

# The Influence of pH on the Forms of Cadmium in Four West Australian Soils

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## *Abstract*

The forms of cadmium in soils affect its uptake by plants and hence its potential toxicity to animals and humans. We studied the effect of pH on the forms of native and added Cd in four West Australian soils which differed in their clay, hydrous oxide and organic matter content. The forms of Cd were extracted sequentially by KCl, BaCl<sub>2</sub>, NaOCl, ammonium oxalate and concentrated acids.

The majority of Cd applied to a sandy soil was found in the soluble (KCl) and the exchangeable (BaCl<sub>2</sub>) forms at all pH values. In the siliceous sand, the proportion of the Cd present in the exchangeable form increased as the soil solution pH increased. However, in the peaty sand, the opposite trend was observed; at pH 5, approximately 50% of the Cd was found in the exchangeable form, while at higher pH values, >60% was bound to organic matter and 20% was in the soluble form. In soils in which the main adsorption surface was dominated by hydrous oxides (mainly goethite), 50–70% of the Cd was extracted as bound to oxides and as the residual fraction at pH ≤ 5. At pH values >5, the majority (90%) of it was extracted in these forms. Soils, containing clay (mainly kaolinite) as the major adsorbent, retained Cd mainly in exchangeable form at all pH values and at all the rates of Cd application. At pH >5, however, some of the Cd was also found in the residual form and bound to organic matter.

This work has shown that the form of added Cd in a soil cannot be elucidated by considering the major adsorbing component alone. It is also necessary to know the pH, the presence of other adsorbing surfaces and the rates of applied Cd.

## **Introduction**

Toxic concentrations of cadmium (Cd) in humans can occur from consumption of plant or animal products grown on soils in which Cd has accumulated. Phosphatic fertilizers contain varying amounts of Cd as an impurity depending on the source of the rock phosphates used (Williams and David 1973). Superphosphate is the most commonly used fertilizer in Australia and nearly 50% of its total Cd content (18–91  $\mu\text{g g}^{-1}$ ) is water-soluble (Mann 1989). The uptake of Cd by plants depends on both soil and plant factors and is influenced by management practices. It has been shown that the Cd content of plants increases with the amount of superphosphate applied (Williams and David 1973) and with a decrease in soil pH (Williams and David 1977; Tiller 1988; Whitten and Ritchie 1991). Since plants take up Cd from the soil solution, any factor that affects its concentration

in solution and the rate of replenishment of the solution concentration (after it has been depleted) will affect the extent of Cd uptake.

Cadmium may exist in the soil in several different forms. When Cd enters the soil it may remain in the soil solution as a free cation or complexed with inorganic or organic ligands (Tills and Alloway 1983), it may adsorb onto exchange sites on clays, hydrous oxides and organic matter (Brown 1954; Sposito and Page 1985) or it may be specifically adsorbed by oxides and hydroxides of Fe, Al and Mn (Tiller *et al.* 1984). Cadmium may be entrapped following diffusion into goethite, Mn oxides and other minerals present in soils (Brummer *et al.* 1988). The reactions of Cd with each soil component will depend upon a number of factors, e.g. soil type, pH, rainfall, temperature, time, management practices and the source of applied Cd. For example, specific adsorption of Cd onto synthetic goethites and onto the edges of clay minerals is pH dependent (e.g. Forbes *et al.* 1976; Tiller *et al.* 1984; Brummer *et al.* 1988). However, understanding the factors that affect the amount of only one possible form of Cd in the soil is not necessarily going to help predict its availability to plants.

The amount of Cd in any one form in the soil could also depend on the extent of saturation of a particular type of site. This could be an important factor for soils which are fertilized regularly with large amounts of Cd-containing, phosphatic fertilizers such as in horticultural enterprises. Saturation of sites that adsorb Cd strongly (and hence are in equilibrium with a low soluble Cd activity) could lead to further added Cd being less strongly adsorbed and hence more readily available for release into the soil solution and subsequent uptake by plants. Therefore, it is important to understand the distribution of Cd into different forms in the soil because each form will have a different ability to release Cd into the soil solution. In turn, we need to understand the relative importance of exterior factors in changing the equilibrium between each solid form and the soil solution.

We studied the effect of pH on the forms of native and added Cd in four West Australian soils which differed in their clay, hydrous oxide and organic matter content. The forms of Cd were extracted sequentially by KCl, BaCl<sub>2</sub>, NaOCl, ammonium oxalate and concentrated acids. The amounts of Cd added were similar to the amounts which would be added over a 20 year period to soils fertilized with low to high rates of superphosphate and which are commonly used in broad-acre agriculture and intensive horticulture. In addition, Cd extracted by EDTA (used as an estimate of labile Cd; Fujii and Corey 1986) was compared with Cd extracted by each solution in the sequential extraction scheme.

The sequential extraction scheme was developed to attempt to distinguish between soluble (KCl), exchangeable (BaCl<sub>2</sub>), organically bound (NaOCl), specifically adsorbed (ammonium oxalate solution) and residual Cd (concentrated acids) which were considered to be the major forms in these non-calcareous soil types which are low in Mn. It is similar to schemes developed for other trace elements by McLaren and Crawford (1973), Tessier *et al.* (1979) and Shuman (1985).

## Materials and Methods

### Soils

Soil was collected from a yellow earth (Soil 1; Northcote classification: Uc1.22; Northcote 1974), lateritic podzolic (Soil 2; Uc5.51), peaty sand (Soil 3; Uc2.33) and siliceous sand

Table 1. Some properties of the soils used

Soil	Northcote classification	Total Cd ( $\mu\text{g g}^{-1}$ )	pH <sup>A</sup>	Org. C (%)	EC ( $\mu\text{S cm}^{-1}$ )	FC <sup>B</sup> (%)	Al <sup>C</sup> ( $\mu\text{g g}^{-1}$ )	Fe <sup>C</sup> ( $\mu\text{g g}^{-1}$ )	Size fraction (%)			Dominant minerals
Yellow earth	Gn 1-22	0.07	5.40	0.31	71	10	84.4	1498	84	2.5	7.8	goethite & kaolinite
Lateritic podzolic	Uc 5.51	0.14	3.74	0.30	372	20	10.0	292	89	0.8	9.9	kaolinite
Peaty sand	Uc 2.33	<0.01	4.04	3.14	35	15	32.6	52	96	1.0	2.5	quartz
Siliceous sand	Uc 2.22	<0.01	5.75	0.12	15	10	6.4	5.5	99	0.4	<0.1	quartz

<sup>A</sup> Soil solution.<sup>B</sup> Field capacity.<sup>C</sup> Acid ammonium oxalate extraction.

Table 2. Detailed sequential extraction scheme used for extraction of forms of Cd from soils

Extraction No.	Forms of Cd	Extractant	Ratio of soil/soln	Procedure
1	soluble	0.005 M KCl	1:5	Shake for 30 min
2	exchangeable	0.1 M BaCl <sub>2</sub>	1:10	Shake residue from (1) for 17 h
3	bound to organic matter	5.3% NaOCl (pH $\approx$ 8.5)	1:2	Residue from (2) placed in water bath at 90°C for 15 min. Repeat two more times agitating in between. Combine the three extracts
4	bound to oxides/clays	0.2 M amm. ox. 0.2 M oxalic acid 0.1 M ascorbic acid (pH $\approx$ 3)	1:40	Residue from (3) shaken in dark for 4 h
5	residual	concentrated HNO <sub>3</sub> /HClO <sub>4</sub> /HF and 6 M HCl acids	—	Transfer residue from (4) to a teflon beaker with double-deionized water washings, dry on hot plate. Add 3 mL HNO <sub>3</sub> and 0.5 mL HClO <sub>4</sub> and heat to dryness. Add 5 mL HF and 0.5 mL HClO <sub>4</sub> , heat to dryness and repeat HF/HClO <sub>4</sub> treatment. Add 5 mL 6 M HCl and 5 mL double-deionized water and heat for 10 min. Make volume to 10 mL with double-deionized water

(Soil 4; Uc 2.22). Soils 1 and 2 were collected from a depth of 25–45 cm whereas soils 3 and 4 were collected from the 0–20 cm layer after removing the vegetation and clearing the debris. The soils were air-dried and ground to pass through a 2 mm sieve. Some properties of the soils are given in Table 1.

#### *Adjustment of Soil Solution pH*

The pH of an aliquot of each soil was adjusted to four different values (4.0, 5.0, 6.0 and 7.0) by adding different concentrations of HCl and KOH in a volume equivalent to the field capacity of each soil and then incubating the soil samples for 1 week at  $40 \pm 1^\circ \text{C}$ . The moisture in the incubated samples was maintained to field capacity throughout the incubation period. The concentrations of HCl and KOH were calculated from the buffer curves (meq  $\text{H}^+$  and  $\text{OH}^-$  per 100 g soil) for each individual soil. Preliminary experiments indicated that the pH after incubation varied by  $\leq \pm 0.1$  unit if this procedure was used. The soils after incubation were centrifuged and the pH of the drained solution was measured.

#### *Addition of Cadmium*

Cadmium was applied as  $\text{Cd}(\text{NO}_3)_2$  at 0, 0.8, 3.2 and  $10.0 \mu\text{g g}^{-1}$  soil in a volume of double-deionized water sufficient to bring 200 g soil to field capacity. Each subsample was incubated at  $40 \pm 1^\circ \text{C}$  for 8 days and then frozen at  $-20 \pm 1^\circ \text{C}$  until analyses were carried out.

#### *Sequential Extraction of Chemical Forms of Cadmium*

Samples to be extracted for different forms of Cd were first thawed to room temperature and were mixed thoroughly. Wet soil, equivalent to 1 g dry soil, was weighed into 50 mL polypropylene centrifuge vials in triplicate. The different forms of Cd were then extracted by the sequential extraction scheme described in Table 2. After each soil sample was shaken with a particular solution, the samples were centrifuged at 2000 rpm and the supernatant was filtered ( $< 0.45 \mu\text{m}$ ) and stored at  $4^\circ \text{C}$  until analysis. The soil residue was washed with double-deionized water before adding the next extracting solution to decrease contamination of Cd in the following extract.

#### *Cadmium Analysis*

Cadmium in all the extracts was analysed by flame atomic absorption spectrophotometry (AAS) on a Perkin–Elmer 5000 atomic absorption spectrophotometer using background correction to eliminate interference from non-atomic absorption.

Cadmium in ammonium oxalate and NaOCl extracts was analysed by using a teflon cup to aspirate the extracts and avoid blockage of the nebulizer (Simmons and Plues-Foster 1977).

Cadmium in KCl,  $\text{BaCl}_2$  and NaOCl extracts which was below the detection limit of the flame was complexed with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into 4-methylpentan-2 one (Syn. methyl isobutyl ketone, MIBK) according to the method of Dudas (1974) in order to eliminate potential matrix effects during analysis. The MIBK extract was then analysed for Cd by furnace AAS using pyrolytically coated platform fitted graphite tubes in a Perkin–Elmer HGA 500 graphite furnace coupled to a Perkin–Elmer 5000 with background correction. The temperature program used for the determination of Cd is given in Table 3.

**Table 3. Temperature program for Cd determination by graphite furnace**

Step No.	Furnace temperature ( $^\circ \text{C}$ )	Ramp	Time Hold (s)	Internal argon gas flow ( $\text{mL min}^{-1}$ )
1	70	1	22	300
2	130	1	10	300
3	400	1	20	300
4	1500	0	5	100
5	2000	1	4	300

Cadmium in ammonium oxalate and acid digested extracts which was below the detection limit of flame AAS was complexed with 40% potassium iodide (KI) and then extracted into MIBK (Aziz-AlRahman *et al.* 1983). The Cd in the MIBK extract was determined using furnace AAS as described above.

#### *Soil Analysis*

All laboratory ware used was cleaned in 0.1 M Na<sub>2</sub>EDTA and 1 M HCl. Solutions of KCl, BaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> were prepared from stock solutions which had been earlier purified with dithiozone extracted in chloroform to remove any trace amounts of Cd (Hewitt 1952). All other solutions were prepared from AR grade reagents.

Total Cd in each soil was estimated by digestion with HNO<sub>3</sub>/HClO<sub>4</sub>/HF/6 M HCl concentrated acids (Elliott and Shields 1988). Soils 1–3 were also extracted by a mixture of 0.005 M EDTA and 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> (Fujii and Corey 1986). Organic carbon was determined by the method of Yeomans and Bremner (1988). The pH was measured in soil solutions extracted by the method of Gillman and Bell (1978). Iron and aluminium (Al) extracted by ammonium oxalate were determined by flame AAS (Searle and Daly 1977). Iron and Al in residual (Table 2) and total digests (HNO<sub>3</sub>/HClO<sub>4</sub>/HF/6 M HCl concentrated acids) were also analysed by flame AAS.

#### **Results**

In all the soils, pH had a marked effect on the amount and percentage of Cd (%Cd) in each form at all the rates of Cd application except when no Cd was applied. The %Cd is the amount of Cd in each form expressed as a percentage of the sum of amounts of Cd extracted by each solution in the sequential scheme.

#### *Forms of Native Cd*

No Cd was extracted from soils 1 and 2 by any of the solutions in the sequential extraction scheme, except by the concentrated acid extraction, i.e. 0.07 and 0.14  $\mu\text{g g}^{-1}$  respectively (data not shown). No Cd was extractable from soils 3 and 4 in any form.

#### *Forms of Added Cd*

The amount of Cd in the KCl extracts decreased exponentially in all the soils with increasing soil solution pH, except soil 3 where it increased linearly with pH (Fig. 1). The rate of decrease for soils 1, 2 and 4 between pH 4 and 6 was greater at higher additions of Cd and was in the order of the soils 1 > 2 > 4 (Figs 1a, 1b and 1d). In soil 3, the rate of increase was greater at the higher rates of Cd application (Fig. 1c).

The variation in the BaCl<sub>2</sub>-extractable Cd with pH depended upon the soil type (Fig. 2). At a constant rate of Cd addition and pH, the amount of Cd in this form was in the order of soil 2 > soil 3 > soil 4 > soil 1 up to pH 5 and at pH 7 the order changed to soil 4 > soil 2 > soil 3 > soil 1. There was approximately twice as much Cd in this form in soil 2 than in soil 1. For both soils, Cd-BaCl<sub>2</sub> increased with pH up to 5 and then decreased. The curvature of the line increased with application rate of Cd (Figs 2a and 2b). In soil 3, Cd-BaCl<sub>2</sub> decreased linearly with pH at all the rates of Cd application (Fig. 2c). In soil 4, Cd-BaCl<sub>2</sub> increased asymptotically except when 0.8  $\mu\text{g g}^{-1}$  Cd was added (Fig. 2d).

Cadmium extracted by NaOCl from soils 1, 2 and 4 represented only a small fraction of the total Cd at all pH values, whereas in soil 3 this fraction represented

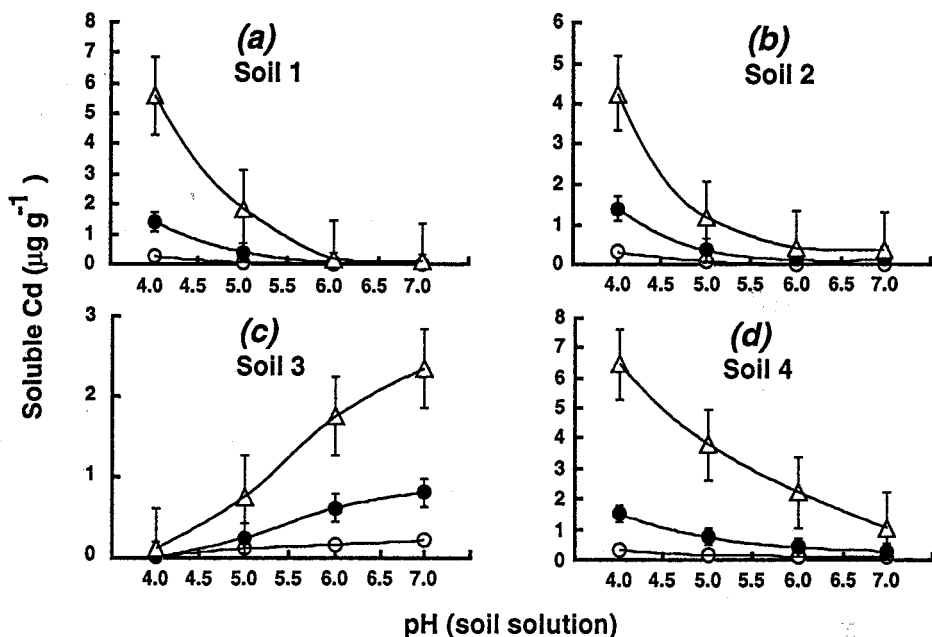


Fig. 1. The relationship between soil solution pH and soluble Cd at application rates of 0.8 (○), 3.2 (●) and 10  $\mu\text{g Cd g}^{-1}$  ( $\Delta$ ) in (a) soil 1, (b) soil 2, (c) soil 3 and (d) soil 4. The vertical bar denotes the standard error.

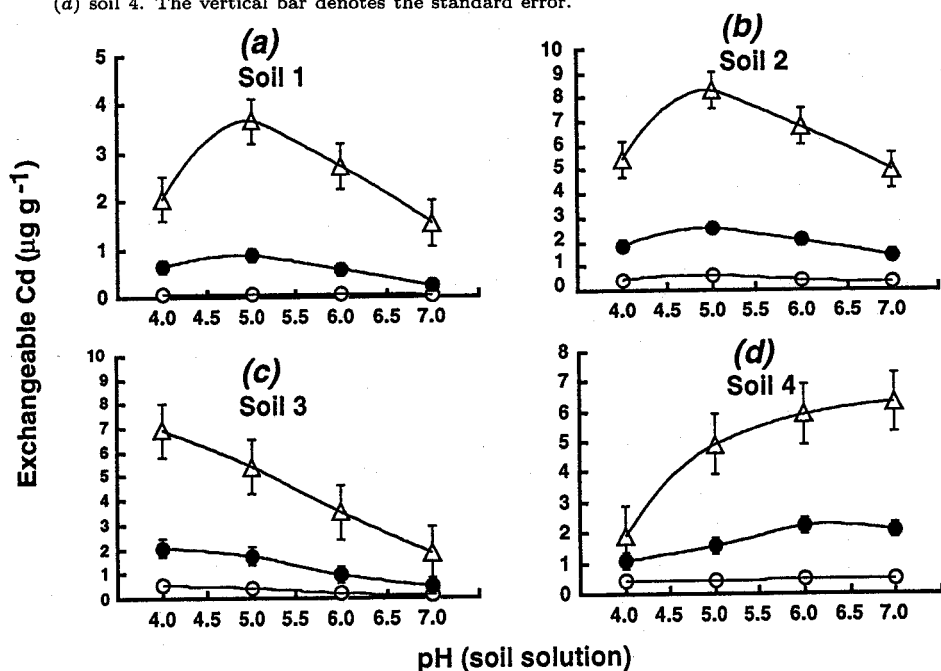


Fig. 2. The relationship between soil solution pH and exchangeable Cd at application rates of 0.8 (○), 3.2 (●) and 10  $\mu\text{g Cd g}^{-1}$  ( $\Delta$ ) in (a) soil 1, (b) soil 2, (c) soil 3 and (d) soil 4. The vertical bar denotes the standard error.

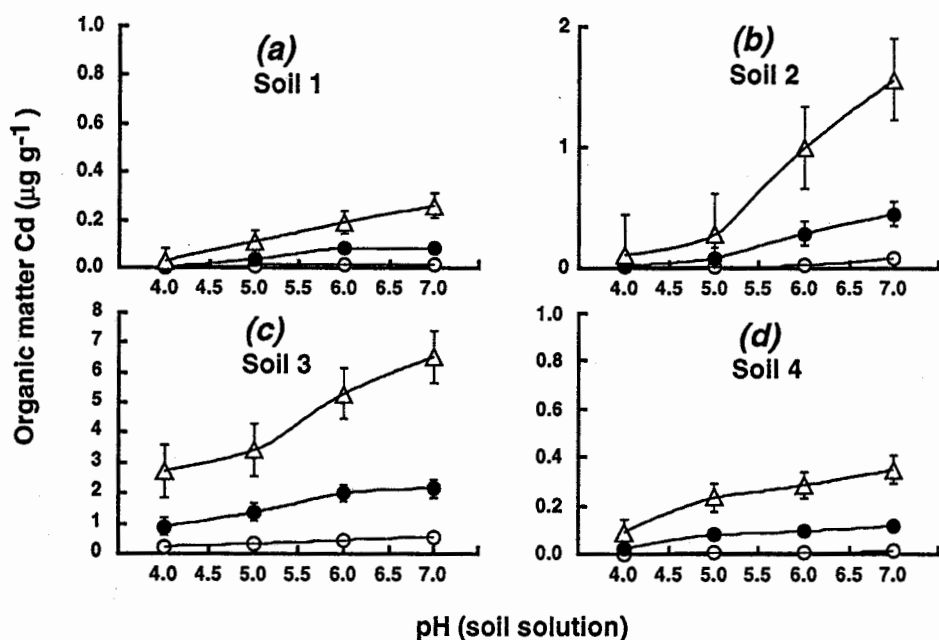


Fig. 3. The relationship between soil solution pH and Cd bound to organic matter at application rates of 0.8 ( $\circ$ ), 3.2 ( $\bullet$ ) and 10  $\mu\text{g Cd g}^{-1}$  ( $\triangle$ ) in (a) soil 1, (b) soil 2, (c) soil 3, and (d) soil 4. The vertical bar denotes the standard error.

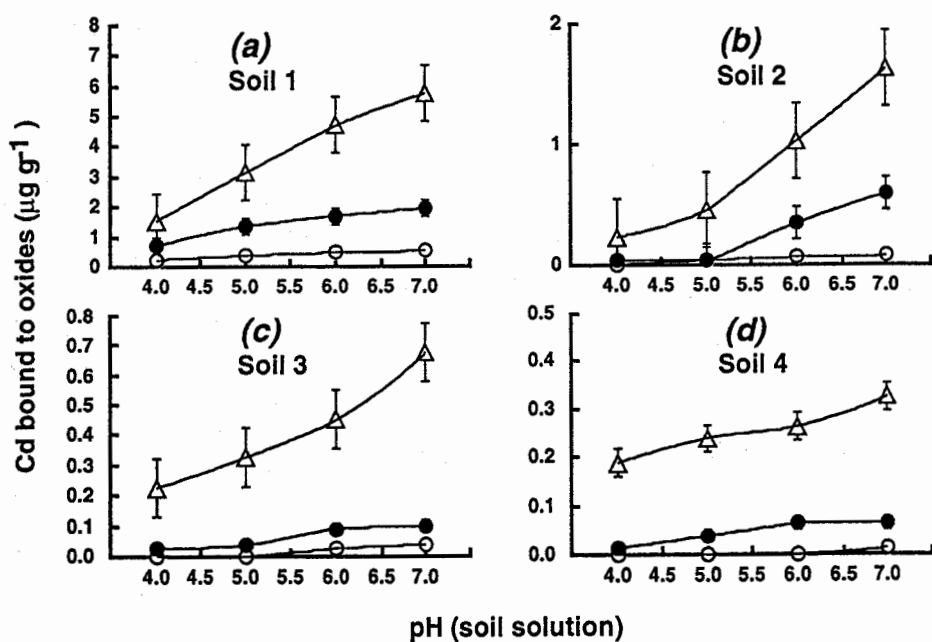


Fig. 4. The relationship between soil solution pH and Cd bound to oxides/clays at application rates of 0.8 ( $\circ$ ), 3.2 ( $\bullet$ ) and 10  $\mu\text{g Cd g}^{-1}$  ( $\triangle$ ) in (a) soil 1, (b) soil 2, (c) soil 3 and (d) soil 4. The vertical bar denotes the standard error.

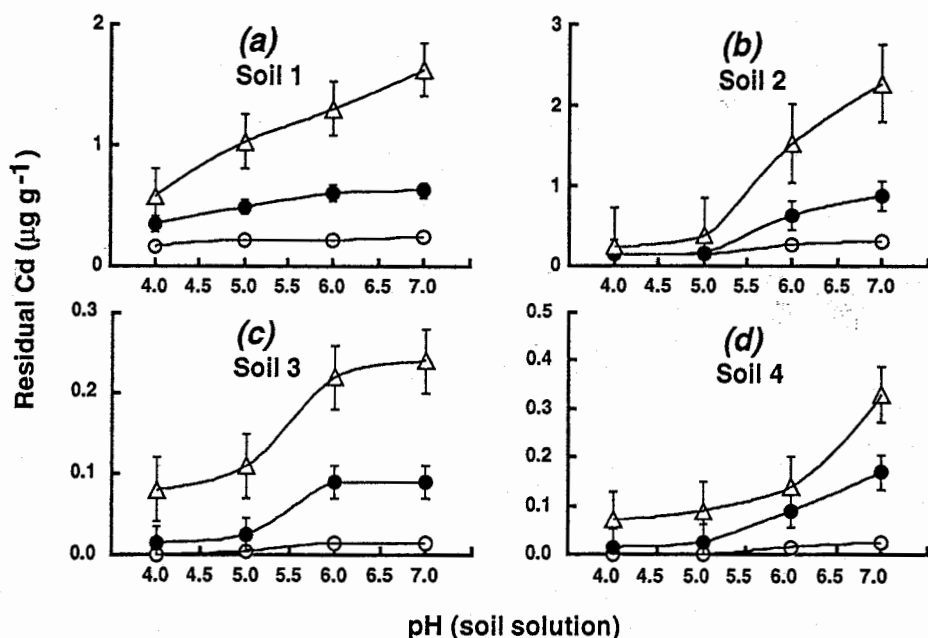


Fig. 5. The relationship between soil solution pH and residual Cd at application rates of 0.8 (○), 3.2 (●) and 10  $\mu\text{g Cd g}^{-1}$  (Δ) in (a) soil 1, (b) soil 2, (c) soil 3 and (d) soil 4. The vertical bar denotes the standard error.

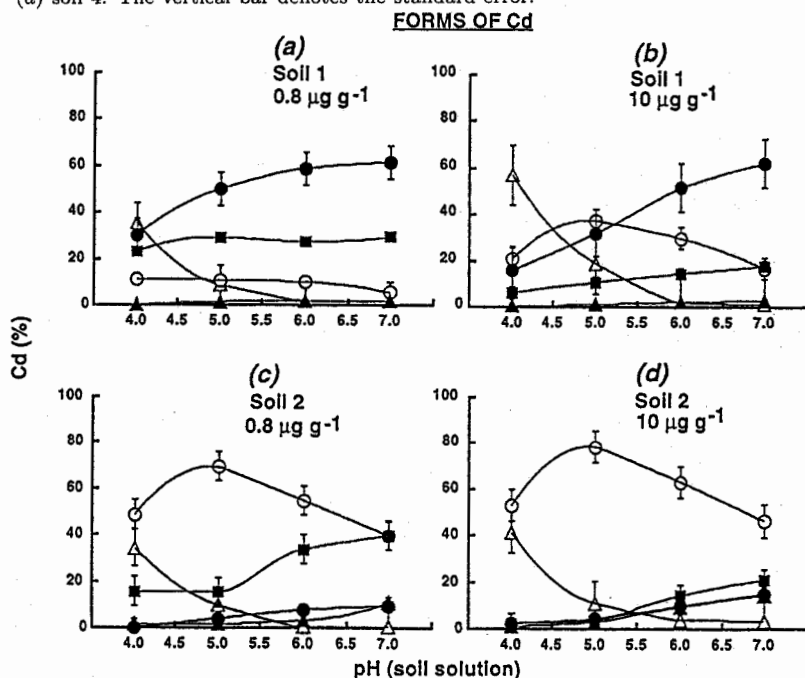


Fig. 6. Effect of soil solution pH in soil 1 at Cd application rates of (a) 0.8  $\mu\text{g g}^{-1}$  and (b) 10  $\mu\text{g g}^{-1}$ , and in soil 2 at (c) 0.8  $\mu\text{g g}^{-1}$  and (d) 10  $\mu\text{g g}^{-1}$  on % soluble Cd (Δ), % exchangeable Cd (○), %Cd bound to organic matter (▲), %Cd bound to oxides/clays (●) and %Cd in the residual form (■).



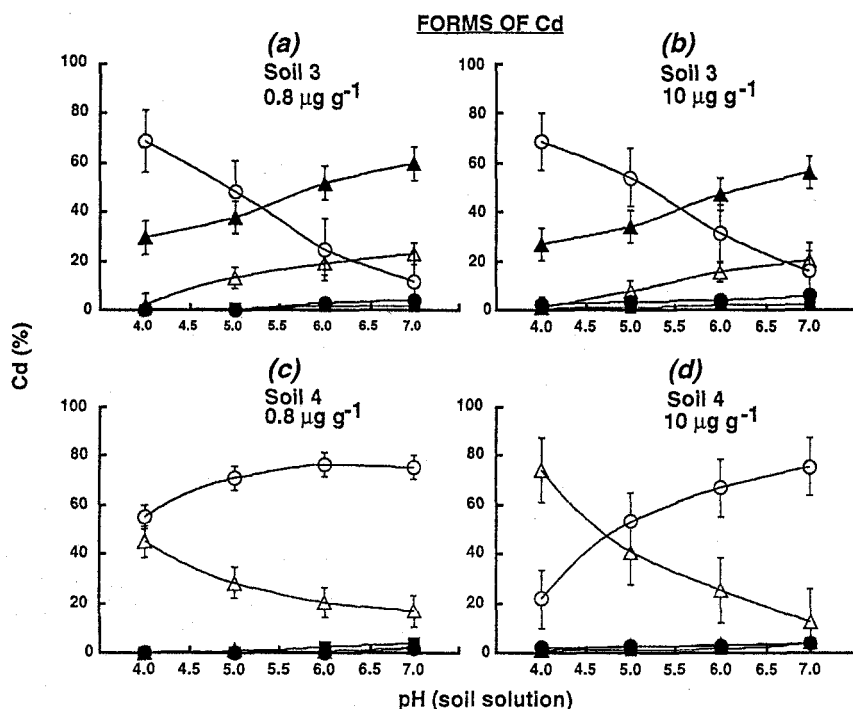


Fig. 7. Effect of soil solution pH in soil 3 at Cd application rates of (a)  $0.8 \mu\text{g g}^{-1}$  and (b)  $10 \mu\text{g g}^{-1}$ , and in soil 4 (c) at  $0.8 \mu\text{g g}^{-1}$  and (d)  $10 \mu\text{g g}^{-1}$  on % soluble Cd ( $\Delta$ ), % exchangeable Cd ( $\circ$ ), %Cd bound to organic matter ( $\blacktriangle$ ), %Cd bound to oxides/clays ( $\bullet$ ) and %Cd in the residual form ( $\blacksquare$ ).

the majority of total Cd at all pH values, (Fig. 3). The amount of Cd-NaOCl increased with increase in pH and with rate of Cd addition and was in the order soil 3  $\gg$  soil 2  $\gg$  soil 1  $\approx$  soil 4.

The amount of Cd extracted by ammonium oxalate (AO) from each soil increased with increase in pH and with the rate of Cd application (Fig. 4). The rate of increase was in the order soil 1  $\gg$  soil 2  $>$  soil 3  $>$  soil 4. The slope of the increase in the amount of AO-extractable Cd with pH increased with increasing rate of Cd addition in all the soils.

The amounts of acid-extractable Cd increased with pH and with rate of Cd application in all four soils and were in the order soil 2  $>$  soil 1  $>$  soil 4  $>$  soil 3 (Fig. 5).

The %Cd extracted by KCl (%Cd-KCl) in soils 1, 2 and 4 decreased exponentially with pH and was similar for all the rates of Cd addition (Fig. 6 and 7). In soil 3, the %Cd-KCl increased linearly with pH from 0–20% at all rates of Cd addition (Fig. 7a and 7b). The % Cd-KCl at pH 4 was highest (75%) in soil 4 and lowest ( $<2\%$ ) in soil 3 at all the rates of Cd application. The largest decrease (30–40%) was observed between pH 4 and 5 in soils 1, 2 and 4. The fraction decreased from approximately 50% to almost zero in soils 1 and 2 when the pH increased from 4 to 6 and no further change was observed between pH 6 and 7.

At the  $10 \mu\text{g g}^{-1}$  Cd rate in soil 4, however, the fraction was 75% at pH 4 and continuously decreased with increase in pH to 15% at pH 7 (Figs 7c and 7d).

The variation in %Cd extracted by  $\text{BaCl}_2$  (% Cd- $\text{BaCl}_2$ ) with pH for soils 1, 2 and 4 was similar to the amounts of Cd- $\text{BaCl}_2$  except that %Cd- $\text{BaCl}_2$  in soil 2 was more or less independent of the Cd application rate (Figs 6c and 6d). In soil 3, %Cd- $\text{BaCl}_2$  decreased with increase in pH and was independent of the application rate (Figs 7a and 7b).

In soils 1 and 4, the variation in %Cd extracted by  $\text{NaOCl}$  (%Cd- $\text{NaOCl}$ ) with pH and rate of Cd addition was inconsistent. The values were <4% of the total Cd extracted by the sequential scheme and hence were considered to be negligible (data not shown). In soils 2 and 3, the %Cd- $\text{NaOCl}$  increased by approximately 12% and 30% respectively with increase in pH from 4 to 7 (Figs 6c and 6d; Figs 7a and 7b).

The %Cd extracted by ammonium oxalate (%Cd-AO) in all the soils increased with increase in pH and was in the order soil 1  $\gg$  soil 2 > soil 3 > soil 4 (Figs 6 and 7). In soil 1, at a constant pH, the %Cd-AO tended to decrease as the rate of Cd application increased. The increase in %Cd-AO in soil 2 with increase in pH from 4 to 7 was almost similar ( $\approx 15\%$ ) at  $3.2$  and  $10.0 \mu\text{g g}^{-1}$  Cd rates, whereas at  $0.8 \mu\text{g g}^{-1}$  this fraction increased by <10%. In soils 3 and 4, the %Cd-AO was almost negligible (<2%) at pH 4 at all the rates of Cd application and, even with an increase in pH from 4 to 7, the fraction increased by <5% (Fig. 7).

The %Cd extracted by acids (%Cd-acid) increased with increase in pH in the four soils and the trend was more or less similar to the amounts of acid-extractable Cd (Figs 6 and 7). The highest amount of %Cd-acid (40%) was found in soil 2 at pH 7 where  $0.8 \mu\text{g g}^{-1}$  of Cd was applied (Fig. 6c). In soil 1, %Cd-acid increased from 5–15% with increase in pH from 4 to 7 at the  $10 \mu\text{g g}^{-1}$  Cd application rate; however, at the lower rate ( $0.8 \mu\text{g g}^{-1}$ ) of Cd application, it remained almost constant ( $\approx 22\%$ ) at all the pH values (Figs 6a and 6b). In soils 3 and 4, %Cd-acid was a small fraction (<6%) and increased slightly with increase in pH; however, it varied inconsistently with rate of Cd addition (Figs 7a–d).

#### *Extraction of Cd with EDTA/ $\text{Ca}(\text{NO}_3)_2$ and its Relationship with the Forms of Cd*

Cadmium extracted by EDTA from soils 1, 2 and 3 did not correlate well with any of the individual amounts of Cd extracted by  $\text{KCl}$ ,  $\text{BaCl}_2$ ,  $\text{NaOCl}$ , AO and the acid digests at any of the pH values and at any of the rates when extracted sequentially. However, Cd-EDTA correlated well with total Cd (extraction by  $\text{HNO}_3/\text{HClO}_4/\text{HF}/6\text{M HCl}$  concentrated acids) and the sum of Cd extracted by  $\text{KCl}$ ,  $\text{BaCl}_2$  and ammonium oxalate ( $r^2 > 0.90$ ). The sum of the Cd extracted by the above three extractants also correlated well with the total Cd in the four soils ( $r^2 > 0.98$ ).

#### **Discussion**

The forms of added Cd after incubation with each soil depended on pH, mineralogy, organic matter and the application rate of Cd.

The major adsorption surface differed between soils and varied with pH for a particular soil. The extent of retention depended on the amount of adsorbing surface and pH. In the siliceous sand, Cd was mainly present as the soluble (KCl) and the exchangeable ( $\text{BaCl}_2$ ) forms because of the lack of soil components with adsorption sites. In the peaty sand, organic matter was the main adsorbing surface present and hence the majority of Cd was extracted by NaOCl and  $\text{BaCl}_2$ . Cadmium extracted by NaOCl would have removed Cd from organic adsorption sites, whereas  $\text{BaCl}_2$  may have extracted exchangeable Cd from both organic and inorganic exchange sites. In the yellow earth, Cd bound to oxides or specifically adsorbed Cd was the dominant form, whereas exchangeable Cd was more prevalent in the lateritic podzolic.

Increasing pH tended to increase the number of exchange and specifically adsorbed sites as well as organic sites. However, the amount and %Cd in these forms only increased with pH if it was the major form in a particular soil or there were sufficient sites onto which Cd could adsorb.

The rate of application of Cd affected the amount of Cd in a particular form when the number of adsorption sites on the main adsorption component became limiting. The excess Cd not adsorbed by the main adsorption component was then retained by another form. For example, when exchangeable sites in the siliceous sand were saturated, %Cd-KCl increased because it was the only other significant form of Cd in that soil. In contrast, when the sites on oxide surfaces became limiting in the yellow earth, the excess Cd was adsorbed at exchange sites.

In the siliceous sand, most of the Cd (>95%) is present in the soluble (%Cd-KCl) and the exchangeable form (%Cd- $\text{BaCl}_2$ ) and the proportion in both forms varied with pH and amount of Cd applied (Figs 7c and 7d). At pH 4, the %Cd that was soluble increased with the amount of Cd applied, presumably because there were no more exchange sites available for adsorption of additional Cd. As pH increased, a greater proportion of Cd was in the exchangeable form due to a concurrent increase in the number of exchange sites with pH. The increase was not as great as that observed by Christensen (1984) who found that Cd adsorption increased by a factor of 3 per pH unit in sandy soils when pH increased from 4 to 7.7. Williams and David (1973) found that >50% of the total Cd in seven yellow podzolic soils (Dy 3.42) was in the exchangeable form but they did not report pH values. The %Cd in the exchangeable fraction at higher pH did not decrease with increase in rate of Cd application because there were more sites available for exchange (Figs 7c and 7d). Cadmium bound to organic matter (%Cd-NaOCl), Fe/Al oxides (%Cd-AO) and that in the residual form (%Cd-acid) was <4% at all the pH values, as may be expected from soils low in organic matter, clay and hydrous oxide content (Table 1).

In the peaty sand, exchangeable Cd and that bound to organic matter were the major forms present. The relative importance depended upon pH and Cd application rate. As pH increased, more organic sites were formed at which Cd was preferentially adsorbed. The organic sites apparently had a higher affinity for Cd than the exchangeable sites. However, as the Cd application rate increased, the number of organic sites per mole of Cd decreased to the extent that some Cd remained in the exchangeable form due to a lack of high affinity organic sites. Hence, the pH at which there was an equal percentage of Cd present as organic

and exchangeable forms rose as the application rate of Cd increased (Figs 7a and 7b). Increases in Cd bound to organic matter as soil pH is increased have been observed previously (Levi-Minzi *et al.* 1976; McBride *et al.* 1981; Gerritse *et al.* 1982).

In the peaty sand at pH <5, the presence of organic matter lowered the amount of Cd-KCl in comparison with that in the siliceous sand. Decreases in Cd mobility under acidic conditions have been shown in the presence of organic matter (Tyler and McBride 1982). Tiller (1988) also suggested that organic matter-rich surfaces had a high Cd affinity at pH values <6. At pH >5, however, an increase in the soluble form of Cd with increase in pH was observed. An increasingly brown coloration of the KCl extract as the pH rose suggested that the dissolution of organic material complexed with Cd could have been occurring. This phenomenon has been observed for Cd in acid soils amended with sodium hydroxide (Kuo and Baker 1980). Cadmium bound to Fe/Al oxides or that in the residual fraction was <4% of total Cd at all pH values and at all the rates of Cd application, as would be expected for soils low in hydrous oxides and clay with a sandy texture (Table 1).

In the yellow earth soil, Cd bound to hydrous oxides was the major form except when the pH was low ( $\leq 6$ ) and the application rate was high ( $10 \mu\text{g g}^{-1}$ , Fig. 6b). In the latter situation, the presence of a small number of sites available for Cd adsorption onto hydrous oxides would have limited the %Cd that could be adsorbed. At pH 4, most of the excess Cd stayed in the soluble form whereas at pH 5 the majority was adsorbed at exchange sites, presumably because of the development of pH-dependent negative sites. As pH increased, an appreciable increase in Cd bound to hydrous oxides occurred even at the higher rates of Cd application, suggesting a further increase in the number of negative sites for specific adsorption. On the other hand, exchangeable Cd reached a maximum at pH 5 and, with further increase in pH, this fraction started to decline, possibly because the higher strength of Cd bonding with oxides favoured specific adsorption of Cd at the expense of exchangeable Cd held by less strength, i.e. coulombic attraction (Tiller 1988). Goethite and kaolinite are the major adsorbing surfaces in this soil (Table 1). The general predominance of specifically adsorbed (Cd-AO) over exchangeable (Cd-BaCl<sub>2</sub>) suggests that the Fe oxide may have been present predominantly as a coating on the kaolinite. Increases in Cd adsorption with increase in pH have been observed by several researchers for soils (Garcia-Miragaya and Page 1977; Jarvis and Jones 1980), clays (Farrah and Pickering 1977), and for goethite (Tiller *et al.* 1984). The increase in residual Cd with application rates at all pH values suggests the occlusion of Cd or its diffusion into less accessible sites from which Cd is not displaced by AO or BaCl<sub>2</sub>.

Exchangeable Cd was the major form of Cd in the lateritic podzolic soil, as may be expected for a soil with kaolinite as the major clay and negligible amounts of hydrous oxides (Table 1). The proportion in the exchangeable form depended mainly on pH, whereas the application rate of Cd had a minimal effect, presumably because there was an excess of exchange sites. At each application rate, exchangeable Cd reached a maximum at pH 5 and then declined with further increase in pH. The decrease in exchangeable Cd at pH >5 could not be explained by a limited number of exchange sites because the %Cd in this form was independent of application rate. The observed decrease in exchangeable Cd

at higher pH values coincided with an increase in residual Cd, possibly indicating that, at higher pH values, some exchange sites are less accessible than others and the Cd adsorbed at such sites is only displaced by an acid extraction. In addition, there was a small but concurrent increase in specifically bound Cd (%Cd-AO) which could indicate the formation of some variable charge negative sites on the edges of kaolinite crystals at high pH values. Organically bound Cd also increased at high pH values, which may have been due to, not only an increase in negative sites, but also an increase in bonding energy.

In the sequential extraction of native Cd from the yellow earth and lateritic podzolic soils, most of the Cd (irrespective of pH) was extracted by acid digestion ( $0.07$  and  $0.14 \mu\text{g g}^{-1}$ , respectively). This suggests that strong binding of Cd to oxides and clays or the occlusion/entrapment of Cd into the layer lattices of oxides and or kaolinite had occurred. Hence, in both soils, the possibility of Cd uptake by plants was decreased. This finding was in complete contrast to the sequential extraction of added Cd. A possible explanation could be that, with time, Cd diffused into the mineral layer lattices of the oxides and or the clays (Brummer *et al.* 1988). Alternatively, the native Cd was originally present in the lattice during formation of the mineral.

#### *Implications for Cd Accumulation in Readily Leachable or Available Forms*

Soluble and exchangeable forms of Cd are considered to be the most labile and available pools for leaching and uptake by plants (Harrison *et al.* 1981; Soon and Bates 1982; Hickey and Kittrick 1984). Hence, the amount of Cd in these forms will be indicative of the potential for Cd accumulation in plants or for Cd contamination of ground waters via leaching. At pH 4, the risk of Cd pollution from these soils is in the order siliceous sand > lateritic podzolic > yellow earth > peaty sand at all rates of Cd application (Figs 6 and 7). However, at pH 7, the risk of Cd pollution from these soils was similar, with the exception that risk from the peaty sand was greater than that from the yellow earth. The results suggest that, at lower pH values, soils with appreciable organic matter would retain more Cd in forms that are unavailable or unleachable in comparison to soils with low organic matter. However, at higher pH values, soils with oxides would contribute more to Cd retention.

In many cases, fertilizers containing Cd as a contaminant are applied to the surface layers of a soil which usually have the highest organic matter content. Hence, it would be expected that the organic matter would adsorb Cd until all the sites were saturated. Any excess Cd would be in the exchangeable or soluble form and thereby be prone to leaching or uptake by plants. In situations where Cd leaches down the soil profile, it may intercept hydrous oxides or clays in subsurface layers and hence could become adsorbed. The amount of Cd adsorbed and that left in more soluble forms will again depend upon the pH of the soil, and the rate at which Cd was applied. However, when we compare the yellow earth and lateritic podzolic soils which contained the same amount of organic matter (Table 1), no Cd was adsorbed onto the organic matter in the yellow earth at any pH value, whereas in the lateritic podzolic, 15–20% of the Cd was adsorbed onto the organic matter at pH 7. This suggests that, when the number of sites on oxides are appreciable, Cd could be preferentially adsorbed by hydrous oxides at the expense of adsorption onto organic matter. In the lateritic podzolic

soil, however, the sites on kaolinite apparently could not compete so effectively with organic matter for Cd (even when present in excess). Alternatively, the kaolinite was partially coated with organic matter so fewer inorganic adsorption sites were available for Cd adsorption.

Uptake of Cd by plants has been shown to increase with a decrease in pH (Williams and David 1977; Whitten and Ritchie 1991). Considering the original soil pH (soil solution) of the siliceous sand (6.0), peaty sand (4.0), lateritic podzolic soil (3.7) and yellow earth (5.4), nearly 90, 70, 80 and 25% of the total Cd applied would be in the soluble and exchangeable forms and be of concern in terms of causing accumulation of Cd in the food chain or contaminating underground water. The estimates decrease to approximately 55, 0, 35 and 10% (respectively) if we assume that only soluble Cd is available to plants. However, the actual concentration of Cd in the soil solution alone cannot account for the amounts taken up by plants. Continuous depletion of Cd from the soil solution will result in its replenishment from solid phase sources in order to maintain equilibrium and would result in higher concentrations of Cd in plants than those that could be attributable to uptake from the soil solution alone (Hardiman *et al.* 1984). The replenishment of Cd in the soil solution of the yellow earth and lateritic podzolic soils may be limited to a certain extent by strong surface reactions, but in the peaty sand, organically bound Cd probably replenishes Cd in the soil solution more quickly (Gibson and Farmer 1986).

The amount of added Cd extracted by EDTA, when compared with total Cd and the forms of Cd extracted by the sequential extraction scheme from all of these soils, indicated that EDTA not only extracts Cd from the soluble and the exchangeable forms but also extracts Cd from the strongly adsorbed pool. Therefore, EDTA (which is commonly used in soil testing procedures for extracting micronutrients that are available to plants) may be more indicative of the total Cd in soils rather than of the available or the mobile forms of Cd. EDTA has a strong chelating ability and has been used to solubilize poorly crystalline Fe oxides and their associated trace metals (Borggaard 1979).

Sequential extraction has limitations because solutions used for extracting particular forms of Cd may also partially extract Cd from some other pool. The sequential scheme used in this work appears to have been reasonably selective and has provided a guide to the potential for Cd to be in a form readily taken up by plants or to be lost by leaching.

## Conclusions

A decrease in pH or the amount of adsorption components in the soil favoured Cd occurring in forms that were more soluble or absorbable by plants. However, the effect of pH on the forms of Cd differed among the soils studied because the nature of the adsorbing component (oxides, clays and organic matter) changed.

The forms of Cd were also influenced by the rate of Cd application. At lower rates, Cd was present as less soluble forms in soils dominated by oxides and the clays, whereas in siliceous and peaty sands, the Cd rate had no significant effect on the forms of Cd. Thus, Cd would be more available to plants when it was applied at higher rates to soils dominated by oxides or clays and equally available in sandy soils and soils with organic matter at all the application rates. However, these generalizations can only be made for the application rates used in this study.

This work has shown that the form of added Cd in a soil cannot be elucidated from considering the major adsorbing component alone. It is also necessary to know the pH, the presence of other adsorbing surfaces and the rates of applied Cd.

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