ISSN: 0128-7680
Pertanika J. Sci. & Technol. **2(2)**: 181-187 (1994)

Effect of pH and Inorganic Reagents on the Immobilization of Cadmium in Some Malaysian Cocoa-growing Soils

K. S. Low and C. K. Lee
Chemistry Department
Faculty of Science and Environmental Studies
Universiti Pertanian Malaysia
43400 UPM Serdang, Selangor, Malaysia

Received 19 February 1993

ABSTRAK

Kesan pH dan berbagai-bagai bahan tak organik ke atas ketakgerakan kadmium pada tiga jenis tanah koko Malaysia (Rengam, Bernam dan Malacca) telah dikaji. Keputusan menunjukkan bahawa $Ca(OH)_2$ adalah paling berkesan terhadap ketakgerakan kadmium. Karbonat dan posfat juga boleh digunakan tetapi tidak begitu berkesan.

ABSTRACT

The effects of pH and various inorganic reagents on the immobility of cadmium in three Malaysian cocoa-growing soils (Rengam, Bernam and Malacca) were investigated. Results show that $Ca(OH)_2$ was most efficient in immobilizing cadmium. Carbonates and phosphates were also effective, though to a lesser extent.

Keywords: cadmium, immobilization, cocoa-growing soils, pH, inorganic reagents

INTRODUCTION

Cadmium is not known to be essential to plants, animals and human beings. Its toxic effects at high concentrations are well documented. Cadmium uptake in mammals and humans occurs through ingestion and inhalation. According to a WHO recommendation, the daily dose of cadmium should not exceed 1 μg per kg body weight.

The presence of cadmium in Malaysian cocoa beans was reported by Knezevic (1979). A more comprehensive survey on cadmium in cocoa beans in various Malaysian cocoa estates was conducted by Lee and Low (1985). The presence of cadmium in cocoa beans is probably due to the geochemical nature of the soil and the application of cadmium-contaminated phosphate fertilisers. It is known that several factors influence the mobility of cadmium in soils. These include soil texture, clay minerals, concentration and type of anions and cations, pH and organic matter. It was found that lowering the pH of soil leads to more cadmium being released from sorption sites and consequently a greater mobility and availability of cadmium to the plants. Ram and Verloo (1985) reported that the mobility of cadmium increased with progressive acidification of soils. The effect of organic matter on the mobility of cadmium in some Malaysian cocoa-growing soils was earlier investigated by Low and Lee (1991). The mobility, and hence availability, of this metal to plants could also be reduced by the addition of calcium carbonate and phosphate through the formation of insoluble cadmium carbonate and phosphate.

In an attempt to reduce cadmium uptake by cocoa plants, investigations were carried out to study the ability of pH and several inorganic substances to immobilize cadmium in three Malaysian cocoa-growing soils. This paper reports the results of this study.

MATERIALS AND METHODS

The three cocoa-growing soils used were Rengam, Bernam and Malacca. They were collected from Merlimau, Sungai Buloh and Selbourne cocoa estates respectively. Soil samples were taken from ten to fifteen cores in each plot at three different depths of 0-15, 15-30 and 30-45 cm. The soils were air-dried, crushed, passed through a 2 mm sieve and composited.

In the study of the effect of pH on the immobilization of Cd on soils, 20 ml of 20 mg/l Cd solution at a particular pH was added to the soil (0.25 g). Solution pH was adjusted by the addition of HNO_3 or NaOH. After shaking the soil mixture for 24 h, it was centrifuged and the supernatant was analysed for Cd using an ICP-AES (Low and Lee 1991). A control without soil was similarly carried out.

In the immobilization study, 1 g of solution containing 100 µg Cd as $CdCl_2 .H_2O$ was added to the soil (5 g) and the mixture was made up to a total volume of 8 ml with distilled deionised water in a 50 ml test tube. It was then shaken on a gyratory shaker at 100 rpm at room temperature until the mixture turned dry. Each treatment was carried out in duplicate. $Fe(OH)_3$ was prepared by mixing appropriate volumes of standard solutions of $Fe(NO)_3$ and KOH.

The following soil mixtures were investigated:

Treatment

1. Soil + Cd
2. Soil + Cd + $Ca(OH)_2$ (0.2 g)
3. Soil + Cd + $CaCO_3$ (0.2 g)
4. Soil + Cd + K_2CO_3 (0.5 meq)
5. Soil + Cd + $Ca_3(PO_4)_2$ (0.2 g)
6. Soil + Cd + $Fe(NO_3)_3$ (0.5 meq)
7. Soil + Cd + KH_2PO_4 (0.5 meq)
8. Soil + Cd + $Fe(OH)_3$ (0.5 meq)

The effectiveness of the various treatments in immobilizing cadmium was assessed by measuring the amounts extracted from the incubated soils by the following extractants:

(a) 1 N NH_4AcO (b) 0.5 N $CaCl_2$
(c) 0.5 N NH_4Cl (d) 0.5 N $Ca(OH)_2$
(e) 0.5 N NH_4AcO (f) 0.5 N KNO_3

Extraction by 1 N NH_4AcO was carried out by shaking the soil mixture with 20 ml NH_4AcO solution for 1 h (Kiekens *et al.* 1984). The soil mixture was then centrifuged and the supernatant was analysed for its cadmium content using an ICP-AES (Low and Lee 1991). The remaining soil mixtures were shaken individually with the other extractants for 10 minutes after standing for 16 h (Sopsito *et al.* 1982). Cadmium content was analysed as before.

RESULTS AND DISCUSSION

Effect of Extractants

Various extractants have been recommended for the determination of available cadmium in soils (Gerritse and Van Driel 1984; Kiekens *et al.* 1984). Table 1 shows the efficiencies of the various chemicals in extracting cadmium from the three cocoa-growing soils.

TABLE 1
Extractable cadmium content in soils (mg/kg)

Soil	Rengam	Malacca	Bernam
NH_4AcO (1 N)	0.76	0.14	0.26
	(34.0)	(19.5)	(7.8)
$CaCl_2$	0.97	0.76	0.62
	(43.5)	(36.2)	(18.5)
NH_4Cl	0.25	0.23	0.63
	(11.2)	(11.0)	(18.9)
$Ca(NO_3)_2$	0.10	0.39	0.35
	(4.5)	(18.6)	(10.5)
NH_4AcO (0.5N)	0.73	0.26	0.36
	(32.7)	(12.4)	(10.8)
KNO_3	0.14	0.09	0.28
	(6.3)	(4.3)	(8.4)

Values in brackets are % of Cd compared to the total amount present in the soil.

The amount of cadmium extracted depends on the nature of the soil. All the three soils studied were acidic –Rengam (pH = 5.68), Malacca (pH = 5.73) and Bernam (pH = 4.52). The greatest difference in extraction is noted with $CaCl_2$ and KNO_3 . More than 30% of cadmium was extracted using $CaCl_2$ whereas KNO_3 gave less than 15%. This could not be due to the weaker exchange of K^+ compared with Ca^{2+} as $Ca(NO_3)_2$ did not extract very well.

Effect of pH

The amounts of cadmium remaining in the solutions after treatment are given in Table 2. In water the immobilization of cadmium increased with increasing pH in the range of 4.18 – 7.42. The increase in immobilization is not very marked because of the rather restricted pH range. Also, all the tested soils were acidic even though it has been reported that pH is a critical factor in controlling the distribution of cadmium between soil and solute. As the cocoa-growing soils in Peninsula Malaysia are mainly acidic, efforts have to be made to neutralize them in order to reduce mobility and hence availability of cadmium to plants. Similar results were also obtained by Christensen (1984) in the study of cadmium-soil sorption at low concentrations. In the pH interval of 4 – 7.7, the sorption capacity of the soil increased approximately threefold for one unit increase in pH. Zhan (1986) ascribed the immobility of cadmium at higher pH to the co-precipitation of cadmium with $Fe(OH)_3$.

TABLE 2
Effect of pH in Cd sorption in soil (0.25 g soil per 20 ml of 20 mg/l Cd)

Soil/pH	4.18	5.18	6.18	7.42
Rengam	13.66*	12.76	12.40	11.64
Bernam	7.26	6.54	6.18	5.91
Malacca	9.17	9.15	8.03	7.80
Control	19.94	20.19	20.82	20.97

*mg/l

Effect of Immobilization Reagents

The pH of the soils upon the addition of inorganic reagents is shown in Table 3. The most pronounced effect is observed by the addition of $Ca(OH)_2$ and $Fe(NO_3)_3$. $Ca(OH)_2$ rendered all the three soils alkaline, whereas the reverse effect is observed with $Fe(NO_3)_3$. The addition of $Ca(OH)_2$ appears to cause co-precipitation of cadmium on soil particles, and thus reduces cadmium availability to plants. Table 4 shows that almost all the added cadmium was immobilized in the soils regardless of the nature of the extractant with the addition of $Ca(OH)_2$.

TABLE 3
pH of soils upon the treatment of inorganic reagents

No.	Inorganic reagents	Rengam	Bernam	Malacca
Control	H_2O	5.68	4.52	5.73
1.	$CdCl_2$(100 μg)	5.65	4.50	5.72
2.	$CdCl_2 + Ca(OH)_2$(0.2 g)	12.43	12.41	12.26
3.	$CdCl_2 + CaCO_3$ (0.2 g)	7.26	6.63	7.13
4.	$CdCl_2 + K_2CO_3$ (0.5 meq)	8.65	6.79	8.54
5.	$CdCl_2 + Ca_3(PO_4)_2$ (0.2 g)	6.14	5.06	6.34
6.	$CdCl_2 + Fe(NO_3)_3$ (0.5 meq)	2.39	2.53	2.48
7.	$CdCl_2 + KH_2PO_4$ (0.5 meq)	5.01	3.76	5.27
8.	$CdCl_2 + Fe(OH)_3$ (0.5 meq)	4.29	3.70	5.22

TABLE 4
Cadmium immobilization under different treatments
(amount extracted from 100 μg Cd added)

Soil/Treatment	Extractants					
	NH_4ACO(1N)	$CaCl_2$	NH_4Cl	$Ca(NO_3)_2$	NH_4ACO(0.5N)	KNO_3
Rengam control	0.76	0.97	0.25	0.10	0.73	0.14
1	49.71	61.68	71.70	38.10	30.00	10.02
2	3.90	0.82	2.48	0.67	1.32	0.22
3	16.76	12.58	8.18	1.73	6.43	0.48
4	14.08	4.98	3.43	1.37	6.43	0.48
5	12.36	20.83	10.98	6.02	4.75	0.72
6	83.00	78.58	102.25	75.00	63.80	102.50
7	31.64	59.33	46.75	24.75	15.28	3.68
Malacca control	0.41	0.76	0.23	0.39	0.09	0.26
1	53.82	51.13	59.18	35.75	30.40	13.60
2	5.64	0.88	2.43	0.32	1.34	0.38
3	25.44	14.26	10.75	2.55	8.85	0.78
4	17.66	3.43	3.84	0.75	3.75	1.71
5	17.94	17.55	12.38	6.00	4.20	1.59
6	87.06	60.53	82.25	67.20	63.48	92.70
Bernam control	0.26	0.62	0.63	0.35	0.28	0.36
1	62.78	61.90	102.0	52.55	47.24	69.61
2	2.02	0.26	1.38	0.66	0.58	0.27
3	12.32	85.90	7.81	1.11	19.01	0.72
4	38.28	50.12	51.06	23.70	18.00	6.22
5	13.64	25.12	27.74	13.33	9.44	4.41
6	82.70	79.93	101.32	67.82	73.76	102.90
7	52.50	71.42	100.27	54.40	39.44	75.67
8	71.61	77.80	105.47	65.73	55.86	88.54

The addition of $Fe(NO_3)_3$ caused the pH of the soils to drop below 3. This could cause the cadmium to be in a mobile state. Some inorganic materials gave 100% recovery of added cadmium, indicating non-sorption of cadmium in soils. In general, $CaCO_3$ is more efficient than K_2CO_3 in immobilizing cadmium in Rengam and Malacca soils. $Ca_3(PO_4)_2$ is more efficient in immobilizing cadmium than KH_2PO_4 in all the tested soils. $Fe(NO_3)_3$ is not useful as an immobilizing agent. In some cases this chemical has a negative effect by releasing the cadmium in the soil, probably caused by its low pH and competition between Cd^{2+} and Fe^{3+} for immobilization reaction sites. The reaction between Cd^{2+} and CO^{2-}_3 and PO^{3-}_4 and other anions in the soil-water system is much more complex than in simple solution. It is due to the various possible reactions of cations and the anions and the soil particles. Precipitation of cadmium as $CdCO_3$ and $Cd_3(PO_4)_2$ is generally not considered significant, as in most cases solubility product could not have been attained. Nucleating effect of soil particles facilitates the surface precipitation of cadmium with the carbonates and the phosphates. A two-stage mechanism is thought to be involved in the sorption. The initial step involves the replacement of the counter cation (Ca^{2+} and Mg^{2+}) by Cd^{2+}. This is followed by chemisorption of Cd^{2+} on CO^{2-}_3 and PO^{3-}_4. The sorption of cadmium by $Fe(OH)_3$ involves the replacement of Cd^{2+} with the surface hydroxyl ions with the release of H^+, followed by chemisorption to form Cd–O bonds (Mckenzie 1980).

CONCLUSION

It is concluded that pH plays an important role in the immobilization of cadmium in soils. Addition of $Ca(OH)_2$ is useful both in neutralizing the acidity of the soil and also in reducing the immobility and hence availability of cadmium to plants. Carbonates and phosphates can also influence cadmium mobility in soils, though to a lesser extent than $Ca(OH)_2$.

ACKNOWLEDGEMENT

The authors are grateful to Majlis Penyelidikan Kemajuan Sains Negara, Malaysia, for their financial support (grant no. 04-07-05-017).

REFERENCES

BROWN, K.W., J.C. THOMAS and J.F. SLOWEY. 1983. The movement of metals applied to soils and sewage effluent. *Water, Air & Soil Pollut.* **19**: 43-54.

CHRISTENSEN, T.H. 1984. Cadmium soil sorption at low concentration. Effect of time, cadmium load, pH, and calcium. *Water, Air & Soil Pollut.* **21**: 105-114.

FASSENBENDER, H.W. and G. SEEKAMP. 1976. Fractions and solubility of heavy metals cadmium, cobalt, chromium, copper, nickel and lead in soils. *Geoderma* **16**: 65-69.

GERRITSE, R.G. and W. Van DRIEL. 1984. The relationship between adsorption of trace metals, organic matter and pH in temperate soils. *J. Environ. Qual.* **13**: 197-204.

KIEKENS, L., A. COTTENIE and C. VAN. 1984. Chemical activity and biological effect of sludge-borne heavy metals and inorganic metal salts added to soils. *Plant and Soil* **79**: 89-99.

KNEZEVIC, G. 1979. Heavy metals in food. Part I. Content of cadmium in raw cocoa beans and in semifinished and finished chocolate products. *Dtsch. Lebensm-Rundsch.* **75(10)**: 305-309.

LEE, C. K. and K.S. LOW. 1985. Determination of cadmium, lead, copper, and arsenic in cocoa, semifinished and finished chocolate products. *Pertanika* **8(2)**: 243-248.

LOW, K.S. and C.K. LEE. 1991. Effect of organic matter on the immobilization of cadmium in four Malaysian cocoa-growing soils. *Pertanika.* **14(1)**: 83-86.

MCKENZIE, R.M. 1980. The adsorption of lead and other heavy metals on iron. *Austral. J. Soil Res.* **18**: 61-73.

RAM, N. and M. VERLOO. 1985. Effect of various organic materials on the mobility of heavy metals in soils. *Environ. Pollut. Ser. B.* **13(10)**: 241-248.

SOPSITO, G., L.J. LUND and A.C. CHANG. 1982. Trace metal chemistry in arid field soils amended with sewage sludge. Fractionations of Ni, Cu, Zn, Cd, and Pb in solid phases. *Soil Sci. Soc. Am. J.* **46**: 260-264.

ZHAN, T. 1986. Laboratory study of the immobilisation of cadmium in soils. *Environ. Pollut. Ser. B.* **13**: 265-280.