

# Revealing the Sources of Cadmium in Rice Plants under Pot and Field Conditions from Its Isotopic Fractionation

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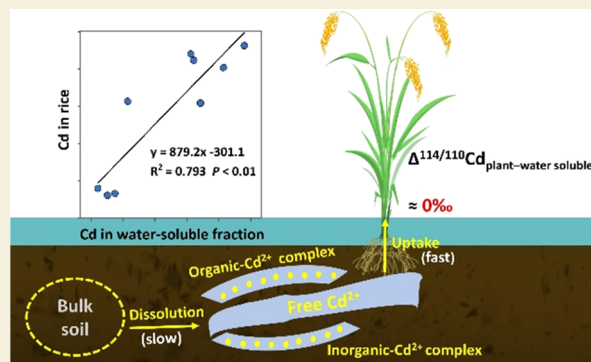
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**ABSTRACT:** The highly excessive uptake of cadmium (Cd) by rice plants is well known, but the transfer pathway and mechanism of Cd in the paddy system remain poorly understood. Herein, pot experiments and field investigation were systematically carried out for the first time to assess the phytoavailability of Cd and fingerprint its transfer pathway in the paddy system under different treatments (slaked lime and biochar amendments), with the aid of a pioneering Cd isotopic technique. Results unveiled that no obvious differences were displayed in the  $\delta^{114/110}\text{Cd}$  of  $\text{Ca}(\text{NO}_3)_2$ -extractable and acid-soluble fractions among different treatments in pot experiments, while the  $\delta^{114/110}\text{Cd}$  of the water-soluble fraction varied considerably from  $-0.88$  to  $-0.27\%$ , similar to those observed in whole rice plant [ $\Delta^{114/110}\text{Cd}_{\text{plant-water}} \approx 0$  ( $-0.06$  to  $-0.03\%$ )]. It indicates that the water-soluble fraction is likely the main source of phytoavailable Cd, which further contributes to its bioaccumulation in paddy systems. However,  $\Delta^{114/110}\text{Cd}_{\text{plant-water}}$  found in field conditions ( $-0.39 \pm 0.05\%$ ) was quite different from those observed in pot experiments, mostly owing to additional contribution derived from atmospheric deposition. All these findings demonstrate that the precise Cd isotopic compositions can provide robust and reliable evidence to reveal different transfer pathways of Cd and its phytoavailability in paddy systems.

**KEYWORDS:** cadmium, rice, isotopic fractionation, phytoavailability, water-soluble fraction, atmospheric deposition



## 1. INTRODUCTION

Cadmium (Cd) is a nonessential and highly toxic element to humans.<sup>1</sup> In recent decades, some agricultural soils in China have experienced an extremely rapid increase in Cd content due to various human activities.<sup>2</sup> Rice, a staple food for half of the human population, provides a dominant source of Cd exposure, especially in Asian countries.<sup>3</sup> For example, rice contributes to around 56% of the total dietary exposure of Cd for general populations in China, and it rises to 65% in the southern part due to higher rice consumption.<sup>4</sup> Therefore, it is of crucial significance to understand the sources of Cd accumulation in rice.

Root uptake from soils is recognized as the primary source of Cd in rice plants.<sup>5</sup> However, phytoavailable Cd, referring to the pool in soil that can be taken up and subsequently accumulated in plants, is still not well characterized. Multiple chemical extractions have suggested that Cd in specific extraction fractions (e.g., the acid-soluble fraction of the BCR sequential extraction procedure<sup>6</sup> and  $\text{Ca}(\text{NO}_3)_2$  extraction<sup>7</sup>) robustly correlates with its accumulation in plants.<sup>6,8</sup> This indicates that these chemical extraction fractions should be included or interrelated with phytoavailable Cd. Interestingly, our previous study observed a better positive relationship between Cd content in rice grains and that in the overlying

water rather than in the acid-soluble fraction in soil.<sup>9</sup> Furthermore, a recent study also showed that pharmaceuticals in soil pore water were the dominant bioavailable fraction for plant uptake.<sup>10</sup> These results imply that the water-soluble fraction may be the direct source of some accumulated pollutants, such as Cd, in plants from the soil. However, this hypothesis still needs to be critically validated.

Besides root uptake, recent studies have revealed that Cd on leaf surfaces, deposited from the atmosphere, could also be assimilated by rice plants.<sup>11,12</sup> Pertinent studies have observed that higher Cd input from atmospheric deposition was interrelated to higher Cd accumulation in rice plants.<sup>13–15</sup> Additionally, foliar spray of Cd has revealed that deposited Cd on rice leaves can be absorbed via the stomata pathway and then accumulated in rice plants.<sup>11</sup> Therefore, the Cd in atmospheric deposition could also be an important Cd source in rice plants from areas with high atmospheric deposition Cd.

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However, the quantitative contributions of soil phytoavailable Cd (root uptake) and atmospheric deposition (foliar uptake) to Cd accumulation in rice plants are not well understood.

Cadmium stable isotopic composition analysis has been demonstrated as a useful approach to unravel its sources and biogeochemical processes in the environment.<sup>16,17</sup> In a soil–rice plant system, Cd isotopes typically exhibit two key behaviors. First, a positive fractionation occurred from bulk soil to the soil solution or extraction. This is attributed to the fact that the Cd–O bonds for aqueous Cd are shorter and stiffer than for adsorbed Cd in soil.<sup>18,19</sup> Second, when Cd was frequently replenished, a negative fractionation occurred from the phytoavailable Cd source to the whole plant. This is because the roots preferentially uptake the light isotopes, which are more mobile than heavy isotopes in soils.<sup>19,20</sup> The isotopic composition of the whole rice plant can be traced back to the soil phytoavailable Cd source.<sup>17,21</sup> Furthermore, the Cd in atmospheric deposition is markedly enriched in light isotopes due to lighter isotopes preferentially released to the vapor phase during high-temperature industrial processes.<sup>22,23</sup> The different Cd isotopic compositions between the phytoavailable Cd in soil and Cd in atmospheric deposition can be used to quantify their respective contributions to the Cd accumulation in the whole rice plant.

In this study, pot and field experiments were performed, combined with total Cd and isotopic composition analysis, to identify Cd sources in a rice plant in a Cd-contaminated rice-producing area. First, rice pot experiments (control, slaked lime, and biochar treatment) were conducted in a greenhouse (without atmospheric deposition of Cd) to (1) identify the source of phytoavailable Cd in soil and (2) evaluate the effects of slaked lime and biochar, two commonly used amendments to increase specific/nonspecific adsorption or formation of Cd precipitation,<sup>9,24,25</sup> on phytoavailable Cd and corresponding isotopic fractionation. Further, field samples from a typical Cd-contaminated rice-producing area within the same soil sampling area as the pot experiments, including mature rice plants, corresponding soil, and atmospheric deposition, were analyzed to quantify the specific contributions of soil phytoavailable Cd and atmospheric deposition to Cd accumulation in whole rice plants under field conditions.

## 2. EXPERIMENTAL SECTION

### 2.1. Sampling Site Overview

Soils used in the pot experiments were sampled from the topsoil (0–20 cm) of a rice-producing field (113.25° E, 27.13° N) in Youxian, Hunan, a typical Cd-contaminated rice-producing area in China.<sup>26</sup> Within 3 km of this field, there are coal-fired power factories, tile factories, and cement industries that could be potential pollution sources of Cd.<sup>26</sup> These soils were air-dried and passed through a 5 mm sieve. The soil pH, organic matter, Cd, and other element concentrations were determined and given in the Supporting Information (SI, Table S1). The soil pH, total organic carbon, and cation exchange capacity were 5.25, 28.50 g kg<sup>-1</sup>, and 5.82 cmol kg<sup>-1</sup>, respectively. The total Cd concentration in bulk soil was 0.44 mg kg<sup>-1</sup>, which slightly exceeds the control standard of China for paddy soil (<0.3 mg kg<sup>-1</sup> when pH ≤ 5.5).<sup>27</sup>

### 2.2. Pot Experiment

The rice plant (*Oryza sativa* L., cultivar Yexiangyoulisi), widely planted at the sampling site, was used in the pot experiments. Three treatments, including the control (CK), slaked lime, and biochar, were chosen for this experiment. In the CK treatment, soils were homogeneously mixed with solid fertilizers (2.15 g of urea, 1.44 g of potassium dihydrogen phosphate, and 0.4 g of potassium chloride

as analytical grade reagents, corresponding to 0.20, 0.33, and 0.08 g kg<sup>-1</sup> soil (dry weight) N, P, and K, respectively), following local rice management practices.<sup>9</sup> In the slaked lime and biochar treatment, soils were homogeneously mixed with 0.5% (w/w) calcium hydroxide (Ca(OH)<sub>2</sub>) as analytical grade reagents or 5% (w/w) rice straw biochar (450 °C, pH 5.12, and sieved 2 mm), respectively, in addition to the solid fertilizers as mentioned above. Deionized water (>18.2 MΩ·cm) was added to these pots to maintain 1 week's flooding to incubate the soil. Then, the germinated rice seedlings were transplanted into the pots (15 cm × 30 cm) with 5 kg of soil. Two rice plants were planted in each pot, and three replicates were performed for each of the treatment. During rice growth, deionized water was added daily to maintain the water level approximately 3 cm above the soil surface until the filling stage. Intermittent flooding (flooding before the overlying water evaporation) was maintained between the filling and harvest stages to simulate field production practices.<sup>9</sup> Details of rice germination and cultivation processes are provided in Text S1.

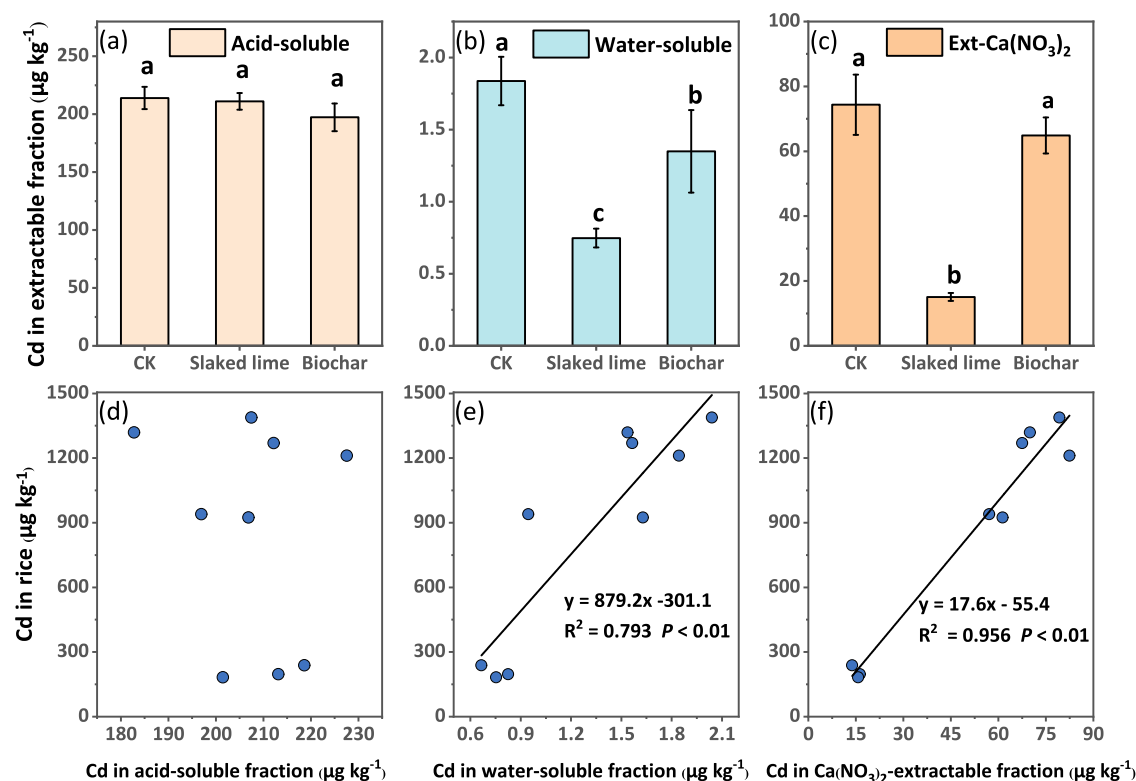
### 2.3. Sample Collection and Preparation

Surface soils (0–20 cm) in every pot were sampled under drained conditions at maturity, freeze-dried, and sieved (<0.147 mm). The soil (0.1 g) was digested with HCl, HNO<sub>3</sub>, and HF (6:2:2, v/v) using a microwave digester (MARS 6, CEM, Matthews, NC) for total Cd analysis.<sup>28</sup> The plant-available Cd pools were extracted as water-soluble Cd and Ca(NO<sub>3</sub>)<sub>2</sub>-extractable Cd. The water-soluble Cd was extracted by dissolving the soluble fraction, including free Cd ions and Cd complexed with dissolved organic matter and other ligands, in deionized water. The Ca(NO<sub>3</sub>)<sub>2</sub>-extractable Cd includes both water-soluble Cd and partially adsorbed onto inorganic/organic soil components through electrostatic interaction, which can be liberated through ion exchange with Ca ions. Briefly, (1) water-soluble Cd was extracted using 10.00 g of soil in 40 mL of deionized water, shaken at 25 °C for 16 h, centrifuged at 3354g for 15 min, and filtered through a 0.45 μm polyethersulfone membrane, and (2) Ca(NO<sub>3</sub>)<sub>2</sub>-extractable Cd was prepared using 3.00 g of soil in 30 mL of a 0.05 mol L<sup>-1</sup> Ca(NO<sub>3</sub>)<sub>2</sub> solution, then shaken, centrifuged, and filtered following the same procedure as water-soluble Cd extraction.<sup>29</sup> In addition, various fractions of Cd, including acid-soluble, reducible, oxidizable, and residual fractions, were also extracted to assess the mobility of Cd in soil according to a modified BCR sequential extraction procedure.<sup>30</sup> Independent soil samples were utilized for the water, Ca(NO<sub>3</sub>)<sub>2</sub>, and BCR sequential extractions. Procedural blanks were conducted with only extraction reagents following the same procedure as the samples. Further details of the modified BCR sequential extraction procedure are provided in Text S2.

At maturity, whole rice plants were collected from each pot under drained conditions. The plant samples were separated into three parts: root, shoot (stem and leaf), and grain (brown rice and husk; Figure S1). All plant samples were washed with running water to remove the surface particles before being washed 3 times with deionized water and then freeze-dried. The dry weight of plant tissues was recorded. The plant samples (0.25 g) were digested with HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and HF (6:2:0.5, v/v) using a microwave digester.<sup>28</sup> For some plant samples under slaked lime treatment with low Cd concentrations, 0.3–0.5 g samples were weighted and digested for total Cd and isotopic composition analysis.

### 2.4. Field Investigation

The surface soils (0–20 cm), rice plants, and dry atmospheric deposition were sampled from the field (Youxian, Hunan) within the same soil sampling area as the pot experiments to track the sources of Cd in rice. Three rice samples (Yexiangyoulisi, the same cultivar as in the pot experiments) at maturity and corresponding soils were randomly collected and prepared following the same procedure as that for the pot experiment. Rice plant samples were washed, freeze-dried, and digested with concentrated HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and HF (6:2:0.5, v/v). The total Cd, water-soluble Cd, and Ca(NO<sub>3</sub>)<sub>2</sub>-extractable Cd of soil samples were extracted as described above. Atmospheric deposition samples were collected during rice growth using a plastic barrel with an inner diameter of 34 cm and a height of 31 cm. Detailed



**Figure 1.** Concentration of Cd in acid-soluble (a), water-soluble (b), and  $\text{Ca}(\text{NO}_3)_2$ -extractable fractions. Three individual replicates of pots were analyzed with the error bars referring to  $\pm$  SD. The letters (a–c) in Figure (a–c) indicate significant differences by LSD at the  $P < 0.05$  level. Figure (d–f) shows the relations between Cd concentration in extractable fractions and the whole rice plant under pot experiments.

information on sampling and preparation procedures is provided in Text S3.

### 2.5. Cadmium Concentration and Isotope Measurement

Concentrations of Cd in bulk soil, soil extracts, and plant tissues were measured by using inductively coupled plasma-mass spectrometry (ICP-MS, iCAP TQ, Thermo Scientific, Bremen, Germany) under kinetic energy discrimination mode to avoid polyatomic interferences on Cd analysis.<sup>9</sup> During measurement, blanks, internal standards (rhodium solution), Cd standard solution, and reference materials (GSS-5 (soil), GSB-1 (rice), and GSB-1a (rice)) were used for quality assurance and quality control. Digestion recoveries of Cd in soil and rice reference materials exceeded 98%.

### 2.6. Cadmium Isotope Measurement

All extracted or digested solutions were evaporated to dryness in the presence of  $^{111}\text{Cd}$ – $^{113}\text{Cd}$  double spike (double spike/sample  $\approx 0.5$ ) and then redissolved in 2 mL of HCl (2 mol  $\text{L}^{-1}$ ) for chemical purification. This process was used to remove matrix elements from samples following a previously reported protocol.<sup>28</sup> In short, the sample solution was loaded into a microcolumn filled with 3 mL of AG-MP-1 M anionic exchange resin. Matrix elements such as Ca, Zr, Mo, Zn, and Sn were removed using different concentrations (2, 0.3, 0.06, and 0.012 mol  $\text{L}^{-1}$ ) of HCl. Cadmium was then eluted by 0.0012 mol  $\text{L}^{-1}$  HCl into Teflon beakers. Procedural blanks and reference materials (NIST 2711a (soil), GSS-5 (soil), and BCR-679 (plant)) were also processed by using the same procedure. The Cd procedural blank was below 0.2 ng (negligible) and equivalent to less than 0.5% of the Cd mass in the sample with the lowest Cd content. The Cd isotopic compositions of all samples were determined by a high-resolution multiple-collector ICP-MS in “dry” plasma conditions (Neptune Plus, Thermo Scientific, Bremen, Germany).<sup>28</sup> Four reference Cd solutions (AAS Cd, Thermo-Cd, GSB-Cd, and NIST 3108 with a double spike) were analyzed to monitor the precision and accuracy of Cd isotopic composition. The long-term precision of NIST 3108 was  $\pm 0.05\%$  (2SD).<sup>28</sup> Furthermore, the measured

isotopic compositions of three reference materials (NIST 2711a, GSS-5, and BCR-679) were in good agreement with the reported values (Table S2).

### 2.7. Data and Statistical Analysis

Cadmium isotopic compositions of samples were reported in delta notation ( $\delta$ ) relative to NIST 3108 Cd isotopic reference solution.

$$\delta^{114/110}\text{Cd} = \left( \frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{sample}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{NIST3108}}} - 1 \right) \times 1000$$

The  $\delta^{114/110}\text{Cd}$  values for different tissues and the whole plant were calculated as follows.<sup>31</sup>

$$\delta^{114/110}\text{Cd}_{\text{tissue}} = \frac{\sum m_i c_i \delta^{114/110}\text{Cd}_i}{\sum m_i c_i}$$

where  $m$ ,  $c$ , and  $i$  represent the mass of dry matter (g), Cd concentration (ng  $\text{g}^{-1}$ ), and different parts of plant tissues, respectively.

The isotopic fractionation between two components A and B (whole plant/plant tissues or soil fraction) was calculated as follows.

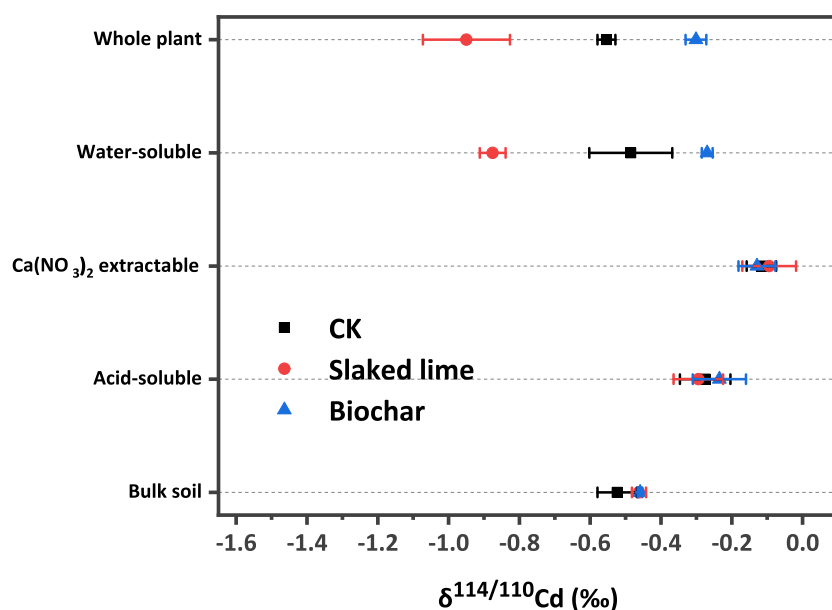
$$\Delta^{114/110}\text{Cd}_{A-B} = \delta^{114/110}\text{Cd}_A - \delta^{114/110}\text{Cd}_B$$

Data were analyzed using IBM SPSS 19.0 software and presented as means  $\pm$  standard deviation ( $n = 3$ ) using Microsoft Excel 2016 (Redmond, WA). One-way analysis of variance (ANOVA) was used to test the differences in treatments, which were compared using the least significant difference (LSD) tests ( $P < 0.05$ ) followed by the homogeneity of variances and normal distribution of the residuals.

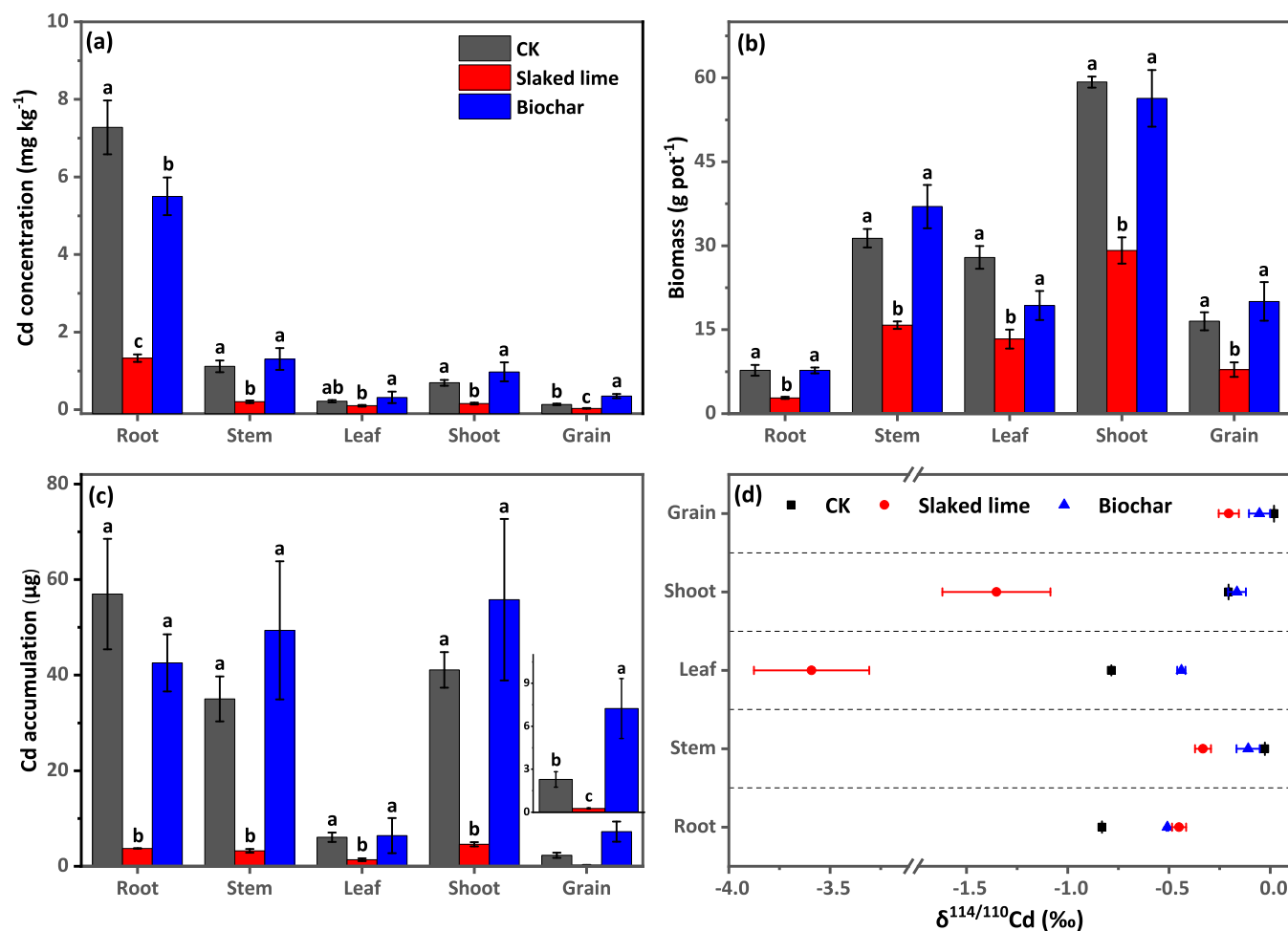
## 3. RESULTS

### 3.1. Cadmium Concentration and Isotopic Composition in Different Soil Fractions under the Pot Experiment

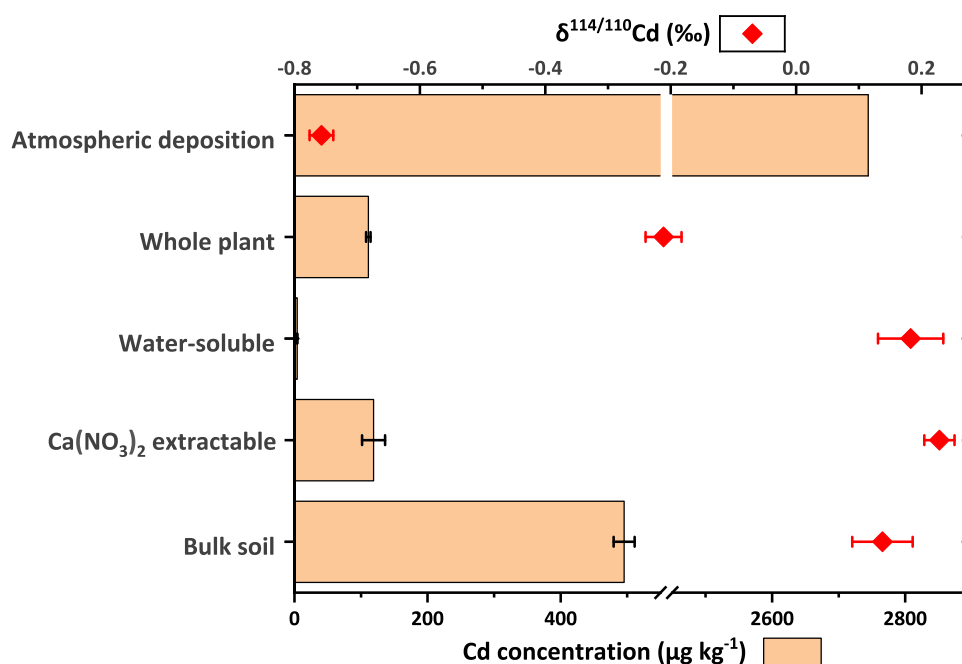
Cadmium concentrations in acid-soluble (CK:  $214.0 \pm 9.6 \mu\text{g kg}^{-1}$ , slaked lime:  $211.1 \pm 7.1 \mu\text{g kg}^{-1}$ , biochar:  $197.3 \pm 12.0$



**Figure 2.** Cadmium isotopic compositions in different soil fractions and the whole rice plant under CK, slaked lime, and biochar amendments. Three individual replicates of pots were analyzed for Cd isotopic composition with the error bars referring to  $\pm$  SD.



**Figure 3.** Cadmium concentration (a), rice biomass (b), Cd accumulation (c), and Cd isotopic composition (d) in various tissues under CK, slaked lime, and biochar treatments at the maturity stage. Three individual replicates of pots were analyzed with the error bars referring to  $\pm$  SD. The letters (a–c) in figure (a–c) indicate significant differences by LSD at the  $P < 0.05$  level.



**Figure 4.** Cadmium concentration and isotopic compositions in various soil fractions, whole rice plant, and atmospheric deposition in the field (Youxian, Hunan). Three replicates of soil samples were analyzed, and the data are expressed as mean  $\pm$  SD. The SD of the  $\delta^{114/110}\text{Cd}$  value in atmospheric deposition was calculated from three replicates of one sample.

$\mu\text{g kg}^{-1}$ ), reducible (CK:  $110.8 \pm 7.2 \mu\text{g kg}^{-1}$ , slaked lime:  $121.1 \pm 5.8 \mu\text{g kg}^{-1}$ , biochar:  $114.4 \pm 9.4 \mu\text{g kg}^{-1}$ ), oxidizable (CK:  $33.0 \pm 1.5 \mu\text{g kg}^{-1}$ , slaked lime:  $32.1 \pm 1.2 \mu\text{g kg}^{-1}$ , biochar:  $32.7 \pm 2.3 \mu\text{g kg}^{-1}$ ), and residual fractions (CK:  $47.6 \pm 4.5 \mu\text{g kg}^{-1}$ , slaked lime:  $47.5 \pm 1.2 \mu\text{g kg}^{-1}$ , biochar:  $49.9 \pm 4.0 \mu\text{g kg}^{-1}$ ) extracted by the BCR procedure among three treatments showed no significant difference ( $P > 0.05$ ; Figures 1a and S2). However, the water-soluble fraction among the three treatments showed significant differences ( $P < 0.05$ ; Figure 1b). Compared with CK, Cd concentrations in the water-soluble fraction under slaked lime and biochar significantly decreased by 59 and 26%, respectively. In addition, Cd concentration in  $\text{Ca}(\text{NO}_3)_2$ -extractable fraction decreased by 79% under slaked lime treatment ( $P < 0.05$ ) and by 11% under biochar treatment (Figure 1c). The order of Cd concentrations in water-soluble or  $\text{Ca}(\text{NO}_3)_2$ -extractable fractions decreased as follows: CK > biochar > slaked lime. These results are opposite to the order of soil pH (CK ( $6.52 \pm 0.04$ ) < biochar ( $6.78 \pm 0.04$ ) < slaked lime ( $7.23 \pm 0.07$ )). Compared with the initial soil pH (5.25), the soil pH in different treatments all increased. It can be attributed to the consumption of protons during the reduction of the oxidized component after soil flooding.<sup>52</sup>

The isotopic compositions of bulk soil ( $\delta^{114/110}\text{Cd}_{\text{soil}}$ ) in the three treatments were essentially the same:  $-0.52 \pm 0.06\%$  (CK),  $-0.50 \pm 0.06\%$  (slaked lime), and  $-0.49 \pm 0.05\%$  (biochar, Figure 2). The  $\delta^{114/110}\text{Cd}$  in  $\text{Ca}(\text{NO}_3)_2$ -extractable ( $\delta^{114/110}\text{Cd}_{\text{Ca-ext}}$ ) (from  $-0.13$  to  $-0.09\%$ ) and acid-soluble fractions ( $\delta^{114/110}\text{Cd}_{\text{acid}}$ ) (from  $-0.29$  to  $-0.23\%$ ) were also indistinguishable among treatments. The indistinguishable  $\delta^{114/110}\text{Cd}_{\text{Ca-ext}}$  or  $\delta^{114/110}\text{Cd}_{\text{acid}}$  among treatments suggests that these methods struggle to accurately evaluate the Cd phytoavailability. However, the  $\delta^{114/110}\text{Cd}$  of water-soluble Cd ( $\delta^{114/110}\text{Cd}_{\text{water}}$ ) differed among treatments. Compared with CK ( $-0.49 \pm 0.12\%$ ), the  $\delta^{114/110}\text{Cd}_{\text{water}}$  in slaked lime treatment ( $-0.88 \pm 0.04\%$ ) was isotopically lighter, while it

was isotopically heavier in biochar treatment ( $-0.27 \pm 0.02\%$ ). Interestingly, the  $\delta^{114/110}\text{Cd}_{\text{water}}$  in different treatments was essentially the same as the corresponding whole rice plant ( $\delta^{114/110}\text{Cd}_{\text{plant}} = -0.55 \pm 0.03\%$  (CK),  $-0.30 \pm 0.03\%$  (biochar), and  $-0.95 \pm 0.12\%$  (slaked lime); Figure 2). In addition, the  $\delta^{114/110}\text{Cd}$  in each fraction extracted by the BCR procedure decreased with the extractability of Cd as follows: acid-soluble (from  $-0.29$  to  $-0.23\%$ ) > reducible (from  $-0.65$  to  $-0.59\%$ ) > oxidizable (from  $-1.70$  to  $-0.92\%$ ) > residual fraction (from  $-1.85$  to  $-1.34\%$ ; Figure S3). The  $\delta^{114/110}\text{Cd}$  values in acid-soluble and reducible fractions were similar between different treatments but with a large deviation in oxidizable and residual fractions.

### 3.2. Cadmium Concentration, Accumulation, and Isotopic Composition in Rice under the Pot Experiment

Compared with CK, Cd concentrations in the root ( $1.33 \pm 0.10 \text{ mg kg}^{-1}$ ), stem ( $0.21 \pm 0.03 \text{ mg kg}^{-1}$ ), leaf ( $0.10 \pm 0.02 \text{ mg kg}^{-1}$ ), shoot ( $0.16 \pm 0.03 \text{ mg kg}^{-1}$ ), and grain ( $0.03 \pm 0.01 \text{ mg kg}^{-1}$ ) under slaked lime treatment significantly decreased by 82, 81, 55, 77, and 75%, respectively (Figure 3a). Under biochar treatment, Cd concentration in the root ( $5.50 \pm 0.49 \text{ mg kg}^{-1}$ ) significantly decreased by 24%, but in the stem ( $1.31 \pm 0.28 \text{ mg kg}^{-1}$ ), leaf ( $0.32 \pm 0.15 \text{ mg kg}^{-1}$ ), shoot ( $0.98 \pm 0.24 \text{ mg kg}^{-1}$ ), and grain ( $0.35 \pm 0.05 \text{ mg kg}^{-1}$ ) increased by 17, 45, 40, and 158%, respectively. The rice plant biomass slightly increased under biochar treatment but significantly decreased under the slaked lime treatment (Figure 3b). Compared with CK, the Cd accumulation in the root ( $3.7 \pm 0.03 \mu\text{g}$ ), stem ( $3.2 \pm 0.38 \mu\text{g}$ ), leaf ( $1.4 \pm 0.3 \mu\text{g}$ ), shoot ( $4.6 \pm 0.4 \mu\text{g}$ ), and grain ( $0.27 \pm 0.04 \mu\text{g}$ ) under slaked lime treatment decreased by 93, 91, 78, 89, and 88%, respectively. However, the Cd accumulation in the root ( $42.6 \pm 6.0 \mu\text{g}$ ) under biochar treatment decreased by 25% but increased in the stem ( $49.4 \pm 14.4 \mu\text{g}$ ), leaf ( $6.4 \pm 3.7 \mu\text{g}$ ), shoot ( $55.8 \pm 16.9$

$\mu\text{g}$ ), and grain ( $7.2 \pm 2.1 \mu\text{g}$ ) by 41, 6, 36, and 216%, respectively (Figure 3c).

The  $\delta^{114/110}\text{Cd}$  in rice plants were ranked as root < shoot < grain, except for the  $\delta^{114/110}\text{Cd}$  in the shoot under slaked lime treatment, which was lighter than that in the root (Figure 3d). The  $\delta^{114/110}\text{Cd}$  in the root under slaked lime ( $-0.45 \pm 0.04\%$ ) and biochar ( $-0.51 \pm 0.01\%$ ) treatment were indistinguishable and isotopically heavier than CK ( $-0.83 \pm 0.03\%$ ). Stems were more enriched in heavy isotopes than roots, and leaves were more enriched in light isotopes than stems across all treatments. The  $\delta^{114/110}\text{Cd}$  in the shoot was similar between CK ( $-0.21 \pm 0.05\%$ ) and biochar ( $-0.16 \pm 0.04\%$ ) treatment but isotopically lighter under slaked lime treatment ( $-1.33 \pm 0.05\%$ ). In grain, the  $\delta^{114/110}\text{Cd}$  (from  $-0.20$  to  $0.02\%$ ) was isotopically heavier than in the corresponding roots for all treatments (Figure 3d).

### 3.3. Cadmium Concentration and Isotopic Composition in the Soil–Rice System under Field Conditions

The total Cd concentration in the field soil was  $495.3 \pm 15.8 \mu\text{g kg}^{-1}$ , similar to that used in pot experiments. According to the soil environmental quality risk control standard for soil contamination of agriculture in China, the soil Cd concentration has exceeded the limit value ( $<300 \mu\text{g kg}^{-1}$  when  $\text{pH} \leq 5.5$ )<sup>27</sup> and was classified as light pollution. The concentrations of  $\text{Ca}(\text{NO}_3)_2$ -extractable and water-soluble Cd fractions were  $118.9 \pm 17.3$  and  $4.06 \pm 0.04 \mu\text{g kg}^{-1}$ , respectively (Figure 4). During the rice growth stage, we collected dry atmospheric deposition near the field ( $0.165 \text{ g}$ ), which had a high concentration of Cd ( $2.74 \text{ mg kg}^{-1}$ ). In rice plants, Cd concentrations in root, stem, leaf, shoot, and grain were  $1363.4 \pm 352.3$ ,  $977.4 \pm 106.8$ ,  $169.7 \pm 8.2$ ,  $773.5 \pm 75.1$ , and  $275.9 \pm 13.5 \mu\text{g kg}^{-1}$ , respectively (Table S3).

The  $\delta^{114/110}\text{Cd}$  in different soil Cd fractions followed the order as  $\delta^{114/110}\text{Cd}_{\text{soil}} < \delta^{114/110}\text{Cd}_{\text{water}} < \delta^{114/110}\text{Cd}_{\text{Ca-ext}}$  (Figure 4). The Cd in atmospheric deposition was enriched in light isotopes ( $\delta^{114/110}\text{Cd}_{\text{deposition}} = -0.76 \pm 0.02\%$ ). The  $\delta^{114/110}\text{Cd}$  in the whole rice plant was  $-0.22 \pm 0.02\%$ . The trend of  $\delta^{114/110}\text{Cd}$  in rice plants under the field was similar to that observed in the pot experiment:  $\delta^{114/110}\text{Cd}_{\text{root}} (-0.34 \pm 0.01\%) < \delta^{114/110}\text{Cd}_{\text{shoot}} (-0.20 \pm 0.02\%) < \delta^{114/110}\text{Cd}_{\text{grain}} (-0.06 \pm 0.01\%)$ ; Table S3). The stems were more enriched in heavy isotopes than roots, while leaves were more enriched in light isotopes than stems.

## 4. DISCUSSION

### 4.1. Water-Soluble Cd is a New Indicator of Cd Phytoavailability in Soil

One dominant factor controlling Cd accumulation in the rice plant is its phytoavailability in soils.<sup>33</sup> Generally, the phytoavailability of toxic heavy metals in soil, including Cd, was often indirectly assessed through chemical extraction.<sup>34</sup> The  $\text{Ca}(\text{NO}_3)_2$ -extractable and acid-soluble fractions are commonly suggested as chemically bioavailable Cd pools in soil.<sup>6,35,36</sup> However, the use of acid-soluble Cd has been criticized because acetic acid can strongly alter the properties of the extracted soil and may extract part of the non-bioavailable Cd in soil.<sup>35,37</sup> In our previous<sup>9</sup> and other<sup>38</sup> studies, it was observed that the concentration of acid-soluble Cd did not correlate with Cd in rice plants. Additionally, the water-soluble Cd is more sensitive to changes in soil than  $\text{Ca}(\text{NO}_3)_2$ -extractable and acid-soluble Cd fractions, which may reflect the Cd phytoavailability in soil.<sup>26,39</sup> Herein, the

acid-soluble,  $\text{Ca}(\text{NO}_3)_2$ -extractable, and water-soluble Cd fractions were extracted and analyzed to assess their applicability as indicators of Cd phytoavailability in soils and their potential contribution to Cd in the rice plant. We found that the concentration of Cd in water-soluble and  $\text{Ca}(\text{NO}_3)_2$ -extractable fractions, but not that in acid-soluble fractions, had correlations with that of Cd in the rice plant (Figure 1d–f). Recently, positive linear correlations have also been observed for Cd concentration in rice tissues and overlying water or soil solution under different water management practices.<sup>9,40</sup> These positive correlations suggest that the water-soluble fraction is suitable as an indicator for Cd phytoavailability in soils as well as the  $\text{Ca}(\text{NO}_3)_2$ -extractable fractions.

The significantly different correlations between extractable Cd fractions and rice Cd content can be attributed to the dramatically different extracted Cd species and concentrations by these three reagents (water,  $\text{Ca}(\text{NO}_3)_2$ , and acetic acid; Figure 1). The Cd isotopic compositions in these three extractable fractions could provide important information about their differential dissolved Cd species in soils. During the dissolution process, the heavy Cd isotopes on the solid phase are preferentially released into the liquid phase,<sup>41–43</sup> and the proportions of Cd in the extractable fractions to the bulk soil Cd correspondingly affect the isotopic composition of the former.<sup>31,42</sup> Compared to water-soluble Cd, the acid-soluble and  $\text{Ca}(\text{NO}_3)_2$ -extractable Cd were isotopically heavier with higher Cd concentrations (Figure 2). These findings indicate that acetic acid and  $\text{Ca}(\text{NO}_3)_2$  solution extracted a greater proportion of heavy isotopes from soils than water. Despite the concentration of Cd in the acid-soluble fraction being higher than that in the  $\text{Ca}(\text{NO}_3)_2$ -extractable fraction,  $\delta^{114/110}\text{Cd}_{\text{acid}}$  was lighter than  $\delta^{114/110}\text{Cd}_{\text{Ca-ext}}$  across all pot treatments. This suggests that acetic acid tends to extract Cd species that are enriched in isotopically light isotopes. In fact, acetic acid can extract part of coprecipitated Cd with carbonate species that were enriched in light isotopes,<sup>43</sup> in addition to water-soluble and exchangeable Cd fractions.<sup>44</sup> Therefore, the acid-soluble fraction may overestimate the Cd phytoavailability in soil, since acetic acid solution extracted more Cd from soil. It should be noted that the  $\text{Ca}(\text{NO}_3)_2$ -extractable fraction generally includes both water-soluble Cd and partially adsorbed onto inorganic/organic soil components through electrostatic interaction.<sup>45</sup> Therefore, it is still a challenge to determine which of the fractions (water-soluble or  $\text{Ca}(\text{NO}_3)_2$ -extractable Cd) is the main source of Cd in rice plants.

### 4.2. Water-Soluble Cd is the Direct Source of Cd in Rice Plant

To clarify the direct source of Cd in rice plants, the isotopic fractionation between whole rice plants and water-soluble or  $\text{Ca}(\text{NO}_3)_2$ -extractable Cd was analyzed. In general, Cd isotopic fractionation can occur when plant roots uptake Cd from phytoavailable pools, mainly caused by different uptake rates of light and heavy isotopes.<sup>18,46,47</sup> In our results, the whole rice plants were more enriched in light isotopes than the  $\text{Ca}(\text{NO}_3)_2$ -extractable fraction ( $\Delta^{114/110}\text{Cd}_{\text{plant-Ca-ext}} = -0.49\%$ ), similar to other studies.<sup>20,31,48</sup> However, there was limited or no isotopic fractionation between the whole rice plant and water-soluble Cd in this study ( $\Delta^{114/110}\text{Cd}_{\text{plant-water}} = -0.06$  to  $-0.03\%$ ; Figure 2). In a previous study, no net Cd isotopic fractionation was found during Cd uptake by phytoplankton from seawater.<sup>49</sup> This can be well explained by the supply-limited uptake by plants under low available Cd

concentration.<sup>49</sup> During rice plant growth, the release or dissolution of Cd from soil to water-soluble fraction was continuous but very slow.<sup>50,51</sup> Herein, the water-soluble Cd, a direct source with high phytoavailability to rice, was lower than  $2 \mu\text{g L}^{-1}$  (Figure 1b). Such low concentration of water-soluble Cd and high plant uptake rate<sup>52,53</sup> jointly contributed to a supply-limited condition in pot experiments. Considering there was no other input source of Cd in the soil–rice system under a pot experiment, the  $\delta^{114/110}\text{Cd}$  of the whole rice plant was essentially similar to that of the water-soluble fraction.

In previous studies, obvious isotopic fractionation ( $\Delta^{114/110}\text{Cd}_{\text{plant-nutrientsolution}} = -0.84$  to  $-0.29\%$ ) was observed between plants and nutrient solutions under high Cd supply ( $>500 \mu\text{g L}^{-1}$ ), which could be attributed to kinetic isotopic fractionation (the light Cd isotopes preferentially absorbed by plant roots).<sup>47,48</sup> Moreover,  $\Delta^{114/110}\text{Cd}_{\text{plant-water}}$  in our study was less than the isotopic fractionation between the plant and soil solution observed in other studies,<sup>18,20</sup> indicating that species in the soil solution are not directly absorbed by plants.<sup>19</sup> In this study, the collection of the water-soluble Cd fraction was achieved by adding deionized water and extracting it through shaking (Section 2.3), theoretically extracting only the water-soluble fraction. The sampling of soil solution in related studies, conducted through suction cups<sup>19</sup> or a Rhizon sampler,<sup>20</sup> could extract Cd fractions beyond the water-soluble fraction from soils. The water-soluble fraction mainly contains free ions and water-soluble inorganic and organic complexes of Cd,<sup>36</sup> while the soil solution could also include colloid-bound Cd besides the water-soluble fraction.<sup>54</sup> The Cd-associated colloid in soil solution was too large to pass the root cell membranes, thereby hindering the phytoavailability of colloidal Cd.<sup>55–57</sup> Meanwhile, colloidal Cd was isotopically heavier than free  $\text{Cd}^{2+}$  ions due to the dominating binding with O ligands.<sup>18,31</sup> Therefore, water-soluble Cd is the direct source of phytoavailable and accumulated Cd in rice plants due to its high phytoavailability and supply limitation. The  $\text{Ca}(\text{NO}_3)_2$ -extractable Cd in soils, although not the direct source of phytoavailable Cd, was quantitatively correlated with water-soluble Cd (Figure S4; partially desorb into the water-soluble fraction) and could be considered potentially phytoavailable.

### 4.3. Distinct Differences from Biochar and Slaked Lime on the Soil Water-Soluble Fraction and Cd Translocation in Rice

In previous studies, soil solution was observed to be preferentially enriched in heavy Cd isotopes due to equilibrium isotope fractionation associated with an enrichment of the heavier isotopes in the phase with the shorter and stiffer bonds.<sup>18–20</sup> However, the  $\delta^{114/110}\text{Cd}_{\text{water}}$  was slightly heavier than their corresponding  $\delta^{114/110}\text{Cd}_{\text{soil}}$  under CK treatment ( $\Delta^{114/110}\text{Cd}_{\text{water-soil}} = 0.04 \pm 0.05\%$ ; Figure 2), while  $\delta^{114/110}\text{Cd}_{\text{water}}$  under biochar treatment was heavier than its  $\delta^{114/110}\text{Cd}_{\text{soil}}$  ( $\Delta^{114/110}\text{Cd}_{\text{water-soil}} = 0.19 \pm 0.01\%$ ). A negative fractionation ( $\Delta^{114/110}\text{Cd}_{\text{water-soil}} = -0.41 \pm 0.06\%$ ) was observed in slaked lime treatment. As discussed in Section 4.2, the Cd speciation in the water-soluble fraction and soil solution should be different. Additionally, the extraction of the water-soluble Cd fraction is primarily a dissolution process. During this process, the preferential release of lighter Cd isotopes may occur due to the typically faster reaction rates of light Cd isotopes, resulting in a light isotopic composition in the water-soluble Cd fraction.<sup>46,58</sup> These distinct differences in isotopic fractionation among treatments can be attributed to

the different adsorption/coprecipitation of Cd with minerals<sup>41</sup> and coordination atoms for Cd complexation in solution under different treatments.<sup>59</sup> Cadmium bound with the oxygen-containing functional groups are the dominant species in the aqueous phase;<sup>19</sup> however, differences in Cd coordination chemistry in the solid phase, organic ligands in water-soluble fraction, and the dissolution processes from the solid phase to the water-soluble fraction would produce distinct Cd isotopic fractionation.<sup>60</sup> Under biochar treatment, insoluble organic matters in biochar preferentially bind with light Cd isotopes.<sup>59</sup> In addition, organic matter could enhance Cd sorption to hematite or kaolinite,<sup>61,62</sup> which also preferentially bind with light Cd isotopes.<sup>41</sup> Both of these would enrich heavy Cd isotopes in the water-soluble fraction. Cadmium is mainly presented in the form of carbonates (i.e., Cd- $\text{CaCO}_3$  and Cd- $\text{CdCO}_3$ ) in flooded alkaline paddy soil,<sup>63</sup> and light isotopes are preferentially enriched in calcite.<sup>43,64</sup> Therefore, the negative  $\Delta^{114/110}\text{Cd}_{\text{water-soil}}$  in slaked lime treatment should be controlled by processes other than coprecipitation. Recent studies showed that high pH can affect the solubility of iron and is favorable for the formation of goethite, which is the major stable iron mineral in aerobic soils.<sup>41,65</sup> Goethite preferentially sequestered heavy Cd isotopes when Cd is incorporated into goethite through substitution for lattice Fe.<sup>41</sup> Therefore, it is possible that the increased soil pH under slaked lime treatment favored the formation of goethite; thus, a negative Cd fractionation occurred.

Root uptake is a critical process that dominates the  $\delta^{114/110}\text{Cd}$  in rice plants.<sup>19</sup> Compared with  $\delta^{114/110}\text{Cd}_{\text{water}}$ ,  $\delta^{114/110}\text{Cd}_{\text{root}}$  was isotopically lighter in both CK ( $\Delta^{114/110}\text{Cd}_{\text{root-water}} = -0.34 \pm 0.14\%$ ) and biochar treatments ( $\Delta^{114/110}\text{Cd}_{\text{root-water}} = -0.19 \pm 0.01\%$ ). Similar isotopic fractionation has been reported before and was attributed to the following: (1) roots preferentially take up the light isotopes from the mobile Cd pool<sup>19,66,67</sup> and (2) heavy Cd isotopes in root cells are preferentially transported to aboveground tissues.<sup>19,20</sup> The shoots correspondingly were enriched in heavy isotopes than roots (Figure 3d), since the isotopically light Cd bound with thiol compounds and retained in root vacuoles during root-to-shoot translocation.<sup>19,31</sup> The magnitude of  $\Delta^{114/110}\text{Cd}_{\text{shoot-root}}$  is associated with the translocation of Cd from roots to shoots,<sup>31,48</sup> which is mainly driven by plant transpiration through the xylem.<sup>68</sup> Herein, the rice growth was improved under biochar treatment (Figure 3b), indicating increased transpiration and enhanced Cd translocation from roots to shoots. Correspondingly, the negative magnitude of the  $\Delta^{114/110}\text{Cd}_{\text{shoot-root}}$  (CK:  $0.62 \pm 0.05\%$ , and biochar:  $0.34 \pm 0.04\%$ ) was observed, in contrast to the increased Cd mass ratio between shoots and roots (CK:  $0.74 \pm 0.09$ , and biochar:  $1.30 \pm 0.33$ ). However, the positive isotopic fractionation between roots and the water-soluble pool ( $\Delta^{114/110}\text{Cd}_{\text{root-water}} = 0.41 \pm 0.06\%$ ) and negative isotopic fractionation between roots and shoots ( $\Delta^{114/110}\text{Cd}_{\text{shoot-root}} = -0.90 \pm 0.30\%$ ) were observed under slaked lime treatment. This result contradicts other treatments in this study and previously reported results.<sup>19,20,69</sup> The specific mechanisms for this result are still not clear, but two possible reasons may contribute to it. First, the addition of slaked lime lightened the isotopic composition of the soil water-soluble Cd, which is the source of Cd accumulation in rice plants. Concurrently, the slaked lime significantly inhibited the growth of rice plants, as evidenced by the changes in its biomass (Figure 3b,c), indicating that the rice plant was under salt and/or alkaline stresses. Therefore,

slaked lime may disrupt the uptake and transport process of Cd in rice plants.<sup>70,71</sup> Second, based on the significant difference in the gene expression in transporters between different water management practices,<sup>20</sup> it was also plausible that gene expression changed under such an adverse growing environment. However, these are hypotheses that require further studies to understand the role and effect of slaked lime on Cd transportation and isotopic fractionation in rice plants.

#### 4.4. Contribution of Atmospheric Deposition to Rice Cd under the Field is Non-Negligible

In the field investigation, we found that the rice plants were enriched in lighter isotopes than  $\text{Ca}(\text{NO}_3)_2$ -extractable or water-soluble fractions ( $\Delta^{114/110}\text{Cd}_{\text{plant-Ca-ext}} = -0.44 \pm 0.03\%$ ,  $\Delta^{114/110}\text{Cd}_{\text{plant-water}} = -0.39 \pm 0.05\%$ ). It suggests that there should be other sources of Cd for the field rice plant. Atmospheric deposition has been identified as a non-negligible or even dominant source of Cd for rice plants in the field.<sup>13–15</sup> In our study, the atmospheric deposition of Cd was up to 2.74 mg kg<sup>-1</sup>, which usually has high bioavailability.<sup>14</sup> The  $\delta^{114/110}\text{Cd}_{\text{plant}}$  was between  $\delta^{114/110}\text{Cd}_{\text{water}}$  and  $\delta^{114/110}\text{Cd}_{\text{deposition}}$  (Figure 4), indicating that both water-soluble and atmospheric-deposited Cd contributed to plant Cd. Therefore, a binary mixing model<sup>72</sup> was used to quantify the specific contributions of the water-soluble fraction and atmospheric deposition to rice Cd

$$\delta_m = f_a \delta_a + f_b \delta_b$$

$$1 = f_a + f_b$$

where  $f_a$  or  $f_b$  is the proportions of two sources,  $\delta_a$  or  $\delta_b$  is the isotopic composition of the source, and  $\delta_m$  is the isotopic composition for the mixture (i.e., whole rice plant). The model and calculation showed that the contributions from the water-soluble fraction and atmospheric depositions were 58.0 and 42.0%, respectively. Studies have found that plant leaves can directly uptake fine particles from atmospheric deposition on the leaf surface through cuticle internalization and stomatal infiltration.<sup>73,74</sup> In addition, plant leaves can also uptake the dissolved elements of atmospheric deposition through hydrophilic diffusion via aqueous pores and stomates.<sup>75</sup> Further, some studies suggest that rice roots preferentially uptake the heavy Cd isotopes in atmospheric wet deposition from the soil, while the leaves are more inclined to uptake heavy Cd isotopes from dry deposition.<sup>12,76</sup> The quantitative assessment of the contribution of soil phytoavailable Cd and atmospheric deposition Cd to rice plants is influenced by the phytoavailability of soil Cd, the input pathway of atmospheric deposition, the bioavailability of Cd in atmospheric deposition, and the growth status of rice plants.<sup>14,77,78</sup> The result of this calculation provides a relatively quantitative assessment and suggests that, besides the soil water-soluble fraction, atmospheric deposition is also a potential and even non-negligible source of Cd in rice plants under field conditions.

## 5. CONCLUSIONS AND IMPLICATIONS

In this study, Cd concentration and isotopic compositions in rice plants and different soil fractions were investigated to probe its phytoavailability and sources in the rice system. Our results suggest that the water-soluble fraction in the soils is an immediate source of Cd for rice plants and is a better indicator, besides the  $\text{Ca}(\text{NO}_3)_2$ -extractable fraction, than the acid-soluble fraction for characterizing the phytoavailability of Cd in

the soil. The effectiveness of different amendments and water management strategies on the phytoavailability of Cd in soils could be accurately and conveniently evaluated by monitoring the changes in water-soluble Cd. Further, the contribution of foliar absorption to Cd accumulation in rice plants cannot be ignored in high atmospheric deposition regions. It should also be noted that the specific species/binding strength of Cd in the water-soluble fraction and its dissolution process need to be fully understood further because the different aqueous species of Cd can induce distinct isotopic fractionation.<sup>79</sup> Especially, precise descriptions of the isotopic fractionation during the process of Cd adsorption/complexation with different soil constituents are needed to clarify for understanding the biogeochemical behavior of Cd in soil–rice systems.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenvironau.3c00067>.

Four texts listing the rice germination and cultivation; BCR sequential extraction procedure; sampling collection and preparation for atmospheric deposition; cadmium isotopic composition in the fractions extracted by the BCR sequential extraction procedure; listing physiochemical properties of the soil for pot culture of rice plants; Cd concentration and isotopic compositions of the standard reference materials; Cd concentration and  $\delta^{114/110}\text{Cd}$  values in rice plants in the field; overview of sampled rice tissues; Cd concentration in different soil fractions extracted following the BCR procedure; Cd isotopic compositions in various soil fractions extracted through the BCR procedure under CK, slaked lime, and biochar amendments; and relation between Cd concentration in water-soluble and  $\text{Ca}(\text{NO}_3)_2$ -extractable fractions in pot experiments (PDF)

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### Notes

The authors declare no competing financial interest.

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