An assessment of cadmium availability in upland field soils using isotope dilution

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Abstract

The isotopically-exchangeable pool of cadmium (Cd), which is referred to as the E-value (Cd_E), was used for evaluating the actual quantity of phytoavailable Cd in soils. We examined the relationship between E-values and L-values (Cd_L), the isotopically-exchangeable pool of Cd as measured from the isotopic composition of rice plants grown on spiked soil. The Cd_L values were generally similar to those of Cd_E, indicating that the rice plants absorbed soil Cd from the same pool assessed by Cd_E. Extraction with 0.1M HCl generally gave similar values to Cd_E. However, the Cd_L values of volcanic ash soils were higher than the Cd_E, and the Cd_E values of those soils were significantly higher than the 0.1M-HCl extractable Cd. Application of organic waste did not affect Cd_E.

Key Words

Cadmium, E-value, L-value, isotope, organic waste, soil.

Introduction

The Codex Alimentarius Commission has enacted regulations on cadmium (Cd) in food (Codex 2005). All possible efforts should be made to reduce Cd levels in staple crops. Risk assessment of Cd in soils has been the subject of a number of investigations. We proposed isotope dilution techniques coupled with an enriched [113]Cd for determining the actual size of the labile Cd pool in soils (Kawasaki and Yada 2008).
This technique gives the quantity of Cd ions in solution together with those in the solid phase, which are in equilibrium with the Cd ions in the solution phase. This quantity is often referred to as the E-value (Cd_E). The isotopically-exchangeable pool of Cd can be measured from the isotopic composition of a plant grown on the spiked soil. In this case, the isotopically-exchangeable pool of Cd is referred to as the L-value (Cd_L). Theoretically, Cd_L gives a similar value to Cd_E. However, there are some reports that Cd_L did not equal Cd_E (Ayoub *et al.* 2002). The objectives of this study were to compare the results of Cd_E with Cd_L, and evaluate the effect of application of organic waste.

Methods

Materials

The surface horizons of 15 upland soils were used. These soils had received continuous low input of Cd by successive applications of various types of organic waste: marine waste compost, cattle manure, or sewage sludge up to 4 years. The sampling sites were as follows. Brown lowland soil A: Hokkaido Prefectural Dohnan Agricultural Experimental Station. Brown lowland soil B and brown forest soil: Hokkaido Central Agricultural Experimental Station. Volcanic ash soil: Kumamoto Prefectural Agricultural Research Center.

Selected soil characteristics

Soil pH was measured in water using a solid : liquid ratio of 1:2.5 (g/ml) after equilibration for 2 h. The organic C content was determined for finely ground and sieved soil (0.5 mm) using a Sumigraph NC-22 NC analyser (Sumika Chemical Analysis Service, Ltd.). The cation-exchange capacity (CEC) using the exchangeable base method employed 1M KCl as the index-exchangeable cation (K) in a 0.1 M NH_4OAc buffer at pH 7.0 (modified from Chapman 1965). Total soil Cd content was measured for digestion using HNO_3-$HClO_4$-HF. The method proposed by Lechler *et al.* (1980) was used. Extractable Cd was measured for extraction with 0.1 M HCl, the method proposed by the Agricultural Land Soil Pollution Prevention Law No. 139 (Japanese Ministry of the Environment 1970). Two replicates of each soil along with blanks were analysed for Cd using an ICP-MS. All soil data, including Cd_E and Cd_L values, are expressed on an oven-dried (105 ˚C) weight basis.

Instrumentation and reagents

An inductively coupled plasma mass spectroscope (ICP-MS; ELAN DRC-e, Perkin Elmer, USA) was used.

The instrument's operating conditions (Table 1) are described in Kawasaki (2008). The spike solution (10.96 µmol Cd L^{-1}) was made from enriched ^{113}Cd (93.29% ^{113}Cd, 0.46% ^{114}Cd, JV Isoflex).

Table 1. Operating conditions of ICP-MS

Plasma condition	RF power	1.1 kW
	Plasma gas flow rate	15 L/min
	Auxiliary gas flow rate	1.2 L/min
	Nebulizer gas flow rate	0.9 /min
Sampling condition	Sampling depth	11 mm
Nebulizer (GE micromist)	Sample uptake flow rate	0.4 L/min
Data acquisition	Data points	1 point/peak
	Dwell time	50 ms/point
	Integration	50 times
	Number of replicate	12

Determination of the Cd E-value, Cd$_E$

Two replicate 15-gram soil samples were equilibrated with 150 mL of water on a magnetic stirrer for more than 2 d. Then, 1.5 mL of enriched ^{113}Cd (93.29% ^{113}Cd, 0.46% ^{114}Cd, 10.96 µmol Cd/L) was added to the suspension and mixed with a stirrer. After exchange times of 1, 4, 10, 40, 100, and 400 minutes, and 1, 4, 7, 11 and 15 days, a 2-mL subsample was collected from the suspensions and immediately filtered through a 0.22-m polyethersulfone (PES) membrane. Determination of the ^{113}Cd/^{114}Cd ratio of the filtrate was determined by ICP-MS after employing a coprecipitation separation procedure proposed by Kawasaki and Yada (2008).

The E-value, Cd$_E$, was calculated using the following equation (Kawasaki and Yada 2007),

$$Cd_E = \frac{C_{spike} M}{m} \times \frac{h^{113}_{spike} - Rh^{114}_{spike}}{Rh^{114}_{sample} - h^{113}_{sample}} \qquad (1)$$

where C$_{spike}$ is the quantity of Cd in the spike solution [µmol], M is the atomic weight of Cd (112.411), m is the soil weight [g], h is the isotopic abundance of the ^{113}Cd or ^{114}Cd in the sample or spike solution, and R is the measured ^{113}Cd/^{114}Cd ratio.

Determination of the Cd L-value, Cd$_L$

Four hundred grams of soil was dispensed into a bag and the moisture content increased to approx. 90% of maximum water capacity using 50 mL of ^{113}Cd (93.29% ^{113}Cd, 0.46% ^{114}Cd, 4.38 µmol Cd L^{-1}) spike solution. Soils were equilibrated for 4 weeks and randomised in five replicate blocks before sowing rice seeds. The growing room had a 24-h cycle of 14 h light and 10 h dark (25 °C). Plant shoots were harvested by cutting at 5 mm above the surface of the soil, 6 weeks after sowing. The shoot material was weighed and dried using a freeze-dryer and digested in hot concentrated HNO$_3$ (1 mL).

Table 2. Selected characteristics of soil samples

Sample	pH	Total C %	CEC mmol/g	Total Cd µg/g	HCl-Cd µg/g
Brown lowland soil A (Un-amended)	4.9	1.3	27	0.70	0.36
Brown lowland soil A + Scallop waste	5.7	1.3	26	0.75	0.41
Brown lowland soil A + Alaskan pollack waste	5.7	1.3	25	0.77	0.38
Brown lowland soil B (Un-amended)	6.1	1.3	21	0.21	0.10
Brown lowland soil B + Sewage sludge (P)[a]	5.6	1.3	21	0.21	0.10
Brown lowland soil B + Sewage sludge (L)[b]	7.0	1.3	20	0.21	0.09
Brown forest soil (Un-amended)	5.7	2.5	24	0.30	0.14
Brown forest soil + Sewage sludge (P)[a]	6.0	2.8	28	0.31	0.17
Brown forest soil + Sewage sludge (L)[b]	6.4	3.0	28	0.33	0.17
Volcanic ash soil (Un-amended)	6.0	7.0	63	0.49	0.11
Volcanic ash soil + manure (2t 10a^{-1})[C]	6.3	7.8	60	0.50	0.10
Volcanic ash soil + manure (4t 10a^{-1})[C]	6.5	8.5	72	0.55	0.07

a) Sewage sludge with polymeric flocculant; b) Sewage sludge with lime flocculant; C) Cattle manure with sawdust.

The L-value, Cd_L, was determined using the same equation as above for digestion using coprecipitation separation method coupling with UV (Kawasaki and Yada 2008).

Results and discussion

Soils

Selected soil characteristics relevant to metal bioavailability are shown in Table 2. The soil pH of each control soils ranged between 4.9 and 6.1. Both the values of pH 7.0 in brown lowland soil B and 6.4 in brown forest soil are the result of application of sewage sludge with lime flocculant. The high values of Total C and CEC in the volcanic ash soils are due to abundant non-crystalline materials such as allophane, imogolite, and Al-humus complexes (Nanzyo 2002).

The concentration of total Cd of control soils ranged from 0.21 to 0.77 mg kg^{-1}. The application of organic waste did not affect the total soil Cd content. These values were similar to world agricultural soil Cd concentrations: 0.27 mg kg^{-1} in the USA (Holmgren *et al.* 1993), 0.7 mg kg^{-1} in the UK (McGrath and Loveland 1992). The amounts of HCl-extractable Cd (HCl-Cd) ranged from 0.07 to 0.38 mg kg^{-1}. Application of organic waste did not increase HCl-Cd in the brown lowland soils or brown forest soils. In contrast, only up to 22 % of total-Cd in volcanic ash soil was 0.1M HCl-extractable, and HCl-Cd decreased with increasing application rate of manure.

E-values of Cd in soils

The Cd_E values were in a range very similar to that of the control soil. No differences in Cd_E between control soil and organic waste-applied soils were observed. The value of Cd_E corresponded to 0.1 M HCl-extractable-Cd in the brown lowland soils and brown forest soils (Figure 1a). However, the values of Cd_E in volcanic ash soils were higher than in the 0.1M HCl-extracted Cd levels. The fact that Cd_E was almost equal to 0.1M-HCl-Cd can be ascribed to the fact that 0.1M-HCl-Cd can be used to estimate the labile Cd pool in brown lowland soils and brown forest soils. In contrast, 0.1M-HCl might not completely dissolve the labile Cd in the volcanic ash soils. When there is a high organic matter content, such as in volcanic ash soils, extraction by 0.1M-HCl is not an alternative to Cd_E obtained by isotopic dilution procedures.

L-values of Cd in soils

Values of Cd_L were, in general, in close agreement with both the corresponding value of Cd_E and HCl-Cd in brown lowland soils and brown forest soils (Figure 1b), indicating that the rice plants utilized the same pool of Cd_E. The fact that Cd_L is equal to Cd_E also can be ascribed to the fact that Cd_E, determined at 15 days of exchangeable time after addition of isotope, can estimate plant labile pool with different contact times (6 W).

a. Comparison between Cd_E and HCl-Cd   **b. Comparison between Cd_L and Cd_E**
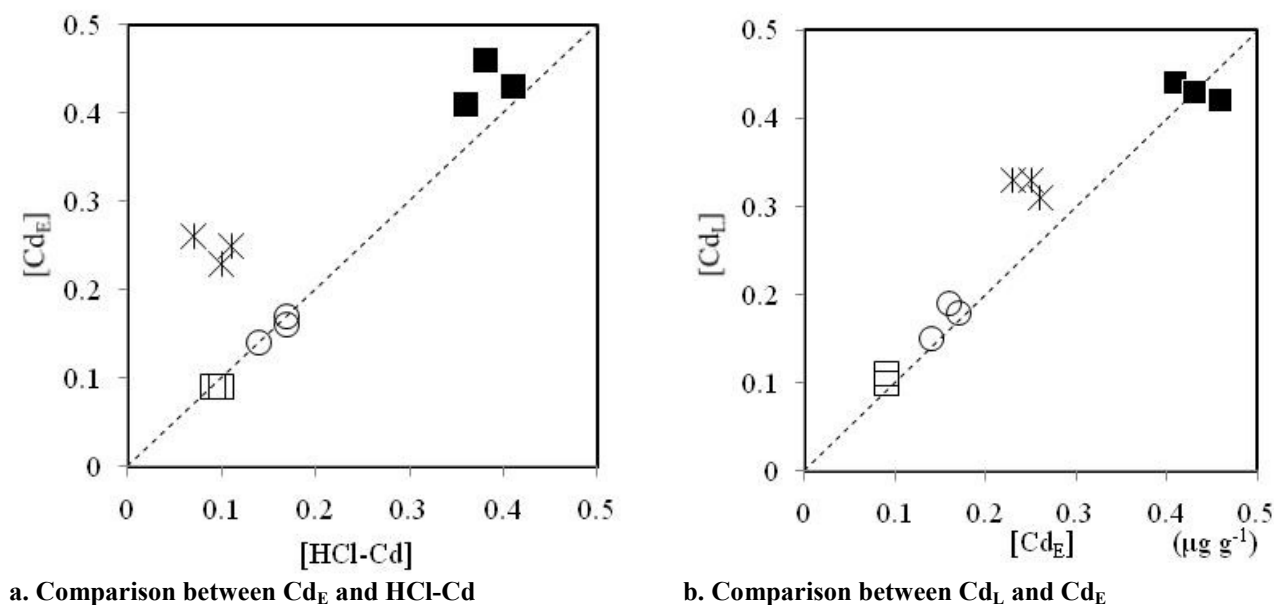
Figure 1. Comparison between measured labile Cd values. ■ indicates brown lowland soil A, □ indicates brown lowland soil B, ○ is brown forest soil, and * is volcanic ash soil.

However, the Cd_L for volcanic ash soil was higher than the corresponding Cd_E (Figure 1b). The differences between Cd_L and Cd_E values in volcanic ash soil suggest that plant-related factors and/or high levels of soil organic matter affect isotope exchange.

Conclusion

The values of Cd_L were in general similar to the values of Cd_E in each soil. The rice plants utilized the same labile Cd pool as that evaluated by Cd_E. Cd_E is a potentially useful tool for assessing the plant labile pool of Cd in soils. No differences between Cd_E in the control soil and organic waste-applied soils were observed. Application of organic waste did not increase Cd_E in soils.

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