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REVIEW

Strategies to manage the risk of heavy metal(loid) contamination in agricultural soils

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Abstract Soil contamination with heavy metal(loid)s threatens soil ecological functions, water quality and food safety; the latter is the focus of this review. Cadmium (Cd) and arsenic (As) are the toxic elements of most concern for food safety because they are relatively easily taken up by food crops. Rice is a major contributor of both Cd and As intakes to the Chinese population. Contamination and soil acidification are the main causes of high Cd levels in rice grains produced in some areas of southern China. The risk of Cd and As accumulation in food crops can be mitigated through agronomic practices and crop breeding. Liming is effective and economical at reducing Cd uptake by rice in acid soils. Paddy water management can produce opposite effects on Cd and As accumulation. Many genes controlling Cd and As uptake and translocation have been characterized, paving the way to breeding low accumulating crop cultivars through marker-assisted molecular breeding or genetic engineering. It is important to protect agricultural soils from future contamination. Long-term monitoring of anthropogenic additions and accumulation of heavy metal(loid)s in agricultural soils should be undertaken. Mass-balance models should be constructed to evaluate future trends of metal(loid)s in agricultural soils at a regional scale.

Keywords arsenic, cadmium, food safety, heavy metals, soil contamination

1 Introduction

Over the last few years there has been increasing concern about heavy metal(loid) contamination in agricultural soils in China. A national survey conducted from 2005 to 2013 reports that 16% of the soil samples collected from 8 km × 8 km grids across the country exceeded the Chinese environmental quality standards for various contaminants, especially heavy metal(loid)s[1]. A much more comprehensive survey, focusing on agricultural soils in potentially contaminated areas, has been completed recently, although the results have not yet been published. As previously discussed[2], the definition of soil contamination is rather subjective because it is difficult to separate natural and anthropogenic sources of contaminants in soils. This is especially true for heavy metal(loid)s as their background levels vary between different soils depending on the parent materials and the pedogenesis processes. In some areas of south-western China, for example, elevated concentrations of cadmium (Cd) in soils are partly attributed to high geogenic background levels of this element[3]. In general, high iron content in soils is associated with high levels of siderophilic elements such as chromium (Cr), cobalt (Co) and nickel (Ni) from geogenic sources[4]. Heavy textured soils also tend to contain higher levels of metals such as Cd, Co, copper (Cu), Cr, Ni and zinc (Zn) than light soils, which are not related to anthropogenic contamination[4]. Considering the difficulties in quantifying geogenic versus anthropogenic sources of heavy metal(loid)s, it is perhaps more pertinent to focus on the assessment and mitigation of the risks of soil contamination and protection of soil against future contamination. Risks of soil contamination with metal(loid)s may arise from transfer of contaminants to the food chain affecting food safety, toxicity to soil microorganisms, fauna and plants causing adverse impacts on the ecological functions of the soil, or transfer of contaminants to surface or groundwaters (Table 1). Transfer of toxic metal(loid)s from soil to the food chain represents one of the most relevant risks of soil contamination which should be assessed and managed carefully to ensure food safety and protect public health.

2 Cadmium and arsenic are high risk metal(loid)s due to their transfer to the food chain

Not all contaminants are readily transferred from soils to the food chain. There are three barriers in the transfer of

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Table 1 Risks of heavy metal(loid) contamination in soils mitigation options

Metal(loid)s	Main risks	Mitigation options
As	• Accumulation in food crops (paddy rice) affecting food safety • High level of As in soil causing toxicity to paddy rice	• Paddy water management: alternate wetting and drying • Screening or breeding of low accumulation cultivars • Silicon fertilizers • Mn/Fe oxides
Cd	• Accumulation in food crops affecting food safety	• Liming (acid soils) • Delay draining paddy water during grain filling • Screening or breeding of low accumulation cultivars • Gene editing/genetic engineering (need approval) • Phytoremediaiton to remove Cd from soil (low-moderate contamination)
Co, Cu, Ni, Zn	• Toxicity to plants, soil microorganisms and soil fauna affecting soil ecological functions	• Liming (acid soils) • Increase soil organic matter
Cr(VI)	• Leaching to groundwater • Toxicity to plants	• Increase soil organic matter to promote microbial reduction of Cr(VI) to Cr(III)
Hg	• Accumulation of methylmercury by paddy rice	• Paddy water management: alternate wetting and drying
Pb	• Inhalation or ingestion of soil dust	• Liming (acid soils) • Addition of phosphate fertilizer to promote immobilization of Pb • Washing/peeling of vegetables to remove surface soil dust

toxic elements from soils to the edible parts of food crops, namely, the solubility barrier, the translocation barrier and the phytotoxicity barrier[5]. Some elements (e.g., Cr(III), mercury (Hg), and plumbum (Pb)) have very low solubility in soil so that they are mostly unavailable for plant uptake. Even when their solubility increases under some specific conditions, plant roots tend to sequester these elements and limit their translocation to the aboveground tissues. Some elements (e.g., Co, Cu, Ni, and Zn) have relatively high solubility in soils and can also be translocated to plant shoots relatively easily. However, excessive accumulation of these elements can cause toxicity to plants and reduce yields (Table 1), and this also makes them less likely to enter the food chain. Among the heavy metal(loid)s, Cd and arsenic (As) can bypass these three barriers relatively easily and are therefore at high risk of transfer from soil to the food chain[5,6]. Cd and As are of course also toxic to plants. However, unlike Cu, Ni and Zn, Cd and As can be toxic to animals and humans at levels that do not cause phytotoxicity, due to the effects from chronic exposure. For these reasons, Cd and As are the toxic elements of most concern for soil contamination and food safety. Rice grain from paddy fields contaminated by Hg mining may contain elevated levels of highly toxic methylmercury[7]. This is because some anaerobic microorganisms in paddy soils can methylate inorganic Hg under anoxic conditions and methylmercury has a greater transferability from soil to rice grain than inorganic Hg[8] (Table 1).

Rice appears to be particularly problematic with regard to both Cd and As accumulation[6]. This is because rice has a relatively high uptake of both elements[9,10] and is also a staple food. A recent total diet study shows that rice contributes 56% of the total dietary intake of Cd for the general population in China, and up to 65% for the population in southern China[11]. In comparison, wheat and vegetables each contribute 10% to 12% of the total Cd intake for the general population in China. Similarly, rice contributes about 60% of the dietary intake of inorganic As for the Chinese population[12]. Therefore, reducing Cd and As accumulation in rice is a top priority in the risk management of contaminated soils.

Recent surveys show considerable proportions of rice grain samples collected from some areas in southern China exceeding the maximum permissible limits of Cd and As[13–19]. In some areas the range and mean values of Cd concentration in rice grain are comparable to those reported for the Itai-Itai disease-affected area in Japan[19,20]. The maximum permissible limit of Cd in rice grain in China is half of the that recommended by FAO/WHO (0.2 versus 0.4 $\mathrm{mg \cdot kg^{-1}}$). This strict limit is deemed necessary because of the high consumption rate of rice by the Chinese population[6]. For example, consumption of 250 g rice per day at a Cd concentration of 0.2 $\mathrm{mg \cdot kg^{-1}}$ would give rise to a Cd intake of 0.83 μg Cd $\mathrm{kg^{-1}}$ bodyweight $\mathrm{d^{-1}}$ (for a person weighing 60 kg), which reaches the tolerable Cd intake limit recommended by FAO/WHO[6]. In some local populations in southern China, estimated average Cd intakes are well over the tolerable intake limit[14,19]. Urgent action is needed now to reduce dietary Cd intake in these populations.

3 Reducing the bioavailability of toxic metal(loid)s in soil

The transferability of toxic elements from soils to the food chain depends on their bioavailability in soils. Bioavailability is influenced by multiple soil and plant factors. One of the key factors affecting Cd bioavailability is soil pH. On average across a range of soils studied, Cd solubility increased 3.5 times when soil pH decreased by one unit[21].

A paired soil-plant survey shows that the median Cd transfer factor from soil to rice grain (i.e., the ratio of grain to soil Cd concentration) increased 10 times, from 0.08 to 0.85, when soil pH decreased from 7.0 to 5.0[13]. A survey of Cd concentration in rice grains collected from different provinces in China shows a clear geographical pattern, increasing markedly from the north to the south[22]. This pattern can be explained by the general trend of increasing soil acidity from the north to the south. Over the last three decades there has been widespread acidification in agricultural soils in many parts of China, caused primarily by the cumulative effects of nitrogen fertilizer applications[23]. Soil acidification is one of the important reasons why Cd concentrations in rice grains produced in some areas of southern China exceed the maximum permissible limit[13,14]. Liming with calcium carbonate to increase soil pH above 6.5 has been shown to be highly effective in decreasing grain Cd concentrations, with the effect lasting for at least three years[19,24]. Liming with calcium carbonate to pH 6.5 had no significant effects on grain yield or As concentrations in the grain[24]. Liming is the most economical method of reducing Cd transfer in acid soils (Table 1). Other materials may also be used to immobilize Cd and other heavy metals in soils if the cost-benefit analysis is favorable.

Arsenic is a metalloid with a relatively high transferability from paddy soils to rice. This is partly because As is mobilized under anaerobic conditions in submerged paddy soils. The most important factor affecting As bioavailability in paddy soils is the redox status[25]. Under submerged conditions in paddy soils, reductive dissolution of iron oxyhydroxides releases As sorbed by the minerals and arsenate is also reduced to the more mobile form of arsenite[26–28]. Growing rice under aerobic conditions can decrease grain As concentrations by more than 10-fold compared to standard flood-irrigated cultivation[29]. Water saving methods such alternate wetting and drying can be effective at reducing As accumulation in rice[30–32] (Table 1). Paddy water management can be an effective method to control As bioavailability, the effect on Cd being opposite to that on As[32,33]. Draining of paddy water during the grain filling period can lead to greatly increased Cd accumulation in rice grain if the soil is acidic[34]. Cd is maintained at low solubility under anaerobic conditions due to the precipitation of cadmium sulfide and increased pH[35]. Once a paddy soil is drained, sulfide is oxidized rapidly and soil pH also decreases, releasing insoluble Cd into the soil solution[36]. The contrasting biogeochemical behaviors of As and Cd mean that managing the risks of As and Cd in paddy soils simultaneously is a difficult task[6]. Applications of silicon fertilizers and materials rich in manganese oxides and iron oxides may mitigate both As and Cd[6] (Table 1). However, more field studies are needed to assess the efficacy of these materials. Unlike Cd, As availability in paddy soil is not sensitive to pH changes within the acidic to neutral range.

4 Breeding or engineering crop cultivars with low metal(loid) accumulation

There are large variations within crop germplasm in the ability to accumulate metal(loid)s[37–39]. Rice cultivars with stably low accumulation of Cd or As have been identified through large scale screening under field conditions[38]. These cultivars can be used in combination with other agronomic methods such as liming and water management to produce a greater effect on reducing the accumulation of metal(loid)s in the edible parts of crops (Table 1).

Large genetic variations also suggest the possibility of breeding crop cultivars with low accumulation of metal(loid)s in the edible parts. Many quantitative trait loci (QTLs) controlling Cd or As accumulation have been reported[2,39]. To date, genes underlying several QTLs for Cd accumulation in rice have been cloned[40–42]. *OsHMA3*, encoding a tonoplast Cd transporter, is a key gene controlling Cd translocation from roots to shoots and grain in rice; weak alleles of *OsHMA3* are associated with high accumulation of Cd in rice grain[40,43–45]. Strong alleles of *OsHMA3* can be used to breed low Cd rice cultivars. For example, by introgressing *qCd7* from the *japonica* cultivar Nipponbare containing a strong allele of *OsHMA3* to *indica* rice hybrids, grain Cd concentration was reduced by about 50%[46]. QTLs for low Cd and for high selenium (Se) or Zn in grain, beneficial to human nutrition, can be introduced into elite rice cultivars through QTL pyramiding and marker-assisted molecular breeding[47]. Allelic variation in *BrHMA3* also has an important role in Cd accumulation in the leaves of *Brassica rapa* vegetables; strong alleles of *BrHMA3* can be used to breed low Cd *Brassica* vegetables[48]. Breeding low As rice cultivars is more challenging because contributions of various As QTLs are small and none of them have been cloned yet. Studies using reverse genetics have shown a number of key genes controlling As uptake and translocation in rice, such as silicon transporters for arsenite uptake[49] and tonoplast transporters for vacuolar sequestration of arsenite-phytochelatin complexes[50]. However, it is not yet known if allelic variations in these genes within rice germplasm can cause variations in As accumulation in rice grain.

Genetic engineering techniques can also be used to reduce Cd and As accumulation in rice grain[6]. Knockout of *OsNRAMP5*, encoding a major influx transporter for both Mn and Cd[51], using CRISPR/Cas9 gene editing technology can decrease Cd accumulation in rice grain by more than 90%[52]. Overexpression of functional *OsHMA3* is also highly effective at reducing Cd accumulation in rice grain by more than 90%[40,53]. Overexpression of a rice aquaporin gene *OsNIP1;1* or of *OsABCC1* together with a bacterial γ-glutamylcysteine synthetase gene has also been shown to reduce As accumulation in rice grain significantly[54,55]. Although technologically feasible and highly effective, genetically engineered crops are not yet allowed in many countries.

5 Need for long-term monitoring and model predictions

While the risks of soil contamination can be managed to a certain extent, it is important to protect agricultural soils from contamination in the future. Anthropogenic additions of heavy metal(loid)s may lead to slow accumulation of these elements in soils. Gradual increases in the concentrations of metal(loid)s in soils are often difficult to detect over a relatively short period of time. Long-term monitoring of both anthropogenic additions and accumulation in soils is necessary. Long-term experiments at Rothamsted, UK, have shown that long-term applications of phosphate fertilizers resulted in significant increases in the concentrations of Cd and As in the soil[56–58]. It is well known that phosphate fertilizers may contain considerable amounts of Cd, although fortunately, rock phosphates in south-west China generally contain very low levels of Cd[2,59]. Imported phosphate fertilizers may have higher levels of Cd, which need to be monitored and regulated. It is a surprise that applications of phosphate fertilizers nearly doubled soil As concentration at the Rothamsted long-term experiment because phosphate fertilizers were not known to contain high levels of As[57]. However, analysis of archived samples shows very high concentrations of As in the phosphate fertilizers used in the experiment during the period from 1925 to 1947, suggesting historical As contamination[57]. In another example of long-term experiments in China, applications of pig manure for 16–17 years increased Cd concentrations in the soils more than 10-fold, most likely due to Cd contamination in the Zn minerals added to animal feeds[60]. In addition to fertilizers and manures, atmospheric deposition and irrigation water may also contribute considerably to the addition of metal(loid)s to soils and should be monitored[2,61]. Changes in the concentrations of metal(loid)s in soils also depends on the losses, such as plant uptake and removal, leaching and runoff. While plant uptake and removal are easily quantifiable, data on leaching and runoff of metal(loid)s and their relationships with soil properties and climatic variables are scarce. More studies are needed to establish and verify predictive models of leaching and runoff of metal(loid)s. Mass balance models can then be constructed to predict future trends of metal(loid)s in soils at a regional scale and under different scenarios[62,63]. A scenario that may lead to a gradual decrease in Cd concentrations in paddy soils is the removal of rice straw[62,63], although this practice would reduce the inputs of organic matter to the soil. In Europe, modeling of the future long-term changes in soil Cd concentrations in agricultural topsoils predicts either increases, decreases or little changes in soil Cd concentration over the next 100 years depending on the region and scenario[64,65]. The modeling outcomes have been used to guide European Union legislation on Cd limits in phosphate fertilizers. Compared with Europe, measurements in China have shown considerably larger additions of Cd and other metal(loid)s from atmospheric deposition and manure applications, but smaller additions from phosphate fertilizers[61,64–66]. Reducing the addition of Cd and other contaminants into agricultural soils is a top priority.

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References

1. Ministry of Ecology and Environment of the People's Republic of China (MEEC). The Ministry of Land and Resources. Report on the national soil contamination survey. Available at MEEC website on April 28, 2020
2. Zhao F J, Ma Y B, Zhu Y G, Tang Z, McGrath S P. Soil contamination in China: current status and mitigation strategies. *Environmental Science & Technology*, 2015, **49**(2): 750–759
3. Chinese Environmental Monitoring Station. Background concentrations of elements in Chinese soils. Beijing: *Chinese Environmental Science Publisher*, 1990 (in Chinese)
4. Zhao F J, McGrath S P, Merrington G. Estimates of ambient background concentrations of trace metals in soils for risk assessment. *Environmental Pollution*, 2007, **148**(1): 221–229
5. Chaney R L. Health risks associated with toxic metals in municipal sludge, In: Bitton G, ed. Sludge: health risks of land applications.. Ann Arbor, Michigan: *Ann Arbor Science Publisher*, 1980, 59–83
6. Zhao F J, Wang P. Arsenic and cadmium accumulation in rice and mitigation strategies. *Plant and Soil*, 2020, **446**(1–2): 1–21
7. Feng X B, Li P, Qiu G L, Wang S F, Li G H, Shang L H, Meng B, Jiang H M, Bai W Y, Li Z G, Fu X W. Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou Province, China. *Environmental Science & Technology*, 2008, **42**(1): 326–332
8. Zhang H, Feng X B, Larssen T, Shang L H, Li P. Bioaccumulation of methylmercury versus inorganic mercury in rice (*Oryza sativa* L.) grain. *Environmental Science & Technology*, 2010, **44**(12): 4499–4504
9. Sui F Q, Chang J D, Tang Z, Liu W J, Huang X Y, Zhao F J. Nramp5 expression and functionality likely explain higher cadmium uptake in rice than in wheat and maize. *Plant and Soil*, 2018, **433**(1–2): 377–389

10. Su Y H, McGrath S P, Zhao F J. Rice is more efficient in arsenite uptake and translocation than wheat and barley. *Plant and Soil*, 2010, **328**(1–2): 27–34
11. Song Y, Wang Y, Mao W F, Sui H X, Yong L, Yang D J, Jiang D G, Zhang L, Gong Y Y. Dietary cadmium exposure assessment among the Chinese population. *PLoS One*, 2017, **12**(5): e0177978
12. Li G, Sun G X, Williams P N, Nunes L, Zhu Y G. Inorganic arsenic in Chinese food and its cancer risk. *Environment International*, 2011, **37**(7): 1219–1225
13. Zhu H H, Chen C, Xu C, Zhu Q H, Huang D Y. Effects of soil acidification and liming on the phytoavailability of cadmium in paddy soils of central subtropical China. *Environmental Pollution*, 2016, **219**: 99–106
14. Chen H P, Yang X P, Wang P, Wang Z X, Li M, Zhao F J. Dietary cadmium intake from rice and vegetables and potential health risk: a case study in Xiangtan, southern China. *Science of the Total Environment*, 2018, **639**: 271–277
15. Du Y, Hu X F, Wu X H, Shu Y, Jiang Y, Yan X J. Affects of mining activities on Cd pollution to the paddy soils and rice grain in Hunan Province, Central South China. *Environmental Monitoring and Assessment*, 2013, **185**(12): 9843–9856
16. Zhu Y G, Sun G X, Lei M, Teng M, Liu Y X, Chen N C, Wang L H, Carey A M, Deacon C, Raab A, Meharg A A, Williams P N. High percentage inorganic arsenic content of mining impacted and nonimpacted Chinese rice. *Environmental Science & Technology*, 2008, **42**(13): 5008–5013
17. Williams P N, Lei M, Sun G X, Huang Q, Lu Y, Deacon C, Meharg A A, Zhu Y G. Occurrence and partitioning of cadmium, arsenic and lead in mine impacted paddy rice: Hunan, China. *Environmental Science & Technology*, 2009, **43**(3): 637–642
18. Wang M E, Chen W P, Peng C. Risk assessment of Cd polluted paddy soils in the industrial and township areas in Hunan, southern China. *Chemosphere*, 2016, **144**: 346–351
19. Wang P, Chen H P, Kopittke P M, Zhao F J. Cadmium contamination in agricultural soils of China and the impact on food safety. *Environmental Pollution*, 2019, **249**: 1038–1048
20. Nogawa K, Sakurai M, Ishizaki M, Kido T, Nakagawa H, Suwazono Y. Threshold limit values of the cadmium concentration in rice in the development of itai-itai disease using benchmark dose analysis. *Journal of Applied Toxicology*, 2017, **37**(8): 962–966
21. Smolders E, Mertens J. Chapter 10. Cadmium. In: Alloway B J, ed. Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability. Dordrecht: *Springer Science + Business Media,* 2013, 283–311
22. Chen H P, Tang Z, Wang P, Zhao F J. Geographical variations of cadmium and arsenic concentrations and arsenic speciation in Chinese rice. *Environmental Pollution*, 2018, **238**: 482–490
23. Guo J H, Liu X J, Zhang Y, Shen J L, Han W X, Zhang W F, Christie P, Goulding K W T, Vitousek P M, Zhang F S. Significant acidification in major Chinese croplands. *Science*, 2010, **327**(5968): 1008–1010
24. Chen H P, Zhang W W, Yang X P, Wang P, McGrath S P, Zhao F J. Effective methods to reduce cadmium accumulation in rice grain. *Chemosphere*, 2018, **207**: 699–707
25. Stroud J L, Khan M A, Norton G J, Islam M R, Dasgupta T, Zhu Y G, Price A H, Meharg A A, McGrath S P, Zhao F J. Assessing the labile arsenic pool in contaminated paddy soils by isotopic dilution techniques and simple extractions. *Environmental Science & Technology*, 2011, **45**(10): 4262–4269
26. Takahashi Y, Minamikawa R, Hattori K H, Kurishima K, Kihou N, Yuita K. Arsenic behavior in paddy fields during the cycle of flooded and non-flooded periods. *Environmental Science & Technology*, 2004, **38**(4): 1038–1044
27. Xu X W, Chen C, Wang P, Kretzschmar R, Zhao F J. Control of arsenic mobilization in paddy soils by manganese and iron oxides. *Environmental Pollution*, 2017, **231**(1): 37–47
28. Weber F A, Hofacker A F, Voegelin A, Kretzschmar R. Temperature dependence and coupling of iron and arsenic reduction and release during flooding of a contaminated soil. *Environmental Science & Technology*, 2010, **44**(1): 116–122
29. Xu X Y, McGrath S P, Meharg A A, Zhao F J. Growing rice aerobically markedly decreases arsenic accumulation. *Environmental Science & Technology*, 2008, **42**(15): 5574–5579
30. Linquist B A, Anders M M, Adviento-Borbe M A A, Chaney R L, Nalley L L, Da Rosa E F F, Van Kessel C. Reducing greenhouse gas emissions, water use, and grain arsenic levels in rice systems. *Global Change Biology*, 2015, **21**(1): 407–417
31. Li R Y, Stroud J L, Ma J F, McGrath S P, Zhao F J. Mitigation of arsenic accumulation in rice with water management and silicon fertilization. *Environmental Science & Technology*, 2009, **43**(10): 3778–3783
32. Arao T, Kawasaki A, Baba K, Mori S, Matsumoto S. Effects of water management on cadmium and arsenic accumulation and dimethylarsinic acid concentrations in Japanese rice. *Environmental Science & Technology*, 2009, **43**(24): 9361–9367
33. Hu P J, Li Z, Yuan C, Ouyang Y N, Zhou L Q, Huang J X, Huang Y J, Luo Y M, Christie P, Wu L H. Effect of water management on cadmium and arsenic accumulation by rice (*Oryza sativa* L.) with different metal accumulation capacities. *Journal of Soils and Sediments*, 2013, **13**(5): 916–924
34. Chen H P, Wang P, Gu Y, Kretzschmar R, Kopittke P M, Zhao F J. The within-field spatial variation in rice grain Cd concentration is determined by soil redox status and pH during grain filling. *Environmental Pollution*, 2020, **261**: 114151
35. de Livera J, McLaughlin M J, Hettiarachchi G M, Kirby J K, Beak D G. Cadmium solubility in paddy soils: effects of soil oxidation, metal sulfides and competitive ions. *Science of the Total Environment*, 2011, **409**(8): 1489–1497
36. Wang J, Wang P M, Gu Y, Kopittke P M, Zhao F J, Wang P. Iron-manganese (oxyhydro)oxides, rather than oxidation of sulfides, determine mobilization of Cd during soil drainage in paddy soil systems. *Environmental Science & Technology*, 2019, **53**(5): 2500–2508
37. Pinson S R M, Tarpley L, Yan W G, Yeater K, Lahner B, Yakubova E, Huang X Y, Zhang M, Guerinot M L, Salt D E. World-wide genetic diversity for mineral element concentrations in rice grain. *Crop Science*, 2015, **55**(1): 294–311
38. Duan G L, Shao G S, Tang Z, Chen H P, Wang B X, Tang Z, Yang Y P, Liu Y C, Zhao F J. Genotypic and environmental variations in grain cadmium and arsenic concentrations among a panel of high yielding rice cultivars. *Rice*, 2017, **10**(1): 9
39. Yang M, Lu K, Zhao F J, Xie W B, Ramakrishna P, Wang G Y, Du

Q Q, Liang L M, Sun C J, Zhao H, Zhang Z Y, Liu Z H, Tian J J, Huang X Y, Wang W S, Dong X H, Hu J T, Ming L C, Xing Y Z, Wang G W, Xiao J H, Salt D E, Lian X M. Genome-wide association studies reveal the genetic basis of ionomic variation in rice. *Plant Cell*, 2018, **30**(11): 2720–2740

40. Ueno D, Yamaji N, Kono I, Huang C F, Ando T, Yano M, Ma J F. Gene limiting cadmium accumulation in rice. *Proceedings of the National Academy of Sciences of the United States of America*, 2010, **107**(38): 16500–16505
41. Luo J S, Huang J, Zeng D L, Peng J S, Zhang G B, Ma H L, Guan Y, Yi H Y, Fu Y L, Han B, Lin H X, Qian Q, Gong J M. A defensin-like protein drives cadmium efflux and allocation in rice. *Nature Communications*, 2018, **9**(1): 645
42. Yan H L, Xu W X, Xie J Y, Gao Y W, Wu L L, Sun L, Feng L, Chen X, Zhang T, Dai C H, Li T, Lin X N, Zhang Z Y, Wang X Q, Li F M, Zhu X Y, Li J J, Li Z C, Chen C Y, Ma M, Zhang H L, He Z Y. Variation of a major facilitator superfamily gene contributes to differential cadmium accumulation between rice subspecies. *Nature Communications*, 2019, **10**(1): 2562
43. Yan J L, Wang P T, Wang P, Yang M, Lian X M, Tang Z, Huang C F, Salt D E, Zhao F J. A loss-of-function allele of *OsHMA3* associated with high cadmium accumulation in shoots and grain of Japonica rice cultivars. *Plant, Cell & Environment*, 2016, **39**(9): 1941–1954
44. Sui F Q, Zhao D K, Zhu H T, Gong Y F, Tang T, Huang X Y, Zhang G Q, Zhao F J. Map-based cloning of a new total loss-of-function allele of *OsHMA3* causes high cadmium accumulation in rice grain. *Journal of Experimental Botany*, 2019, **70**(10): 2857–2871
45. Sun C J, Yang M, Li Y, Tian J J, Zhang Y Y, Liang L M, Liu Z H, Chen K, Li Y T, Lv K, Lian X M. Comprehensive analysis of variation of cadmium accumulation in rice and detection of a new weak allele of *OsHMA3*. *Journal of Experimental Botany*, 2019, **70**(21): 6389–6400
46. Zhou J Q, Jiang Y R, Ming X Q, Wang J R, Tang W B, Sun L. Introgressing the allelic variation of a major locus in reducing the grain cadmium accumulation in indica rice hybrids. *Molecular Breeding*, 2019, **39**(6): 84
47. Liu C L, Ding S L, Zhang A P, Hong K, Jiang H Z, Yang S L, Ruan B P, Zhang B, Dong G J, Guo L B, Zeng D L, Qian Q, Gao Z Y. Development of nutritious rice with high zinc/selenium and low cadmium in grains through QTL pyramiding. *Journal of Integrative Plant Biology*, 2020, **62**(3): 349–359
48. Zhang L X, Wu J, Tang Z, Huang X Y, Wang X W, Salt D E, Zhao F J. Variation in the *BrHMA3* coding region controls natural variation in cadmium accumulation in *Brassica rapa* vegetables. *Journal of Experimental Botany*, 2019, **70**(20): 5865–5878
49. Ma J F, Yamaji N, Mitani N, Xu X Y, Su Y H, McGrath S P, Zhao F J. Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. *Proceedings of the National Academy of Sciences of the United States of America*, 2008, **105**(29): 9931–9935
50. Song W Y, Yamaki T, Yamaji N, Ko D, Jung K H, Fujii-Kashino M, An G, Martinoia E, Lee Y, Ma J F. A rice ABC transporter, *OsABCC1*, reduces arsenic accumulation in the grain. *Proceedings of the National Academy of Sciences of the United States of America*, 2014, **111**(44): 15699–15704
51. Sasaki A, Yamaji N, Yokosho K, Ma J F. Nramp5 is a major transporter responsible for manganese and cadmium uptake in rice. *Plant Cell*, 2012, **24**(5): 2155–2167
52. Tang L, Mao B G, Li Y K, Lv Q M, Zhang L P, Chen C Y, He H J, Wang W P, Zeng X F, Shao Y, Pan Y L, Hu Y Y, Peng Y, Fu X Q, Li H Q, Xia S T, Zhao B R. Knockout of *OsNramp5* using the CRISPR/Cas9 system produces low Cd-accumulating indica rice without compromising yield. *Scientific Reports*, 2017, **7**(1): 14438
53. Lu C N, Zhang L X, Tang Z, Huang X Y, Ma J F, Zhao F J. Producing cadmium-free Indica rice by overexpressing *OsHMA3*. *Environment International*, 2019, **126**: 619–626
54. Sun S K, Chen Y, Che J, Konishi N, Tang Z, Miller A J, Ma J F, Zhao F J. Decreasing arsenic accumulation in rice by overexpressing *OsNIP1;1* and *OsNIP3;3* through disrupting arsenite radial transport in roots. *New Phytologist*, 2018, **219**(2): 641–653
55. Deng F L, Yamaji N, Ma J F, Lee S K, Jeon J S, Martinoia E, Lee Y, Song W Y. Engineering rice with lower grain arsenic. *Plant Biotechnology Journal*, 2018, **16**(10): 1691–1699
56. Nicholson F A, Jones K C, Johnston A E. Effect of phosphate fertilizers and atmospheric deposition on long-term changes in the cadmium content of soils and crops. *Environmental Science & Technology*, 1994, **28**(12): 2170–2175
57. Hartley T N, Macdonald A J, McGrath S P, Zhao F J. Historical arsenic contamination of soil due to long-term phosphate fertiliser applications. *Environmental Pollution*, 2013, **180**: 259–264
58. Jones K C, Symon C J, Johnston A E. Retrospective analysis of an archived soil collection 2. Cadmium. *Science of the Total Environment*, 1987, **67**(1): 75–89
59. Verbeeck M, Salaets P, Smolders E. Trace element concentrations in mineral phosphate fertilizers used in Europe: a balanced survey. *Science of the Total Environment*, 2020, **712**: 136419
60. Wu L H, Tan C Y, Liu L, Zhu P, Peng C, Luo Y M, Christie P. Cadmium bioavailability in surface soils receiving long-term applications of inorganic fertilizers and pig manure. *Geoderma*, 2012, **173–174**: 224–230
61. Luo L, Ma Y B, Zhang S Z, Wei D P, Zhu Y G. An inventory of trace element inputs to agricultural soils in China. *Journal of Environmental Management*, 2009, **90**(8): 2524–2530
62. Peng C, Wang M E, Chen W P. Modelling cadmium contamination in paddy soils under long-term remediation measures: model development and stochastic simulations. *Environmental Pollution*, 2016, **216**: 146–155
63. Feng W L, Guo Z H, Peng C, Xiao X Y, Shi L, Han X Q, Ran H Z. Modelling mass balance of cadmium in paddy soils under long term control scenarios. *Environmental Science: Processes & Impacts*, 2018, **20**(8): 1158–1166
64. Six L, Smolders E. Future trends in soil cadmium concentration under current cadmium fluxes to European agricultural soils. *Science of the Total Environment*, 2014, **485–486**: 319–328
65. Sterckeman T, Gossiaux L, Guimont S, Sirguey C, Lin Z B. Cadmium mass balance in French soils under annual crops: scenarios for the next century. *Science of the Total Environment*, 2018, **639**: 1440–1452
66. Feng W L, Guo Z H, Peng C, Xiao X Y, Shi L, Zeng P, Ran H Z, Xue Q H. Atmospheric bulk deposition of heavy metal(loid)s in central south China: fluxes, influencing factors and implication for paddy soils. *Journal of Hazardous Materials*, 2019, **371**: 634–642