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DISTRIBUTION OF DIFFERENT FORMS OF COPPER IN FRESHWATER POND SOILS OF ORISSA, INDIA

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Key words: copper distribution, copper fractions, India, pond soil properties

Abstract

The distribution of native copper fractions in freshwater pond soils of Orissa and their relationship to important soil properties were studied. Total Cu and diethylene triamine penta acetic acid (DTPA) extractable Cu ranged 7.0-24.0 and 2.0-4.9 mg/kg soil, respectively, with mean values of 12.7 and 3.1 mg/kg. The amounts of exchangeable, weakly adsorbed, moderately adsorbed, strongly adsorbed and organic matter associated Cu ranged 1.7-2.6%, 3.5-6.0%, 3.3-6.6%, 0.7-2.2% and 0.8-7.2% of the total Cu, respectively. Cu occluded or bound by carbonates or other acid-soluble mineral fractions was 1.5-6.1% of the total Cu. Most of the Cu (58-91%) was in the residual fraction. All the chemical fractions of Cu significantly correlated with each other and with the organic carbon status of the soils.

Introduction

Copper is commonly applied to aquaculture ponds to inhibit phytoplankton growth, kill organisms which produce odorous compounds responsible for off-flavor in fish and shrimp and control fish diseases (Boyd, 1990; Tucker and Robinson, 1990). However, copper quickly disappears from the water. Some of the copper is absorbed by plants, but most of it is precipitated as insoluble tenorite (CuO) or malachite [$Cu_2(OH)_2CO_3$; Stumm and Morgan, 1970] or is adsorbed by bottom muds (Reimer and Toth, 1970). The adsorbed copper can be desorbed from the sediment into the water. The magnitude of desorption depends on pH, salinity and the presence of natural and/or synthetic chelating agents (Moore and Ramamoorthy, 1984; Adhikari and Saha, 1999). In this regard, the

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association of Cu with different ligands, Fe/Mn oxides or organic matter in the pond sediment could also play a role. Knowing the different chemical forms of Cu in the pond soil can help to understand its fixation, mobility and availability.

The sequential extraction technique (McLaren and Crawford, 1973) is widely used to distinguish between chemical forms of Cu in soils. Information on native soil Cu fractions in freshwater pond soils is inadequate. Hence, the present investigation was undertaken to study the distribution of Cu fractions in freshwater pond soils of Orissa, India, in relation to soil properties.

Materials and Methods

Surface soil samples (0-0.15 m) were collected from 48 freshwater ponds representing four major agro-ecological subregions of Orissa: the eastern plateau (Mayurbhanj and Dhenkanal districts), the eastern plateau and eastern Ghat subregion (Sambalpur, Bolangir and Koraput districts), eastern Ghat and part of the eastern plateau (Cuttack, Dhenkanal and Ganjam districts) and the eastern coastal plain (Puri and Khurda districts). Characteristics of the soils (<2 mm) were determined according to procedures outlined by Page et al. (1982). Copper fractions were determined using a modified version of the sequential fractionation scheme (Smith and Shoukry, 1968; Chandi and Takkar, 1982). Exchangeable Cu was extracted with IM NH_4OAC (pH 7.0). Weakly, moderately and strongly complexed or adsorbed Cu was extracted in three successions with 0.005 M diethylene triamine penta acetic acid (DTPA; pH 7.3). Cu associated with organic matter was extracted with 30% H_2O_2 and 0.005 M DTPA (pH 7.3). Occluded Cu was extracted with 0.1 M HCl. Residual Cu was obtained by substracting the Cu fractions from the total Cu. Concentrations of Cu, Fe and Mn in the extracts were determined using an atomic absorption spectrophotometer.

Results and Discussion

The available (DTPA-extractable) Cu content of the pond soils varied 2.0-4.9 with a mean of 3.1 mg/kg soil (Table 1). The mean Cu content was much higher than the critical limit for plant growth of 0.2 mg/kg soil (Follet and Lindsay, 1970).

The amounts of Cu in the exchangeable, weakly adsorbed, moderately adsorbed, strongly adsorbed, organic matter associated and occluded fractions ranged 0.05-0.7, 0.1-1.5, 0.1-1.7, 0.02-0.6, 0.03-1.8 and 0.06-1.6 mg/kg, respectively (Table 2), comprising 1.7-2.6%, 3.5-6.0%, 3.3-6.6%, 0.7-2.2%, 0.8-7.2% and 1.5-6.1% of the total Cu. Residual Cu varied 6.0-16.8 mg/kg (58-91%), indicating that the majority of total Cu was held within the silicate mineral structure. In comparison, in Lake Ontario, Canada, all the copper in the sediments was bound to humic acids (Nriagu and Coker, 1980).

The exchangeable Cu content in our pond soils (0.05-0.7 mg/kg soil) was comparable with that of the soils of Haryana (0.06-0.9 mg/kg; Singh et al., 1988) and Punjab (0.1-0.4 mg/kg; Randhawa and Singh, 1996). The weakly, moderately and strongly adsrobed fractions (0.7-6.6%) were higher than the 0.2-2.7% reported by McLaren and Crawford (1973).

The organically bound Cu in our soils (0.8-7.2%) was comparable to the amount in Punjab soils (0.4-13.3%; Randhawa and Singh, 1996) but lower than the findings of Singh et al. (1989; 6.9-11.7%). This may be due to the low organic carbon content of the pond soils of Orissa. This value also differed from the Amazon and Yukon Rivers where the organic Cu was 8-15% (Gibbs, 1977). Tessier et al. (1980) reported a high percentage of organic-bound copper in the particulates of Canada's Yamaska and St. Francois Rivers (31% and 52%, respectively). The percent of total Cu that was occluded and bound by carbonates and other acid soluble minerals (1.5-6.1%) was lower than the 11.6-21.7% reported by Singh et al. (1989).

Simple correlations (Table 3) between the Cu fractions and soil properties show that, for all fractions except organically bound Cu, DTPA-extractable Cu and residual Cu, the amounts of Cu significantly correlated with each other. These relationships suggest the

Table 1. Characteristics of freshwater pond soils from Orissa, India.

.	*pH*	*Electrical conductivity (dS/m)*	*Organic C (g/kg)*	*$CaCO_3$ (g/kg)*	*Sand (%)*	*Silt (%)*	*Clay (%)*	*Phosphorus* (mg/kg)*	*Free oxides of*		*DTPA – extractable*
									Fe (g/kg)	*Mn (mg/kg)*	*Cu (mg/kg)*
Eastern plateau subregion (Ustorthents, Ustochrepts), n = 12											
Range	7.3-8.4	0.18-0.21	3.8-12.5	5.0-30.0	61.2-80.3	7.0-40.2	12.7-21.4	12.4-17.0	4.0- 7.2	121-166	3.7-4.9
Mean	7.8	0.19	8.8	20.0	66.4	15.4	18.2	14.0	5.0	138	4.0
Eastern plateau and eastern Ghat subregion (Ustorthents, Ustochrepts, Haplustalfs), n = 14											
Range	6.1-7.9	0.07-0.19	2.8-7.8	6.0-17.0	66.6-81.4	6.5-12.8	11.7-17.8	7.8-28.3	4.9-7.6	144-182	2.0-3.3
Mean	7.1	0.10	4.2	10.0	76.0	9.6	14.4	14.5	5.8	162	2.7
Eastern Ghat and eastern plateau subregion (Haplustalfs, Paleustalfs, Ustochrepts, Ustropepts), n = 10											
Range	6.3-8.3	0.14-0.22	2.6-5.4	8.0-24.0	60.8-78.8	6.0-16.6	12.0-20.8	9.1-12.2	4.2-7.3	82-161	2.0-3.6
Mean	7.2	0.18	3.6	18.0	74.0	11.4	14.6	9.8	4.8	131	2.6
Eastern coastal plain subregion (Tropaquepts, Ustipsamments), n = 12											
Range	6.0-7.6	0.08-0.28	3.6-11.3	10.0-22.0	54.8-84.3	8.5-16.8	10.8-18.8	4.3-12.5	4.6-7.4	76-168	2.8-3.7
Mean	7.0	0.18	7.4	15.0	76.0	10.6	13.4	8.6	5.2	134	3.1
Overall, n =48											
Range	6.0-8.4	0.07-0.28	2.6-12.5	5.0-30.0	54.8-84.3	6.0-40.2	10.8-21.4	4.3-28.3	4.0-7.6	76-182	2.0-4.9
Mean	7.3	0.16	6.4	15.7	73.1	11.8	15.1	11.7	5.2	141	3.1

* Extracted by the method of Olsen et al. (1954)

Table 2. Total Cu and Cu fractions (mg/kg soil) of freshwater pond soils from Orissa, India.

	Total Cu	*Exchangeable Cu*	*Weakly adsorbed Cu*	*Moderately adsorbed Cu*	*Strongly adsorbed Cu*	*Organic matter associated Cu*	*Occluded Cu*	*Residual Cu*
Eastern plateau subregion								
Range	7.1-20.6	0.1-0.7	0.2-1.5	0.2-1.6	0.04-0.6	0.06-1.8	0.1-1.5	6.3-12.8
Mean	11.7	0.4	0.6	0.6	0.3	0.3	0.6	8.6
Eastern plateau and eastern Ghat subregion								
Range	7.0-24.0	0.05-0.6	0.1-1.4	0.1-1.6	0.02-0.5	0.03-1.7	0.06-1.4	6.5-16.8
Mean	15.4	0.2	0.5	0.7	0.2	0.3	0.4	12.0
Eastern Ghat and eastern plateau subregion								
Range	7.0-21.8	0.2-0.6	0.3-1.4	0.2-1.6	0.06-0.5	0.07-1.7	0.1-1.4	6.0-14.6
Mean	12.6	0.3	0.6	0.7	0.2	0.4	0.4	9.9
Eastern coastal plain subregion								
Range	8.0-23.2	0.2-0.7	0.4-1.5	0.4-1.7	0.08-0.6	0.08-1.8	0.2-1.6	6.6-15.2
Mean	11.1	0.3	0.7	0.8	0.2	0.4	0.6	8.0
Overall								
Range	7.0-24.0	0.05-0.7	0.1-1.5	0.1-1.7	0.02-0.6	0.03-1.8	0.06-1.6	6.0-16.8
Mean	12.7	0.3	0.6	0.7	0.2	0.4	0.5	9.6

Table 3. Simple correlation coefficients between Cu fractions and soil properties.

	Total Cu	*Exchangeable Cu*	*Weakly adsorbed Cu*	*Moderately adsorbed Cu*	*Strongly adsorbed Cu*	*Organic matter associated Cu*	*Occluded Cu*	*Residual Cu*
Exchangeable Cu	0.56*							
Weakly adsorbed Cu	0.78*	0.48*						
Moderately adsorbed Cu	0.80*	0.51*	0.97*					
Strongly adsorbed Cu	0.82*	0.49*	0.95*	0.95*				
Organic matter associated Cu	0.47*	0.39*	0.44*	0.46*	0.53*			
Occluded Cu	0.72*	0.49*	0.78*	0.75*	0.76*	0.69*		
Residual Cu	0.92*	0.36*	0.70*	0.71*	0.69*	0.28	0.48*	
pH	0.06	0.07	-0.06	-0.06	-0.04	-0.10	-0.04	0.04
Organic C	0.72*	0.52*	0.68*	0.70*	0.80*	0.54*	0.60*	0.58*
$CaCO_3$	0.37*	0.42*	0.16	0.13	0.26	0.41*	0.43*	0.28
Clay	0.68*	0.16	0.73*	0.70*	0.68*	0.10	0.22	0.76*
Phosphorus	0.06	0.12	0.36*	0.36*	0.40*	0.22	0.40*	-0.02
Free Fe oxides	0.68*	0.29	0.52*	0.49*	0.48*	0.17	0.43*	0.74*
Free Mn oxides	0.72*	0.32*	0.71*	0.68*	0.62*	0.12	0.48*	0.74*
DTPA-extractable Cu	0.68*	0.40*	0.84*	0.78*	0.80*	0.27	0.60*	0.60*

* Significant at $p<0.05$

existence of a reversible dynamic equilibrium among the chemical pools of Cu. All the chemical fractions of Cu significantly correlated with the organic carbon content of the soils. The highly significant correlation between Cu associated with the organic matter fraction and the amount of organic matter was also observed by Domingues and Vieira e Silva (1990), suggesting that Cu is preferentially bound to organic matter. The amounts of total, adsorbed and residual Cu significantly correlated with the clay content and with the free Fe and Mn oxides of the soils. Domingues and Vieira e Silva (1990) also reported a highly significant correlation between the amount of clay and the presence of Cu in the clay fraction, showing that Cu bound mainly to the structure of clay minerals.

Since the majority of Cu in the studied soils is contained within silicate minerals, the problem of using Cu in aquaculture will be less critical. However, there is a possibility of pond bottom pollution since some of the Cu exists in exchangeable or weakly and moderately adsorbed forms and may, therefore, be desorbed into the water in the course of time.

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