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FERTILIZATION OF FRESHWATER FISH PONDS WITH COBALT AND ITS ADSORPTION AND DESORPTION IN THE POND SEDIMENT

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Abstract

The use of cobalt as a micro-nutrient fertilizer in the culture of the freshwater *Labeo rohita* was evaluated in terms of primary productivity, Chlorophyll *a* production, plankton volume and fish growth. Three cobalt doses (5, 10 and 15 kg $CoCl_2$/ha) were tested. In the 5 and 10 kg $CoCl_2$/ha treatments, primary productivity, Chlorophyll *a* production, plankton volume and growth of *Labeo rohita* increased ($p<0.05$). The highest increment was obtained in the 10 kg $CoCl_2$/ha treatment. The adsorption and desorption of the cobalt in the pond sediment fit the Langmuir isotherm. The highest adsorption and desorption values were found in pond sediments from the Dhenkanal area, due to its higher clay content, total Mn content and pH, indicating that sediments with a higher capacity to adsorb cobalt also have a higher capacity to desorb cobalt.

Introduction

Cobalt plays an important role in nitrogen fixation by rhizobium (Baddesha et al., 1997). An adequate supply of cobalt is essential for the healthy growth of ruminants. Goldman and Horne (1983) reported that cobalt could stimulate production in some oligotrophic lakes. Sen and Chatterjee (1976, 1978) reported enhanced survival and growth of carp fry with the application of cobalt singly or in combination with supplementary feed. However, information regarding the role of cobalt as a micro-nutrient fertilizer in fish production and its availability in fishpond sediments is scanty or nonexistent. The concentration of cobalt in pond sediments is most likely controlled by adsorption and desorption. Thus, it is important to understand these processes to determine the availability of

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cobalt to plankton and, therefore, fish, and the movement of cobalt through pond sediments. This experiment was conducted to study the use of cobalt as a micro-nutrient fertilizer for increasing the production of plankton and the adsorption and desorption patterns of cobalt in different freshwater pond sediments in Orissa, India.

Materials and Methods

Fish growth. This experiment was conducted in twelve cement cisterns (1.0 x 0.7 x 1.0 m, 0.5 m^3). Soil from a pond at the Central Institute of Freshwater Aquaculture (CIFA) fish farm was collected, dried, powdered and spread uniformly on the bottom of the cisterns to a thickness of about 15 cm. The soil had a sandy loam texture, 6.8 pH, cation exchange capacity of 11.8 cmol (P+)/kg, organic carbon of 0.74% and available cobalt at 0.50 ppm. The cisterns were then filled with water from the parent pond. One week was allowed to establish the soil and water conditions before fertilization with the standard dose of N:P:K (200:100:40 kg/ha). The experimental treatments consisted of three levels of cobalt (0, 5, 10 and 15 kg/ha Co as $CoCl_2$) with three replications. Three additional cisterns received no cobalt and served as the control. Hydrological conditions, primary production, Chlorophyll *a* production and phytoplankton volume were determined fortnightly following standard procedures (APHA, 1989). After 15 days of cobalt application, ten Indian major carp (*Labeo rohita*) fingerlings (average length 70 mm, average weight 4.0 g) were stocked into each cistern. Their growth was monitored 75 days and expressed as yield in g/cistern.

Adsorption and desorption of cobalt. Sediment samples from the bottoms (0-0.15 m) of fish ponds in six districts of Orissa, India (Dhenkanal, Bolangir, Puri, Mayurbhanj, Sambalpur and Ganjam) were collected. They were equilibrated for six days with Co solutions (0.01 M calcium chloride containing 10-350 mg Co/kg), to maintain a sediment to solution ratio of 1:10 (2.0 g sediment to 20 ml 0.01 M $CaCl_2$). Two drops of toluene were added to each sample to minimize microbial activity. After equilibration, the samples were centrifuged and extracts were analyzed for Co with an atomic absorption spectrophotometer. The adsorbed cobalt was desorbed in 30 ml of a 0.01 M $CaCl_2$ solution by equilibrating it for six hours and the amount of cobalt desorbed was estimated.

Results and Discussion

Fish growth. The pH of the water ranged 7.3-8.1, total alkalinity as $CaCO_3$ ranged 94-116 mg/l, total hardness was 75-110 mg/l and dissolved cobalt was 0.003-0.030 mg/l. The effects of cobalt on primary productivity, Chlorophyll *a* and plankton production are presented in Table 1. In the 5 kg and 10 kg $CoCl_2$/ha treatments, the increases in primary

Table 1. Effects* of cobalt on primary productivity, Chlorophyll *a* and plankton production.

	Control	*5 kg $CoCl_2$/ha*	*10 kg $CoCl_2$/ha*	*15 kg $CoCl_2$/ha*
Gross primary production (g C/m^2/day)	0.026-0.034 (0.031)[a]	0.047-0.071 (0.059)[b]	0.072-0.116 (0.089)[c]	0.034-0.049 (0.044)[a]
Chlorophyll *a* production (µg/l)	50-78 (68)[a]	75-115 (99)[b]	89-128 (112)[c]	54-85 (78)[a]
Plankton volume (g/10 l)	0.16-0.24 (0.21)[a]	0.27-0.34 (0.30)[b]	0.36-0.48 (0.41)[c]	0.22-0.29 (0.26)[a]

Treatment means followed by the same superscript were not significantly different at the 0.05 level.
* Figures in parentheses are mean values.

productivity, Chlorophyll *a* and plankton volume were significantly higher (at 5% level) than in the control. The 10 kg $CoCl_2$/ha treatment produced the highest values. The lower primary productivity, Chlorophyll *a* and plankton volume achieved in the 15 kg $CoCl_2$/ha treatment may be due to cobalt toxicity. Although cobalt is an essential micro-nutrient for animals and some plants since it is required for vitamin B_{12} formation (Lehninger, 1972), several studies report on cobalt thresholds in the range of 50-100 µg/l cobalt for algae (Holm-Hansen et al., 1954), bacteria (Sawada et al., 1955) and yeast (Enari, 1958). Studies by Coleman et al. (1971) and Young (1979) suggest that cobalt concentrations above 40-50 µg/l retard growth in freshwater algae.

In this experiment, the *L. rohita* fingerling yield in the 10 kg $CoCl_2$/ha treatment was significantly higher (5% level) than in the control (Table 2). The 10 kg $CoCl_2$/ha treatment resulted in the highest fish yield, possibly because plankton production was highest in this treatment. The lower yield in the 15 kg $CoCl_2$/ha treatment may have been due to cobalt toxicity. Toxicity data suggest that daphnids are more sensitive than other genera to cobalt. Cobalt LC_{50} (48 h) for *Daphnia magna* ranged from 1110 µg/l (45.3 mg/l hardness as $CaCO_3$) to 3400 µg/l (124-128 mg/l hardness) to 5150 µg/l (220 mg/l hardness). Chronic toxicity data for *D. magna* and *Pimephales promelas* (fathead minnow) ranged between 5.1 µg/l (*D. magna*) and 560 µg/l (*P. promelas*). Acute to chronic ratios using the two available *D. magna* chronic test results (10 and 5.1 µg/l) were 111 and 1163 under soft (45.3 mg/l) and hard water (220 mg/l) regimes, respectively. Thus, extremely hard water significantly reduced acute toxicity of cobalt to indicator freshwater species (Diamond et al., 1992). Soil liming or a naturally high level of calcium carbonate (as in limestone derived soils) decreases the solubility and bioavailability of cobalt to plants and animals (Young, 1979).

Adsorption and desorption. Characteristics of the soils are given in Table 3. The amount of adsorbed cobalt increased as the level of added cobalt increased (Table 4). The highest amount of Co adsorbed in the 350 mg/kg treatment was in the Dhenkanal sediment (95.8%) which had the highest pH (8.6); the lowest amount of Co adsorbed in this treatment was in the Bolangir sediment (53.7%) which had the lowest pH (7.3). These results are similar to those of Baddesha et al. (1997) who found that Co adsorption increased as the pH increased in agricultural soils.

The cobalt adsorption data were fitted to the Langmuir adsorption isotherm and the various parameters of the Langmuir adsorption isotherm were calculated (Table 5). The data indicate that adsorption differed from sediment to sediment. The highest adsorption in all treatments was found in the Dhenkanal sedi-

Table 2. Growth of *Labeo rohita* fingerlings with different levels of cobalt application.

Cobalt application	*Cobalt concentration in water (mg/l)*	*Fish yield (g/cistern/75days)*
Control	0.003	64.0 ± 4.0
5 kg $CoCl_2$/ha	0.012	70.0 ± 6.0
10 kg $CoCl_2$/ha	0.024	90.8 ± 9.2
15 kg $CoCl_2$/ha	0.030	69.0 ± 9.0
Critical difference (5%)*		8.6

* If the difference between fish yields in different treatments is greater than 8.6, then the difference is significant at the 5% level.

Table 3. Pond sediment characteristics.

Sediment	*pH*	*Electrical conductivity (ds/m)*	*Cation exchange capacity [cmol (P+)/kg]*	*$CaCO_3$ (%)*	*Organic carbon (%)*	*Sand (%)*	*Clay (%)*	*Available Co (mg/kg)*	*Total Mn (mg/kg)*
Dhenkanal	8.6	0.21	9.07	1.32	0.51	74.8	18.2	0.21	335
Bolangir	7.3	0.24	13.78	2.67	0.26	81.8	11.7	0.07	196
Puri	7.4	0.26	8.49	1.17	0.36	79.8	12.2	0.40	319
Mayurbhanj	7.6	0.17	5.90	1.08	0.51	37.8	12.2	0.94	325
Sambalpur	7.9	0.21	7.17	1.39	0.31	80.8	12.2	0.65	203
Ganjam	8.3	0.16	12.40	2.57	0.28	81.8	12.2	0.47	224

ment while the lowest was found in the Bolangir sediment. The high adsorption in the Dhenkanal sediment may be due to its high clay content, total Mn content and pH. The low adsorption in the Bolangir sediment may be due to its low clay, total Mn, organic carbon and pH values. The effect of various properties such as clay, pH, organic carbon, total Mn and available Co on cobalt adsorption was explained by the following relationship: maximum adsorption = 0.712 available Co - 0.006 clay + 0.029 pH - 0.041 organic carbon + 0.0005 total Mn (R^2 = 0.931**). However, the partial contributions of the properties to maximum Co adsorption were clay 42.3%, available Co 42.8%, pH 49% and $CaCO_3$ 48.7%.

The desorption of cobalt increased as the cobalt adsorption increased (Table 5). The desorption data were fitted to the Langmuir isotherm to calculate the desorption parameters. The highest maximum desorption was in the Dhenkanal sediment, which had the highest clay and total Mn contents and the highest pH. The lowest maximum desorption was in the Bolangir sediment with the lowest clay and total Mn contents and lowest pH. These results indicate that sediments with a higher capacity for adsorbing Co have a higher capacity for desorbing Co to the overlying waters for uptake by plankton and fish. Sediment properties such as clay, total Mn and available Co contributed to 73.2% variation in maximum desorption as explained by the following relationship: maximum desorption = 12.77 available Co + 0.013 total Mn - 0.053 clay - 2.23 (R^2 = 0.732**). However, the partial contributions of the properties to maximum Co desorption were total Mn 62%, clay 51% and $CaCO_3$ 43%.

The mobility constant was highest in the Mayurbhanj sediment and lowest in the Puri sediment. The contribution of linear and quadratic term of pH on the mobility constant of Co was 67.8%. However, the contribution of pH and clay on the Co mobility constant was 71.2%, as determined by the following relationship: mobility constant of cobalt (K_d) = 5.778 pH - 0.363 pH^2 - 22.25 (R^2 = 0.678*); mobility constant of cobalt (K_d) = 0.142 clay - 0.006 $clay^2$ - 0.847 (R^2 = 0.712*).

Table 4. Amounts of cobalt adsorbed and desorbed (mg/kg) in sediments in relation to level of cobalt added.

Sediment		*Amount of cobalt added (mg/kg soil)*					
		10	*50*	*100*	*150*	*250*	*350*
Dhenkanal	adsorbed	9.9	49.9	96.9	144.4	240.4	335.6
	desorbed	0.2	0.6	0.8	2.0	3.1	5.0
Bolangir	adsorbed	8.8	44.9	83.8	94.6	138.6	188.0
	desorbed	0.3	0.7	2.0	19.4	40.0	51.1
Puri	adsorbed	9.6	48.4	83.6	110.2	167.6	204.8
	desorbed	0.3	1.2	1.4	17.0	24.8	47.0
Mayurbhanj	adsorbed	9.9	49.7	97.8	144.4	240.3	330
	desorbed	0.2	0.7	1.0	2.3	3.0	4.8
Sambalpur	adsorbed	9.9	49.6	95.5	139.7	229.0	316.0
	desorbed	0.3	0.6	0.9	3.7	5.4	9.2
Ganjam	adsorbed	9.9	49.8	97.9	144.5	237.3	327.5
	desorbed	0.2	0.7	1.0	2.5	3.7	5.5

Table 5. Maximum adsorption and desorption according to Langmuir adsorption isotherm.

Sediment	*Maximum adsorption (mg/kg)*	*Maximum desorption (mg/kg)*	*Constant related to mobility of cobalt (ml/g)*
Dhenkanal	0.404[a]	10.27[a]	0.098[a]
Bolangir	0.207[b]	1.87[b]	0.160[b]
Puri	0.237[b]	2.26[b]	0.053[c]
Mayurbhanj	0.378[c]	8.44[c]	0.198[d]
Sambalpur	0.317[d]	4.65[d]	0.138[e]
Ganjam	0.357[c]	6.33[e]	0.187[d]

Values followed by the same superscript are not significantly different at the 0.05 level.

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