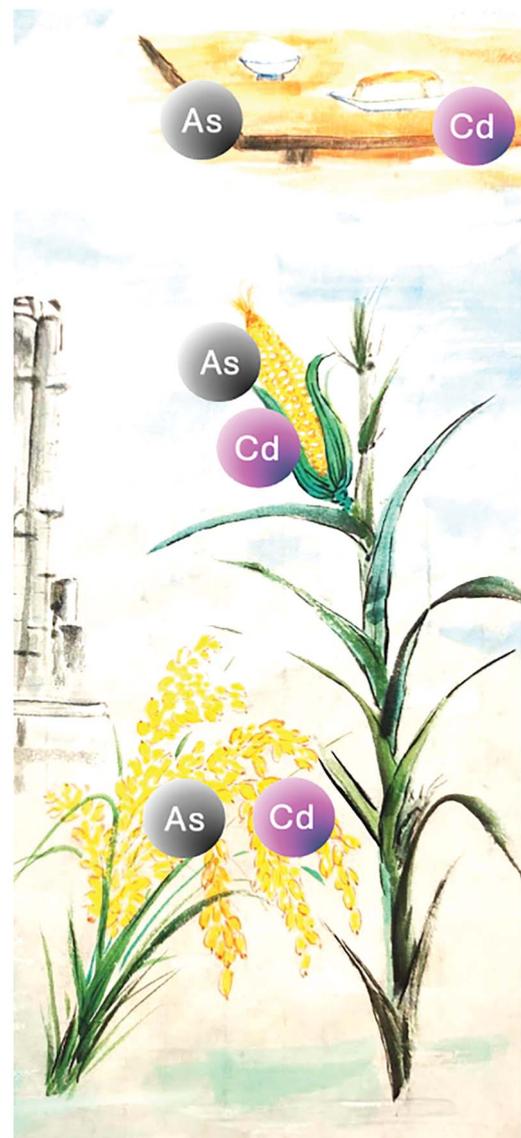


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**PAPER**

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## Multi-mode soil chemical passivation and crop protection of severe cadmium and arsenic polluted soils with engineered silica†

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Large tracts of agricultural land are enriched in toxic trace elements (TTE), particularly cadmium and arsenic. Functionalized mesoporous silica (FMS) is used extensively as an advanced process and waste-stream management tool for TTE removal in the chemical industries. Their adoption in agriculture though is extremely limited, encompassing only a narrow selection of FMS materials and crop/soil types. Understanding the function of FMS in diverse and relevant agri-settings is a priority. Not only in terms of their ability to immobilize TTE, but also in relation to the uncharacterized risks they pose to the soil's supply of essential nutrients, concurrent plant ionome responses and crop performance. Here, a series of plant mesocosm experiments were conducted on seriously degraded soils from zinc smelting operations. Two different crops, *Oryza sativa* and *Brassica rapa* with opposing redox managements were studied to understand the mechanisms of the FMS–soil–plant interactions. Companion FMS-incubations were undertaken on urban-industry impacted and mining-accident/“cancer-village” soils, to test performance across a wider range of contamination scenarios. In addition to the multi-functionality of FMS for targeted TTE immobilization along with the chemical inertia for needed plant nutrients, its abilities as a vector for plant growth/soil remediation stimulants was also investigated. Growth/protection enhancers were preloaded on FMS and then trials were performed to characterize their release. The plant mesocosm experiment demonstrated FMS can effectively immobilize ~36% of the total Cd and ~37% of the bioavailable Cd in soil into a highly recalcitrant/plant unavailable fraction. This significantly reduced in planta Cd accumulation by >80% across contrasting soil redox scenarios. Bioavailability of Cd and As decreased simultaneously by 98% and 57%, in companion soil incubations. Finally, FMS successfully accumulated and released dosed agri-chemicals in solution-based experiments. These findings establish FMS as a multi-functional soil amendment, offering a novel and integrated solution for complex agricultural soil issues.

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### Environmental significance

TTE pollution in soil is extensive and poses a significant threat to environmental and human health. Extraction of metal contaminants in soil is technically challenging, whereas immobilization provides a more practical solution. This study demonstrates that FMS can substantially reduce in solium bioavailability of TTE. This results in safe crop production even in severely contaminated soils. The ion affinities of FMS are specific to target TTEs, with minimal impact on the crop's nutrient ionome. In addition, enhanced crop protection is provided by nutrients/agri-chemicals preloaded in the FMS. This multi-faceted approach to soil pollution is a promising new tool for agricultural soil remediation.

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## 1. Introduction

Cadmium (Cd) and arsenic (As) are among the most problematic toxic trace elements (TTE) that threaten food safety.<sup>1–4</sup> Preventing the transfer of TTE in the soil-plant system through soil remediation is a key strategic solution.<sup>5</sup> There are numerous remediation approaches but the addition to contaminated soil of binders that immobilize TTE *via* processes of chemical passivation are the most popular because of convenience, cost, and rapid implementation.<sup>6,7</sup> Other



technologies, such as phytoremediation, only work under specific conditions and require a long time to be effective.<sup>5</sup> Physical measures, such as soil washing, are expensive and can cause lasting damage to the treated soil.<sup>8</sup> Soil amendments, work *via* stabilization. Traditional remediation materials used for immobilizing TTE in soil include lime ( $\text{CaCO}_3/\text{CaO}$ ) and metal oxides ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$ ). Additionally, phosphorus-containing compounds (*e.g.*, hydroxyapatite, phosphate rock), natural or synthetic minerals (such as sepiolite, zeolite, and montmorillonite), and biochar (BC) are also popular amendment technologies.

Lime increases soil pH, enhancing the soil's adsorption capacity for cation TTE.<sup>9</sup> The immobilization principle of metal oxides and phosphorus-containing substances is to induce TTE adsorption or produce precipitation to reduce bioavailability.<sup>9–11</sup> The immobilization mechanism of natural/synthetic minerals is mainly through ion exchange.<sup>12,13</sup> The surface area and porosity, which varies with feedstock and pyrolysis method, primarily determine the adsorption capacity of the biochar (BC).<sup>14</sup> Biochar, especially, has been used extensively in trials, showing strong performance in reducing the bioavailability of soil Cd and decreasing the accumulation of Cd in rice grains.<sup>15</sup> In addition, to immobilization, the effect of BC in reducing Cd uptake by rice, is thought to relate to improved Si supply.<sup>16,17</sup>

FMS is the gold standard for metal recovery treatments in the pharmaceutical and commercial/industrial chemistry sector. It is favoured for its high capacity, selectively and resilience to problematic matrixes, especially low pH.<sup>18</sup> However, the application of functionalized mesoporous silica (FMS) in soil remediation is recent, with only a few reported studies to date.<sup>19,20</sup> A reason why FMS has not been used more extensively is due to limited access to suppliers and cost, but this is changing, as methods for FMS synthesis improve. FMS can be chemically synthesized based on mesoporous silica (MS). MS differs from silicon fertilizer due to its extensive internal network of pores/channels, but the underpinning raw material Si is readily available. More detail on the form and synthesis of FMS is provided in Yang *et al.*, (2020).<sup>18</sup> In brief, FMS offers variable pore sizes, high surface areas, stability, and strong/targeted adsorption ability. This makes it attractive for soil remediation applications, especially severely contaminated scenarios.

Land management plays a defining role in how TTE mobilize, with bio-geochemical processes in cropping systems such as dryland vegetables being vastly different to that of flooded lowland rice. Here, soil oxygen ( $\text{O}_2$ ) concentrations, soil redox potential (Eh), and pH strongly influence biogeochemical cycling, especially for both As and Cd which have a marked dichotomy of behaviors as redox conditions change.<sup>21</sup> This is further modulated by the rhizosphere. For example, scales of iron and manganese (hydro)oxides, attached to the surface of rice roots in wetland scenarios play a major role in altering TTE uptake. These can act to both sequester and supply.<sup>22,23</sup> In non-saturated soil conditions, the mobilization of TTE by root exudates can be more dominant. In both cases though, simultaneously, phosphate and Si ions act as competitive inhibitors for As uptake in roots, whilst Mn and Fe perform a similar function for Cd.<sup>24,25</sup> Overlaid on this are plant metabolic

responses, with growth, stress and defense responses being regulated by secondary metabolites. For example, salicylic acid has been found to increase plant tolerance to Cd.<sup>26</sup>

In this research, these intertwined biogeochemical processes were explored in severely TTE contaminated soils, using a new multi-mode soil chemical passivation technology based on engineered crystalline silica, and the dual role of FMS in TTE immobilization and controlled metabolite release were studied. Plant mesocosm trials were conducted to study/evaluate a specific Cd targeted FMS as a soil-crop remediation strategy in severely Cd contaminated soils. Two common crops, rice (*Oryza sativa* L.) and pakchoi (*Brassica chinensis* L.), which are widely grown in the Cd-contaminated soil collection sites, were selected to explore the ability of FMS to reduce the accumulation of Cd in two redox diverse cropping systems. To compare the effects of different amendment methods, the application of non-functionalized MS and a common BC were also included in the trial design, along with a control. To understand how soil Cd fractionation is changed by FMS additions, common sequential extraction/BCR procedures were performed. Whilst the impact of the FMS on other trace element cycles, such as As, Fe, Mn and Cu were investigated from both the perspective of soil chemical behaviors, but also plant performance (yield), ionome changes, internal element transfer and root iron plaque formation/characterization. A soil incubation experiment was conducted, and the As and Cd bioavailability of FMS-treated soil was measured using Diffusive Gradients in Thin Films (DGT). In addition, FMS was spiked/pre-loaded with plant-beneficial elements/compounds (K, Mn, P, and salicylic acid). The loading capacity of FMS and the release performance of spiked FMS in water were studied, and its possibility as a rhizosphere regulator was evaluated.

## 2. Material and methods

### 2.1. Soil collection, sourcing of seed and soil additives

Soil was collected from 3 provinces in southern China. Cd contaminated soil was sampled from Bijie City (BJ soil) and Liupanshui City (LSP soil), Guizhou province. The pH value of BJ soil is 6.6, and the concentration of Cd is  $1.9 \text{ mg kg}^{-1}$ ; the pH value of LPS soil is 6.7, and the concentration of Cd is  $9.5 \text{ mg kg}^{-1}$  (Table S1†). As contaminated soil was collected from Chenzhou City (CZ soil) (As:  $73 \text{ mg kg}^{-1}$  pH<sup>-1</sup>: 6.9), Hunan Province (Table S2†). Mining and industry contaminated soil was collected from near the Dabaoshan mine (GD soil) and a peri-urban farming zone in Gaoming City (GG soil), Guangdong Province (Tables S2–S4†). Rice and pakchoi seeds were purchased at an agricultural supplies market in Guizhou City, Guiyang Province, China (Table S5†). FMS and MS were purchased from the Golden Keys High-Tech Materials Co., Ltd, detail information is shown in Table S6.† Food-grade commercial BC was purchased from Henan Zhongju Purification Materials Co., Ltd.

### 2.2. Experimental design

**2.2.1. Rice and pakchoi pot trial.** Four treatments (FMS, MS, BC, and no amendment/control) were implemented, with 4



replicates per treatment for rice Chuanyou 670 (CY67) and Yiyou1787 (YY17); 5 replicates per treatment for the pakchoi. Potted experiments were carried out in plastic mesocosms (14 × 15 × 9.5 cm) with a diameter of 14 cm, and each container was filled with 1 kg of soil, the dosages of FMS, MS, and BC were 5% (wt%), mixed with soil. BJ soil was used in the rice mesocosm trial; LPS soil was used in the pakchoi trial. Dithionite–citrate–bicarbonate (DCB) experiments were conducted on fresh harvested rice roots, and TTE composition analysis was conducted on plant samples and soil samples. Detailed information is described in Text S1.†

**2.2.2. Soil incubation.** 150 g CZ soils (CZ-L) were treated with different doses (wt%) of FMS (0%, 0.1%, 0.5%, and 1%) (2 weeks incubation), while the 0.5%-FMS treated CZ-L were incubated for a further 4 and 8 weeks. In addition, different soil scale (150 g vs. 50 g) was set up for different dose treatment groups, each treatment was replicated ( $n = 4$ ). For GD and GG soil incubation experiments, control group (CT) and treatment group (1% FMS) were set up. The incubation time was 2 weeks, 50 g soil each pot, 3 replication each group. The Diffuse Gradients in Thin films (DGT) technique, DGT-induced fluxes in sediments and soils (DIFS), and pore water analysis were used to evaluate the performance of FMS in various soil incubation experiments. Detailed information is described in Text S2.†

**2.2.3. Nutrients/agri-chemical pre-loading and release.** The detailed pre-loading process of K/Mn/P spiked FMS and the calculation of loading capacity (LC) is described in Text S3.† In the release experiment, spiked FMS (1 g) was added to 40 mL of Milli-Q water (18.2 MΩ cm) (container: 50 mL glass bottle) and shaken (200 RCF) for 12 h at room temperature using a mechanical oscillator (Jipad-200TLMS). Sampling was carried out at 4 h, 8 h, and 12 h. The specific sampling operation was as follows: collect the supernatant, 20 mL of Milli-Q was used to rinse the spiked FMS in a glass bottle, repeating 3 times. Then 40 mL of Milli-Q water was added, with the bottle agitated with gentle shaking. Collected supernatant was filtered (PES membrane, pore size: 0.45 μm, 270 mm × 10 m), and ICP-OES (Varian Vista MPX CCD) was used to determine the content of elements in the supernatant. Detailed information on salicylic acid (SA) spiked FMS experimental design is described in Text S3.† HPLC (Agilent 1260 infinity 2 series HPLC) was used to determine the content of SA in the supernatant (detailed described in Text S4†).

### 2.3. Sample analysis and quality control

Rice tissues and pakchoi digestion samples, DCB extraction samples, porewater samples, soil BCR extraction samples, and soil anti-aqua regia digestion samples were analyzed by ICP-MS (Agilent 7700X), the isotopes monitored included <sup>75</sup>As, <sup>111</sup>Cd, <sup>63</sup>Cu, <sup>55</sup>Mn, and <sup>66</sup>Zn. DGT elution samples were analyzed by ICP-MS (NexION 300X, PerkinElmer), the isotopes monitored being <sup>75</sup>As and <sup>111</sup>Cd. Fe concentration of DCB extraction samples, soil BCR extraction samples, and soil anti-aqua regia digestion samples were determined by ICP-OES (Varian Vista MPX CCD). Detailed ICP-MS and ICP-OES instrument set up is described in

Table S9.† XRF was used to determine the Fe and Si content in rice and pakchoi samples (detailed described in Text S4†).

The efficiency of the analysis was evaluated by analyzing the recovery values of certified material for each element. The overall performance of quality control is shown in Table S10.† In ICP-MS measurement, the CRM (GBW10010 rice flour) recoveries vary from 88–104% in rice tissues and pakchoi analysis (104% for Cd); the CRM (GBW07405 soil flour) recoveries vary from 102–119% in soil AAR digestion samples analysis (112% for Cd); the CRM (1640a) recoveries for As and Cd vary from 101–102% in porewater sample analysis. The Fe recovery of soil CRM (GBW07405) is 99% in the ICP-OES analysis. Fe and Si recoveries of plant CRM (NCS ZC73018) for ED-XRF analysis were also within acceptable levels. BCR extraction result validation was conducted, and the Cd recovery of BCR/AAR is 90–101% (Table S11†).

### 2.4. Statistical analysis

Data was analyzed with Minitab statistical software (Version 21.4) and GraphPad Prism (Version 10.0.1). The normal distribution of all variables was checked by Kolmogorov–Smirnov test by Minitab, and Winsorization performed on any identified outliers ( $\pm 2$  standard deviations was used to define the threshold of outliers). Principal Component Analysis (PCA) and General Linear Model (GLM) (followed by Tukey Pairwise Comparisons or Dunnett Multiple post-hoc test) were performed using Minitab. Regression analyses were performed by using GraphPad. Pearson correlations analysis performed by using Origin 2021.

## 3. Results

### 3.1. Performance of FMS in soil-plant system

#### 3.1.1. Plant system response

**3.1.1.1. Plant yield and Cd profile.** Plant yield of different treatments is reported in Table S12.† Compared with the control/no-amendment group (CT), the FMS/BC amendment significantly increased the yield of CY67 rice grain ( $P < 0.05$ ) but did not show a significant impact on the grains of YY17 ( $P > 0.05$ ), the observed differences in grain yield may result from inherent genetic variation among the rice cultivars. Rice grain and total plant weight of both rice cultivars increased significantly by MS amendment ( $P < 0.05$ ). However, different amendment methods did not affect the pakchoi yield.

Fig. 1 and 2 show the effects of different treatments on Cd accumulation in plant tissues. FMS treatment reduced the Cd concentration in CY67 and YY17 rice grains by 80% and 68%, respectively (Fig. 1A). Subsequently, Cd concentrations in rice grains fell to 0.07 mg kg<sup>-1</sup> for CY67 and 0.18 mg kg<sup>-1</sup> for YY17, both below the Chinese safety standard limit (0.2 mg kg<sup>-1</sup>, d. wt.) (GB 2762-2017). Post FMS amendment application, Cd concentrations in the leaves, straw, and roots of CY67 reduced by 77%, 84%, and 66%, respectively, while YY17 saw reductions of 58%, 73%, and 40% in the same tissues (Fig. 2A–C). YY17 showed a higher accumulation of Cd. CY67 exhibited more Cd reduction than YY17 under FMS treatment. Indicating differing



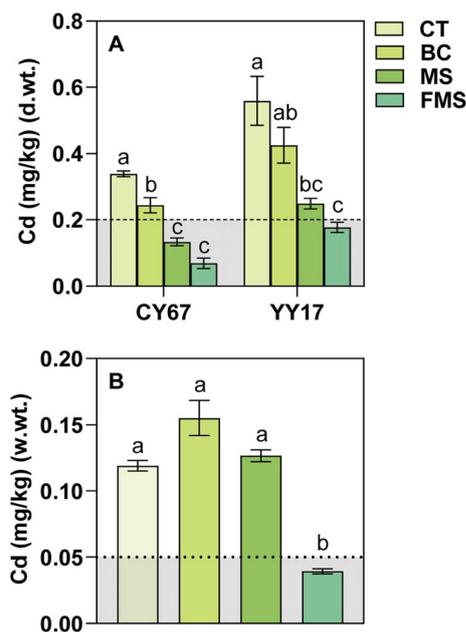


Fig. 1 Cd content in rice grain (A) (Mean  $\pm$  s.e.  $n = 4$ ) and pakchoi (B) (Mean  $\pm$  s.e.  $n = 5$ ). Bar that does not share a letter are significantly different. FMS: functionalized mesoporous silica, MS: mesoporous silica, BC: biochar, CT: control/no-amendment. Gray shading: below the safety standard (GB 2762-2017).

Cd accumulation capacities between the two rice cultivars ( $P < 0.05$ ). This trend shows that the capacity of different rice cultivars for Cd uptake will affect the effectiveness of using FMS. MS treatment significantly reduced the Cd concentration in the grains, leaves, and straw of both rice cultivars by 55–60%, 40–61%, and 64–67%, respectively (Fig. 1 and 2.). The Cd concentration in grains with MS amendment was  $0.13 \text{ mg kg}^{-1}$  (CY67) and  $0.25 \text{ mg kg}^{-1}$  (YY17). BC amendment did not significantly affect Cd concentration in the leaves, straw, and roots of either rice cultivar but reduced Cd accumulation in the grains by approximately 28%, resulting in grain Cd concentrations for CY67 and YY17 of  $0.24 \text{ mg kg}^{-1}$  and  $0.43 \text{ mg kg}^{-1}$ , respectively. In pakchoi, the Cd concentration under FMS amendment was  $0.04 \text{ mg kg}^{-1}$ , representing a 67% reduction compared to the CT at  $0.12 \text{ mg kg}^{-1}$  (Fig. 1B), aligning with the Chinese national safety standard ( $0.05 \text{ mg kg}^{-1}$ , w. wt.) (GB 2762-2017). However, neither MS nor BC treatments reduced Cd accumulation in pakchoi. Concerning Cd offtake in plants, FMS treatment significantly reduced Cd offtake in rice and pakchoi, with similar results unobserved in MS and BC amendments. For FMS-amended rice, Cd offtake in CY67 significantly decreased from  $67.5 \text{ } \mu\text{g per pot}$  to  $18.9 \text{ } \mu\text{g per pot}$  ( $P < 0.05$ ), and in YY17, it dropped from  $76.9 \text{ } \mu\text{g per pot}$  to  $37.3 \text{ } \mu\text{g per pot}$  ( $P < 0.05$ ). The Cd offtake in MS-amended rice (CY67:  $49.8 \text{ } \mu\text{g per pot}$ ; YY17:  $56.1 \text{ } \mu\text{g per pot}$ ) and BC-amended rice (CY67:  $44.9 \text{ } \mu\text{g per pot}$ ; YY17:  $63.1 \text{ } \mu\text{g per pot}$ ) also decreased, but was not significantly different compared with CT. Furthermore, Cd offtake in pakchoi under FMS treatment was significantly reduced to  $1.3 \text{ } \mu\text{g per pot}$  from that in the CT ( $3.8 \text{ } \mu\text{g per pot}$ ) ( $P < 0.05$ ), while the

Cd offtake in MS-amended pakchoi and BC-amended pakchoi was  $3.9 \text{ } \mu\text{g per pot}$  and  $4.6 \text{ } \mu\text{g per pot}$ , respectively.

The correlation of Cd concentration between different rice tissues is shown in Fig. 2D–F. A positive correlation was observed between the Cd concentration in grains and straw ( $R^2 = 0.67$ ;  $P < 0.01$ ) (Fig. 2D), similar positive correlation also applied to the relationship between Cd concentrations in leaves and straw ( $R^2 = 0.54$ ;  $P < 0.01$ ) (Fig. 2E). At the same time, the Cd translocations in rice tissues were assessed using translocation factors (TF) (Table S13<sup>†</sup>). No significant difference was observed in the  $\text{TF}_{(\text{Grain}/\text{straw})}$  and  $\text{TF}_{(\text{Leaf}/\text{straw})}$  of Cd between FMS, MS, BC, and CT. However, a weaker positive correlation was found between Cd contents in straw and root ( $R^2 = 0.26$ ;  $P < 0.01$ ) (Fig. 2F), the  $\text{TF}_{(\text{Straw}/\text{root})}$  of Cd in FMS (CY67: 0.64; YY17: 0.70) and MS (CY67: 0.68; YY17: 0.70) treatment significantly decreased compared to CT (CY67: 0.79; YY17: 0.82).

**3.1.1.2. Plant multi-elemental ionome responses.** Fig. S1 and S2<sup>†</sup> exhibit the responses of the plant multi-elemental ionome under different treatments. FMS treatment significantly increased the Si content by 522–666% in both cultivars of rice leaves and straws (Fig. S1D and G<sup>†</sup>), while MS treatment has a higher Si increase trend in leaves and straws by 564–885% (Fig. S1E and H<sup>†</sup>). Both FMS and MS slightly increased the content of Si by 31% and 42% in YY17 rice roots, respectively. In CY67 rice roots, the increased Si content by MS treatment was about 5-fold that of the FMS treatment (Fig. S1J and K<sup>†</sup>). The Si content of YY17 grain with the FMS treatment increased by 418%, while in CY67 grain, Si content increased by 20% (Fig. S1A<sup>†</sup>). MS treatment increased Si in the YY17 grain by 248% but the Si in the CY67 grain dropped by 9% (Fig. S1B<sup>†</sup>). BC has less impact on rice tissues' Si contents compared to FMS and MS, grain Si content increased 24–41% with BC treatment (Fig. S1C<sup>†</sup>). In addition, the Si content in FMS-amended and MS-amended pakchoi slightly increased (Fig. S2<sup>†</sup>), and the BC amendment did not significantly disturb the Si content in pakchoi.

The rice grain Fe and Mn concentrations of the two cultivars were unaffected by the FMS treatment, but the concentrations of Cu and Zn were reduced by 32% and 23% respectively (Fig. S1A<sup>†</sup>). A 45% decrease in As was observed in the CY67 grain with FMS treatment, while 4% As increases were observed in the YY17 grain (Fig. S1A<sup>†</sup>). The effects of MS treatment on Cu, Fe, and Zn in rice grains were similar to those in the FMS treatment, but the decrease of As was not observed (Fig. S1A and B<sup>†</sup>). FMS treatment reduced the As concentration in CY67 leaves by 72% and the As in straw by 68%, while As decreased by 30% in leaves and 32% in straw of YY17 (Fig. S1D and G<sup>†</sup>). For the MS treatment, the As concentration in CY67 leaves and straw decreased by 51% and 34%, 43% and 51% decreasing in YY17 leaves and straw (Fig. S1E and H<sup>†</sup>). However, MS significantly increased the contents of As in the CY67 root by 42%. Compared with FMS and MS, BC has relatively limited effects on elements in various rice tissues. And its effects on different tissues of the two rice species were not consistent. Regarding the pakchoi, FMS significantly increased Mn concentration in pakchoi by 140%, the contents of As and Fe slightly increased (Fig. S2<sup>†</sup>). The As concentration in FMS treatment pakchoi is  $0.04 \text{ mg}$



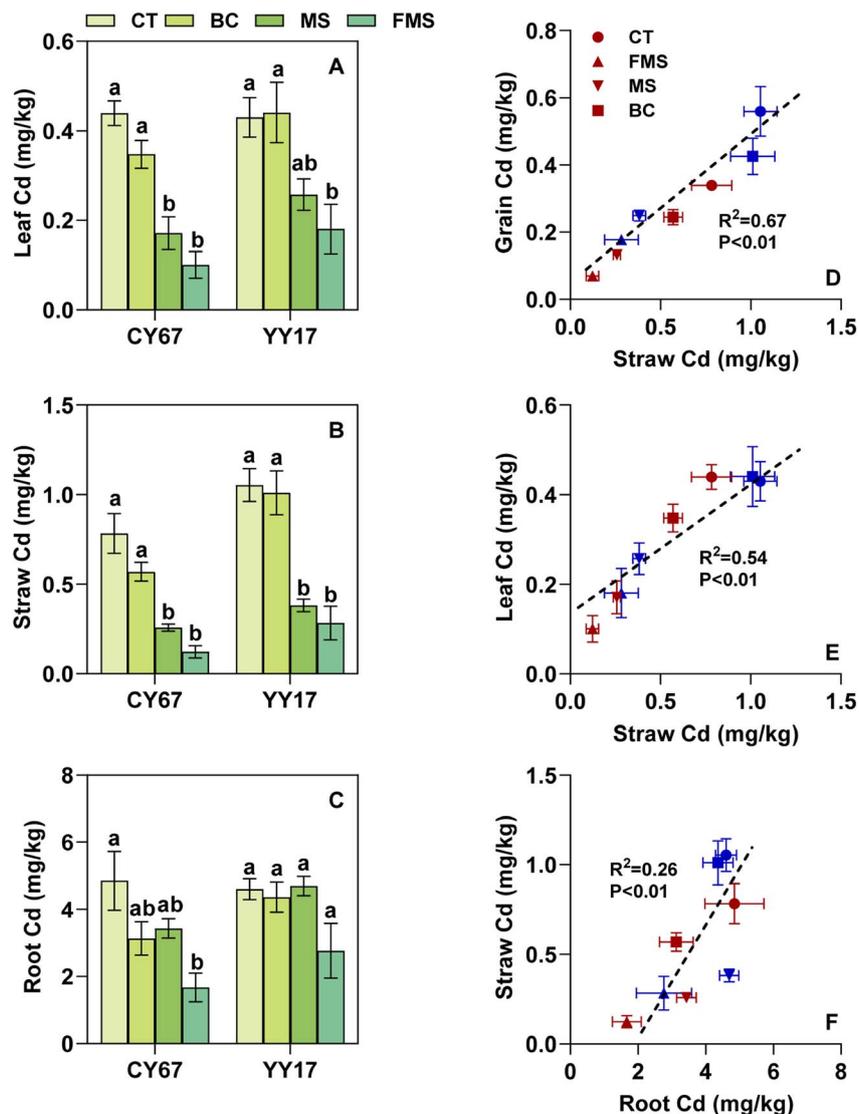


Fig. 2 Cd concentration in rice tissues and correlations (d. wt.) (Mean  $\pm$  s.e.  $n = 4$ ). The correlation calculation includes each replicate, showing in the graph as mean and standard error (Red: CY67; Blue: YY17). A: Cd concentration in rice leaf. B: Cd concentration in rice straw. C: Cd concentration in rice root. D: grain and straw. E: leaf and straw. F: straw and root.

$\text{kg}^{-1}$ , still within the national safety standard ( $0.5 \text{ mg kg}^{-1}$ ) (w.wt.) (GB 2762-2017). MS did not significantly disturb element levels in pakchoi. Conversely, BC treatment significantly increased As by 187% and Cu by 60% in pakchoi. The As offtake in plants was evaluated (Table S14<sup>†</sup>), FMS treatment reduced As offtake in CY67 and YY17, but increased As offtake in pakchoi.

Pearson's correlation analysis was conducted to explore the relationships between As, Cd, Cu, Fe, Mn, Si and Zn in rice straw and pakchoi (Fig. S3<sup>†</sup>). Results show that the behavior of Si is different in rice straw and pakchoi. Si exhibited moderate negative correlations with As ( $r = -0.73$ ), Cd ( $r = -0.78$ ), Cu ( $r = -0.69$ ) and Zn ( $r = -0.62$ ), but weak correlations with Fe ( $r = 0.41$ ) and Mn ( $r = -0.35$ ) in the rice straw. However, in the pakchoi, Si showed negligible correlations with As ( $r = 0.02$ ), Cd ( $r = -0.26$ ), Cu ( $r = -0.10$ ) and Zn ( $r = 0.11$ ), a weak positive correlation with Mn ( $r = 0.33$ ) and a significant positive correlation with Fe ( $r = 0.87$ ).

### 3.1.2. Effect of FMS on soil

**3.1.2.1. Change of soil pH, Eh, and Cd fraction.** With the application of FMS, the pH of rice planted soil slightly decreased from 6.59 to 6.46, the Eh increased from 24 mV to 30 mV. Similar trends observed in the pakchoi planted soil, FMS amendment decreased the soil pH from 6.72 to 6.67 but increased the Eh from 17 mV to 19 mV. The fraction of Cd in soil was evaluated based on BCR extraction after plant harvest. Fig. 3 shows the changes in Cd in soil fractions under FMS treatment. The results showed that Cd can be strongly bound to FMS, forming an FMS-fraction in the soil, which is resistant to extraction by aqua regia. In the FMS-amended CY67 planted soil, YY17 planted soil and pakchoi planted soil, the proportion of FMS-fraction Cd is 29%, 36% and 13%, respectively (Fig. 3).

The bioavailability of Cd (Bio-Cd) in soils was determined by BCR extraction. Considering that acid-extractable, reducible, and oxidizable fractions were bioavailable in the rice growth



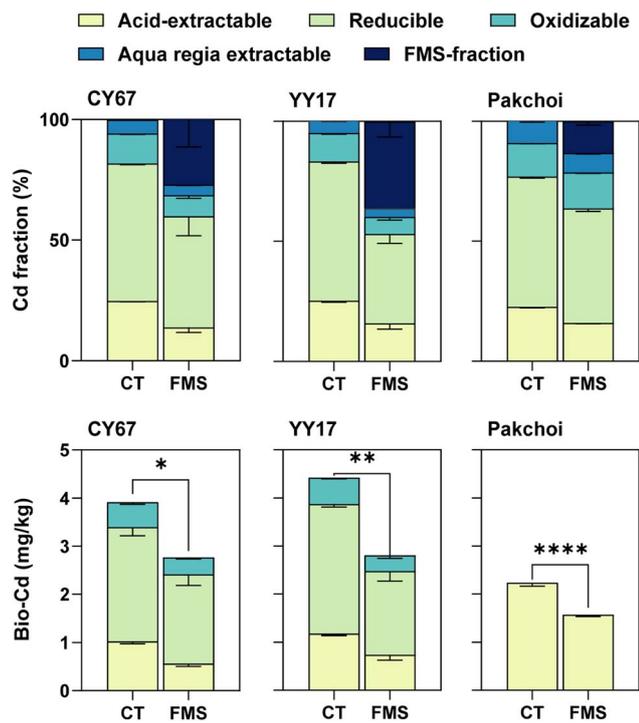


Fig. 3 Soil Cd profile (Mean  $\pm$  s.e.). The FMS-fraction is calculated from the total amount of Cd extracted by BCR in the CT group and FMS amendment group (FMS-fraction = BCR extracted Cd<sub>(CT)</sub> – BCR extracted Cd<sub>(FMS)</sub>).

environment, and the acid-extractable fraction was bioavailable in the pakchoi plant soil, compared with the CT, the Bio-Cd in the soil of CY67, YY17, and pakchoi decreased by 29%, 37% and 30% respectively under the action of FMS (Fig. 3). FMS reduced 37–45% of acid-extractable Cd, 21–35% of reducible Cd and 31–39% of oxidizable Cd in rice-planted soil. However, in the pakchoi-planted soil, ~30% of acid-extractable Cd and ~12% reducible Cd was decreased by FMS, but oxidizable Cd increased by ~7%.

3.1.2.2. As, Cu, Fe, Mn, and Zn in soil. The BCR extracted As in the FMS amended CY67 planted soil decreased from 39 mg kg<sup>-1</sup> to 36 mg kg<sup>-1</sup> (reduced by 8%), while in the YY17 planted soil there was a decrease from 38 mg kg<sup>-1</sup> to 35 mg kg<sup>-1</sup> (reduced by 9%) compared to CT (Fig. S4A†). Additionally, a significant drop in BCR extracted As was found in the soil of pakchoi plants modified with FMS; it reduced from 52 mg kg<sup>-1</sup> to 45 mg kg<sup>-1</sup> (reduced 15%). However, compared with the CT, the Bio-As in the FMS-amended soil of CY67, YY17 and pakchoi increased by 60%, 44% and 70% respectively (Fig. S4B†). It was also observed that the BCR extracted Cu, Fe, Mn, and Zn decreased in FMS-amended CY67 planted soil by 12%, 10%, 27% and 11% respectively (Fig. S4A†). Similarly, in YY17 FMS-amended soil, the BCR extracted Cu, Fe, Mn, and Zn reduced about 18%, 13%, 31% and 16% respectively. The bioavailability of Cu, Mn, and Zn in the rice-planted soil also decreased with the FMS amendment (11–36%) (Fig. S4B†). However, the FMS amendment increased the Bio-Fe by 36% and 5% in the CY67

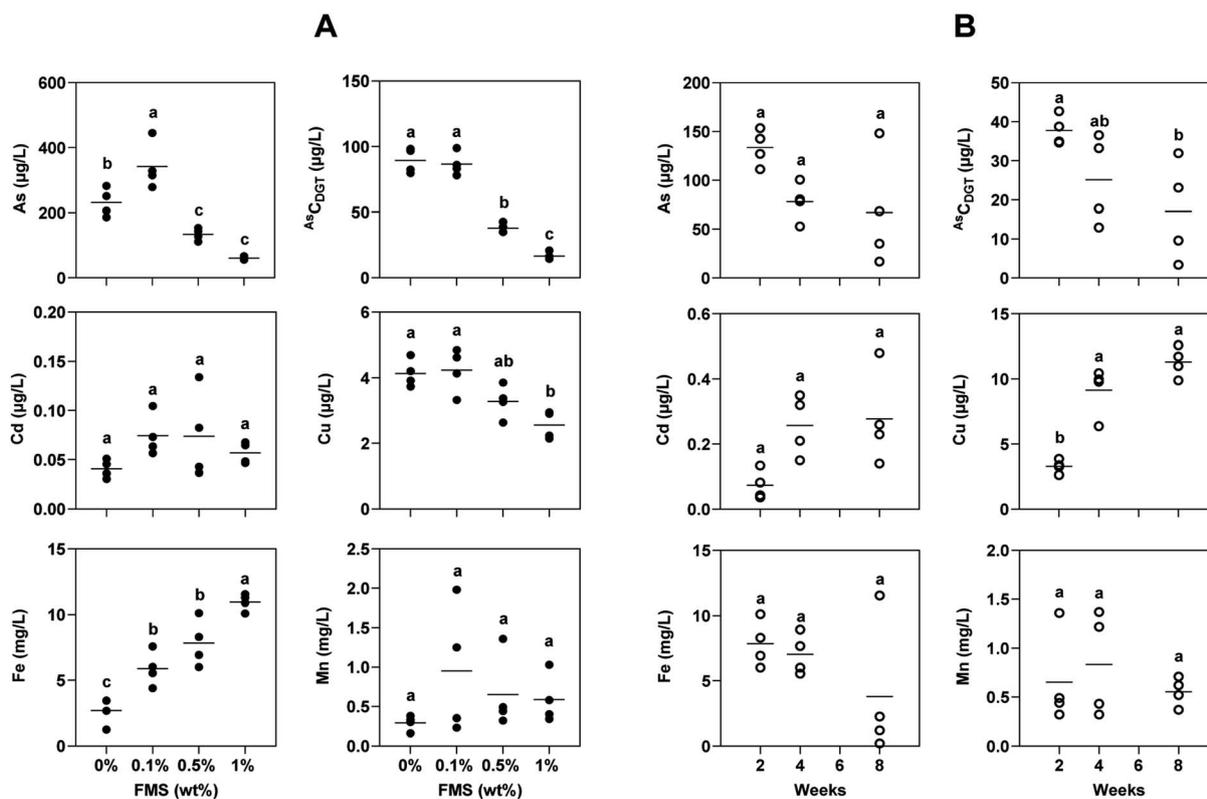


Fig. 4 Effect of FMS on element concentration in soil pore-water ( $C_{sol}$ ) and DGT measured As ( $As_{CDGT}$ ) (Mean,  $n = 4$ ). (GLM, post hoc analysis was carried out using Tukey Pairwise Comparisons). Different letters above each bar represent significant differences between treatments ( $P < 0.05$ ). (A): Dose. (B): Time.



planted soil and YY17 planted soil. The BCR extracted Cu, Fe, Mn, and Zn decreased in FMS-amended pakchoi planted soil by 10%, 12%, 5% and 9% respectively. The bioavailability of Cu, Mn, and Zn was not significantly affected by FMS, but the Bio-Fe significantly increased by 131%.

**3.1.2.3. Rice rhizosphere.** The content of As and Cd in rice root iron plaques under the FMS amendment decreased compared to the CT group. As significantly decreased from  $49.8 \mu\text{g kg}^{-1}$  to  $28.2 \mu\text{g kg}^{-1}$ , and Cd significantly decreased from  $1.52 \mu\text{g kg}^{-1}$  to  $0.32 \mu\text{g kg}^{-1}$  in CY67 root iron plaque (Table S15<sup>†</sup>). In the YY17 root iron plaque, the concentration of As decreases from  $47.9 \mu\text{g kg}^{-1}$  to  $41.0 \mu\text{g kg}^{-1}$ , and Cd decreased from  $2.11 \mu\text{g kg}^{-1}$  to  $1.22 \mu\text{g kg}^{-1}$ . In addition, the Fe concentration in the iron plaques of rice roots is enhanced by the application of FMS amendment, the Fe concentration of CY67 root iron plaque significantly increased from  $21.2 \text{ mg kg}^{-1}$  to  $50.9 \text{ mg kg}^{-1}$ , and YY17 root iron plaque Fe concentration significantly increased from  $18.3 \text{ mg kg}^{-1}$  to  $49.9 \text{ mg kg}^{-1}$  (Table S15<sup>†</sup>).

To study the impact of FMS on the rice rhizosphere Principal Component Analysis (PCA) was carried out on the dataset

comprising As, Cd, Fe, and Mn, concentrations of rice roots, rice root iron plaques and soil (Fig. S5<sup>†</sup>). In the initial two principal components (PC) in combination account for 62% of the total variation. The PC1 contributes to 45% of the variance, while the PC2 explain 17%. Both CY67-FMS and YY17-FMS segregate from CY67-CT and YY17-CT (Fig. S5<sup>†</sup>), CY67-CT and YY17-CT are positioned in the negative range of PC1, whereas CY67-FMS and YY17-FMS are situated in the positive range of PC1. In PC2, CY67-CT did not segregate from YY17-CT, CY67-FMS slightly differentiated from YY17-FMS. The concentrations of R-Fe, R-Mn, IP-Fe, IP-Mn, B-As, and B-Fe contribute to the positive range of PC1 driving the CY67-FMS and YY17-FMS. The R-As, R-Cd, IP-As, IP-Cd, B-Cd, and B-Mn contribute to the negative range of PC1 driving the CY67-CT and YY17-CT.

### 3.2. Performance of mixed FMS in soil

**3.2.1. Impact of different deployment conditions on the soil remediation effects of FMS.** Fig. 4 shows that as the FMS dosage and deployment time increased, the As content in the soil solution decreased. When the dose of FMS was 0.5% and

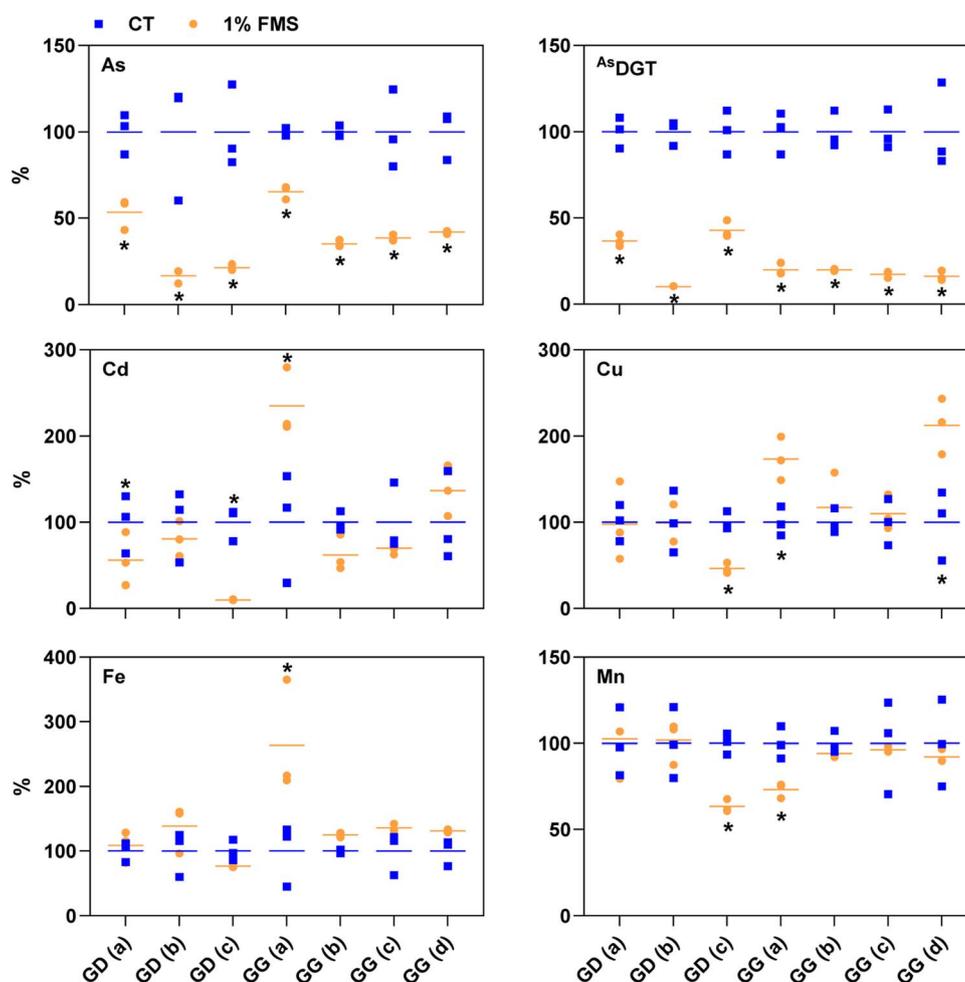


Fig. 5 Element concentration in pore-water of different Guangzhou soils (Dabaoshan soil and Gaoming soil) expressed as a percentage relative to the mean of the control group (Mean,  $n = 3$ ). (GLM, post hoc analysis was carried out using Tukey Pairwise Comparisons). \* Indicated significant differences between treatment and control ( $P < 0.05$ ).



1%, the porewater As concentration in CZ-L soil was significantly reduced by 42% and 74% ( $P < 0.05$ ) (Fig. 4A). However, when the FMS dose was 0.1%, the As concentration in porewater increased by 48%. Cd and Mn content was not significantly disturbed by the addition of FMS ( $P > 0.05$ ). Cu concentration decreased with the dose of FMS, but Fe concentration increased. In addition, it was observed that the  $^{As}C_{DGT}$  exhibited a similar trend to that of porewater As concentration ( $^{As}C_{sol}$ ) as the addition of FMS increased (Fig. 4A). When the dose of FMS  $> 0.1\%$  the  $^{As}C_{DGT}$  decreases,  $^{As}C_{DGT}$  reduced by 82% in CZ-L soil with 1% FMS treatment. The lowest  $^{As}C_E$  was found at 1% FMS treatment ( $270 \mu\text{g L}^{-1}$ ), the  $^{As}R$  value ranging from 0.25 to 0.28 with the 0.1–1% FMS treatment which is lower than that of the CT group ( $^{As}R: 0.39$ ) (Table S16†).

When the incubation time of 0.5% FMS treatment CZ-L soil reached 4 weeks, the As concentration of the porewater was  $78 \mu\text{g L}^{-1}$ , which was 42% lower than week 2 ( $134 \mu\text{g L}^{-1}$ ) (Fig. 4B). At 8 weeks, the porewater As concentration was  $67 \mu\text{g L}^{-1}$ , which was 14% lower than at week 4. The concentrations of Cd and Cu in

the porewater increased with incubation time, but the concentrations of Fe decreased (Fig. 4B).  $^{As}C_{DGT}$  also decreased with increasing incubation time, and the lowest value of  $^{As}C_E$  was observed at week 8 ( $279 \mu\text{g L}^{-1}$ ),  $^{As}R$  value ranged from 0.25 to 0.32 during the incubation period; the lowest  $^{As}R$  value also occurred at the 8th week (0.25) (Table S16†).

In addition, FMS dose treatment experiments were also conducted on small-scale CZ soil (CZ-S), and results showed that there was no significant difference between the porewater element concentrations and  $^{As}C_{DGT}$  concentration in the CZ-L and CZ-S (Table S16 and Fig. S6†). However, the  $^{Cd}C_{DGT}$  obtained from the whole CZ soil incubation experiment was lower than the DGT Method Detection Limits ( $^{Cd}MDL: 0.04 \mu\text{g L}^{-1}$ ) reported by Panther *et al.* (2014) (Table S16†).

**3.2.2. Environmental application of mixed FMS.** Fig. 5 shows the changes in elements in the pore water of different soils with the FMS treatment, and that As concentration has decreased. GD soil and GG soil exhibited a significant decrease in As concentration in the porewater with 1% FMS amendment

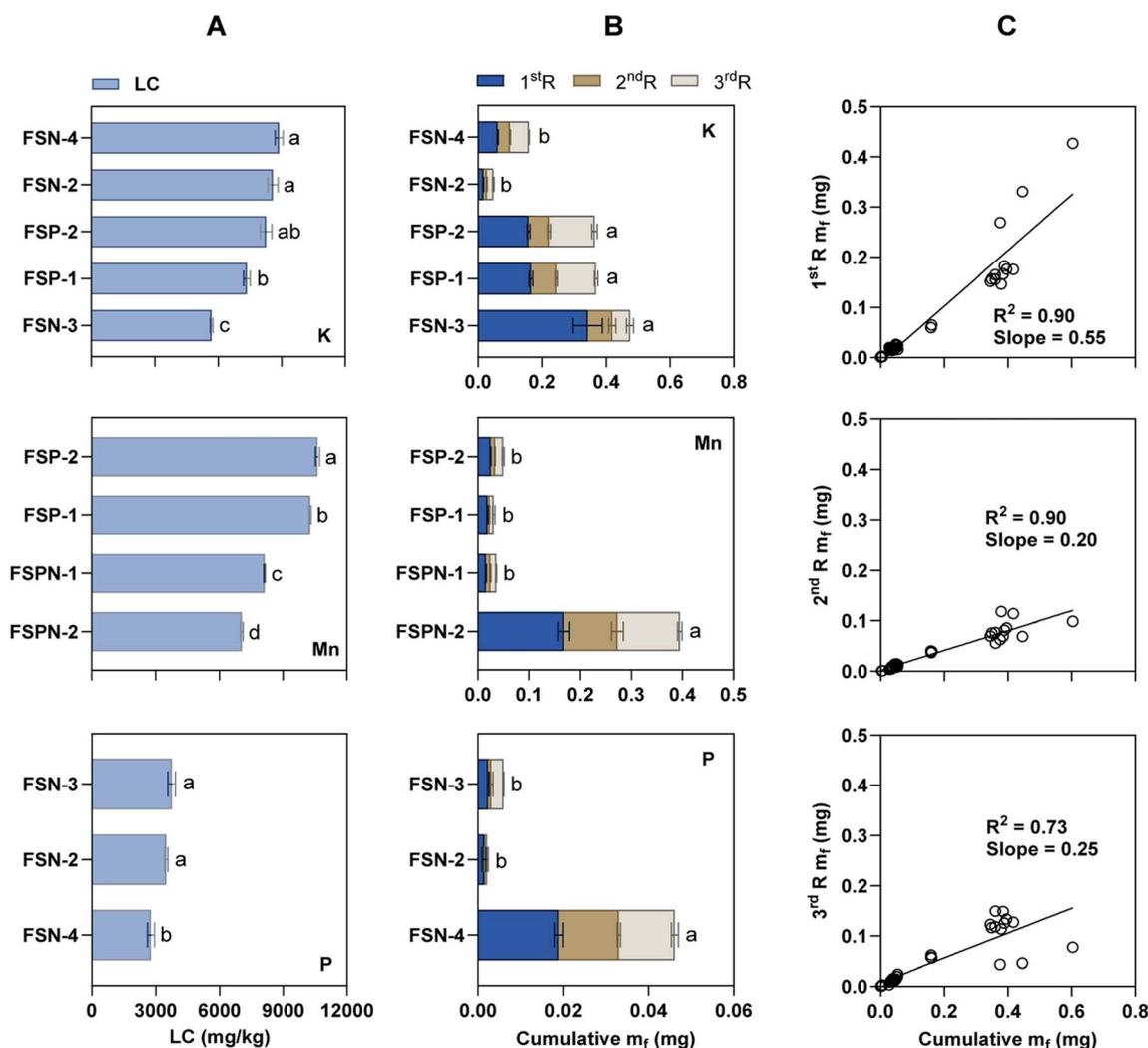


Fig. 6 Spiked FMS profile. (A): The loading capacity (LC) of FMS for K, Mn, and P (Mean  $\pm$  s.e.,  $n = 3$ ). (B): The cumulative  $m_f$  of FMS for K, Mn, and P (Mean  $\pm$  s.e.,  $n = 3$ ) (1<sup>st</sup> R: first sampling, 2<sup>nd</sup> R: second sampling, 3<sup>rd</sup> R: third sampling.  $m_f$ : the weight of the element released from spiked FMS.). (C): Correlation analysis between the  $m_f$  in the 1<sup>st</sup> R, 2<sup>nd</sup> R, and 3<sup>rd</sup> R and the cumulative  $m_f$ .



( $P < 0.05$ ) (Fig. 5). The highest value of the measured  $^{As}C_{sol}$  appears in the CT of GD (c) ( $213 \mu\text{g L}^{-1}$ ) followed by the CT of GD (b) ( $135 \mu\text{g L}^{-1}$ ), and the lowest value appears in the CT of GG (a) ( $44 \mu\text{g L}^{-1}$ ) (Table S17†). At the same time, the largest decrease in  $^{As}C_{sol}$  was observed in GD (b) (83%) followed by GD (c) (78%), while the smallest decrease was observed in GG (a) (34%). However, the changes in  $^{Cd}C_{sol}$  are more complicated,  $^{Cd}C_{sol}$  significantly increased from  $0.17 \mu\text{g L}^{-1}$  to  $0.40 \mu\text{g L}^{-1}$  in GG (a) (Table S18†), but the  $^{Cd}C_{sol}$  significantly decreased by 38% and 90% in GG (b) and GD (c). The Cd and Cu dynamics in porewater across the different soils caused by the addition of 1% FMS are similar. Except for the porewater of the GD (c), which showed a decrease in Fe concentration (24%) by FMS treatment, the Fe concentrations in the other samples exhibited an upward trend, among which the Fe concentration in GG (a) increased significantly (164%) ( $P < 0.05$ ). At the same time, the highest porewater Fe concentration measured was in the CT of GD (c) ( $186 \text{ mg L}^{-1}$ ), while the lowest Fe concentration was in the CT of GG (a) ( $5 \text{ mg L}^{-1}$ ). In addition, the highest porewater Mn concentration was found in the CT of GD (c) ( $9.6 \text{ mg L}^{-1}$ ), and the reduction of Mn concentration by FMS is significant (37%) ( $P < 0.05$ ).

The values of  $^{As}C_{DGT}$  in the FMS treatment groups were lower than those in the related CT groups (Fig. 5). FMS reduced the  $^{As}C_E$  in different soils, with the lowest reduction being 57% (GD (c)) and the largest reduction occurring in GD (b) (90%). Except for GD (c), the  $^{As}R$  values in other FMS-treated soils decreased, the FMS-treated  $^{As}R$  values of GG (b), (c), and (d) were even lower than  $^{As}R_{diff}$  (Table S17†). Valid  $^{Cd}C_{DGT}$  values are obtained from GD (a), (b), and (c); the  $^{Cd}C_{DGT}$  of other soils is lower than the  $^{Cd}MDL$  ( $0.04 \mu\text{g L}^{-1}$ ) (Table S18†). FMS treatment decreased  $^{Cd}C_{DGT}$  and  $^{Cd}C_E$ , and the largest reduction of  $^{Cd}C_E$  was observed in GD (c) (98%). However, only the  $^{Cd}R$  value of GD (c) shows a decrease with FMS treatment (a decrease from 0.66 to 0.11) (Table S18†).

### 3.3. Pre-loading and release performance of plant-promoting components by FMS

The LC of FMS for K, Mn, and P are shown in Fig. 6A. FMS materials show a larger LC for K and Mn. FSN-4 exhibited the largest LC for K, which is  $8873 \text{ mg kg}^{-1}$ , and the highest LC for Mn was observed in the FSP-2 ( $10\,623 \text{ mg kg}^{-1}$ ). In addition, FSN-3 exhibited the largest LC for P, which is  $3753 \text{ mg kg}^{-1}$ . The release performance of nutrient-spiked FMS was evaluated (Fig. 6B), spiked FMS can release preloaded elements into solution, the corresponding experimental results for each element show that the FMS with larger  $m_f$  values tend to have smaller LC. The correlation between the  $m_f$  in the 1st R, 2nd R, and 3rd R and the cumulative  $m_f$  was analyzed (Fig. 6C). It can be concluded from the slope value that the  $m_f$  of the spiked FMS in the 1st R accounts for the largest proportion of the cumulative  $m_f$ , which is 55%. The  $m_f$  in the 2nd R and 3rd R accounts for 20% and 25% of the cumulative  $m_f$ . In addition, the LC of FMS to SA reached  $21\,002 \text{ mg kg}^{-1}$ , and the SA-spiked FMS showed an SA releasable in the solution, similar to nutrients-spiked FMS, the  $m_f$  decreases and then stabilizes as the release experiment proceeds (Fig. S7†).

## 4. Discussion

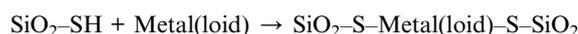
### 4.1. Characteristics of FMS-soil-plant systems

**4.1.1. FMS-amended soil fraction.** The primary mechanism of FMS adsorption/immobilization of toxic trace elements involves forming dative bonds with the target elements through its functional groups. Wang *et al.* (2019) verified that Cd predominantly forms S–Cd and O–Cd complexes by interacting with FMS which are loaded with –SH and –OH groups, to form metal silicates.<sup>20</sup> However, owing to the absence of hydrofluoric acid (HF) in our extraction method, elements in FMS-amended soil cannot be completely extracted.<sup>27</sup> Consequently, the fraction of elemental components strongly associated with FMS is quantified by calculating the difference between the BCR extraction results of the no-amendment soil and the FMS-amended soil, with these unextracted components labeled as the FMS-fraction.

As a result, the BCR extracted As, Cd, Cu, Fe, Mn, and Zn in FMS-amended soil was lower than in the no-amendment/control soil. Under FMS treatment, the Cd content within the FMS-fraction of the soil used for rice cultivation constituted 25–30% of the soil Cd fraction, whereas it accounted for approximately 13% in soil designated for pakchoi growth. Differences in soil Cd immobilization performance were evident because the primary mechanism through which FMS adsorbs Cd involves the formation of covalent bonds between Cd and the sulfur atoms in thiol groups. The chemisorption process is more effective when metal ions are readily available in solution, and this availability is facilitated by adequate water content (*e.g.*, long-term flooding during rice cultivation).

However, the FMS-fraction quantified *via* BCR calculations represents the irreversible components resulting from the strong interaction between FMS and elements. This cannot accurately reflect the dynamics of element-FMS interactions in real-environment applications. The interaction between FMS and elements in the environment encompasses not only irreversible components but also exchangeable ones with weaker bonding strengths.<sup>28</sup> Consequently, BCR extraction experiments might alter the coordination environment of the elements bound in FMS and release them, thereby affecting the interpretation of labile metal fractions. Leading to an over-interpretation of exchangeable metal, which affects environmental risk assessments.

**4.1.2. Rhizosphere effect of FMS.** The pH values decreased slightly in FMS-amended soil. This is because during the element ion and FMS interaction, hydrogen ions from the FMS functional groups may liberate (eqn (1)). Therefore, –SH group in FMS can influence the environment of the rice rhizosphere.



or



Eqn (1) mechanism of metal(loid) adsorption by thiol-functionalized silica in soil.



In FMS-amended soil, the redox potential (Eh) is relatively higher than in unamended soil, indicating less reducing conditions. Since Mn is more easily reduced than Fe, Mn oxides (Mn(IV)) are converted to soluble Mn(II) earlier and more readily than Fe oxides. As a result, Mn is more likely to leach out under mildly reducing conditions, while Fe remains in a less mobile form until stronger reducing conditions occur. This explains the higher proportion of reducible Fe in FMS-treated soils. Additionally, As and Fe associated with Mn oxides are released more easily under these conditions. The microbial reduction of As(V) to the more mobile As(III) further increases As availability in the soil.<sup>29–31</sup> Under flooded conditions, rice root respiration promotes Fe(II) accumulation in the rhizosphere, leading to the formation of iron plaques.<sup>23</sup>



Eqn (2) reaction mechanism for iron plaque formation on rice roots.

DCB extraction experiment results show that the Fe content in the FMS-amended CY67 and YY17 IP was 2.4-fold and 2.7-fold that of the no-amendment group, respectively. But the As content in the IP was reduced under FMS treatment, this is explained by –SH loaded on the FMS having a higher affinity for As compared to Fe, especially for the trivalent arsenic species (arsenite, As(III)). This strong affinity is due to the soft–soft interaction between arsenic (a soft acid) and sulfur in the sulfhydryl group (–SH) (a soft base) according to the Hard and Soft Acids and Bases (HSAB) principle, which evolves into a covalent bond formed between sulfur and As. However, Fe commonly occurs in two oxidation states: ferrous (Fe(II)) and ferric (Fe(III)). While Fe(II) can participate in covalent bonding, it is generally considered a borderline acid according to the HSAB theory, meaning it does not have as strong a preference for soft bases like sulfur in sulfhydryl groups compared to soft acids like As. Fe(III), with its higher charge and smaller ionic radius, acts more like a hard acid and tends to form more ionic bonds, which are less specific and not as strong with soft bases like –SH groups. Therefore, we consider that the exchangeable fraction formed by Fe and FMS is easy to interact with the rice rhizosphere environment, but the exchangeable fraction formed by As and FMS is relatively more stable.

Generally, IP is considered as the primary link and first interface of As and Cd entering rice roots.<sup>17</sup> This intermittent porous layer, predominantly consist of ferrihydrite,<sup>32</sup> the layer has a considerable specific surface area, characterized by –OH functional groups, which demonstrates a propensity to interact with metallic elements, additional cationic species, and anionic entities.<sup>33</sup> Tian *et al.*, (2023) reported that the increase in IP Fe content is generally accompanied by an increase in the adsorption of As and Cd.<sup>22</sup> However, in our result, the content of As and Cd in FMS-amended IP decreased, this should be because the adsorption of As and Cd by hydroxyl groups (–OH) mainly involves physisorption or ion exchange mechanisms, which are generally less strong and specific than chemisorption where a chemical bond forms between As or Cd and –SH. What is more, rice rhizosphere PCA analysis show that the B–As and

B–Cd contribute to the positive range of PC1 driving the FMS treatment, but the R–As and R–Cd contribute to the negative range of PC1 driving the CT group. Thus, we infer that in the rhizosphere region of rice, the original free state As and Cd are more incorporated in the FMS rather than on the IP, which reduces the As and Cd uptake by rice root.

Moreover, –SH groups on FMS might participate in redox-sensitive sulfur cycling, potentially serving as electron donors or acceptors for specific microbial guilds. This may favor the growth of sulfur-oxidizing or -reducing bacteria, thereby reshaping microbial composition. The free Cd<sup>2+</sup> concentration in FMS amendment soil solution was lower. This can alleviate heavy metal stress on microbes, leading to shifts toward more metal-sensitive but functionally beneficial populations (*e.g.*, nitrifiers, plant growth-promoting rhizobacteria).

**4.1.3. Plant ionome evaluation.** Negative correlations were found between Si and As ( $r = -0.73$ ), along with Si and Cd ( $r = -0.78$ ) in rice straw. Increased Si content in rice straw led to a lower As and Cd content. The reason is Si suppresses the expression of *Lsi1/Lsi2* and competes with As for the transporters directly.<sup>34,35</sup> Moreover, Si can also inhibit the expression of *OsNRAMP5* and *OsHMA2* which reduces Cd uptake.<sup>36</sup> This mechanism further assists FMS in reducing As and Cd accumulation by the rice plant. It is also the main mechanism of decreasing in planta As/Cd accumulation *via* MS amendment, which decreased the TF of Cd between straw and root. Thus, the reduction in the TF<sub>(Straw/root)</sub> by FMS can be attributed to the Cd transfer inhibited by Si and the decrease in root Cd uptake in caused by FMS's capacity to immobilize Cd in the soil.

The Cd and As offtake in the whole rice plant was evaluated. It was observed that the Cd offtake in the rice plant significantly decreased with FMS treatment, and slightly decreased by MS and BC treatments. Differences in the uptake of Cd between different rice cultivars were observed, which may be related to variety-specific root or microbial interactions. The iron plaques formed on the roots of YY17 (18.3  $\mu\text{g kg}^{-1}$ ) was slightly lower than that of CY67 (21.2  $\mu\text{g kg}^{-1}$ ) (Table S15†). This may be because the radial oxygen loss of YY17 roots is slightly weaker than that of CY67, resulting in higher Cd uptake in YY17. However, the performance of As offtake is relatively different, the responses of CY67 and YY17 to MS and BC treatments were not consistent. In the CY67, MS (219  $\mu\text{g per pot}$ ) and BC (178  $\mu\text{g per pot}$ ) increased the As offtake in the rice plant compared to the CT (147  $\mu\text{g per pot}$ ); in the YY17, MS (112  $\mu\text{g per pot}$ ) and BC (114  $\mu\text{g per pot}$ ) decreased the As offtake in the rice plant compared to the CT (147  $\mu\text{g per pot}$ ). The reasons underlying these results are multifaceted. Initially, the behavior of As in soil is more complex, and compared with Cd, it has a tendency to be methylated. Many organisms, including some archaea, bacteria, fungi, algae and animals, can methylate inorganic As into different methylated species, with the most common species being monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and trimethylarsine (TMA).<sup>21</sup> Furthermore, the ability of different rice cultivars to uptake As varies, as do the microbial communities within their rhizospheres. Moreover, the addition of soil remediation agents may alter the microbial community surrounding the rice rhizosphere.<sup>37</sup> Nevertheless, the impact of



FMS on As offtake in various rice plants remains relatively consistent, with reductions of 52% in CY67 and 28% in YY17, respectively. However, it is still necessary to focus on the effects of different soil types and microbial communities on plant As uptake in subsequent FMS studies. For instance, soils with high clay content or organic matter may exhibit stronger metal-binding capacity, potentially competing with FMS for As adsorption. Microbial communities involved in As redox transformations, such as arsenate-reducing bacteria and arsenite-oxidizing bacteria, may change as a result of FMS deployment.

The accumulation of Fe and Mn in rice grain was not disturbed by FMS, but lower Cu and Zn concentrations were found in rice grain, leaf, and straw in both FMS and MS treatment rice. Content of micronutrient Zn in rice grains may have positive impact on human health,<sup>38</sup> and more than 25% of the world's population is at risk of Zn deficiency.<sup>39,40</sup> Unlike Zn, Cu deficiency in humans does not present a widespread global problem.<sup>41</sup> For the plant, Zn deficiency can lead to stunted growth, poor grain filling, and lower nutritional value; Cu deficiency will affect lignin synthesis, weaken plant structural integrity and reduce disease resistance. Norton *et al.* (2014) reported that the average concentration of Zn in brown rice (collected from Bangladesh, China, and the United States) ranged from 16.5 mg kg<sup>-1</sup> to 30 mg kg<sup>-1</sup>, while the average concentration of Cu ranged from 0.8 mg kg<sup>-1</sup> to 3.7 mg kg<sup>-1</sup>.<sup>40</sup> In our study, the Zn concentration in FMS-treated brown rice ranged from 14.7 mg kg<sup>-1</sup> to 19.7 mg kg<sup>-1</sup>, whereas the Cu concentration ranged from 2.2 mg kg<sup>-1</sup> to 2.4 mg kg<sup>-1</sup>. Therefore, we suggest that the Zn and Cu concentrations in FMS-treated rice grains remain within permissible limits. It was observed that the Si exhibited moderate negative correlations with Cu ( $r = -0.69$ ) and Zn ( $r = -0.62$ ) in rice straw. This is because the *OsHMA2* affected by Si is also involved in the root-to-straw translocation of Zn.<sup>42</sup> But Si and Cu are taken up by different transporters (*e.g.*, *Lsi1/Lsi2* for Si, *CsCTR1/CsCTR2* and *CsCOPT1/CsCOPT2* for Cu), an indirect effect might occur if the presence of high levels of Si alters the expression or activity of transporters or channels in a way that impacts Cu uptake. However, this would be a secondary effect rather than direct competition at the transporter level.

The concentration of Cu and Zn in pakchoi was not affected by FMS and MS. But a weak negative correlation between Si and Cd ( $r = -0.26$ ), and a negligible correlation between Si and As ( $r = 0.04$ ) was observed in pakchoi. The Cd offtake ( $\mu\text{g}$  per pot) in the pakchoi ranked as BC (4.6) > MS (3.9) > CT (3.8) > FMS (1.3), the As offtake ( $\mu\text{g}$  per pot) in the pakchoi ranked as BC (1.9) > FMS (1.2) > CT (0.7) > MS (0.6). The MS amendment should inhibit the accumulation of Cd and As in pakchoi; however, the low dry matter content and high water content in pakchoi may reduce the effectiveness of Si in mitigating Cd and As uptake. In this study, we cannot infer how stable the exchangeable state formed between As and FMS is in the pakchoi-planted soil system, but FMS-treated pakchoi exhibited a higher As offtake. Thus, the lower water content in the soil-FMS system may limit the adsorption ability of FMS. Which also led to a higher Fe and Mn concentration in FMS-treated pakchoi.

## 4.2. Behavior of mixed FMS in soil remediation

**4.2.1. Mechanism of action of mixed FMS.** Mixed FMS may contribute to the dissolution of Fe/Mn (hydro)oxide, one reason is mixed FMS may release H<sup>+</sup> from -SH, -SO<sub>3</sub>H, and -PO<sub>3</sub>H<sub>2</sub> loaded in FMS upon interaction with elements. The increased H<sup>+</sup> concentration results in greater solubility of Fe and Mn,<sup>45</sup> further releasing As and Cd which are absorbed in and on these mineral phases. Due to the limited dosage of 0.1% mixed FMS, the amounts of As and Cd adsorbed by FMS were lower than those of the elements released from the Fe/Mn (hydro)oxide phase. However, as the FMS dosage increased, more As and Cd were adsorbed by FMS, leading to a significant reduction in the As and Cd concentrations in porewater.

In addition, it was observed that the concentration of Fe in porewater decreases with incubation time. However, the concentration of Cd and Cu continues increasing with incubation time. Considering that during the beginning of the flooding period, the reduction of sulphate to sulphide mediated by sulphate-reducing bacteria can lead to the precipitation of cadmium sulphide (CdS),<sup>43,44</sup> and the competing ions such as Cu which can form even more insoluble CuS.<sup>45</sup> However, the dissolution of sulfides will happen when H<sup>+</sup> concentration increases.<sup>21,46</sup> Thus, when the sulfides formation increased during the flooding period, H<sup>+</sup> produced by FMS occurred in reaction with sulfides and released the Cd and Cu into the soil solution. It is inferred that when the incubation time increased from 2 weeks to 8 weeks, the increased solubility of Cd and Cu was mainly due to the dissolution of sulfides instead of the dissolution of Fe/Mn (hydro)oxide.

**4.2.2. Performance of mixed FMS in different soils.** The mixed FMS effectively reduced porewater As concentration and bioavailability in the GD soil and GG soil. After FMS treatment of GG (b), (c), and (d), which contain relatively low As content in the soil, the <sup>As</sup>R value is even lower than <sup>As</sup>R<sub>diff</sub>. This illustrates the strong ability of FMS to immobilize As in soil. However, the changes in Cd in different soils after mixed FMS treatment are not consistent, only the bioavailability (<sup>Cd</sup>C<sub>E</sub>) and <sup>Cd</sup>R of Cd in GD (c) soil were significantly reduced, and the pH value of GD (c) is relatively lower (4.98). Cd sorption on the soil solid phases is strongly dependent on pH,<sup>47,48</sup> whereas sorption of As(III), the predominant As species in flooded paddy soils, is only weakly dependent on pH.<sup>49</sup> On average, Cd solubility in soil increased by approximately 4-fold with one unit decrease in pH.<sup>46</sup> Also, the porewater Cd concentration in the CT of GD (c) was 5.19  $\mu\text{g L}^{-1}$ , which is higher than that of other GD and GG soils (Table S18<sup>†</sup>). Suggesting that: (i) When the content of soluble Cd in the soil solution reaches a higher level, mixed FMS will have a significant adsorption effect on the Cd. (ii) A lower pH value may facilitate the binding of Cd to mixed FMS.

## 4.3. The potential regulatory effect of spiked FMS on element interaction

FMS with higher LC tend to exhibit lower  $m_f$ , and thus, the FMS can be further tuned based on this property. In addition, during the release process of spiked FMS, it can be observed that



spiked FMS tends to have the highest  $m_f$  value in the first stage (1st  $R$ ) during the entire release experiment. Because the elements that are weakly bound to FMS (physical binding/weak chemical binding) were first released into the solution. Then, the elements present as the exchangeable component of the spiked FMS interact with the outside environment and are slowly released into the solution. The ability of spiked FMS to release secondary components can be used to modulate the interactions of plant rhizosphere substances. For example, Cd is mainly uptake by rice roots by the Mn transporter OsNRAMP5,<sup>50</sup> and the competition uptake between Cd and Mn was found.<sup>51</sup> K and P are the main nutrients of plants, and many studies have reported the correlation between As and P in rice.<sup>52–54</sup> Arsenate, as an analogue of phosphate, is transported across the plasma membrane through the phosphate transport system,<sup>55</sup> and the addition of phosphate may reduce arsenate uptake, potentially reducing arsenic toxicity.<sup>56</sup> Arsenate sensitivity is closely related to phosphate nutrition, and the increased phosphate status will contribute to decreased arsenate uptake by inhibiting the high-affinity arsenate/phosphate uptake system.<sup>24</sup> As(v) is taken up by the phosphate uptake pathway, and As(III) is primarily assimilated by rice roots *via* the Si transporters.<sup>21</sup> It is well known that Si can inhibit As(III) uptake by rice plants *via* decreasing the expression of *lsi1* or *lsi2* or directly compete for the transporters.<sup>35</sup> Furthermore, the effect of SA on reducing Cd stress in rice has been reported.<sup>26,57</sup> SA's enhanced tolerance to Cd in rice can be attributed to SA's enhancement of enzymatic and non-enzymatic antioxidants and non-protein thiol, as well as SA's regulation of Cd absorption, distribution, and transport in plant organs.<sup>58</sup> Thus, spiked FMS can promote plant growth and indirectly protect plant health.

## 5. Conclusion

FMS can significantly reduce the bioavailability of target TTE in severely polluted soil (by ~37%) through its specific ion affinity (the functional group in the FMS forms a covalent bond with the target TTE). The impact of FMS on the nutrient ion balance of crops is minimal, which benefits and protects crop quality. Preloading FMS with nutrients or agrochemicals can further enhance crop protection. Although the application of FMS in agricultural and environmental fields still requires further research (*e.g.*, long-term impacts on soil health, crop yield, or ecological effects), its comprehensive efficacy for soil pollution mitigation suggests that this material could serve as a promising solution for addressing complex environmental challenges.

## Data availability

The data supporting this article have been included as part of the ESL.† Data for this article, are also available from Queen's University, Belfast at <https://pureadmin.qub.ac.uk/admin/editor/dk/atira/pure/api/shared/model/studentthesis/editor/studentthesiseditor.xhtml?scheme=&type=&id=613137253> and <https://doi.org/10.6084/m9.figshare.29223440.v1>.

## Author contributions

Jiawei Yang: Data curation, formal analysis, investigation, methodology, visualization, writing – original draft. Paul N. Williams: Conceptualization, funding acquisition, methodology, project administration, supervision, writing – review & editing. Xiaoxia Cao: Investigation, methodology. Jun Luo: Resources, supervision. Hongyan Liu: Resources, supervision. Yingjian Xu: Resources, supervision.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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