UNIVERSITY OF BIRMINGHAM
University of Birmingham Research at Birmingham

The effect of Fenton reaction using H_2O_2 and water control on the distribution and accumulation of As speciation within the soil-rice system

Wang, Shaorui; Li, Qiaowen; Stubbings, William; Li, Lili; Qin, Junhao; Li, Huashao

DOI:
https://doi.org/10.1016/j.chemosphere.2021.129633

License:
Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version
Peer reviewed version

Citation for published version (Harvard):
Wang, S, Li, Q, Stubbings, W, Li, L, Qin, J & Li, H 2021, 'The effect of Fenton reaction using H_2O_2 and water control on the distribution and accumulation of As speciation within the soil-rice system', *Chemosphere*, vol. 274, 129633. https://doi.org/10.1016/j.chemosphere.2021.129633

Link to publication on Research at Birmingham portal

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

•Users may freely distribute the URL that is used to identify this publication.
•Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
•User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
•Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Download date: 20. Apr. 2024

The effect of Fenton reaction using H_2O_2 and water control on the distribution and accumulation of As speciation within the soil-rice system

Shaorui Wang[b,c], Qiaowen Li[a,d], William A. Stubbings[e], Lili Li[f], Junhao Qin[a,d], Huashou Li[a,d*]

a *College of Natural Resources and Environment, South China Agricultural University, Guangzhou, 510642, China*

b Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management, Institute of Eco-environmental and Soil Sciences, Guangdong Academy of Sciences, Guangzhou, 510650, China

c National-Regional Joint Engineering Research Center for Soil Pollution Control and Remediation in South China, Guangzhou, 510650, China

d Guangdong Engineering Research Center for Modern Eco-agriculture and Circular Agriculture/Key Laboratory of Agroecology and Rural Environment of Guangzhou Regular Higher Education Institutions, Guangzhou, 510642, China

e School of Geography, Earth, & Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK.

f School of Environmental Science and Engineering, Zhongkai University of Agriculture and Engineering, Guangzhou 510225, China

* Author for correspondence: E-mail: lihuashou@scau.edu.cn; Tel.: +86-20-85280211;

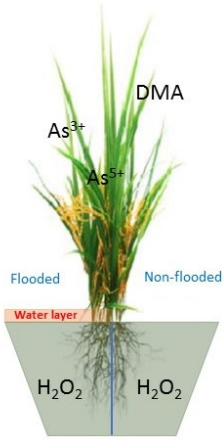
24

25

26

27

28 **TOC**



29

Abstract

The behavior of arsenic (As) in paddy soil is of great interest because rice is an efficient As accumulator, which can result in potential health risks to humans. In this study, we investigated the distribution and translocation of As speciation within the soil-rice system in the presence of Fenton solution (100 μM H_2O_2 and 100 μM Fe^{2+}). The results showed that the iron plaque concentrations were enhanced either by the addition of Fenton solution or under flooded condition. In addition, total As, As^{5+}, and As^{3+} concentrations were lower in rice tissues treated with Fenton solution than those without Fenton solution treatments. Therefore the addition of Fenton solution can reduce As speciation accumulation in rice tissue. This study revealed the function of Fenton solution on the fate of As speciation distribution within soil-rice system and the link between iron plaque and As accumulation in rice tissue under flooded and non-flooded conditions.

Introduction

Inorganic arsenic (As) is a potent carcinogen for humans with no safe exposure limit, while organic arsenic can exist in the terrestrial environment, with the most common As speciation: dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA).[1-3] The toxicity of As to humans varies greatly with chemical speciation. For example, trivalent MMA was found to be the most cytotoxic As species to human cell cultures while the pentavalent methylated species, such as DMA, is thought to be less toxic than inorganic As.[4, 5]

The impact of soil As distribution and its transfer from soil to the food chain depends on the bioavailability of soil As.[6] Due to favorable anaerobic conditions in the paddy soils and the efficient uptake of arsenite by rice,[7, 8] As can be intensively accumulated within rice tissue in comparison with other cereals.[9] The distinct cycle of flooded and non-flooded periods for paddy soil, accompanied by natural redox changes, combine to result in significant impacts on the environmental behavior of As, which can be attributed to the redox-sensitivity of As.[10, 11] Firstly, soil microbes are effected by the flooding condition of paddy soil, resulting in the enhancement of anaerobic microorganisms such as iron-reducing bacteria and the formation of iron plaques.[12] Iron plaques are commonly formed on the surfaces of rice roots which are generally related to oxidants and oxygen existing in the rhizosphere. Additionally, the formation of iron plaques can benefit from the artificial addition of ferrous iron (Fe^{2+}) in solutions, which has a strong affinity for arsenate.[13] In paddy soils, As can be sequestered in iron oxides during the non-flooded period.[10] Moreover, under anaerobic conditions, arsenite can be mobilized into the soil solution, subsequently resulting in the enhancement of the availability of the substrate for methylation. Previous studies

have demonstrated that arsenite was the predominant speciation when arsenate and arsenite coexist in flooded paddy soils.[14] Thirdly, arsenite shares the highly efficient silicon uptake pathway in rice which is a significant way in rice roots. Therefore, unlike other terrestrial food crops, rice grains can contain considerable amounts of methylated As, especially DMA [15, 16] which is highly mobile during both xylem and phloem transport in rice, unlike arsenite where the main route of transport is *via* the phloem. The accumulation of As in rice tissue and the fate of As within the paddy soil-rice system are one of the major global concerns, especially in Asia where rice diets dominate.[17]

Fenton-type reactions aimed to eliminate the water-borne chemicals have been investigated previously with the major mechanism related to an advanced oxidation process. For instance, Fe^{2+} and a hydroxyl radical can be generated once the Fe^{2+} and hydrogen peroxide (H_2O_2) coexist, which plays an important role in the biogeochemical cycles of As.[13, 18] As a consequence, it is possible to oxidize arsenite to arsenate in the presence of iron oxides which have great adsorption capacity for inorganic anions, especially for arsenate.[19] Therefore, the ubiquity of iron plaques on rice roots and the potential As sequestration in iron plaque has a large impact on As uptake by rice roots, As speciation and distribution within rice tissue. Additionally, the ingredients for triggering the Fenton reaction may be naturally present during rainfall events, since H_2O_2 is a common constituent of rainwater and Fe^{2+} is present in many surface water environments, especially in paddy soils.[20-23] The concentration of H_2O_2 in rainwater varies greatly according to the season, geographic and climatic conditions, regional contamination emission characteristics, and monitoring time.[24] Our previous study has demonstrated that the H_2O_2 in rainwater in summer was below 19 uM.[24] However, whether or not the interaction between Fe and As in the presence of H_2O_2 will influence

the As transportation within the soil-plant system is still unknown. Therefore, the objective of this study is to investigate the potential effect of Fenton solution and water control on the distribution and transportation of As speciation within the soil-rice system under different As levels.

Materials and methods

Experimental set-up

Surface loamy soil was collected from a rice paddy at the South China Agricultural University campus, Guangzhou. The soil was air-dried, sieved through a 2 mm mesh and then blended thoroughly with two concentrations of As. Specifically, soil was separately spiked with arsenic trioxide (As_2O_3), with a final concentration of 30 mg kg^{-1} total As (As_{30}) and 60 mg kg^{-1} total As (As_{60}), respectively. Soil without As addition was used as a control (CK). After spiking, the soils were stirred for 30 min every day, and then homogenized for 1 month at room temperature to allow the contaminants to equilibrate. The physicochemical properties of the spiked soil can be found in Table S1.

Rice seeds (*Oryza sativa*, Tianyou 122) were surface sterilized with 30% H_2O_2, rinsed thoroughly with deionized water and then germinated in matrix for 2 weeks. Four uniform rice seedlings were transplanted into a root bag (40 μm aperture, 10 cm i.d. × 15 cm height) containing 200g quartz sand and spiked soil. Subsequently, the root bags were transplanted into individual ceramic pots (30 cm diameter, 25 cm height) containing 10 kg spiked soil in total. During the cultivation, four irrigation methods were included during the pot experiment; (1) water-flooded (CF), soils were continuously covered by a 2 cm thick water layer; (2) wet-dry alternation (IF), soils were cyclically covered by a 2 cm thick water layer and then allowed to dry naturally by vertical flow,

105 the a 2 cm thick water layer is then replenished, such circulation was continuous performed during
106 the cultivation; (3) water-flooded soil was spiked with Fenton solutions containing 100 μM H_2O_2
107 and 100 μM Fe^{2+} ($FeSO_4$) (F + CF); (4) wet-dry alternation soil was spiked with Fenton solutions
108 mentioned above (F + IF). In total, 12 treatments were involved in the current study, with four
109 irrigation methods applied to each of the two spiked soil concentrations and the control soil. Each
110 treatment has three duplicates. All the pots were rotated randomly during the cultivation to ensure
111 plant were exposed to the same environmental conditions. The pot experiments were conducted
112 from April, 2015 to July, 2015, in a greenhouse located in South China Agricultural University. The
113 temperature is ranged from 25 to 31°C during the cultivation. At the end of cultivation, the soil in
114 the root bags were collected as rhizosphere soil (RS), and the soil outside of the root bags was
115 collected as non-rhizosphere soil (NRS).

116 ***Chemical analysis***

117 ***As concentration and speciation analysis***

118 The rice plants were collected at the end of cultivation and dried in the oven at 75 °C for 48
119 hours until obtaining constant weight. The total concentrations of As in soil and rice tissue (root,
120 shoot, leave, and grain) were determined by an atomic fluorescence spectrometer (AFS) after strong
121 acid digestion (HNO_3) of about 500 mg of ground plant and soil samples. For analysis of As
122 speciation, plant samples were weighed and ground into powder using agate mortar. 0.2-0.5 g plant
123 tissue were extracted with 5 mL mixture of methanol/water (2:1, v:v) for 20 min at 60 °C, and
124 centrifuged at 10,000 r/min for 20 min.[25] This extraction was repeated twice and the collected
125 supernatants were combined. Samples were stored in a -40 °C freezer until analysis *via* inductively
126 coupled plasma mass spectrometry (ICP). Detailed information on ICP analysis can be found

127 elsewhere.[21]

128 For determining As speciation in soil, 1 g soil was extracted with 10 mL H_3PO_4 for 6 hours and
129 centrifuged at 10,000 r/min for 5 mins. Subsequently, 10 mL NaOH was added to the soil for 6 hours,
130 and the supernatants collected after a further round of centrifugation. The samples were then stored
131 at -40 °C until ICP analysis.

132 In the analysis of As, certified standard reference materials (SRM 1515 for plants and SRM
133 2709 for soils) of the National Institute of Standards and Technology (NIST), USA, were used as
134 the QA/QC protocol in the As analysis. The recovery rates for all various arsenic species in the soil
135 and plant reference materials ranged from 82.8% to 109% and from 89.6% to 122%, respectively.

136 ***Iron plaques***

137 Iron plaques on fresh root surfaces were extracted using the dithionite-citrate-bicarbonate
138 (DCB) method. Briefly, the whole root of each seedling was incubated in 50 mL solution containing
139 0.03 M sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) and 0.125 M sodium bicarbonate ($NaHCO_3$) at room
140 temperature (20-25 °C) for 60 min. The roots were first rinsed three times with deionized water and
141 then combined with the DCB extracts and topped up to 100 mL with deionized water. After DCB
142 extraction, the roots were oven dried at 70 °C until a constant weight could be read. The iron plaque
143 concentration (g Fe/kg RDW) was calculated as: iron concentration in DCB extracts divided by dry
144 weight of root (RDW).

145 ***Data analysis***

146 The statistical significance of differences and correlation (p-value < 0.05) of As accumulation
147 in plants among the different treatments was performed using a one-way ANOVA and Pearson's test
148 using Minitab 19.0.

Results and discussion

Iron plaque formation and As distribution in iron plaque

Regarding the As treatments, the average concentrations of iron plaques on root surfaces ranged from 2.7 to 15.4 g Fe/kg RDW in treatments of Fenton solution and from 3.6 to 7.1 g Fe/kg RDW in treatments without Fenton solution application. In general, the concentrations of iron plaques were enhanced by the addition of Fenton solution (Fig.1). Previous studies have demonstrated that the iron plaque formation was correlated with greater oxygen and oxidant concentrations.[26] As expected, in the current study, the iron plaque concentrations in treatments of Fenton solution are higher than those in treatments without Fenton solution indicating that the addition of Fenton solution enhanced iron plaque formation. The CF irrigation method increased the iron plaque concentration compared to IF irrigation method (Fig.1).

More importantly, higher concentrations of As^{5+} and As^{3+} in iron plaques were also observed in CF treatments than the IF treatments (Fig.2). For instance, the concentrations of As^{5+} and As^{3+} in iron plaques of CF treatments were significantly higher than those observed in IF treatments. However, the concentration of DMA among treatments remained indistinguishable. Under the CF irrigation method (flooded condition), the predominant As species of arsenite is less retained by soil colloids. Moreover, the reductive dissolution of Fe-oxides could further mobilize the arsenic into the environment. These results suggest that iron plaque formation can benefit from the CF irrigation method which in turn enhances the accumulation of chemical species As^{5+} and As^{3+}.

In a previous study, Liu et al. demonstrated a significant correlation between the concentrations of As in iron plaques and the concentration of iron plaques forming naturally in the soil.[27] Normally, a portion of rhizospheric arsenite can be oxidized to arsenate, co-precipitated with Fe^{3+},

and finally absorbed on to the plaque owing to the strong affinity between iron plaques and arsenate. [19] The siderophores or phyto-siderophores induced by rhizospheric microbes or rice roots at the root-plaque interface may also form a complex with Fe^{3+} and mobilize Fe-bound arsenate which can be driven by the phosphate co-transporters. As a result, Fe and arsenate are simultaneously taken up by plant in this case. Additionally, arsenite may accumulate on Fe plaques in the form of H_3AsO_3 and then be transported into rice roots via aquaporins.[28] This is an indication that the formation of iron plaques strongly depends on the environmental factor in the rhizosphere, particularly the oxidation condition and also that iron plaque formation is the critical controlling factor on the eventual accumulation of chemical species As^{5+} and As^{3+}.

Distribution and speciation of As in soil and rice tissue

Total As In general, the total As concentrations in RS were lower than that in NRS (Fig.S1). Much to be expected, the total As concentrations in rice tissues increased with the increasing concentration of As applied to the soil, both in shoot and root, with the highest As concentration (1.56 mg/kg for shoot and 9.58 mg/kg for root) observed in the treatment of As_{60}+CF. Similar to the distribution of soil As, the total As concentrations in rice tissues of treatments of Fenton solution were lower than that of treatments without Fenton solution. For total As concentration in rice grains, the highest As concentration was observed in the treatment of As_{60}+CF, with value of 0.95 mg/kg. However, the lowest As concentration in rice grains were observed in the treatments of As_{30}+F+IF, with a value of 0.32 mg/kg (Fig.S2).

Regarding the effect of the Fenton solution on the distribution of As chemical species in soil and rice tissue, the addition of the Fenton solution resulted in the lowest soil As concentrations both in RS and NRS. Also, the addition of the Fenton solution significantly reduced the As accumulation

in grains of As treatments, with the highest reduction of 57% observed in treatment of As_{30}+F+IF. Overall, the IF irrigation increased the As accumulation in grains in comparison with treatments of CF.

As speciation Concentrations of As^{5+}, As^{3+}, and DMA selected to evaluate the distribution of As speciation in soil and rice tissue are presented in Fig.3. In general, As^{5+} is the dominant speciation among the three As species, both in soil and rice tissues. The DMA concentration is much lower than As^{5+} and As^{3+} in all analyzed matrices with the exception of rice grains.

Specifically, the As^{5+} concentration ranged from 27.2 to 96.8 mg/kg in NRS and from 38 to 77.6 mg/kg in RS, respectively. As^{5+} concentration in RS was comparable with that in NRS in the absence of the Fenton solution. However, lower concentrations of As^{5+} were found in RS in comparison with those in NRS with the addition of the Fenton solution. Higher As^{3+} concentrations were observed in RS than in NRS of treatments with Fenton solution, while no constant trend was observed between RS and NRS of treatments without Fenton solution. For soil DMA, the addition of the Fenton solution reduces the DMA concentration in RS; adversely, a different trend was observed in NRS, with lower DMA concentration found in treatments in the absence of Fenton solution.

The highest concentration of As^{5+} in rice tissue was observed in the root, followed by the stem, leaf, and grain where the As^{5+} concentration ranged from 0.14 to 0.62 mg/kg. However, the highest As^{3+} concentrations in rice tissues were found in the root ranging from 0.23 to 28 mg/kg, while As^{3+} concentration in the stem, leaf, and grain were comparable. The highest DMA concentrations in rice tissue were also observed in the grain, ranging from 0.3 to 0.66 mg/kg. It is notable that the addition of the Fenton solution reduces the As^{5+}, As^{3+}, and DMA concentrations in all rice tissue, when

compared to the treatments without Fenton solution.

Numerous studies have demonstrated that plant roots are able to take up DMA, however, the uptake rates of DMA are lower than that of inorganic As species. The uptake rate of DMA is also reduced with increasing numbers of the methyl groups.[29-34] For example, previous research on the uptake of arsenate and DMA by 46 plant species in hydroponic experiments indicated that the mean root absorption factor for arsenate was 5 times higher than that for DMA. Increasing hydrophobicity may be a reason for the reduced uptake rate of methylated As species.[32] However, in the current study, the concentration of DMA in grain, which is comparable with As^{5+}, is higher than As^{3+} in grain. Although the DMA concentrations were lower than As^{3+} concentrations in soil and iron plaques, higher DMA concentrations were observed in grain in comparison with As^{3+} among the treatments. Such discrepancy could be attributed to two reasons: firstly, the genetic variation in the arsenic speciation in rice grain varied greatly among rice cultivars. For example, a previous study showed that the percentage of inorganic As and DMA in twenty rice cultivars ranged from 19% to 95% and 2% to 81%, respectively.[35] Another publication elucidated that the percentage of inorganic As varied from 40% to 70% and that of DMA ranged from 30% to 55% among six rice cultivars grown in pot experiments.[18] It is known that the main transport route of arsenite is *via* the phloem; while DMA is highly mobile during both xylem and phloem transport in rice. As such, the translocation efficiency of DMA within rice tissue may be potentially higher than As^{5+} and As^{3+}. Secondly, the origin of DMA in rice grains is also of concern, since DMA represents a substantial proportion of the total As in rice grains. It is well accepted that inorganic As taken up by plant was dominated by the As^{3+} and As^{5+} forms. The uptake mechanism for As^{5+} is mostly via the high-affinity phosphate transporters and the amount can be influenced to some extent by

phosphate concentration in soil.[36] While As^{3+} in most likely taken up via glycerol transporters, which are not related to the amount of phosphate present.[37] The uptake mechanisms for DMA which is dominantly driven either by the root system or by the shoot system is still unknown; however, it is known that inorganic As species are taken up *via* both root and shoot.[38] Contradictory results were observed in previous publications.[16, 39, 40] Several publications indicated that, whether from field surveys or laboratory studies, the presence of methylated As in plants tissue usually represented only a small fraction of the total As in plant tissue.[32, 41-43] In the present study, the proportion of DMA in soil ranged from 0.1% to 12%, while those in grain from 37% to 61%. The higher proportion of DMA in grain can potentially be attributed to the methylation of As within rice tissue. However, it was reported methylated As in plant tissues could be originated from soil microorganisms.[11] limited information is available on the potential for As methylation in rice, with only one publication reporting inconclusive results that rice grown in nonsterile solution can reduce the trimethylarsine oxide to volatile trimethylarsine.[29] Additionally, methylated As species were not observed in the tissue of rice, tomato, and clover grown on axenic cultures with additions of either arsenate or arsenite.[11] The authors conclude that methylated As species in plants grown in soil or other nonsterile media could not have occurred within plant tissue. Other sources for methylated As are more likely, for example, methylated As can also originate from the use of methylated As compound residues and the methylation products of microbes.[3] Taken together, the possibility for rice to convert inorganic As into organic forms during their uptake and translocation is still unknown.

Environmental influences* on *As speciation in soil and As accumulation in grains

Irrigation methods and pH The effect of environmental parameters on As speciation in rice grains have been investigated by laboratory studies using different environmental conditions or soils but the same rice genotype.[44, 45] Overall, As bioavailability and As accumulation in rice grains can be increased by maintaining anaerobic soil conditions during the period of rice growth, which can also influence the distribution of As speciation in grain.[31, 44] Our findings corresponded well with these results. Furthermore, as shown in Table 1, the addition of the Fenton solution significantly lowers the soil pH when compared to treatments without the Fenton solution. The positive correlation between soil pH and soil As^{5+} and As^{3+} ($p < 0.05$) indicates that soil pH might influence the distribution of As in soil. This finding is supported by a previous study that reported that As speciation in soil is relevant to soil pH and higher As^{3+} was observed in higher pH soils.[46] The cycle of flooded and non-flooded periods associated with rice paddy cultivation significantly affects the soil pH and Eh which in turn influences the soil As speciation.[12] Subsequently, the redox change accompanied by paddy soil has a significant impact on the behavior of As in water, soil, and plant, as the mobility of As is redox-sensitive. For instance, more arsenite is mobilized into the soil solution under anaerobic conditions, thus increasing the availability of the substrate for methylation. Hence, the distribution of As speciation in soil is influenced by many factors.

Addition of Fenton solution Fig.4 shows that the total As accumulation in grains increases with the total As in soils while similar trends were observed between total As in grains and total As^{5+}, As^{3+}, and DMA in soil. More importantly, the increasing rates of total As, As^{5+}, and As^{3+} in treatments without Fenton solution were higher than those observed in treatments with Fenton solution. Translocation factor (TF) calculated by the As concentration in shoot (sum of stem, leaf, and grain) divided by the As concentration in root was also presented in Table S4 to illustrate the

effect of Fenton solution on As transportation within plant tissues. The TFs for treatments with Fenton solution were generally lower than those observed for treatments without Fenton solution. These results indicate that the addition of Fenton solution reduced As accumulation in rice grains. As mentioned previously, the enhanced iron plaque formation by the addition of Fenton solution mainly controlled the As speciation in soil and their translocation within the soil-plant system. Besides, it was reported that the uptake of As from root to shoot and sequestration depends on the transporters involved in As uptake, which are mediated by the constitutive expression of genes encoding various transporters.[47] Previous study also indicated that H_2O_2 probably induced the constitutive expression of genes that encode various transporters.[48] Hence, the inhibition of As uptake in rice grain currently was potentially related to the effects on As transporters and protected rice plant from As-induced oxidative stress damage on growth and photosynthesis which has been validated previously.[48] These results suggest that rice cultivation would benefit from the addition of Fenton solution to reduce concentration of As in grains. Previous studies have demonstrated that the ingredients for triggering Fenton reaction may be naturally present during rainfall events since H_2O_2 is a common constituent of rainwater.[23, 49] Therefore the application of H_2O_2 can, to some extent, represent real paddy soil conditions and application of H_2O_2 might be a reliable tool in regulating As accumulation in rice tissue, especially in rice grain.

Conclusion

Chronic arsenic poisoning is a major threat to large sections of the global population, and rice consumption, as a major food staple, is one of the biggest contributors to human arsenic exposure. In this study, we demonstrate that the application of a Fenton solution can reduce As accumulation

in rice grains. The Fenton solution enhances iron plaque formation in soils, and due to the strong affinity of As with these plaques, it thus reduces the As available to rice roots by sequestering the As. Our findings imply that Fenton reaction is a potential satisfactory tool to reduce the As uptake and translocation within rice tissue. Further study on the effect of Fenton reaction on the As speciation in different soil types is needed. The study provides elementary data regarding the distribution of As speciation within soil-rice system and will therefore potentially improve the ecological risk assessment of As.

Acknowledgement

This study was supported by the National Key Research and Development Program of China (2020YFC1807805, 2017YFD0800903), and the National Natural Science Foundation of China (31770479, 41271469).

Appendix Supporting information

The physicochemical properties of test soil are included in Table S1. The total As concentrations in soil and rice tissue are presented in Figure S1. As speciation in rice grains are presented in Figure S2. The translocation factor for As^{5+} and As^{3+} are presented in Table S4.

References

[1] F.J. Zhao, J.L. Stroud, T. Eagling, S.J. Dunham, S.P. McGrath, P.R. Shewry, Accumulation, Distribution, and Speciation of Arsenic in Wheat Grain, Environ. Sci. Technol., 44 (2010) 5464-5468.

[2] F.J. Zhao, S.P. McGrath, A.A. Meharg, Arsenic as a Food Chain Contaminant: Mechanisms of Plant Uptake and Metabolism and Mitigation Strategies, in: S. Merchant, W.R. Briggs, D. Ort (Eds.) Annual Review of Plant Biology, Vol 61, 2010, pp. 535-559.

[3] P.B. Tchounwou, J.A. Centeno, A.K. Patlolla, Arsenic toxicity, mutagenesis, and carcinogenesis a health risk assessment and management approach, Mol. Cell. Biochem., 255 (2004) 47-55.

[4] M. Styblo, L.M. Del Razo, L. Vega, D.R. Germolec, E.L. LeCluyse, G.A. Hamilton, W. Reed, C. Wang, W.R. Cullen, D.J. Thomas, Comparative toxicity of trivalent and pentavalent inorganic and methylated arsenicals in rat and human cells, Arch. Toxicol., 74 (2000) 289-299.

[5] D.J. Thomas, M. Styblo, S. Lin, The cellular metabolism and systemic toxicity of arsenic, Toxicol. Appl. Pharmacol., 176 (2001) 127-144.

[6] M.A. Khan, J.L. Stroud, Y.G. Zhu, S.P. McGrath, F.J. Zhao, Arsenic Bioavailability to Rice Is Elevated in Bangladeshi Paddy Soils, Environ. Sci. Technol., 44 (2010) 8515-8521.

[7] J.-t. Qiao, X.-m. Li, M. Hu, F.-b. Li, L.Y. Young, W.-m. Sun, W. Huang, J.-h. Cui, Transcriptional Activity of Arsenic-Reducing Bacteria and Genes Regulated by Lactate and Biochar during Arsenic Transformation in Flooded Paddy Soil, Environmental Science & Technology, 52 (2018) 61-70.

[8] J.-t. Qiao, T.-x. Liu, X.-q. Wang, F.-b. Li, Y.-h. Lv, J.-h. Cui, X.-d. Zeng, Y.-z. Yuan, C.-p. Liu, Simultaneous alleviation of cadmium and arsenic accumulation in rice by applying zero-valent iron and biochar to contaminated paddy soils, Chemosphere, 195 (2018) 260-271.

[9] Z. Wu, H. Ren, S.P. McGrath, P. Wu, F.-J. Zhao, Investigating the contribution of the phosphate transport pathway to arsenic accumulation in rice, Plant Physiol., 157 (2011) 498-508.

[10] Y. Takahashi, R. Minamikawa, K.H. Hattori, K. Kurishima, N. Kihou, K. Yuita, Arsenic behavior in paddy fields during the cycle of flooded and non-flooded periods, Environ. Sci. Technol., 38 (2004) 1038-1044.

[11] C. Lomax, W.J. Liu, L.Y. Wu, K. Xue, J.B. Xiong, J.Z. Zhou, S.P. McGrath, A.A. Meharg, A.J. Miller, F.J. Zhao, Methylated arsenic species in plants originate from soil microorganisms, New Phytol., 193 (2012) 665-672.

[12] T. Hori, A. Müller, Y. Igarashi, R. Conrad, M.W. Friedrich, Identification of iron-reducing microorganisms in anoxic rice paddy soil by 13C-acetate probing, The ISME journal, 4 (2010) 267.

[13] W.J. Liu, Y.G. Zhu, F.A. Smith, S.E. Smith, Do iron plaque and genotypes affect arsenate uptake and translocation by rice seedlings (Oryza sativa L.) grown in solution culture?, J. Exp. Bot., 55 (2004) 1707-1713.

[14] M.J. Abedin, J. Feldmann, A.A. Meharg, Uptake kinetics of arsenic species in rice plants, Plant Physiol., 128 (2002) 1120-1128.

[15] A.A. Meharg, P.N. Williams, E. Adomako, Y.Y. Lawgali, C. Deacon, A. Villada, R.C. Cambell, G. Sun, Y.-G. Zhu, J. Feldmann, Geographical variation in total and inorganic arsenic content of polished (white) rice, Environ. Sci. Technol., 43 (2009) 1612-1617.

[16] Y.J. Zavala, R. Gerads, H. Gürleyük, J.M. Duxbury, Arsenic in rice: II. Arsenic speciation in USA grain and implications for human health, Environ. Sci. Technol., 42 (2008) 3861-3866.

[17] A.A. Carbonell-Barrachina, X.C. Wu, A. Ramirez-Gandolfo, G.J. Norton, F. Burlo, C. Deacon, A.A. Meharg, Inorganic arsenic contents in rice-based infant foods from Spain, UK, China and USA, Environ.

Pollut., 163 (2012) 77-83.
[18] W. Liu, Y. Zhu, Y. Hu, P. Williams, A. Gault, A. Meharg, J. Charnock, F. Smith, Arsenic sequestration in iron plaque, its accumulation and speciation in mature rice plants (Oryza sativa L.), Environ. Sci. Technol., 40 (2006) 5730-5736.
[19] M. Otte, I. Dekkers, J. Rozema, R. Broekman, Uptake of arsenic by Aster tripolium in relation to rhizosphere oxidation, Can. J. Bot., 69 (1991) 2670-2677.
[20] M. Becker, F. Asch, Iron toxicity in rice-conditions and management concepts, J. Plant Nutr. Soil Sci., 168 (2005) 558-573.
[21] J.H. Qin, H.S. Li, C.X. Lin, G. Chen, Can rainwater induce Fenton-driven degradation of herbicides in natural waters?, Chemosphere, 92 (2013) 1048-1052.
[22] J. Qin, C. Lin, Effects of micro-molar H2O2 on inhibiting soil nitrification, Geoderma, 333 (2019) 145-148.
[23] J.D. Willey, R.J. Kieber, R.D. Lancaster, Coastal rainwater hydrogen peroxide: Concentration and deposition, J. Atmos. Chem., 25 (1996) 149-165.
[24] X. Lin, L. He, R. Zhang, X. Guo, H. Li, Rainwater in Guangzhou, China: Oxidizing properties and physicochemical characteristics, Atmos. Pollut. Res., 10 (2019) 303-312.
[25] P.-y. Xue, C.-z. Yan, Arsenic accumulation and translocation in the submerged macrophyte Hydrilla verticillata (L.f.) Royle, Chemosphere, 85 (2011) 1176-1181.
[26] Z. Chen, Y.G. Zhu, W.J. Liu, A.A. Meharg, Direct evidence showing the effect of root surface iron plaque on arsenite and arsenate uptake into rice (Oryza sativa) roots, New Phytol., 165 (2005) 91-97.
[27] W.-J. Liu, Y.-G. Zhu, F. Smith, Effects of iron and manganese plaques on arsenic uptake by rice seedlings (Oryza sativa L.) grown in solution culture supplied with arsenate and arsenite, Plant Soil, 277 (2005) 127-138.
[28] A.A. Meharg, L. Jardine, Arsenite transport into paddy rice (Oryza sativa) roots, New Phytol., 157 (2003) 39-44.
[29] Y. Jia, H. Huang, G.X. Sun, F.J. Zhao, Y.G. Zhu, Pathways and Relative Contributions to Arsenic Volatilization from Rice Plants and Paddy Soil, Environ. Sci. Technol., 46 (2012) 8090-8096.
[30] R.Y. Li, J.L. Stroud, J.F. Ma, S.P. McGrath, F.J. Zhao, Mitigation of Arsenic Accumulation in Rice with Water Management and Silicon Fertilization, Environ. Sci. Technol., 43 (2009) 3778-3783.
[31] W.R. Cullen, D.I. Hettipathirana, The effect of arsenic on alkaloid producation by cell-suspension cultures of catharanthus-roses, Appl. Organomet. Chem., 7 (1993) 477-486.
[32] A. Raab, P.N. Williams, A. Meharg, J. Feldmann, Uptake and translocation of inorganic and methylated arsenic species by plants, Environ. Chem., 4 (2007) 197-203.
[33] A.A. Carbonell-Barrachina, M.A. Aarabi, R.D. DeLaune, R.P. Gambrell, W.H. Patrick, The influence of arsenic chemical form and concentration on Spartina patens and Spartina alterniflora growth and tissue arsenic concentration, Plant Soil, 198 (1998) 33-43.
[34] F. Burlo, I. Guijarro, A.A. Carbonell-Barrachina, D. Valero, F. Martinez-Sanchez, Arsenic species: Effects on and accumulation by tomato plants, J. Agric. Food Chem., 47 (1999) 1247-1253.
[35] C. Wu, Z.H. Ye, W.S. Shu, Y.G. Zhu, M.H. Wong, Arsenic accumulation and speciation in rice are affected by root aeration and variation of genotypes, J. Exp. Bot., 62 (2011) 2889-2898.
[36] I.J. Pickering, R.C. Prince, M.J. George, R.D. Smith, G.N. George, D.E. Salt, Reduction and coordination of arsenic in Indian mustard, Plant Physiol., 122 (2000) 1171-1177.
[37] Z.J. Liu, J.M. Carbrey, P. Agre, B.P. Rosen, Arsenic trioxide uptake by human and rat aquaglyceroporins, Biochem. Biophys. Res. Commun., 316 (2004) 1178-1185.

[38] A.A. Abdelghani, A.C. Anderson, J.W. Mason, Screening study for the uptake of monosodium methanearsonate in the blackberry following dosing at 4 apllication rates, Bull. Environ. Contam. Toxicol., 23 (1979) 797-799.
[39] J.H. Wu, R. Zhang, R.M. Lilley, Methylation of arsenic in vitro by cell extracts from bentgrass (Agrostis tenuis): effect of acute exposure of plants to arsenate, Funct. Plant Biol., 29 (2002) 73-80.
[40] P. Nissen, A.A. Benson, Arsenic metabolism in fresh-water and terrestrial plants, Physiol. Plant., 54 (1982) 446-450.
[41] A.A. Meharg, J. Hartley‐Whitaker, Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species, New Phytologist, 154 (2002) 29-43.
[42] I. Koch, L.X. Wang, C.A. Ollson, W.R. Cullen, K.J. Reimer, The predominance of inorganic arsenic species in plants from Yellowknife, Northwest Territories, Canada, Environ. Sci. Technol., 34 (2000) 22-26.
[43] R. Zhao, M.X. Zhao, H. Wang, Y. Taneike, X.R. Zhang, Arsenic speciation in moso bamboo shoot - A terrestrial plant that contains organoarsenic species, Sci. Total Environ., 371 (2006) 293-303.
[44] X.Y. Xu, S.P. McGrath, A.A. Meharg, F.J. Zhao, Growing rice aerobically markedly decreases arsenic accumulation, Environ. Sci. Technol., 42 (2008) 5574-5579.
[45] T. Arao, A. Kawasaki, K. Baba, S. Mori, S. Matsumoto, Effects of Water Management on Cadmium and Arsenic Accumulation and Dimethylarsinic Acid Concentrations in Japanese Rice, Environ. Sci. Technol., 43 (2009) 9361-9367.
[46] N. Yamaguchi, T. Nakamura, D. Dong, Y. Takahashi, S. Amachi, T. Makino, Arsenic release from flooded paddy soils is influenced by speciation, Eh, pH, and iron dissolution, Chemosphere, 83 (2011) 925-932.
[47] M. Hasanuzzaman, K. Nahar, K.R. Hakeem, M. Öztürk, M. Fujita, Chapter 16 - Arsenic Toxicity in Plants and Possible Remediation, in: K.R. Hakeem, M. Sabir, M. Öztürk, A.R. Mermut (Eds.) Soil Remediation and Plants, Academic Press, San Diego, 2015, pp. 433-501.
[48] M. Asgher, S. Ahmed, Z. Sehar, H. Gautam, S.G. Gandhi, N.A. Khan, Hydrogen peroxide modulates activity and expression of antioxidant enzymes and protects photosynthetic activity from arsenic damage in rice (Oryza sativa L.), Journal of Hazardous Materials, 401 (2021) 123365.
[49] C. Gonçalves, M.A.d. Santos, A. Fornaro, J.J. Pedrotti, Hydrogen peroxide in the rainwater of Sao Paulo megacity: measurements and controlling factors, J. Braz. Chem. Soc., 21 (2010) 331-339.

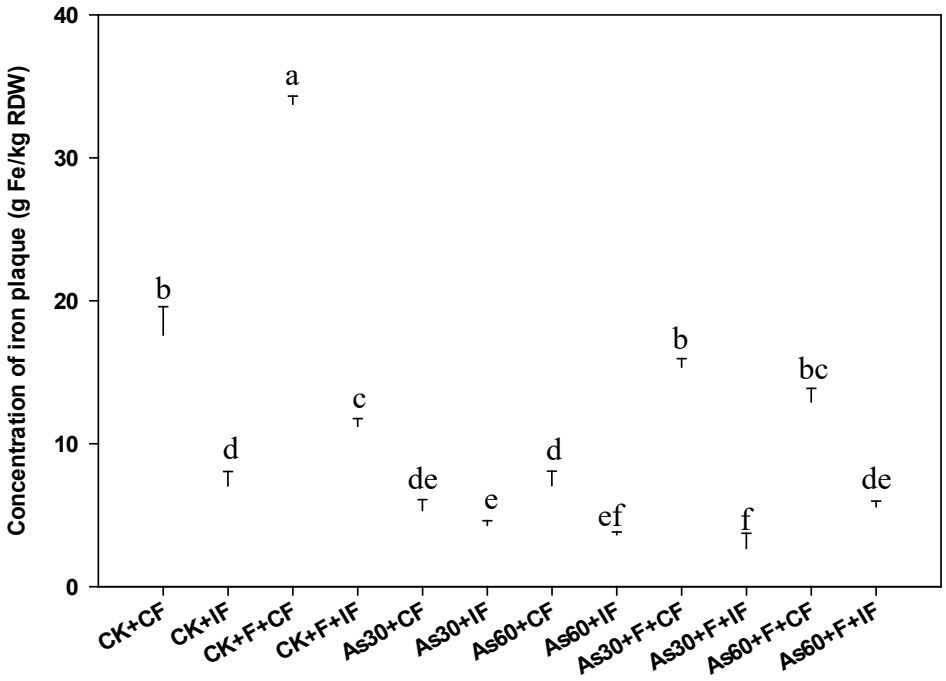


Figure 1. Averaged concentrations of iron plaques (g Fe/kg RDW). The total As concentrations for CK, As_{30}, and As_{60} are 0, 30, 60 mg/kg, respectively. CF and IF represent flooded and wet-dry alternation irrigation methods, respectively. F represents the Fenton solution (100 μM H_2O_2 and 100 μM $FeSO_4$). Concentrations sharing the same letter are not significantly different at a $p < 0.05$ level. The whiskers above each bar represent the standard error of three duplicates of each treatment.

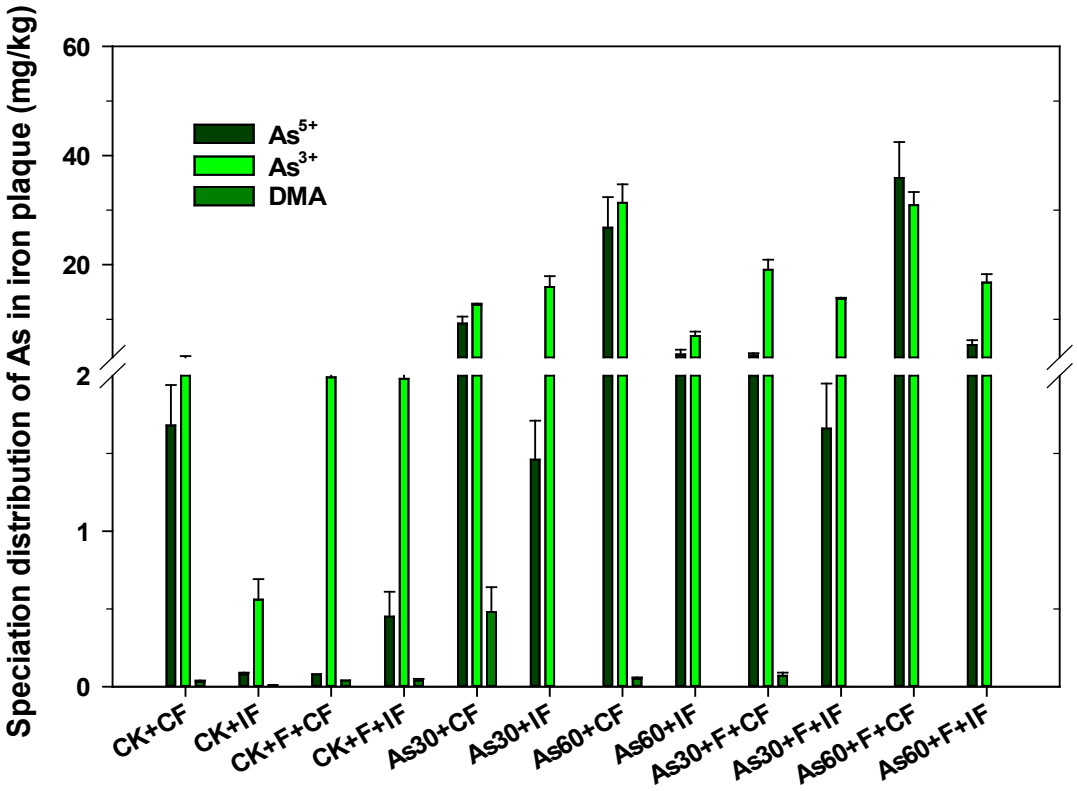
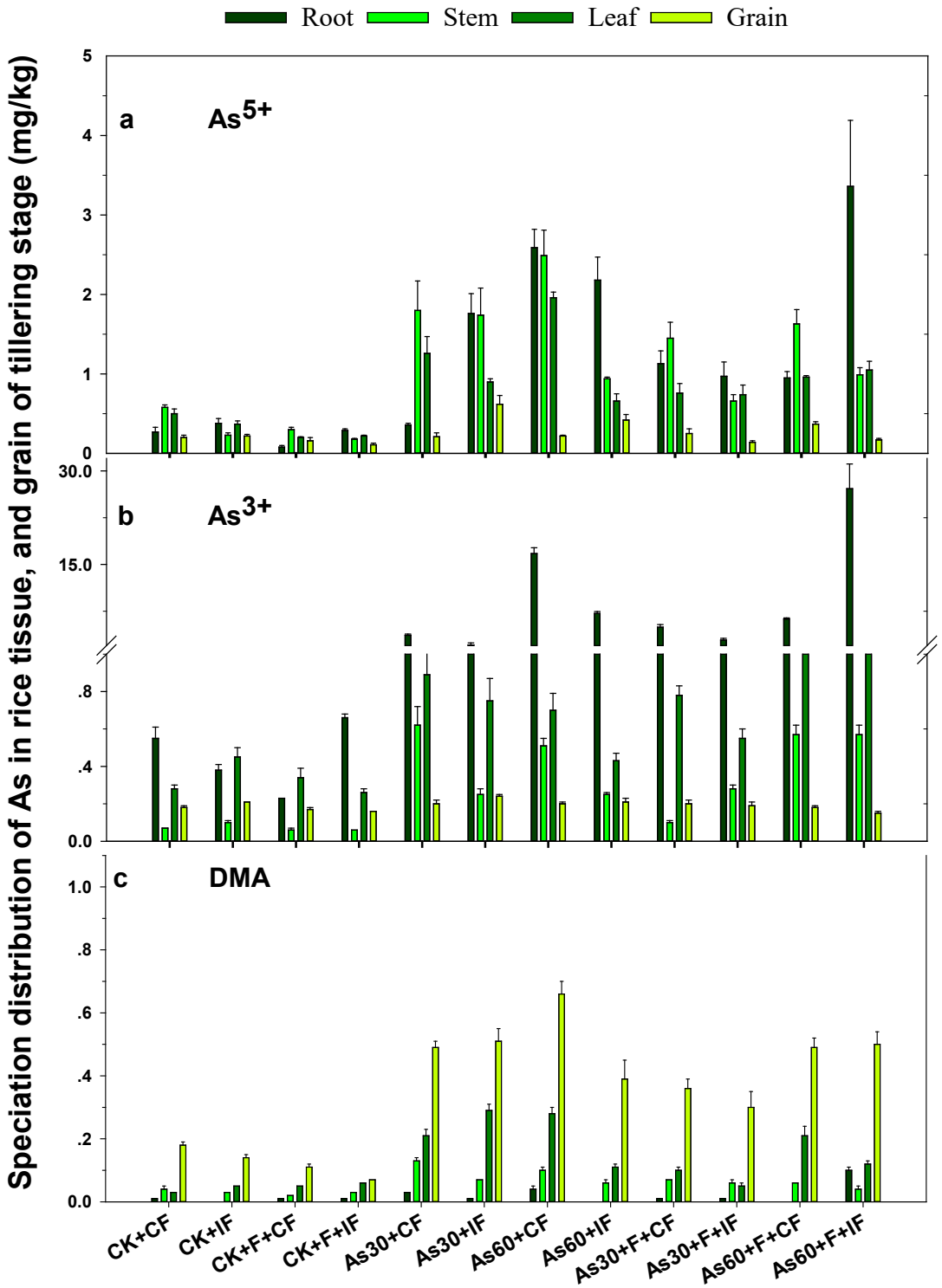
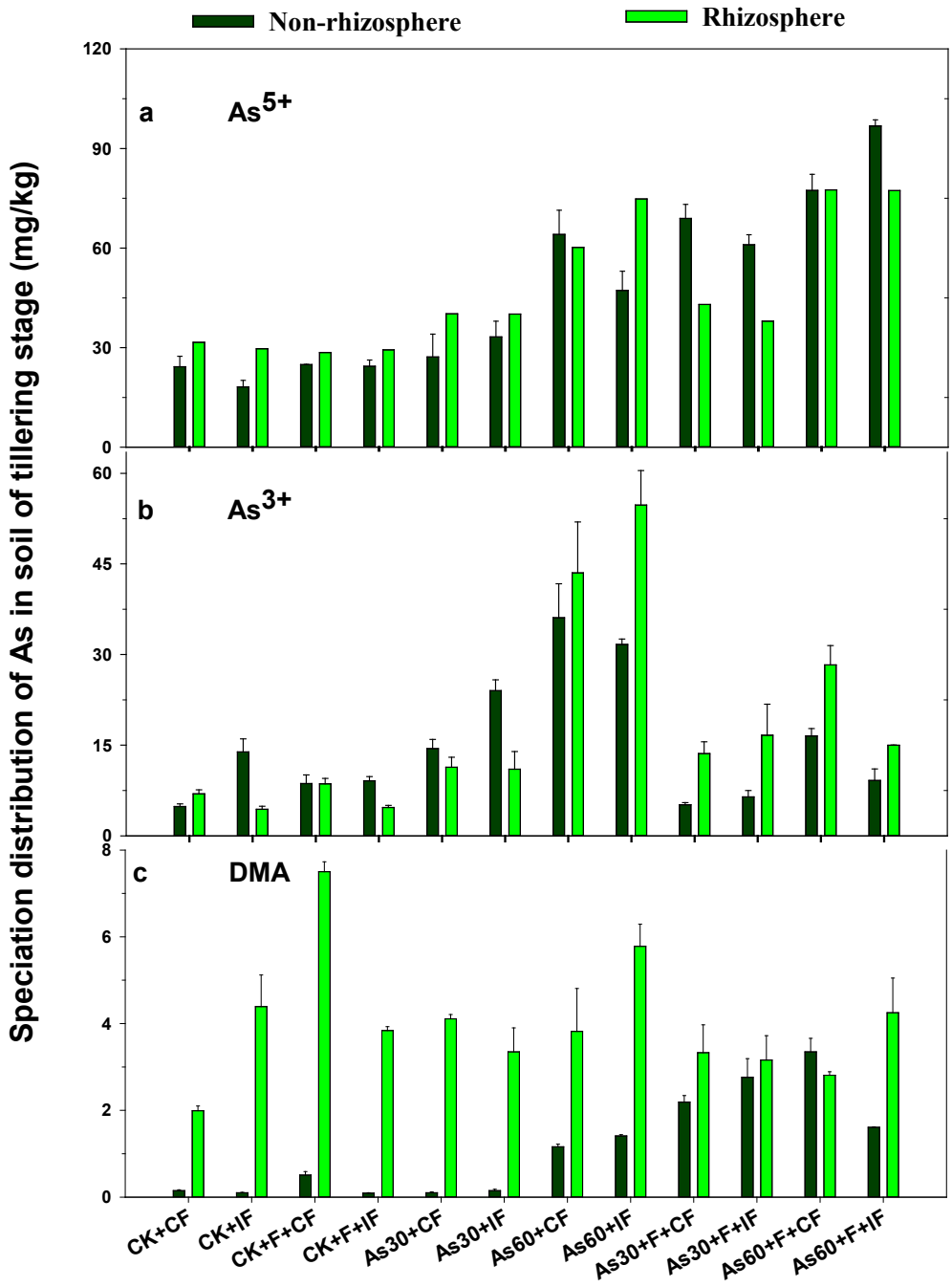


Figure 2. Concentrations of As speciation, including As^{5+}, As^{3+}, and dimethylarsinic acid (DMA), in iron plaques (mg/kg, averaged concentration ± standard error). The total As concentration for CK, As_{30}, and As_{60} is 0, 30, 60 mg/kg, respectively. CF and IF were represent the flooded and wet-dry alternation irrigation methods, respectively. F represents the Fenton solution (100 μM H_2O_2 and 100 μM $FeSO_4$). The whiskers above each bar represent the standard error of three duplicates of each treatment.


Root
Stem
Leaf
Grain
Speciation distribution of As in rice tissue, and grain of tillering stage (mg/kg)
a
As5+
b
As3+
c
DMA
CK+CF
CK+IF
CK+F+CF
CK+F+IF
As30+CF
As30+IF
As60+CF
As60+IF
As30+F+CF
As30+F+IF
As60+F+CF
As60+F+IF

458



459

460 **Figure 3.** Distribution of As chemical species, including As^{5+} (a), As^{3+} (b), and dimethylarsinic acid
461 (DMA, c) in rhizosphere soil, non-rhizosphere soil, and rice tissues (mg/kg, averaged concentration
462 ± standard error). The total As concentrations for CK, As_{30}, and As_{60} are 0, 30, 60 mg/kg,
463 respectively. CF and IF represent flooded and wet-dry alternation irrigation methods, respectively.
464 F represents the Fenton solution (100 μM H_2O_2 and 100 μM $FeSO_4$). The whiskers above each bar
465 represent the standard error of three duplicates of each treatment.

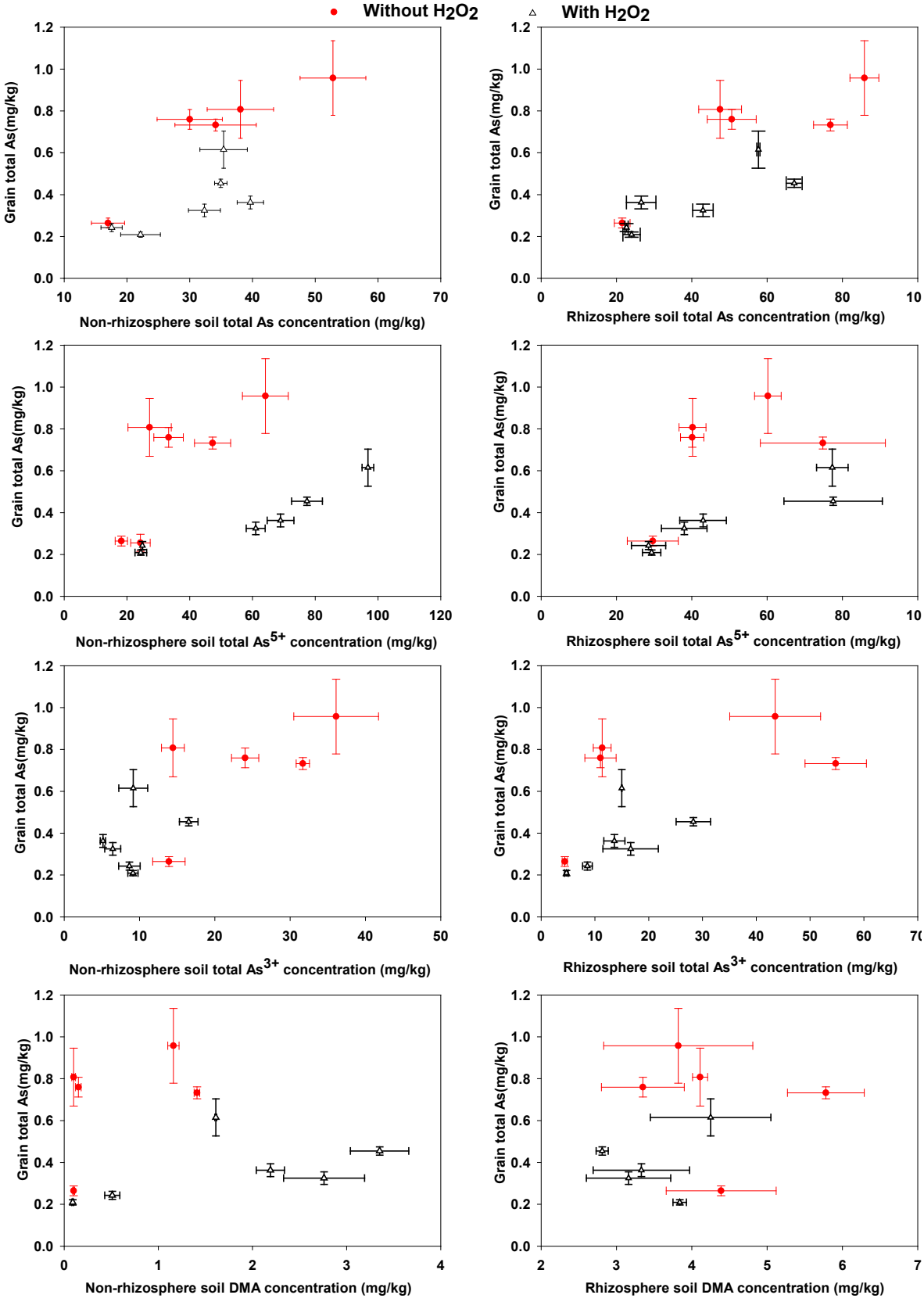


Figure 4. Effect of Fenton solution on the distribution of As chemical species in soil and rice grains. The vertical and horizontal lines represent the standard error of three duplicates of each treatment.

Table 1. Soil pH of different treatments. The total As concentrations for CK, As_{30}, and As_{60} are 0, 30, 60 mg/kg, respectively. CF and IF represent flooded and wet-dry alternation irrigation methods, respectively. F represents the Fenton solution (100 μM H_2O_2 and 100 μM $FeSO_4$).

Treatments	rhizosphere soil	non-rhizosphere soil
CK+CF	5.76±0.28a	5.92±0.04ab
CK+IF	5.33±0.05b	5.71±0.06bd
CK+F+CF	5.21±0.06bc	5.79±0.02bc
CK+F+IF	5.24±0.02bc	6.09±0.04a
As_{30}+CF	5.26±0.02bc	5.73±0.06be
As_{30}+IF	5.37±0.01b	5.72±0.12be
As_{60}+CF	5.18±0.15bcd	5.56±0.16dcef
As_{60}+IF	5.12±0.0bcd	5.40±0.11f
As_{30}+F+CF	5.01±0.15d	5.44±0.09def
As_{30}+F+IF	5.26±0.02bcd	5.48±0.03def
As_{60}+F+CF	5.15±0.08bcd	5.44±0.17def
As_{60}+F+IF	5.05±0.06cd	5.40±0.14f