

An Assessment of Cadmium Availability in Cadmium-Contaminated Soils using Isotope Exchange Kinetics

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ABSTRACT

There has been much research conducted to find suitable methods for the determination of available Cd in soils. In recent years, an isotope exchange kinetics (IEK) technique has been tested to describe the kinetic transfer of ions from the soil solution to the solid phase. Although the IEK technique has been successful in describing nutrient availability in soils, it has not been widely applied to study contaminant availability. In this study, experimental conditions to determine exchangeable Cd in soils using IEK were determined along with a measurement of Cd availability using the IEK technique for 20 topsoils. The results indicated that isotopically exchangeable Cd [$E_{(t)}$ values] predicted from short-term isotopic kinetics (≤ 60 min) were only successful in predicting exchangeable Cd up to 24 h of exchange. After 24 h, $E_{(t)}$ values were significantly overestimated when compared with measured $E_{(t)}$ values. A compartmental analysis revealed that there were differences in the distribution of Cd in exchange pools between soils contaminated with Cd from different sources. The percentage of Cd located in the $E_{(1 \text{ min})}$ pool, was on average 21% of total Cd for the P-fertilizer soils compared with 13% for the biosolids-amended soils. In contrast, the biosolids-amended soils had on average 42% of total Cd located in the $E_{(1 \text{ min}-24 \text{ h})}$ pool compared with 25% for the P-fertilizer soil. The $E_{(>24 \text{ h})}$ pool averaged 57% for the P-fertilizer soil compared with 46% for the biosolids-amended soil. The IEK technique may be a useful tool to provide information on Cd availability in soils.

CADMIUM is a biotoxic heavy metal regarded as an important environmental pollutant in agricultural soils because of the potential adverse effects it may pose to food quality, soil health and the environment. It is generally recognized that it is the labile fraction rather than the total soil Cd content which is critical when assessing Cd availability in soils. In response to this concept, there has been a great deal of research conducted to find suitable methods for the determination of available Cd in contaminated soils. Some of these methods include chemical extractants such as dilute salts, complexing agents and mild acids (Gray et al., 1999), ion-exchange resins (Hooda et al., 1999), sequential extraction procedures (Almås et al., 1999), and isotope dilution techniques (Hamon et al., 1997; Young et al., 2000). The relative advantages or limitations of many of these techniques have recently been reviewed by McLaughlin et al. (2000).

Cadmium availability to plants and soil microorganisms, like other nutrient or contaminant ions, is a function of the concentration of the dissolved metal species in the soil solution and the ability of the soil solid phase

to replenish the soil solution. These two components are the intensity factor (I) and quantity factor (Q) respectively and the relationship between the two is referred to as the buffering capacity (C) of the soil. While many of the techniques proposed above provide information on either one or two of these factors describing ion availability in soils, often estimation of all three factors is not achieved by these techniques.

In recent years, an IEK technique has been developed and tested to describe the kinetic transfer of $^{32}\text{PO}_4$ ions from the soil solution to the soil solid phase (Frossard and Sinaj, 1997). It has been shown that the IEK technique is very useful in describing P availability in terms of the concepts of intensity, quantity, and capacity factors. More recently, the IEK technique has been applied successfully to study soil Zn exchangeability in soils (Sinaj et al., 1999), and Echevarria et al. (1998) used IEK to assess Ni phytoavailability in Ni polluted soils, while Gérard et al. (2000, 2001) used IEK to study Cd availability in four alkaline soils with a large range in total soil Cd concentration. We were interested to determine whether IEK could be applied to study Cd exchangeability in acid soils with relative low Cd concentrations.

The objectives of this study were therefore: (i) develop experimental conditions suitable for the determination of the rate and amount of exchangeable Cd in soils using the IEK technique; (ii) investigate whether it is possible to predict isotopically exchangeable Cd for long-term exchange intervals, that is, up to 18 d, from short-term exchange intervals (≤ 60 min); and (iii) determine whether IEK can provide information on the rate of exchange and amount of exchangeable Cd in a range Cd-contaminated soils.

MATERIALS AND METHODS

Soil Samples

Twenty topsoils were sampled from sites that had different histories of Cd contamination that included long-term land application of biosolids (sewage sludge) and from P-fertilizer application (Table 1). The soil samples were air-dried and passed through a stainless steel sieve to obtain the < 2 -mm fraction before analysis. Soil pH was measured in a water suspension using a soil/solution ratio of 1:2.5 after the suspensions were shaken for 24 h, on a reciprocating shaker at 20°C (Blakemore et al., 1987). Total C content was analyzed by LECO CNS 2000 analyzer (LECO, Australia). Soil texture was measured by the Malvern Laser Sizer method (Singer et al., 1988). Cation exchange capacity (CEC) was determined by ammonium acetate leaching at pH 7.0 (Blakemore et al., 1987). Amorphous Fe and Al oxides were measured by acid oxalate extraction (Blakemore et al., 1987). Manganese oxides

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Abbreviations: IEK, isotope exchange kinetics.

Table 1. Selected characteristic of the soils studied.

Soil	Soil type [†]	pH	Total organic C	Sand	Silt	Clay	CEC	Am-Fe	Am-Al	Mn	Total Cd
				g kg ⁻¹			cmol, kg ⁻¹	g kg ⁻¹		mg kg ⁻¹	
Biosolids soils											
63	Entisol	6.5	92.5	420	510	70	21	4.3	2.1	120	3.00
66	Entisol	6.0	89.7	520	440	50	26	4.6	2.5	104	2.88
67	Entisol	6.4	79.3	600	350	50	22	4.3	1.7	153	2.57
68	Entisol	6.1	68.4	550	400	50	19	4.1	2.1	83	2.73
70	Entisol	7.0	102.1	440	480	80	35	10.3	1.9	131	0.97
71	Entisol	6.5	64.5	620	330	50	18	3.0	1.8	82	2.54
72	Entisol	6.4	62.5	600	340	60	17	2.9	1.5	102	0.98
73	Entisol	6.7	95.5	390	530	90	23	4.8	1.7	108	1.63
74	Entisol	6.4	72.6	600	340	60	26	3.4	0.9	192	0.60
75	Entisol	6.2	38.0	710	240	50	11	1.7	0.8	45	1.06
76	Entisol	5.9	119.7	240	610	150	36	10.0	2.1	72	0.73
77	Entisol	6.4	83.2	570	380	40	21	4.1	2.0	96	2.27
78	Entisol	6.0	118.0	240	560	200	46	9.6	2.5	110	1.00
Fertilizer soils											
200	Udand	4.9	123.0	590	120	290	7	13.0	36.5	1092	0.53
201	Udand	5.4	66.0	400	360	240	7	5.7	23.0	1335	0.52
202	Vitrand	5.3	46.0	410	400	190	5	2.7	5.5	120	0.69
203	Dystrochrepts	5.6	64.0	390	400	210	14	9.5	3.6	531	0.41
204	Eutrochrepts	5.9	33.0	370	430	210	17	5.7	1.6	633	0.19
205	Haplustalf	5.4	62.0	420	490	90	14	4.5	1.6	1747	0.45
206	Humult	5.9	31.0	380	430	190	13	4.0	1.5	406	0.26

[†] U.S. soil taxonomy.

were determined by dithionite-citrate extraction (Jackson et al., 1986). Total Cd was determined by digestion in 5 mL H₂O₂ and 5 mL HNO₃ for 5 h as outlined by Kovacs et al. (2000), and made up to 50 mL with deionized water before being filtered through Whatman 42 filter paper. Cadmium was measured in the digest by graphite furnace atomic absorption spectrometry (GFAAS) with deuterium arc background correction and 0.1% (v/v) H₃PO₄ acid used as a modifier. Ethylene diamine tetraacetic acid (EDTA) extractable Cd was determined by extracting five grams of soil with 20 mL of 0.04 EDTA at 20°C for 2 h on an end-over-end shaker. After extraction the suspension was centrifuged at 9400 × *g* for 10 min and filtered through Whatman 42 filter paper before analysis of Cd by flame atomic absorption spectrophotometry (FAAS) with deuterium arc background correction. Calcium chloride extractable Cd was determined by extracting four grams of soil with 30 mL of 1 M CaCl₂ at 20°C for 24 h on an end-over-end shaker. After extraction the suspension was centrifuged at 9400 × *g* for 10 min and filtered through a Whatman 42 filter paper before analysis of Cd by FAAS or GFAAS depending upon the concentration of Cd in the extract.

THEORY

Isotope Exchange Kinetics

The principle of IEK has been described in a number of recent papers (e.g., Echevarria et al., 1998; Sinaj et al., 1999). Essentially, when ions such as ⁶⁵Zn or ⁶³Ni are added carrier free to a soil solution system at a steady state, the radioactivity in solution decreases with time (*t*, expressed in minutes) according to Eq. [1] (Fardeau, 1996):

$$r(t)/R = [r(1)/R]\{t + [r(1)/R]^{1/n}\}^{-n} + r(\infty)/R \quad [1]$$

where *R* is the total amount of radioactivity introduced into the system, *r*(1) and *r*(∞) are the radioactivity remaining in the solution after 1 min and an infinite exchange time respectively, and *n* is a parameter describing the rate of disappearance of the radioactive tracer from the solution for time longer than 1 min of exchange. The parameter *n* is calculated as the slope of the linear regression between log *r*(*t*)/*R* and log (*t*) for exchange *t* ≤ 60 min. The ratio *r*(∞)/*R* is the maximum possible dilution of the isotope, and is approximated by the

ratio of water soluble Cd to the total soil Cd concentration Eq. [2] (Sinaj et al., 1999; Fardeau, 1996):

$$r(\infty)/R = 10C_{Cd}/CdT \quad [2]$$

where *C*_{Cd} is total water-soluble Cd (mg Cd L⁻¹) and CdT is total Cd digested in concentrated HNO₃ and H₂O₂ expressed in mg kg⁻¹ soil. The factor 10 arises from the soil/solution ratio of 1:10 so that 10 × *C*_{Cd} is equivalent to the water-soluble Cd quantity in the soil expressed in milligrams per kilogram (mg kg⁻¹).

Given that the soil system is at a steady state before the introduction of the isotope, the decrease in the radioisotope with time is assumed to be the result of ionic exchange between radioactive ions, for example, ¹⁰⁹Cd added to the soil solution and stable Cd ions on exchange sites on the soil solid phase. Therefore the quantity *E*(*t*) (mg Cd kg⁻¹) of isotopically exchangeable Cd at a time (*t*) can then be calculated using Eq. [3] assuming that (i) stable Cd and ¹⁰⁹Cd ions have the same fate in the soil-solution system and (ii) whatever the time (*t*), the specific activity of the ¹⁰⁹Cd ions in the soil solution is identical to that of the stable isotopically exchangeable Cd ions in the whole system:

$$E(t) = 10C_{Cd}[R/r(t)] \quad [3]$$

Experiment

Experimentally, 10 g of soil was equilibrated with 99 mL of deionized water on an end-over-end shaker for 5 d. This was the mixing interval used to equilibrate the soil solution. After this time, at *t* = 0, 1 mL of carrier free ¹⁰⁹Cd was added to the suspension and mixed with a magnetic stirrer. Subsamples of between 0.5 to 1.0 mL were collected from the suspensions after 1, 10, 30, and 60 min (short-term kinetics) and also at 1, 3, 7, 11, and 18 d where long-term kinetics were performed on selected samples, the suspensions immediately filtered through a 0.2-μm cellulose acetate membrane filter and measured for radioactivity. The radioactivity in solution was determined with a liquid scintillation counter (Packard 2500 TR) using Packard Ultima Gold scintillation liquid with a volume/volume ratio of 1 mL of sample to 5 mL of scintillation liquid. The initial amount of ¹⁰⁹Cd introduced (*R*), was counted to-

gether with the concentration of ^{109}Cd remaining in the soil solution after each exchange time $r(t)$ for each sample, hence there was no need to correct for radioactive decay. Before the addition of the radioisotope, a 2-mL subsample of soil solution was collected and filtered through a 0.2- μm cellulose acetate membrane and soluble Cd determined by GFAAS. The proportion of Cd^{2+} in the filtered soil water extracts was estimated in five samples (i.e., 71, 72, 73, 75, and 205) with the GEOCHEM speciation model (Parker et al., 1995).

Data Analysis

For all 20 samples, short-term IEKs were performed. Isotopically exchangeable Cd, $E_{(t)}$ values, were calculated using $r(1)/R$ and n along with C_{Cd} and total Cd using Eq. [1], [2], and [3]. We refer to these calculated values as short-term predicted $E_{(t)}$ values.

For six samples (i.e., 71, 72, 73, 74, 75, and 205) that varied in soil properties and total soil Cd concentration (Table 1), long-term isotopic kinetics were performed. Data obtained were then fitted with an iterative nonlinear regression algorithm (i.e., Gauss–Newton model, SYSTAT Version 10) to obtain $r(1)/R$, n , and $r(\infty)/R$ kinetic parameters, and $E_{(t)}$ values were again calculated. We refer to these as long-term predicted $E_{(t)}$ values. The experimental data for these six samples, that is, $r(t)/R$ and C_{Cd} were also used to calculate directly isotopically exchangeable Cd using Eq. [3], up to 18 d. We refer to these data as measured $E_{(t)}$ values.

Using the IEK approach, ion exchange data can be interpreted on a compartmental basis, where a compartment is defined as a homogenous unit in which all the ions have the same kinetic properties and exchange at the same rate with the same ions present in other compartments (Atkins, 1973). A pool can be defined as a volume that contains at least one compartment (Atkins, 1973). Hence using IEK, a nutrient such as P or contaminant such as Cd is not divided into two pools, that is, labile and nonlabile Cd, rather the exchange is considered a continuum that theoretically therefore could result in the exchange of all the Cd in the soil. The amount of exchangeable Cd for example will therefore depend upon the exchange time. By analogy to IEK studies of P and Zn (Frossard and Sinaj, 1997; Sinaj et al., 1999) and based on the results obtained by IEK in the present investigation for Cd, we propose a three-compartmental model to describe exchangeable Cd in our soils.

Preliminary Study

Equilibration Time

The effect of equilibration time on the concentration of Cd in soil solution was assessed for two soils with contrasting soil properties and their source of Cd contamination, that is, a biosolids (Soil 63) and a phosphate fertilizer-amended soil (Soil 202). The samples were equilibrated on an end-over-end shaker in a background of deionized water at a 1:10 soil solution ratio for periods of 1, 3, 5, and 10 d. After shaking, soil water suspensions were filtered through a 0.2- μm cellulose acetate membrane and analyzed in triplicate for water soluble Cd by GFAAS.

Recovery of Added Cadmium

The effect of filtering on the recovery of Cd was determined for a P-fertilized amended soil (Soil 202). Cadmium was added at amounts of either 0, 0.5, or 1 $\mu\text{g Cd L}^{-1}$ as $\text{Cd}(\text{NO}_3)_2$ to either deionized water or a soil solution extract and then

filtered through a 0.2- μm cellulose acetate membrane. Aliquots were then analyzed in triplicate for Cd by GFAAS.

The recovery of ^{109}Cd added to either deionized water, 1 mM $\text{Ca}(\text{NO}_3)_2$, or soil solution extract (Soil 202) and then ^{109}Cd measured in the unfiltered solutions or in solution which had been filtered through either a 0.2- or 0.1- μm membrane was investigated.

Quality Control

Soil Samples

Analysis of a sewage sludge amended soil, that is, Natural Matrix Certified Reference Material CRM005-050 (Resource Technology Corp., Laramie, WY) and a soil standard (NIST 2709) produced recoveries of Cd within the certified limits for both of these standard reference materials.

Soil Solution Cadmium Concentrations

Soil solution Cd analyses were performed on an AAnalyst 800 (Perkin Elmer, Norwalk, CT) GFAAS with Zeeman background correction with magnesium nitrate (6%) used as modifier. Samples were measured in batches of 10, followed by a quality control standard (NIST 1640). The quality range was set to 5% of the certified value of the standard. The limit of detection for Cd was 0.1 $\mu\text{g L}^{-1}$.

Statistical Analysis

All statistical analysis was performed in triplicate using Minitab version 11. Long-term n , $r(1)/R$, and $r(\infty)/R$ parameters were obtained using the nonlinear Gauss–Newton function (SYSTAT versions 10).

RESULTS AND DISCUSSION

Soils

Total soil Cd content ranged between background concentrations found in New Zealand soils (i.e., 0.2 mg kg^{-1}) (Roberts et al., 1994) to Cd concentrations up to the New Zealand Department of Health (1992) guidelines of 3 mg kg^{-1} (Table 1). Other soil properties that have been identified as likely to influence Cd availability also varied between soils (Table 1). Soil texture varied between loamy sand to silt loam, soil pH ranged between 4.9 to 7.0, total C ranged between 3.1 to 12 g kg^{-1} , and oxides of Fe, Al, and Mn also varied between soils.

Preliminary Study

The effect of equilibration interval on the concentration of Cd in solution indicated that after 5 d of shaking, a steady state was obtained for both the biosolids-amended and P-fertilizer soil (data not shown). Young et al. (2000) needed 5 d to achieve equilibration in their investigation of labile Cd and Zn in soils. However, Smolders et al. (1999) reported that desorption of stable Cd did not change appreciably between 1 and 14 d and chose a 7-d equilibration time for their investigation of Cd availability using radioisotopes. In comparison, Gérard et al., (2001) showed that there were no significant differences in solution Cd concentrations between 7 and 72 h. We used a 5-d equilibrium period for all IEK studies.

Table 2. Recovery of Cd added to deionized water or a soil solution extract filtered through a 0.2- μm membrane.

Cadmium added to Solution	Deionized water		Soil water extract	
	Mean	SEM	Mean	SEM
	$\mu\text{g Cd L}^{-1}$			
0	<0.1		0.22	0.02
0.5	0.59	0.03	0.76	0.01
1	0.93	0.05	1.27	0.01

SEM standard error of mean three replicates.

The effect of filtering on the recovery of stable Cd (Table 2) indicated that there was in general a total recovery of Cd added to either deionized water or a soil solution extract, indicating that there was neither significant sorption nor contamination of Cd from the 0.2- μm membrane filter.

It has been previously noted that there can be a significant adsorption of ^{109}Cd onto filter membranes during filtration in a background of water (Morel, 1985; Gérard et al., 2001). This is important if an accurate estimation of the total radioactivity introduced into the soil solution system, (R), is to be made. It was observed in the present study that the percentage recovery of ^{109}Cd in deionized water was only 3.5% of that added, compared with nearly total recovery in a background of 1 mM $\text{Ca}(\text{NO}_3)_2$ or in soil solution extract (Table 3). This was likely the result of the large amount of competing Ca ions in the dilute electrolyte or other cations in the soil solution, which prevented significant sorption of ^{109}Cd . It was also noted that filtering through a 0.2- μm filter membrane produced better recoveries than the 0.1- μm filter (Table 3) and that there were better recoveries for the P fertilizer compared with the biosolids-amended soil. The lower recovery of ^{109}Cd for the 0.1- μm membranes is likely due to greater amounts of colloids in solution, while a lower recovery of ^{109}Cd in the biosolids-amended soil maybe a function of greater amounts of organic colloidal particles. We therefore made all measurements in a background of soil solution and used 0.2- μm membrane filters.

The GEOCHEM speciation model indicated that Cd in the filtered soil solution extracts (C_{Cd}) was present principally as Cd^{2+} , with values ranging between 61 and 85%.

Measurement of variance between samples produced average coefficients of variation (CV%) of 9, 6, and 24% for $r(1)/R$, n , and C_{Cd} respectively and 9, 14, and 12% for $E_{1 \text{ min}}$, $E_{1 \text{ min}-24 \text{ h}}$, and $E_{>24 \text{ h}}$ respectively.

Changes in E-Values with Time

For the six soils where IEK was performed for both short (≤ 60 min) and long-term (i.e., 18 d) exchange, results indicated that the amount of isotopically exchangeable Cd increased with time. It was observed that there was a relatively large increase in exchangeable Cd for exchange intervals between 1 min and 24 h, after which time, although there was still exchange of Cd taking place, the rate of increase in exchangeable Cd was much smaller (Fig. 1).

Young et al. (2000) investigated the effect of increas-

Table 3. The percentage recovery of ^{109}Cd in de-ionized water, 1mM $\text{Ca}(\text{NO}_3)_2$ and in soil water extracts from a biosolids-amended and P-fertilizer soil before and after filtration through a 0.2- or 0.1- μm membrane filter.

	Deionized water	1 mM $\text{Ca}(\text{NO}_3)_2$	Biosolids amended soil	P-fertilizer soil
	%			
Unfiltered	100	100	100	100
0.2 μm	3.5 (0.1)	99.2 (0.3)	97.8 (0.5)	99.8 (0.6)
0.1 μm	3.4 (0.1)	98.9 (0.1)	90.9 (1.8)	96.6 (0.2)

The results are mean and SEM in parentheses of five replicates.

ing the contact time of an isotope added to two mine spoil contaminated soils to determine whether there was a significant transfer of ^{109}Cd to nonlabile pools during equilibration. Their results indicated that for one soil, there was no significant change in the E-value after 24 h of contact, while only a small change after 48 h for the other soil. Smolders et al. (1999) similarly showed that there was no appreciable sorption of ^{109}Cd between 1 and 14 d of equilibrium and the E-value for the soil they studied was unaffected by contact time. These results were similar to what was observed in the present investigation, which clearly indicates that the isotopic exchange process for Cd takes place over a shorter interval compared with what has been previously shown for other ions such as Zn or P.

When the amount of measured exchangeable Cd was compared with $E_{(t)}$ values predicted from short-term kinetics, it was found that data from short-term kinetics were only successful in predicting exchangeable Cd for two of the six soils, that is, Soil 74 and 205. For the other four samples tested, $E_{(t)}$ values from short-term kinetics could predict exchangeable Cd only up to 24 h of exchange. After 24 h, $E_{(t)}$ values were significantly overestimated (e.g., Fig. 1a). This was in contrast to the results of $E_{(t)}$ values calculated from long-term kinetics, where there were no statistically significant differences with experimentally measured data in most soils (e.g., Fig. 1b). The one exception being Soil 205, where data from long-term kinetics statistically underestimated $E_{(t)}$ values, the reasons for which were unclear.

When a comparison was made of the $r(\infty)/R$ parameter calculated from Eq. [2], between short-term and long-term kinetics, with the exception of Soils 74 and 205, the $r(\infty)/R$ parameter was significantly greater when estimated for long-term compared with short-term kinetics (Table 4). One of the assumptions made using this function is that the total soil Cd content, in this instance Cd solubilized by concentrated HNO_3 and H_2O_2 digestion, is all potentially exchangeable. This assumption maybe unrealistic given that a number of studies have shown that often substantial proportions of total soil Cd are considered nonlabile in soils (Young et al., 2000; Gray et al., 2003). This idea maybe supported by the observation that when EDTA-extractable Cd was substituted into Eq. [2] in place of total soil Cd content, for some soils, e.g., Soils 72 and 75 there was no longer a significant difference between $E_{(t)}$ values calculated using short-term kinetics and measured values, and for other soils (i.e., Soil [71, 73] Fig. 1c) the relationship was improved. It is therefore apparent that estimating the

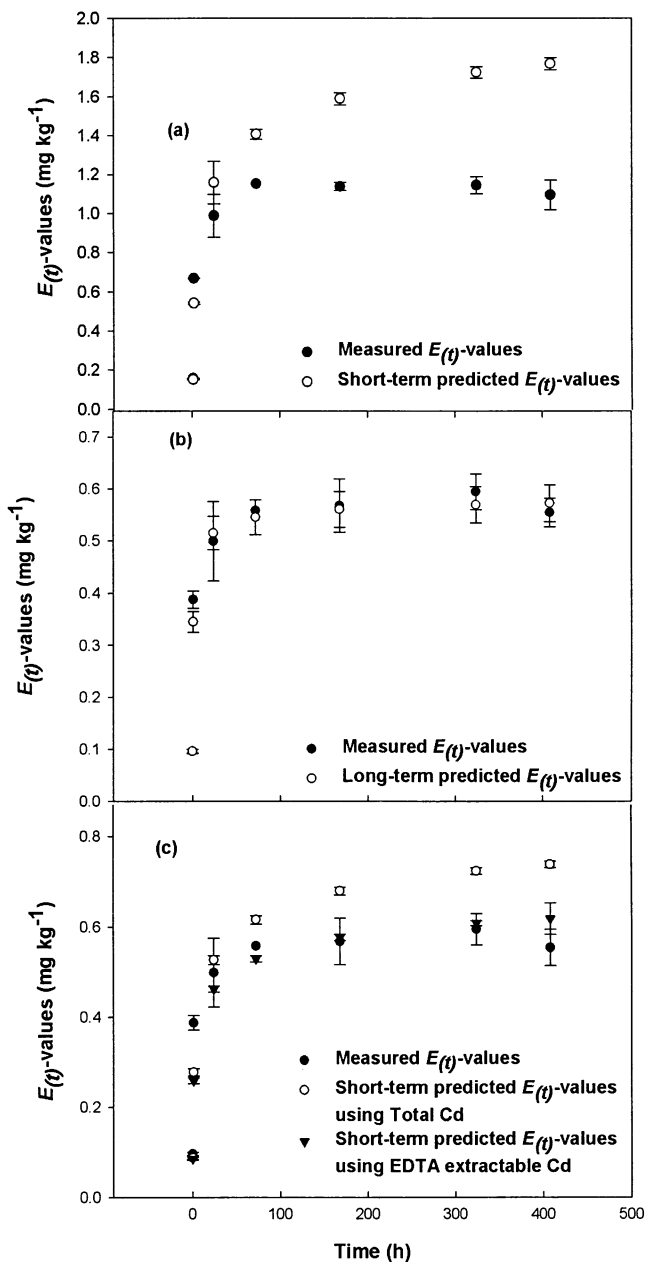


Fig. 1. (a) Comparison between measured and short-term predicted $E(t)$ values for Soil 71; (b) Comparison between measured and long-term predicted $E(t)$ values for Soil 72; (c) Comparison between measured and predicted $E(t)$ values calculated from short-term kinetics using Total or EDTA extractable Cd as an estimator of exchangeable Cd for Soil 72. Error bars are S.E.M. of triplicate determinations.

$r(\infty)/R$ parameter using Eq. [2], may lead to an underestimation of the parameter. A similar observation was made by Diesing et al. (2002) for two of the six Zn-polluted soils they were comparing using the IEK technique. It was suggested that total Zn may not necessarily reflect exchangeable Zn concentrations in their soils and that another chemical extractant may be more suitable. Obviously this is something which requires further investigation if we are to use the IEK technique to provide an accurate long-term estimation of exchangeable Cd in soils.

Table 4. Comparison of kinetic parameters using IEK data between short-term and long-term exchange.

Exchange	$r(1)/R$	n	$r(\infty)/R$
Short-term			
Soil 71	0.045	0.356	0.003*
Soil 72	0.043*	0.341*	0.005*
Soil 73	0.023*	0.322*	0.002*
Soil 74	0.049	0.339*	0.008
Soil 75	0.054	0.340*	0.004*
Soil 205	0.010	0.267*	0.002
Long-term			
Soil 71	0.041	0.493	0.006
Soil 72	0.037	0.480	0.007
Soil 73	0.019	0.479	0.004
Soil 74	0.043	0.494	0.008
Soil 75	0.047	0.478	0.008
Soil 205	0.007	0.467	0.003

* Significant at the 0.05 probability level.

Isotopic Exchange Kinetic Parameters

The ratio of the radioactivity remaining in solution after 1 min of exchange $r(1)$, to the total introduced radioactivity (R), that is, $r(1)/R$ ranged between 0.010 for Soil 205 and 0.060 for Soil 67, with an average value of 0.037 (Table 5). Gérard et al. (2000) estimated $r(1)/R$ values of between 0.003 and 0.0053 for four alkaline soils with a large range in total soil Cd concentration. However, the $r(1)/R$ values were within the ranges calculated for Zn in some polluted and nonpolluted soils (Sinaj et al., 1999; Diesing et al., 2002). The rate of decrease of radioactivity for exchange times greater than 1 min, that is, n values, ranged between 0.131 to 0.385 with an average value of 0.293. The values were generally within the range reported for other trace metals. For example, Gérard et al. (2000) found n values of between 0.19 to 0.31 for Cd, while Sinaj et al. (1999) and Diesing et al. (2002) calculated n values for Zn between 0.065 to 0.270 and Echevarria et al. (1998) calculated n values for Ni of 0.188 and 0.244.

The $r(1)/R$ parameter has been identified as indicative of a soils fixing capacity for ions such as P, K, and SO_4 and the soil buffering capacity (Frossard and Sinaj, 1997). The higher the $r(1)/R$ value, the less the ion is removed from solution hence the more highly buffered the soil. In the present study there was a significant positive relationship between $r(1)/R$ and soil solution Cd concentration (Table 6). This may be related to the soil Mn content in these soils, which was related to the $r(1)/R$ function and has been shown in a number of studies to be important in sorbing Cd in soils. Sinaj et al. (1999) similarly reported a significant relationship between soil Mn content and $r(1)/R$ in a study of Zn exchangeability in polluted and nonpolluted soils. Interestingly, there were no significant relationships with other soil properties such as pH, which is often regarded as the most important soil factor influencing solution Cd concentrations. However, this is not to say that soil pH is not an important soil property within a given soil type. For example, Schwartz et al. (2003) demonstrated that there were significantly greater C_{Cd} and $E(t)$ values in an acidic soil sample compared with the same soil that had a higher pH as a result of being amended with lime.

Table 5. Isotope exchange kinetic parameters and isotopically exchangeable Cd [$E_{(t)pred}$] for 20 soil samples.

Sample	$r(1)/R$	n	C_{Cd} $\mu\text{g L}^{-1}$	$E_{(t)pred}$		$E_{(>24\text{ h})pred}$
				$E_{(1\text{ min})pred}$	$E_{(1\text{ min}-24\text{ h})pred}$	
				mg kg^{-1}		
Biosolids						
63	0.031	0.336	0.889	0.283	1.268	1.449
66	0.058	0.385	1.402	0.236	1.411	1.233
67	0.060	0.306	1.772	0.295	1.028	1.247
68	0.048	0.342	0.908	0.188	1.046	1.496
70	0.041	0.336	0.306	0.110	0.432	0.428
71	0.029	0.355	0.862	0.194	1.065	1.281
72	0.045	0.341	0.454	0.105	0.443	0.431
73	0.043	0.322	0.327	0.143	0.631	0.856
74	0.023	0.339	0.494	0.103	0.294	0.203
75	0.049	0.320	0.467	0.086	0.395	0.579
76	0.054	0.240	1.413	0.257	0.231	0.242
77	0.055	0.344	1.500	0.252	1.029	0.989
78	0.059	0.256	0.648	0.236	0.358	0.406
Fertilizers						
200	0.025	0.320	0.088	0.035	0.172	0.323
201	0.021	0.247	0.109	0.053	0.126	0.341
202	0.041	0.288	0.147	0.040	0.165	0.485
203	0.030	0.164	0.161	0.054	0.069	0.287
204	0.015	0.194	0.142	0.097	0.030	0.064
205	0.010	0.267	0.092	0.091	0.172	0.187
206	0.012	0.153	0.106	0.088	0.041	0.131

When a comparison of $r(1)/R$ and n parameters was made between soils amended with Cd from either biosolids or P fertilizer, the results indicate clear differences between the source of contamination. The average $r(1)/R$ value was 0.022 for the P-fertilizer soil compared with 0.044 for the biosolids-amended soils. Similarly the n value was lower in the P-fertilizer soils, that is, 0.233, when compared with 0.327 for the biosolids-amended soils. The differences between the soils will be discussed in detail in the next section.

Compartmental Analysis of Soil Exchangeable Cadmium

In the present investigation, Cd availability in soils was considered a temporal process and availability was not simply a matter of labile and nonlabile pools. Figure 1 indicated that initially there was a large increase in isotopically exchangeable Cd up to 1 min, and then a change in the amount of exchangeable Cd between 1 min and 24 h and then the rate of increase in Cd exchangeability after 24 h was much smaller. Based on these observations we have proposed three compartments for exchangeable Cd in these soils:

- i) $E_{1\text{ min}}$, which are Cd ions in soil solution and exchangeable Cd on soil surfaces considered with both the same kinetic properties;
- ii) $E_{1\text{ min}-24\text{ h}}$, Cd ions exchangeable between 1 min and 24 h;
- iii) $E_{>24\text{ h}}$, Cd ions not exchangeable within 24 h.

The amounts of exchangeable Cd predicted for exchange times of $E_{1\text{ min}}$, $E_{1\text{ min}-24\text{ h}}$, and $E_{>24\text{ h}}$ indicated that $E_{1\text{ min}}$ contained the smallest amount of Cd ranging between 0.035 and 0.295 mg kg^{-1} , $E_{1\text{ min}-24\text{ h}}$ ranged between 0.030 and 1.411 mg kg^{-1} and $E_{>24\text{ h}}$ contained the largest amount of Cd ranging between 0.064 and 1.496 mg kg^{-1} .

The compartment analysis conducted revealed that there were clear differences in the distribution of Cd in exchange pools between those soils where Cd was derived from phosphate fertilizer or from biosolids. For example, the percentage of Cd located in the $E_{1\text{ min}}$ pool, which estimates soil solution and instantaneously exchangeable Cd, was on average 21% for the P-fertilizer soils compared with 13% for the same pool for the biosolids-amended soils. This may in part have been a result of Cd being supplied in relatively more soluble forms via annual applications of superphosphate fertilizer compared with the biosolids-amended soils that likely, as a consequence of the processing of biosolids before land application had part of its Cd in recalcitrant forms.

In contrast, the biosolids-amended soils had on average 42% of the total Cd located in the $E_{1\text{ min}-24\text{ h}}$ pool compared with 25% for the P-fertilizer soil. Cadmium in this pool was labile, and has the potential to replenish soil solution Cd when processes such as root uptake or leaching remove it. The kinetic parameter $r(1)/R$ provides information on rapid exchange processes, and was on average twice as fast in the P-fertilizer compared with the biosolids-amended soil (i.e., 0.022 versus 0.046). The smaller $r(1)/R$ values in the P-amended soil may

Table 6. Correlations (r) between the soil Cd buffering capacity and soil variables.

Soil variable	$r(1)/R$	N
pH	0.371	0.441
Total C, g kg^{-1}	0.443	0.339
Cation exchange capacity, $\text{cmol}_c \text{ kg}^{-1}$	0.514*	0.143
Manganese oxides, mg kg^{-1}	-0.682**	-0.364
Clay content, g kg^{-1}	-0.414	-0.677**
Soluble Cd concentration, $\mu\text{g L}^{-1}$	0.726**	0.437
Total Cd, mg kg^{-1}	0.538*	0.679**
$E_{1\text{ min}}$, mg kg^{-1}	0.626**	0.356
$E_{1\text{ min}-24\text{ h}}$, mg kg^{-1}	0.530*	0.722***
$E_{>24\text{ h}}$, mg kg^{-1}	0.491*	0.647**

* $P < 0.05$.** $P < 0.01$.*** $P < 0.001$.

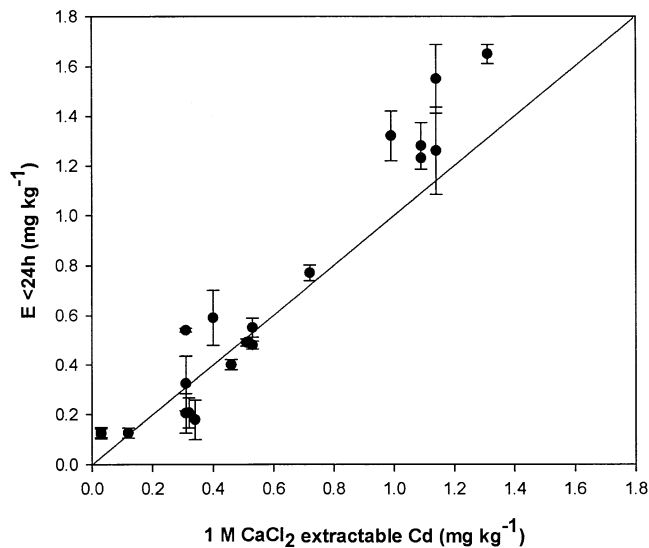


Fig. 2. Relationship between Cd extracted by 1 M CaCl₂ and the amount of isotopically exchangeable Cd calculated up to 24 h ($E < 24$). Error bars are S.E.M. of triplicate determination. The straight line is the 1:1 line.

be a result of the greater amounts of amorphous Fe, Al and Mn oxides, and clay content in these soils compared with the biosolids-amended soils (Table 1). The n value provides information on slower exchange processes, and was larger for the biosolids-amended compared with the P-fertilizer soils (i.e., 0.325 versus 0.233) (Table 5). This may be in part related to the significantly higher total C values found in the biosolids-amended soils (Table 1), which have been shown in previous studies to be very important with regard to Cd sorption and desorption, especially in soils with large amounts of total C (Gray et al., 1998).

The $E_{>24h}$ pool contains Cd not isotopically exchangeable within 24 h and was considered nonlabile. Values averaged 57% for the P-fertilizer soil compared with 46% for the biosolids-amended soil that are similar to results found in other investigations of Cd availability using isotope dilution techniques. For example, Stanhope et al. (2000) found in an investigation of Cd mobilization in soils that on average, 52% of the Cd was in nonlabile forms in a sludge amended soil. Nakhone and Young (1993) measured Cd availability for 33 soils that had been contaminated with mine spoil or sewage sludge using a radioisotope technique and found for the sludge amended soils, the nonlabile fraction of Cd ranged between 11 to 71% with an average of 52%. Gray et al. (2001) calculated that between 40 and 56% of Cd was nonlabile from soils containing Cd from phosphate fertilizer addition.

Clearly, the proportion of nonlabile Cd in soils varies depending upon the source of the Cd, the soils physical and chemical characteristics and the length of time the Cd has been in contact with the soil. The P-fertilizer compared with the biosolids-amended soils had substantially more Fe, Al, and Mn oxides, which are soil components shown to be involved in Cd fixation (Gray et al., 1998). In addition, a recent study of the some of the biosolids-amended soils used in this investigation indi-

cated that the affinity of the soil inorganic phase to retain Cd was extremely small (i.e., 1.8–18%) in relation to the affinity of the soil organic fraction (Zamzam et al., 2002).

Almås et al. (2000) has similarly proposed a three-compartment model to describe the kinetics of ¹⁰⁹Cd transfer in soils. The compartment model proposed describes water soluble, reversibly sorbed and irreversibly sorbed ¹⁰⁹Cd in soils where the compartments are related to amounts of metals extracted using a sequential extraction procedure. In a sequential extraction experiment, Almås et al. (1999) indicated that the reversible sorption of ¹⁰⁹Cd, which is the transfer of ¹⁰⁹Cd from water soluble to reversible compartments in a soil occurs readily, and that a pseudoequilibrium was attained within 0.5 h of sorption. In fact <1% of the total ¹⁰⁹Cd was recovered after 0.5 h of contact time in the water-soluble fraction and <10% were recovered in a 1 M NH₄OAc extract or exchangeable Cd (Almås et al., 1999). These results are in line with what was found in the present study where for the most part Cd exchangeability was complete with 24 h. Almås et al. (2000) also found that the transfer of ¹⁰⁹Cd from solution to irreversible forms was a significantly slower process.

Correlation was performed between the amounts of Cd associated with each exchange pool and soil properties along with the amounts of Cd extracted by different soil extractants commonly used to estimate Cd availability in soils. A comparison between the amount of Cd isotopically exchangeable up to 24 h, considered labile, and Cd extracted using 1 M CaCl₂ is given in Fig. 2. There was a highly significant ($P < 0.001$) relationship between the two estimators of labile Cd, although it appears that for some samples 1 M CaCl₂ was quantitatively extracting approximately 24% less Cd than the amount isotopically exchangeable up to 24 h. Nonetheless, the results were similar to those reported by Gray et al. (2003) and Young et al. (2000) who demonstrated that the amount of Cd extracted with 1 M CaCl₂ corresponded with the proportion of radiolabile Cd estimated by isotope dilution in soils contaminated by either mine spoil and sewage sludge. Young et al. (2000) suggested that 1 M CaCl₂ might be a feasible alternative to using isotope techniques to estimate labile Cd in soils. They suggested that the chloride ion is a moderately strong complexing agent for Cd, while the Ca ion competes with Cd for sorption sites in soils and neither ions (i.e., Cd²⁺ or Cl⁻) dissolve soil minerals for example, hydrous oxide within which Cd may form nonlabile complexes.

CONCLUSIONS

Cadmium availability in soils with relatively low Cd concentrations can be assessed in soils using the IEK technique. The IEK technique approach could simultaneously provide information on the intensity factor (C_{cd}) the quantity factor [$E_{(t)}$] and a parameter related to Cd sorption/desorption in soils [$r(1)/R$]. A compartment analysis revealed that there were differences in the distribution of Cd in exchange pools between soils contaminated with Cd from either long-term land application

of treated biosolids or from annual applications of phosphate fertilizer. Extraction of soils with 1 M CaCl₂ can provide a useful estimation of potentially isotopically exchangeable Cd in soils. Isotopic exchange kinetics has potential as a technique to provide useful information on Cd availability in soils although further work is still required to find a robust measure of the potentially exchangeable parameter that is, $r(\infty)/R$ which is required in the IEK equation.

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