

WATER SOLUBLE IRON (Fe) CONCENTRATION IN ALKALINE AND CALCAREOUS SOILS INFLUENCED BY VARIOUS Fe SOURCES

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Iron availability in alkaline and calcareous soils is limited because of high pH and calcium carbonate contents. Various sources may have different solubilities within soil and may result in varying degrees of Fe availability. An incubation study was conducted to evaluate effectiveness of different sources of Fe to maintain water soluble Fe in different soils over passage of time. For this purpose, three different soils were incubated with various organic (Fe-EDDHA, Fe-DTPA, FYM) and inorganic (ferrous sulphate, vivianite) Fe sources for the period of four weeks. All amendments were adjusted to maintain 20 mg kg⁻¹ of soil Fe except FYM. Iron sources showed significantly different behavior in maintaining soil Fe in different soils. The chelates of Fe proved very effective in maintaining soil solution Fe throughout the incubation period. Fe-EDDHA maintained 12 mg kg⁻¹ with 56% recovery of total Fe added Followed by Fe-DTPA (with 30% recovery). Recovery of ferrous sulphate was negligible on the first day of incubation. Vivianite which was prepared by mixing DAP fertilizer with FeSO₄.7H₂O also rapidly converted in to insoluble fractions on first contact to soils but maintained slightly more amount of soluble Fe as compared ferrous sulphate.

Keywords: Fe, DTPA, EDDHA, calcareous, vivianite, ferrous sulphate

INTRODUCTION

Plants growing on alkaline and calcareous soils commonly suffer from Fe deficiency called as "Iron chlorosis" (Mengel, 1994) and is the second most important micronutrient disorder in arid calcareous environment after zinc (Zn) (Rashid *et al.*, 1997). Legumes, citrus, and deciduous fruits growing on these soils are more susceptible to Fe chlorosis (Rashid and Ryan, 2004; Ahmed *et al.*, 2012).

A number of strategies have been proposed to cure Fe chlorosis, among which the use of various soil amendments is common. Ferrous sulphate (FeSO₄.7H₂O) is the cheapest source hence the first choice of farmers but it rapidly oxidizes and becomes insoluble as hydroxide (Loupassaki *et al.*, 1997). Its effectiveness can be increased after mixing with some organic substrates. Organic manures contain different organic compounds which can chelate Fe and increase its solubility and mobility in the soil (Marschner, 1995; Cesco *et al.*, 2000). Use of chelates proved very effective in controlling Fe chlorosis in different crops but these chelated compounds are expensive (Lucena, 2003). Synthetic iron (II)-phosphate (also known as Vivianite) showed promising results in controlling Fe chlorosis in fruit trees (de-Santiago *et al.*, 2008). The performance of any Fe source depends on soil type and the chemical properties and/or purity of these products (Cantera *et al.*, 2002).

In cultivated alkaline and calcareous soils, the potential of applied Fe compounds depends upon the capacity of compounds to maintain soluble Fe and capacity of roots to assimilate Fe from these applied compounds (Garcia-Mina *et al.*, 2003). Stability of compound depends upon sorption, chelating agent, soil texture, pH and time (Norvell, 1999). A possible way to evaluate the potential effectiveness of the Fe compound under soil conditions would be to study the changes in concentration of the total Fe and the Fe compound in soil solution over time (Alvarez-Fernández *et al.*, 1997; Siebner-Freinbach *et al.*, 2004). For this purpose a study was conducted to evaluate ability of different Fe sources to maintain water soluble Fe in calcareous soils over time.

MATERIALS AND METHODS

Soil sampling and preparation: Three soils with different physicochemical properties were collected from different citrus orchards of Sargodha District (Table 1). Collected soils were air dried and ground to pass through 2 mm sieve. Different physical and chemical properties were determined according to standard methods (Ryan *et al.*, 2001).

Fe Sources: Five different sources of Fe were used and prepared soils were incubated with Fe different sources for 4 weeks. Five sources of Fe viz; ferrous sulphate (FeSO₄.7H₂O), chelates (Fe-DTPA, Fe-EDDHA), farm yard

Table 1. General description of soils used in study and total Fe concentration of FYM

	Soil Series	ECe (dS m ⁻¹)	pH _s	DTPA-Fe (ppm)	CaCO ₃ %	Texture	Total Fe ppm (oven dry basis)
Soil-1	Rasalpur	0.8±0.1	8.1±0.1	2.6±0.2	5.0±1.2	Sandy Loam	
Soil-2	Bhalwal	1.2±0.2	7.9±0.1	7.2±0.3	4.3±0.8	Silt Loam	
Soil-3	Jakkar	1.1±0.1	8.4±0.1	9.1±0.2	8.0±1.1	Loam	
FYM	-	-	-	-	-	-	70±5.0

Values are means of replicates ± standard deviation

manure (FYM) and modified vivianite (Diammonium Phosphate plus FeSO₄) were used. Vivianite was prepared by mixing DAP fertilizer with ferrous sulphate at the ratio of 1:3(w/w). The solution was shaken on a reciprocating shaker until a grayish color appeared.

Incubation: Twenty gram of each soil was taken in plastic bottles and incubated for 1 day, 7 days, 14 days and 28 days. All soils were kept at their field capacity during the whole incubation period and kept in dark. All treatments were adjusted to maintain 20 mg kg⁻¹ of Fe in incubated soils except FYM. Well decomposed FYM (cow dung) was applied at rate of 10 tons ha⁻¹ with and without FeSO₄.7H₂O. The vivianite solution was applied to soil by continuous shaking.

Measurements: The water soluble Fe contents of soils were measured using the method explained by Siebner-Freinbach *et al.* (2004). On extraction day, soils were tumbled mixed with distilled water for 2 hours. For 20mg of soil, 40ml of deionized water was used. After shaking, the supernatant was collected and filtered. Atomic Absorbance Spectrophotometer (Varian, SpectraAA 220) was used to

measure Fe concentration from filtrate. FYM was analyzed for Total Fe contents with wet digestion process (Chapman, 1975) and digested material was subsequently analyzed on Atomic Absorption Spectrophotometer.

Statistical Analysis: Statistical analysis was done in CRD with three repeats of each treatment. All means and graphs were drawn with Microsoft Excel. Means were compared by using the least significant difference (LSD) at a 5% level (Steel *et al.*, 1997).

RESULTS AND DISCUSSION

Different Fe sources used for incubation were found to have significantly varied in their ability to provide soil-Fe (Table 2). However, different textured soils did not vary significantly in maintaining water soluble Fe concentration over period of time. Interaction was found significant between days of incubation and soil types (p<0.05).

With respect to Fe sources, the soils incubated with chelates were found to have significant amount of water extractable soil Fe as compared to other sources. During the whole

Table 2. Water soluble Fe concentration (mg kg⁻¹) in different soils incubated with different source of Fe.

Soils	Sources	Time				Mean
		Day1	Day-7	Day-14	Day-28	
Soil-1	Fe-EDDHA	11.22	10.79	11.94	9.40	10.84AB
	Fe-DTPA	5.04	5.50	6.87	4.63	5.51D
	FeSO ₄	0.09	0.27	0.11	0.09	0.14E
	Vivianite	0.35	1.34	0.34	0.35	0.59E
	FYM	0.11	0.30	0.29	0.11	0.20E
	FYM + FeSO ₄	0.25	0.38	0.38	0.25	0.31E
Soil-2	Fe-EDDHA	11.60	11.71	13.70	8.99	11.50A
	Fe-DTPA	5.54	5.68	7.60	4.97	5.95C
	FeSO ₄	0.34	0.44	0.05	0.34	0.29E
	Vivianite	0.84	1.00	0.23	0.84	0.73E
	FYM	0.47	0.42	0.09	0.47	0.36E
	FYM + FeSO ₄	0.66	0.62	0.21	0.66	0.54E
Soil-3	Fe-EDDHA	11.30	11.88	12.20	8.65	11.01B
	Fe-DTPA	6.36	8.69	4.40	3.29	5.68CD
	FeSO ₄	0.41	0.20	0.12	0.44	0.30E
	Vivianite	1.36	0.90	0.24	0.35	0.71E
	FYM	0.29	0.25	0.19	0.29	0.25E
	FYM + FeSO ₄	1.37	0.36	0.50	1.30	0.90E

Means with the same letter were not significantly different (p<0.05)

incubation period, the highest soil solution Fe (13.7 mg kg^{-1}) was maintained by Fe-EDDHA in Bhalwal soil series. Average over all values, Fe concentration of 10.5 mg kg^{-1} was observed when incubated with Fe-EDDHA followed by Fe-DTPA (5.8 mg kg^{-1}). The other sources remained statistically non-significant. The lowest Fe concentration (0.09 mg kg^{-1}) was observed where ferrous sulphate was applied. Maximum of Fe concentration of 0.47 mg kg^{-1} was observed in soils incubated with FYM.

Behavior of Ferrous sulphate over time in different soils:

On first day of incubation, little or no Fe was detected in all soils treated with ferrous sulphate (Fig. 1). All soils showed a similar trend with recovery percentage of almost zero. This indicates that ferrous sulphate rapidly oxidizes to insoluble forms in alkaline and calcareous soils (Rosado *et al.*, 2002). Slightly higher soil solution Fe in Soil-3 on day one can be attributed to dispersion of soil due to high pH of Soil-3. This happens when soils are extracted with water rather than with buffer solution. But if 0.2 ppm detection of atomic absorbance is considered as error then Soil-3 will have zero concentration of water soluble Fe. Soil solution concentration of Fe with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ application was almost zero in all incubation periods. This indicated that higher rates of ferrous sulphate are needed to alleviate Fe chlorosis with repeated applications. Some researchers suggested its band placement with seeds and use of polymers to prevent soil reactions (Godsey *et al.*, 2003).

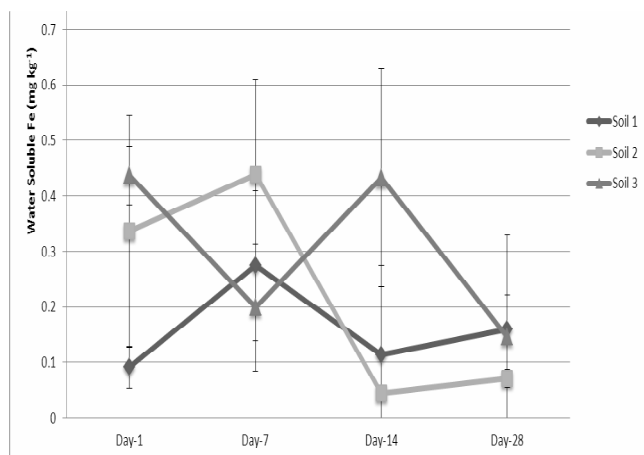


Figure 1. Time course action of FeSO_4 in regulating water soluble Fe of three soils. Error bars on figure shows standard deviation of means.

Behavior of Fe-EDDHA over period of time in different soils:

The amount of Fe in soil solution maintained by EDDHA on first day was 12.3 mg kg^{-1} with the recovery of 56% of total Fe added (Fig. 2). This recoverable percentage was significantly higher than any other treatment. After a significant drop of over half of amount of the Fe-EDDHA on first contact with soils, the solubility of Fe declined very

slowly afterward. Although the solubility of Fe-EDDHA decreased with time yet Fe-EDDHA maintained a significantly higher concentration of Fe as compared to the other Fe sources after all incubation periods. The behavior of Fe-EDDHA differed significantly with soil types. Moreover, the behavior of Fe-EDDHA changed with time in soils with different physicochemical properties. Length of incubation period also affected the pattern behavior of Fe-EDDHA among different soils. Soil-3 maintained a higher amount of Fe concentration after first day of incubation. Although Soil-3 had a higher pH value and CaCO_3 content as compared to other soils, it maintained the higher concentration of water extractable Fe as compared to other soils after the first day. This might be due to the fact that the Soil-3 had high DTPA-Fe contents as compared to other soils. Fe-EDDHA has the ability to solublize the reactive Fe oxides and thus chelate a little amount of Fe from poorly crystalline Fe oxide surface. The other possibility could be that pH and CaCO_3 had nothing to do with EDDHA in that short period of time (Ahrland *et al.*, 1990). However, after 4 weeks of incubation time, Soil-3 had lower contents of solution Fe as compared to other soils. This indicates that during the early days soil alkalinity and calcareousness of soils had little effect on stability of EDDHA. The competition of Fe^{3+} and Ca^{++} affect the stability of Fe-chelates in calcareous soils (Norvell, 1991). Soil-3 (pH=8.4) maintained a higher concentration of Fe as compared to other soils in early days. After 2 weeks a sharp decline in water soluble Fe concentration was observed in Soil-3 as compared to other soils. This explains that reaction time in alkaline calcareous soil is a very important factor that regulates the availability of Fe. Soil-1 and Soil-2 which had lower concentrations of water soluble Fe in early days as compared to Soil-3 maintained slightly higher amount of Fe in solution after 2 and 4 weeks.

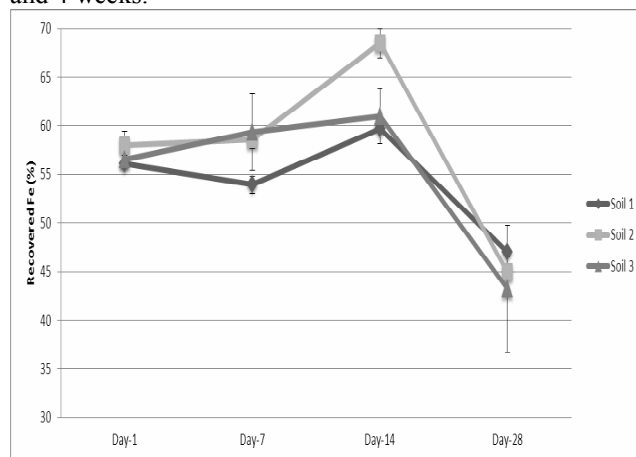


Figure 2. Time course action of Fe-EDDHA in regulating water soluble Fe of three soils. Error bars on figure shows standard deviation of means.

Behavior of Fe-DTPA over period of time in different soils:

The adsorption of Fe-DTPA was very high on first contact with 70% of chelate adsorbed to soil surfaces (Fig. 3). In Soil-3, about 15% increase in its recovery was observed in the first eight days of its application, but dropped thereafter. Several studies have explained this rise in Fe solubility could be due to desorption of DTPA after first day (Goos and Germain, 2001, Garcia-Mina *et al.*, 2003). However, in Soil-1 and Soil-2 this rise in Fe concentration was observed in third week. DTPA performed second to EDDHA in maintaining soil soluble Fe level with 30% recovery on average basis.

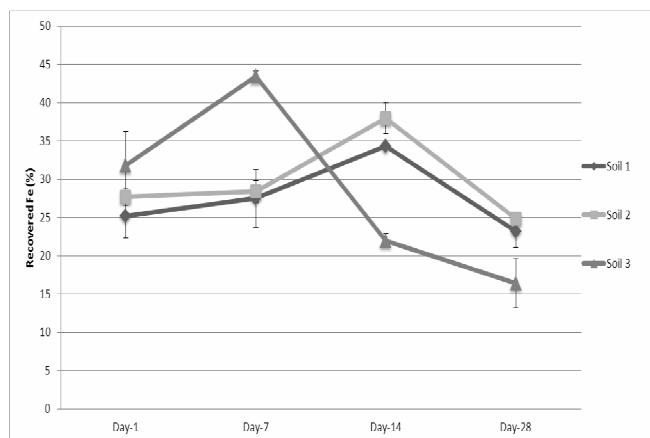


Figure 3. Time course action of Fe-DTPA in regulating water soluble Fe of three soils. Error bars on figure shows standard deviation of means.

Behavior of vivianite over period of time in different soils:

Vivianite maintained a measureable level of soluble Fe in the solution throughout the incubation period (Fig. 4). The concentration of Fe (1.24 mg kg^{-1}) maintained by vivianite was slight more to the amount (0.73 mg kg^{-1}) maintained by the ferrous sulphate. After one day of incubation, the concentration of Fe maintained by vivianite was higher than that from ferrous sulphate. But for the rest of period, vivianite behaved very similar to ferrous sulphate. Its conversion to insoluble forms was rapid on first contact to soil similar to ferrous sulphate. However, use of vivianite has proved very effective in controlling Fe chlorosis in different crops and many researchers found it very affective like Fe chelates (Rombolà *et al.*, 2003). In our study vivianite maintained very low detectable Fe levels as compared to chelates. The behavior of Fe-vivianite can be best judged by applying it to plants where rhizosphere can modify the vivianite over period of time. de-Santiago *et al.*, (2013) found ferrous sulphate more effective in increasing the leaf Fe concentration in first crop as compared to vivianite, whereas in the second crop, vivianite treated plant were found with significantly higher Fe concentration in leaf portion as compared to $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

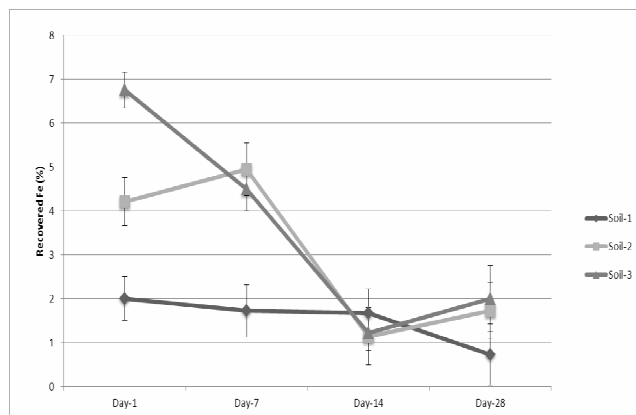


Figure 4. Time course action of Fe-Vivianite in regulating water soluble Fe of three soils. Error bars on figure shows standard deviation of means.

Behavior of FYM over period of time in different soils:

Water soluble Fe concentration was lower in all soils where only FYM was applied as compared to all other treatments. There was no significant change in Fe concentration observed over entire period of incubation in all soils. This may be due the fact that FYM is very low in soluble Fe contents. However, in many field trials, application of FYM manure has shown significant affect in increasing the plant growth and leaf Fe concentration especially in second and third crops (Singh and Dahiya, 1980; Özdemir and Tangolar, 2007). This may be also due to improvement of soil conditions associated with addition of organic matter (Chen *et al.*, 1998).

Conclusion: All Fe sources behaved differently on different soils. Fe-EDDHA and Fe-DTPA chelates maintained significant amount of soluble Fe for four weeks of incubation period. DTPA ranked second to EDDHA in solubilizing the soil Fe. Ferrous sulphate rapidly oxidized to insoluble forms on very first contact in all soils regardless of soil properties. Vivianite prepared by mixing ferrous sulphate and DAP showed better ability to maintain Fe as compared to sole application of ferrous sulphate. In the future, studies should involve variety of new chelates, humic substances and mixing with inorganic substances on more number of soils.

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