Research Article

Relationship between Cadmium Fractions Obtained by Sequential Extraction of Soil and the Soil Properties in Contaminated and Uncontaminated Paddy Soils

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The method for the sequential extraction of cadmium from soil was adapted to investigate the relationship between different chemical forms of cadmium in soils and the soil properties of Cd-contaminated and uncontaminated paddy soils. Air-dried soil samples from each field site were sequentially fractionated into five forms: exchangeable Cd, inorganically bound Cd, organically bound Cd, oxide-occluded fraction, and residual Cd. The average and range of soil properties such as pH, total C, total N, CEC, exchangeable Ca, Mg, K, base saturation, available phosphate, particle size distribution, free iron oxide, oxalate extractable Al, and Fe were somewhat similar between uncontaminated and contaminated soils. The average total Cd in uncontaminated and contaminated soils was 0.26 and 0.65 mg kg⁻¹, respectively. The proportions of soil Cd fractions did not differ between the uncontaminated and contaminated soils, although the Cd concentration of several fractions in contaminated soils was statistically higher than those in uncontaminated soils except for residual fraction. The proportion of exchangeable Cd was correlated with the CEC and phosphate absorption coefficient in contaminated soil but not in uncontaminated soil. Thus, soil properties appear to affect the proportions of soil Cd fractions in contaminated soil and should be considered when evaluating soil Cd mobility.

1. Introduction

Under Japan's *Food Sanitation Act*, the Cd concentration of unpolished rice must not be higher than 0.4 mg kg⁻¹ on or after February 28, 2011 [1]. The official method for extracting soil Cd to estimate the extent of soil contamination generally uses a 0.1 mol L⁻¹ HCl solution, but the concentration of Cd estimated by this method tends to be unrelated to the Cd concentration of unpolished rice grains [2, 3]. Therefore, various extraction methods have been tested to determine the plant-available Cd concentration in contaminated soil, and the Cd concentrations in some upland plants have shown high correlations with plant-available soil Cd concentrations [4, 5].

Despite this progress, the association of soil properties with the Cd concentration of paddy rice—especially the rice

grain—has not been evaluated [2] because the rapid shifts between submerged and drained conditions affect the solubility of soil Cd due to the change in oxidation-reduction potential. Chino [6] reported that most of the Cd taken up by rice plants in the 10 days after heading was transported to the grain but that the final Cd concentration was determined by the oxidation-reduction potential in this period. The Cd concentration of rice grown in paddy soil was greatly affected by the number of days of dry conditions after heading [7]. It is therefore difficult to estimate the Cd concentration of rice grains by analyzing dried soil. Nevertheless, an assessment of potential risk apart from the influence of the water condition of soils is useful for zoning high-risk fields and deciding on countermeasures or remediation.

The sequential extraction of soil Cd can be used to evaluate Cd behavior in soil and its availability to plants.

The proportion of exchangeable Cd (ex-Cd) is much higher in contaminated soil than in uncontaminated soil [8]. Hattori et al. [9] found that it is possible to estimate the Cd concentration of brown rice from the ex-Cd concentration in the soil at the time of heading. This result suggests that the Cd concentration in rice grains may be affected by the ex-Cd concentration in the soil. However, the ex-Cd concentration decreases with increasing soil pH [10], submergence [11], or the application of organic matter [12]. Correlation analysis also revealed that pH was the most dominant soil variable affecting soil solution Cd concentration and sorption and desorption of native and added Cd in 29 New Zealand soils. However, organic matter (OM), cation exchange capacity (CEC), and total soil Cd were also found to be important [13]. The exchangeable fraction of Cd as determined by 1 M MgCl_2 in the sequential extraction procedure increased, whereas the Fe-Mn oxide bound fraction decreased, with increasing levels of organic matter addition [14]. As mentioned above, some soil properties could influence the solubility and mobility of soils Cd, and the degree of the influence is thought to be different between contaminated and uncontaminated soils. Thus, there is a need to compare the relation between Cd fractions and soil characteristics in both contaminated and uncontaminated soil. Furthermore, any changes in the proportion of ex-Cd lead to changes in the proportions of inorganically bound, organically bound, and oxide-occluded Cd. However, few articles have compared the relationships between Cd fractions in soil and soil properties in uncontaminated and contaminated soils of similar character. Therefore, to support the assessment of potential Cd risk in arable soils, it is important to determine the proportions of each soil Cd fraction by sequential extraction of soils.

The aim of this study was to evaluate the relationships between Cd fractions and soil properties in uncontaminated and contaminated soils.

2. Materials and Methods

2.1. Soils. Samples of Cd-contaminated soil were collected from 10 paddy fields in Hokuriku district that were contaminated with Cd by mining waste water and sediments deposited by flooding from the 1930s to 1960s [15]. It is probable that fields in this area produce rice grains with Cd concentrations above $0.4 \text{ mg Cd kg}^{-1}$, the new international threshold established by the Codex Alimentarius Commission [16] for Cd concentrations in brown rice. Uncontaminated soil samples were collected from 10 other paddy fields. All soils were collected from the plow layer from five points in each field and were bulked before analysis.

2.2. Analysis of Soil Physicochemical Properties. All samples were air-dried and passed through a 2-mm-mesh sieve before analysis. Soil pH was determined using a glass electrode (TOA pH meter HM-30S, Japan) with a 1:2.5 w/w ratio of soil to either water or 1 mol L^{-1} KCl. The total carbon and total nitrogen concentrations were measured using an elemental analyzer (Perkin Elmer 2400 II, USA). There is no replication of the soil chemical analysis and the sequential

extraction, because we applied the regression analysis for the data analysis.

2.3. Sequential Extraction of Soil Cd. We extracted the soil Cd by means of a single-extraction method with 0.1 mol L^{-1} HCl solution (1:5 w/v) by shaking side-to-side for 1 h [17]. The sequential extraction of Cd from soil was performed as follows (modified from [18]) using 3 g of dry soil and 30 mL of extraction solution. First, the ex-Cd fraction was obtained by extraction with 0.05 mol L^{-1} $\text{Ca}(\text{NO}_3)_2$ (1:10 w/v, 24 h shaking), and the extract was separated by centrifugation. Next, to obtain the inorganically bound Cd (in-Cd), the residue of the ex-Cd fraction was reextracted with 2.5% acetic acid (1:10 w/v, 24 h shaking). The organically bound Cd (or-Cd) was obtained by extraction with 2.5% acetic acid (1:10 w/v, 24 h shaking) after the decomposition of organic matter from the residue of the in-Cd fraction with 6% H_2O_2 . Finally, the oxide-occluded Cd (oc-Cd) was extracted from the residue of the or-Cd fraction with a mixture of 0.1 mol L^{-1} oxalate and 0.175 mol L^{-1} ammonium oxalate (1:30 w/v) in a boiling water bath for 1 h with occasional stirring. Total soil Cd was quantified by digestion with concentrated HNO_3 and 60% HClO_4 . The difference between total Cd and the summed extracted fractions gave the residual fraction (re-Cd). The particle size distribution was determined using the pipette method [19]. The cation exchange capacity (CEC) and exchangeable cations were analyzed after extraction with 1 mol L^{-1} $\text{CH}_3\text{COOHNH}_4$ (pH 7.0) [20]. Other analyses were performed based on the methods described by [21].

2.4. Statistical Analysis. The relationship between soil Cd fraction and soil properties was investigated using Pearson's correlation coefficient test at $P = 0.05$, 0.01 , and 0.001 in Statcel 2 software [22]. Soil properties identified as statistically significant at $P < 0.001$ in contaminated soil were compared with those in uncontaminated soil.

3. Results

3.1. Soil Properties. The chemical property values for the uncontaminated and contaminated soils were mentioned in Table 1. The soil textures ranged from sandy loam to light clay. None of the soil chemical and physical properties differed significantly between uncontaminated and contaminated soils ($P > 0.05$).

3.2. Chemical Forms of Cd in Uncontaminated and Contaminated Soils. Table 2 shows the concentration of each form of Cd and its proportion of the total. The average total Cd concentration was 0.26 mg kg^{-1} with a range from 0.21 to 0.36 mg kg^{-1} in uncontaminated soils. In contaminated soils, the average Cd concentration was 0.65 mg kg^{-1} ranging from 0.43 to 0.88 mg kg^{-1} . The average concentration of each form of Cd (mg kg^{-1}) in uncontaminated and contaminated soils was exchangeable (0.07, 0.16); inorganically bound (0.07, 0.17); organically bound (0.08, 0.19); oxide occluded (0.03, 0.11); and residue (0.02, 0.03). The concentration of each form

TABLE 1: Soil properties.

Soil	Soil type ^a	pH (H ₂ O)	pH (KCl)	T-C (g kg ⁻¹)	T-N (g kg ⁻¹)	Exchangeable cations				Base saturation (%)	Available phosphate (mg kg ⁻¹)	PAC (g kg ⁻¹)	Particle size distr.			Free iron oxide (g kg ⁻¹)		Oxalate extractable		
						CEC (cmol _c kg ⁻¹)	Ca (cmol _c kg ⁻¹)	Mg (cmol _c kg ⁻¹)	K (cmol _c kg ⁻¹)				Clay (10 ⁻² kg kg ⁻¹)	Silt (10 ⁻² kg kg ⁻¹)	Sand (10 ⁻² kg kg ⁻¹)			Alo	Feo	Alo + 1/2 Feo (g kg ⁻¹)
Uncontaminated-1	Fluvaquents	5.5	4.0	25.4	2.7	18.7	5.2	1.7	0.3	38.0	272	9.2	28.2	34.1	37.7	8.9	3.2	3.2	5.5	6.0
Uncontaminated-2	Fluvaquents	6.5	5.5	20.7	1.6	9.1	6.0	1.5	0.3	86.7	912	4.7	4.4	18.2	77.4	9.4	3.1	2.8	4.4	4.4
Uncontaminated-3	Endoaquands	5.8	4.8	62.1	4.4	25.8	9.8	2.7	0.8	51.7	434	10.5	38.4	31.5	30.0	8.5	4.7	3.8	6.6	6.6
Uncontaminated-4	Fluvaquents	5.8	4.2	15.8	0.9	8.7	2.7	0.7	0.2	41.7	188	3.8	8.6	12.3	79.1	5.5	2.0	1.8	3.8	3.8
Uncontaminated-5	Fluvaquents	5.9	4.3	24.4	1.8	16.1	6.3	1.4	0.3	49.6	327	5.8	16.4	19.7	63.9	5.0	2.7	1.6	4.3	4.3
Uncontaminated-6	Fluvaquents	5.5	4.0	22.9	1.8	13.3	3.6	1.1	0.4	38.5	148	6.0	13.8	17.8	68.5	3.1	2.2	2.2	4.4	4.4
Uncontaminated-7	Epiaquepts	5.5	4.1	33.6	2.2	20.6	5.4	2.1	0.2	38.1	145	9.8	22.8	23.7	53.5	10.9	3.4	4.7	8.1	8.1
Uncontaminated-8	Fluvaquents	5.5	4.0	25.5	1.6	17.6	5.4	2.0	0.5	45.4	160	7.7	17.5	30.4	52.1	11.0	2.4	5.4	7.9	7.9
Uncontaminated-9	Fluvaquents	6.1	4.6	19.6	1.7	9.9	3.8	1.3	0.3	54.8	236	5.6	11.6	19.1	69.3	9.2	3.9	1.9	5.8	5.8
Uncontaminated-10	Fluvaquents	6.0	4.4	18.8	2.1	15.2	7.2	2.6	0.3	66.2	224	7.2	18.8	23.7	57.6	9.6	2.4	4.9	7.3	7.3
Contaminated-1	Fluvaquents	5.7	4.5	32.0	2.6	14.3	4.3	0.9	0.1	37.0	570	6.6	14.1	17.3	68.6	7.7	3.1	2.9	4.6	4.6
Contaminated-2	Fluvaquents	5.5	4.3	32.6	2.5	10.6	3.1	0.8	0.2	38.4	277	4.3	10.1	15.0	74.9	4.7	2.2	2.0	3.2	3.2
Contaminated-3	Fluvaquents	5.6	4.7	46.3	3.7	17.6	6.0	1.9	0.6	47.9	708	7.6	14.8	22.1	63.1	9.1	4.1	4.7	6.5	6.5
Contaminated-4	Fluvaquents	6.1	4.5	32.6	2.6	12.1	3.4	1.0	0.3	38.8	401	4.2	14.4	14.7	70.9	4.5	2.7	2.9	4.2	4.2
Contaminated-5	Fluvaquents	5.9	4.9	37.8	2.8	15.4	6.2	1.3	0.3	50.7	514	6.6	10.2	23.5	66.3	6.3	3.7	2.2	4.8	4.8
Contaminated-6	Endoaquands	6.2	5.1	43.5	2.9	20.5	6.9	2.7	0.4	48.8	880	10.4	16.5	17.1	66.4	9.6	5.8	2.7	7.1	7.1
Contaminated-7	Endoaquands	5.6	4.5	48.2	3.7	17.4	5.2	1.2	0.5	39.6	349	9.0	23.7	31.6	44.7	11.4	4.6	3.4	6.3	6.3
Contaminated-8	Fluvaquents	5.7	4.5	12.7	1.0	8.2	2.0	0.6	0.2	34.0	143	2.9	5.6	7.8	86.6	12.3	0.9	3.4	2.6	2.6
Contaminated-9	Fluvaquents	5.9	4.7	15.2	1.2	8.3	2.9	1.1	0.3	51.8	175	3.6	7.0	11.7	81.3	9.7	1.0	3.1	2.5	2.5
Contaminated-10	Fluvaquents	5.9	4.9	33.5	2.6	18.4	7.9	1.9	0.2	54.7	528	8.5	22.3	36.2	41.5	13.9	4.2	5.4	6.9	6.9
Uncontaminated-AV		5.8	4.4	26.9	2.1	15.5	5.5	1.0	0.3	51.0	305	7.0	18.1	23.1	58.9	8.1	3.0	3.5	5.9	5.9
Contaminated-AV		5.8	4.7	33.4	2.6	14.3	4.8	0.8	0.3	44.2	455	6.4	13.9	19.7	66.4	8.9	3.2	3.3	4.9	4.9

T-C, total carbon; T-N, total nitrogen; CEC, cation exchange capacity; PAC, phosphate absorption coefficient.
^aClassified by Soil Taxonomy [23].

TABLE 2: Soil Cd content and fractions of total Cd.

Soil	Cd content by sequential extraction							Fraction of total Cd					
	Total (mg kg ⁻¹)	0.1 M HCl ^a (mg kg ⁻¹)	Exchangeable	Inorganically bound	Organically bound	Oxide occluded	Residue	0.1 M HCl	Exchangeable	Inorganically bound	Organically bound	Oxide occluded	Residue
					(mg kg ⁻¹)					(%)			
Untaminated-1	0.22	0.11	0.069	0.037	0.046	0.045	0.022	50.3	31.5	16.7	21.1	20.6	10.2
Untaminated-2	0.36	0.21	0.043	0.131	0.105	0.036	0.042	58.7	12.0	36.8	29.5	10.0	11.7
Untaminated-3	0.33	0.18	0.051	0.119	0.108	0.024	0.024	56.4	15.7	36.5	33.0	7.4	7.4
Untaminated-4	0.27	0.18	0.105	0.053	0.073	0.021	0.017	65.2	39.0	19.5	27.2	7.9	6.3
Untaminated-5	0.29	0.23	0.079	0.085	0.091	0.017	0.022	78.0	27.0	28.8	30.9	5.8	7.5
Untaminated-6	0.23	0.16	0.092	0.058	0.059	0.012	0.013	68.0	39.3	24.9	25.0	5.1	5.7
Untaminated-7	0.21	0.17	0.047	0.052	0.079	0.012	0.019	79.6	22.5	24.7	38.0	5.9	8.9
Untaminated-8	0.21	0.15	0.064	0.050	0.063	0.015	0.018	73.4	30.4	23.9	30.0	7.3	8.5
Untaminated-9	0.22	0.10	0.035	0.048	0.061	0.039	0.036	44.1	15.9	21.7	28.0	17.8	16.6
Untaminated-10	0.28	0.18	0.073	0.057	0.070	0.052	0.027	65.3	26.2	20.3	25.0	18.6	9.8
Contaminated-1	0.43	0.33	0.096	0.113	0.140	0.063	0.020	76.1	22.2	26.2	32.4	14.5	4.6
Contaminated-2	0.55	0.31	0.166	0.118	0.163	0.083	0.019	56.9	30.2	21.5	29.6	15.1	3.5
Contaminated-3	0.58	0.43	0.113	0.167	0.200	0.079	0.025	73.3	19.4	28.6	34.2	13.4	4.3
Contaminated-4	0.61	0.39	0.224	0.126	0.164	0.070	0.023	63.7	36.8	20.8	27.1	11.5	3.7
Contaminated-5	0.62	0.43	0.107	0.187	0.184	0.104	0.038	69.2	17.2	30.2	29.7	16.7	6.1
Contaminated-6	0.67	0.50	0.048	0.192	0.258	0.141	0.031	73.8	7.2	28.6	38.4	21.0	4.7
Contaminated-7	0.67	0.60	0.137	0.193	0.218	0.077	0.049	89.2	20.3	28.6	32.3	11.5	7.3
Contaminated-8	0.74	0.45	0.288	0.129	0.132	0.155	0.032	60.4	39.1	17.5	18.0	21.1	4.3
Contaminated-9	0.79	0.62	0.272	0.202	0.168	0.117	0.031	78.9	34.4	25.6	21.3	14.8	3.9
Contaminated-10	0.88	0.75	0.142	0.280	0.231	0.166	0.061	85.5	16.1	31.8	26.2	18.9	7.0
Untaminated-AV	0.26	0.17	0.07	0.07	0.08	0.03	0.02	63.9	25.9	25.4	28.8	10.6	9.2
Contaminated-AV	0.65	0.48	0.16	0.17	0.19	0.11	0.03	72.7	24.3	26.0	28.9	15.9	4.9
<i>t</i> -test	<i>P</i> < 0.001	<i>P</i> < 0.001	<i>P</i> < 0.01	<i>P</i> < 0.001	<i>P</i> < 0.001	<i>P</i> < 0.001	<i>P</i> < 0.001	<i>P</i> < 0.05	<i>P</i> < 0.001				<i>P</i> < 0.001

^aCd content extracted with 0.1 mol L⁻¹ HCl (1:5 w/v).

TABLE 3: Correlation between proportions of Cd chemical forms and soil properties^a.

Soil properties	Uncontaminated soils					Contaminated soils				
	Exchangeable	Inorganically bound	Organically bound	Oxide occluded	Residue	Exchangeable	Inorganically bound	Organically bound	Oxide occluded	Residue
pH(H ₂ O)	(-)*									
pH(KCl)	(-)**	(+)*				(-)*	(+)*			
T-C						(-)*		(+)**		
T-N						(-)*		(+)**		
CEC						(-)**	(+)**	(+)**		
Ex-Ca						(-)**	(+)**			(+)*
Ex-Mg						(-)**	(+)*			
Ex-K										
Base saturation	(-)*						(+)**			
Available phosphate	(-)*	(+)*				(-)**		(+)**		
PAC						(-)**	(+)**	(+)**		
Free iron oxide										
Sand						(+)*	(-)*			(-)**
Silt							(+)**			(+)**
Clay										(+)*
Alo + 1/2 Feo ^b						(-)**	(+)**	(+)*		

^a(+): positive correlation, (-): negative correlation, * ($P < 0.05$), ** ($P < 0.01$), and *** ($P < 0.001$).

^bExtracted with acid oxalate.

of Cd (except re-Cd) was significantly higher in contaminated soils than in uncontaminated soils ($P < 0.01$). The proportions of ex-Cd, in-Cd, and or-Cd were not significantly different between the soil types, but those of ox-Cd ($P < 0.05$) and re-Cd ($P < 0.001$) were different. The sum of the proportions of ex-Cd, in-Cd, and or-Cd ranged from 65% to 90% in both soils and did not differ significantly.

3.3. Proportions of Chemical Forms of Cd and Soil Properties.

The proportions of most chemical forms of Cd exhibited correlations with several soil properties (Table 3). In uncontaminated soils, ex-Cd displayed negative correlations with pH (H₂O), pH (KCl), base saturation, and available phosphate ($P < 0.05$ or 0.01), and in-Cd was positively correlated with pH (KCl) and available phosphate ($P < 0.05$). No other soil properties displayed any correlation with any Cd fractions in uncontaminated soils.

In the contaminated soils, ex-Cd showed strong negative correlations with CEC, ex-Ca, ex-Mg, available phosphate, PAC, and amorphous iron and aluminum oxides ($P < 0.001$ or $P < 0.01$), and in-Cd showed strong positive correlations with CEC, ex-Ca, base saturation, PAC, silt content, and amorphous iron and aluminum oxides ($P < 0.001$ or 0.01). Additionally, strong positive correlations were observed between or-Cd and total C, total N, CEC, available phosphate, and PAC ($P < 0.001$ or 0.01); and re-Cd was correlated negatively with sand content ($P < 0.01$) and positively with silt content ($P < 0.001$). The remaining properties pH (H₂O),

ex-K, and free iron oxide were not correlated with any Cd fractions in either type of soil. Also, there are no correlations between ox-Cd and soil properties.

The soil properties that exhibited strong correlations with the proportions of Cd fractions in contaminated soils are shown in Figure 1. It is suggested that several of the soil properties in Figure 1 affect the proportions of Cd chemical forms and specifically the transformation of ex-Cd into in-Cd or or-Cd.

4. Discussion

4.1. Comparison of the Relationships between Soil Properties and Proportion of Exchangeable Cd between Uncontaminated and Contaminated Soils.

Few articles have compared the relationships between Cd fractions and soil properties in uncontaminated and contaminated soils in detail. Sadamoto et al. [18] reported that the proportion of ex-Cd was approximately 20% in uncontaminated soil but approximately 30 to 40% in contaminated soil. However, we found no statistical difference in this proportion between uncontaminated and contaminated soils. Sadamoto et al. [18] used only three fluvic paddy soils (two contaminated, one uncontaminated), which did not represent a wide variety of properties such as particle size and total C content. Moreover, their contaminated soils contained large amounts of copper (Cu) and a higher organic fraction than ours. The solubility constants of chelates formed between Cd and soil humic acid at pH 5 and 7 are lower

FIGURE 1: Correlation between proportions of Cd chemical forms and soil properties in contaminated soil.

than those of Cu [24], so we consider that the Cd was distributed primarily in the exchangeable fraction due to its lower covalent bonding to humic acid compared to Cu. Morera et al. [25] studied the competitive adsorption of heavy

metals in different soils and reported that Cd was scarcely adsorbed in the presence of Cu. These results may identify the reason why the proportion of ex-Cd in the contaminated soil was not higher than that in the uncontaminated soil.

FIGURE 2: Relationships between cation exchange capacity (CEC), phosphate absorption coefficient (PAC), and relevant soil properties.

We suggest that the proportion of ex-Cd depends on the soil type and especially on differences in humic acid and Cu contents.

As the proportion of ex-Cd increased, the proportions of in-Cd and or-Cd decreased in both contaminated and uncontaminated soils (Table 2). Furthermore, there was no correlation between in-Cd and or-Cd. These fractions exist in equilibrium [26], so we consider that changes in soil moisture, soil pH, oxidation-reduction state, and/or the decomposition of organic matter led to changes in the chemical forms of Cd in soil. During the extraction process by using a mixture of oxalate and ascorbic acid, ferrous oxalate dehydrate could be precipitate, which induced coprecipitation of some metals except As and Cu in Andisols [27]. This provides question validity of the extraction method, while it was used even recently. In our experiment, the existence ratios of ox-Cd and re-Cd are relatively low compared to other fractions, suggesting minor role of those fractions to plant availability and dynamics in soils. The effect of changes in soil conditions on the forms of Cd should be analyzed further.

4.2. Relationship between Cd Chemical Forms and Soil Properties. Heavy metals in soils are adsorbed to clay minerals, free oxides, and humic substances. Many methods have been used to fractionate these heavy metals [28–30]. As the proportion of ex-Cd in contaminated soils was not significantly higher than that in uncontaminated soils, we examined the relationships between the proportion of ex-Cd and soil properties in contaminated soil in detail. In general, soil pH plays a major role in the adsorption of heavy metals: with decreasing soil pH, the proportion of ex-Cd increases [31] and the proportion of in-Cd decreases [32]. As the pH of our contaminated soils ranged from 5.5 to 6.2 and there was no correlation between soil pH and any of the Cd fractions under the experimental conditions, the soil pH had no effect on the soil Cd fractions in these soils. Humic substances have many surface functional groups and can bind specific heavy metals. The total C content, which indicates the humic substance content, was strongly correlated with the proportion of or-Cd in the contaminated soils. However, it was only slightly correlated with ex-Cd and

was not correlated with in-Cd. Therefore, the total C content primarily affected the or-Cd fraction. CEC and PAC were very strongly negatively correlated with ex-Cd and strongly positively correlated with in-Cd. We therefore investigated the relationships between the contents of total C, clay, and amorphous iron and aluminum oxides, which are considered to affect CEC and PAC [33, 34] (Figure 2). The total C and clay contents were strongly correlated, and the amorphous iron and aluminum oxides correlated very strongly with CEC and PAC. Thus, the main Cd adsorbents in our soil samples were amorphous iron and aluminum oxides.

The binding of metals to inorganic soil constituents involves a continuum of reactive sites, ranging from those where there are weak physical forces (van der Waals forces) and electrostatic outer-sphere complexes (e.g., ion exchange) to those where precipitation [35] or strong chemical bonds occur (by inner-sphere complexation). The outer-sphere complex is formed on a negative electron charge resulting from isomorphous substitution. Because this complex can release metals easily with changes in the soil solution, its contents are available to plants. In contrast, the inner-sphere complex forms on clay edges or on the surfaces of metal hydroxides, the active surface hydroxide groups of which are able to bind to metals via coordinate bonds [36]. Because these bonds are stronger than the outer-sphere ones, the plant availability of those adsorbed metals is relatively lower. We consider that the reduction in the proportion of ex-Cd with increasing CEC and PAC (Figure 1) was due to the formation of inner-sphere complexes with amorphous iron and aluminum oxides.

Yanagisawa et al. [2] suggested that the influence of soil texture, soil permeability, CEC, soil moisture, and other factors masks the correlation between soil properties and Cd content in brown rice. Because soil properties were correlated with the proportions of various Cd forms in our contaminated soils, we suggest that the soil properties determined the distribution of Cd forms derived from the same source.

Cd uptake by cabbage [10] and paddy rice [37] is affected by the fractions of Cd in the soil. Furthermore, the Cd content of soybean is affected by soil pH, soil Cd content as extracted by 0.1M HCl, and PAC [38]. Thus, soil properties are very important for Cd uptake and are major factors to consider in estimating potential Cd risk in soils.

5. Conclusion

The sequential extraction of cadmium from soil revealed the relationship between chemical forms of soil Cd and properties in contaminated and uncontaminated paddy soils. The proportions of soil Cd fractions were almost the same between the two soil groups, although the Cd concentration of several fractions in contaminated soils was statistically higher than those in uncontaminated soils except for residual fraction. The proportion of exchangeable Cd was correlated with the CEC and PAC in contaminated soil but not in uncontaminated soil, suggesting a new finding on the difference of Cd-chemical form between the two soil groups. Soil properties appear to affect the proportions of soil Cd

fractions in contaminated soil and should be considered when evaluating soil Cd mobility.

Conflict of Interests

The authors declare that there is no conflict of interests.

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