



## Amendments mediated iron immobilization under different moisture regimes in metal contaminated soil

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### ABSTRACT

The present study was performed to evaluate the effect of lime, poultry manure and farmyard manure (FYM) application on the immobilization of soil iron (Fe) under both submergence and alternate wetting-drying (AWD) soil moisture regimes. Effect of soil amendments (organic and inorganic) and soil moisture regimes on the dry matter yield, total Fe content in plant, the DTPA-extractable soil Fe and the distribution of Fe in various chemical fractions of contaminated soil was explored in the greenhouse pot experiment during 2018 at IARI, New Delhi. Results indicated that the mean DTPA-extractable Fe content in post-harvest soil was found significantly lower under AWD (84.8 mg/kg) as compared to submergence (118 mg/kg). The mean DTPA-extractable Fe was significantly reduced by 14.7% due to the application of lime over control. Poultry manure and FYM application were ineffective in altering the mean DTPA-extractable Fe. Water soluble and exchangeable Fe content in post-harvest soil was decreased significantly by 17.7% under AWD compared with submergence and it was reduced significantly by 25.2% due to the lime application over control. Whereas, carbonate bound Fe content was increased significantly by 8.0% due to the lime application over control while it was decreased significantly by 5.3% due to the poultry manure over control. Therefore, lime application under AWD soil moisture regime was the best practice for remediation of metal contaminated soil and poultry manure and FYM could be include in management practices for improving crop yield.

**Key words:** Contaminated soil, DTPA-extractable Fe, Lime, Poultry manure, Soil moisture regimes

Unlike organic contaminants, metals do not undergo microbial or chemical degradation and persist for a long time after their introduction (Adriano *et al.* 2004). Bioavailability of metals plays a vital role in the remediation of contaminated soils. Immobilizing amendments such of precipitating agents and sorbent materials decrease the bioavailability and mobility of metals, and reduce the transfer to metals to food chain via plant uptake and leaching to groundwater. Traditional methods of soil removal and replacement of clean soil is often cost prohibitive. Park *et al.* (2011) reported that bioavailability can be minimized through chemical and biological immobilization of metals using a range of inorganic compounds such as lime and phosphate (P) compounds, and organic compounds. Application of organic amendments to agricultural soils can be beneficial because they can provide nitrogen, phosphorus, and other nutrients, improve the structure of degraded soils and increase beneficial organic matter. Organic amendments have been used as chemical barriers for heavy metal movement (Ludwig *et al.* 2002). The mobility of trace metals, their

bioavailability and related toxicity to plants strongly depend on their specific chemical forms or the way that they are bound.

### MATERIALS AND METHODS

Bulk surface soil sample was collected from contaminated site (Budhanala, Ludhiana, Punjab, India) which is situated at 30° 58' 20.53" N latitude, 75° 39' 01.64" E longitude. Initial characteristics of experimental soil were determined following standard procedures (Jackson 1973). pH and electrical conductivity (EC) of experimental soil was 8.01 and 0.57 dS/m, respectively. The experimental soil was sandy clayin texture with 1.31% organic carbon content. Available N, P and K content were 376, 260 and 326 kg/ha, respectively. DTPA-extractable Pb, Cd, Cr, Ni, Zn, Mn, Fe and Cu contents were 2.55, 0.19, 0.09, 15.6, 71.3, 8.52, 123 and 21.4 mg/kg, respectively. Olsen-extractable as content in soil was 0.62 mg/kg. Total (Aqua-regia extractable) Pb, Cd, Cr, Ni, Zn, Mn, Cu and As contents were 86.6, 0.58, 278, 172, 725, 240, 82.2 and 4.49 mg/kg, respectively. Total Fe content in heavy metal contaminated soil was 2.39%. The processed soil was used for conducting greenhouse pot experiment on rice (cv. Pusa Basmati 1509) during the monsoon of 2018 at Indian Agricultural Research Institute, New Delhi to study the immobilization of Fe in metal contaminated soil using

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inorganic and organic amendments under different soil moisture regimes. All eight treatment combinations [two soil moisture regimes (Submergence and alternate wetting-drying)  $\times$  three soil amendments (Lime, poultry manure and farm yard manure) + two controls (without amendments under both moisture regimes)] were replicated thrice and experiments were laid out in completely randomised design. A uniform basal dose of N: P<sub>2</sub>O<sub>5</sub>: K<sub>2</sub>O @ 80.4:40.2: 40.2 mg/kg soils were added in solution form to the soil of each pot through urea, diammonium phosphate and muriate of potash, respectively. Lime was added @ 1 % (w/w) of soil as inorganic amendment and farmyard manure (FYM) and poultry manure were added @ 1% (w/w) of soil as organic amendment. Two soil moisture regimes were maintained for whole crop season, viz. submergence and alternate wetting-drying (AWD). One set of pot in both soil moisture regimes was maintained as a control (No lime, FYM and poultry manure). One set of the pots were maintained at submergence and another set of pots were maintained at AWD with the help of appropriate irrigation scheduling. After harvest of rice, dry matter (grain and straw) yield was recorded and soil and plant samples were collected for their analysis. Grain, husk and straw of rice were wet digested by using di-acid mixture (HNO<sub>3</sub> and HClO<sub>4</sub>, ratio 9:4) (Jackson 1973). Iron content in the digest material was determined on atomic absorption spectrophotometer (ZEEnit 700) at 248.3 nm. The DTPA-extractable Fe in post-harvest soil was extracted (soil to extractant ratio of 1:2) with 0.005 M DTPA + 0.01 M CaCl<sub>2</sub> + 0.1 M TEA solution adjusted at pH 7.3 (Lindsay and Norvell 1978) and analysed for Fe content on atomic absorption spectrophotometer (ZEEnit 700).

The water soluble and exchangeable, carbonate bound, Fe/Mn oxides bound and organically bound Fe fractions of post-harvest soil were analysed by Phillips and Chappie (1995). Analysis of variance method was followed to assess the effect of applied lime, FYM and poultry manure and soil moisture regimes on soil DTPA-extractable Fe, plant Fe content, dry matter yield of plant and different fractions of soil Fe adopting factorial concept through completely

randomized design and statistical analysis system (SAS 9.4).

## RESULTS AND DISCUSSION

*DTPA-extractable Fe in post-harvest soil:* The mean DTPA-extractable Fe content in post-harvest soil was significantly lower under AWD (84.8 mg/kg) compared with submergence moisture regime (118 mg/kg) (Table 1). Submergence reduced Fe<sup>3+</sup> to Fe<sup>2+</sup>, thus enhancing solubility (Nogiya *et al.* 2019). The DTPA-extractable Fe content in post-harvest soil was found significantly lower due to lime application under both submergence (103 mg/kg) and AWD moisture regimes (75.7 mg/kg) over control. The mean DTPA-extractable Fe was ~14.7% lower under lime application compared with control. The increase in pH due to liming might have resulted in the precipitation of metals as metal hydroxides in soil (Ok *et al.* 2011). Poultry manure and FYM were ineffective in altering the mean DTPA-extractable Fe content in post-harvest soil.

*Redistribution of Fe in different fractions of soil Fe:* Readily available (water soluble and exchangeable) Fe content in post-harvest soil was ~ 17.7% lower under AWD moisture regime compared with submergence (Table 1) and it was ~ 25.2% lower under lime application over control. The efficacy of lime in reducing metal content in water soluble and exchangeable fraction may be attributed to increase in pH (Datta and Young 2005, Meena *et al.* 2016). On an average, carbonate bound Fe content was significantly higher under AWD (538 mg/kg) compared with submergence (523 mg/kg) (Table 1). The highest mean carbonate bound Fe was found under lime application (574 mg/kg) followed by control (528 mg/kg), FYM application (519 mg/kg) and poultry manure (500 mg/kg). Carbonate bound Fe was ~ 8.0% higher under lime application over control. On the other hand, carbonate bound Fe was ~ 5.3% lower under poultry manure application over control. In contrast to our finding, Alvareng *et al.* (2009) reported conversion of available metals into SOM-associated, metal oxides and carbonates due to application of organic amendments. Oxide bound Fe in post-harvest soil was ~14.6% higher under AWD compared

Table 1 Effect of different soil amendments and soil moisture regimes on DTPA-extractable iron and various fractions of soil Fe in post-harvest soil

Amendment	DTPA-extractable Fe (mg/kg)			Water soluble and exchangeable Fe (mg/kg)			Carbonate bound Fe (mg/kg)			Fe & Mn oxide bound Fe (mg/kg)			Organically bound Fe (mg/kg)		
	S	AWD	Mean	S	AWD	Mean	S	AWD	Mean	S	AWD	Mean	S	AWD	Mean
Control	123 <sup>a</sup>	86.4 <sup>c</sup>	105 <sup>a</sup>	1.40 <sup>ba</sup>	1.14 <sup>bdc</sup>	1.27 <sup>a</sup>	519 <sup>dc</sup>	536 <sup>bc</sup>	528 <sup>b</sup>	2503 <sup>b</sup>	2880 <sup>ba</sup>	2692 <sup>ba</sup>	365 <sup>a</sup>	299 <sup>de</sup>	332 <sup>a</sup>
Lime	103 <sup>b</sup>	75.7 <sup>d</sup>	89.5 <sup>b</sup>	1.03 <sup>dc</sup>	0.87 <sup>d</sup>	0.95 <sup>b</sup>	567 <sup>ba</sup>	582 <sup>a</sup>	574 <sup>a</sup>	2735 <sup>ba</sup>	3217 <sup>a</sup>	2976 <sup>a</sup>	310 <sup>dc</sup>	281 <sup>e</sup>	296 <sup>b</sup>
PM	125 <sup>a</sup>	89.6 <sup>c</sup>	107 <sup>a</sup>	1.54 <sup>a</sup>	1.26 <sup>bac</sup>	1.40 <sup>a</sup>	491 <sup>d</sup>	510 <sup>dc</sup>	500 <sup>c</sup>	2307 <sup>b</sup>	2758 <sup>ba</sup>	2532 <sup>b</sup>	345 <sup>ba</sup>	339 <sup>b</sup>	342 <sup>a</sup>
FYM	123 <sup>a</sup>	87.4 <sup>c</sup>	105 <sup>a</sup>	1.43 <sup>ba</sup>	1.18 <sup>bdc</sup>	1.31 <sup>a</sup>	514 <sup>dc</sup>	525 <sup>c</sup>	519 <sup>b</sup>	2429 <sup>b</sup>	2826 <sup>ba</sup>	2628 <sup>ba</sup>	335 <sup>b</sup>	327 <sup>bc</sup>	331 <sup>a</sup>
Mean	118 <sup>a</sup>	84.8 <sup>b</sup>		1.35 <sup>a</sup>	1.11 <sup>b</sup>		523 <sup>b</sup>	538 <sup>a</sup>		2493 <sup>b</sup>	2920 <sup>a</sup>		339 <sup>a</sup>	311 <sup>b</sup>	

DTPA-extractable iron, water soluble and exchangeable, carbonate bound, Fe & Mn bound and organically bound soil Fe under different amendments and soil moisture regimes followed by same letter in same column and same row are not significant ( $p \leq 0.05$ ) according to Tukey's LSD test. S: Submergence; AWD: Alternate wetting-drying; PM: Poultry manure and FYM: Farmyard manure

Table 2 Effect of different soil amendments and soil moisture regimes on iron content in rice plant parts, grain yield and straw yield

Amendment	Fe content in grain (mg/kg)			Fe content in husk (mg/kg)			Fe content in straw (mg/kg)			Grain yield (g/pot)			Straw yield (g/pot)		
	Soil moisture regime														
	S	AWD	Mean	S	AWD	Mean	S	AWD	Mean	S	AWD	Mean	S	AWD	Mean
Control	51.8 <sup>a</sup>	43.4 <sup>b</sup>	47.6 <sup>a</sup>	190 <sup>a</sup>	154 <sup>b</sup>	172 <sup>a</sup>	676 <sup>ba</sup>	571 <sup>c</sup>	623 <sup>a</sup>	9.39 <sup>b</sup>	10.2 <sup>b</sup>	9.79 <sup>b</sup>	15.9 <sup>c</sup>	16.5 <sup>c</sup>	16.2 <sup>b</sup>
Lime	42.5 <sup>cb</sup>	37.2 <sup>c</sup>	39.8 <sup>b</sup>	165 <sup>b</sup>	136 <sup>c</sup>	151 <sup>b</sup>	593 <sup>bc</sup>	535 <sup>c</sup>	564 <sup>b</sup>	13.0 <sup>ba</sup>	15.5 <sup>a</sup>	14.3 <sup>a</sup>	19.8 <sup>bc</sup>	23.1 <sup>ba</sup>	21.4 <sup>a</sup>
PM	54.3 <sup>a</sup>	45.4 <sup>b</sup>	49.8 <sup>a</sup>	195 <sup>a</sup>	158 <sup>b</sup>	177 <sup>a</sup>	714 <sup>a</sup>	605 <sup>bc</sup>	660 <sup>a</sup>	13.2 <sup>ba</sup>	15.3 <sup>a</sup>	14.3 <sup>a</sup>	21.0 <sup>b</sup>	22.5 <sup>ba</sup>	21.7 <sup>a</sup>
FYM	52.3 <sup>a</sup>	44.3 <sup>b</sup>	48.3 <sup>a</sup>	194 <sup>a</sup>	157 <sup>b</sup>	176 <sup>a</sup>	693 <sup>a</sup>	584 <sup>c</sup>	639 <sup>a</sup>	13.6 <sup>ba</sup>	16.2 <sup>b</sup>	14.9 <sup>a</sup>	21.6 <sup>b</sup>	25.7 <sup>a</sup>	23.6 <sup>a</sup>
Mean	50.2 <sup>a</sup>	42.6 <sup>b</sup>		186 <sup>a</sup>	152 <sup>b</sup>		669 <sup>a</sup>	574 <sup>b</sup>		12.3 <sup>b</sup>	14.3 <sup>a</sup>		19.6 <sup>b</sup>	21.9 <sup>a</sup>	

Fe content in grain, Fe content in husk, Fe content in straw, grain yield and straw yield under different amendments and soil moisture regimes followed by same letter in same column and same row are not significant ( $p \leq 0.05$ ) according to Tukey's LSD test. S: Submergence; AWD: alternate wetting-drying; PM: Poultry manure and FYM: Farm yard manure.

with submergence (Table 1). Organic amendments did not alter oxide bound Fe (Table 1). Organically bound Fe was significantly lower under AWD compared with submergence. Lime application significantly lowered organically bound Fe compared with control.

*Fe content in rice grain, husk and straw:* The mean Fe content in rice grain was found significantly lower under AWD as compared with submergence (Table 2). Lime application significantly lowered Fe content in rice grain over control. The effectiveness of lime in lowering Fe content in different rice plant parts may be attributed to the reduced solubility of iron in limed soil as evidenced from the DTPA-extractable Fe content in soil after harvest of rice. The findings of our study are in concurrence with the findings of various researchers (Datta *et al.* 2007, Paulose *et al.* 2007). The mean Fe content in rice husk was also significantly reduced by 34 mg/kg under AWD compared to submergence. Results indicated that mean Fe content in rice husk significantly reduced (by ~12.2%) due to the application of lime over control.

The mean Fe content in rice straw was significantly lower under AWD (574 mg/kg) compared to submergence (669 mg/kg). Similar finding was reported by Nogiya *et al.* (2019) in which they found highest Fe content in leaves of iron deficiency tolerant rice genotype (IDTR) as well as iron deficiency susceptible rice genotype (IDSR) at tillering stage was observed under submergence followed by foliar application and recommended dose of Fe. Results indicated that mean Fe content in rice straw significantly reduced by 9.4% due to the application of lime over control. Similarly, a decreasing mobility of elements such as Cd, Cu, Zn, Ni, and Pb in limed soil and effective decrease of their element uptake by several crops was intensively investigated in both pot and field regimes (Hooda *et al.* 1997).

*Grain and straw yield:* On an average, grain yield of rice increased significantly by 1.16 fold under AWD over submergence (Table 2). Mean grain yield was ~ 1.46, 1.46 and 1.52 times higher under application of lime, poultry manure and FYM, respectively over control. In case of straw yield, significantly higher yield observed under AWD (21.9 g/pot) as compared to submergence (19.6 g/

pot). Lime application resulted in significant increased in mean straw yield by 1.32 times over control. The highest mean straw yield was observed under FYM application (23.6 g/pot) followed by poultry manure (21.7 g/pot) which was statistically at par with lime application (21.4 g/pot). Hence, application of organic amendments improved grain yield and plant biomass due to enhanced SOM (Bolan *et al.* 2014).

In metal contaminated soil, lime application was found to be the most effective strategy for immobilization of DTPA-extractable Fe. Poultry manure and FYM were relatively ineffective in terms of immobilization of Fe in the contaminated soil, although these manures brought significant increase in yield over control. Lime application was most effective in decreasing water soluble and exchangeable bound Fe while increasing carbonate bound Fe in post-harvest soil. The AWD moisture regime was found most favorable to arresting the transfer of Fe from metal contaminated soil to basmati rice grain. The purpose of this study was to suggest amendments for immobilization of metals in contaminated soils with very high metal/metalloid content, posing potential risk to human health by consumption of crops grown on these soils. The study was not meant for immobilization of metallic micronutrient (Fe) under normal (non-contaminated) basmati growing soils. Findings of the present investigation regarding effect of amendments (especially lime) may, therefore, be interpreted in right perspective.

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