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Assessment of 0.1 M HCl Extraction Protocol in Determining Available Cd in Andisol

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Summary

In Japan, 0.1 M HCl method was stipulated as a tool to evaluate the available cadmium content of soils. Its feasibility on available cadmium determination for Andisol was assessed and the extraction conditions were investigated through Cd recovery experiments. The results showed that only about 80% of Cd added was recovered in paddy soil from Kawatabi Andisol and 23.1% to 92.4% of Cd added were recovered from other Andisols, when extracted by the stipulated method. Improving of extraction concentration did not result in enough recovery, but the increase of soil : solution ratio did increase Cd recoveries of Andisol. Most Andisols had full Cd recoveries when extracted with a soil : solution ratio of 1 : 20. Therefore, it is suggested that the soil : solution ratio of the stipulated method should be changed to 1 : 20 for Andisol.

Introduction

Cadmium is one of the most wellknown environmental toxins to humans. Long term exposure to cadmium can cause lung cancer and kidney dysfunction. Except professional exposure, humans get cadmium mainly through the food chain, especially in those areas with soils polluted by cadmium. Anthropogenic addition of cadmium to soils occur via short- or long-range atmospheric deposition, application of fertilizers, municipal sewage wastes, urban composts and industrial sludges (1). Though the total content of cadmium in soils gives some indication of contamination, Cd content in plants does not always correlate to Cd content in soils because Cd in soils is associated with a number of physicochemical forms with different availability to plants (2). Soil cadmium forms vary with soil factors such as pH, soil texture, organic matter content, type of soil colloids, soil Eh and so on, thus the availability of soil cadmium changes with soil factors. Therefore, the availability of soil cadmium is used to evaluate the degree of soil pollution by Cd. The amount of soil available Cd varies both with extractants and extraction conditions. Up to date, a lot of extractants were developed, for example, water (3), DTPA, double-acid (0.05 M HCl and H_2SO_4), 0.1 M HCl (4), 1 M NH_4NO_3 (5), 0.1 M $CaCl_2$ (6), 1 M $Ca(NO_3)_2$ (7). Among these extractants, DTPA, 0.1 M HCl and the double acid extractants are most commonly used (4). The DTPA method was developed for calcareous soils and the 0.1 M HCl method was used to estimate Cd availability in acid soils.

Soils in Japan are mainly acid soils and 0.1 M HCl method was stipulated as a tool to evaluate the degree of soil pollution by cadmium, copper and zinc. In this article, the protocol in determining available cadmium of soils was assessed through a recovery experiment. The limitations of this method were also documented.

Materials and Methods

Soils including Alluvial paddy $soil_1$ from Furukawa (APS_1), Alluvial paddy $soil_2$ from Yamagata (APS_2), Sulfate soil from Naruko (SS), and paddy soil from Kawatabi Andisol (KAPS) were collected and air-dried. Soils were screened to pass a 2 mm sieve after the coarse materials were removed by hand, then stored for the experiment.

The basic procedure was as follows:

① Weigh 10 g of air-dried sample into 100 ml polyethylene bottle. Add 50 ml 0.1 M HCl to the bottles and cap them. Place them on a horizontal reciprocating shaker at 30°C, 145 cycles min^{-1} for 1 hour

② Filter the slurry through No. 5C filter paper

③ Analyze Cd concentration in filtrate by AAS (Hitachi Z-1600, Japan)

Concentration of HCl and soil : solution ratio were changed to investigate their effects on available cadmium extraction of Andisol. Alluvial $soil_2$ was chosen as the control.

Results and Discussion

Recovery of Cadmium

Available Cd contents of several soils extracted by the stipulated protocol were shown in Table 1. Of these soils, Sulfate soil had the lowest available Cd content. The available Cd contents of Andisol and Alluvial soils were 0.28 ppm and 0.28～0.84 ppm, respectively. The recoveries of Cd from Alluvial $soil_1$, Alluvial $soil_2$, Sulfate soil and Andisol (from Kawatabi) were 100.1%～101.2%, 99.9%～100.0%, 98.4%～99.8% and 78.5%～82.5%, respectively. Only Andisol from Kawatabi did not exhibit full Cd recovery. This showed that the Andisol still had a very high ability to absorb Cd from the solution under the extraction conditions of stipulated protocol. Therefore the extraction conditions were stud-

TABLE 1. *Cd Recoveries of Several Soils Extracted by Stipulated Protocol*

Soil	Available Cd ppm	Cd recovery (%)		
		1 ppm added	2 ppm added	4 ppm added
APS1	0.267	101.2	100.7	100.1
APS2	0.830	100.0	100.0	99.9
SS	0.005	98.5	99.8	98.4
KAPS	0.275	82.5	78.5	79.1

* : APS_1 was the Alluvial paddy $soil_1$ collected from Furukawa, APS_2 was the Alluvial paddy $soil_2$ collected from Yamagata, SS was the Sulfate soil collected from Naruko and KAPS was the paddy soil collected from Kawatabi Andisol.

ied further.

Cd Recoveries with Different Soil : Solution Ratios

Effect of soil : solution ratio on the content of available cadmium and Cd recovery was shown in Table 2.

Increasing soil : solution ratio resulted in more Cd extracted from soil, thus increased the content of soil available Cd. The amount of Cd extracted by 50 ml 0.1MHCl increased from 0.27 ppm at 10 g of KAPS to 0.44 ppm at 2.5 g soil, and from 0.84 ppm at 10 g of APS_2 to 0.92 ppm at 2.5 g of soil. In spite of the soil : solution ratio, APS_2 exhibited full recoveries, while the Cd recoveries of KAPS increased with the increasing soil : solution ratio. With a soil : solution ratio of 1 : 10 (5 g/50 ml), the soil had more than 95% Cd recoveries, and with a soil : solution ratio of 1 : 20 (2.5 g/50 ml), the soil exhibited full Cd recoveries. This illustrated that an increase of soil : solution ratio could prevent Andisol from

TABLE 2. *Cd Recoveries of Soils Extracted with Different Soil : Solution Ratios*

Soil	Ratio of soil : solution	Soil (W)/ solution (V) g/ml	Soil available Cd ppm	Cd recovery (%)		
				1 ppm added	2 ppm added	4 ppm added
APS2	1 : 5	10/50	0.835	101.5	99.4	97.6
	1 : 10	5/50	0.875	101.0	101.3	100.0
	1 : 20	2.5/50	0.920	99.0	99.5	100.3
KAPS	1 : 5	10/50	0.270	80.1	82.0	81.7
	1 : 10	5/50	0.364	96.0	95.7	96.7
	1 : 20	2.5/50	0.438	100.0	99.0	101.2

* : APS_2 was the Alluvial paddy $soil_2$ collected from Yamagata and KAPS was the paddy soil collected from Kawatabi Andisol.

re-absorption of Cd from extraction solution.

Cd Recoveries with Different Concentration of HCl

Effects of different HCl concentration on soil available Cd content and Cd recovery were shown in Fig. 1 and Table 3. Improvement of extraction concentration increased H^+ concentration of extraction solution and resulted in more

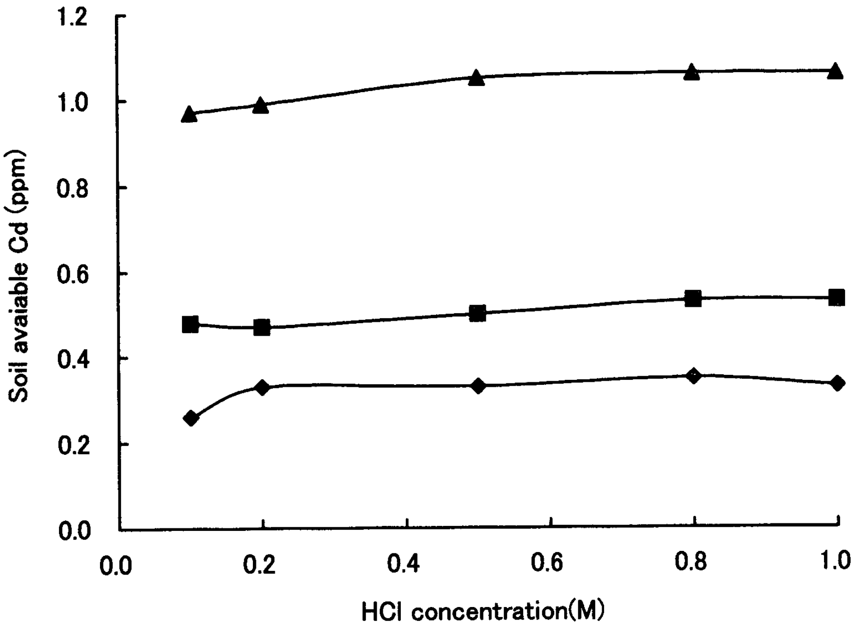

FIG. 1. Soil available Cd content extracted with different acid concentration.
—◆— Andisol 1 : 5 —■— Andisol 1 : 20 —▲— Alluvial soil 1 : 5

TABLE 3. *Effect of Concentrations of Extractant on Cd recovery of Andisol and Alluvial soil*

Soil	Soil : solution ratio	Cd added ppm	Recovery of Cd				
			0.1 M	0.2 M	0.5 M	0.8 M	1.0 M
APS2	1 : 5	1	100.5				100.0
		2	100.0				98.8
		4	101.5				99.0
KAPS	1 : 5	1	84.5	92.0	94.5	92.0	96.1
		2	84.7	91.0	94.3	91.5	93.8
		4	85.0	92.4	94.8	91.5	94.3
KAPS	1 : 20	4	101.3	101.5	100.3	102.5	101.5
		16	100.4	102.4	98.9	101.2	102.5

* : APS_2 was the Alluvial paddy $soil_2$ collected from Yamagata, and KAPS was the paddy soil collected from Kawatabi Andisol.

Cd^{2+} released from the soil. Soil available Cd contents of both soils increased with the increasing HCl concentrations. However, when it was more than 0.5 M, the concentration of HCl had little influence on soil available Cd extraction (Fig. 1).

With a soil : solution ratio of 1 : 5, the Cd recoveries of KAPS varied with HCl concentrations. When the soil was extracted by 0.1 M HCl, the recovery was 84.5%~85.0%, but when it was extracted by HCl with concentrations from 0.2 M to 1.0 M, the recoveries were in the range of 91.0% to 96.0%. Increase of extractant concentration in this range did not increase the Cd recovery obviously. While for APS_2, all concentrations employed here showed full recoveries.

With a soil : solution ratio of 1 : 20, the Cd recoveries of KAPS were in the range of 98.9% to 102.5%. Soils did not reabsorb the Cd from extraction solution, though the Cd concentration in extraction slurry was very high.

Cd Recoveries of Different Andisols

Data in Table 4 showed that the Cd recoveries of Andisols ranged from 23.1% to 92.4% when extracted by the stipulated protocol, and thus almost all of Andisols did not exhibit high or full recoveries of Cd. This illustrated further that Andisols had a high absorption capacity and they reabsorbed Cd that had

TABLE 4. *Soil Available Cd Contents and Their Recoveries of Different Andisols*

Soil : solution ratio	Soils	Location	Soil Cd content (ppm)	Cd recovery (%)
1 : 5	Allophanic soil (A)	Takizawa A1	0.151	71.9
		Takizawa A2	0.047	72.8
		Utsunomiya A	0.080	65.9
	Allophanic soil (B)	Takizawa B	0.053	87.8
		Utsunomiya B	0.055	82.1
	Non-allophanic soil	Mukaiyama A1	0.220	62.4
		Mukaiyama A3	0.045	23.1
		Kawatabi A	0.278	82.1
		Hitsujigaoka	0.121	92.4
1 : 20	Allophanic soil (A)	Takizawa A1	0.250	97.6
		Takizawa A2	0.081	98.0
		Utsunomiya A	0.137	99.2
	Allophanic soil (B)	Takizawa B	0.127	102.1
		Utsunomiya B	0.115	99.8
	Non-allophanic soil	Mukaiyama A1	0.372	96.8
		Mukaiyama A3	0.132	76.1
		Kawatabi A	0.429	98.0
		Hitsujigaoka	0.152	100.9

been released from soils. The increase of soil : solution ratio or the decrease of soil weight not only resulted in an increase of cadmium extracted from soils, but also full Cd recoveries of soils used in this experiment except Mukaiyama A3 soil. This also indicated that for most of Andisols, soil-extractant equilibrium had been reached at the soil : solution ratio of 1 : 20.

Conclusion

This experiment showed that there were some doubts in determining available Cd of Andisols by the method stipulated in Japan. Because Andisols had very high ion absorption ability, soil-extraction equilibrium had not been reached under the extraction condition, and soils still absorbed Cd from extraction slurry. It is very important to determine available Cd in Andisol correctly, because Andisol is one of the most widely distributed soils in Japan. The results showed that soil : solution ratio of 1 : 20 (2.5 g/50 ml) was better than that of 1 : 5 (10 g/50 ml) and could get good result, while increasing extractant concentration did little good for available Cd determination of Andisol. The following protocol was recommended by the authors :

Weigh 2.5 g of air-dried sample into 100 ml polyethylene bottle. Add 50 ml 0.1 MHCl and cap them. Place on a horizontal reciprocating shaker at 30°C, 145 cycles min^{-1} for 1 hour. Filter the slurry through No. 5C filter paper, and then determine the Cd concentration in filtrate by AAS or ICP.

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