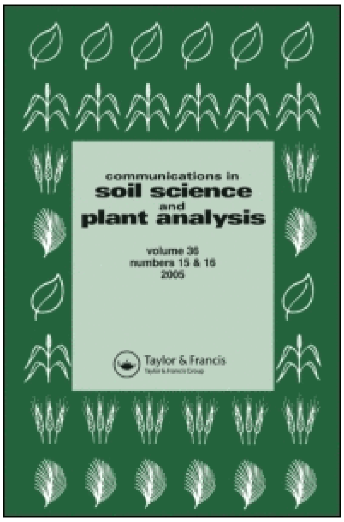

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Interrelationship of Organic Acids and Aluminum Concentrations in Rhizosphere and Nonrhizosphere Soil Solution of Rice in Acidic Soil

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To study the interrelationship of organic acids and aluminum concentrations in rhizosphere and nonrhizosphere soil solution of rice (var. Satabdi and IR 64) in acidic soil, plants were grown in plastic pots containing 500 g soil. Three organic acids (viz., tartaric, oxalic, and citric acids) were identified and quantified in rice rhizosphere and nonrhizosphere soils. Organic acids were found more in the rhizosphere soil and at early stages of crop growth, decreased sharply after 30 days of germination, and found in negligible quantity after 45 days of germination. Regression analysis revealed a significant and negative relationship between solution aluminum and organic acid. Satabdi showed greater organic acid concentration in rhizosphere soil, leading to significantly lower root and shoot aluminum concentrations and consequently significantly greater dry-matter production as well as root volume, compared to IR 64. The findings established that organic acids can effectively reduce aluminum concentration in soil solution.

Keywords Aluminum, complexation, dry matter, organic acids, rice, root aluminum, root volume, shoot aluminum

Introduction

The rhizosphere is an area of intensive interaction between plant root and soil. These interactions are of considerable significance for nutrient availability to the plant roots. Aluminum (Al) is one of the most abundant elements in the earth's crust after only oxygen and silicon, comprising about 8.13% of its mass. Although Al is abundant in the soil environment, it is not an essential element and is toxic to most organisms. In many countries with naturally acidic soils, which constitute about 40% of the world's arable soil, Al toxicity is a major factor constraining crop production, and therefore the level of Al in soil is important for soil management. Most of the Al occurs as harmless oxides and aluminosilicates when soil pH is more than 5.5. As the soil pH decreases to less than 5.5, the solubility of Al increases and phytotoxic Al accumulates in soil solution as well as on the cation exchange complex (Aitken 1992; Helyar, Conyers, and Munns 1993; Guo et al. 2004). The mobility of Al in soil and aquatic environments is controlled by its distribution between immobile solid phases and dissolved species (Driscoll and Postek 1996).

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There are several factors affecting the adsorption, desorption, and dissolution of Al in soil. These factors include the ionic forms of Al itself, quantity of organic anions capable of forming complexes with Al ions, and the surface charge of clay minerals. Furthermore, the ability of different organic anions to form complexes with Al, expressed as the stability constant of the Al complexes, may be of even more significance. The processes controlling the retention and release of Al in acidic soils are still subject to controversy, and therefore a universal hypothesis as to what mechanisms are operating has not been firmly established. Adsorption–desorption and dissolution studies have been extended to include many heavy-metal pollutants. There appears to be no definitive information in the literature on the adsorption–desorption and dissolution behavior of Al under well-defined experimental conditions. We still lack the knowledge about the influence of different levels of organic acids in the rhizosphere in regulating the kinetics of Al dissolution, so the amount of Al mobilized in the rhizosphere is hardly predictable.

The effects of Al on plant growth, crop yield, uptake, and nutrient distribution in vegetative and reproductive parts are still not fully understood. Micromolar concentration of Al can inhibit root growth within minutes or hours in many agriculturally important plant species (Kochian 1995). Inhibition of root hair formation in soybean takes place if the sum of the activities of the cationic monomeric Al species is only 2 μM (Brady et al. 1993). Plasma membrane of root cells, particularly of the root apex, seems to be the major target of Al toxicity. The most prominent symptom of Al toxicity is inhibition of root elongation, which occurs within 60 min (Sivaguru and Horst 1998), resulting in an undeveloped root system. Affected roots are usually stubby and brittle, and root tips and lateral roots become thick and may turn brown. The poor root system prevents the plants from taking up sufficient water and nutrients to support normal growth (Marschner 1995). Some plant species and cultivars have developed resistance to Al. The proposed mechanisms for such resistance include immobilization at the cell wall, selective permeability of plasma membrane, chelation by ligands in the cytosol, induction of Al-tolerant enzymes and special proteins, and exudation of low-molecular-weight organic acids from the roots (Guo et al. 2004). Hypothetically organic acid anions complex Al in the root apoplast and/or rhizosphere and thus avoid its interaction with root cellular components and its entry in the root symplast (Silva et al. 2001; Barcelo and Poschenrieder 2002; Li, Ma, and Matsumoto 2002).

Hardly any report has been obtained either to identify or quantify the release of organic acids in soil from roots in relation to Al availability. With this background, the objectives of this study were to identify and quantify the major organic acids in rhizosphere and nonrhizosphere soils of rice, to determine the interrelationship of Al and organic acid concentrations, and to correlate Al and organic acid concentrations with dry matter, root volume, and root and shoot Al concentrations of rice varieties.

Materials and Methods

Collection, Processing of Bulk Soil Samples, and Analysis of Initial Soil Properties

Surface (0–15 cm deep) soil sample classified as Haplaquept was collected from the central research farm of Orissa University of Agriculture and Technology (OUAT), Bhubaneswar, Orissa. Bhubaneswar is located at 20.5° N latitude, 85.5° E longitude at an altitude of 100 m above mean sea level. The average annual temperature of this location is 27 °C, and average annual rainfall is 1500 mm. Rice is the common crop grown in that area. The soil was air dried, crushed, and sieved (2 mm). The initial soil sample was analyzed for pH in 1:2 soil/water suspension using a combined electrode (Richards 1954). Electrical conductivity (EC; dS m^{-1}) was measured in the supernatant liquid of soil water suspension (1:2) with conductivity bridge (Richards 1954). Wet oxidation method of Walkley and Black (1934) was followed to measure organic carbon (C) content of the soil. Soil texture was determined from the textural diagram as proposed by the U.S. Department of Agriculture, based on the result of mechanical analysis by the hydrometer method (Bouyoucos 1962). Cation exchange capacity (CEC) of soil was determined as per the procedure outlined by Jackson (1974). Available nitrogen (N) was measured by the alkaline permanganate method as described by Subbiah and Asija (1956). Available phosphorus (P) was extracted following the method of Bray and Kurtz (1945), and P content in the extract was measured spectrophotometrically by the ascorbic acid method (Watanabe and Olsen 1965). Exchangeable potassium (K) was determined by the ammonium acetate method as described by Hanway and Heidel (1952). Selected physicochemical properties of the soil are pH (soil/water 1:2), 4.6; EC (soil/water 1:2), 0.30 dS m^{-1}; textural class, sandy loam (69% sand, 13% silt, and 18% clay); organic C, 0.41%; available N, 185.0 kg ha^{-1}; available P, 10.31 kg ha^{-1}; exchangeable K, 19.74 mg kg^{-1}; CEC, 8.87 cmol(p^+) kg^{-1}; and exchangeable Al, 132 mg kg^{-1} soil.

Pot Culture Experiment

Rice (*Oryza sativa*, var. Satabdi and IR 64) was grown in plastic pots containing 500 g soil in the greenhouse of the National Phytotron Facility at Indian Agricultural Research Institute (IARI), New Delhi (28° 37′ to 28° 39′ N, 77° 9′ to 77° 11′ E) for a period up to 45 days after germination. The bottoms of the pots were plugged with glass wool and cotton, and soil was placed on filter paper in the pot. The experiment was laid out in a completely randomized design (CRD) with three replications. Five rice plants were grown in each pot, and standard doses of N (54 mg kg^{-1}), P pentoxide (P_2O_5) (27 mg kg^{-1}), and K oxide (K_2O) (60 mg kg^{-1}) were applied. Destructive sampling was done to collect soil and plant samples at 15, 30, and 45 days after germination (DAG) of rice.

Collection, Processing, and Analysis of Soil Solution

Soil solution was extracted from moist soil of the pots using the immiscible displacement technique (Whelan and Barrow 1980; Percival 1990) and carefully stored carefully at 4 °C to inhibit biological activity prior to analysis. The Al content in soil solution was measured by the colorimetric procedure of Krishnamurti, Sarma, and Rengasamy (1974). The soil solution was subjected to filtration at high suction by passing through 0.1-μm-pore-size Whatman (Whatman, Kent UK) membrane filter. The Al concentration in the filtrate (i.e., monomeric Al) and Al in the residue remaining over the filter paper (i.e., complexed Al) were determined by the colorimetric procedure of Krishnamurti, Sarma, and Rengasamy (1974). The soil was extracted with 1 N potassium chloride (KCl) following the procedure of Jackson (1974), and exchangeable Al content of the soil was determined by conductometric titration. Total weak ligand concentration in soil solution was determined by conductometric titration.

Organic Acid Concentrations in Soil Solution

For estimation of organic acids, measured quantity of soil solutions were evaporated to dryness in a hot plate. The residues were esterified with diazomethane (in ether) to convert the organic acid into corresponding ester. The ether was distilled off, and the residue containing methyl ester was dissolved in 0.5 mL hexane, 3 μL of which was injected in Gas Liquid Chromatography (GLC) (Hewlett Packard, GLC model 5890A; Hewlett Packard, Palo Alto, Calif.). The specific conditions of GLC were as follows: Column: OV-17 (3%); type of column: Megabore (10 m × 0.53 mm; 2.65-μm film thickness); initial column temperature: 90 °C; temperature programming: 10 °C per minute; injector and detector temperature: 250 °C; N_2 flow: 20 mL per minute; and detector: flame ionization detector.

Standards of the acids of known concentrations were esterified and estimated in the same condition. The amounts of organic acids were quantified after comparing the peak areas of the standards and samples.

Analysis of Plant Samples

Root volume of the plants was determined by the water-displacement method. Total dry weight was determined by the standard procedure. For determining Al concentrations in root and shoot tissues, oven-dried ground plant root and shoot samples were digested separately in a triacid [nitric acid (HNO_3) / perchloric acid ($HClO_4$) / sulfuric acid (H_2SO_4); 10:4:1] mixture and in hydrochloric acid (HCl) as per the procedure outlined by Jackson (1974). Aluminum concentrations in root and shoot tissues were determined separately by the method of Krishnamurti, Sarma, and Rengasamy (1974).

Statistical Analysis

Data obtained in the greenhouse pot culture experiment were subjected to analysis of variance (ANOVA) appropriate to the experimental design. For statistical analysis of data, Microsoft Excel (Microsoft Corporation, Redmond, Wash.) and MSTATC packages (MSTAT, Michigan State, East Lansing, Mich.) were used. The relationships between Al and organic acid concentrations and between Al concentrations in plant root and shoot tissues were studied by stepwise multiple regression analysis and Pearson's correlation matrix using SPSS Window, version 14 (SPSS Inc., Chicago, Ill.).

Results and Discussion

Organic Acids in Rhizosphere and Nonrhizosphere Soils

In the present study, there were three organic acids (viz., tartaric, oxalic, and citric acids) identified and quantified in the rice rhizosphere, with the concentration of tartaric acid being the greatest (Bhattacharyya, Datta, and Dureja 2003), followed by oxalic and citric acids. Tartaric acid concentration was significantly greater at 15 days after germination (636.1, 601.0, and 255.4 mg L^{-1} for Satabdi, IR 64, and nonrhizosphere soil, respectively), decreased sharply at 30 days after germination (345.2, 301.6, and 113.7 mg L^{-1} for Satabdi, IR 64, and nonrhizosphere soil, respectively), and became negligible at 45 days after germination (50.35, 20.1, and 0 mg L^{-1} for Satabdi, IR 64, and nonrhizosphere soil, respectively). Tartaric acid concentration was significantly affected by rhizosphere, varieties, as well as stages. The interactions of rhizosphere with varieties as well as stages were also found to be significant. A similar trend was found in the cases of citric and oxalic acid also, though the varietal effect was nonsignificant in the case of both (Table 1). The concentrations of all the organic acids including total weak ligands were significantly greater in the Satabdi rhizosphere as compared to the IR 64 rhizosphere.

Table 1
Organic acid concentrations in nonrhizosphere and rice rhizosphere

DAG	Nonrhizosphere	IR 64 rhizosphere	Satabdi rhizosphere
Tartaric acid (mg L^{-1})			
15	255.40	601.00	636.10
30	113.70	301.60	345.20
45	0.00	20.10	50.35
Citric acid (mg L^{-1})			
15	2.67	35.63	36.06
30	0.00	16.13	16.57
45	0.00	0.00	0.00
Oxalic acid (mg L^{-1})			
15	11.61	54.29	57.33
30	0.00	30.14	33.17
45	0.00	0.00	0.00
Total weak ligand (meq L^{-1})			
15	7.80	14.60	18.9
30	10.67	17.48	21.75
45	9.57	16.34	20.66

Notes. Least significant differences at the 5% probability level, where R is rhizosphere, V is variety, S is stage, and NS is nonsignificant: Tartaric acid: R (20.19), S (21.63), V (17.68), R × S (30.60), R × V (24.98), V × S (NS), R × V × S (NS). Citric acid: R (6.05), S (7.51), V (NS), R × S (10.60), R × V (NS), V × S (NS), R × V × S (NS). Oxalic acid: R (5.64), S (6.88), V (NS), R × S (9.71), R × V (NS), V × S (NS), R × V × S (NS). Total weak ligand: R (0.68), S (0.44), V (0.36), R × S (NS), R × V (0.49), V × S (NS), R × V × S (NS).

The presence of various organic acids in the rhizosphere of cereals, legumes, pulses, as well as horticultural crops have been reported by several workers (Hinsinger 1998; Otani, Noriharu, and Tanaka 1996; Jones and Darrah 1994). Curl and Truelove (1986) reported as many as 12 low-molecular-weight organic acids in the rhizosphere. The reason for the greater organic acid concentration at the initial period is vigorous root growth in initial stages of crop growth, leading to greater root excretion of organic acids. Similar kinds of organic acids are produced by root exudation, partial decomposition of organic matter, as well as by microbial activities, which are clearly indicated by the presence of organic acids in nonrhizosphere soil but in smaller quantity.

Measurement of total weak acid concentration takes into account a number of weak acids other than tartaric, oxalic, and citric acids, which are produced by metabolic activities of plant roots and microorganisms. Therefore, a greater concentration of total weak acid was found in rhizosphere than in nonrhizosphere soils. The concentration of total weak ligands increased significantly from 15 to 30 DAG and decreased thereafter, and the concentration was significantly affected by rhizosphere, varieties, and stages. The interaction between rhizosphere and varieties was also significant. The presence of organic acids in later stages of growth was dependent not only on initial secretion of roots but also on the stability of particular acids in soils (Bhattacharyya, Datta, and Dureja 2003). In soil, organic acids suffer a number of fates such as sorption, biodegradation, and metal complexation, making their behavior difficult to predict (Jones et al. 2003).

The presence of low-molecular-weight organic acids such as citric, malic, oxalic (Ma and Hirdate 2000; Jones et al. 2003), and humic acids (Gerke 1994; Elkins and Nelson 2002) often alleviates Al phytotoxicity. Low-molecular-weight organic acids originate from several sources, including microbial activity, root exudation, and decomposition of plant residues (Jones et al. 2003). Depending on the capacity to form complexes with Al, organic acids are classified into three groups: (i) strong complexers: citric, oxalic, and 2,3-dihydroxybenzoic acid; (ii) moderate complexers: malic, malonic, and salicylic acid; and (iii) weak complexers: succinic, lactic, formic, acetic, phthalic, and benzoic acid (Hue, Craddock, and Adams 1986; Tam and McColl 1990; Martell et al. 1996). Since the realization that the release of organic acids from roots may confer Al resistance in plants, there has been great interest in identifying and quantifying organic acids in the rhizosphere (Ryan, Delhaize, and Jones 2001). The rates of organic acid production at different stages of crop growth under various soil conditions are also needed to be quantified in order to understand the interactions between organic acids and metals that may influence bioavailability to plants and microorganisms (Ahumada et al. 2001). However, the extent to which organic anions can decrease the concentration of toxic Al species in the soil solution and on the exchange sites is not well known. An understanding of the importance of the different organic acids to complex Al, and how this affects the availability of Al, is required to develop more effective amelioration procedures for acidic soil.

Solution, Monomeric, Complexed, and Exchangeable Aluminum in Rhizosphere and Nonrhizosphere Soils

Solution Al concentration was significantly weaker in the Satabdi rhizosphere (9.25, 13.79, and 17.27 mg L^{-1} at 15, 30, and 45 DAG, respectively) as compared to IR 64 rhizosphere (11.49, 15.68, and 19.39 mg L^{-1}, at 15, 30, and 45 DAG, respectively) and nonrhizosphere soil (11.81, 16.25, and 19.83 mg L^{-1} at 15, 30, and 45 DAG, respectively) at all the crop growth stages. Significant increase in solution Al was found with increase in DAG (Table 2). Monomeric Al concentration was significantly weaker in the Satabdi rhizosphere (2.48, 3.64, and 5.34 mg L^{-1} at 15, 30, and 45 DAG, respectively) as compared to the IR 64 rhizosphere (4.02, 4.42, and 4.88 mg L^{-1} at 15, 30, and 45 DAG, respectively) and nonrhizosphere (3.32, 4.39, and 6.21 mg L^{-1} at 15, 30, and 45 DAG, respectively). Complexed Al concentration was significantly greater in the Satabdi rhizosphere (6.24, 9.84, and 11.50 mg L^{-1} at 15, 30, and 45 DAG, respectively) as compared to the IR 64 rhizosphere (6.19, 8.97, and 10.04 mg L^{-1} at 15, 30, and 45 DAG, respectively) and nonrhizosphere soil (4.65, 8.13, and 9.89 mg L^{-1} at 15, 30, and 45 DAG, respectively). The effects of rhizosphere, varieties, as well as stages were also significant. Exchangeable Al followed a similar trend as that of solution Al, though the influence of varieties and staged were not significant.

In the present investigation, Al concentration in soil solution as well as exchangeable Al were less in the rhizosphere as compared to nonrhizosphere soils, and with an increase in organic acid concentration, Al concentration decreased. The lower concentration of Al in the rhizosphere are attributed to the formation of Al organic complexes as the rhizosphere contains a wide range of low-molecular-weight organic acids produced by metabolic activities of plant roots and microorganisms. This is in conformity with the findings of Porebska and Mulder (1996), who tested this hypothesis under field conditions and reported that mobilized Al originates largely from the organically found fraction of soil Al.

In the Satabdi rhizosphere, a greater percentage of complexed Al was found as compared to the IR 64 rhizosphere, which is because of greater organic acid production in

Table 2

Aluminum concentrations in nonrhizosphere and rice rhizosphere

DAG	Nonrhizosphere	IR 64 rhizosphere	Satabdi rhizosphere
Solution Al (mg L^{-1})			
15	11.81	11.49	9.25
30	16.25	15.68	13.79
45	19.83	19.39	17.27
Monomeric Al (mg L^{-1})			
15	3.32	4.02	2.48
30	4.39	4.42	3.64
45	6.21	4.88	5.34
Complexed Al (mg L^{-1})			
15	4.65	6.19	6.24
30	8.13	8.97	9.84
45	9.89	10.04	11.50
Exchangeable Al (mg kg^{-1})			
15	181.25	119.10	159.67
30	152.50	117.08	126.13
45	133.21	117.00	124.05

Notes. Least significant differences at the 5% probability level, where R is rhizosphere, V is variety, S is stage, and NS is nonsignificant: Solution Al: R (1.51), V (2.01), S (2.96), R × S (NS), R × V (NS), V × S (NS), R × V × S (NS). Monomeric Al: R (0.50), V (NS), S (NS), R × S (NS), R × V (NS), V × S (NS), R × V × S (NS). Complexed Al: R (0.94), V (2.13), S (2.94), R × S (NS), R × V (NS), V × S (NS), R × V × S (NS). Exchangeable Al: R (14.55), V (NS), S (NS), R × S (NS), R × V (NS), V × S (NS), R × V × S (NS).

the Satabdi rhizosphere. This result is in accord with the findings of Muhrizal et al. (2003), who reported that application of organic materials produced organic acids in soil and thus promoted complexation and chelation of monomeric Al by forming Al–organic acid complexes. As a consequence, Al toxicity was reduced. It was also reported that relative root length of mung bean increased with decreasing total and monomeric Al concentration. Thus, Al organic acid interaction promotes better plant growth at low pH values.

The present research revealed that the majority of the Al in soil solution was in the form of Al organic complexes. The fraction of monomeric Al was more in nonrhizosphere soils as compared to the rhizosphere, and over time, the monomeric Al fraction decreased and the complexed Al fraction increased. The presence of significantly greater amount of organic acids in the rhizosphere as compared to nonrhizosphere soils led to a lower percentage of monomeric Al and higher complexed Al in rhizosphere. With the progress in the crop growing period, the amount of organic acids decreased rapidly in soil and thus leading to a lower percentage of complexed Al.

Dry Matter, Root Volume, and Aluminum Concentration in Root and Shoot of Rice

Dry-matter production by Satabdi variety (11.47, 24.1, and 37 g pot^{-1} at 15, 30, and 45 DAG, respectively) was significantly greater as compared to IR 64 (8, 20.75, and

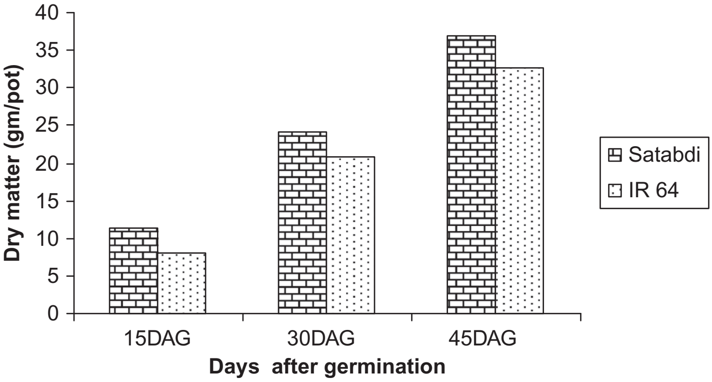

Figure 1. Dry-matter production by rice varieties. $LSD_{0.05}$: Variety, 1.03; stage, 1.26; variety × stage, NS. NS refers to not significant.

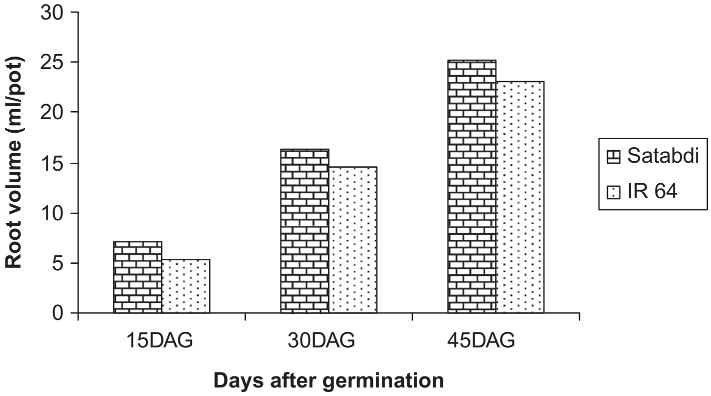

Figure 2. Root volume of rice varieties. $LSD_{0.05}$: Variety, 1.42; stage, 2.31; variety × stage, NS. NS refers to not significant.

32.64 g pot^{-1} at 15, 30, and 45 DAG, respectively) at all the crop growth stages (Figure 1). Root volume also followed a trend similar to that of dry-matter production (Figure 2). A significantly lower root as well as shoot Al concentration was found in the case of the Satabdi variety as compared to IR 64 at all the crop growth stages (Figures 3 and 4).

Under low soil pH (<pH 4.5), Al readily moves into solution, often dominates the exchange and solution chemistry of the soil (Sposito 1989), and becomes toxic to plant roots, resulting in poor root growth and reduced crop yields. In the current research, it was revealed that the Satabdi variety released more organic acids as compared to IR 64 in all the crop growth stages, resulting in better performance in acidic soil under Al-stress conditions. This finding closely follows the report that roots of Al-resistant wheat and maize cultivars rapidly excrete large amounts of low-molecular-weight organic acids (malate and citrate) into solution in response to toxic levels of Al (Pellet, Grunes, and Kochian 1995). Moreover, root tolerance to Al has been shown to be highly correlated with organic acid release in 36 wheat genotypes (Ryan, Delhaize, and Randall 1995). In a simple salt solution culture, these organic acids have been shown to render Al nontoxic (Delhaize, Ryan, and Randall 1993).

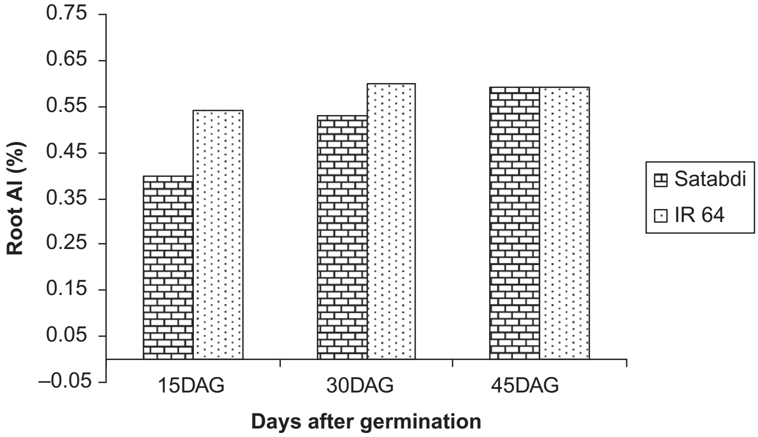

Figure 3. Aluminum concentration in roots of rice varieties. $LSD_{0.05}$: Variety, 0.009; stage, 0.006; variety × stage, NS. NS refers to not significant.

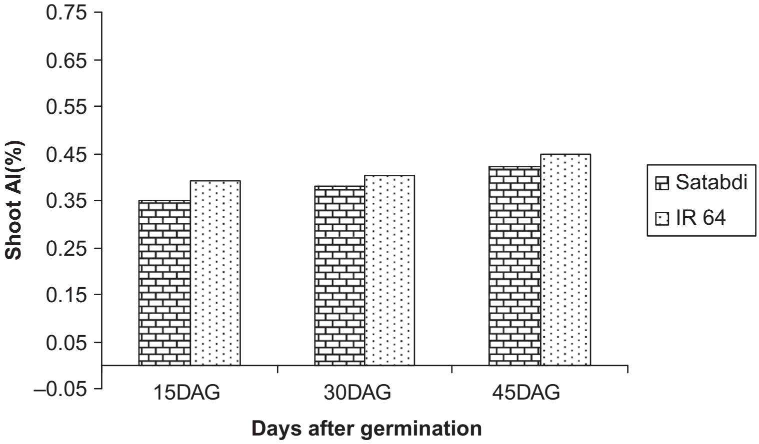

Figure 4. Aluminum concentration in shoots of rice varieties. $LSD_{0.05}$: Variety, 0.004; stage, 0.003; variety × stage, NS. NS refers to not significant.

Relationship of Organic Acids and Aluminum Concentrations

Regression analysis (Table 3) indicated the significant influence of tartaric and citric acids on solution Al concentration. Citric acid positively influenced Al concentration, but tartaric acid affected solution Al concentration negatively. No significant relationship was found between solution Al concentration with the concentration of oxalic acid and total weak ligand. Low partial correlation coefficients of variables indicates nonsignificant relationships with each other. A negative relationship of solution Al concentration with tartaric acid indicates more acid excretion by roots under Al-stress condition in acidic soil. Chemical equilibria model predictions indicated that under acidic conditions, addition of citrate was sufficient to reduce free solution Al by about 85%, while a reduction of 73% was found in case of malate (Porebska and Mulder 1996). Jones and Darrah (1994) reported that 18% of the citrate added to an acidic soil was complexed with Al and the degree of Al–citrate complexation was highly dependent on the pH of the soil solution.

Table 3
Stepwise multiple regression of aluminum and organic acid concentrations

Acid	Partial correlation coefficients (r^2)	Level of significance of r^2 (%)
Significant variables		
Tartaric acid	0.837	0.10
Citric acid	0.651	1.50
Nonsignificant variables		
Oxalic acid	0.008	84.70
Total weak ligand	0.058	60.30

Note. Solution Al = 19.77 – 0.03 Tartaric acid + 0.316 Citric acid; $R^2 = 0.968$.

It has been widely believed that low-molecular-weight organic ligands in soil environments, particularly in the rhizosphere, released by plant roots or by microorganisms, play important roles in the weathering of Al-bearing rocks and minerals, in transport of Al in soils, and in reducing Al toxicity (Poulsen and Hansen 2000; Taniguchi, Yamagata, and Sakurai 2000; Jones and Darrah 1994; Ma and Furukawa 2003). As is the case with inorganic anions, these organic ligands could be specifically adsorbed on surfaces, forming inner-sphere complexes (Henrichs and Sugai 1993; Wang and Lee 1993; Gu et al. 1994), or coordinate with Al and inhibit the hydrolytic reactions of the cation (Violante and Huang 1985). The basis of these chemical reactions relies on the complexation reaction between the carboxyl groups of the organic acids and metal cations present either in soil solution or held in the solid matrix (Jones, Prabowo, and Kochian 1996). The presence of organic anions, particularly those with a strong affinity for Al ions, can induce a change in the distribution of Al between the mineral surface and the solution through the formation of Al–organic complexes. The extent of the effect is dependent on the nature of the anion species, including the molecular structure and acid dissociation constant of the anions and the stability constant of the complex.

Correlation between Soil and Plant Parameters

Root volume was significantly and negatively influenced by solution (-0.779^{**}) and monomeric (-0.572^{*}) Al concentration, whereas complexed Al (0.747^{**}), tartaric acid (0.959^{**}), and total weak ligand (0.851^{**}) affected root volume positively. Dry-matter production also followed a trend similar to that of root volume (Table 4). The concentration of complexed Al, tartaric acid, and total weak ligand affected root volume and dry-matter production positively. Aluminum concentrations in root and shoot were significantly and positively influenced by solution and monomeric Al concentration and negatively influenced by complexed Al, tartaric acid, and oxalic acid concentrations. Thus, the results indicate that with increase in organic acid concentration, root and shoot Al concentrations decreased, leading to greater root volume and dry-matter production.

Conclusions

Three organic acids were identified and quantified in the rice rhizosphere, among which the concentration of tartaric acid was maximum, followed by those of oxalic and citric acids.

Table 4
Correlation between different soil and plant parameters

Parameter	Root volume	Dry matter	Al concentration in root	Al concentration in shoot
Aluminum				
Sol Al	−0.779**	−0.773**	0.436**	0.457**
Mono Al	−0.572*	−0.578*	0.427*	0.521*
Com Al	0.747**	0.757**	−0.995**	−0.419**
Ex Al	NS	NS	NS	NS
Organic acid				
TA	0.959**	0.953**	−0.558**	−0.630**
CA	NS	NS	NS	NS
OA	NS	NS	−0.669*	−0.598*
TWL	0.851**	0.839**	NS	NS

Notes. Sol Al, solution aluminium; mono Al, monomeric aluminum; com Al, complexed aluminum; ex Al, exchangeable aluminum; TA, tartaric acid; CA, citric acid; OA, oxalic acid; TWL, total weak ligand; NS, nonsignificant.

**Significant at the 1% level of significance.

*Significant at the 5% level of significance.

Organic acid concentration in the rhizosphere was found to be greater than in nonrhizosphere soils at all the stages of crop growth. Organic acid production was greater at the initial stage of crop growth and decreased later. Organic acid concentration in the Satabdi rhizosphere was found to be greater as compared to IR 64 rhizosphere. The Satabdi variety can perform better under Al toxic conditions, because its high organic acid–secreting capacity. Tartaric acid application can effectively reduce Al concentration in soil solution. Thus, rice varieties with high organic acid secretion capacity will perform better in Al-toxic acidic soils.

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