agriculture

Article

Evaluating Water Management Efficiency in Regulating Cadmium and Arsenic Accumulation in Rice in Typical Japonica Paddy Soils at Varied pH Levels

Xianxin Wu, Qiujun Lin, Guang Li, Chunjing Guo, Lina Li and Jianzhong Wang *

Institute of Agricultural Quality Standards and Testing Technology, Liaoning Academy of Agricultural Sciences, Shenyang 110161, China; wuxianxin1225@163.com (X.W.); linqiujun85@163.com (Q.L.); lngtgh@163.com (G.L.); guocj464@163.com (C.G.); lln231118@163.com (L.L.)
* Correspondence: zbswjz72@163.com

Abstract: There is growing concern regarding cadmium (Cd) exposure through rice consumption. Compared with alternate wetting and drying (AWD), continuous flooding (CF) is usually considered as an effective approach for reducing Cd enrichment in rice but increases the risk of pollution from arsenic (As). In this study, the field trial was conducted to investigate remediation effects of two water management (CF and AWD) techniques on Cd pollution in rice in typical japonica rice cultivation areas with varied soil pH levels. The results indicate that soil pH was a crucial factor in regulating CF-mediated Cd/As accumulation and migration in rice plants, and grains at all stages of rice growth. In acidic fields, compared with AWD, the use of CF reduced the accumulation of Cd in plants during the tillering stage; CF during the milk stage promotes the risk of contamination of Cd in rice grains and any form of As in plants and inhibits the content of any forms of As in grains. During the mature stage, CF reduced the levels of Cd in the plants and grains while promoting the accumulation of As(V) and total As(T-As) in plants and As(III) in grains. In alkaline fields, compared with AWD, CF during the tillering stage promoted the accumulation of various forms of As in plants. During the milk stage, CF increased and decreased the Cd content in plants and grains, respectively, and reduced the accumulation of T-As in plants and As(III) in grains; during the mature stage, CF promoted the accumulation of Cd in plants and grains, induced the accumulation of T-As plants, and inhibited the accumulation of any form of As in grains. From the perspective of food safety, the impact of CF conditions on the accumulation of Cd and As in rice from acidic fields exhibited a pattern of reduction in Cd and increase in As during the maturity period, as compared to that on the AWD. Conversely, CF increased the Cd risk while simultaneously reducing the As accumulation in rice grains to a safe level in alkaline fields. CF is not recommended as a remediation strategy for Cd pollution in rice in low Cd pollution areas, but it can be considered as a potential strategy for As pollution remediation in rice in alkaline fields with low Cd pollution.

Keywords: cadmium; arsenic; continuous flooding; alternate wetting and drying; soil pH; rice

check for updates

Citation: Wu, X.; Lin, Q.; Li, G.; Guo, C.; Li, L.; Wang, J. Evaluating Water Management Efficiency in Regulating Cadmium and Arsenic Accumulation in Rice in Typical Japonica Paddy Soils at Varied pH Levels. *Agriculture* **2024**, *14*, 407. https://doi.org/10.3390/agriculture14030407

Academic Editor: Matevz Likar

Received: 29 January 2024
Revised: 16 February 2024
Accepted: 1 March 2024
Published: 3 March 2024

1. Introduction

Cadmium (Cd) and arsenic (As) have no biological function in plants but can adversely affect crops by inducing protein denaturation in plants, interfering with antioxidant capacity, and limiting nutrient absorption [1,2]. Both elements are considered major carcinogenic heavy metals with high toxicity, and their accumulation in the soil, drinking water, and food chain is a major concern [1]. Exposure to Cd can cause renal dysfunction, osteoporosis, and cancer [3]. Long-term exposure to As in the human body can lead to toxic effects such as skin lesions, keratosis, diabetes, and various types of cancer [4,5]. Unfortunately, human activities, such as the application of agricultural inputs, including fertilizers, herbicides, and insecticides, as well as metal mining and smelting, industrial activities, and irrigation with contaminated groundwater, exacerbate the accumulation of Cd and As in the soil [2,6].

Rice (*Oryza sativa* L.), a stable carbohydrate source for the majority of the global population, can efficiently uptake Cd and As from soil solutions, with greater accumulation in roots, shoots, panicles, and grains than in other cereal crops [7]. Consequently, rice has become a main medium for Cd and As to enter the human food chain, posing a significant threat to public health [8]. In addition, excessive amounts of heavy metals such as Cd and As can inhibit plant growth, development, and yield by inducing protein denaturation in plants, interfering with antioxidant capacity, and limiting nutrient absorption [9]. Therefore, the development of effective strategies to reduce the Cd/As content in soil and limit their uptake and accumulation in rice grains is crucial for minimizing yield losses caused by Cd or As and ensuring the safety of rice as a food source for human consumption [10].

In recent years, researchers have identified agronomic practices for reducing and controlling Cd enrichment in rice, including fertilizer (nitrogen, phosphorous, and selenite) and irrigation regulation, among which water management is considered the most cost-effective strategy [11,12]. The primary irrigation modes available for rice cultivation are typically categorized into continuous flooding (CF) and alternate wetting and drying (AWD) [13]. AWD is a widely utilized irrigation mode that can maintain crop yields, reduce water usage, and minimize greenhouse gas emissions [14,15]. Compared with AWD, CF during the rice-growing season can significantly reduce Cd accumulation in rice grains [16], as the low soil oxidation–reduction potential during flooding can facilitate Cd to combine with sulfur (S) to form CdS, a less soluble compound in water [17]. In contrast, anaerobic conditions in paddy soils caused by flooding typically promote the reduction in arsenate (As(V)) to arsenite (As(III)), which enhances the solubility of As in the soil and the bioavailability of rice [18]. Given the opposing effects of water management on the speciation and bioavailability of Cd and As in the soil and their subsequent accumulation in rice, it is crucial to exercise caution when using continuous flooding as an agronomic measure to reduce Cd pollution in rice. In addition, although most studies have indicated that the Cd content decreases under flooding and anaerobic conditions, some studies have produced different results [11]. This intricate phenomenon suggests that changes in heavy metal concentrations in rice due to flooding may be influenced by other undefined factors.

Northeast China is known for its high-quality rice cultivation, accounting for more than half of the country's japonica rice production. The heavy metal pollution in soil and rice in this region is relatively low compared to that in the southern indica rice planting area [19]. Moreover, the rice cultivation areas in Northeast China, particularly in Liaoning, are divided into typical acidic and alkaline field planting areas due to the different pHs of paddy soil. However, the efficacy of CF in reducing Cd residue in rice grains in areas with low Cd pollution requires further evaluation, and it is unclear how soil background pH affects the accumulation of Cd and As in rice through water management. This study aimed to assess the impact of water management on the accumulation of Cd and As in rice in low-pollution areas and examine the role of soil pH in this process.

2. Materials and Methods

2.1. Selection of Test Base

The high Cd pollution areas in China are mainly the southern indica rice planting areas, and CF has been widely promoted and validated as a Cd remediation strategy in rice. However, the effectiveness of CF in the Northeast Japonica rice planting area with low Cd pollution is not yet clear. Therefore, in this study, the low Cd pollution Japonica rice planting area was selected. This study was conducted in typical rice-producing regions of Liaoning Province, China, using a fixed-point tracking technique. The fixed-point experimental fields were divided into acidic and alkaline fields. The monitoring point for acidic soil was located in Xujiatun Village, Pudong Street, Liaozhong District, Shenyang City, with a soil pH of 4.9 measured prior to flooding. In contrast, the monitoring point for acidic soil was in Huangjia Village, Gaokan Town, Dashiqiao County, Yingkou City, with a soil pH of 7.6 measured prior to flooding. The other soil properties of the two fields are similar except for the pH (Table 1).

Table 1. Basic soil properties of acidic and alkaline fields for testing.

Soil Type	pH	Organic Matter (g/kg)	Total Nitrogen (g/kg)	Effective Phosphorus (mg/kg)	Total Potassium (g/100 g)
Acid field	4.9 ± 0.2	19.2 ± 0.8	1.24 ± 0.06	633.4 ± 139.8	1.9 ± 0.2
Alkaline field	7.6 ± 0.1	19.3 ± 1.1	1.34 ± 0.15	656.3 ± 166.7	2.2 ± 0.1

2.2. Field Experiment Design

This investigation was conducted with a rice variety known as Liaoxing 168. The experiment was conducted in two treatments, each focusing on a distinct irrigation mode, CF or AWD, to investigate the impacts of various water management practices on Cd and As accumulation in rice crops. The CF group maintained a field surface water level of 3–5 cm throughout the growth period. The AWD group, after the initial irrigation in the field, maintained a surface water layer of 3–5 cm until the rice dried once in the late tillering stage, and conducted two "flooding-drying" tests during the filling stage. "Drying" referred to the phenomenon in which the field soil dried for 5–7 d until there were microcracks on the surface, resulting in a soil moisture content between 70% and 90%, presenting a "wet hard" state. The CF and AWD treatment groups each comprised three plots, serving as three biological replicates, with each area no less than 30 m^2. In total, there were 12 experimental plots in the two fields. The design incorporated isolation rows between the CF and AWD treatment fields and covered the ridges between the experimental plots with plastic film to prevent water leakage in each experimental zone. This design scheme was adopted for both alkaline and acidic fields. Before the experiment, the heavy metal pollution in the soil and irrigation water commonly used in acidic and alkaline fields were specifically tested. The background Cd and As contents in acidic soil are 0.17 mg/kg and 7.22 mg/kg, respectively. The background Cd and As contents in alkaline soil are 0.13 mg/kg and 9.67 mg/kg, respectively. The Cd and As contents in the irrigation water of both fields were lower than the detection limit (0.0005 mg/L), which can exclude the possibility of Cd and As pollution introduced by the irrigation water.

2.3. Field Management and Sample Collection

A unified approach to the management of fertilizers and the control of diseases, pests, and weeds across all experimental areas was outlined by Sun et al. [2]. Soil samples were collected at three distinct stages: late tillering stage, milk stage, and harvest stage using the five-point sampling method [20]. Sampling should be conducted at the diagonal and focal points of each experimental community, with a sampling depth of 0–20 cm. Avoid sampling at the edges of the four corners to ensure the representativeness of the samples. The mixture of five soil samples taken from each sampling area is used as the test sample. Then, synchronously collect samples of rice roots, plants, and grains corresponding to the soil.

2.4. Determination of Cd and As

Determination of Cd content in soil: accurately weigh about 1 g of soil sample passing through a 0.149 mm sieve, add a little distilled water to moisten the soil sample, and add 3~4 small glass beads. Soak the entire sample in 10 mL of HNO_3 (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) solution and heat it for 20 min in a slightly boiling state on an electric heating plate. Add 20 mL of HCl (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), cover with a Petri dish, heat on an electric heating plate for 2 h. Remove all acid solution to a wet salt state, dissolve in 10 mL of water, filter, and make up to 50 mL. Then, the Cd content in the soil is measured using the graphite furnace method [21]. For the determination of Cd in rice roots, plants, and grains, weigh 0.3 g~0.5 g of dry sample and place it in a microwave digestion tank. Add 5 mL of HNO_3 and 2 mL of H_2O_2. After the digestion is completed, wait for the digestion tank to cool down, heat and drive the acid to near dryness. Rinse the digestion tank three times with a small amount of HNO_3 (1%), transfer the solution to a 10 mL volumetric flask, and mix with HNO_3 (1%) to a constant volume. Then, the Cd content is determined by graphite furnace atomic absorption spectroscopy [22]. Determination of T-As content in soil: weigh 0.5 g of air-dried soil that has passed through a 0.149 mm sieve and place it in a 50 mL conical flask. Wet the soil with a small amount of water, then add 10 mL of aqua regia (HCl:HNO_3 = 3:1), dilute with ddH_2O twice, shake well, and seal the membrane. Leave it at room temperature overnight, heat and digest in a boiling water bath for 2 h, shake once during the process, filter, and volume. Measure the T-As content using an atomic fluorescence spectrophotometer [23]. For the determination of inorganic As content in soil, weigh 0.5 g of dried soil sample and place it in a 50 mL centrifuge tube. Add 10 mL of ultrapure water and extract with ultrasonic assistance for 30 min. Centrifuge at 3500 r/min for 15 min, repeat the extraction three times, and combine the extraction solutions. Filter and determine the content of various forms of As using high-performance liquid chromatography hydride generation atomic fluorescence method. For the determination of T-As and inorganic As contents in rice roots, plants, and grains, weigh approximately 1 g of finely ground sample into a 50 mL centrifuge tube, add 20 mL of HNO_3 (0.15 mol/L), and leave overnight. Hot soak in a 90 °C constant temperature incubator for 2.5 h, shake for 1 min every half hour, cool to room temperature, centrifuge at 8000 r/min for 15 min, take the upper clear liquid, and pass it over 0.45 μM organic microporous filter membrane for HPLC-ICP-MS (Agilent, CA, USA) determination [24].

2.5. Statistical Analysis of Data

Statistical analysis was performed using Prism software (version 5.0; GraphPad, San Diego, CA, USA), and one-way analysis of variance (ANOVA) was utilized to compare significant differences between multiple groups. Data were presented as the mean ± standard error of three independent replicates. Differences between groups were considered statistically significant with at least $p < 0.05$.

3. Results

3.1. Effect of Water Management on Cd Accumulation in Paddy Soils and Rice Roots

The impacts of water management on Cd accumulation in acidic field soils and alkaline soils are shown in Figure 1a and Figure 1b, respectively. The effects of CF on Cd accumulation in rice roots in acidic and alkaline fields are shown in Figure 1c and Figure 1d, respectively. Upon comparing the two management modes, the Cd content both in the soil and in rice roots from acidic and alkaline fields showed no significant difference between the CF and AWD during any rice growth stage. In addition, in acidic field soils (Figure 1c), the accumulation of Cd in rice roots increases with the development of rice and reaches a higher level at maturation stage. In alkaline field soils (Figure 1d), with the development of rice, the Cd level in rice roots shows a trend of first increasing and then decreasing, reaching the highest accumulation level during the milk stage.

3.2. Effect of Water Management on Cd Accumulation in Rice Plants

In fields with acidic soil, the extension of the rice growth period led to a gradual increase in the accumulation of Cd in plants under the CF management mode (Figure 2a). Under the AWD management mode, the enrichment of Cd demonstrated a trend of initially decreasing and then increasing (Figure 2a). When comparing the two management modes, the order of Cd content in plant samples collected at each period was consistently higher under the AWD management mode, especially during the tillering and maturation stages (Figure 2a). These findings suggest that the CF management model was effective in reducing the risk of Cd accumulation in rice plants grown in acidic fields.

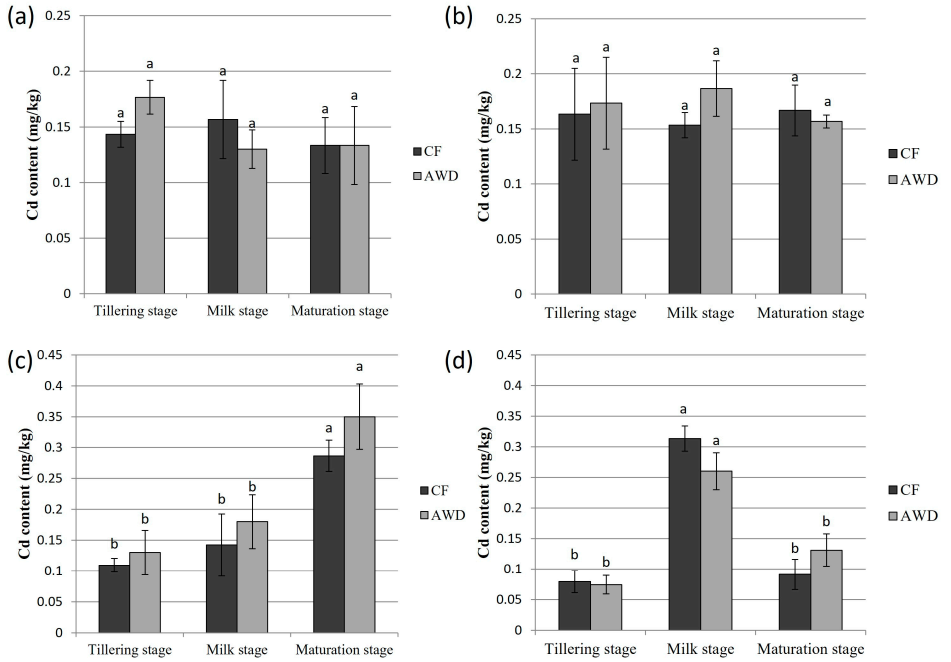

Figure 1. Water management effects on Cd accumulation in paddy soils and rice roots. (**a**,**b**); Effect of different water management methods on Cd accumulation in soil under acidic fields (**a**) and alkaline fields (**b**); (**c**,**d**); Effect of different water management methods on Cd accumulation in rice roots under acidic fields (**c**) and alkaline fields (**d**). CF represents continuous flooding, and AWD represents alternate wetting and drying. Error bars represent standard error of the mean (SE). Different letters indicate statistically significant differences ($p < 0.05$).

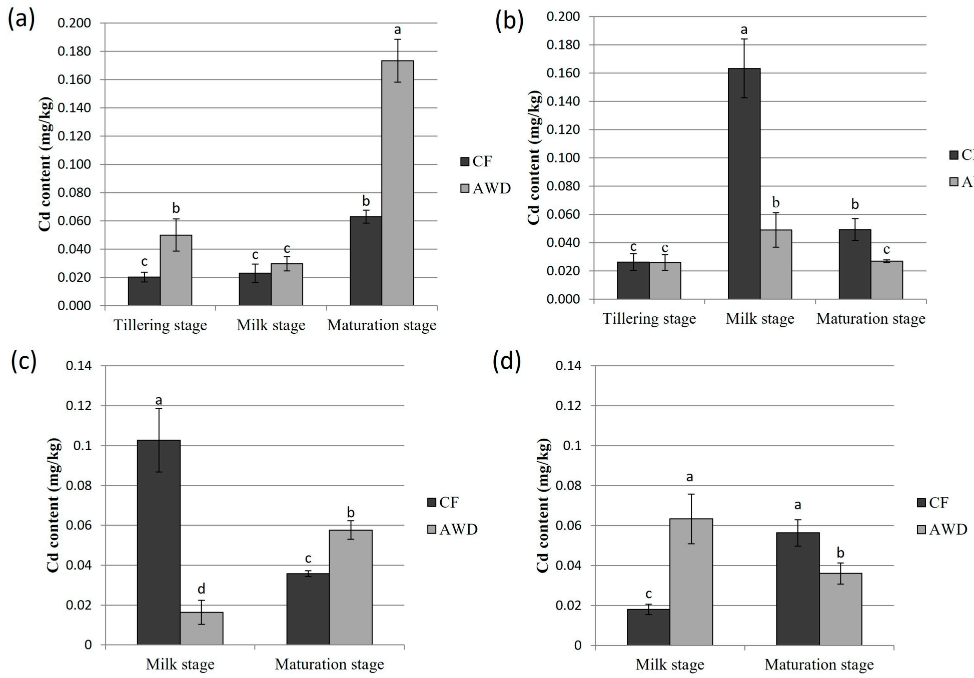

Figure 2. Water management effects on Cd accumulation in rice plants and grains. (**a**,**b**); Effect of different water management methods on Cd content in rice plants under acidic fields (**a**) and alkaline fields (**b**). (**c**,**d**); Effect of different water management methods on Cd content in rice grains under acidic fields (**c**) and alkaline fields (**d**). CF represents continuous flooding, and AWD represents alternate wetting and drying. Error bars represent standard error of the mean (SE). Different letters indicate statistically significant difference ($p < 0.05$).

The effects of water management on Cd accumulation in rice plants under alkaline conditions are illustrated in Figure 2b. The concentration of Cd in plants under both CF and AWD management initially increased and then decreased as the rice growth period was extended. During the milk stage, Cd accumulation was more pronounced in the CF management mode than in the AWD mode. When comparing the two management modes, the order of Cd content in the plant samples collected during the milk and mature stages was CF > AWD. This indicated that the CF management model did not mitigate the risk of Cd accumulation in rice plants in alkaline fields but rather exacerbated Cd pollution, which was contrary to the findings in acidic fields.

3.3. Effect of Water Management on Cd Accumulation in Rice Grains

The effect of water management on the accumulation of Cd in rice grains in acidic fields is shown in Figure 2c. At the milk stage, the Cd content in rice grain samples collected under the CF mode was significantly higher than that under the AWD mode. However, during the ripening period, the Cd content accumulated in the rice grains under the AWD mode was significantly higher than that under the CF mode. This suggested that employing the CF method from the milk stage to the mature stage can effectively reduce the risk of Cd accumulation in the rice grains during the harvest period.

The impact of water management on Cd pollution in rice grains in alkaline fields is shown in Figure 2d. During the milk stage, the Cd levels in rice grain samples obtained through the AWD mode were higher than those collected through the CF mode. Conversely, during the maturation phase, the accumulation of Cd in the rice grains produced in the AWD mode was lower than that observed in the CF. This suggested that, in alkaline fields, the CF management approach increased the likelihood of Cd accumulation in rice grains during the harvest period, which was contrary to the findings obtained in acidic fields.

3.4. Effect of Water Management on As Accumulation in Rice Soils

The impact of water management on As pollution in paddy fields with acidic soil is illustrated in Figure 3a. During the tillering stage, the concentrations of As(V) in the soil in the AWD mode were higher than those in the CF mode. During the milking stage, the levels of As(III) in the soil under the different management modes followed the order CF > AWD, while the content of As(V) remained largely unchanged under the two management modes. During the mature stage, the levels of As(III) in the soil were generally consistent across the various water management modes. However, the levels of As(V) under AWD were considerably higher than those under CF conditions. Throughout the growth period of rice under either AWD or CF, the T-As content in soil is similar.

The impact of water management on As pollution in paddy fields with alkaline soil is shown in Figure 3b. There was no discernible difference in As(III), As(V), and T-As content between the two water management methods at any stage of rice development.

3.5. Effect of Water Management on As Accumulation in Rice Roots

In acidic field soils (Figure 3c), the accumulation of As(III), As(V), and T-As content in rice roots under two water management modes is similar during the tillering stage. During the milk stage, CF significantly reduced the accumulation of any form of As in rice roots compared to AWD. During the mature stage, the accumulation of As(III) and T-As in rice roots under CF mode was significantly lower than that under the AWD mode, while the content of As(V) in rice roots was not significantly different between the two water management modes.

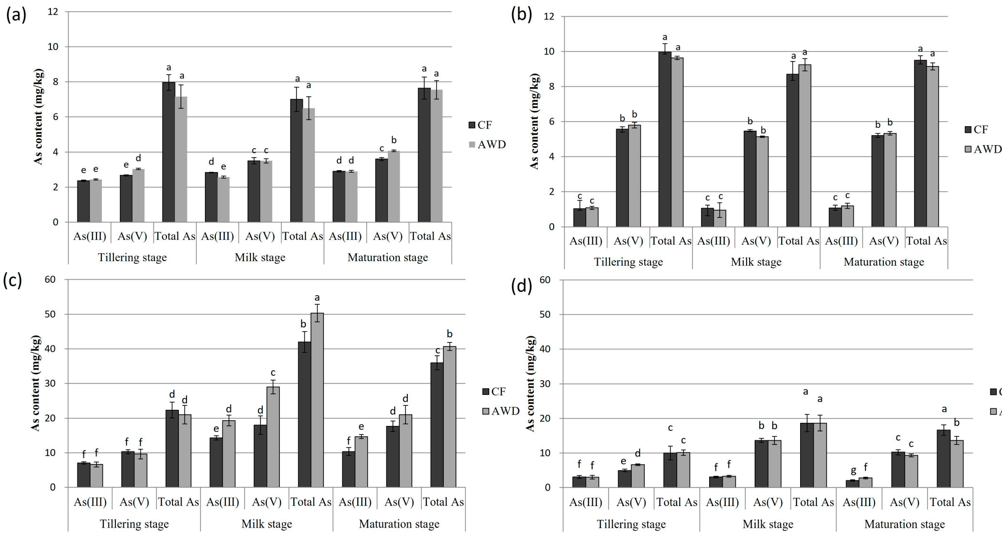

Figure 3. Water management effects on As accumulation in paddy soils and rice roots. (**a**,**b**); Effect of different water management on As content in paddy soils under acidic fields (**a**) and alkaline fields (**b**); (**c**,**d**); Effect of different water management on As content in rice roots under acidic fields (**c**) and alkaline fields (**d**). CF represents continuous flooding, and AWD represents alternate wetting and drying. Error bars represent standard error of the mean (SE). Different letters indicate statistically significant difference ($p < 0.05$).

In alkaline field soils (Figure 3d), compared with AWD, CF significantly inhibited the As(V) content in rice roots at the tillering stage, but did not affect the content of As(III) and T-As. There is no significant difference of As level in any form in rice roots between CF and AWD modes during the milk stage. In the mature stage, compared with AWD, the CF mode reduced and increased the accumulation of As(III) and T-As in rice roots, respectively. The content of As(V) in rice roots does not differ significantly between the two water management modes.

3.6. Effect of Water Management on As Accumulation in Rice Plants

In an acidic soil environment, no significant differences were observed in the effects of different water management practices on As(III), As(V), or T-As in rice plants during the tillering stage (Figure 4a). However, CF exacerbated the accumulation of As in any form in the rice plants during the milk stage (Figure 4a). At the maturity stage, the accumulation of As(III) in rice plants under both water management modes was similar, while the enrichment of As(V) and T-As in rice plants was significantly higher under CF mode than under the AWD mode (Figure 4a). Overall, CF increased the risk of As enrichment in rice plants in fields with acidic soil conditions.

In alkaline fields, the CF mode was found to significantly promote the accumulation of both As(III) and As(V) in rice plants during the tillering stage, whereas no significant differences were observed in the accumulation levels of these species in rice plants during the milk and maturation stages between the two irrigation modes (Figure 4b). In addition, the T-As content accumulated in rice plants during the tillering stage was significantly higher in the CF mode than in the AWD mode, while during milky stage, the T-As content in rice plants under the two water management modes followed the order AWD > CF (Figure 4b).

3.7. Effect of Water Management on As Accumulation in Rice Grains

In soil with an acidic environment, the application of CF during the milk stage of rice growth resulted in a reduction in the accumulation of any form of As in the rice grains compared to the AWD method (Figure 4c). However, at the maturity stage, the application of CF increased the risk of As(III) pollution in rice, and its impact on As(V) and T-As was similar to that of the AWD method (Figure 4c).

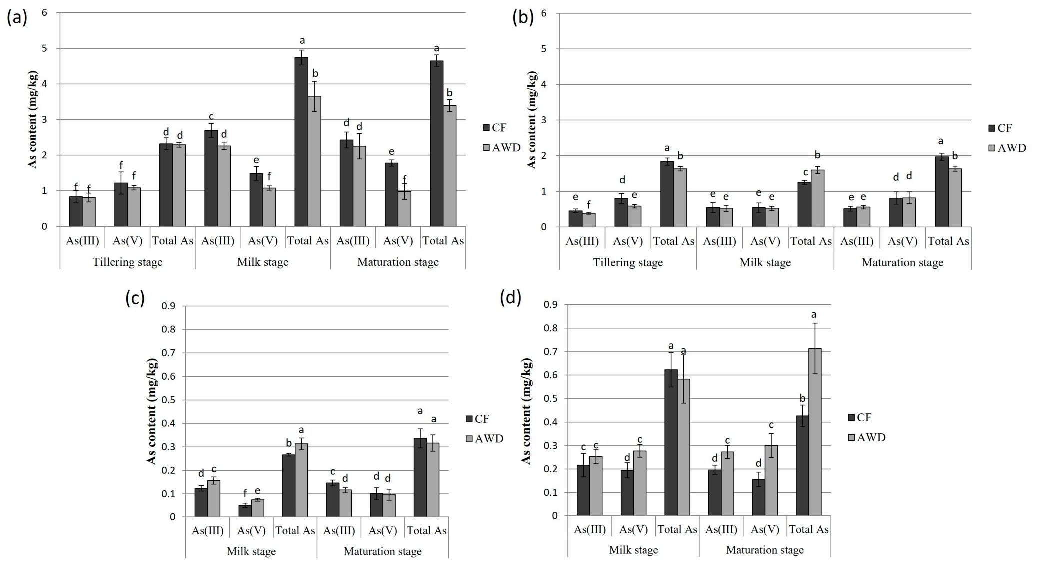

Figure 4. Water management effects on As accumulation in rice plants and grains. (**a**,**b**); Effect of different water management methods on As content in rice plants under acidic fields (**a**) and alkaline fields (**b**). (**c**,**d**); Effect of different water management methods on As content in rice grains under acidic fields (**c**) and alkaline fields (**d**). CF represents continuous flooding, and AWD represents alternate wetting and drying. Error bars represent standard error of the mean (SE). Different letters indicate statistically significant difference ($p < 0.05$).

In alkaline soils, the concentration of As species (As(III) and As(V)) in rice grains under the CF mode was significantly lower than that under the AWD mode during the milk and maturation stages (Figure 4d). Regarding the T-As content, only the T-As content in rice grains under the CF treatment during the milk stage was similar to that under the AWD mode, whereas during the maturity stage, the CF treatment significantly inhibited the accumulation of T-As in rice grains compared to the AWD mode (Figure 4d). These findings suggest that CF can effectively reduce the levels of As pollution in rice grains in alkaline soil environments.

4. Discussion

In this study, it was observed that, during the rice harvest period, the use of CF in acidic fields, as opposed to the commonly utilized AWD mode of production, resulted in a reduction in the risk of Cd pollution in both the rice plants and grains (Figures 2a,c and 5c). This result proves that CF is an effective mode of reducing Cd enrichment in rice, as reported in numerous studies [14,15], but only under acidic conditions. Although CF is traditionally considered an effective method for controlling and reducing Cd pollution in rice, recent evidence suggests that the accumulation of Cd in rice due to CF may be contrary to the findings of previous studies under certain specific conditions [11]. Research has indicated that the accumulation of Cd in rice grains under unsaturated irrigation conditions, such as sprinkler irrigation, is significantly lower than that in CF [25]. Another study also demonstrated that the application of CF under conditions of low phosphorus fertilizer supply led to a higher accumulation of Cd in rice than that of AWD [26]. In this study, we found a similar conclusion in alkaline fields during the harvest stage according to which CF significantly increased the risk of Cd accumulation in rice plants and grains compared to AWD (Figures 2b,d and 5c). These findings highlight the intricate and regulated nature of Cd accumulation in rice resulting from irrigation systems, and this process may be regulated by undefined factors. The contrasting result between acidic and alkaline fields in this study demonstrated that the pH of the paddy soil is a key factor affecting Cd enrichment in rice mediated by water management. The findings presented here partially elucidate the dynamic nature of CF in reducing Cd accumulation in rice [11]. Furthermore, this study highlights that the reduction and control in Cd pollution in rice through CF were limited to acidic soil environments and are not applicable to alkaline soil conditions. Previous investigations on pot experiments have suggested that bioavailability and Cd availability in contaminated rice field soil are influenced by various factors, including alkaline fertilizer, water management, and soil pH [27]. The pH of paddy soils has been reported to significantly affect Cd bioavailability [28]. The concentration of Cd in both dryland and flooded rice decreased as the pH of the paddy soil increased from 6.1 to 6.9 [29]. Future research should focus on the physiological, biochemical, and molecular mechanisms underlying pH-dependent regulation of Cd accumulation in rice via CF.

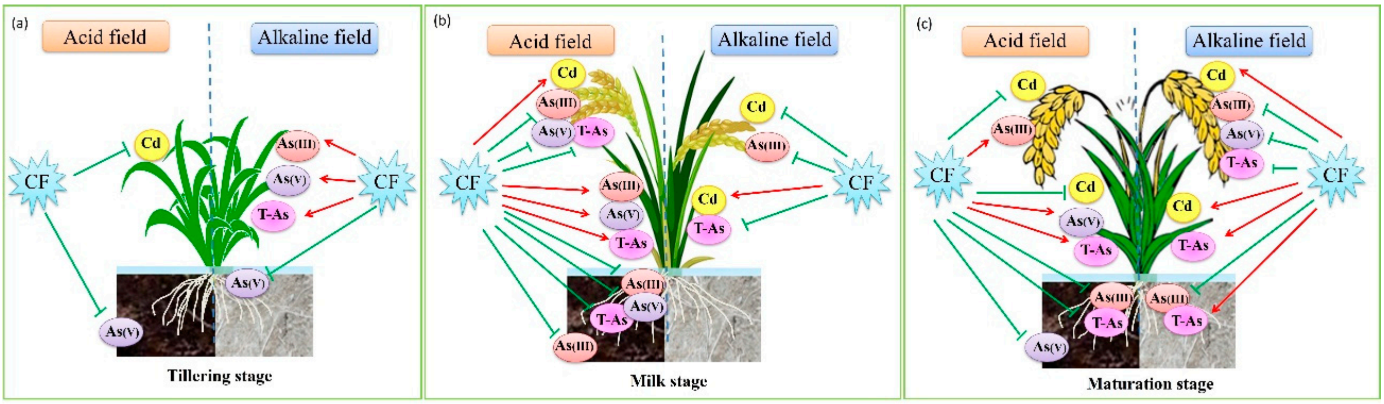

Figure 5. Role of soil pH in CF-mediated Cd and As accumulation. (**a**); Effect of CF on Cd and As accumulation in soils, rice roots, plants, and grains compared to AWD at different pH fields during tillering stage. (**b**); Effect of CF on Cd and As accumulation in soils, rice roots, plants, and grains compared to AWD at different pH fields during milk stage; (**c**); Effect of CF on Cd and As accumulation in soils, rice roots, plants, and grains compared to AWD at different pH fields during maturation stage. CF represents continuous flooding, and AWD represents alternate wetting and drying. Red arrows represent a promoting effect on heavy metal accumulation. The green cutoff line represents an inhibitory effect on heavy metal accumulation.

Numerous studies have demonstrated that, although CF is effective in reducing the accumulation of Cd in rice, it increases the risk of As enrichment [30,31]. On the basis of determining that pH is a key factor affecting Cd enrichment mediated by CF in rice, this study further confirms that the soil's pH value also affects the accumulation of As in rice. In acidic soil conditions, the application of CF resulted in a significant increase in the accumulation of As(III) in rice grains during the maturation period compared to AWD (Figure 5), and As(III) was the most toxic form of As [32]. Additionally, CF also increased the accumulation of As(V) and T-As in plants (Figure 5), while reducing the content of As(III) and T-As in roots as well as As(V) in acidic paddy soil (Figure 5), suggesting that the implementation of CF during the mature stage promotes the transfer of As(V) from soil to plants, As(III) from roots to grains, and T-As from roots to plants compared with AWD. In alkaline soil conditions, CF reduced the risk of enrichment of As(III), As(V), and T-As in mature rice grains (Figure 5). Moreover, during the mature stage, CF increased the accumulation of T-As in rice roots and plants while it reduced the As(III) content in roots (Figure 5). It can be seen that, compared with AWD, the use of CF during the mature stage limits the transfer of T-As from roots and plants to grains. Furthermore, CF seems to reduce the accumulation of As(III) in grains by reducing the uptake of As(III) by roots from the soil. However, the current results cannot explain why the As(V) content in rice grains is significantly lower under the action of CF than AWD.

A thorough examination of the accumulation patterns of Cd and As in acidic and alkaline soils, as well as in rice at different growth stages, revealed that the soil pH significantly influenced the uptake and accumulation of the heavy metals in rice roots, plants, and grains at any stage (Figure 5). In acidic fields, following the development process of rice seedlings to maturity, both CF and AWD did not change the enrichment status of Cd in the soils, and both promoted the availability of As(III) and As(V) in the soil. However, compared with AWD, CF reduces the efficiency of Cd transfer from roots to plants and effectively limits the dynamic migration of Cd from plants to grains. Moreover, CF promotes the transfer of T-As from roots to plants by reducing the increase in T-As content in roots and increasing the increase in T-As content in plants compared with AWD. From the changes in As(III) and As(V) throughout the entire growth period in rice, it can be seen that, contrary to the inhibition of As(III) migration from plants to grains by AWD, CF significantly promotes the accumulation of As(III) in grains. CF also promoted the mobilization of As(V) from roots to plants, and then from plants to grains, especially with a significantly higher promotion of As(V) transfer from plants to grains than AWD. In alkaline fields, with the extension of the rice growth period, compared with AWD, CF increased the risk of Cd pollution in grains by promoting the accumulation of Cd in plants. In alkaline fields, with the extension of the rice growth period, compared with AWD, CF increases the risk of cadmium pollution in grains by promoting the accumulation of Cd in plants. From the migration pattern of As from the rice seedling stage to the maturity stage, compared with AWD, CF seems to reduce the accumulation of T-As in grains by blocking the transfer of T-As from roots to plants, and reduce the accumulation of As(III) in grains by inhibiting the uptake of As(III) in roots. These results indicate that soil pH also affects the migration dynamics of heavy metals mediated by irrigation during the rice growth period between soil, roots, plants, and grains. Although the underlying mechanism is not yet fully understood, pH is a crucial factor that cannot be ignored when evaluating the effectiveness of improving heavy metal pollution in rice through water management.

Notably, from a food safety perspective, the level of heavy metal pollution in rice grains during the maturity stage was particularly noteworthy. In acidic fields, the application of CF reduced the residual risk of Cd in rice plants and grains during the maturity stage, but it also promoted the enrichment of As (Figure 5c). It seems that, under acidic soil conditions, the mobilization of Cd into grains only occurs during the rice growing season rather than the mature stage, which may be due to the low pH-dependent synthesis of certain Cd transfer inhibitors or dilution factors during the mature stage. In alkaline soil environments, CF was unable to reduce the Cd content of mature rice grains as it did in acidic fields, but instead increased the risk of Cd accumulation in the rice plants and grains. However, the application of the CF model in alkaline fields reduced the accumulation of As in rice grains (Figure 5c). It is worth noting that, according to the Chinese food safety standards, the maximum residual limit of Cd in brown rice is 0.2 mg/kg. Whether in acidic or alkaline fields, the accumulation level of Cd in brown rice under both water management modes is at a safe level. According to the maximum residue limit of 0.35 mg/kg of inorganic As in brown rice stipulated in Chinese food safety standards, the pollution level of inorganic As in acidic fields is relatively low. However, in alkaline fields, there is a risk of exceeding the limit for inorganic arsenic in brown rice under the AWD mode, while CF can reduce the accumulation of inorganic As to a safe level. These findings suggest that the dynamics of Cd and As in rice were strongly affected by the pH of the paddy soil and that the accumulation of these elements in brown rice mediated by CF displayed an opposite trend under both acidic and alkaline conditions. This is consistent with the results of numerous previous studies that have reported opposite biogeochemical behaviors of As and Cd [31], which indicates that the opposite biochemical behavior of Cd and As in rice mediated by CF is not affected by the pH of the cultivated soil. Previous studies have shown that water management can affect the dynamics of Cd and As in soil by affecting soil physical and chemical properties, such as pH and soil redox potential (Eh), and by regulating the forms and contents of soil iron, manganese, and sulfur [10,33]. The results of this study partly reveal that pH was not the main reason for the opposite accumulation effect of Cd and As in rice grains. In the future, the role of soil Eh and element (iron, manganese, and sulfur) features in the opposite enrichment behavior of Cd and As in rice grains should be given special attention.

This study utilized actual rice production fields in Liaoning, which were typical japonica rice cultivation areas and belonged to relatively low-Cd pollution areas with little dietary risk. These results indicate that CF had a promoting effect on As enrichment in mature rice grains under acidic conditions, and it was not suitable as a remediation strategy for Cd pollution in rice under acidic soil environments. Although CF exacerbated the accumulation of Cd in brown rice in alkaline fields, it can reduce the risk of As pollution in brown rice to a safe level. Therefore, CF management was unsuitable for repairing Cd pollution in rice in areas with low Cd pollution, but it can be considered as a potential strategy for As pollution remediation in rice in alkaline fields with low Cd pollution.

5. Conclusions

Soil pH is a crucial element in regulating the accumulation and migration of Cd and As in paddy soils, rice roots, plants, and grains at any stage of rice growth under CF-mediated conditions (Figure 5). In acidic fields, compared with the AWD, the effects of the CF on the accumulation of Cd and As in mature rice grains followed the pattern of reducing Cd and increasing As, whereas in alkaline fields, the opposite result was obtained, where CF promoted Cd accumulation but reduced As accumulation. The opposite biochemical behavior of Cd and As in rice grains mediated by CF was not affected by the pH of the cultivated soil. When selecting water management as an agronomic measure to remediate Cd pollution in rice production, it was essential to fully consider the pH of the paddy soils. Further research is required to investigate the physiological, biochemical, and molecular mechanisms underlying the influence of pH on the growth and decline of Cd and As mediated by irrigation. In conclusion, the application of CF is not recommended as a remediation strategy for Cd pollution in rice in areas with low Cd pollution resulting from the increased As accumulation in rice grains under acidic soil environments and induced the Cd pollution risk of rice under alkaline soil conditions. However, CF can be considered as a potential strategy for As pollution remediation in rice in alkaline fields with low Cd pollution. Our findings provide valuable insights for ensuring food security and remediating heavy metal pollution in japonica rice-producing areas of Northeast China.

Author Contributions: Investigation, Q.L. and C.G.; Resources, G.L. and L.L.; Data curation, X.W.; Writing—original draft, X.W.; Writing—review & editing, X.W.; Project administration, J.W.; Funding acquisition, J.W. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Fundamental Research Funds of Liaoning Academy of Agricultural Sciences (2024DD113318), and Risk Assessment of Agricultural Product Quality and Safety (14225024, 14234045).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: We are very grateful to Li Tianya at the College of Plant Protection, Shenyang Agricultural University for his guidance and editing of the text.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Verbruggen, N.; Hermans, C.; Schat, H. Mechanisms to cope with arsenic or cadmium excess in plants. *Curr. Opin. Plant Biol.* **2009**, *12*, 364–372. [CrossRef]
2. Sun, L.M.; Zheng, M.N.; Liu, H.Y.; Peng, S.B.; Huang, J.L.; Cui, K.H.; Nie, L.X. Water management practices affect arsenic and cadmium accumulation in rice grains. *Sci. World J.* **2014**, *2014*, 596438.
3. Rikans, L.E.; Yamano, T. Mechanisms of cadmium-mediated acute hepatotoxicity. *J. Biochem. Mol. Toxicol.* **2000**, *14*, 110–117. [CrossRef]

4. Rahman, M.; Sohel, N.; Yunus, F.M.; Alam, N.; Nahar, Q.; Streatfield, P.K.; Yunus, M. Arsenic exposure and young adult's mortality risk: A 13-year follow-up study in Matlab, Bangladesh. *Environ. Int.* **2019**, *123*, 358–367. [CrossRef]
5. Xu, Y.; Fu, J.; Wang, H.; Hou, Y.; Pi, J. Arsenic Exposure and Lifestyle-Related Diseases. In *Arsenic Contamination in Asia. Current Topics in Environmental Health and Preventive Medicine*; Yamauchi, H., Sun, G., Eds.; Springer: Singapore, 2019. [CrossRef]
6. Zhao, F.J.; Wang, P. Arsenic and cadmium accumulation in rice and mitigation strategies. *Plant Soil* **2020**, *446*, 1–21. [CrossRef]
7. Mlangeni, A.T.; Perez, M.; Raab, A.; Krupp, E.M.; Norton, G.J.; Feldmann, J. Simultaneous stimulation of arsenic methylation and inhibition of cadmium bioaccumulation in rice grain using zero valent iron and alternate wetting and drying water management. *Sci. Total Environ.* **2020**, *711*, 134696. [CrossRef]
8. Michio, H.; Shahdat, H.; Kentaro, M.; Osamu, S.; Katsumi, Y. The journey from white rice to ultra-high hydrostatic pressurized brown rice: An excellent endeavor for ideal nutrition from staple food. *Crit. Rev. Food Sci. Nutr.* **2022**, *62*, 1502–1520.
9. Zhu, T.; Li, L.; Duan, Q.; Liu, X.; Chen, M. Progress in our understanding of plant responses to the stress of heavy metal cadmium. *Plant Signal. Behav.* **2021**, *16*, 1836884. [CrossRef] [PubMed]
10. Zhao, F.J.; McGrath, S.P.; Meharg, A. Arsenic as a food chain contaminant: Mechanisms of plant uptake and metabolism and mitigation strategies. *Annu. Rev. Plant Biol.* **2010**, *61*, 535–559. [CrossRef]
11. Li, H.; Zhang, H.; Yang, Y.; Fu, G.; Tao, L.; Xiong, J. Effects and oxygen-regulated mechanisms of water management on cadmium (Cd) accumulation in rice (*Oryza sativa*). *Sci. Total Environ.* **2022**, *846*, 157484. [CrossRef]
12. Raghuvanshi, R.; Raut, V.V.; Pandey, M.; Jeyakumar, S.; Verulkar, S.; Suprasanna, P.; Srivastava, A.K. Arsenic and cadmium induced macronutrient deficiencies trigger contrasting gene expression changes in rice. *Environ. Pollut.* **2022**, *300*, 118923. [CrossRef]
13. Spanu, A.; Valente, M.; Langasco, I.; Barracu, F.; Orlandoni, A.M.; Sanna, G. Sprinkler irrigation is effective in reducing cadmium concentration in rice (*Oryza sativa* L.) grain: A new twist on an old tale? *Sci. Total Environ.* **2018**, *628*, 1567–1581. [CrossRef]
14. Wang, J.; Li, D.; Lu, Q.; Zhang, Y.; Xu, H.; Wang, X.; Li, Y. Effect of water driven changes in rice rhizosphere on cd lability in three soils with different pH. *J. Environ. Sci.* **2020**, *87*, 82–92. [CrossRef]
15. Huang, B.; Zhao, F.; Wang, P. The relative contributions of root uptake and remobilization to the loading of Cd and As into rice grains: Implications in simultaneously controlling grain Cd and As accumulation using a segmented water management strategy. *Environ. Pollut.* **2022**, *293*, 118497. [CrossRef]
16. Xu, W.; Hou, S.; Muhammad, A.; Chao, Y.; Xiao, L.; Ruan, Z.; Hong, L.; Chen, Z.; Ceng, S.; Ye, Z.; et al. Effect of water and fertilization management on Cd immobilization and bioavailability in Cd-polluted paddy soil. *Chemosphere* **2021**, *276*, 130168.
17. Wiggenhauser, M.; Aucour, A.M.; Bureau, S.; Campillo, S.; Telouk, P.; Romani, M.; Ma, J.F.; Landrot, G.; Sarret, G. Cadmium transfer in contaminated soil-rice systems: Insights from solid-state speciation analysis and stable isotope fractionation. *Environ. Pollut.* **2021**, *269*, 115934. [CrossRef]
18. Hu, P.; Ouyang, Y.; Wu, L.; Shen, L.; Luo, Y.; Christie, P. Effects of water management on arsenic and cadmium speciation and accumulation in an upland rice cultivar. *J. Environ. Sci.-China* **2015**, *27*, 225–231. [CrossRef] [PubMed]
19. Shi, R.G.; Lv, J.G.; Liu, Y.Z. Spatial Distribution and Bio-accumulation of Cadmium and Lead in Soil, Rice and Vegetables in Typical Pollution Areas, China. *Bull. Environ. Contam. Toxicol.* **2020**, *104*, 307–313. [CrossRef] [PubMed]
20. *HJ/T 166-2004*; Technical Specification for Soil Environmental Monitoring. Environmental Protection Industry Standards of the People's Republic of China: Beijing, China, 2004.
21. Liu, F.; Cai, Y.; Liu, Y.; Liu, M.; Xu, Y.; Yang, Y.; Zhan, X. *Soil Quality-Analysis of Soil Heavy Metals-Atomic Absorption Spectrometry with Aqua Regia Digestion*; NY/T 1613-2008; China Agricul Ture Press: Bejing, China, 2008.
22. *GB 5009.15-2014*; National Food Safety Standard—Determination of Cadmium in Food. National Standard of the People's Republic of China: Beijing, China, 2014.
23. *NY/T 1121.11-2006*; Soil Testing. Part 11: Method for Determination of Soil Total Arsenic. Agricultural Industry Standards of the People's Republic of China: Beijing, China, 2014.
24. *GB 5009.11-2014*; National Food Safety Standard—Determination of Total Arsenic and Inorganic Arsenic in Foods. National Standard of the People's Republic of China: Beijing, China, 2014.
25. Spanu, A.; Valente, M.; Langasco, I.; Leardi, R.; Orlandoni, A.M.; Ciulu, M.; Deroma, M.A.; Spano, N.; Barracu, F.; Pilo, M.I.; et al. Effect of the irrigation method and genotype on the bioaccumulation of toxic and trace elements in rice. *Sci. Total Environ.* **2020**, *748*, 142484. [CrossRef] [PubMed]
26. Song, T.; Das, D.; Hu, Q.; Yang, F.; Zhang, J. Alternate wetting and drying irrigation and phosphorus rates affect grain yield and quality and heavy metal accumulation in rice. *Sci. Total Environ.* **2021**, *752*, 141862. [CrossRef] [PubMed]
27. Ye, X.; Li, H.; Zhang, L.; Chai, R.; Tu, R.; Gao, H. Amendment damages the function of continuous flooding in decreasing Cd and Pb uptake by rice in acid paddy soil. *Ecotoxicol. Environ. Saf.* **2018**, *147*, 708–714. [CrossRef] [PubMed]
28. Yang, Y.J.; Chen, J.; Huang, Q.; Tang, S.; Wang, J.; Hu, P.; Shao, G. Can liming reduce cadmium (Cd) accumulation in rice (*Oryza sativa*) in slightly acidic soils? A contradictory dynamic equilibrium between Cd uptake capacity of roots and Cd immobilisation in soils. *Chemosphere* **2018**, *193*, 547–556. [CrossRef] [PubMed]
29. Kikuchi, T.; Okazaki, M.; Kimura, S.D.; Motobayashi, T.; Baasansuren, J.; Hattori, T.; Abe, T. Suppressive effects of magnesium oxide materials on cadmium uptake and accumulation into rice grains: II: Suppression of cadmium uptake and accumulation into rice grains due to application of magnesium oxide materials. *J. Hazard. Mater.* **2008**, *154*, 294–299. [CrossRef] [PubMed]

30. Silva, J.O.T.; Paniz, F.P.; Sanchez, F.E.S.; Pedron, T.; Torres, D.P.; Rocha, C.F.I.G.D.; Barbat, P.J.M.; Batista, B.L. Selected soil water tensions at phenological phases and mineral content of trace elements in rice grains–mitigating arsenic by water management. *Agric. Water Manag.* **2020**, *228*, 105884. [CrossRef]
31. Carrijo, D.R.; LaHue, G.T.; Parikh, S.J.; Chaney, R.L.; Linquist, B.A. Mitigating the accumulation of arsenic and cadmium in rice grain: A quantitative review of the role of water management. *Sci. Total Environ.* **2022**, *839*, 156245. [CrossRef]
32. Zavala, Y.J.; Gerads, R.; Gürleyük, H.; Duxbury, J.M. Arsenic in rice: II. Arsenic speciation in USA grain and implications for human health. *Environ. Sci. Technol.-Env.* **2008**, *42*, 3861–3866. [CrossRef]
33. Kawasaki, A.; Arao, T.; Ishikawa, S. Reducing cadmium content of rice grains by means of flooding and a few problems. *J. Food Hyg. Soc. Jpn.* **2012**, *67*, 478–483. [CrossRef]