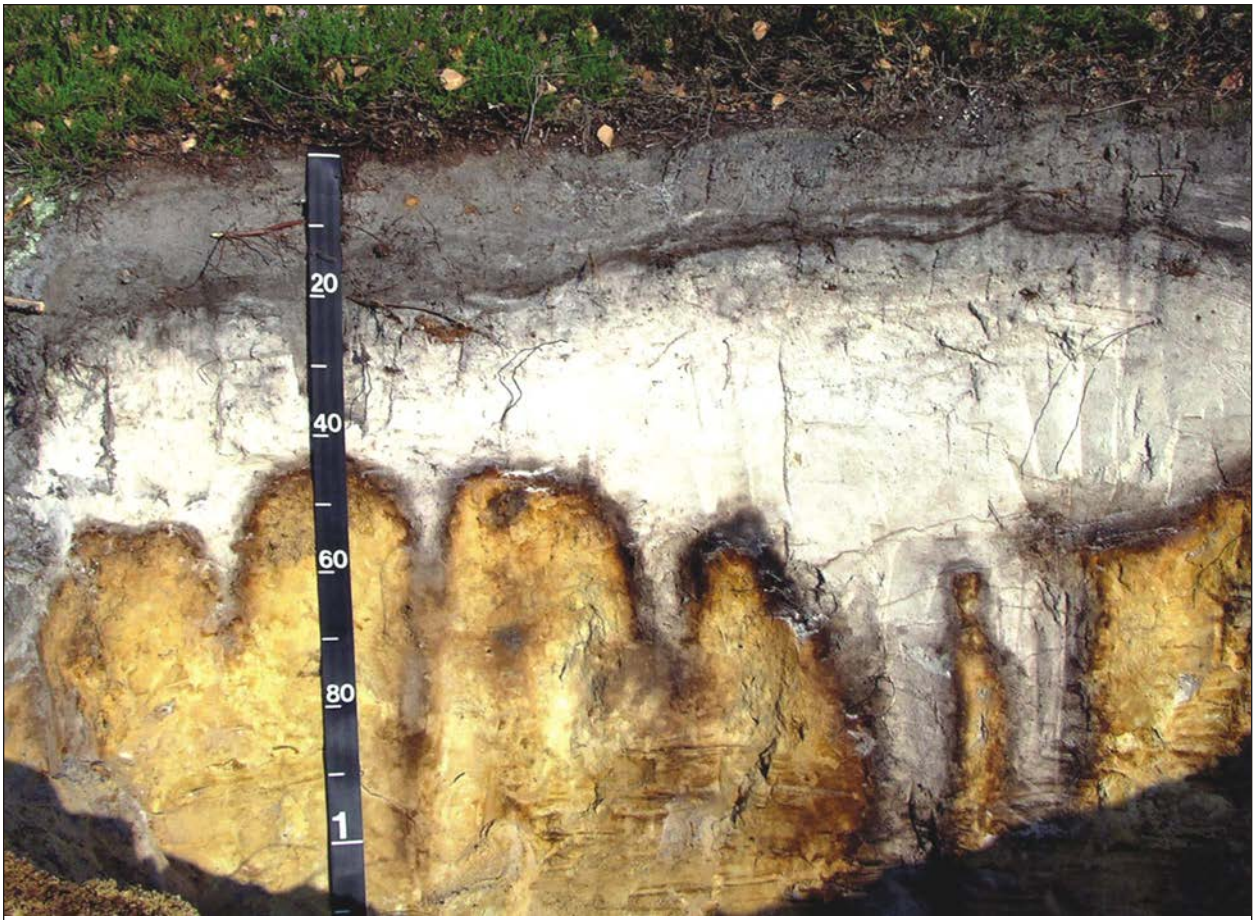

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Effects of Liming and Soil Moisture Regimes on Time Changes of Soil pH, Redox Potential, Availability of Native Sulfur and Micronutrients to Rice (*Oryza sativa* L.) in Acid Soils

[1]Ashok Kumar Karan, [1]Sandipta Kar, [1]Vikas Kumar Singh and [2]Chandra Vir Singh
[1]Department of Agricultural and Food Engineering, IIT Kharagpur, West Bengal, India
[2]Central Rainfed Upland Rice Research Station, Hazaribag, Jharkhand, India

Corresponding Author: Ashok Kumar Karan, Vikas Kumar Singh, Department of Agricultural and Food Engineering, IIT Kharagpur, West Bengal, India

ABSTRACT

The productivity of wetland rice is constrained by the reduced availability of Sulfur (S) and micronutrients in acid alluvial and laterite soils of West Bengal, India. In an attempt to increase the soil and plant availability of S and micronutrients; the effects of liming and soil moisture regimes were assessed on the time changes of soil pH and Eh, soil and plant availability of S and micronutrients. The acid alluvial and laterite soils were deficient in B but had toxic concentration of Fe Mn and Al. Prolonged submergence of soils increased pH and reduced Eh which in turn decreased the availability of S, B, Cu and Zn in these acid soils. Liming of these acid soils significantly reduced the availability of S, Cu, Zn, Fe, Mn and Al but increased B availability, irrespective of soil moisture regime. Continuous flooding during rice growing season decreased the plant availability of S, Cu, Zn and Al but increased that of B, Fe and Mn. Alternate Flooding and Drying (AFD) was more beneficial to rice than continuous flooding as it significantly increased the plant availability of S, B, Cu, Zn and decreased that of Fe and Mn.

Key words: Acid soil, pH, Eh, liming, soil moisture regimes, native S, micronutrients

INTRODUCTION

Rice is the most important food for more than 50% of the world population and it is cultivated on almost 155 million hectares of the world land area. World rice production in 2008 was approximately 661 million tons and about 90% produce in Asia (Kogel-Knabner *et al*., 2010).

The productivity of rice in India is oscillating around 2 tons ha^{-1} (Mishra, 2004) when the average productivity of the world is 3-4 tons ha^{-1} (Genon *et al*., 1994) and the estimated yield potential of the crop is 15 tons ha^{-1} (Smil, 2005). There is a large variation among national average yield with a factor of 5 to 6 tons per hectare among industrialized and developing countries (Bruinsena, 2003). The production function of rice is not responding to the increasing application rates of major fertilizer nutrients. The productivity of rice is handicapped by the degraded soil conditions, which are becoming increasingly unfavourable to the availability of secondary and micronutrients.

The acids soils of West Bengal, India are formed from acid granite and sedimentary deposit constituting shale and sand stone. Predominantly Kaolinit 1:1 type clay minerals in soil order ultisols. Paddy soil development is driven by the specific soil management practices that mask the soil's original character (Kirk, 2004). These are artificial submergence and drainage, ploughing and puddling, organic manuring, liming and fertilization. The management induced changes of oxic and anoxic conditions results in temporal and spatial (vertical, horizontal) variation in reduction and oxidation (redox) reactions are the dynamics of organic and mineral soil constitution (Cheng *et al.*, 2009). The critical Eh value for Fe reduction and consequence dissolution is 100 mv at pH 7.0.

Availability of sulfur is limited by the shallow root system in submerged soil as more than 90% of root confined to the top 20 cm of the soil. Low redox potential causes reduction of sulfates to sulfides, some of which are toxic (H_2S) and other low in solubility (FeS, ZnS). The availability of sulfur to rice in submerged soils decreases because of slower mineralization of organically bound sulfur (Bell and Dell, 2008).

Al is the most abundant component in the cultivated soil and considered as one of the primary cause of low rice productivity in acid soil if it is found in high concentration. It can be found in different forms depending on the pH of the soil solution. Al is toxic for plants when pH of soil is lower than 5.0 (Xue *et al.*, 2006). Liming is recommended for acidic soil as soil pH affect nutrient availability and the toxicity of elements such as Al (Dietzel *et al.*, 2009). Al toxicity is severe during drought period as soil becomes oxidized and pH falls (Romheld, 1998). In two acids sandy soil of Thailand (pH H_2O 4.0 and 4.5). Positive response of rice yield to lime in continuously flooded soil was observed by (Khunthasuvon *et al.*, 1998). Both soils contained a high level of exchangeable Al under air dry conditions (Seng *et al.*, 2001).

One process is the generation of H in the oxidation of Fe^2+by O_2 released from the roots. Root porosity and wall permeability should be just sufficient to meet the root respiratory requirement and perhaps to oxidize some of the toxic product of anaerobic respiration in the soil. Similar argument should apply to zinc, which should be mobilized like P in rice (Kirk *et al.*, 1994). However, zinc uptake can be inhibited by strong adsorption of Zn^{2+} on Fe hydroxide precipitate as iron plaque on rice root (Zhang *et al.*, 1998).

Under flooded condition the availability of sulfur is also reduced as most of the sulfur occurs in sulfide form. Thus, the flooded rice soils may develop unfavourable soil conditions that reduce the availability of micronutrients and sulfur due to high concentration of iron, manganese, aluminium, sulfide and dissolved carbon dioxide. The magnitude of such reduction in the availability of micronutrients due to increase in iron and bicarbonate concentration is largely influenced by the period of submergence and changes in pH and Eh (Patnaik and Mandal, 1982; Hazra *et al.*, 1987). When soils are submerged, the diffusion of O_2 into the soil and CO_2 out of the soil is greatly restricted, resulting in the accumulation of CO_2. This increases the concentration of H_2CO_3, HCO_3^- and CO_3^{2-} in the soil solution (Ponnamperuma, 1972), which may cause precipitation of Zn and Cu as their carbonates (Dutta *et al.*, 1989) and reduce their availability in flooded rice soils (Forno *et al.*, 1975). Keeping these deficiencies of knowledge in mind, the present research has been undertaken in acid laterite (Ultisols) and alluvial (Inseptisols) soils of west Bengal to evaluate the effect of liming and soil moisture regimes on the changes in pH, Eh and availability of native S and micronutrients to the rice (*Oryza sativa* L).

MATERIALS AND METHODS

Characterization of soil: The soil used in this experiment was collected from acid soils of West Bengal, India (0-20 cm depth). The climate of West Bengal is subtropical where annual rainfall varies from 1250 to 2000 mm and temperature ranges from 15 to 40°C. The soil was air dried and

Table 1: Physicochemical properties of soil

Properties	Laterite soil	Alluvial soil
Sand (%)	63.7	49.0
Silt (%)	19.4	31.2
Clay (%)	16.9	19.8
pH	4.8	5.2
CEC (CmolC kg^{-1})	4.65	7.19
Organic carbon (g kg^{-1})	5.0	5.4
Organic matter (g kg^{-1})	8.6	9.31
Calcium carbonate (g kg^{-1})	4.5	5.0
Total S (mg kg^{-1})	437	303
Total B (mg kg^{-1})	10.81	18.02
Total Cu (mg kg^{-1})	17.50	12.50
Total Zn (mg kg^{-1})	41.90	25.39
Total Fe (mg kg^{-1})	18700	12500
Total Mn (mg kg^{-1})	533	167
Total Al (mg kg^{-1})	54890	48650

passed through 0.2 mm sieve for total nutrient of soil and 2 mm sieve for exchangeable nutrient of soil. Some soil physico-chemical properties were selected (Table 1). Soil particle size was examined by hydrometer method (Bouyoucos, 1936). Soil pH was measured in a 1:2.5 soil to distilled water ratio using pH meter and soil cation exchange capacity was measured by using ammonium acetate leachate method (Jackson, 1973). Organic carbon and organic matter was determined by rapid titration method (Walkley and Black, 1934). Calcium carbonate was estimated by rapid titration method (Piper, 1950). Total content of S, B, Cu, Zn, Fe, Mn and Al in this soil were determined using anhydrous Na_2CO_3 fusion method (Jackson, 1973). Available S in exchangeable form was determined by 0.15% $CaCl_2$ extractable method (Williams and Stainberg, 1962). Soil available B as hot water soluble form was determined by hot water extractable method (Berger and Truog, 1944). Soil available Cu, Zn, Fe and Mn were estimated in exchangeable and organic bonded form by 0.005 DTPA (pH 7.3) extractable method (Lindsay and Norvell, 1978). Soil available Al in exchangeable form was determined by 1 N KCl extractable method (Black, 1965). Lime requirement in laterite and alluvial soil were evaluated by pH buffer method. The equilibrium pH method for lime requirement was adopted considering the buffer capacity of soil (Jackson, 1973).

The Details of the treatments arranged in the Split Plot Design of the experiment and replicated thrice as stated below:

Treatments
Main plot:

- L_0 = Soil without liming
- L_1 = Soil with liming @ 2 tons ha^{-1}

Sub-plot:

- FC = Field Capacity (0-30 Kpa soil matric potential)
- F = 5±1 Flooding
- AFD = Alternate Flooding (5±1) and Drying (30 Kpa soil matric potential)

Incubation studies: Two typical strongly acidic rice soils, one 'Salboni loam' from laterite (Ultisol) and the other 'Durgapur Silty loam' from alluvial (Inceptisols) groups, having pH of, respectively 4.8 and 5.2 and different concentration of sesquioxides, were selected for the controlled incubation and greenhouse studies to assess the effects of liming (0 and 2 ton ha^{-1}) and three soil moisture regime namely Field capacity (30 Kpa) 5±1 cm Flooding (F) and Alternate flooding (5±1 cm) and drying (30 Kpa), (AFD). FC moisture was maintained by replenishing water as and when required by weighing in the laboratory incubation study. In this study, 10 g soil sample was taken in a series of test tubes and wide mouth plastic bottles. The treatments of liming and soil moisture regime as stated above were imposed.

Green house studies: Two typical acidic rice soils, one 'Salboni loam' from laterite (Ultisol) and the other 'Durgapur Silty loam' from alluvial (Inceptisols) groups, having pH of respectively 4.8 and 5.2 and different concentration of sesquioxides, were selected for the controlled green house studies to assess the effects of liming (0 and 2 ton ha^{-1}) and three soil moisture regime namely Field capacity (30 Kpa) 5±1 cm Flooding (F) and Alternate flooding (5±1 cm) and drying (30 Kpa), (AFD).

For the greenhouse experiment, plastic pots were filled with 5 kg air dry soil and mixed with N, P, K fertilizers at the rate of respectively, 60 mg N, 30 mg P_2O_5 and 30 mg K_2O per kg of soil. Soils were wetted to saturation and equilibrated for two days. All the treatments were replicated thrice in the experiment. Two 10 days old rice seedlings (IR36) grown in distilled water, were transplanted in saturated soil. The changes in pH and redox potential were measured at regular intervals with the help of respectively, Grip pH meter and TOA-ORP meter at 2 cm depth of the soil. Experiment was conducted in wet (Kharif) season (June to September) and in dry (Rabi) season (November to February) (2007-08).

Soil and plant analysis: After 60 days of incubation period and growth period of rice, the soil and plant samples were analyzed for available sulfur and micronutrients. Soil pH and Eh was measured after 15, 30, 45 and 60 days of incubation. After 60 days of incubation period, the soil extractable available content of S, B, Cu, Zn, Fe and Mn were analyzed following standard methods.

The plant samples of rice, were washed with double distilled water, dried in air and then in oven at 70°C and ground by Pestle and mortar. 1 g processed plant sample was taken in a 100 mL conical flask and digested with a diacid mixture (HNO_3:$HClO_4$::10:4) on hot plate for the analyses of sulfur, copper, zinc, iron and manganese. For boron, 0.5 g processed plant sample was taken in a quartz dish and dry ashed in muffle furnace at 550°C overnight and cooled. 10 mL of 0.1 M HCl was added in the quartz dish to dissolve the dry ash. The solution was covered by glass and allowed to stand for 4 hours. Subsequently, it was filtered into a test tube. The diacid extract of plant sample was analyzed for copper, zinc, iron and manganese with the help of Atomic Absorption Spectrophotometer (Pye-Unicam-SP-9, 800, made in U.K). For boron, 0.1 M hydrochloric acid extract was analyzed calorimetrically with the help of Autoanalyser (CFA system 4, Chemlab, made in U.K) by using Azomethine-H indicator (Basson *et al.*, 1969). The plant extract was analyzed for sulfur by the Turbidimetric method using a colorimeter. A series of known Standards of S, B, Cu, Zn, Fe, Mn and Al were used to compare as reference of the soil and plant samples.

Statistical analysis: Statistical analyses were performed with the help of the MSTAT computer package to estimate the regression equations relating dependent variables with independent variables. In order to test the significance of different treatments individually as well as in combinations the experimental ANOVA was performed for the split plot design by the method described by Gomez and Gomez (1984). The comparisons between the treatment means were tested and Least Significant Difference (LSD) were calculated at 5 and 1% level of significance.

RESULTS

Controlled incubation and greenhouse studies have been conducted to evaluate the effects of liming and soil moisture regime on the time changes of pH and redox potential, availability of S and micronutrients. The studies were carried out with two typical acidic rice soils: one from laterite and the other from alluvial groups, which were maintained at two levels of liming: 0 and 2 tons ha^{-1} and three soil moisture regimes: Field capacity (FC), (5±1 cm) Flooding (F) and Alternate flooding (5±1 cm) and drying (AFD). Following superimposition of the soil moisture regimes, soil pH and Eh were measured after 15, 30, 45 and 60 days. After 60 days of incubation period and growth period of rice, which was planted in the potted soil in the greenhouse experiment, the soils and plants were analysed for available S and micronutrients. The results obtained in these studies are presented below.

Changes in pH and extractable S, B, Cu, Zn, Fe, Mn and Al in air dry and flooded acid soil: Initial air dry soil of pH values were 4.8 and 5.2 and after 60 days of incubation of continuous flooding pH values were increased and reached a peak of 6.9 and 7.1 in laterite and alluvial soil, respectively. In air dry soil 0.15% calcium chloride extractable values of S were 16.6 and 22.2 mg kg^{-1} and after 60 days of flooding values were decreased to substantial level 4.54 and 6.81 mg kg^{-1} with a percentage decrease of 73 and 69 in laterite and alluvial soils, respectively. In air dry soil before flooding hot water extractable B values were 0.22 and 0.35 mg kg^{-1} and after 60 days of flooding values were decreased to 0.08 and 0.23 mg kg^{-1} with a percentage of decrease about 64 and 34 in the laterite and alluvial soil, respectively. In air dry soil DTPA pH 7.3 extractable Cu values were 1.57 and 1.75 mg kg^{-1} and after 60 days of flooding values were decreased to substantial level 0.23 and 0.22 mg kg^{-1} with a percentage of decrease about 85 and 87 in the laterite and alluvial soil, respectively. In air dry soil before flooding DTPA pH 7.3 extractable Zn values were 1.50 and 0.94 mg kg^{-1} and after flooding values were decrease to 1.11 and 0.32 mg kg^{-1} with a percentage of decrease about 26 and 66 in laterite and alluvial soils, respectively. In air dry soil before flooding DTPA pH 7.3 extractable Fe values were 96 and 160 mg kg^{-1} and after flooding values were increased and reached a peak of 217 and 467 mg kg^{-1} with a percentage of increase about 126 and 192 in laterite and alluvial soils, respectively. In air dry soil before flooding DTPA pH 7.3 extractable Mn values were 118 and 10 mg kg^{-1} and after flooding values were increased and reached a peak of 282 and 56 mg kg^{-1} with a percentage of increased about 139 and 460 in laterite and alluvial soils, respectively. In air dry soil before flooding 1N KCl extractable Al values were 75.5 and 67.3 mg kg^{-1} and after 60 days of flooding values were decrease to 16.6 and 7.4 mg kg^{-1} with a percentage of decreased about 78 and 89 in laterite and alluvial soils, respectively (Table 2).

Effects on the time changes of pH and redox potential: The time changes of pH and redox potential (Eh), which was characterized by Pe + pH, in the potted soil planted with rice, revealed that pH of both laterite and alluvial soils increased gradually up to 45 days and then remained stable (Fig. 1, 2). The initial pH was 4.8 and 5.2, respectively of unlimed laterite and alluvial soils, while for limed laterite and alluvial soils the initial pH that was measured 15 days after mixing with lime and watering was, respectively 6.4 and 6.5. After 60 days of transplanting, pH

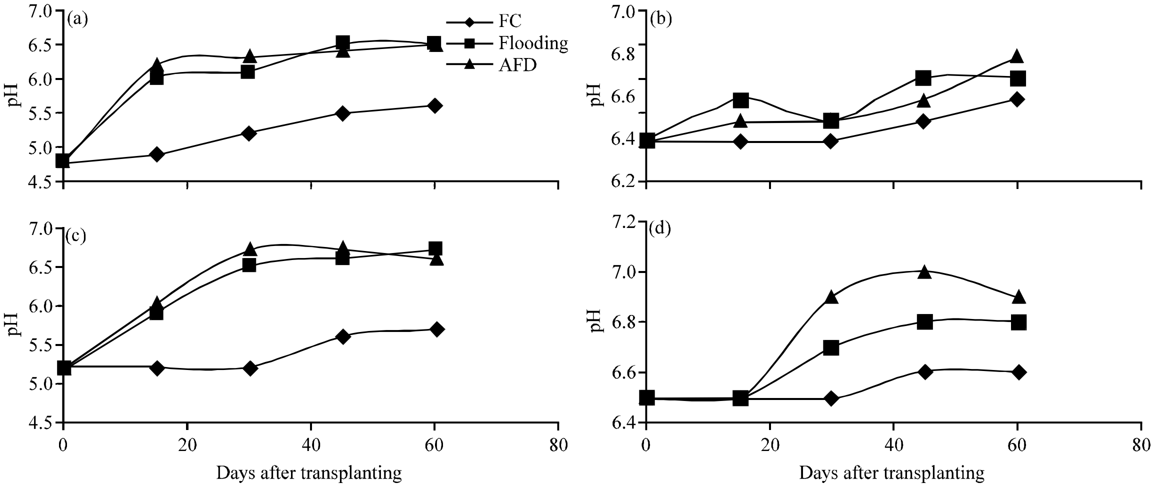

Fig. 1(a-d): (a) Changes in pH of unlimed laterite soil at 2 cm depth, (b) Changes in pH of limed laterite soil at 2 cm depth, (c) Changes in pH of unlimed alluvial soil at 2 cm depth and (d) Changes in pH of limed alluvial soil at 2 cm depth

Table 2: Effect of 60 days incubation of flooding on the changes of pH and available S, B, Cu, Zn, Al, Fe and Mn in acid soils

	Laterite soil			Alluvial soil		
Parameters (mg kg^{-1})	I	F	Decrease (%)	I	F	Decrease (%)
S	16.6	4.54	73	22.2	6.81	69
B	0.22	0.08	64	0.35	0.23	34
Cu	1.57	0.23	85	1.75	0.22	87
Zn	1.50	1.11	26	0.94	0.32	66
Al	75.5	16.6	78	67.3	7.4	89
	I	F	Increase (%)	I	F	Increase (%)
Fe	96	217	126	160	467	192
Mn	118	282	139	10	56	460
pH	4.8	6.9	44	5.2	7.1	37

I: Initial air dry soil, F: Flooded soil

of unlimed laterite and alluvial soils increased, respectively from 4.9 to 5.6 and 5.2 to 5.7 under FC, 4.9 to 6.5 and 5.2 to 6.7 under Flooding and from 4.9 to 6.5 and 5.2 to 6.6 under AFD. The pH of limed laterite and alluvial soils increased, respectively from 6.4 to 6.6 and 6.5 to 6.6 under FC, 6.4 to 6.7 and 6.5 to 6.8 under F and 6.4 to 6.8 and 6.5 to 6.9 under AFD moisture regimes. The increase in pH was, in general, more in laterite than alluvial soils. In the greenhouse experiment with rice, the initial values of Pe+pH following imposition of soil moisture regimes were 9.88 and 10.35, respectively in unlimed laterite and alluvial soils, whereas in limed laterite and alluvial soils the values of Pe+pH were 12.39 and 12.42. Pe+pH of both laterite and alluvial soils was found to decrease gradually to attain the minimum value after 60 days of transplanting.

Effect on soil and plant availability of S, B, Cu, Zn, Fe and Mn: The data on the concentration of soil extractable and rice plant available native S, B, Cu, Zn, Fe and Mn after 60 days of incubation were analysed statistically to assess the effects of liming and soil moisture

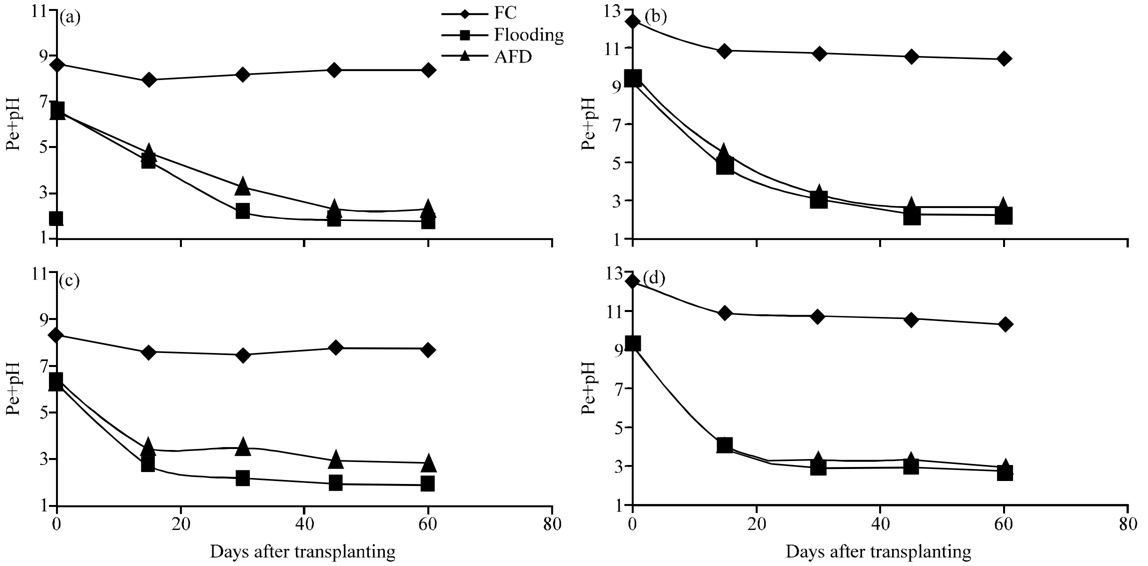

Fig. 2(a-d): (a) Changes in redox potential of unlimed laterite soil at 2 cm depth, (b) Changes in redox potential of limed laterite soil at 2 cm depth, (c) Changes in redox potential of unlimed alluvial soil at 2 cm depth and (d) Changes in redox potential of limed alluvial soil at 2 cm depth

Table 3: Effects of liming and soil moisture regime on the concentration of soil extractable and rice plant available native S, B, Cu, Zn, Fe and Mn after 60 days of incubation in laterite soil

	Conc. of soil extractable nutrients (mg kg^{-1})						Conc. of plant available nutrients (mg kg^{-1})					
	S	B	Cu	Zn	Fe	Mn	S	B	Cu	Zn	Fe	Mn
Liming												
Unlimed	13.6	0.1	0.8	1.6	174.0	233.0	2404.0	29.7	14.9	45.9	657.0	2873.0
Limed	7.6	0.2	0.7	1.4	159.0	217.0	2267.0	40.8	13.3	43.4	432.0	1500.0
LSD (p = 0.05)	0.1	0.0	0.3	0.1	0.4	1.1	24.3	2.2	0.1	0.5	23.3	45.3
Moisture regimes												
Field capacity	14.8	0.2	1.5	1.6	104.0	96.0	2451.0	33.6	16.9	54.1	561.0	2180.0
Flooding	4.3	0.1	0.3	1.3	210.0	282.0	2206.0	34.7	12.3	39.4	615.0	2370.0
AFD	12.7	0.2	0.5	1.4	185.0	295.0	2350.0	37.6	13.1	40.4	457.0	2010.0
LSD (p = 0.05)	0.2	0.0	0.2	0.2	0.8	1.0	84.0	0.3	0.3	0.4	15.7	41.6

regime on their availability. The results are presented in Table 3 and 4, respectively for laterite and alluvial soils. Liming significantly decreased the concentration of available S, Zn and Mn in laterite soil, but increased that of B irrespective of soil moisture regime. The concentrations of available Cu and Fe however, were not decreased significantly. Due to this effect of liming, the concentration of plant available S, Cu, Zn, Fe and Mn decreased and that of B increased significantly. Similarly in alluvial soil liming significantly reduced the concentration of available S, Cu, Zn, Fe and Mn, but increased the concentration of B (Table 4).

Relationships of pH and Pe+pH with soil availability of S and micronutrients: After 60 days of incubation and rice growing period, the measured concentrations of soil available S, B,

Table 4: Effects of liming and soil moisture regime on the concentration of soil extractable and rice plant available native S, B, Cu, Zn, Fe and Mn after 60 days of incubation in alluvial soil

	Conc. of soil extractable nutrients (mg kg^{-1})						Conc. of plant available nutrients (mg kg^{-1})					
	S	B	Cu	Zn	Fe	Mn	S	B	Cu	Zn	Fe	Mn
Liming												
Unlimed	14.6	0.3	0.8	0.6	341.0	48.0	2364.0	37.0	26.2	64.3	655.0	727.0
Limed	9.8	0.4	0.6	0.5	223.0	39.0	1491.0	37.7	18.0	53.0	558.0	478.0
LSD (p = 0.05)	0.1	0.0	0.1	0.0	1.1	0.4	43.1	2.2	0.4	0.3	2.9	5.0
Moisture regimes												
Field capacity	17.9	0.4	1.6	0.9	95.0	23.0	2051.0	35.9	25.0	64.0	613.0	802.0
Flooding	6.4	0.4	0.2	0.3	386.0	52.0	1753.0	35.3	20.3	55.4	694.0	551.0
AFD	12.4	0.4	0.2	0.4	364.0	55.0	1979.0	40.9	21.0	56.5	511.0	455.0
LSD (p = 0.05)	0.3	0.0	0.2	0.0	1.0	0.8	60.0	1.1	0.2	0.7	3.1	6.2

AFD: Alternate flooding and drying

Table 5: Linear correlation coefficients (r) for the relationships of soil pH and Pe+pH with the native soil available concentration of S, B, Cu, Zn, Fe and Mn after 60 days of incubation

			Concentration in soil					
			(0.15% $CaCl_2$)	(Hot water)	DTPA			
Soil group	Treatment	Soil parameters	Sulfur	Boron	Copper	Zinc	Iron	Manganese
Laterite	Unlimed	PH	-0.645*	-0.704*	-0.965***	-0.513	0.972***	0.982***
		Pe+pH	0.708*	0.803**	0.995***	0.601	-0.995***	-0.991***
	Limed	PH	-0.111	-0.283	-0.498	-0.395	0.499	0.773*
		Pe+pH	0.670*	0.939***	0.981***	0.937***	-0.971***	-0.865**
Alluvial	Unlimed	PH	-0.939***	-0.121	-0.979***	-0.979***	0.984***	0.972***
		Pe+pH	0.973***	0.255	0.989***	0.997***	-0.994***	-0.960***
	Limed	PH	-0.438	-0.454	-0.777*	0.733*	0.768*	0.839**
		Pe+pH	0.789**	0.906***	1.000***	0.995***	-0.998***	-0.993***

*, ** and ***Significant at the 0.05, 0.01 and 0.001 probability levels, respectively

Cu, Zn, Fe and Mn were regressed with pH and Pe+pH and the linear correlation coefficients obtained for these relationships are presented in Table 5. The available concentration of native S was significantly and negatively correlated with pH of unlimed laterite soil. However, this relationship was nonsignificant in limed laterite soil. In alluvial soil also available S was highly significantly and negatively related with pH, but the relationship was nonsignificant in limed alluvial soil (Table 5).

Relationships of pH and Pe+pH with plant availability of S and micronutrients: As observed with soil available S, the concentration of plant available S was significantly and negatively related with pH in unlimed laterite and alluvial soils, but the same relationships were nonsignificant in limed soils. Unlike soil available B, plant available B was positively and significantly related with pH in laterite soil. However, the relationship of plant available B with pH of alluvial soil was nonsignificant. In both laterite and alluvial soils Pe+pH was not significantly related to plant available B are presented in Table 6.

Table 6: Linear correlation coefficients (r) for the relationships of soil pH and Pe+pH with the concentration of Plant available S, B, Cu, Zn, Fe and Mn after 60 days of transplanting of rice plant

			Concentration in plant					
Soil group	Treatment	Soil parameters	Sulfur	Boron	Copper	Zinc	Iron	Manganese
Laterite	Unlimed	PH	-0.661*	0.666*	-0.969***	-0.852*	0.764*	0.403
		Pe+pH	0.725*	-0.625	0.997***	0.902***	-0.817**	-0.472
	Limed	PH	-0.379	0.714*	-0.543	-0.395	-0.669*	-0.399
		Pe+pH	0.912***	-0.906***	0.988***	0.920***	0.646	0.925***
Alluvial	Unlimed	PH	-0.819**	0.430	-0.864**	-0.709*	0.477	-0.924***
		Pe+pH	0.870**	-0.371	0.912***	0.769*	-0.544	0.914***
	Limed	PH	0.083	0.499	-0.768*	-0.785*	-0.569	-0.832**
		Pe+pH	0.264	-0.276	0.999***	1.000***	0.389	0.948***

*, ** and ***Significant at the 0.05, 0.01 and 0.001 probability levels, respectively

Table 7: Linear correlation coefficients (r) for the relationships of plant concentration of S, B, Cu, Zn, Fe and Mn with native available concentration of S, B, Cu, Zn, Fe and Mn in laterite soil

	Soil available conc.					
	(0.15% $CaCl_2$)	(Hot water)	DTPA			
Plant conc.	S	B	Cu	Zn	Fe	Mn
S	0.867***	0.305	0.775***	0.930***	-0.626**	0.596**
B	-0.46	0.510*	-0.232	0.301	0.012	0.108
Cu	0.544*	0.422	0.853***	0.945***	-0.739***	-0.830***
Zn	0.308	0.448	0.723***	0.878***	-0.640**	-0.784***
Fe	0.11	-0.514*	0.035	0.301	0.182	-0.083
Mn	0.231	-0.646**	0.028	0.31	0.2	0.052

*, ** and ***Significant at the 0.05, 0.01 and 0.001 probability levels, respectively

Table 8: Linear correlation coefficients (r) for the relationships of plant concentration of S, B, Cu, Zn, Fe and Mn with native available concentration of S, B, Cu, Zn, Fe and Mn in alluvial soil

	Soil available conc.					
	(0.15% $CaCl_2$)	(Hot water)	DTPA			
Plant conc.	S	B	Cu	Zn	Fe	Mn
S	0.695**	-0.776***	0.308	0.398	0.155	0.122
B	0.006	0.288	-0.418	-0.302	0.280	0.425
Cu	0.610**	-0.582**	0.481*	0.553*	0.024	-0.161
Zn	0.591**	-0.457	0.534*	0.601**	-0.054	-0.262
Fe	0.183	-0.565*	0.053	0.004	0.285	0.021
Mn	0.759***	-0.501*	0.793***	0.791***	-0.426	-0.504*

*, ** and ***Significant at the 0.05, 0.01 and 0.001 probability levels, respectively

Relationships of plant concentration of S and micronutrients with their available concentration in soil: The plant concentration of S, B, Cu, Zn, Fe and Mn were regressed with their soil available concentration and the correlation coefficients for the relationships are presented Table 7 and 8, respectively for laterite and alluvial soils. In laterite soil, plant S concentration was highly significantly related with all nutrients except B. In laterite soil the relationships of plant Mn with soil available S, Cu, Zn, Fe and Mn were nonsignificant (Table 7), but in alluvial soil it was highly significantly and positively related with the soil available concentration of S, Cu and Zn (Table 8).

DISCUSSION

Changes in pH and extractable S, B, Cu, Zn, Fe, Mn and Al in air dry and flooded acid soil In continuous flooding there was increase in pH value approaching to neutral in acid laterite and alluvial soils. In submersed acid soil under rice cultivation due to low redox potential (Eh) and pH around 7 lead to non availability of S, Cu, Zn (Harmsen and Vlek, 1985). Due to reduction and dissolution of Fe and Mn in flooded acid soil Zn, Cu, B get occluded in these oxide forms and become unavailable in soil. Under continuous flooded condition the availability of S is also reduced as most of the S occurs in sulfide form, some of which are toxic H_2S and other low in solubility (FeS, ZnS). The slower mineralization of organically bound sulfur decreases the availability of sulfur to rise in submersed soil (Bell and Dell, 2008).

In acid soil rice productivity is constraint by either aluminum toxicity as commonly prevalent in upland soil having pH less than 5.5 or by iron and manganese toxicity that usually occur in low land soil with low oxidation- reduction potential (Eh) and pH around 7 on flooding. Considering toxic level of aluminum 25 mg kg^{-1} of soil (Tanaka *et al*., 1966), air dry acid laterite and alluvial soil contain toxic concentration of aluminum and Al toxicity problem will be enhanced during drought period as soil become oxidized and pH fall (Romheld, 1998). Strongly acidic soil after loss of soil water moisture saturation extractable aluminum increased to 1.0 c molC kg^{-1} a potential harmful level of rice (Seng *et al*., 2004). The similar observation of aluminum availability in relation to loss of soil water saturation may be associated by excess soluble Al, by contrast, flooding decreased exchangeable Al to level below the threshold for toxicity in rice (Seng *et al*., 2006). Air dry acid laterite and alluvial soil contain toxic concentration of Fe, Mn and Al considering toxic limit of DTPA extractable Fe 300 mg kg^{-1} (Lindsay and Norvell, 1978) and DTPA extractable Mn as 200 mg kg^{-1} (Lindsay and Cox, 1985). Submersed acid laterite soil contains toxic concentration of Mn and alluvial soil contains toxic concentration of Fe for rice plants. Submersed acid laterite and alluvial soil contains Al level below the toxic concentration for rice.

Considering critical deficiency limit in soils 0.15% $CaCl_2$ extractable S 10 mg kg^{-1} (Williams and Stainberg, 1962), hot water soluble B 0.36 mg kg^{-1} (Berger and Truog, 1944), DTPA extractable Cu 0.2 mg kg^{-1} and Zn 0.6 mg kg^{-1} (Lindsay and Norvell, 1978), air dry acid laterite and alluvial soils contain deficient level of available B. Submersed acid alluvial soil contains deficient level of available S, B, Cu and Zn and laterite soil contains deficient level of available S, B and Cu for rice plant.

Effects on the time changes of pH and redox potential: The redox cycling and pH condition in flooded rice soil reduction accompanied by changes in pH. Increase in pH of acid soils due to consumption of proton. Soil solution reaction is neutral at the beginning of rice cropping season (Kirk, 2004). Sajwan and Lindsay (1986) observed that below the soil-water interface Pe+pH dropped rapidly and leveled off after 30 days at 2 cm depth, the stabilized Pe+pH was approximately 4.2. The decrease was minimum under FC and maximum under F moisture regime. After 60 days of growth period Pe+pH of unlimed laterite and alluvial soils was, respectively 9.60 and 9.53 under FC, 1.95 and 2.15 under F, 2.54 and 3.42 under AFD, whereas in limed soil Pe+pH of laterite and alluvial soils was, respectively 10.51 and 10.24 under FC, 2.20 and 2.73 under F, 2.67 and 2.93 under AFD. The results of this study showed that liming increased the oxidation process as evidenced by higher values of Pe+pH compared to unlimed soil. Due to this the values of Pe+pH in limed soil was higher than those in unlimed soil even after 60 days of growth period of rice. The values of Pe+pH under FC and AFD moisture regimes were higher than those under continuous flooding (F) in both limed and unlimed soils. Higher Pe+pH under AFD can be explained by the resupply of oxygen during drying, which was depleted during flooding. Since oxygen is not available as an electron acceptor under flooding, the electron activity increased in flooded soil. As a consequence of which there was a decrease of Pe+pH in flooded soil (Sajwan and Lindsay, 1986).

In the acid laterite and alluvial soils, pH was found to be highly significantly and negatively correlated with both Eh and Pe+pH, but after liming the level of significance for the relationships decreased (lower r-values) in alluvial soils and became nonsignificant in laterite soils.

Effect on soil and plant availability of S, B, Cu, Zn, Fe and Mn: In response to effect of liming the plant available concentration of S, Cu, Zn, Fe and Mn decreased in alluvial soil after 60 days of incubation. However, the concentration of plant available B was not significantly affected by liming in alluvial soil.

The availability of S and micronutrients was also significantly affected by soil moisture regime irrespective of liming. The available concentration of S, B, Cu and Zn in laterite soil was significantly lower under continuous flooding (F) than FC and AFD moisture regimes. Sulfur deficiency has increased in prevalence in wet land rice due to low redox potential causes reduction of sulfates to sulfides and slower mineralization of organically bound sulfur decrease the availability of sulfur to rice in submerged soil (Bell and Dell, 2008). FC induced higher availability of S, B and Cu compared to AFD. The difference in Zn concentration between FC and AFD was however not significant. The concentration of available Fe in laterite soil was maximum under F closely followed by that under AFD, which had the highest concentration of available Mn. The concentration of soil available Mn under F was significantly lower than that under AFD. Soil available concentration of Fe and Mn under FC was significantly lower than those under AFD and FC. As observed with laterite soil, in alluvial soil also continuous flooding significantly reduced the availability of S, B, Cu, Zn compared to AFD and FC moisture regimes. The concentration of soil extractable S, Cu, Zn was significantly higher under FC than AFD. The difference in availability of B between FC and AFD was however, not significant. The trends observed with respect to the effects of soil moisture regime on Fe and Mn availability in alluvial soil were similar to those observed in laterite soil. In response to the effects of soil moisture regime on the availability of S and micronutrients, the plant availability of S, Cu and Zn was significantly lower under F than FC and AFD in both laterite and alluvial soils. Due to increase in soil pH under flooding, the availability of B was not significantly reduced compared to that under FC. In fact the plant availability of B significantly increased over those under AFD and FC in both laterite and alluvial soils. Plant availability of Zn as found to be significantly higher under FC than F and AFD. Rice plant availability of Fe was maximum under flooding. It was significantly reduced under AFD and FC moisture regimes in both the soils. The maximum plant availability of Mn occurred under F in laterite soil and under FC in alluvial soil. AFD induced the minimum availability of Mn in rice plant in both the soils.

The effects of liming and soil moisture regime on the availability of micronutrients are largely brought about by the changes in pH and redox potential. With increase in pH in limed soil the availabilities of Fe, Mn, Zn and Cu tend to decrease. Similarly, the increases in soil pH under F and AFD moisture regimes reduced the availability of Cu and Zn. However, the availability of B may increase with increase in pH due to either liming or flooding of soil in the neutral range of pH. Increases in availability of Fe and Mn under F and AFD moisture regimes are largely due to decrease in redox potential of the soil. As the redox potential decreases under flooding, insoluble sulfides of Cu and Zn may be formed, which make these elements unavailable to rice plant (Harmsen and Vlek, 1985). Zinc uptake can be inhibited by strong adsorption of zinc+ on Fe hydroxide precipitate as iron plaque on rice root (Zhang *et al.*, 1998). However, when the submerged soils are drained off and redox potential increases, the formation of insoluble sulfides is restricted and as a result the availability of Cu and Zn increases. Such increase in redox potential, which occurs under FC and AFD moisture regimes, helps decrease the soil and plant availabilities of Fe and Mn. Due to decrease in the availability of Fe and Mn, the reduction in the availability of B, Cu and Zn as affected by Fe and Mn, is also restricted. Under flooded condition low Eh and neutral pH may also enhance the sulfate reduction and sulfur immobilization (Islam and Ponnamperuma, 1982), which in turn decrease the availability of S to rice plant. Liming and AFD moisture regime reduced the availability of toxic concentration of Fe and Mn in acid laterite and alluvial soils and as a result availability of Fe and Mn also reduced in rice plant. Considering the critical limit of Fe in rice plant as 300 mg per kg (Tanaka and Yoshida, 1970); it has been observed that toxic concentration of Fe in rice plant is a inhibiting factor for growth of rice in acid soil.

Relationships of pH and Pe+pH with soil availability of S and micronutrients: In both the soils available S was significantly and positively related to Pe+pH; the relationships being highly significant in alluvial soil. Like S, B was also significantly and negatively related with pH in unlimed laterite soil, but the same relationship was nonsignificant in limed laterite soil. In alluvial soil the availability of B was not much affected by pH; the relationship being nonsignificant both in limed and unlimed soils. Available B was highly significantly and positively related with Pe+pH in limed alluvial soil, but in unlimed alluvial soil the same relationship was nonsignificant. The available concentration of Cu was found to be highly significantly and negatively related to pH in unlimed laterite and alluvial soils. However, in limed soil the relationship became weaker and it was nonsignificant in limed laterite soil. The relationships between Cu and Pe+pH was highly significant in both laterite and alluvial soil irrespective of liming. The pH of laterite soil was not significantly related with available Zn, but in alluvial soil available Zn was significantly and negatively related to pH. With Pe+pH Zn was highly significantly and positively related in limed laterite and alluvial soils. In unlimed alluvial soil also available Zn was highly significantly and negatively related with Pe+pH. Unlike S, B, Cu and Zn, Fe and Mn were found to be positively and highly significantly related to soil pH. The relationships of available Fe and Mn with Pe+pH were however, negatively and highly significantly related. The results of the regression analyses clearly indicate that in sesquioxide rich acid laterite and alluvial soils, the changes in pH and redox potential under prolonged wet soil moisture regime, significantly affected the availability of S and micronutrients.

Relationships of pH and Pe+pH with plant availability of S and micronutrients: The available concentration of Cu and Zn in rice plant after 60 days of transplanting was, in general, significantly and negatively related to soil pH irrespective of liming. The relationships of plant available Cu and Zn with Pe+pH were however, highly significant and positive both in limed and unlimed soils. Plant available Fe was significantly and positively related with pH in laterite soils, but the same relationship was nonsignificant in alluvial soils. Liming had little influence on the availability of Fe to rice plant. In unlimed laterite soil plant available Fe was highly significantly and negatively related to Pe+pH, but the same relationship was nonsignificant in alluvial soil. Plant available Mn was highly significantly and negatively with pH in alluvial soil, but the same relationship was nonsignificant in laterite soil. Pe+pH had highly significant positive relationship with plant available Mn in alluvial soil irrespective of liming. In limed laterite soil also Pe+pH was highly significantly and positively related with plant available Mn. The results thus indicate that plant available Cu and Zn are strongly related to the changes in pH and Pe+pH in unlimed and limed acid soils.

Relationships of plant concentration of S and micronutrients with their available concentration in soil: The relationship between plant S and available Fe was negative indicating the decrease in plant S concentration with increase in soil available Fe. The relationship between plant S and available B was non significant, which indicates antagonistic effect of soil available B on S availability. Plant Zn was highly significantly and positively related with soil available Zn and Cu in laterite soil, but the degree of significance decreased in alluvial soil. The relationships between plant Fe and soil available concentration of S, Cu, Zn, Fe and Mn were nonsignificant in both the soils. However, the relationship of plant Fe with soil available B was significant and negative. Similarly, plant Mn was significantly and negatively related with soil available B in both the soils.

CONCLUSION

Liming of acid laterite and alluvial soils significantly reduces the availability of S, Cu, Zn, Fe and Mn but increases the availability of B irrespective of soil moisture regime. Hot water extractable B is significantly and positively related with pH in acid alluvial soil. Continuous flooding during rice growing season decreases the plant availability of S, Cu and Zn but increases that of B, Fe and Mn in both limed and unlimed acid laterite and alluvial soils. In acid laterite and alluvial soils alternate flooding and drying is more beneficial to rice than continuous flooding, as it significantly increases the plant availability of S, B, Cu, Zn and decreases that of Fe and Mn which are liable to attain toxic concentration under flooded condition.

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