Geoderma 161 (2011) 18–29

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Air-drying and liming effects on exchangeable cadmium mobilization in contaminated soils: A repeated batch extraction study

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ARTICLE INFO

Article history:
Received 4 June 2010
Received in revised form 14 November 2010
Accepted 21 November 2010
Available online 23 December 2010

Keywords:
Cadmium
Desorption
Liming
Air-drying
Exchange selectivity coefficient

ABSTRACT

Air-drying of soil samples is known to increase the exchangeable fraction of cadmium (Cd) in soil. Liming, on the other hand, reduces bioavailability of heavy metals in soil by metal hydrolysis reactions and/or coprecipitation with carbonate. However, due attention has not been paid to desorption and mobilization of Cd from air-dried and limed soils at realistic ionic strengths. We compared Cd desorption from moist and air-dried samples of two texture-contrasting soils which had been spiked with 3 or 30 mg-Cd kg^{-1} after liming with 25 mmol kg^{-1} of $Ca(OH)_2$, or without prior liming. Repeated batch extraction with water and 1–10 mM $CaCl_2$ solutions was carried out, and chemical speciation of dissolved Cd performed using Visual MINTEQ. Desorption of Cd from the exchangeable pool in the soils was not exhaustive, with smaller fractions of Cd remaining after five extractions in the coarse-textured Chiba soil having lower CEC than the fine-textured Takada soil. Air-drying enhanced Cd desorption from the both soils particularly in the first extraction, with the cumulative Cd desorption after five extractions 1.5 times, on average, as large as that from the unlimed moist soils. Liming suppressed the Cd release, resulting in cumulative desorptions 0.14–0.19 times those from the unlimed counterparts. The air-drying and liming effects on Cd desorption were reflected in the apparent Cd^{2+}/Ca^{2+} exchange selectivity coefficient, which was lowest in the first extraction upon air-drying, and significantly increased upon liming. Alternatively, assuming that constant Cd^{2+}/Ca^{2+} exchange selectivities obtained from the moist unlimed soils apply, exchangeable Cd pools in the air-dried and limed soils were evaluated. The exchangeable pool was found to increase, on average, by 26% and 30% upon air-drying, and decrease by 79% and 86% upon liming in the Takada and Chiba soils, respectively. These results demonstrate that the size of exchangeable Cd in contaminated soils is prone to change upon drying and liming, and that the potentially desorbable Cd is only slowly mobilized under ionic strength conditions prevailing in the field.

1. Introduction

Cadmium (Cd) is one of the most toxic metallic elements in soil, and occurs as a result of natural and anthropogenic activities. Sorption of Cd in soils has two facets: (i) like other heavy metals, Cd is readily sorbed on soil clays and Fe, Mn, and Al oxides/hydroxides, with the sorption influenced by soil pH (Gray et al., 1999; Jobstmann and Singh, 2001; Naidu et al., 1994), and (ii) the sorption is, however, weaker than other heavy metals, with a considerable proportion in the exchangeable fraction (Tang et al., 2006; Voegelin et al., 2003). Consequently, electrolyte cations like Ca^{2+} can displace the exchangeable Cd and mobilize it in the soil environment (Escrig and Morell, 1998; Pardo, 1997).

This propensity of Cd toward mobilization by cation exchange emphasizes the importance of correctly assessing the size of exchangeable Cd pool in soil and its desorbability under different conditions. Air-drying is known to increase the exchangeable fraction of Fe, Mn, Co, Cu and Zn together with the release of dissolved organic carbon (DOC) (Bartlett and James, 1980; Makino et al., 2000; Shuman, 1980). Makino (2001) envisaged that the dissolution of manganese oxides by reductive sugars released from the corpses of microorganisms was responsible for the increase in the metal solubility and exchangeability upon soil drying. While the amounts of extractable Cd were not always directly affected by DOC (Strobel et al., 2005), strong influences of complex-forming DOC on Cd migration in the environment have been reported (Mahara et al., 2007). Liming, on the other hand, reduces the mobility and bioavailability of heavy metals in soil by metal hydrolysis reactions and/or coprecipitation with carbonate (Kabata-Pendias and Pendias, 1992).

In the present study, we focus on Cd desorption through cation exchange at ionic strengths typically encountered in field soils, where

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doi:10.1016/j.geoderma.2010.11.012

Cd desorption and mobilization may occur during rainfall events. In the preceding studies, Cd sorption/desorption experiments using dilute (as low as 1 mM, e.g., Christensen, 1984) salt solutions are rather exceptional. Widely-adopted single extraction batch experiments (e.g., Boekhold et al., 1993; Gray et al., 1999) as well as the sequential extraction methods for chemical fractionation of Cd in soil (Tessier et al., 1979; Wang et al., 2002) use high-ionic strength extractant solutions (e.g., 1 M $MgCl_2$), so that the results may not be directly applicable to predicting Cd desorption and transport under field conditions. In addition, the sequential extraction method also suffers from non-selectivity of the extractants and redistribution of Cd among different chemical forms during the extraction process (Rapin et al., 1986).

Repeated extraction method (Gray et al., 1999; Mustafa et al., 2004, 2006) is an alternative and has an advantage that the use of high-ionic strength extractants can be avoided. Changes in the released Cd concentrations reflect changes in the exchangeable pool and its desorbability caused by the continual Cd release. In addition, exchange selectivity coefficients for the replacement of Cd by other cations determined at each extraction step provide information about Cd release behavior distinctively under different conditions. Use of salt solutions (e.g., $CaCl_2$) at different concentrations enables the effects of Cl^- complex formation (Boekhold et al., 1993; Doner, 1978) and changes in the DOC solubility (Römkens and Dolfing, 1998) on Cd desorption to be investigated as well.

The objective of the present study was to reveal the effects of air-drying and liming on the desorption of exchangeable Cd at ionic strengths typically found in the field. Repeated batch extraction from Cd-added soils was carried out using dilute $CaCl_2$ solutions, and chemical speciation of dissolved Cd performed using Visual MINTEQ. Air-drying and liming effects were compared in terms of stepwise and cumulative Cd releases from the soil as well as the apparent Cd^{2+}/Ca^{2+} exchange selectivity coefficients. We also show that assuming a constant Cd^{2+}/Ca^{2+} exchange selectivity, alternatively, enables the size of exchangeable Cd pool in differently treated soils to be estimated, and that the size considerably changes upon drying and liming.

2. Materials and methods

2.1. Soils

Two topsoils (0–20 cm depth), Takada soil (Typic Epiaquept) collected from experimental fields of Hokuriku Research Center of the National Agricultural Research Center (37°6′59″ N, 138°16′28″ E), Joetsu, and Chiba soil (Typic Fluvaquent) from Chiba Prefectural Agriculture and Forestry Research Center (35°32′50″ N, 140°09′29″ E), Chiba, Japan, were used. The experimental field at the Hokuriku Research Center was converted from a paddy field, and had been used mainly for soybean and cabbage since 1996. The soil was heavy-clayey and had a pH of 5.8, with the clay fraction dominated by smectite. The Chiba soil with a similar land use history had a coarser texture and a pH of 5.4, with the clay minerals dominated by smectite and halloysite. Selected properties of the two soils are shown in Table 1.

2.2. Preparation of Cd-contaminated soils

Cadmium-contaminated soils were prepared by soaking the soils in $CdCl_2$ solutions with or without prior liming. During the preparation, care was taken to avoid soil drying beyond the soil water potential of −1.5 MPa, which could lead to changes in the soil properties (Katou et al., 1985; Toriyama et al., 1988). Takada and Chiba soils were passed through a 4-mm sieve after slowly lowering the water content from field-moist to near the plastic limit. After incorporating 0 or 25 mmol kg^{-1} of powder $Ca(OH)_2$ and ageing for a week, the soils were soaked in $CdCl_2$ solutions containing 2.65 or 26.5 mg-Cd L^{-1} at a solution/soil ratio of 1.13 L kg^{-1}, to obtain target contamination levels of 3 and 30 mg-Cd kg^{-1}. The Cd-contaminated soils were kept in a muddy state for 2 months. The soils were then slowly dried to gravimetric water contents of 0.25 kg kg^{-1} for Takada soil, and 0.35 kg kg^{-1} for Chiba soil, and gently passed through a 2-mm sieve. The sieved moist soils were further stored for 3 months in sealed plastic bags for further ageing under moist conditions. Portions of the moist samples were then air-dried for the subsequent experiments. In

Table 1
Selected properties of the experimental soils.

Soil		Takada				Chiba			
		3 mg-Cd kg^{-1}		30 mg-Cd kg^{-1}		3 mg-Cd kg^{-1}		30 mg-Cd kg^{-1}	
		Moist	Air-dried	Moist	Air-dried	Moist	Air-dried	Moist	Air-dried
Cd content	mg kg^{-1}								
Background Cd		0.40				0.33			
Total Cd after addition		3.29		28.7		3.27		30.0	
Water content pH (1:5[a])	kg kg^{-1}	0.24	0.046	0.22	0.045	0.35	0.039	0.36	0.037
Water		5.8	6.0	6.1	6.0	5.8	6.0	5.8	5.9
0.01 M $CaCl_2$		5.5	5.6	5.7	5.7	5.7	5.7	5.7	5.5
Exchangeable cations	$mmol_c$ kg^{-1}								
Ca^{2+}		206	203	208	204	127	126	130	130
Mg^{2+}		44.8	42.2	46.8	46.3	37.1	37.4	39.8	38.7
K^+		8.9	8.5	9.1	8.7	5.6	5.4	5.8	5.3
Na^+		1.6	1.4	1.7	1.4	1.9	1.5	1.7	1.6
CEC	$mmol_c$ kg^{-1}			253				173	
Fe_o[b]	g kg^{-1}	8.85				6.80			
Fe_d[c]	g kg^{-1}	14.4				7.76			
Mn_o[b]	g kg^{-1}	0.16				0.22			
Mn_d[c]	g kg^{-1}	0.36				0.49			
$CaCO_3$	g kg^{-1}	5.20				5.16			
Organic C	g kg^{-1}	20.4				17.5			
Total N	g kg^{-1}	3.7				4.7			
Textural composition	%								
Sand (0.02–2 mm)		16.9				51.8			
Silt (2–20 μm)		38.1				18.6			
Clay (<2 μm)		45.0				29.6			

[a] Soil to solution ratio.

[b] Fe_o, Ammonium oxalate-extractable Fe; Mn_o, Ammonium oxalate-extractable Mn (Schwertmann, 1964).

[c] Fe_d, dithionite–citrate–bicarbonate-extractable Fe; Mn_d, dithionite–citrate–bicarbonate-extractable Mn (Mehra and Jackson, 1960).