RELEASE KINETICS OF IRON, ZINC AND MANGANESE FROM SOIL CONCRETIONS

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Nodules (2-15 mm) from Gujranwala (Udic Haplustalf) Btc2 (96-130 cm) and Satghara (Typic Natrargid) 2 Btcknob2 (80-108cm) soil horizons were wet ground in acetone, sonicated and passed through a 300 mesh sieve. They were extracted at room temperature by gently shaking with 0.005 M DTPA in duplicate at a 1:50 solid: solution ratio for 0.5, 2, 4, 16, 24 and 96 hrs. Cumulative release of Mn, Fe and Zn in Gujranwala was 24, 4 and 12%, respectively of the total composed to 12, 1.2 and 14%, respectively in the Satghara horizon. Release of either Zn, Mn or Fe from mineral matrix in the two samples by diffusion controlled process was suggested by significant coefficients of determination (r^2) for parabolic diffusion, power function and Elovich equations. Two different mechanisms contrtolling the release of Fe and Mn from Gujranwala nodules were suggested by adjustment in t_0. Initial (intercept a) and time dependent (slope b) release of Zn, Mn and Fe from the two samples in relation to their mineral composition is discussed.

Key words: Release kinetics, Trace elements, Soil concretions.

Introduction

Concentration of total Mn and Fe in the nodules (2-15 mm) from subsurface horizons of two alkaline calcareous flooded rice soils had a significant positive correlation with Zn [7]. These nodules contained the Mn minerals birnessite and lithiophorite, in addition to some phyllosilicates, quartz, mica and calcite [7]. Manganese minerals in marine environment are important in sorption-desorption processes of heavy metals (2 and 10). Therefore, information on kinetics of sorption-desorption in the nodular fraction, containing Mn minerals, could be important for soil pedogensis and for micronutrient nutrition of flooded rice.

A 0.005 M DTPA solution, buffered to pH 7.3 with $CaCl_2$ and TEA, is commonly used to estimate bioavailability of micronutrients in calcareous soils [3]. Zinc, Fe and Mn were released by DTPA at variable time intervals from nodule fraction of the two soils and four different mathematical models were employed to characterize desorption kinetics of Fe, Zn and Mn.

Materials and Methods

Two nodule (2-15 mm) samples, separated by wet sieving from a Gujranwala (Udic Haplustalf) Btc_2 (96-130 cm) and a Satghara (typic Natrargid) 2 $Btcknb_2$ (80-108 cm) soil horizons of two alkaline calcareous rice growing soils were studied for their Zn, Mn and Fe release kinetics. Detailed properties of the two soils including morphology and mineralogical composition of the two nodule specimens, are reported elsewhere [7]. The two samples were wet ground in acetone in an agate mortar, suspended in water and dispersed by sonicating with an ultrasonic fitted with a microtip (40 watts for 60 secs). The dispersed samples were wet sieved through 300 mesh sieve. The sieved samples (< 50 μm) were centrifuged

and sediments were freeze dried in a vacuum freeze - dryer. Samples composed of 200 mg of crushed nodules from Gujranwala and Satghara soils were taken in duplicate in clean 40 ml plastic centrifuge tubes fitted with airtight cover. The crushed nodular material (<50 μm) was extracted with 0.005 M DTPA [3] at 1:50 solid: solution ratio for 0.5, 2, 4, 16, 24 and 96 hrs at room temperature by gentle shaking on a reciprocating shaker.

Every DTPA - nodule suspension after each time interval was centrifuged at 2000 rpm for 5 mins and fresh DTPA solution was added to the same tube after saving the clear supernatant for Zn, Mn and Fe determination by atomic absorption spectroscopy. All glassware and equipment were washed with a laboratory detergent, dilute HCl and distilled deionized water. Extracted quantities of Zn, Mn and Fe were calculated and four different mathematical models were employed to characterize their release kinetics [1].

Results and Discussion

Structural features like nodules used in this investigation developed in situ in sub-surface horizons of the two alkaline calcareous soils. Flooded rice cultivation is practiced on these soils year after year. Nodules, developed under special pedogenic environment of a reduced soil by precipitation of soluble ions had highly variable Fe/Mn content similar to earlier reports [5]. The Gujranwala sample had brinessite and lithiophorite Mn mineral phase, goethite iron, mica, quartz, smectite, kaolinite and calcite. Manganese containing calcite was suggested in Satghara which also had mica, vermiculite, and kaolinite (Table.1). The nodular materials used in this study were not pure mineral phases. Gujranwala sample contained birnessite and lithiophorite Mn minerals and goethite whereas Satghara sample had some Mn substituted calcite.

Cumulative release of Mn through 96 hrs was 24 and 12% of the total Mn in the Gujranwala and Satghara samples, respectively. The proportion of total Fe release was 4% in Gujranwala sample and 12% in Satghara sample. Converse to Mn and Fe, a higher proportion of Zn (14%) was released from Satghara than 12% from Gujranwala sample. Each desorption curve was characterized by an initial fast release followed by a slower release over time.

Four different kinetic models, first order, parabolic diffusion, power function and Elovich equations, were used to characterize release kinetics of Zn, Mn and Fe from crushed nodules from the two soils (Table 2). Coefficient of determination (r^2) calculated by least square method [9] was used to judge the best fit of the four models in describing the release of the three elements. The Elovich equation, power function and parabolic diffusion equation best described the release of Zn, Fe and Mn from the two sample (Table 2). On the basis of r^2 value, release of Zn as described by the four different mathematical models followed the order: Elovich> power function> parabolic diffusion> first order. The four models described the release of Mn and Fe in the fashion viz. Elo vich< power function $\geq$ parabolic diffusion > first order. Coefficient of determination of 0.86 and 0.83 calculated for Elovich equation for the release of Mn and Fe in Gujranwala, respectively,

TABLE 1. CHARACTERISTICS OF THE NODULE FRACTIONS.

Property	Unit	Gujranwala	Satghara
Shape	–	Rounded	Irregular
Total Zn	mg/gm	0.19	0.18
" Cu	"	0.12	0.05
" Mn	%	1.45	0.39
" Fe	"	7.16	2.66
Fe & Mn mineral		Birnessite Mn substituted Calcite	
		Lithiophorite	Goethite
		Goethite	
Other minerals		Mica, Quartz	Calcite
		Smectite, Kaolimite	Mica
		and Calcite	Vermiculite
			Chlorite kaolinite

TABLE 2. COEFFICIENT OF DETERMINATION (r^2), INTERCEPT (a) AND SLOPE (b) VALUES FOR VARIOUS KINETIC MODELS USED TO DESCRIBE ZN, MN AND FE RELEASE FROM NODULE (2-15 MM) FRACTION OF GUJRANWALA AND SATGHARA.

Kinetic equation	Gujranwala nodules			Satghara nodules		
	Zn	Mn	Fe	Zn	Mn	Fe
Y = a +b ln t (Elovich)						
r^2	0.97	0.86	0.83	0.97	0.90	0.97
a	5.87	-28.13	-47.44	4.35	23.16	65.17
b	3.44	621.83	506.27	4.84	85.65	57.48
Y = a + b ln (t + t$_o$) -a (Elovich)						
r^2	–	0.99	0.99	–	–	–
a	–	-2329.07	-2399.47	–	–	–
b	–	1220.73	1105.46	–	–	–
t_0	–	6.00	8.00	–	–	–
Iny = Ina + b ln t (Power function)						
r^2	0.89	0.99	0.99	0.88	0.99	0.93
a	1.70	5.07	4.75	1.27	3.75	4.14
b	0.34	0.71	0.74	0.52	0.56	0.41
Y = a + bt$^{1/2}$ (Parabolic diffusion)						
r^2	0.85	0.99	0.99	0.80	0.97	0.83
a	5.77	-239.77	236.55	4.48	1.14	64.24
b	1.82	379.92	313.73	2.49	50.45	30.22
Iny = l na - bt (first order)						
r^2	0.42	0.59	0.59	0.35	0.77	0.44
a	2.09	5.81	5.51	1.90	4.33	4.62
b	0.01	0.03	0.03	0.02	0.02	0.02

can be improved by adjusting abt >> 1. Because the Elovich equation used to described the release of Mn and Fe was:

$$dy/dt = ae^{-by} \qquad (1)$$

Where Y is the amount of metal cation released (or complexed by DTPA) at time t, a and b are constants (1). The $dy/dt \longrightarrow a$, initial rate, as $Y \longrightarrow O$. Therefore, integration of Eq. (1) yields:

$$Y = 1/b \ln (1+abt) \qquad (2)$$
$$\text{or} \quad Y = 1/b \ln (t+t_o) - (1/b) \ln t \qquad (3)$$

if $Y = 0$ at $t = 0$. where

$t_o = 1/ab$ if abt >> 1 then Eq. (2) can be simplifed to
$$Y = (1/b) \ln (ab) + (1/b) \ln t \qquad (4)$$

Thus, a plot of Y vs. ln t for Eq. (4) should be linear with slope 1/b and intercept 1/b ln (ab), where b is the rate constant. Substitution of 6 and 8 in Eq. (3) for t_o for Mn and Fe, respectively, would yield abt >> 1 [1] which resulted in a linear plot of Y vs. ln $(t+t_o)$ which slope 1/b and intercept as determined from $t_o = 1/ab$. It improved the coefficient of determination (r^2) values from 0.86 to 0.99 and 0.83 to 0.99 for Mn and Fe, respectively.

Release of Zn, Fe and Mn from mineral matrix, as indicated by better r^2 - values for the Elovich, parabolic diffusion and power function equation, was a diffusion controlled process (Figs. 1-3). Improved linear fit of Elovich model by adjusting for Fe and Mn suggested two different mechanisms controlling their release from Gujranwala
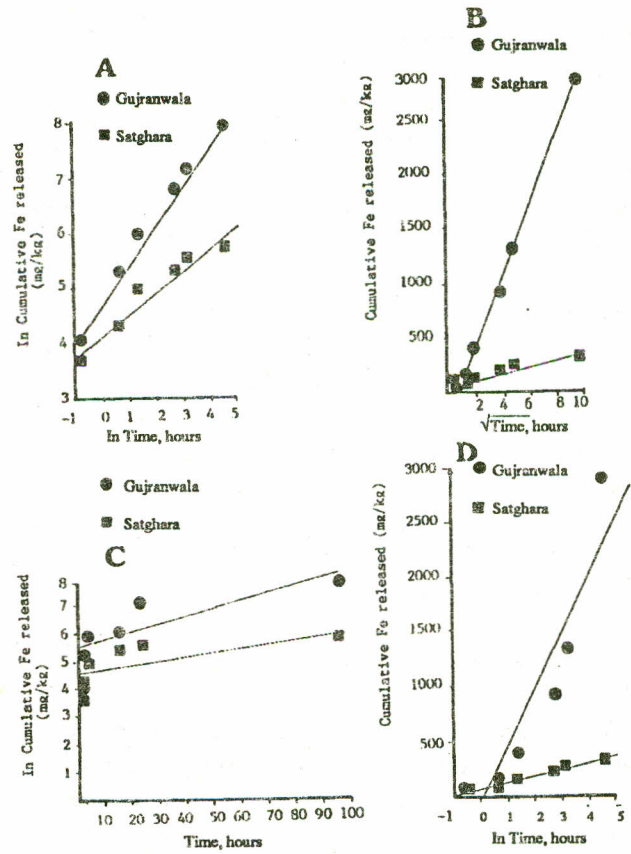
Fig. 2. Expression of iron desorbed to DTPA as a function of time from Gujranwala and Satghara nodules by (A) power function, (B) para bolic diffusion, (C) first order and (D) Elovich equation.
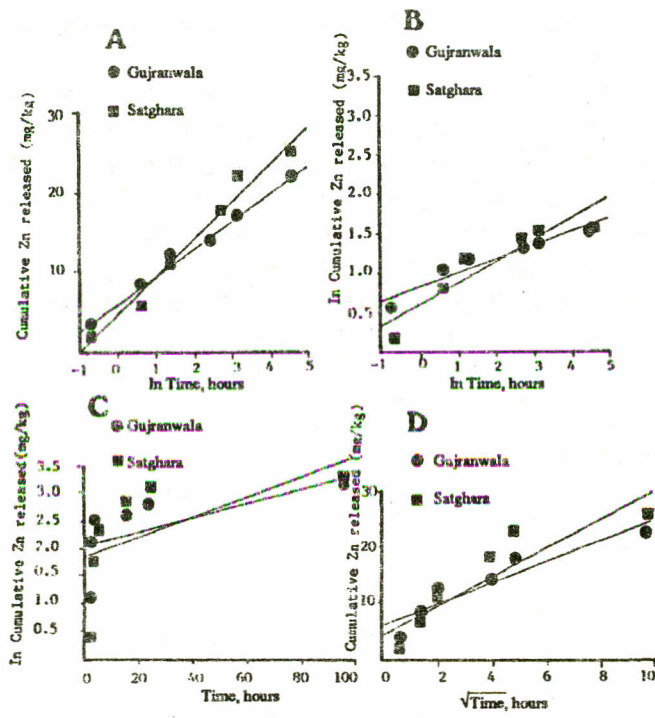
Fig. 1. Description of zinc desorption of DTPA as a function of time from Gujranwala and Satghara nodules by (A) Elovich, (B) power function, (C) first order and (D) parabolic diffusion equation.
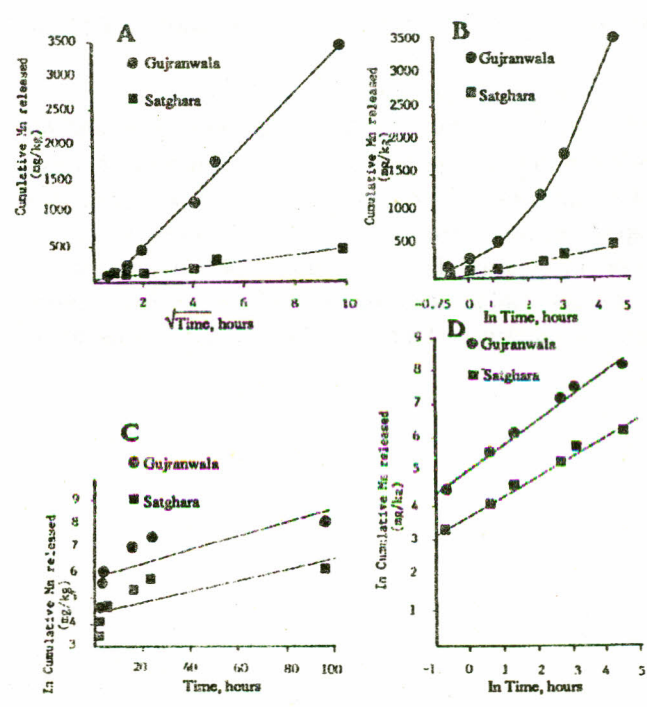
Fig. 3. Description of manganese desorption to DTPA as a function of time from Gujranwala and Satghara nodules by (A) parabolic diffusion, (B) Elovich, (C) first power and (D) power function equations.

nodules which had two different phases of Mn (birnessite and lithiophorite).

The two samples were highly heterogenous developed in situ in natural environment. The nodules recovered from Satghar soil contained more carbonates than the Gujranwala nodules while the later had birnessite and lithiophorite compared to poorly defined Mn minerals in the former. The rest of their mineral components were quite similar. Considering the three best fitted models (Elovich, parabolic diffusion and power function) initial rate of Zn release, a (intercept), was always higher in Gujranwala than satghara sample. But rate of release predicted as slope, b, as a function of time t, was lower in Gujranwala than in Satghara samples. Hence, oxide minerals present in Gujranwala had higher affinities for Zn. Unlike Zn, release of Fe and Mn as a function of time, was higher in Gujranwala than Satghara. Initial contents of Zn and Mn at t_o (intercept a) was low in Gujranwala than Satghara.

Practical implications. Rice, in Pakistan, is cultivated under submerged soil conditions. Extent of Zn deficiency in flooded rice follows N and P deficiency. Zinc accumulation away from active root zone had a significant positive correlation with Fe and Mn precipitated in the nodules found in subsurface horizons of the Gujranwala and Satghara rice soils [7] Zinc was strongly held by Fe and Mn precipitated in nodules present in the Gujranwala soil.

Elevated concentration of dissolved Fe and Mn in reduced soil environment under rice cultivation also inhibits Zn absorption by rice plants [6].

Alternate wetting and drying helps to aleviate Zn deficiency in rice by reoxidizing the reduced Fe and Mn present in soil soultion. On the other had it increases N losses [11]. Improving fertilizer use efficiency in our agricultural crop production system is of prime concern during the present era of energy crisis. Dry incorporation of N fertilizer in rice field is associated with improved fertilizer use efficiency and with low incidence of Zn deficiency. These considerations warrant the investigation of utility of submerged as compared to upland rice cultivation.

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