

Cadmium adsorption by some alkaline soils of Punjab state

H.S. Hundal, Raj Kumar and C.L. Arora

Department of Soils, Punjab Agricultural University, Ludhiana-141 004, India

Abstract

Cadmium adsorption on five alkaline soils of north-west India followed Langmuir equation. The analogous shape of Linear Langmuir plot in each soil at 293 and 313°K elucidate that temperature does not change the nature of reaction but influence the bonding energy constant and adsorption maxima for Cd ion. The magnitude of adsorption maxima enhanced with increase in CaCO₃ and organic content in soils. The positive and constant value of differential isosteric heat of adsorption (ΔH) on each soil between 298 and 313°K indicate that adsorption of Cd is an endothermic process which leads to precipitation of Cd rather than physical adsorption. However, the variation of ΔH within soils might be due to variation in their physico-chemical characteristics. Solubility isotherm diagram revealed that CdCO₃ reaction product formed in equilibrated soil-Cd system used for adsorption study. It is inferred from Linear Langmuir plots, differential isosteric heat of adsorption and solubility isotherm studies that adsorption of Cd in alkaline soils occurred due to precipitation of CaCO₃ mineral.

Additional keywords : Cadmium adsorption, isotherm, solubility isotherm, differential isosteric heat of adsorption.

Introduction

Cadmium is a potentially toxic pollutant in environment and the excessive accumulation of cadmium in man causes bronchitis (Lewis *et al.* 1969), hypertension (Schroeder 1965), cardiovascular (Page and Bingham 1973) and "ouch-ouch" (Tsuchiya 1969) diseases. Cadmium exposure also enhances susceptibility to bacterial, protozoal and viral infections and that result in impaired humoral and cell-mediated immune responses (Blakley and Rajpal 1986). Cadmium contamination of the environment has been attributed to industrial activities like smelting and electroplating of metals, combustion of lubricating oils, vulcanisation of rubber for motor vehicle tires and use of cadmium compounds as fungicide sprays and due to accumulation of Cd in soils as a result of excessive use of phosphatic fertilizers (John 1972, Lengerwerff and Specht 1970, Ross and Stewart 1969, Robert *et al.* 1994). The divalent Cd is slightly soluble in an aqueous solution when associated with carbonate anions and in alkaline soils and therefore their leaching must be limited (Holmgren *et al.*

1993). Thus higher Cd status of surface soils entails its accumulation in plants and eventually in food stuffs (Hundal and Arora 1993, Wagner 1993, and Singh 1998). Hodgson (1970) found that cadmium content in plants depends primarily on soil adsorption capacity which, in turn, is governed by the physico-chemical characteristics of the soils (Adhikari and Singh 2000). An attempt was, therefore, made to study cadmium adsorption in the alkaline soils of Punjab state of India.

Materials and methods

Surface samples (S1 to S5) of alkaline soils representing alluvial plains were collected from different locations in Punjab. The physical and chemical characteristics of soils were determined following standard procedures. For adsorption study, 1 g of soil in duplicate was equilibrated for 24 hours in polyethylene bottles containing 50 ml of 0.01 M NaNO₃ solution of different Cd [added as Cd(NO₃)₂] concentrations ranging from 0.25 to 1.35 $\mu\text{mol Cd cm}^{-3}$. Adsorption isotherms were determined by equilibrating the soil suspension at 20°C and 40°C. A clear solution was separated from soil-solution suspension with Whatman No.42 filter paper. The pH and EC of the filtrate solution at 25°C was determined by pH meter and conductivity bridge, respectively. The Langmuir equation was used to interpret the equilibrium adsorption data. The linear form of the Langmuir equation is:

$$C/x/m = 1/Kb + C/b$$

Where C is the equilibrium Cd concentration ($\mu\text{mol Cd cm}^{-3}$); x/m is the amount of Cd adsorbed ($\mu\text{mol Cd g}^{-1}$ soil); b is the adsorption maxima ($\mu\text{mol Cd g}^{-1}$ soil) and k is the constant related to the bonding energy of the soil for Cd ($\text{cm}^{-3} \mu\text{mol Cd}$).

The isosteric heat of Cd adsorption, ΔH , was obtained from the adsorption data at 293 and 313°K by way of applying the Clausius-Clapeyron equation to the system. For a given surface coverage ?,

$$\text{Log } (C_2/C_1)\theta = \Delta H_{\text{ads}}/2.303R (1/T_1 - 1/T_2)$$

Where C₁ and C₂ are the equilibrium concentration ($\mu\text{mol Cd cm}^{-3}$) at temperature T₁ (293°K) and T₂ (313°K), respectively and R is the molar gas constant (Kcal mol⁻¹). The differential isosteric heat of adsorption (ΔH) is related to heat adsorbed or liberated during adsorption reaction at constant surface coverage but at different temperatures (Hayward and Trapnell 1964). By convention, it is equal but opposite in sign to that portion of the change in enthalpy of the system attributable to adsorption (Roy *et al.* 1989)

$$\Delta H = \Delta H_{\text{ads}}$$

For solubility isotherm, pCd values, the negative logarithm of the cadmium activities were calculated for soils equilibrated with 0.01 M NaNO₃ solution containing no initial Cd and with the equilibrated initial Cd concentrations of 40, 70, 90 and 140 $\mu\text{mol Cd cm}^{-3}$. For study of solubility of cadmium minerals, equilibrium reaction of octavite (CdCO₃) and cadmium hydroxide [Cd(OH)₂] phase was considered at 0.003 atmospheric pressure of CO₂. Corrections for the following ion-pairs were made: CdHCO₃⁺, CdCO₃⁰, Cd(NO₃)₂⁰ and CdHPO₄⁰.

Results and discussion

Some important characteristics of soils are given in Table 1. All studied soils are very deep, alkaline in reaction and low in available carbon. S1 to S4 soils have mixed mineralogy with illite and kaolinite as the dominant clay minerals. Cation exchange capacity (CEC) of these soils (S1-S4) vary from 4.7 to 8.2 cmol(+)kg⁻¹. Smectite is dominant in the clay fraction of S5 soil. Its CEC is 26.3 cmol(+)kg⁻¹.

Table 1. Some soils properties

Soils	Location	Taxonomic	Sand	Silt	Clay	pH	CaCO ₃	O.C.	CEC	
Village	District	Classification	------(%)-----				--(g kg ⁻¹ --		cmol (+) kg ⁻¹	
S1	Sardulgarh	Mansa	Coarse-loamy, Fluventic Haplustept	75.8	15.0	9.2	7.8	10.0	1.9	4.7
S2	Chohal	Hosiarpur	Coarse-loamy, Typic Ustorthent	82.4	6.0	11.6	7.8	—	5.7	5.5
S3	Bagha- purana	Moga	Fine-loamy, Typic Haplustept	51.0	29.0	20.0	7.9	5.0	4.2	8.0
S4	Nurmahal	Jalandhar	Fine-loamy, Typic Haplustept	58.0	24.0	18.0	7.9	—	2.0	7.2
S5	Sadhugarh	Fatehgarh Sahib	Fine, Vertic Haplustept	11.8	29.9	58.3	8.6	3.8	6.9	26.3

Adsorption of cadmium by these soils at 293 and 313°K temperature showed single linear Langmuir plots (Fig. 1). Thus, Cd adsorption on these soils as adsorbent are described by the Langmuir equation. The bonding energy for Cd adsorption was high in Fluventic Haplustept (S1) and Typic Ustorthent (S2), whereas it declined in Typic

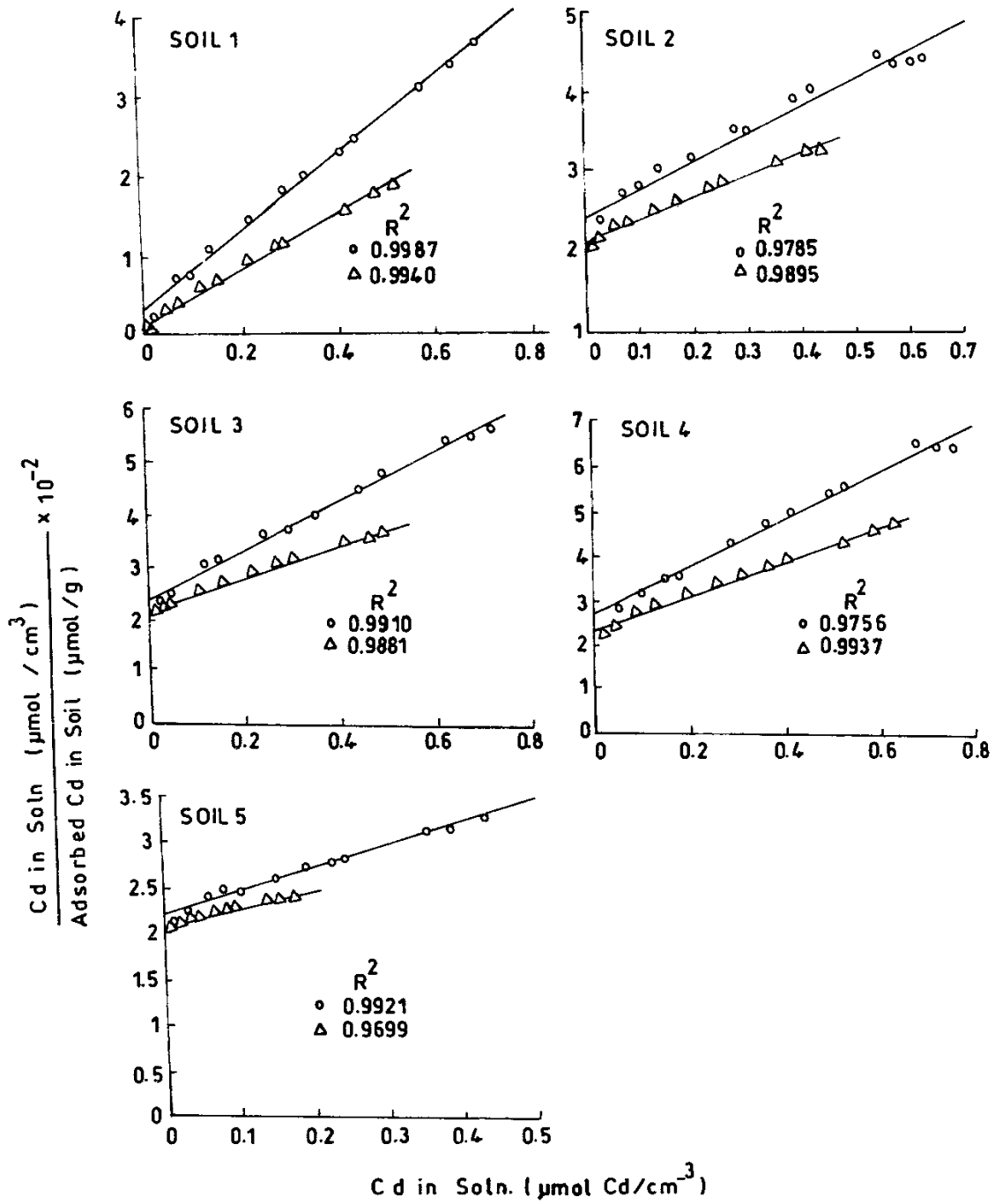


Fig. 1. Langmuir isotherm for cadmium adsorption at 293^oK(O) and 313^oK (Δ) by alkaline soils

Haplustept (S3 and S4) and Vertic Haplustept (S5) with increase in temperature of the soil solution suspension for equilibrium from 293 to 313°K. K was lower in S2 than that of S3 and S4 at both the temperatures (Table 2).

The adsorption maxima of Cd adsorption in these soils increased with an increase in temperature of the soil solution suspension for equilibration from 293 to 313°K suspension. Fluventic Haplustept had the highest magnitude of bonding energy for Cd adsorption as 11.3 ml μmol^{-1} Cd at 293°K and 18.6 ml μmol^{-1} Cd at 313°K as compared to the other soils might be due to the presence of higher amount of CaCO_3 as compared to other soils. The highest amount of Cd adsorption maxima of 41.7 μmol Cd g^{-1} soil at 293°K and 52.1 μmol Cd g^{-1} soil at 313°K were observed in the Vertic Haplustept (Table 2) owing to higher clay and CEC of the soils.

Table 2. Langmuir parameters for Cd adsorption on alkaline soils determined at 293 and 313°K

Soils	293°K		313°K		ΔH (kcal mol^{-1})
	K (ml μmol^{-1} Cd)	b (ml μmol^{-1} Cd)	K (ml μmol^{-1} Cd)	b (ml μmol^{-1} Cd)	
S1	11.3	22.2	18.7	31.6	3.24
S2	1.1	30.9	1.3	36.5	1.52
S3	1.9	21.6	1.4	32.9	3.74
S4	1.7	20.5	1.5	27.3	2.58
S5	1.1	41.7	0.9	52.1	2.00

The values of ΔH over the temperature range of 293°K to 313°K were computed using the Clausius-Clapeyron equation and plotted as a function of cadmium adsorbed (Fig.2). This shows that Cd adsorption process is energy consuming (endothermic), with positive and constant ΔH values for each soil, but it varies in soils due to their different physico-chemical characteristics. The ΔH values were 3.24, 1.52, 3.74, 2.58 and 2.00 kcal mol^{-1} for S1, S2, S3, S4 and S5 soils, respectively. The constant ΔH values as a function of cadmium adsorbed indicate that mechanism for cadmium-soil surface interaction remained essentially the same, even with increasing amount of cadmium adsorbed. The adsorption of Cd in these soils was endothermic. It elucidates that adsorption occurs due to the chemisorption precipitation of cadmium solid phase minerals. Physical adsorption on the other hand is always characterized by exothermic reaction and thus an increase in temperature eventually would lead to decrease in adsorption. The values of differential isosteric heat of cadmium adsorption remained constant in different soils, which suggests that precipitation of cadmium occurs only in single form of Cd solid phase mineral.

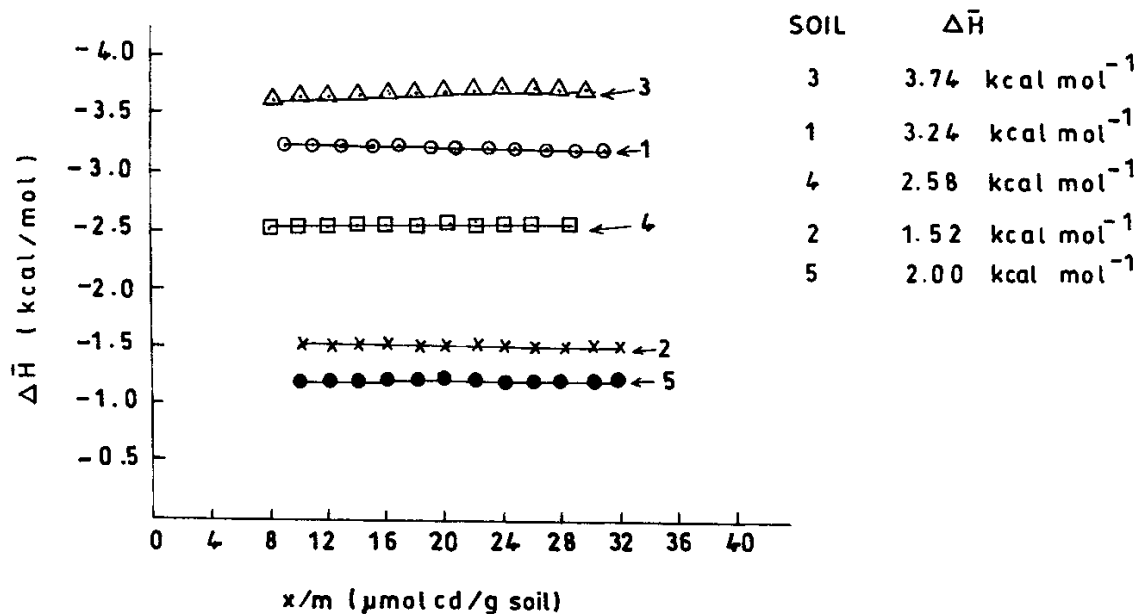


Fig.2. The isothermal differential heat of adsorption ΔH , as a function of Cd Adsorbed x/cm ($\mu\text{mol Cd g}^{-1}$ soil) on alkaline soils of Punjab

While admitting that a true thermodynamic equilibrium condition does not exist in soil system and that solubility criteria are thus often not strictly applicable, it is nevertheless, worthwhile to apply these relationship criteria to the equilibrated soil systems containing no initial Cd to $1.13 \mu\text{mol Cd cm}^{-3}$ $0.01M \text{NaNO}_3$ electrolytic solution. The solubility relationships in the equilibrated soil systems are plotted as the negative logarithm of activities of Cd ion in relation to pH (Fig.3). The equilibrated soil-systems for different soils containing no initial Cd were undersaturated with respect to octavite (CdCO_3) mineral. All the equilibrated soil systems containing 0.34 to $1.13 \mu\text{mol Cd cm}^{-3}$ in $0.01M \text{NaNO}_3$ remained undersaturated with respect to $\beta\text{-Cd}(\text{OH})_2$, but supersaturated with respect to CdCO_3 . This suggests that at these levels of Cd concentration, adsorption of Cd in different soils occurred due to precipitation of CdCO_3 . The cadmium carbonate in alkaline soils has low solubility and therefore leaching of Cd in these soils (Holmgren *et al.* 1993) is limited. Thus, cadmium contamination due to industrial activities or use of cadmium compounds as fungicide sprays entails to higher Cd status of surface soils. This could result in accumulation in plants and eventually in their respective food stuffs (Wagner 1993; Hundal and Arora 1993; and Singh 1998).

The linear Langmuir isotherm plot and constant differential isosteric heat of adsorption (ΔH) as a function of Cd adsorbed revealed that Cd adsorption in alkaline soils was mainly due to single adsorption mechanism. Since the reaction is endothermic, precipitation is the likely process for Cd adsorption in these soils.

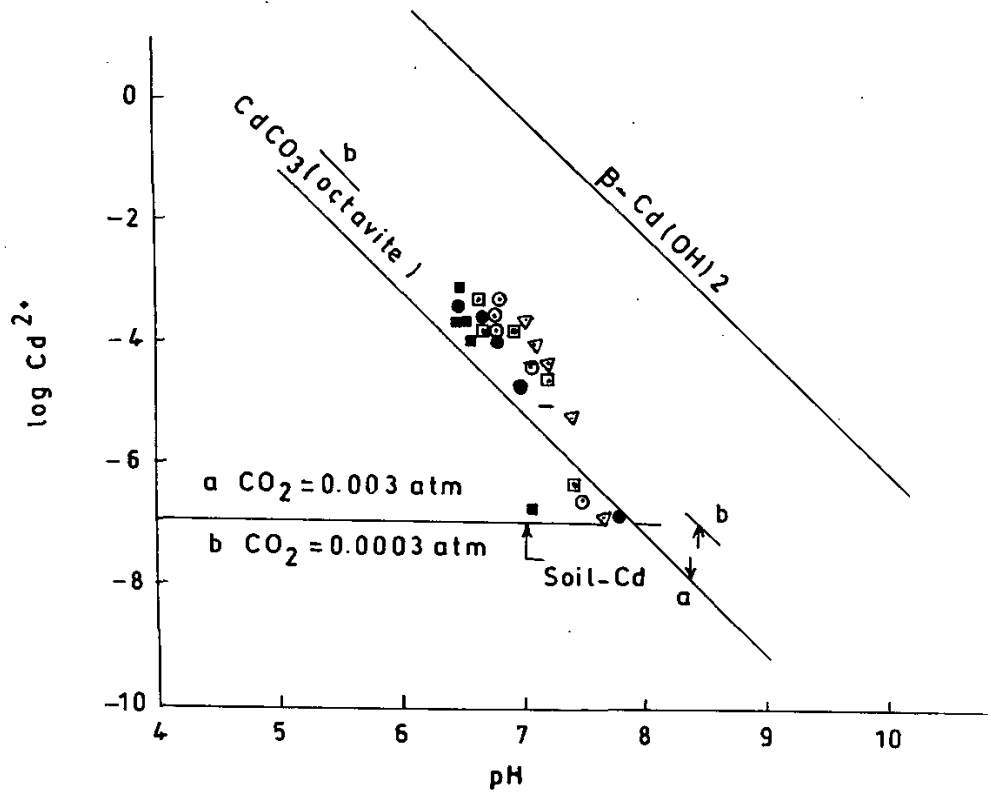


Fig.3. Identification of Cd solid phase formed in soil equilibrated with 0.01M NaNO₃ solution containing no initial Cd and with equilibrated initial Cd Concentration of 40, 70, 90 and 140 $\mu\text{mol Cd cm}^{-3}$ Soil 1 (\circ), Soil 2 (\bullet), Soil 3 (\square), Soil 4 (\blacksquare), Soil 5 (∇).

Solubility criteria used to identify the solid phase formed inferred the precipitation of Cd as CdCO₃ phase in all the soil equilibrated systems used for adsorption study.

References

- Adhikari, T., and Singh, M.V. (2000). Cadmium sorption characteristics of major soils of India in relation to soil properties. *Journal of the Indian Society of Soil Science* **48**, 757-92.
- Blakley, B.R., and Rajpal, S.T. (1996). The effect of cadmium on antibody responses to antigens with different cellular requirements. *International Journal of Immunopharmacology* **88**, 1009-1015.
- Hayward, D.O., and Trapnell, B.M.W. (1964). 'Chemisorption', Butterworth, London.
- Hodgson, J.F. (1970). Trace Substances in Environmental Health'. D.d. Emphill (ed) Vol.III, 45-58. Univ. Missouri Press, Columbia.

- Holmgren, G.G.S., Meyer, M.W., Chaney, R.L., and Daniels, R.B. (1993). Cadmium, lead, zinc, copper and nickel in agricultural soils of the United States of America. *Journal of Environmental Quality* **22**, 335-348.
- Hundal, H.S., and Arora, C.L. (1993). Studies on toxic trace elements in vegetables and corresponding soils. *Indian Journal of Horticulture* **50**, 273-278.
- John, M.K. (1972). Cadmium adsorption maxima of soils as measured by the Langmuir isotherm. *Canadian Journal of Soil Science* **52**, 273-290.
- Lengerwerff, J.V., and Specht, A.W. (1970). Contamination of roadside soil and vegetation with cadmium, nickel, lead and zinc. *Environmental Science Technology* **4**, 583-586.
- Lewis, G.P., Iyle, H., and Miller, S. (1969). Association between hepatic water soluble protein-bound cadmium levels and chronic bronchitis and/or emphysema. *Lancet II*, 1330-1333.
- Page, A.H., and Bingham, E.T. (1973). Cadmium residue in the environment. *Residue Review* **98**, 1-44.
- Robert, A.H.C., Longhurst, R.D., and Brown, M.V. (1994). Cadmium status of soils, plants and grazing animals in Newzeland. *Newzeland Journal of Agricultural Research* **37**, 119-129.
- Ross, R.G., and Stewart, D.K.R. (1969). Cadmium residues in apple fruit and foliage following spray of cadmium chloride. *Canadian Journal of Plant Science* **49**, 49-52.
- Roy, W.R., Hasset, J.J., and Griffin, R.A. (1989). Quasi-thermodynamic basis of competitive-adsorption coefficients for anionic mixtures in soils. *Journal of Soil Science* **40**, 9-15.
- Schroeder, H.A. (1965). Cadmium as a factor in hypertension. *Journal of Chronic Diseases* **18**, 647-656.
- Singh, M.V. (1998). Progress Report of All India Coordinated Research Project of Micro and Secondary and Pollutant Elements in Soil and Plants. IISS, Bhopal, pp.1-99.
- Tsuchiya, K. (1969). Causation of ouch-ouch disease. *Keio Journal of Medicine* **18**, 181-194.
- Wagner, G.J. (1993) Accumulation of cadmium in crop, plants and its consequences to human health. *Advances in Agronomy* **51**, 173-212.