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Transformation of zinc and iron in submerged rice soils of Kashmir

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ABSTRACT

Thirty five alluvial rice (*Oryza sativa* L.) growing soils of Kashmir (India) were studied for transformation and distribution of different forms of Zn and Fe on submergence out of forty soils. The results revealed that more than 83% of total Zn occurred in the relatively inactive clay lattice-bound form while a smaller fraction, viz. 1.09, 1.82, 11.70 and 2.27% of the total zinc occurred as water-soluble plus exchangeable, organic complexed, amorphous sesquioxide-bound and crystalline sesquioxide bound forms, respectively. All these four Zn forms showed significant negative correlations with soil pH (r = –0.637**, –0.419*, –0.539** and –0.528**, respectively), while the latter two Zn forms showed significant positive correlations with Fe_2O_3 (r = 0.510** and 0.540**) and $A1_2O_3$ (r = 0.698** and 0.536**) content of the soils. The different Zn forms were found to have positive and significant correlations amongst each other, suggesting the existence of a dynamic equilibrium of these forms in soil. There was a marked increase in NH_4OAc and $AlCl_3$ extractable Fe with concomitant decrease in CBD-Fe. Much of Fe^{3+} in crystalline sesquioxides underwent dissolution due to reduction to Fe^{2+}.

Key words: Rice, Soils, Submergence, Transformation, Zinc fractions

Submergence of soil is known to cause drastic changes in the availability of nutrients like iron, manganese, zinc and phosphorus and thereby influencing the nutrition of the rice plant. Zinc deficiency is prevalent worldwide in temperate and tropical climates (Slaton *et al.* 2005, Prasad 2006, Fageria *et al.* 2011). Many cases of deficiency occur in developing (Third world) countries, where there is an urgent need to increase food production in order to feed their population without relying on food imports. Growing modern, high yielding varieties of crops with appropriate use of macronutrient fertilizers and irrigation is a major development in food self sufficiency. However, the sensitivity of new crop hybrids to zinc deficiency, the adverse effects of high P levels and flooding soils for rice production, can all result in a failure to realize potentially high yields due to an increase in the incidence in zinc deficiency. Widespread occurrence of zinc deficiency has been reported from many parts of the world where high yielding, fertilizer-responsive rice varieties are being grown intensively under wetland conditions. Zinc deficiency in rice has been reported in lowland rice soils of India and Kashmir by Mandal *et al.* (2000) and Wani *et al.* (2013), respectively. Zinc deficiency continues to be one of the key factors in determining rice production in several parts of the country (Chaudhary *et al.* 2007). It is now recognized as the fifth leading risk factor in developing Asian countries (Anonymous 2007) and efforts are made to reduce Zn deficiency in soils as it is not only a barrier to achieving crop yield goals but also results in low Zn content in grains and straw leading to poor Zn nutrition of humans and animals, a subject which recently received considerable attention (Schardt 2006).

Zn is essential for several biochemical processes in the rice plant, such as cytochrome and nucleotide synthesis, auxin metabolism, chlorophyll production, enzyme activation, and membrane integrity (IRRI 2000). The studies carried out in IRRI (2000) indicated that under severe Zn deficiencies, tillering decreased or could stop completely, and time to crop maturity increased. Zn deficiencies could also increase spikelet sterility in rice. The content of DTPA Zn in the soils ranged from 0.03 to 3.26 mg/kg with the mean value of 0.92 mg/kg (Table 2). Srivastava *et al.* (1999) observed that additional Zn application increased grain and straw Zn concentration. Mandal and Mandal (1986) observed that the four soil Zn pools namely (i) water-soluble plus exchangeable, (ii) organically complexed, (ii) amorphous sesquioxide-bound, and (iv) crystalline sesquioxide-bound combinedly could explain 95% of the variability of Zn concentration in lowland rice. Banin *et al.* (1990) found that zinc in Israeli soils was mainly in the residual fraction (40-54%) and the

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reducible oxide (iron oxide) fraction (20-33%). More than 47% of the land in India is deficient in zinc due to the fact that 80-96% of the zinc is in the residual fraction (Takkar 1996). Han and Zhu (1992) reported that zinc in calcareous paddy soils in China was predominantly in the residual fraction (97-99%). The results of such investigations, therefore, emphasize the importance of soil Zn pools in Zn nutrition of rice.

Rice is the staple food for more than half of the world population and it provides 21% and 15% per capita of dietary energy and protein, respectively (Maclean *et al.,* 2002). The area under rice in Jammu and Kashmir is 2.55 million hectares and the average productivity is 22.41 quintals per hectare. Rice is usually grown in soils under flooded condition. Flooding the soils brings about a number of dynamic changes in soils, which may influence Zn availability in the soil. It is known that much of the Zn remains in soil bound by oxides of iron. On submergence these oxides undergo reduction, due to anaerobiosis, to the lower valent forms which are more soluble. The bound Zn, therefore, is released and becomes available to the rice plants.

Information regarding the distribution of different pools of Zn in rice soils and their changes on submergence which are very pertinent to Zn nutrition of lowland rice are limited. The present investigation was, therefore, aimed at obtaining a more detailed and critical information on these aspects.

MATERIALS AND METHODS

The experiment was conducted in the laboratory with thirty five soils out of forty soils collected from the surface layer (0-30 cm) of typical lowland rice fields situated in the rice growing region of Kashmir, India (Table 1). The soils have been classified as Inceptisols. They collected soil samples were air-dried, pulverized and sieved through a 2-mm nylon sieve and analyzed for their various physico-chemical properties (Table 2) following the standard methods as described by Jackson (1967). Five gram portion of prepared soil sample was placed in a 100 ml polyethylene centrifuge tube. These soil samples were sequentially extracted with 20 mL of neutral 1.0M NH_4OAc (pH 7.0) and 0.05 M $Cu(OAc)_2$ solution to obtain water-soluble plus exchangeable and organic-complexed forms of Zn, respectively. The soil residue after $Cu(OAc)_2$ extraction was suspended in 20 ml of 0.2 M ammonium oxalate (pH 3.0) solution and a dithionate-citrate system buffered with $NaHCO_3$ to solvate Zn bound to amorphous and crystalline sesquioxides, respectively (Murthy 1982, Mandal and Mandal 1986). A similar set of soil samples was also extracted sequentially with (i) 1.0 M NH_4OAc (pH 4.5), (ii) 2.0% $AlCl_3$ (pH 2.8) and (iii) dithionate-citrate system buffered with $NaHCO_3$ to obtain: (i) water-soluble plus exchangeable Fe, (ii) insoluble ferrous iron and (iii) crystalline Fe oxide form, respectively (Mehra and Jackson 1960, Mandal 1961). Total Zn was extracted by digesting the soils with perchloric acid. The residual Zn fraction was found by the difference between the total Zn and the sum of other extractable fractions.

Five-gram of each of the fresh soil samples were put in a number of small containers made of Corning glass and submerged with double distilled water to a height of 5 ± 0.5 cm above the soil surface and incubated in the laboratory at the ambient temperature. Any loss of water through evaporation was compensated for by periodic addition of double distilled water. After 45 days of incubation, the soil samples were again sequentially extracted with different extractants as described previously to provide a solution in which different forms of Zn and Fe in the soil were determined. There were always three replications of each soil sample for each set of extractions. Zinc and iron in the extracts were determined with an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Distribution of total and different forms of zinc in soil

The results (Table 3) show that the total content of zinc in the soils varied within a narrow range of 117 to 240 mg/kg with a mean value of 144.5 mg/kg. The water-soluble plus exchangeable form of Zn, which represents the most readily available source of Zn was comparatively low ranging from 1.29 to 2.90 mg/kg with a mean value of 1.57 mg/kg constituting only 1.09% of the total amount. Similar results were reported by Pal *et al.* (1997). The organically complexed zinc, which is known to play a significant role in zinc nutrition of lowland rice (Mandal and Mandal 1986) was found to vary from 1.78 to 4.10 mg/kg with a mean value of 2.61 mg/kg constituting 1.82% of the total content. Similar results were reported by Katyal and Rattan (1993).The amorphous sesquioxide-bound zinc formed the major fraction amongst the four active forms of soil zinc. It ranged from 14.15 to 18.90 mg/kg with a mean value of 16.60 mg/kg and constituted 11.70% of the total amount. Similar results were reported by Hazara *et al.* (1987) and Pal *et al.* (1997). The crystalline sesquioxide-bound zinc content, which is apparently, more stable particularly under upland conditions of soil was comparatively low, ranging from 2.48 to 4.60 mg/kg with a mean value of 3.24 mg/kg, and constituted 2.27% of the total amount. In the presence of trace metals (e.g. Cu and Zn) the crystallinity or crystal growth of Fe-oxide precipitates is interfered with and hence the possibility of zinc being occluded in the crystalline sesquioxides becomes comparatively less. Moreover, the amorphous sesquioxides have a greater ability to adsorb zinc because of their high specific surface area (Davis and Leckie 1978). This may explain the occurrence of a higher proportion of zinc in the amorphous than in the crystalline sesquioxide-bound form. The results, therefore, show that about 17% of the total zinc in these soils was in the active forms, and the remaining 83% was in highly unavailable forms, apparently not contributing

Table 1 Location of surface samples in the study area.

Village	Location		Soils	Latitude	Longitude	Altitude
	Tehsil	District		(deg, min, sec)	(deg, min, sec)	
Adipora	Sopore	Baramulla	S_{1}	341816.06	742956.44	1575
Warpora	Sopore	Baramulla	S_{2}	341941.22	742932.27	1582
Hathlung	Sopore	Baramulla	S_{3}	342114.85	743035.83	1581
Malmapanpur	Sopore	Baramulla	S_{4}	342138.78	743034.33	1580
Watlab (Zoor Manz)	Sopore	Baramulla	S_{5}	342138.11	743116.83	1577
Kehnoosa	Bandipora	Bandipora	S_{6}	342300.13	743132.82	1583
Ashtough	Bandipora	Bandipora	S_{7}	342435.15	743240.24	1581
Aloosa Ghat	Bandipora	Bandipora	S_{8}	342458.22	743307.51	1580
Keemah	Bandipora	Bandipora	S_{9}	342528.71	743450.26	1584
Patushia	Bandipora	Bandipora	S_{10}	342505.96	743528.73	1578
Watapora	Bandipora	Bandipora	S_{11}	342424.18	743533.27	1582
Nathpora	Bandipora	Bandipora	S_{12}	342509.90	743715.80	1582
Bandipora	Bandipora	Bandipora	S_{13}	342456.21	743812.37	1582
Dajigam	Bandipora	Bandipora	S_{14}	342440.82	743744.41	1582
Nasoo	Bandipora	Bandipora	S_{15}	342359.82	743840.88	1582
Nadihal	Bandipora	Bandipora	S_{16}	342256.88	744008.94	1577
Garoora	Bandipora	Bandipora	S_{17}	342219.74	744010.18	1578
Gund Ajas	Sonawari	Bandipora	S_{18}	341937.97	743955.62	1575
Ajas	Sonawari	Bandipora	S_{19}	341908.60	744048.96	1583
Chewa	Sonawari	Bandipora	S_{20}	341700.98	744003.47	1578
S.K.Bala	Sonawari	Bandipora	S_{21}	341806.47	743902.67	1578
Sadunara	Sonawari	Bandipora	S_{22}	341935.71	743858.89	1578
Banyari	Sonawari	Bandipora	S_{23}	342000.05	743820.10	1578
Paribal	Sonawari	Bandipora	S_{24}	341826.60	743750.06	1577
Hajin	Sonawari	Bandipora	S_{25}	341808.29	743657.27	1578
Shahgund	Sonawari	Bandipora	S_{26}	341658.61	743427.05	1576
Tarzoo	Sopore	Baramulla	S_{27}	341616.36	743012.15	1580
Naidkhai	Sonawari	Bandipora	S_{28}	341423.40	743303.50	1575
Sumbal	Sonawari	Bandipora	S_{29}	341413.08	743835.90	1580
Nowgam	Sonawari	Bandipora	S_{30}	341328.03	743739.80	1577
Kanpeth	Pattan	Baramulla	S_{31}	34133.94	743644.66	1580
Chack Ganasthan	Pattan	Baramulla	S_{32}	341308.01	743612.16	1580
Gadah Khud	Pattan	Baramulla	S_{33}	3413.30.39	743522.24	1577
Goshbug	Pattan	Baramulla	S_{34}	341130.79	743425.35	1579
Shilwat	Sopore	Baramulla	S_{35}	341224.50	743924.25	1583
Mujgund	N.Srinagar	Srinagar	S_{36}	340802.50	744201.20	1578
Malroo- B	N.Srinagar	Srinagar	S_{37}	340709.50	744352.18	1579
Malroo- A	N.Srinagar	Srinagar	S_{38}	340704.60	744404.87	1580
Mirgund	Pattan	Baramulla	S_{39}	340900.32	743710.96	1580
Haigam	Sopore	Baramulla	S_{40}	341526.77	743034.74	1579

to the provision of the immediate zinc requirement of the plants.

The water-soluble plus exchangeable zinc showed a significant negative correlation (r = – 0.637**) with soil pH (Table 4). This is obviously due to the increased solubility of zinc at low pH and its subsequent adsorption by soil exchange complex (Bar-Yosef 1979). The organically complexed zinc showed a highly significant positive correlation (r = 0.616**) with the organic carbon content of the soils. Both the amorphous and crystalline sesquioxide-bound forms of zinc showed significant negative correlations (r = – 0.539** and – 0.528**) with pH, but significant positive correlations with Fe_2O_3 (r = 0.510** and 0.540**) and Al_2O_3 (r = 0.698** and 0.536**). The results, therefore, suggest that soils rich in oxides of iron and aluminium contain much of their zinc in the amorphous and crystalline sesquioxide-bound forms. They

Table 2 Physico-chemical characteristics of the soils

	pH (I: 2.5)	OC (%)	CEC (cmol/kg)	Clay (%)	Fe_2O_3(%)	Al_2O_3 (%)	Zn (mg/kg)	Fe (mg/kg)
Range	5.5–7.5	0.6–2.4	8–17	19–39	0.20–0.39	0.22–1.19	0.03–3.26	0.14–30.62
Mean	6.59	1.53	12	30	0.31	0.85	0.92	15.35
SD	0.64	0.47	3	6	0.05	0.29	0.51	7.34

Table 3 Distribution of different forms of Zn in the soils

	Zinc (mg/kg) extracted by				
	NH_4OAc	$Cu(OAc)_2$	$(NH_4)_2C_2O_4$	CBD	Total
Range	1.29–2.90	1.78–4.10	14.15–18.90	2.48–4.60	117.0–240.0
Mean	1.57 (1.09)	2.61 (1.82)	16.60 (11.70)	3.24 (2.27)	144.5
SD	0.306 (0.096)	0.464 (0.291)	1.171(1.553)	0.470 (0.308)	23.81

Figures between parentheses represent per cent of total content

Table 4 Linear correlation coefficients (r) between soil characteristics and different forms of zinc in the soils

Extractants	pH	Organic carbon	Clay	Fe_2O_3	AI_2O_3
NH_4OAc	–0.637**	0.346	0.348	–0.310	–0.370*
$Cu(OAc)_2$	–0.419*	0.616**	0.561**	0.486*	0.557**
$(NH_4)_2C_2O_4$	–0.539**	0.277	0.574**	0.510**	0.698**
CBD	–0.528**	0.481*	0.523**	0.540**	0.536**

* and ** denote significant differences at 0.05 and 0.01 probability levels, respectively.

are supposed to play a less important role in supplying zinc to crops grown in soils under upland condition, although they are likely to be important for the rice crop, which is grown mostly in soil under submerged condition. The different forms of zinc were found to be significantly and positively correlated amongst each other (Fig 1), which suggests the existence of a dynamic equilibrium between them. The findings are also in conformity with those of Mandal *et al.* (1986).

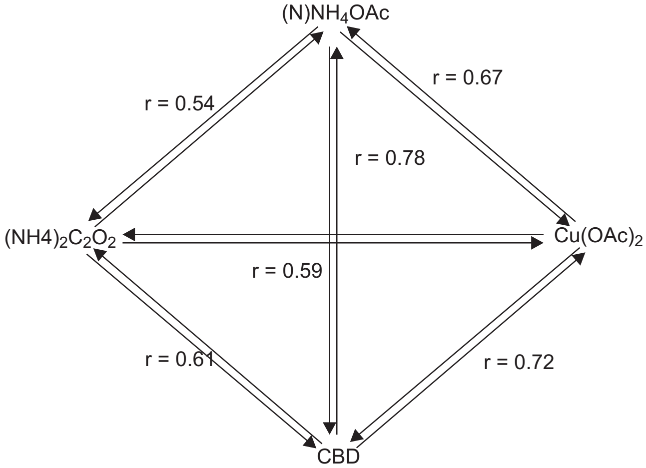

Fig. 1 Schematic diagram of the dynamic equilibrium between different zinc pools in soil

Effect of submergence on the transformation of different Zn pools in soil

The results (Table 5) show that after incubation for 45 days under flooded conditions, the amount of Zn in the water-soluble plus exchangeable form recorded a decrease from the initial amounts in all the soils. The magnitude of such decrease ranged from 5.7 to 53.6% with a mean of 31.7% of the initial amounts. The soils used in the experiment were mostly acidic in reaction. On flooding, the pH values of the soils increased, which caused a decrease in the solubility of native soil zinc. The increased pH might have also favoured precipitation of some amount of Zn as hydroxides and carbonates, and also its adsorption on the surface of freshly formed hydrated oxides of Fe and Mn, which are known to have a strong scavenging action for Zn because of their high specific surface area (Jenne 1968).

The amounts of Zn in the organically complexed form also showed a decrease, from the initial values, in all the soils and the magnitude of decrease ranged from 6.2 to 52.5%, with a mean of 20.7% of the initial amounts. In soils, there are many naturally occurring chelating agents ranging from simple organic acids to complex fulvic and humic acids. It has been shown (Reddy and Patrick 1977) that under reducing conditions, the stability of the Zn organic complexes decreases, and the Zn that is released from such complexes because of the decreased solubility, might have subsequently undergone the same changes as that of water-soluble plus

Table 5 Changes in the concentration of Zn in different forms in the soils upon submergence

Soil no.	Zn (mg/kg) extracted by				Net change
	NH_4OAc	$Cu(OAc)_2$	$(NH_4)_2C_2O_4$	CBD	
1	–0.28 (20.9)	–0.54 (43.5)	+0.85 (5.5)	–0.28 (12.0)	–0.25
2	–0.36 (32.1)	–0.53 (37.1)	+0.70 (3.9)	–0.30 (13.5)	–0.49
3	–0.18 (12.8)	–0.23 (11.7)	+0.68 (4.3)	–0.35 (11.8)	–0.08
4	–0.43 (43.4)	–0.64 (52.5)	+1.04 (6.5)	–0.52 (26.5)	–0.55
5	–0.51 (44.3)	–0.73 (45.9)	+1.18 (7.1)	–0.62 (17.7)	–0.68
6	–0.21 (16.8)	–0.67 (34.7)	+ 1.08 (6.0)	–0.48 (I9.0)	–0.28
7	–0.39 (34.8)	–0.57 (33.3)	+ 1.35 (7.8)	–0.52 (24.8)	–0.13
8	–0.44 (44.9)	–0.27 (09.2)	+ 1.42 (7.9)	–0.83 (39.7)	– 0.12
9	–0.45 (34.6)	–0.43 (25.0)	+ 1.01 (6.7)	–0.39 (13.5)	–0.26
10	–0.19 (14.6)	–0.54 (25.5)	+ 1.41 (7.8)	–0.81 (35.4)	–0.13
11	–0.16 (13.8)	–0.42 (19.7)	+ 1.35 (6.8)	–0.91 (41.2)	–0.14
12	–0.42 (40.4)	–0.46 (22.8)	+ 1.48 (8.0)	–0.63 (26.8)	– 0.03
13	–0.43 (43.9)	–0.53 (28.2)	+ 1.21 (6.7)	–0.51 (20.8)	–0.26
14	–0.35 (31.8)	–0.26 (11.9)	+ 1.65 (8.1)	–1.17 (57.6)	–0.13
15	–0.12 (05.7)	–0.24 (08.4)	+ 1.33 (7.2)	–1.27 (44.9)	–0.30
16	–0.23 (17.2)	–0.24 (09.4)	+0.95 (4.9)	–0.52 (18.3)	–0.04
17	–0.44 (33.8)	–0.35 (12.7)	+1.15 (6.7)	–0.44 (13.8)	–0.08
18	–0.47 (37.6)	–0.45 (19.1)	+1.24 (7.2)	–0.48 (16.2)	–0.16
19	–0.46 (46.9)	–0.45 (20.9)	+1.05 (6.0)	–0.51 (19.5)	–0.37
20	–0.39 (34.8)	–0.24 (12.9)	+1.36 (7.6)	–0.81 (30.6)	–0.08
21	–0.24 (18.8)	–0.27 (11.0)	+1.25 (6.8)	–1.07 (42.3)	–0.33
22	–0.48 (45.3)	–0.47 (22.1)	+ 0.65 (3.7)	–0.44 (I5.3)	–0.74
23	–0.45 (53.6)	–0.45 (27.3)	+ 0.75 (4.4)	–0.62 (26.1)	–0.77
24	–1.15 (37.2)	–0.46 (24.7)	+ 0.85 (5.0)	–0.31 (12.4)	–0.27
25	–0.26 (21.3)	–0.26 (11.7)	+ 1.05 (5.9)	–0.75 (35.5)	–0.22
26	–0.38 (33.6)	–0.40 (16.5)	+ 0.84 (4.7)	–0.38 (13.9)	–0.32
27	–0.34 (37.8)	–0.46 (23.2)	+ 0.85 (5.2)	–0.62 (26.3)	–0.57
28	–0.34 (32.7)	–0.47 (20.0)	+ 1.00 (5.8)	–0.46 (16.1)	–0.27
29	–0.43 (50.0)	–0.31 (14.4)	+ 0.65 (4.0)	–0.72 (33.0)	–0.81
30	–0.47 (51.1)	–0.25 (10.7)	+ 1.18 (7.0)	–0.62 (26.7)	–0.16
31	–0.44 (40.0)	–0.55 (24.4)	+ 1.25 (7.2)	–0.64(23.9)	–0.38
32	–0.52 (38.5)	–0.26 (08.6)	+0.60 (3.3)	–0.18 (0.5.0)	–0.36
33	–0.24 (09.0)	–0.24 (06.2)	+1.82 (8.8)	–1.45 (46.0)	–0.11
34	–0.27 (16.1)	–0.27 (09.2)	+1.94 (9.4)	–1.67 (77.7)	–0.27
35	–0.25 (17.6)	–0.24 (08.4)	+1.65 (8.5)	–1.61 (78.5)	–0.45
Range	–0.12 (5.7 to to – 0.52 53.6)	–0.23 (6.2 to to –0.73 52.5)	+0.60 (3.3 to to + 1.94 9.4)	–0.18 (7.9 to to –1.67 30.7)	–0.03 to – 0.81
Mean	–0.35 (31.7)	–0.40 (20.7)	1.14 (6.4)	–0.68 (28.1)	–0.30
SD	0.11 (13.3)	0.14 (11.7)	0.34 (1.56)	0.37 (17.3)	0.21

Figures between parentheses represent per cents of the initial amounts, and (–) and (+) indicate decreases and increases, respectively.

exchangeable Zn. The soils were rich in organic matter, much of which was in unhumified condition. On flooding, the population of facultative anaerobes and obligate anaerobes might have increased, particularly in the presence of fairly adequate amounts of soil organic matter. Hence, a decrease in the content of organically complexed form of Zn may partly be attributed to microbial immobilization. This may also be partly due to adsorption on the surface of the hydrated oxides of Fe and Mn.

The amorphous sesquioxide-bound Zn in the soil increased over the initial amount in each of the soils. The magnitude of such increases ranged from 0.60 to 1.94 mg/kg with a mean of 1.14 mg/kg, which constituted 6.4% of the initial amounts. Under the reducing conditions in submerged soil there is an increase in the formation of hydrated oxides of Fe^{2+}-iron and Mn^{2+}-manganese which, when freshly formed, have a high surface area and hence possess strong adsorptive capacity. The water soluble Zn already present in the soil or that released from the other forms might have been adsorbed on the surface of these freshly precipitated hydrated oxides, resulting in an increase in the amorphous sesquioxide-bound form of Zn. The higher content of amorphous sesquioxide bound zinc than crystalline sesquioxide bound zinc could be attributed to greater ability of amorphous sesquioxide to adsorb zinc because of their high specific surface area (Devis and Leckie 1978).

On the other hand, the crystalline sesquioxide bound form of Zn, decreased below the initial amounts found in all the soils. The magnitude of such decreases ranged from 0.18 to 1.67 mg/kg with a mean value of 0.68 mg/kg, which constituted 28.1% of the initial amounts. Under reducing conditions in submerged soils some of the crystalline sesquioxides might have undergone transformation to an amorphous form resulting in the release of a part of the Zn occluded by the former and the subsequent adsorption of this by the latter. Similar results were reported by Pal *et al.* (1997).

The overall results (Table 5), therefore, show a net decrease in the total contents of the above mentioned four forms of Zn in soil upon submergence, which corroborates the general observations of the occurrence of Zn deficiency in lowland rice. It has been shown earlier by Mandal and Mandal (1986) that the above four forms of Zn account for more than 95% variability of Zn concentration in rice plants.

The decreases in all three Zn forms, viz. (i) water soluble plus exchangeable, (ii) organic complexed and (iii) crystalline sesquioxides-bound showed highly significant correlations with the initial contents of these forms in soil (Table 6), which implies that soils rich in these Zn forms will show greater decreases in their contents upon submergence. The decreases in water-soluble plus exchangeable and crystalline sesquioxides-bound Zn also showed significant negative correlations with initial pH values of the soils, which suggests that the decreases in these two forms of Zn increase with decreasing initial pH. It is shown that upon submergence the pH of acid soils increases and tends to attain the neutral value (Ponnamperuma 1972). The lower the initial pH value of the soils, the higher is the magnitude of its rise upon submergence. With increasing pH, the Zn in solution undergoes precipitation, co-precipitation and adsorption. The observed significant correlation, therefore, lends support to the hypothesis put forward earlier to explain the decrease in water-soluble plus exchangeable Zn in soil upon submergence. The increase in pH of soils upon submergence is attributed to the reduction of Fe^{3+} to Fe^{2+} and its subsequent conversion to $Fe(OH)_2$. The higher pH rise obviously necessitates a greater formation of $Fe(OH)_2$ from Fe_2O_3 resulting in a release of Zn, which explains the negative significant correlation between the decrease in crystalline sesquioxide-bound Zn and soil pH. The positive correlation between the decreases in organically complexed Zn in soil upon submergence with soil organic carbon lends support to the suggestion made earlier that the decrease was partly due to microbial immobilization.

Table 6 Linear correlation coefficients (r) between changes in the different forms of zinc and characteristics of the soils

	Initial values	pH	Organic carbon
NH_4OAc—Zn	0.364*	–0.515**	0.099
$Cu(OAc)_2$— Zn	0.515**	–0.388*	0.672**
$(NH_4)_2C_2O_4$— Zn	0.676**	–0.380*	0.215
CBD—Zn	0.080	–0.663**	0.102

* and ** denote significant differences at 0.01 and 0.05 probability levels, respectively.

Keeping the soils submerged for 45 days resulted in a marked increase in the NH_4OAc-and $AlCl_3$-extractable forms of iron with a concomitant decrease in the CBD-extractable form (Table 7). Under submerged condition much of the Fe^{3+} iron in crystalline sesquioxides had undergone dissolution due to its reduction to the Fe^{2+} form, a portion of which entered into the soil exchange complex or remained in solution while a greater fraction was precipitated as hydroxides and carbonates. The decreases in the water-soluble plus exchangeable and the organic-complexed forms of Zn were found to be correlated with increases in the insoluble ferrous compounds as well as with increases in the amorphous sesquioxides-bound Zn (Table 8), which lends strong support to the explanation given earlier that the decrease in the above two forms of Zn was due to their adsorption on the surface of the freshly formed hydrated oxides of iron.

The highly significant positive correlation between the increase in the amorphous sesquioxide bound Zn and that in the $AlCl_3$-extractable Fe also give strong support to the hypothesis, given earlier, to explain the increase in the above form of Zn upon flooding of the soils. It has been stated before that the decrease in the crystalline sesquioxide bound Zn in soil on submergence was due to the release of Zn resulting from the dissolution of Fe_2O_3 under reducing conditions. This is supported by the existence of a strong significant correlation between the decreases in both the contents. The results, therefore, very clearly show that the transformation of different forms of Zn in soil upon submergence is very much related to changes in the different forms of iron particularly the reduction of Fe_2O_3 and the subsequent formation of insoluble hydroxides of iron.

The native zinc in soils occur in different chemical pools, availability of soil zinc to plants is governed by dynamic equilibrium among the different form rather than the total content of zinc in soils. The relative distribution of these chemical pools depends upon the physical and chemical properties of soils. Studies on zinc fraction in native soil

Table 7 Effect of submergence on the changes in different forms of iron in the soils

Soils	NH_4OAc-extractable (mg/kg)			$AlCl_3$-extractable (mg/kg)			CBD-extractable (mg/kg)		
	Initial	After submergence	Difference	Initial	After submergence	Difference	Initial	After submergence	Difference
1	27	72	+45	121	313	+192	584	517	–67
2	34	98	+64	239	387	+148	645	533	–92
3	26	88	+62	205	392	+187	750	601	–149
4	23	63	+40	131	328	+197	578	480	–98
5	18	45	+27	150	277	+127	719	527	–192
6	27	92	+65	195	341	+146	774	579	–195
7	27	88	+61	193	383	+190	816	625	–191
8	17	64	+47	183	373	+190	719	463	–256
9	33	102	+69	215	368	+153	800	618	–182
10	21	85	+64	221	347	+126	855	597	–258
11	12	52	+40	185	350	+165	837	583	–254
12	21	61	+40	197	387	+190	909	661	–248
13	18	48	+30	171	330	+159	767	567	–200
14	20	64	+44	193	360	+167	669	417	–252
15	19	52	+33	177	366	+189	513	411	–102
16	22	68	+46	220	403	+183	467	375	–92
17	15	34	+19	163	281	+118	743	465	–278
18	46	102	+56	217	333	+116	644	509	–135
19	28	82	+54	191	377	+186	763	545	–218
20	47	78	+31	175	303	+128	791	593	–198
21	46	95	+49	121	250	+129	743	467	–276
22	27	120	+93	245	397	+152	493	381	–112
23	18	123	+105	219	413	+194	515	417	–98
24	24	74	+50	135	247	+112	767	569	–198
25	38	96	+58	193	291	+98	867	659	–208
26	41	106	+65	169	343	+174	823	647	–176
27	29	60	+31	177	366	+189	855	603	–252
28	31	95	+64	153	297	+144	827	639	–188
29	20	88	+68	209	381	+172	695	593	–102
30	27	75	+48	221	399	+178	737	653	–84
31	10	29	+19	180	297	+117	813	627	–186
32	09	32	+23	193	359	+166	849	591	–258
33	11	36	+25	215	329	+114	727	479	–248
34	10	44	+34	137	267	+130	700	503	–197
35	11	40	+29	159	273	+114	881	623	–258

(+) and (–) indicate increases and decreases, respectively.

Table 8 Linear correlation coefficients (r) between changes in the different forms of zinc and iron in the soils

	Extractable forms			
	$Cu(OAc)_2$-Zn	$(NH_4)_2C_2O_4$-Zn	$AlCl_3$-Fe	CBD-Fe
NH_4OAc	0.136	0.350*	0.315	0.290
$Cu(OAc)_2$		0.511**	0.451*	0.578**
$(NH_4)_2C_2O_4$	0.511**		0.561**	0.354*
CBD	0.280	0.371*	0.229	0.508**

* and ** denote significant differences at 0.05 and 0.01 probability levels, respectively.

revealed that concentration of different zinc fractions varied from soil to soil and the order of magnitude of different zinc fractions remained same, viz. water soluble plus exchangeable zinc < organically bound zinc < crystalline bound zinc < amorphous sesquioxide bound zinc. Both the content and per cent contribution of water soluble plus exchangeable zinc to total zinc was the lowest among all the zinc fractions. Amorphous sesquioxide bound zinc was the dominant fraction in all soils. The soil pH mainly influenced the water soluble plus exchangeable zinc content in soils. The different fractions of Zn have significant correlations among each other, suggesting the existence of a dynamic equilibrium of these fractions in soils.

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