

Long-Term Changes in Cadmium Bioavailability in Soil

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A study was conducted to examine changes in total and phytoavailable Cd in a soil that had received inputs of Cd due to fertilization with single superphosphate (SSP) at various rates since 1948. Accumulation of Cd in the soil was highly correlated to the application rate of SSP. No evidence was found to indicate offsite movement of Cd, either through horizontal transfer or via leaching through the profile. Increases in soil Cd led to an increase in the Cd content of wheat that was grown in the soil. However, using a radioisotope dilution technique, a significant proportion of the added Cd was found to exist in a non-bioavailable pool in the soil. A model was developed which estimated that Cd was being fixed in this soil at a rate of 1–1.5% of the total added Cd per year.

Introduction

Applications of phosphate fertilizers, which contain Cd as an impurity, are largely responsible for the increasing Cd load in agricultural soils worldwide (1). The long-term sustainability of this practice is limited by the strict maximum permissible concentrations (MPC) of Cd allowed in crops for human consumption [e.g., 0.1 mg kg⁻¹ for staple crops in Australia (2)]. While total concentrations of Cd are steadily increasing in soils, it is unknown whether this will lead to a proportionate increase in concentrations of Cd in crops as total concentrations of Cd in soils are often a poor indicator of Cd phytoavailability (3, 4).

One factor that may reduce Cd phytoavailability is fixation of Cd in soil pools that are inaccessible to plants. Significant reductions in the long-term plant availability of Zn, a metal considered to have similar chemical behavior in soils to Cd, are recognized (5). The mechanisms responsible for declines in Zn availability have not been conclusively established but may involve migration into micropores (6) or movement of Zn into the soil matrix through other solid-phase diffusion processes (7). Soil aging has also been demonstrated to lead to increased Cd sorption to soils (8–10), but the direct effect of this on Cd phytoavailability was not ascertained in these studies. The aim of this study was to determine whether the phytoavailability of Cd can decline with time due to fixation of Cd in the soil.

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Materials and Methods

Soil. Soil (clay loam, Plinthic Paleustalf) from experimental field plots at Armidale NSW [Upper Kirwans Sites (11)] was sampled in 1995 to a depth of 10 cm using a stainless steel auger. The plots have received different application rates of single superphosphate (SSP) since 1948, and hence soil from the plots was expected to contain different concentrations of Cd. Specifically, plots used in the current experiment had annual applications equivalent to 62.5, 125, and 250 kg of SSP/ha. In 1975 the plots were split such that fertilizer applications were terminated on one half [rundown (R) plots] while the same application rates of fertilizers were maintained on the other half of each plot until the present time [continuous (C) plots]. Pasture species are established on the plots that have also been individually grazed by sheep since 1952 (12). The air-dried soil was sieved to less than 2 mm using a stainless steel sieve. The sieved soil was spiked with a solution of carrier-free ¹⁰⁹Cd to give a final mean soil activity of 245 (SD = 21) kBq/kg and thoroughly mixed. Moist soil (equivalent to 240 g dry weight) was then placed into acid-washed plastic pots and the moisture content increased to 50% of the water holding capacity. The pots were covered and left to incubate in the dark in a controlled environment growth chamber (15/20 °C, 8/16 h) for 2 weeks until seeds were sown. Three replicates of the R and C soils receiving 62.5 or 250 kg of SSP/ha were potted, and six replicates of the intermediate (125 kg/ha) SSP treatments were potted. Samples of soil (0.25 g) from each of the treatments were digested in hot concentrated HNO₃/HClO₄ (3:1, v/v), and Cd concentrations were determined as described below.

Plants. Seeds of wheat (*Triticum turgidum* cv. Yallaroi) were sown in the spiked soil and thinned following seedling development to remove late germinating or unhealthy seedlings. Plants were grown in a controlled environment growth chamber (15/20 °C, 8 h dark/16 h light). The moisture content was maintained at 50% of the water holding capacity by watering to weight daily with deionized H₂O. The amount of water lost through transpiration was calculated by deducting the amount lost by evaporation (measured by weighing two unplanted control pots of soil) from the daily weight loss of the planted pots. Nutrients (AR grade) were provided in the water replenishing that lost through transpiration. The nutrients added in this solution were KNO₃ (6.5 mM), NH₄NO₃ (7.5 mM), MgSO₄ (2 mM), and KH₂PO₄ (0.2 mM).

Plant shoots were harvested 28 days after sowing, at which time there was sufficient material for analysis. Plants were rinsed in deionized H₂O and then dried at 80 °C for 16 h, the dry weights were recorded, and the plants were then ground using an agate mortar and pestle. Samples of ground plant material (0.5–1 g) were then digested in hot, concentrated HNO₃ (5 mL).

Analyses. Following acid digestion, plant and soil samples were made up to 20 mL using acidified, deionized H₂O and stored at 4 °C until analysis. Inclusion of plant and soil certified reference material with each of the digests ensured reliability of the final results. The Cd concentrations in the digest solutions were determined using a graphite furnace atomic absorption spectrophotometer (GFAAS) with deuterium background correction and orthophosphoric acid as a modifier. The activity of ¹⁰⁹Cd soil and plant digests was assessed by γ-spectroscopy.

Labile Cd. The amount of soil Cd available for uptake by the plants (labile Cd) (L) was calculated according to the

TABLE 1. Influence of the Application Rate of Single Super Phosphate on Cd Content in Soils and Yields of Wheat Shoots

plot	total soil Cd ^a (mg kg ⁻¹)	increase in soil Cd (mg kg ⁻¹ yr ⁻¹)	shoot dry weight ^a (g)
nil SSP	0.026 (0.008)	nil	
62.5 R	0.070 (0.006)	0.0016	0.061 (0.003)
62.5 C	0.115 (0.003)	0.0019	0.084 (0.006)
125 R	0.147 (0.005)	0.0045	0.081 (0.006)
125 C	0.198 (0.005)	0.0037	0.149 (0.009)
250 R	0.195 (0.002)	0.0063	0.097 (0.009)
250 C	0.339 (0.014)	0.0067	0.179 (0.012)

^a SE in parentheses.

method of Larsen (13) as follows:

$$\% L = [\text{specific activity of Cd}_{\text{soil}} (\text{Bq}/\mu\text{g}) / \text{specific activity of Cd}_{\text{plant}} (\text{Bq}/\mu\text{g})] \times 100 \quad (1)$$

This approach assumes that the added ¹⁰⁹Cd equilibrates with the immediately phytoavailable Cd in the soil, which in soils with pH < 7 is composed primarily of aqueous and easily exchangeable forms of the metal (14). Hence, the radioisotope is diluted by the phytoavailable unlabeled soil Cd with the end result being the larger the phytoavailable pool of soil Cd, the lower the specific activity of Cd in the plant with respect to the specific activity of Cd in the spiked soil. The method also requires that the contribution of seed Cd to the final total plant concentration of Cd be minimal. In the present experiment, Cd in the seed contributed less than 5% to the total amount of Cd taken up by the plant.

Results and Discussion

Soils. Application of superphosphate at different rates appeared to have no effect on soil pH with the mean value (\pm SE) for all the plots found to be 5.95 ± 0.08 .

The total cadmium concentration of soils from the R and C series ranged from 0.05 to 0.20 and from 0.10 to 0.35 mg of Cd (kg of soil)⁻¹, respectively (Table 1). A nominal background concentration of Cd of 0.026 mg kg⁻¹ was determined in soil collected adjacent to the plots that had not received any direct inputs of phosphatic fertilizer. When this background concentration was subtracted from the total Cd concentration in soil from each of the plots, a linear correlation was found between soil Cd and rate of application of SSP (Figure 1). The approximate annual Cd input rates were calculated by dividing the background corrected total soil concentrations of Cd by the number of years of SSP application (27 or 47 years, R and C plots, respectively) and are given in Table 1. Visual inspection of the plots at the time of sampling the soil indicated that different plant species dominated on different fertilizer treatments. However, neither plant composition differences nor the fact that the plots were grazed by sheep appear to have had any effect on the total content of Cd in individual plots, as evidenced by the excellent linear fit obtained in Figure 1. Moreover the linearity of the data in Figure 1 provides a strong indication that the concentration of Cd in the SSP applied to these plots did not change significantly during the last 20 years of application: if Cd concentrations in the fertilizer had decreased, then the slope of the relationship for the C plot data would have been lower than the slope for the R plot data. Similarly, there appears to have been no movement of Cd down the soil profile or off-site for at least the last 20 years, as the calculated annual increase of soil Cd at a given rate of SSP was not significantly lower ($P > 0.7$) in R plots as compared to C plots (Table 1).

Assuming (i) a bulk density of 1.4 Mg/m³ for this soil and (ii) no significant movement of Cd from the 10 cm surface

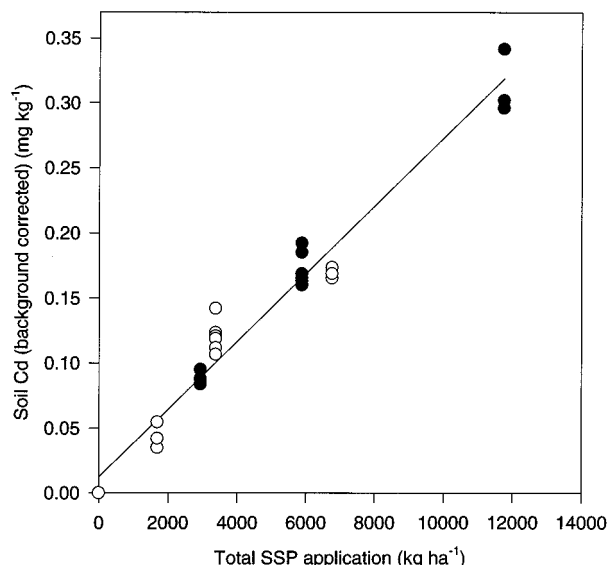


FIGURE 1. Background corrected concentration of Cd in the soil versus total cumulative application of single super phosphate (open symbols = data from R plots, filled symbols = data from C plots).

layer, an estimation of the concentration of Cd in the applied SSP of 40 mg/kg was obtained. This value falls in the middle of the range of Cd concentrations (25–50) reported for SSP in use in Australia (15). The absence of significant loss of Cd from the soil surface due to leaching or removal of crops is consistent with data from several studies. For example, Chang et al. (16) observed no decrease in Cd concentration from sludge-amended soils up to 9 years after termination of sludge treatment. Loganathan and Hedley (17) found that, even on highly fertilized pasture in highly acidic soils and in a high rainfall environment, Cd applied over 10 years in phosphate fertilizers was retained in the top 12 cm of the soil profile. Calculations by McGrath (18) have estimated that the residence time for Cd in soils is in the order of thousands of years.

Plants. Plant growth was different between soils, with increased yields noted in soils from plots that had received the highest rates of SSP application (Table 1). The total concentration of Cd in the wheat increased with increasing concentration of Cd in the soil. Cadmium concentrations in the wheat ranged from 0.19 (plot 62.5 R) to 1.40 mg/kg (plot 250 C). A curvilinear relationship between concentration of Cd in the plants and concentration of Cd in the soil gave the best fit to the data ($r^2 = 0.81$) (Figure 2); however, this relationship was strongly influenced by the high values for Cd concentration in the plants growing in the 250 C soil. Exclusion of these latter values resulted in a poorer ($r^2 = 0.35$) but still positive linear correlation.

The positive trend between concentration of Cd in the soil and the Cd content of plants contrasts with results of several authors (19–21), who concluded that there was no evidence to suggest that Cd concentrations in herbage increased due to long-term applications of phosphatic fertilizers that contain Cd as an impurity. However, such statements should be treated with caution. In these studies, comparisons were made between plants growing in unfertilized (control) soil and plants growing in soil in which there was either no observable increase in soil Cd following long-term use of phosphatic fertilizers or the addition of fertilizers not only led to an increase in Cd concentration in the soil but also to a significant increase in plant yield. Hence, a possibly large confounding factor, acknowledged by these authors, was 'dilution' of Cd in herbage due to the higher yields (22). Therefore, to conclude that the use of phosphatic

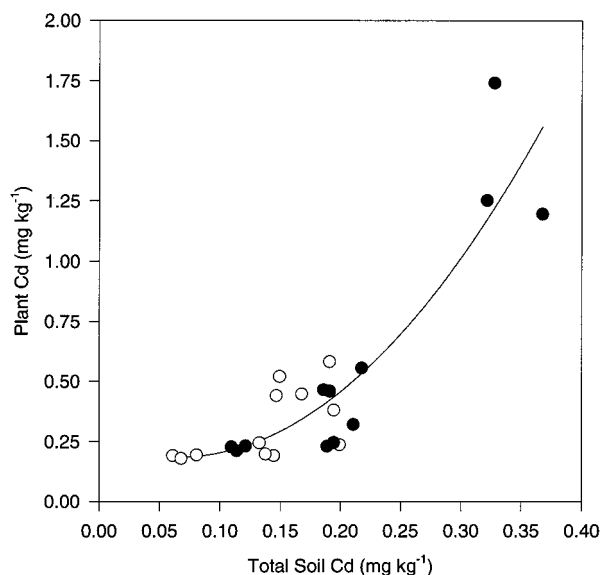


FIGURE 2. Relationship between the concentration of Cd in wheat and the total concentration of Cd in the soil (open symbols = data from R plots, filled symbols = data from C plots).

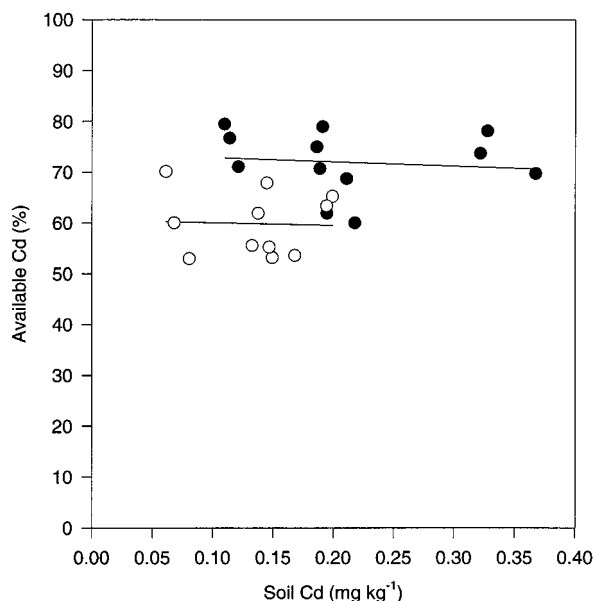


FIGURE 3. Percent of total soil Cd that is available for plant uptake versus the concentration of Cd in the soil (open symbols = data from R plots, filled symbols = data from C plots).

fertilizers does not increase Cd concentration in crops, it would be necessary either to periodically measure the concentrations of Cd in crops growing in a regularly fertilized soil or to use soils in which equivalent amounts of P but not Cd have been applied, as controls.

Labile Cd. Evaluation of the percentage of total soil Cd that was available for uptake by the plants (% *L*) showed that in soil from the R plots approximately 40% of the Cd was in a plant unavailable form (Figure 3). Cadmium was generally more phytoavailable in the C plot soils with a mean of 72% of the total Cd in a plant available form (Figure 3). It should be noted that a distinct advantage of using % *L* values to assess the availability of elements is that differences in relative growth rates of plants are canceled out in the calculation, so available Cd could be determined despite the yield differences obtained in this experiment. Moreover, given the relatively small pot size used in these experiments, it is likely that the values reported for % *L* Cd are, if anything, overestimated in

this experiment as compared to a field setting. In the confined space of a pot, the extraction power of roots per unit soil is much greater (i.e., more roots per unit soil resulting in higher concentration gradients) than in a nonconfined field setting, hence pools of Cd that may be unavailable except in the presence of high concentration gradients will now form part of the labile pool.

For both types of plots, the total concentration of Cd in the soil had little or no effect on the % *L* Cd as indicated by slopes of the lines of best fit approaching zero (Figure 3). In light of the fact that additions of SSP did not affect soil pH, this result is not entirely unexpected. For example, it can be assumed that in a specific soil a given set of physicochemical reactions would facilitate metal fixation and that the amount of metal fixed would be proportional to the concentration of metal (hence percent metal reacted is independent of concentration), providing the metal is not added to the soil at concentrations high enough to lead to nonspecific sorption processes dominating exchange equilibria (3, 23) or changes in pH (24). If the reactions responsible for metal fixation became saturated with excess metal, these latter processes would cause percent labile metal to increase as a function of the total soil concentration. This result therefore provides evidence (i) that pools of non-phytoavailable Cd can exist in the soil, which supports our previous findings with a different soil (25), and (ii) that at low concentrations of Cd in the soil, the amount of Cd fixed is proportional to the concentration of soil Cd. While Cd sorption to the solid phase may be increased in the presence of phosphate (26), the effect of phosphate on Cd fixation was minimal as % *L* Cd was independent of the total concentration of P in the soil (data not shown). Since SSP is highly water soluble, it is also unlikely that Cd locked inside recently applied SSP contributed significantly to the non-phytoavailable pool of Cd in either the R or C plots. It is possible that diffusion of Cd into the soil matrix (8, 27) was the process responsible for the reduction in the phytoavailability of the added Cd.

For a given concentration of Cd in the soil, Cd was significantly less phytoavailable ($P < 0.001$) in plots that had received their last input of Cd in 1975 (R plots) as compared to those still subject to Cd inputs (C plots) (Figure 3). Providing the sward composition differences associated with the different rates of P application did not affect Cd fixation in the soil; this segregation in % *L* Cd between R and C plots (Figure 3) further implies that there is a time-dependent component associated with declines in Cd phytoavailability.

From these data, it was possible to calculate an approximate annual rate of Cd fixation in the soil using a model derived as follows. Given an application of a units of available Cd and assuming a constant rate k of fixation of Cd in the soil, the amount of Cd that is available (labile Cd) (L) at time t is

$$L_t = ae^{-kt} \quad (2)$$

This is a first-order reaction that concurs with the observation that the amount of Cd fixed in the soil was concentration limited and not process limited (i.e., there was no saturation of the mechanism responsible for Cd fixation in the soil).

The percentage of Cd that is available is then

$$\% L = (ae^{-kt}/a) \times 100 = e^{-kt} \times 100 \quad (3)$$

Assuming a constant addition rate of available Cd, after t years of applications the amount of Cd that remains available in the soil (T) will be the sum of the contributions from 0, 1, 2, ... t years i.e.:

$$T = a + ae^{-k} + ae^{-2k} + \dots + ae^{-kt} \quad (4)$$

TABLE 2. Annual Rate of Fixation (k) of Cd as a Percent of either Total Cd in the Soil (unadjusted) or Background-Corrected Soil Cd

	fertilizer treatment		
	62.5 kg of SSP yr ⁻¹	125 kg of SSP yr ⁻¹	250 kg of SSP yr ⁻¹
rundown, unadjusted	1.52	1.69	1.36
rundown, background corrected	0.06	1.08	0.92
continuous, unadjusted	1.30	1.72	1.39
continuous, background corrected	0.18	1.03	0.97

Summing the geometric series in eq 4 gives

$$T = a(1 - e^{-kt}/1 - e^{-k}) \quad (5)$$

After t years of additions, a total of $(a \times t)$ units of Cd would have been applied. The percent of Cd available at that stage would then be

$$\% L_1 = (T/at) \times 100 = (1 - e^{-kt})/t(1 - e^{-k}) \quad (6)$$

If there are no further additions of Cd for the next n years, the percent available Cd will decrease according to eq 2 giving

$$\% L_2 = [e^{-kn}(1 - e^{-kt})/t(1 - e^{-k})] \times 100 \quad (7)$$

Values for $\% L$ were derived experimentally, hence the annual rate of fixation of Cd in the C and R soils could be estimated by solving eqs 6 and 7, respectively, for k . Note that no explicit solution is possible for eqs 6 and 7, but they can be solved by simple iteration. The model for fixation of Cd relies on the following assumptions: (i) during the years when SSP was applied, Cd was added to the soil at a constant rate. (ii) There was no movement of Cd away from the surface horizon in each plot. (iii) Cd added to the soil was initially all available. (iv) The rate of fixation was constant over time.

Using this model, the values obtained for k in each plot are shown in Table 2. Assuming that the original background concentration of Cd in the soil was 0, approximately 1.5% of the total available Cd was estimated to be fixed per year. Assuming that the original background concentration of Cd was 0.026 mg/kg and that none of this Cd was available at the onset of SSP applications, approximately 1% of the total available Cd was estimated to be fixed per year in the plots receiving the two highest application rates of SSP. Incongruous values for plots receiving 62.5 kg of SSP/yr (Table 2) are probably the result of the assumed background concentration of Cd being very close in value to the amount of unavailable Cd in the soil in these plots.

A similar study (28) using the L value technique to examine Cd lability in soils sourced from house foundations that had remained sealed for at least 200 years concluded that there was no change in Cd lability during this time. However, to reach this conclusion, the authors were forced to make the assumption that at least 30% of the Cd in each of the plants was derived through foliar uptake from an unknown atmospheric source, despite the plants being grown in the laboratory. Without this assumption, the calculated size of the labile pools of Cd in the different soils would have been 120–150% of the amount of total soil Cd. Apart from creating a huge potential source of error, this assumption is theoretically unjustified as there is no reason the amount of Cd deposited on the leaves should be consistently related to the internal plant Cd concentration when a majority of the plant Cd is soil derived. Studies with solution cultured plants (29) have shown that the specific activity of Cd in plants was

equal to that in the culture solutions, verifying that at least in our facilities there are no significant atmospheric sources of Cd. A more plausible explanation for the results obtained in the above study (28) is that the ¹⁰⁹Cd spike was not mixed homogeneously throughout the soil and was physically less available to plant roots than the nonradioactive, native soil Cd.

In the only other study we are aware of where the L value technique has been used to assess Cd lability, 10–20% of Cd in soils contaminated with very high concentrations of Cd from long-term sludge utilization farms was found to exist in nonlabile pools (30). The total length of incubation of Cd in the soil in this study is, however, unclear. Other studies that have assessed Cd availability through an examination of changes in total Cd uptake by plants were reviewed by McLaughlin et al. (1) and results found to conflict, with Cd phytoavailability being reported both to decrease and remain constant over time. Lack of evidence for decline in Cd phytoavailability with time may be a function of individual soil types, with the constituents responsible for the slow reactions that fix Cd not being present in all soils, or due to the presence of agents that may inhibit fixation (27). However, the inability to discern decreases in Cd phytoavailability with time may also be the result of shortcomings in experimental design; for example, the short-term nature of many studies and/or relatively high concentrations of Cd being applied to the soil so that any decreases in plant concentrations with time are analytically nonsignificant when compared to the total plant concentration of Cd. The sensitivity of the L value technique should overcome problems associated with this latter aspect.

Though only 1–1.5% of the total Cd was being immobilized in this soil per year, it is apparent that in the long term this might lead to a significant proportion of the total soil Cd being excluded from the equilibrium reactions between the solid and solution phases, which are important determinants of plant uptake. The fact that Cd can exist in non-phytoavailable pools in soils adds further impetus to arguments that the totals-based approach, which is widely in use for delimiting maximum allowable concentrations of metals in soil (31), is inappropriate. Moreover evidence that Cd and other metals can be fixed in soils suggests that to alleviate potential health risks of contaminated soils, in which the risk is primarily associated with soil–plant–animal/human transfers of metal, it may be unnecessary to achieve huge reductions in the total concentration of Cd in the soil. Providing remediation treatments significantly deplete the labile pool of the metal (or other contaminant), a process we have termed 'bioavailable contaminant stripping' (BCS), and this pool is not readily replenished by the contaminant migrating from nonlabile pools, risks to health may be mitigated even without a significant reduction in the total soil content of metal.

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