Effects of water-fertilizer coupling on immobilization remediation technology using sepiolite

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Abstract

Sepiolite shows great potential to reduce the pollution risk of cadmium (Cd)-contaminated rice in acidic paddy soils, but the efficiency in practical application was synergy of water-fertilizer coupling. We studied the effect of goat manure in sepiolite amended soil under aerobic, intermittent, and flooded irrigation condition. The results showed that the application of sepiolite alone increased soil pH, as a consequence, sepiolite decreased available Cd under flooded condition. The application of goat manure alone increased DOM content in unamended and sepiolite amended soil. As a result, goat manure increased available Cd under aerobic and flooded water condition in sepiolite amended soil. Under intermittent water condition, the combined application of sepiolite and goat manure inhibited the transfer of Cd from roots to unpolished rice to the greatest extent. The application of sepiolite in Cd polluted soil decreased the accumulation of Cd in unpolished rice at the first year, but Cd content witnessed slight increase at the second year. But, the application of goat manure in sepiolite amended soil further decreased Cd content in unpolished rice under intermittent irrigation condition. As a result, the application of goat manure and intermittent irrigation pattern could present a water-fertilizer coupling effect in sepiolite amended soil and further increased the long-term passivation effect of sepiolite.

1. Introduction

Soil is the main gathering place for metals and acts as a barrier to prevent them from transferring through food chain to protect food safety and human health. It’s reported that around $2.35 \times 10^8$ hectares farmland worldwide are contaminated with trace metal elements (Bermudez et al., 2012). In China, due to improper disposal of industrial wastes and the excessive use of pesticides, fertilizers and plastic films, heavy metal contamination is getting serious and the pollution area is gradually expanding (Liang et al., 2016). According to a general survey of soil pollution status released in 2014, Cadmium (Cd) is the most widely distributed soil pollutant in China. In addition to natural sources (which cause fewer changes), human activities are changing soil functions and properties more rapidly and more intensively. More than 90% of Cd release in the environment is caused by man-made sources (Bi et al., 2006). Therefore, the prevention and control of Cd pollution has become a hotspot in the field of soil environment.

Engineered soil remediation technology (such as mixing of soil method) and bioremediation technology (such as phytoremediation and microbial remediation) are difficult to realize in practical applications due to high cost and low remediation efficiency. Therefore, as soon as the in-situ chemical immobilization remediation technology appeared, it has attracted widespread attention for its advantages of high cost-effectiveness, easy to operate, suitable for large-area soil treatment, and environmental friendliness.

Immobilization remediation is a process of converting metals with high mobility into solid or physicochemical stable form through chemical interactions among heavy metals, soil particles, and binders while agricultural production (He et al. 2020). Numerous soil amendments, i.e., alkaline compounds (Liu et al, 2020), clay minerals (Xie et al, 2018), metal oxides (Lin et al, 2021), organic scraps (Jin et al, 2020) and phosphate sulfides (Song et al, 2021) have been proposed and evaluated for their ability to immobilize heavy metals in soil environment. The mechanism involved in Cd adsorption of natural clay mineral containing redox potential (Fulda et al. 2013), soil pH (Yin et al., 2017), ion-exchange (Bolan et al., 2013; Luo et al., 2013), surface complexation (Liang et al., 2017) and precipitation reactions (Khaokaew et al., 2011; Agrawal and Sahu, 2006).

Therefore, in the past two decades, the research on heavy metal pollution using immobilization remediation method has mainly focused on the screening and synthesis of immobilizing agents. Our previous study found that the application of natural sepiolite could decrease available content of Cd in soil and reduce the pollution risk of Cd on plant. However, natural sepiolite might not achieve the desired effect during planting and other soil biogeochemical process, like acid-soluble and complexation effects. As a consequence, development of agronomic management technologies to prevent Cd remobilization was an important pathway to control the food safety of agricultural products in soils.
As we all know, continuous flooding irrigation dramatically reduced Cd accumulation in rice grains (Wiggenhauser et al., 2020). Because, radial oxygen loss from rice roots temporarily oxygenates the rhizosphere and causes redox oscillations in the soil (Maisch et al., 2019). Rinklebe(2016) and Ye(2018) found that the reduction of sulfate to sulfide and the formation of insoluble CdS consequently reduced available Cd in the flooded soil. Intermittent flooding promote rice growth through regulate of soil permeability. The periodic variation in rhizosphere soil may affect the dominant biogeochemical reactions of redox-sensitive elements such as Fe, nitrogen (N), sulfur (S) and carbon (C)(Zhu et al., 2014). Meanwhile, intermittent irrigation improves rainfall utilization rate and facilitate water conservation (Lv et al., 2014).

As the main source of plant nutrition, the application of chemical and organic fertilizer also affects the distribution of soil heavy metal fractions (Li et al. 2016). Wang et al(2021) found that ammonia (NH\textsubscript{4}+\textsuperscript{+}-N) accelerated the remobilization of immobilized Cd. However, the impact of OM on mobility and phytotoxicity of heavy metal remains controversial. On one hand, OM reduces available Cd in the process of complexation or chelation (Ren et al. 2016, Mohamed et al. 2010). OM influences the Cd translocation into plants during soil nutrient uptake, root exudates, rice transpiration and transport protein activity (Rizwan et al., 2015). In contrast, OM may induce metal mobilization through the formation of small molecular organic acids (Spaccini et al. 2008, Richard et al. 2009, Salati et al. 2010).

Accordingly, the objectives of this study were to investigate the effects of common water management and goat manure on sepiolite amended paddy soil.

2. Materials And Methods

2.1 Physicochemical properties of sepiolite, goat manure and soil

Soil specimen with natural Cd was collected from the 0 to 20 cm layer in Chenzhou, Hunan, China (112º43’48”N, 25º43’48”E). The basic characteristics of soil are showed in Table 1. Natural sepiolite was purchased from Hebei Huakai Environmental Protection Material Co. Ltd. The goat manure (GM) was purchased from a local fertilizer market in Tianjin, China. Selected characteristics of goat manure were listed in Table 2.

2.2 Experimental setup and water management

Pot experiment in the first year.

Pot experiments were performed in a greenhouse in the Agro-Environmental Protection Institute, Tianjin, China. The soil samples were air-dried, homogenized and passed through a 4mm sieve. Soil (6 kg) was placed in each pot (23.3 cm in diameter, 34 cm in height). Basal fertilizer, containing 3.87 g urea and 6.24 g monopotassium phosphate, was added to soil and mixed thoroughly (Xiao et al., 2015). SP and GM were mixed in to each pot as shown in Table 3. Then, soils were equilibrated for one month, maintaining approximately 75% of field water-holding capacity with tap water (without Cd).

Seedlings of rice (Oryza sativa L.) were germinated on perlite and transplanted on June 11, 2019. The rice plants were grown under uniform flooded conditions for 21 d before the water treatment. There were three water management conditions, involving continuous flooded (CF, maintained 2–3 cm water layer in pot throughout the growth period), intermittent water condition (IW, repeated every 7-d with 3-d flooding followed by 4-d drainage), and aerobic condition (AO, soil maintained moisture during the growth period). Drainage from the pots was prevented during the experiments, and the pots were arranged in random blocks and rotated intermittently to ensure the same conditions for each pot.

Pot experiment in the second year.

In order to test and verify the long-term stability and effectiveness of sepiolite, the pot experiment with the same design was conducted in the second year. The pot have applied goat manure in the first year were added with the same dosage of GM to replenish soil fertility.
2.3 Sample preparation and analysis

After 135 d of growth, the plants were harvested and separated into root, straw, rachis, husk, and rice grains. The rice grains were oven-dried at 75 °C and weighed immediately after removing the husk and unfilled grains. Each part of the plant were ground and passed a 1.85-mm sieve for further analysis. Cd contents in plant samples were digested using a block digester and soil solutions was determined by inductively coupled plasma mass spectrometry (iCAP Q; Thermo Scientific, Waltham, MA, USA). (Yin et al., 2017).

Rhizosphere soil was collected from a small amount of soil shaken directly from the plant roots. Soil samples were air-dried at room temperature and sieved to <1 mm, and stored in a plastic container for further analysis.

Soil pH was measured with a pH meter (PB-10, Sartorius, Germany) at the solid-to-liquid ratio (m:v) of 1:2.5(Zhou et al. 2018a).

DOM content was measured using a total organic carbon analyzer (Vario TOC, Elementar Germany element) at a solid-to-water ratio of 1:5(Gao et al. 2018).

The bioavailability of Cd in soil was determined by diethylenetriaminepentaacetic acid (DTPA) at a solid-to-water ratio of 1:5 (Liang et al. 2016; Wang et al. 2016).

Changes in the fractions of Cd in paddy soil were analyzed by sequential extraction (Tessier et al., 1979), which separates heavy metals into five different fractions: extractable with 1.0 M MgCl$_2$ (pH=7) (exchangeable, EXC-Cd), extractable with 1.0 M NaOAc (pH=5) (carbonate-bound, CB-Cd), extractable with 0.04 M NH$_2$OH·HCl in 25% (vol.%) HOAc solution (associated with Fe–Mn oxides, OX-Cd), extractable with 0.02 M HNO$_3$ in 30% (wt.%) H$_2$O$_2$ (complexed with organic matter, OM-Cd), and HNO$_3$–HF–HClO$_4$ digested (residual, Res-Cd).

2.4 Quality control

To monitor the accuracy and quality of chemical analyses, quality control measures were adopted using soil (GBW(E)-070009) and plant reference materials (GBW-10045 (GSB-23)) obtained from the Institute of Geophysical and Geochemical Exploration (IGGE, China). Three reagent blanks and three standard reference materials were included in each batch of extraction, preparation, and analysis of every 40 samples. The recovery rate were 95–103% and 92–100% for Cd of plants and soil, respectively.

2.5 Statistical analyses

All treatments were replicated three times. The means and standard deviations (SD) were calculated using Microsoft Office Excel 2003. Two way analysis of variance was carried out with SAS 9.2 (SAS Inc., NC, USA). The mean values of the experimental parameters were compared using Student’s t-test at p ≤ 0.05 (significant).

3. Results

3.1 Effects of GM on grain yield under different water management treatments

As shown in Fig.1, grain yield was higher in intermittent irrigation condition, comparing to aerobic and flooded condition. The application of GM increased grain yield by 9.4% and 30.1% in the aerobic and intermittent condition, but decreased grain yield by 20.3% in the flooded paddy soil. In sepiolite amended soil, the application of GM increased grain yield by 34.3% and 40.2% in the aerobic and flooded paddy soil, while decreased grain yield by 11.9% in intermittent irrigation. Song et al (2021) observed higher grain yield in intermittent irrigation than flooded condition. Further, grain yield improved with the increase in P rates.
3.2 Effects of GM on soil DOM and pH under different water management treatments

As shown in Fig.2, soil pH slightly increased in intermittent and flooded paddy soil. The application of sepiolite and goat manure also increased soil pH. The application of GM increased DOM by 244.3%, in contrast, the application of sepiolite decreased DOM by 31.5%. So, the application of GM in SP amended soil increased DOM by 135.2%. Dissolved organic matters refers to the organic matter that can be extracted by water passing 0.45μm membrane. Bian et al (2020) found that the application of silkworm excrement organic fertilizer increased DOM by 124.6%.

3.3 Effects of GM on Cd accumulation factor in different parts

The translocation factors of different parts were directly related to the Cd accumulation character. The translocation factors (TF) from roots to straws were between 0.08—0.24. The transfer factors from straws to rachis were between 0.31—0.55. The translocation factors from rachis to husk showed great disparity under different water management. The translocation factors from rachis to husk were between 0.31—0.67 under aerobic and intermittent irrigation condition, whilst the translocation factors from rachis to husk were 0.86—2.00 under flooded condition. As for the translocation factor from husk to unpolished rice, the only TF=1 was obtained for sepiolite-amended soil with the application of goat manure under intermittent irrigation condition.

3.4 Effects of GM on Cd concentration of unpolished rice in two consecutive years

Table 5 showed the effects of GM on Cd of unpolished rice under different water condition. During the first year, Cd concentration of unpolished rice were 0.2908 mg·kg⁻¹ under flooded water treatment, whilst, Cd concentration were 4.85 times and 6.88 times higher under aerobic and intermittent water condition. The application of SP alone decreased Cd concentration by 51.3—76.9%. The application of GM on unamended soil decreased Cd concentration by 49.7—73.1%. The application of GM on sepiolite-amended soil decreased Cd concentration by 61.0, 62.5% under aerobic and intermittent condition, whilst increased Cd concentration under flooded condition. In the following year, Cd concentration of unpolished rice were 0.4868, 0.3944, and 0.2385 mg·kg⁻¹ under aerobic, intermittent, and flooded water treatment, respectively. Sepiolite-amended treatment decreased Cd concentration by 33.6% to 46.7%. GM treatment decreased Cd concentration by 10.0% to 47.3%. GM treatment on sepiolite-amended soil decreased Cd concentration by 32.6 to 58.5%.

3.5 Effects of GM on available Cd of soil extracted by DTPA

Fig.3 showed the available Cd in soil of different treatment. The application of GM in unamended-soil increased available Cd extracted by DTPA under different water management. The application of GM on sepiolite-amended soil showed different effect on available Cd. Under intermittent irrigation condition, the application of GM in sepiolite-amended soil decreased available Cd by 17.5%. However, the application of GM in sepiolite-amended soil increased available Cd under aerobic and flooded water condition.

3.6 Effects of GM on species distribution of Cd

Sequentially extractable Cd fraction percentages in the soil affected by GM were shown in Fig.4. In the bulk soil of CK group, residual fraction accounted for a large proportion of the total Cd concentration (44.4%, 51.7, and 53.6, respectively). The application of SP decreased exchangeable fraction, and increased Fe-Mn-oxides bounded fraction. The application of GM decreased the residual fraction, whilst increased carbonate bounded fraction in unamended soil. As for sepiolite-amended soil, the application of GM decreased exchangeable fraction, increased the residual fraction simultaneously under intermittent irrigation condition. Whilst, under aerobic and flooded condition, the application of GM increased exchangeable fraction.

4 Discussion
Yield is the chief element to indicate the growth and development of crops that are affected by excess concentration of noxious substance in soil. Water management affects the bioavailability of cadmium (Cd) in the soil and hence their accumulation in rice and grain yields. Lv (2014) found that the intermittent irrigation increased grain yield by 7.55%-29.58%. Compared with flooding, both aerobic and intermittent irrigation enhanced Cd distribution in the root and reduced it in the straw and grain. It is reported that Cd might promoted the growth of plants when the concentration below 5 mg·kg\(^{-1}\) (Tang et al., 2020). Song (2020) found that comparing to continuous flooding, grain yield was higher under alternate wetting and drying (intermittent) irrigation condition. Besides, the application of phosphorus fertilizer slightly increased grain yield. Coincidentally, we found the same tendency in our research. Grain yield were higher under intermittent water condition comparing with flooded and aerobic water condition. The application of goat manure showed different effect on grain yield in unamended and sepiolite amended soil. It might ascribe to the substantial reduction of dissolved Cd in soil.

Soil acidity is a major yield-limiting factor that adversely affects crop productivity (Nanda and Adriano, 2014). In our study, the application of sepiolite alone decreased grain yield under aerobic and flooded irrigation condition. As a result, grain yield decreased by 9.7%-18.3%. Lahori (2017) found that tobacco biochar and zeolite significantly decreased the dry biomass yield of *Brassica campestris L.* due to the increase in the soil pH compared to the control. However, Ran (2019) reported that the combine application of sepiolite and organic fertilizer increased soil pH by 1.0-1.2, yet, some treatments appeared to increase the dry biomass yield relative to the CK. In our study, the application of sepiolite and goat manure increased soil pH by 1.2-1.5 under different water condition, meanwhile grain yield increased by 9.7%-26.6%. This finding indicated that the combined application of sepiolite and organic manure can be used as a suitable choice for remediating Cd contaminated soil.

Soil pH and soluble carbon are important factors that influence the movement of heavy metals and bioactivity (Jiang et al. 2012). Zhou et al. (2014) described a negative correlation between soil pH values and bioavailable concentrations of soil Cd. Because with increasing soil pH values, concentrations of OH\(^{-}\) increased, followed by the OH\(^{-}\) and heavy metals forming a precipitate of hydroxide. Sepiolite, as well known, is a pH-regulating immobilizing agent. When absorbed to ion exchange sites, sepiolite could also fix some heavy metals. After rice planting, the soil pH is close to neutral, while soluble organic carbon increases. However, as the seasons change, these two factors differently affect the chemical forms and bioactivity of the soil Cd (Kögel-Knabner et al. 2010). Research also suggests that soluble organic carbon is the most important in terms of exchangeable Cd with high bioactivity (Xiao et al. 2006). In our study, soil DOM increased for 3.44 times while applied goat manure alone, but decreased by 31.5% while applied sepiolite alone. Hence, DOM almost doubled while the combined application of sepiolite and goat manure. Li et al(2018) found that soluble carbon increased significantly by 15% (P ≤ 0.05) under the farmyard manure treatments.

As a result of large decreases in biomass inputs and soil organic carbon (SOC) concentrations due to the long-term effects of metal pollution on soil microorganisms and vegetation, Ekaterina et al (2005) found that SOM had greater diversity and bond intensity of functional groups in unpolluted soils than in polluted soils. Zhou et al (2017) studied the effects of organic matter fraction on distribution of Cd in long-term polluted paddy soils, the results showed that SOM fractions had higher Cd concentration than other soil constituents. In our study, the application of goat manure slightly increased available Cd extracted by DTPA under aerobic intermittent irrigation condition, but the effect did not reach a significant level.

The root is widely recognized as the most major connection between rice plant and soil environment. Compared to aerobic and intermittent irrigation, flooded irrigation decreased Cd content of root by 73.4%-93.0%. Meanwhile, the accumulation pattern of Cd in other parts of rice plant was similar to that in root. Cd content in different part of rice ranked in the following order root>straw>brachis>husk.

Translocation factors (TFs) were also the most perceptual intuition of the concentration between different parts. A decrease of Cd concentrations in unpolished rice was relevant to TFs in all parts of the rice plant, but different organs had different
TFs. With the addition of different amendment, the TFs of Cd from roots to straw, straw to rachis, rachis to husks, husks to unpolished rice, and roots to unpolished rice changed to different degrees (Table 4). However, TFs are inversely proportional to biomass of different plant parts. We found that TFs from roots to straw all lower than 0.20. Because, the biomass of straws were much higher than roots. Wang (2020) found that the application of hydroxyapatite decreased TF of maize, besides the effect increased with the increase of application rate. Chen (2021) found that the amendments the ability of Cd to be transferred to the grains was effectively inhibited as the values of $\text{TF}_G$ were lower than those of $\text{TF}_S$ ($\text{TF}_G$, Translocation factor from straw to grains; $\text{TF}_S$, Translocation factor from root to straw). In our study, the TFs from husks to unpolished rice exceeded 1.0 in most of the treatments. This results indicated that ability of husks to transport Cd was greater than that of other rice organs. Table 4 showed that under intermittent water condition, the combined application of sepiolite and goat manure inhibited the transfer of Cd from roots to unpolished rice to the greatest extent.

In the first year, the combined application of sepiolite and goat manure decreased Cd by 83.1%, but did not reach the recommended tolerable levels as proposed in the national food pollutants standards (GB2762-2012; 0.20 mg·kg$^{-1}$). However, under flooded irrigation condition, the application of sepiolite alone, goat manure alone, and the combination all reduced the rice contamination risk. Cd content all below 0.20 mg·kg$^{-1}$ in the amended treatments. In the second year, the application of sepiolite alone decreased Cd content of unpolished rice by 66.7%, 45.5% under aerobic and intermittent irrigation condition compared to the first year. But, under flooded condition, the application of sepiolite alone increased Cd content of unpolished rice in the second year. The results indicated that cropping pattern affected has a negative effect on the long-term stability of the sepiolite. But, the combined application of sepiolite and goat manure further decreased Cd content of unpolished rice under flooded condition. Therefore, the application of goat manure enhanced the effect and long-term stability of sepiolite.

It is well known that bioavailable fraction of metal is more important for plant uptake than the total concentrations of heavy metals in the soil which might be due to the presence of different chemical forms of heavy metals (Rizwan et al., 2016). Bioavailable Cd is the fraction of total Cd in the interstitial water and soil particles that is readily available to the receptor organisms. The DTPA-extractable metal concentration in the 10-20 cm profiles is adapted to assess the phytoavailable proportion of Cd. Therefore, the uptake and transportation of Cd by rice plants was also greatly influenced by DTPA-Cd (Fellet et al., 2014). Wang (2016) reported that the application of biochar decreased DTPA-Cd by 14%-51%, as a result, Cd in edible part decreased by 46%-86%. In this study, the application of goat manure increased DTPA-Cd in most treatments. Because organic manure increased -COOH of soil particle, which can promoted the mobility of Cd by forming complexes. Zhou (2018b) found that rice straw(RS) increased phytoextraction efficiency of Cd, and RS has positive effects on plant Cd uptakes.

In our study, the application of sepiolite decreased exchangeable Cd and increased the fraction bound to organic matter. The reason is that CaCO$_3$ occupied a large proportion in sepiolite. Besides, the application of goat manure increased exchangeable Cd and decreased residual form of Cd in unamended soil. But in the sepiolite-amended soil, the application of goat manure decreased exchangeable Cd and increased residual form of Cd under intermittent irrigation condition. The results showed that intermittent irrigation regime was a safe and effective pattern for Cd remediation using sepiolite. Besides, the application of goat manure in sepiolite amendment was also a recommended measure to promote crop growth and achieve safe production in Cd polluted soil.

5 Conclusion

1. The application of sepiolite alone increased soil pH, as a consequence, sepiolite decreased available Cd under flooded condition.
2. The application of goat manure alone increased DOM content in unamended and sepiolite amended soil. As a result, goat manure increased available Cd under aerobic and flooded water condition in sepiolite amended soil.
3. Under intermittent water condition, the combined application of sepiolite and goat manure inhibited the transfer of Cd from roots to unpolished rice to the greatest extent.

4. The application of sepiolite in Cd polluted soil decreased the accumulation of Cd in unpolished rice at the first year, but Cd content witnessed slight increase at the second year. But, the application of goat manure in sepiolite amended soil further decreased Cd content in unpolished rice under intermittent irrigation condition. As a result, the application of goat manure and intermittent irrigation pattern could present a water-fertilizer coupling effect in sepiolite amended soil and further increased the long-term passivation effect of sepiolite.

**Declarations**

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**Competing Interests**

The authors have no relevant financial or non-financial interests to disclose.

**Author Contributions**

All authors contributed to the study conception and design. Yiyun Liu and Yingming Xu contributed to the conception of the study. Yiyun Liu, Qinging Huang and Qin Xu performed the experiment. Lijie Zhao contributed significantly to data collection. Xuefeng Liang, Lin Wang, and Yuebing Sun helped perform the analysis with constructive discussions. The first draft of the manuscript was written by Yiyun Liu and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Tables

Table 1 Basic Characteristics of soil

| Properties       | Value |
|------------------|-------|
| pH(H_2O)         | 6.21  |
| OM(g·kg\(^{-1}\)) | 34.6  |
| Total N(mg·kg\(^{-1}\)) | 42.9 |
| Available P(mg·kg\(^{-1}\)) | 9.3  |
| Available K(mg·kg\(^{-1}\)) | 182.7 |
| CEC(cmol·kg\(^{-1}\)) | 25.3 |
| Total Cd(mg·kg\(^{-1}\)) | 2.5  |

Table 2 Basic Characteristics of goat manure

| Properties       | Value |
|------------------|-------|
| pH               | 10.1  |
| OM(%)            | 92.1  |
| Total N(%)       | 2.54  |
| Total P(%)       | 0.56  |
| Total K(%)       | 1.09  |
| Total S(%)       | 0.56  |
| Total Cd(mg·kg\(^{-1}\)) | 0.74 |

Table 3 Summary of pot experiment treatments
### Table 4 Cd content in different part of rice plant (mg/kg) and translocation factor

| Treatments      | Cd\textsubscript{Root} | TF\textsubscript{1} | Cd\textsubscript{Straw} | TF\textsubscript{2} | Cd\textsubscript{Rachis} | TF\textsubscript{3} | Cd\textsubscript{Husk} | TF\textsubscript{4} | TF\textsubscript{p} |
|-----------------|-------------------------|----------------------|--------------------------|----------------------|--------------------------|----------------------|--------------------------|----------------------|----------------------|
| **Aerobic**     |                         |                      |                          |                      |                          |                      |                          |                      |                      |
| CK              | 46.42±2.30              | 0.19                 | 8.86±0.80                | 0.49                 | 4.33±0.29                | 0.39                 | 1.70±0.07                | 1.00                 | 0.0366               |
| GM              | 8.67±0.18               | 0.16                 | 1.43±0.16                | 0.31                 | 0.44±0.01                | 0.57                 | 0.25±0.02                | 1.83                 | 0.052                |
| SP              | 16.16±2.00              | 0.10                 | 1.65±0.36                | 0.53                 | 0.88±0.002               | 0.31                 | 0.27±0.008               | 2.85                 | 0.047                |
| SG              | 6.42±0.60               | 0.13                 | 0.85±0.11                | 0.35                 | 0.30±0.02                | 0.57                 | 0.17±0.02                | 1.68                 | 0.044                |
| **Intermittent**|                         |                      |                          |                      |                          |                      |                          |                      |                      |
| CK              | 42.21±5.86              | 0.24                 | 10.37±0.28               | 0.55                 | 5.70±0.25                | 0.39                 | 2.20±0.17                | 1.04                 | 0.054                |
| GM              | 15.72±2.79              | 0.16                 | 2.55±0.05                | 0.44                 | 1.12±0.20                | 0.49                 | 0.55±0.001               | 1.65                 | 0.057                |
| SP              | 17.09±1.40              | 0.11                 | 1.83±0.004               | 0.42                 | 0.76±0.15                | 0.33                 | 0.25±0.02                | 2.12                 | 0.032                |
| SG              | 9.09±0.33               | 0.09                 | 0.86±0.01                | 0.42                 | 0.36±0.07                | 0.67                 | 0.24±0.01                | 0.86                 | 0.022                |
| **Flooded**     |                         |                      |                          |                      |                          |                      |                          |                      |                      |
| CK              | 3.24±0.56               | 0.12                 | 0.38±0.002               | 0.37                 | 0.14±0.01                | 0.86                 | 0.12±0.001               | 2.42                 | 0.092                |
| GM              | 2.06±0.09               | 0.10                 | 0.21±0.02                | 0.48                 | 0.10±0.01                | 2.00                 | 0.20±0.005               | 0.73                 | 0.070                |
| SP              | 4.54±0.20               | 0.08                 | 0.37±0.05                | 0.43                 | 0.16±0.00                | 0.87                 | 0.14±0.01                | 1.01                 | 0.030                |
| SG              | 2.12±0.09               | 0.11                 | 0.24±0.01                | 0.42                 | 0.10±0.02                | 1.80                 | 0.18±0.002               | 0.95                 | 0.079                |

Note: TF\textsubscript{1}, Translocation factor from root to straw; TF\textsubscript{2}, Translocation factor from straw to rachis; TF\textsubscript{3}, Translocation factor from rachis to husk; TF\textsubscript{4}, Translocation factor from husk to unpolished rice; TF\textsubscript{p}, product of TF\textsubscript{1}, TF\textsubscript{2}, TF\textsubscript{3} and TF\textsubscript{4}.

### Table 5 Effects of GM on Cd of unpolished rice
| Treatments | Cd concentration (mg·kg⁻¹) |
|------------|-----------------------------|
|            | CK                  | GM       | SP       | SG       |
| 1st year   |                     |          |          |          |
| aerobic    | 1.6999±0.0649        | 0.4570±0.0001 | 0.7700±0.0308 | 0.2866±0.0116 |
| intermittent | 2.2920±0.1706      | 0.9089±0.0711 | 0.5290±0.0417 | 0.2062±0.0190 |
| flooded    | 0.2908±0.0008        | 0.1464±0.0020 | 0.1415±0.0077 | 0.1702±0.0113 |
| 2nd year   |                     |          |          |          |
| aerobic    | 0.4868±0.0418        | 0.2596±0.0139 | 0.2566±0.0105 | 0.1729±0.0074 |
| intermittent | 0.3944±0.0328      | 0.2234±0.0155 | 0.2885±0.0157 | 0.1605±0.0088 |
| flooded    | 0.2385±0.0093        | 0.1583±0.0101 | 0.2146±0.0115 | 0.0891±0.0061 |

**Figures**

**Figure 1**

Effects of goat manure on grain yield under different water management treatments (CK, no material was applied, GM, 1.0% (w/w, the same below) GM was applied to the pots; SP, 1.0% SP was applied to the pots; SG, 1.0% GM and SP was applied to the pots.)
Figure 2
Effects of goat manure on pH and DOM under different water management treatments

Figure 3
Available Cd extracted by DTPA
Figure 4

**Cd fractions of Tessier sequential extraction** (EXC-Cd, proportion of exchangeable Cd; CB-Cd, proportion of Cd in carbonate-bound; OX-Cd, proportion of Cd bounded with Fe–Mn oxides; OM-Cd, proportion of Cd complexed with organic matter; RES-Cd, proportion of Cd in residual form)

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