и овчије ђубриво и вермикомпост) на отпуштање гвожђа из кречњачког тла и одређивање најбољих модела за описивање кинетике ове десорпције. Органске супстанце су додаване земљиштима у концентрацијама по 3 %. У сваку посуду је посејано семе босиљка (*Ocimum basilicum* L.) и посуде одржаване на температурама 24–25 °C, приближно при капацитету земљишта током 90 дана. Након 90 дана, биљке су пожњевене и узорци земљишта подвгнути анализи десорпије гвожђа. Седам кинетичких модела је испробано за карактерисање брзине ове десорпције, екстракцијом помоћу DTPA. Резултати су показали да се ослобађање гвожђа дешава најпре брзо, а затим се успоравало. Ослобађање гвожђа третманом органским супстанцама је

било изразитије него из недирнутог земљишта, а најбоље је описано параболичном дифузијом са две кинетичке константе и Еловичевом (Elovich) једначином.

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