

EFFECT OF PHOSPHATE ON CADMIUM SORPTION IN SOME ARID AND SEMI-ARID SOILS OF HARYANA, INDIA

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INTRODUCTION

Heavy metals existence and behaviour in soil is the main source of human food. It also poses serious threat to the aquatic environment because of their toxicity, accumulation and magnification in organisms, causing severe damage to the organ-systems leading to innumerable health hazards (Roy, 2010). The toxic cadmium (Cd) enters agricultural soils as a result of both natural and anthropogenic activities. The fate of Cd that reaches soil from anthropogenic sources, like industrial effluents, sewage sludge, use of phosphatic fertilizers, municipal wastes, etc. depends upon ability of host medium, which in turn depends on soil properties (Garcia-Miragaya and Page, 1978, Barrow, 1986). Thus, elevation of soil cadmium levels and its potential cycling through food chain is of considerable concern. Significant reduction in Cd, Zn, and Pb heavy metals was reported in untreated industrial effluent inoculated with *A. niger* and *A. flavus* biomass with respect to industrial treated effluent (Shivakumar *et al.*, 2011).

The persistence and transport of Cd is governed to a large extent by sorption into soil colloidal components (Azeez *et al.*, 2010). Sorption is one of the processes that determine the availability of the metals to plant and their mobility in the soil through adsorption on soil colloidal surfaces. Heterogeneous soil systems consist of both organic and inorganic constituents with different affinities for heavy metals. In addition, heavy metals themselves exhibit varying affinities for soil surfaces. Variability in heavy metals affinity for soil sorption sites has been attributed to a given metal's hydrolysis constant (pKH), electronegativity, Lewis acidity, charge density and solubility (K_{sp}) of precipitates, including hydroxide and carbonate, adsorbent dose, contact time and initial metal ion concentration (McBride, 1994; Pardo, 2000; Sparks, 2003, Sandeep and Suresha, 2013). Numerous studies have indicated that toxic heavy metals and micronutrients have high affinity for ferric and aluminum hydrous oxides, calcite and clay mineral (McBride, 1980, Bolan *et al.*, 1999, Thakur *et al.*, 2004). Investigations have also shown that calcium carbonate, alumino-silicate clay minerals, hydrous oxides and exchangeable Ca^{2+} , Al^{3+} and Fe^{3+} are important phosphate sorbents in soils (Kuo and Lotse, 1972, Griffin and Jurinak, 1974, Tomar and Gautam, 1998). The adsorption of phosphate anions by soils and increase in the pH of the system has been reported to influence the adsorption of Cd by the soils, possibly due to increase in surface negative charge (Kuo and McNeal, 1984, Bolan *et al.*, 1999; Singh and Tomar, 1996, Thakur *et al.*, 2013). These evidences indicate that Cd and Phosphate may influence the sorption of each other, either by competing for sorption sites or by influencing the surface charge potential of the sorbate. Adhikari and Singh (2008) reported that when Cd was added along with phosphate, the increase in negative charge due to phosphate sorption resulted in a corresponding increase in Cd sorption. Hence, sorption of Cd and P in different soil types is of potential interest for determining their loading capacity and distribution in the soil profile. The present investigation was therefore, carried out to investigate the

ABSTRACT

The effect of phosphate pretreatment of cadmium sorption was examined on soils, varying in calcium carbonate and clay to elucidate the mechanism of cadmium retention in phosphorus treated soils. The soils were treated with 200 mg P kg⁻¹ and incubated (30 ± 4°C) for 45 days giving six wetting and drying cycles. The enrichment of soils with phosphorus decreased the Cd sorption and distribution coefficient over untreated soils. Soils of relatively lower pH (7.1-7.6), Cd²⁺ concentration in solution seem to be controlled by solubility of CdCO₃ and/or Cd₃(PO₄)₂ whereas, in soils of relatively higher pH (8.5-9.5), Cd²⁺ concentration in solution were manifold higher than predicated from solubility of CdCO₃ or Cd₃(PO₄)₂ probably due to formation of CdOH⁺ and CdH₂PO₄⁺ owing to hydrolysis of Cd²⁺ at higher pH. Cadmium sorption by soils followed by release of cations like Ca²⁺, Mg²⁺, Na⁺ and K⁺ from solid phase into solution phase

KEY WORDS

Sorption
Phosphate cadmium
Clay
Soil

Received : 10.03.2015

Revised : 18.05.2015

Accepted : 11.07.2015

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influence of phosphate on cadmium sorption on soils of variable CaCO_3 and clay.

MATERIALS AND METHODS

Preparation of soil samples

Eight surface (0-0.15 m) soil samples varying in calcium carbonate and clay were collected from arid and semi-arid parts of Haryana. These soil samples were crushed, mixed and passed through 2 mm sieve. The soil samples were analyzed at various physico-chemical properties by standard procedure (Jackson, 1973). The soils (sand 20.4 to 87.9%, silt 5.3 to 42.8%, clay 6.8 to 43.4%) were clayey to loamy sand in texture and showed pH 7.14 to 9.45, EC 0.20 to 2.30 dSm^{-1} , organic carbon 0.13 to 0.92 %, CaCO_3 0.00 to 9.78% and CEC 3.82 to 29.96 $\text{cmol}(\text{p}^+)\text{kg}^{-1}$. The total and Olsen's P contents of these soils ranged from 281.25 to 781.25 and 0.500 to 2.200 mg kg^{-1} , respectively (Table 1).

Preparation of phosphated soil samples

The soils 250 g of each soil samples were spreaded over a polythene sheet separately in a very thin uniform layer and 25 ml KH_2PO_4 solution containing 50 mg P was sprayed and mixed thoroughly. Thereafter, the soil samples were transferred to 600 ml beakers and 150 ml distilled water was added and covered with polythene sheet and allowed to dry at room temperature ($30 \pm 4^\circ\text{C}$). Six such wetting and drying cycles were repeated in 45 days. Thereafter, the soil samples were air dried ground and passed through 2 mm sieve. Both P- treated and untreated soil samples were used for Cd sorption.

Method of Cd sorption

The Cd sorption by original (untreated) and phosphated (P-treated) soil samples was allowed to take place by equilibrating 2 g soil with 25 mL of CdCl_2 solution of various cadmium concentrations ranging from 0.5×10^{-5} to 1×10^{-3} $\text{mol Cd}^{2+} \text{L}^{-1}$ in 100 mL plastic bottles separately. The 25mL of CdCl_2 solution of each Cd concentration was added in each bottle. The plastic bottles were stopped and shaken intermittently and kept for 24 hours incubator-cum-shaker to attain equilibrium at $25 \pm 2^\circ\text{C}$. Thereafter, the suspensions were centrifuged at 5000 rpm for 20 minutes. The centrifugate suspension was passed through filter paper Whatman 42 to get clear solution. The filtrate was analysed for Cd^{2+} by Atomic Absorption Spectrophotometer. The centrifugates were also analysed for Ca^{2+} , Mg^{2+} , Na^+ and K^+ by standard methods (Hesse, 1971). Sorbed Cd was calculated from the difference between the initial and corresponding equilibrium concentration. The percent of added Cd sorbed (X_{Ad}) and distribution coefficient (K_d) were calculated. $K_d = \text{Cd sorbed}(\text{cmol})$ per kg of sorbent used/Cd in solution (cmol) per litre at equilibrium.

RESULTS AND DISCUSSION

Sorption isotherms

The amount of Cd sorbed (x/m) varied from 0.059 to 12.385 m mol kg^{-1} in untreated (P_0) and 0.050 to 12.385 m mol kg^{-1} in P-treated (P_1) soils while, the percent of added Cd sorbed (X_{Ad}) varied from 91.10 to 99.10 in untreated and 79.35 to 99.02 in P-treated soils (Table 2). These results indicated that the $x/$

Table 1: Physico-chemical properties of soils.

Location	Bardha(S_1)		Dabra(S_2)		Chaudharywas(S_3)		Bhojraj(S_4)		Jui(S_5)		Ambala(S_6)		Kaul(S_7)		Hisar(S_8)	
	Climate	Arid	Semi-arid	Arid	Arid	Semi-arid	Semi-arid	Semi-arid	Arid	Arid	Semi-arid	Semi-arid	Arid	Arid	Semi-arid	Semi-arid
Taxonomic classification	Typic Torripsamment	Typic Camborthid	Typic Camborthid	Typic Camborthid	Typic Camborthid	Typic Camborthid	Fallow-Mustard	Typic Torripsamment	Typic Torripsamment	Typic Torripsamment	Typic Haplustept	Typic Haplustept	Typic Haplustept	Typic Haplustept	Typic Haplustept	Typic Haplustept
Land use	Bajra-Wheat	Bajra-Wheat	Bajra-Mustard	Bajra-Mustard	Bajra-Mustard	Fallow-Mustard	Bajra-Wheat	Bajra-Wheat	Bajra-Wheat	Bajra-Wheat	Paddy-Wheat	Paddy-Wheat	Paddy-Wheat	Paddy-Wheat	Paddy-Wheat	Bajra-Wheat
Sand (%)	87.9	58.6	78.3	78.3	78.3	59.7	53.2	53.2	53.2	53.2	46.6	46.6	20.4	20.4	45.6	45.6
Silt (%)	5.3	22.6	13.4	13.4	13.4	32.6	9.4	9.4	9.4	9.4	42.8	42.8	36.2	36.2	36.4	36.4
Clay (%)	6.8	18.8	8.3	8.3	8.3	7.7	7.4	7.4	7.4	7.4	10.6	10.6	43.4	43.4	18.0	18.0
Texture	Loamy sand	Sandy loam	Loamy sand	Loamy sand	Loamy sand	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Silt loam	Silt loam	Clay	Clay	Silt loam	Silt loam
CaCO_3 (%)	1.00	2.60	3.90	3.90	3.90	9.78	0.72	0.72	0.72	0.72	0.00	0.00	0.00	0.00	0.00	0.00
CEC [$\text{cmol}(\text{p}^+)\text{kg}^{-1}$]	3.82	12.17	5.95	5.95	5.95	5.47	5.21	5.21	5.21	5.21	9.34	9.34	29.96	29.96	13.04	13.04
pH	8.55	7.81	8.35	8.35	8.35	9.45	8.55	8.55	8.55	8.55	7.55	7.55	7.60	7.60	7.14	7.14
EC (dSm^{-1})	0.30	2.30	0.22	0.22	0.22	0.29	0.22	0.22	0.22	0.22	0.34	0.34	0.20	0.20	0.62	0.62
Organic carbon (%)	0.56	0.57	0.38	0.38	0.38	0.13	0.24	0.24	0.24	0.24	0.92	0.92	0.67	0.67	0.83	0.83
Total P (mg/kg)	281.25	625.00	500.00	500.00	500.00	562.50	281.25	281.25	281.25	281.25	312.50	312.50	500.00	500.00	781.25	781.25
Olsen's P (mg/kg)	0.852	2.200	0.500	0.500	0.500	0.768	0.500	0.500	0.500	0.500	1.006	1.006	0.500	0.500	1.828	1.828

Table 2: The amount of Cd sorbed (x/m , m mol kg^{-1}), percent of added Cd sorbed (X_{Ad}) and distribution coefficient (K_d) of untreated (P_0) and P-treated (P_1) soils at different initial (C_0) Cd^{2+} concentration.

	Bardha (S_1)		Dabra (S_2)		Chaudharywas (S_3)		Bhojraj (S_4)		Jui (S_5)		Ambala (S_6)		Kaul (S_7)		Hisar (S_8)	
	P_0	P_1	P_0	P_1	P_0	P_1	P_0	P_1	P_0	P_1	P_0	P_1	P_0	P_1	P_0	P_1
x/m	0.059	0.052	0.059	0.052	0.062	0.057	0.062	0.054	0.059	0.054	0.059	0.060	0.062	0.059	0.060	0.058
X_{Ad}	94.60	85.23	91.10	85.23	100.00	91.10	100.00	87.54	93.59	87.54	95.90	84.66	100.00	84.66	95.90	92.35
K_d	217.15	128.06	184.08	70.36	"	128.03	"	94.67	184.08	94.67	293.11	220.89	"	220.89	292.97	151.51
	$C_0 = 0.5 \times 10^{-5} M$															
x/m	0.121	0.115	0.119	0.115	0.122	0.119	0.123	0.114	0.119	0.114	0.121	0.118	0.122	0.120	0.121	0.119
X_{Ad}	96.79	93.23	95.63	91.98	97.95	95.54	98.57	91.45	95.54	91.45	96.97	95.01	97.59	96.79	97.32	95.54
K_d	377.53	169.97	272.81	143.52	591.10	218.38	863.15	133.36	267.29	133.36	399.73	236.66	685.39	374.41	453.01	267.29
	$C_0 = 0.2 \times 10^{-4} M$															
x/m	0.242	0.236	0.241	0.237	0.245	0.243	0.247	0.232	0.244	0.232	0.244	0.242	0.247	0.244	0.246	0.244
X_{Ad}	96.99	95.42	96.61	95.10	98.39	97.50	98.97	93.05	97.50	93.05	97.64	96.88	98.66	97.64	98.39	97.50
K_d	403.27	257.33	356.19	197.05	764.43	487.36	1206.64	167.02	489.37	167.02	517.05	388.32	935.25	517.05	767.55	489.37
	$C_0 = 1 \times 10^{-4} M$															
x/m	1.218	1.217	1.210	1.199	1.232	1.230	1.237	1.211	1.222	1.211	1.226	1.225	1.235	1.233	1.234	1.230
X_{Ad}	97.50	97.42	96.84	95.98	98.59	98.49	98.97	96.95	97.83	96.95	98.19	97.19	98.79	98.64	98.77	98.41
K_d	488.57	472.95	382.81	298.58	875.75	817.43	1197.71	397.69	564.80	397.69	678.28	432.84	1027.45	911.04	1004.31	812.63
	$C_0 = 1 \times 10^{-3} M$															
x/m	12.198	12.216	12.162	12.188	12.349	12.340	12.383	12.385	12.229	12.385	12.279	12.332	12.385	12.270	12.344	12.376
X_{Ad}	97.59	97.75	97.31	97.50	98.80	98.80	99.07	99.00	97.84	99.00	98.24	98.64	99.10	98.86	98.83	99.02
K_d	507.76	543.57	453.79	489.39	1035.01	1028.89	1337.25	1354.32	564.97	1354.32	697.90	912.39	1382.67	1076.60	1058.72	1263.36

m , X_{Ad} and K_d progressively increased with increasing Cd^{2+} concentration in solution. The distribution coefficient (K_d) varied from 184.08 to 1382.67 on untreated while, 48.41 to 1354.32 on P-treated soils. The higher values of K_d are indicative of more efficient removal of Cd from the solution by soils due to higher affinity of Cd for sorbents than for solvent (water). The amount of Cd sorbed by untreated soil was highest (100%) in Chaudharywas (S_3), Bhojraj (S_4) and Kaul (S_7) at 0.5×10^{-5} mol L^{-1} solution Cd^{2+} concentration. This may be due to presence of higher amounts of $CaCO_3$ and clay in these soils. The effect of $CaCO_3$ content on Cd sorption was highly marked in Bardha (1%), Chaudharywas (3.90%) and Bhojraj (9.78% $CaCO_3$) soils. The x/m , X_{Ad} and K_d progressively increased with increasing $CaCO_3$ content. These soils contain almost similar amounts of clay (6.8 to 8.3%). Maftoun *et al.* (2004) reported that soluble Cd compounds added to calcareous soils were effectively and rapidly retained by the solid phase of the soils. The adsorption of Cd increased with increasing solution Cd concentration and the soils had different Cd sorption capacity. Similarly, the effect of clay on Cd sorption was evident in non-calcareous soils of Kaul (43.4%). Hisar (18.0%) and Ambala (10.6% clay) where, the x/m , X_{Ad} and K_d at a given concentration increased with increasing clay content. The results are in agreement with the reports of Thakur *et al.* (2013).

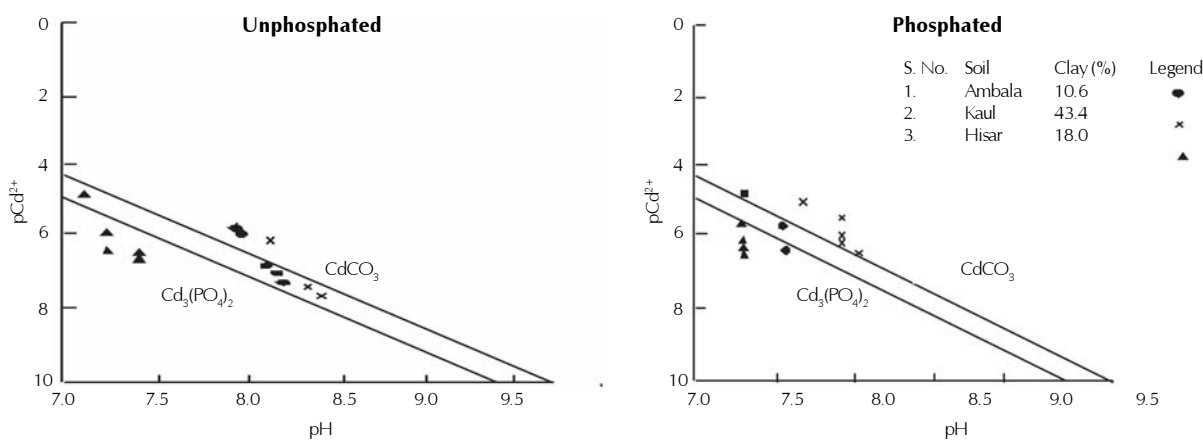
The phosphate enrichment of soils in general decreased the values of x/m and K_d as compared to untreated soils. The magnitude of reduction however, varied with the soil and Cd^{2+} concentration in solution. It was observed that effect of phosphate pretreatment was more pronounced at lower Cd^{2+} concentration in all the soils. These observations are consistent with earlier reports of Krishnamurti *et al.*, (1999) and Thakur *et al.* (2006). As the pH of the experimental soils is in alkaline range (7.14 to 9.45), it appears that effect of P-treatment of $CaCO_3$ predominated over the effect of phosphatization of clay, in respect of net reduction in Cd sorption due to phosphate pre-treatment of soils. It can be attributed to (i) phosphate treatment causes nucleation of different phosphate ion species on $CaCO_3$ (Tomar, 2000), (ii) solubility product contents of calcium phosphates are lower than that of calcium carbonate (Novozamsky and Beek, 1976), suggesting that calcites surface has more affinity for Cd compared to that of calcium phosphate or in other words, phosphate is bound more strongly than CO_3^{2-} , with Cd^{2+} causing a more difficult release of Cd^{2+} from Ca-P surface than that of $CaCO_3$ and (iii) formation of Cd phosphate complexes such as $Cd H_2PO_4^+$ ($\log K_{sp} Cd H_2PO_4^+ = 2.91$, Martell *et al.*, 1997). This would lead to increase in Cd^{2+} concentration in solution, resulting in a decreased Cd sorption in presence of phosphate.

Solubility relationship of Cd^{2+} in soils

Solubility diagrams were constructed between the negative logarithmic Cd^{2+} concentrations versus pH to investigate, whether Cd sorption in the soils resulted due to precipitation as $CdCO_3$ and/or $Cd_3(PO_4)_2$ or whether, Cd^{2+} concentration in solution is controlled by the solubility of these compounds. It can be observed (Fig. 1) that in Ambala (S_6), Kaul (S_7) and Hisar (S_8) soils (pH 7.14 to 7.60), the Cd^{2+} concentration in solution appears to be controlled by $CdCO_3$ and/or $Cd(PO_4)_2$, suggesting that Cd sorption in soils took place by the precipitation as $CdCO_3$ and $Cd_3(PO_4)_2$. In highly alkaline

Table 3: The amount of cation released (m eqv kg⁻¹) and their contribution to Cd sorption (%) in untreated (P₀) and P- treated (P₁) soils

Soils	Treatments	Initial Cd ²⁺ concentration in solution		1 x 10 ⁻³ M	
		1 x 10 ⁻⁵ M	Contribution of cations to Cd sorption	Total amount of cation released	Contribution of cations to Cd sorption
S ₁	P ₀	0.124	51.33	2.549	10.44
	P ₁	0.149	64.20	2.975	12.41
S ₂	P ₀	0.124	52.99	1.512	6.20
	P ₁	0.199	62.23	2.761	11.37
S ₃	P ₀	0.136	55.71	1.249	5.05
	P ₁	0.149	62.60	1.474	5.96
S ₄	P ₀	0.112	45.10	1.137	4.57
	P ₁	0.175	76.73	2.099	8.45
S ₅	P ₀	0.150	62.59	2.161	8.82
	P ₁	0.187	88.19	4.011	16.35
S ₆	P ₀	0.087	35.94	1.537	6.25
	P ₁	0.087	36.85	2.061	8.34
S ₇	P ₀	0.074	30.31	1.986	7.99
	P ₁	0.100	41.66	3.362	13.67
S ₈	P ₀	0.087	36.46	1.875	7.58
	P ₁	0.174	49.27	2.275	9.09

**Figure 1: pCd²⁺ - pH Solubility relationship for unphosphated and phosphate soils with varying clay content. Solid lines represent theoretical pCd²⁺ from CdCO₃ and Cd₃(PO₄)₂****Table 4: Average contribution of different adsorbed soil cations to sorption**

Cations	Initial Cd ²⁺ concentration in solution			
	1 x 10 ⁻⁵ M	1 x 10 ⁻³ M		
	P ₀	P ₁	P ₀	P ₁
Ca	9.61	12.14	1.86	1.54
Mg	5.68	8.69	1.30	1.41
Na	13.46	15.67	2.76	5.45
K	17.53	23.70	1.18	2.25
Total	46.28	60.20	7.10	10.65

calcareous soils of Bardha (S₁), Chaudharywas (S₃) and Bhojraj (S₄) (pH 8.35 to 9.45), Cd²⁺ concentration in equilibrium solution were manifold higher than predicted from the solubility of CdCO₃ or Cd₃(PO₄)₂ (Fig. 2 of diagram, the formation of CdH₂PO₄⁺ and CdOH⁺ due to hydrolysis of Cd²⁺ was not taken into consideration. Bolan *et al.* (1999) and Krishnamurti *et al.* (1999) contended that inorganic anions form ion pair complexes with heavy metals which may reduce the sorption of heavy metals. Furthermore, it has also been

suggested that besides precipitation reaction, complex forming reaction between metal ions and hydroxyl ions are taking place leading to the formation of hydroxyl-co-complex containing one or more metal (Bolt, 1976). This tendency becomes more stronger with rise in pH. According to Davis and Leckie (1978) and Kuo and McNeal (1984), the Cd could undergo hydrolysis particularly above the pH of the adsorption edge. Martell *et al.* (1997) also opined that due to formation of Cadmium phosphate complexes such as CdH₂PO₄⁺, Cd sorption would decrease the amount of Cd in solution as Cd phosphate complexes would increase. This causes a substantial increase in the solubility of the solid Cd leading to the increase in total metal concentration in solution. Therefore, in highly alkaline calcareous soils, sorbed as well as solution Cd²⁺ would undergo hydrolysis forming co-complexes with OH⁻ such as CdOH⁺, Cd(OH)₂⁰, resulting in substantial higher values of Cd concentration in the solution than predicted from the solubility of CdCO₃ and Cd₃(PO₄)₂. Thakur *et al.* (2013) also reported that in unphosphated system, the Cd concentration in solution was controlled by

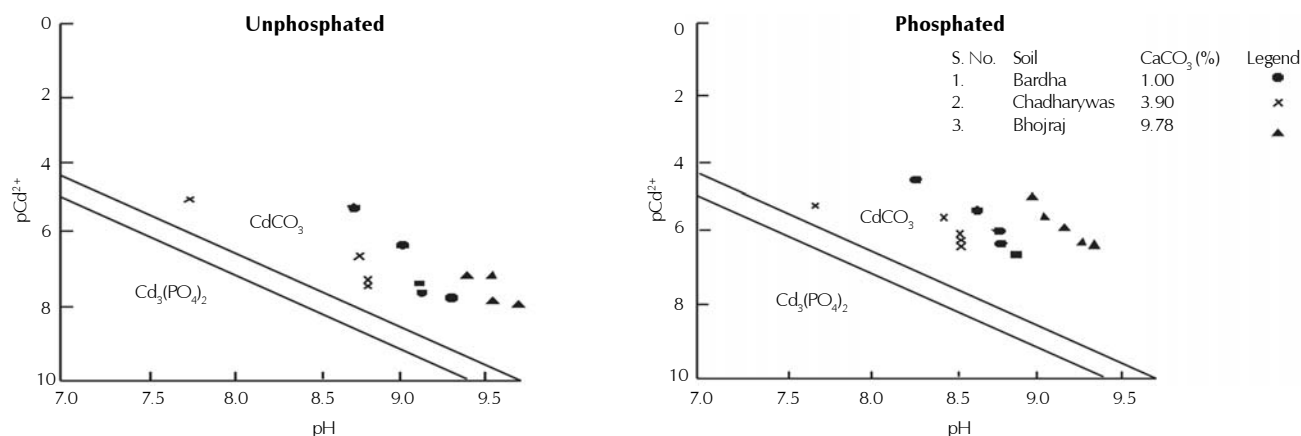


Figure 2: pCd^{2+} - pH Solubility relationship for unphosphated and phosphate soils with varying $CaCO_3$ content. Solid lines represent $CdCO_3$ and $Cd_3(PO_4)_2$

the solubility of $CdCO_3$ plus soil Cd while, in phosphated system it was controlled by the solubility of $Cd_3(PO_4)_2$.

Release and contribution of adsorbed (exchangeable) cations in Cd sorption

The release of cation was calculated by subtracting the cation concentration in pure water at equilibrium with soil from its corresponding concentration at 10^{-5} mol and 10^{-3} mol Cd^{2+} L⁻¹ concentration in equilibrium with soils. The contribution of total adsorbed cations ($Ca^{2+} + Mg^{2+} + Na^+ + K^+$) to Cd sorption at 10^{-5} mol Cd^{2+} L⁻¹ concentration ranged from 30.31 to 62.59 per cent in untreated soil and 36.85 to 88.19 per cent in P-treated soils (Table 3), while, at 10^{-3} mol Cd^{2+} concentration, the contribution were 4.57 to 10.44 per cent in untreated and 5.96 to 16.35 per cent in P-treated indicates that cationic contribution to total Cd sorption was manifold at 10^{-5} than at 10^{-3} mol Cd^{2+} concentration. These results are consistent with earlier reports of Soon (1981). The sorption of Cd or other metal is multistep process involving initial fast adsorption at relatively lower concentrations, followed by slow adsorption probably by diffusion into process of inner soil surface and precipitation at higher concentration (Brunner *et al.* 1988). Thus it is logical to conclude that adsorption of Cd^{2+} on exchange sites was the dominant mechanism at lower concentration whereas, at higher (10^{-3} mol) concentration, precipitation of $CdCO_3$ or $Cd_3(PO_4)_2$ predominated. Thakur *et al.* (2006) also reported that cadmium was effectively retained on $CaCO_3$ by the mechanism of chemisorptions at lower concentrations while, at higher concentration, precipitation of $CdCO_3$ on $CaCO_3$ surface predominated. These results further illustrate that contribution of adsorbed cations was higher in P-treated soils, which may be due to increase in the negative charge on soil due to phosphatization. The average contribution of different cations at 10^{-5} mol Cd^{2+} concentration were in order $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ both in untreated and P-treated soils while, at 10^{-3} mol the average cation contribution was in order $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in untreated and $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$ in P-treated soils (Table 4). These results are in conformity with Garcia-Miragaya and Page (1977). These results further reveal that at lower concentration monovalent cations (Na^+ and K^+) contributed more than divalent cations (Ca^{2+} and Mg^{2+}) to Cd sorption

presumably due to more easier replacement than divalent cations.

Thus, it can be inferred that the application of phosphate to the soils decreased its Cd sorbing ability. Cadmium sorption by soils was followed by release of Ca^{2+} , Mg^{2+} , Na^+ and K^+ from solid phase into the solution phase indicating that Cd sorption in part was taking place by the process of cation exchange. The effect of phosphate pretreatment on Cd sorption was more pronounced at lower Cd^{2+} concentration in solution phase as adsorption of Cd^{2+} on exchange sites was dominant mechanism whereas, at higher concentration precipitation of $CdCO_3$ or $Cd_3(PO_4)_2$ predominated.

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