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Growing Rice Aerobically Markedly Decreases Arsenic Accumulation

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Arsenic (As) exposure from consumption of rice can be substantial, particularly for the population on a subsistence rice diet in South Asia. Paddy rice has a much enhanced As accumulation compared with other cereal crops, and practical measures are urgently needed to decrease As transfer from soil to grain. We investigated the dynamics of As speciation in the soil solution under both flooded and aerobic conditions and compared As accumulation in rice shoot and grain in a greenhouse experiment. Flooding of soil led to a rapid mobilization of As, mainly as arsenite, in the soil solution. Arsenic concentrations in the soil solution were 7−16 and 4−13 times higher under the flooded than under the aerobic conditions in the control without As addition and in the +As treatments (10 mg As kg^{-1} as arsenite or arsenate), respectively. Arsenate was the main As species in the aerobic soil. Arsenic accumulation in rice shoots and grain was markedly increased under flooded conditions; grain As concentrations were 10−15-fold higher in flooded than in aerobically grown rice. With increasing total As concentrations in grain, the proportion of inorganic As decreased, while that of dimethylarsinic acid (DMA) increased. The concentration of inorganic As was 2.6−2.9 fold higher in the grain from the flooded treatment than in that from the aerobic treatment. The results demonstrate that a greatly increased bioavailability of As under the flooded conditions is the main reason for an enhanced As accumulation by flooded rice, and growing rice aerobically can dramatically decrease the As transfer from soil to grain.

Introduction

More than 40 million people worldwide are at risk from drinking As-contaminated water (*1*). A large portion (>36 million) live in Bangladesh and West Bengal, India, where water from shallow tube-wells containing elevated levels of As has been used for drinking over the last two to three decades. Long-term exposure to As has caused serious health problems among the population in the affected areas (*2*). Furthermore, As-contaminated tube-well water is also widely used for irrigating crops during dry (boro) season rice production in Bangladesh and West Bengal (*3, 4*). It has been estimated that irrigation water from shallow aquifers adds more than 1000 t of As per year to the arable soils of Bangladesh (*3, 5*). This has resulted in an accumulation of As in soils and elevated uptake of As by crops (*3, 6–10*), thus further increasing exposure of the local population to As.

Recent studies have shown that human As intake from consumption of rice can be substantial, and in some cases exceeds that from drinking water (*9–12*). Arsenic is present in rice grain both as inorganic As (mainly arsenite) and dimethylarsinic acid (DMA), with inorganic As representing between 20% and 90% of the total As (*9, 11–13*). Inorganic As is generally considered to be more toxic than methylated As compounds (*13, 14*). It is also a class 1 carcinogen (*15*). In populations not suffering from elevated As in drinking water, exposure to inorganic As is dominated by the intake from the consumption of rice (*13, 16*). Polished rice grain typically contains 0.05−0.3 mg kg^{-1} total As (*12, 17, 18*). Rice produced from As-contaminated areas can have even higher concentrations; up to 1.8 mg kg^{-1} has been reported in some Bangladesh rice originating from As-contaminated soils (*6*). Because As intake from rice represents an important route of exposure, especially for people consuming a lot of rice in their diet, mitigation measures to reduce As accumulation in rice are urgently needed.

Compared with other cereals (wheat, barley, and maize), rice accumulates much higher levels of As in the shoots and grain (*3, 19*). For example, the As transfer factor, i.e., (shoot As)/(soil As), was found to be ~0.8 for rice compared with 0.1−0.2 for wheat and barley (*19*). This difference was thought to be due to the higher bioavailability of As in flooded soil in which paddy rice grows (*19*), although differences in root uptake and/or root to shoot translocation may also play a role. In the present study, we investigated the dynamics of As speciation under flooded and aerobic conditions and the effects of watering regimes on As uptake by rice. Furthermore, we evaluated the effect of environmental factors (As additions and watering regimes) on the speciation of As in rice grain, which is important for assessing the risk posed by As in rice.

Materials and Methods

Pot Experiment. Soil was collected from the plow layer (0−20 cm) of an arable field on the Rothamsted farm, Southeast England. The soil is a moderately well drained Aquic Paleudalf (USDA classification) with a silty clay loam, containing 26% clay, 53% silt, and 21% sand. Other soil properties are 2.03% organic C, 0.19% total N, pH 6.4, and total As concentration of 15.1 mg kg^{-1}. The soil total As is slightly elevated compared with background values of <10 mg kg^{-1} in uncontaminated soils (*20*), but within the range found in the paddy soils in Bangladesh and West Bengal, India, that have received irrigation with As-contaminated groundwater (*6–8*). The contents of amorphous Fe and Mn oxides (extracted with ammonium oxalate (*21*)) were 5.93 g Fe kg^{-1} and 1.08 g Mn kg^{-1}, respectively, and the concentration of As extracted by this extractant was 3.2 mg kg^{-1}. The soil was air-dried, sieved to <8 mm, and homogenized. One kg of soil was placed in a plastic pot. A factorial experimental design was used with two methods of watering (aerobic and flooded) and three As treatments: control, and +10 mg As kg^{-1} soil in the form of arsenate (Na_2HAsO_4, $7H_2O$) or arsenite ($NaAsO_2$). There were 4 replicates per treatment, randomly arranged on a bench inside a glasshouse (day/night temperatures 28/25 °C, light period 16 h per day with natural sunlight supplemented with sodium vapor lamps to maintain light intensity of >350 μmol m^{-2} s^{-1}). To grow rice aerobically, pots with holes at the bottom were placed on saucers, while for the flooded

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treatment pots without holes were used and a standing head of water was maintained in the pots. Arsenic and basal fertilizers (120 mg N kg^{-1} soil as $NH_4NO_3/(NH_4)_2SO_4$, 30 mg P kg^{-1} and 75.5 mg K kg^{-1} soil as K_2HPO_4) were added to the soil and mixed thoroughly. A sampling device (Rhizon MOM 10 cm length, 2.5 mm OD, Rhizosphere Research Products, Wageningen, The Netherlands) was buried diagonally in the middle of the soil of each pot for collecting soil solution. Deionized water was then added to full saturation with 2 cm of standing water for flooded rice, and to 70% of the soil's water holding capacity for aerobic rice. The two watering regimes were maintained throughout the experiment by daily additions of deionized water. Two days later, five pregerminated rice seeds (*Oryza sativa* L. cv. Oochikara, a japonica cultivar commonly grown in Japan) were planted in each pot. Two further doses of 50 mg of N (NH_4NO_3) were added to each pot at 33 and 70 days after planting. Two plants per pot were removed at the growth stage of stem extension (45 days after planting). The remaining plants were harvested at grain maturity (117 days after planting). Stems were cut at 2 cm above soil surface, rinsed with deionized water, and dried at 60 °C for 48 h. The samples were separated into straw, husk, and unpolished rice grain. Soil solutions were collected on days 3, 12, 26, 45, and 97.

Analysis of Total As and As Speciation. Soil solution was diluted with a phosphate-EDTA buffer solution (2 mM NaH_2PO_4 and 0.2 mM Na_2EDTA, pH 6.0) at 1:1 ratio immediately after collection, filtered through a sterilized 0.2 μm filter, and analyzed for As speciation using HPLC-ICP-MS (Agilent LC1100 series and Agilent ICP-MS 7500ce, Agilent Technologies, Santa Clara, CA) within 12 h of collection (*22*). A preliminary study showed that there were no changes in As speciation during storage for 2 weeks (Supporting Information (SI), Figure S1). Arsenic species (arsenite, arsenate, DMA, and monomethylarsonic acid (MMA)) were separated using an anion-exchange As speciation column (Agilent G3154-65001) fitted with a guard column (Agilent G3154-65002). Details of the As speciation method were described previously (*22*). A preliminary study showed an excellent agreement between the sum of all As species determined by HPLC-ICP-MS and the total As concentration in soil solutions determined by ICP-MS (SI, Figure S2). The concentrations of Fe, Mn, and P in the soil solutions were determined using ICP-AES (Fisons ARL Accuris, Ecublens, Switzerland).

Ground root and shoot samples (0.2−0.5 g) were digested with 5 mL of high-purity $HNO_3/HClO_4$ (85/15 v/v). Grain and husk samples, which contain lower levels of As, were digested with high-purity HNO_3 and H_2O_2 in a microwave digester (*23*). The As concentration in the digest solution was determined by ICP-MS (Agilent 7500ce) operating in reaction cell mode with helium gas. Certified reference materials (NIST 1568a rice flour, IAEA-140/TM seaweed, and NIST1573a tomato leaves) and blanks were included for quality assurance (SI, Table S1).

Arsenic speciation in the rice grain was determined by HPLC-ICP-MS following an extraction of the rice flour with 2 M trifluoroacetic acid (TFA) according to the method developed by Heitkemper et al. (*24*) and modified by Williams et al. (*12*). Subsamples (0.25 g) of rice flour were weighed into graduated digestion tubes and 2 mL of 2 M TFA was added. The mixture was allowed to stand overnight at room temperature. The tubes were then placed on a heating block at 100 °C for 5 h, by when the solution had been evaporated. The digests were cooled and made up to 10 mL with ultrapure (>18 MΩ) deionized water. HPLC-ICP-MS analysis showed that the rice grain samples contained mostly arsenite and DMA, with trace amounts of arsenate. However, because arsenate may be partially reduced to arsenite during TFA extraction (*24*), the sum of arsenite and arsenate was presented as inorganic As. Recent risk assessments of As in foods have considered inorganic As as a whole rather than as individual species (*13, 16*). The certified reference material NIST1568a rice flour was included for As speciation analysis, and the results obtained were in good agreement with those reported previously (*12, 24*) (SI, Table S1).

Results

Dynamics of As Speciation in Soil Solution. Analysis of As speciation in the soil solutions revealed a marked difference between the aerobic and the flooded treatments (Figure 1). With few exceptions, arsenite was the predominant species of As in the flooded treatments, accounting for 81−95% of the total As in the soil solution samples collected between 12 and 97 days after soil flooding. Arsenate was present in appreciable amounts only in the first samples collected 3 days after flooding. In contrast, arsenate was the main species in the aerobic treatments, accounting for >88% of the total solution As, except on day 45 when there were similar concentrations of arsenate and arsenite, probably because the soil in the aerobic treatment was slightly overwatered in the days prior to the sampling. DMA was detected at low concentrations in some of the soil solution samples, while MMA was not detectable. Regardless whether arsenate or arsenite was added to the soil, As speciation in the soil solution was dominated by arsenite under the flooded conditions, and by arsenate under the aerobic conditions.

Soil solutions from the flooded treatment contained markedly higher concentrations of As (sum of all species) than those from the aerobic treatment (Figure 1). In the control without addition of As, the concentration of total As (mainly arsenite) increased 4 fold, from 4 to 16.9 μg L^{-1}, under the flooded conditions from day 3 to day 97, whereas in the aerobic treatment it decreased from 3.3 to 1.0 μg L^{-1}. In the two +As treatments, total As concentrations in the soil solution remained at an elevated level (between 35 and 60 μg L^{-1}) in the flooded treatment, but decreased in the aerobic treatment from 23 to 27 μg L^{-1} on day 3 to around 4 μg L^{-1} on day 97.

Similar to the pattern of As in soil solution, there was a marked mobilization of Fe and Mn in the flooded treatment, whereas their concentrations remained very low in the aerobic treatment (SI, Figure S3). There was a slight increase in the Mn concentration in the aerobic treatment on day 45, again probably a result of slight overwatering prior to the sampling of soil solution. Soil solution pH was 0.5−1 unit higher in the flooded treatment than in the aerobic treatment in the first two samplings, but approached neutrality in both treatments during the latter phase of the experiment (SI, Figure S4). The concentrations of P and dissolved organic C generally decreased with time and were higher in the flooded than in the aerobic treatments (SI, Figures S5 and S6).

Plant Growth. Rice produced grain in both aerobic and flooded treatments. Two-way analysis of variance (ANOVA) revealed a significant effect of watering regimes and As treatments on grain yield of rice ($P < 0.001$ and <0.05 for the water and As treatments, respectively; SI, Figure S7). Grain yield was not significantly different between the flooded and aerobic treatments when no As was added to the soil. In contrast, additions of 10 mg As kg^{-1} soil decreased grain yield significantly (by 20−25%) under the flooded conditions, but had no significant effect under the aerobic conditions. Rice grown in the +As treatments under the flooded conditions produced some unfilled grain, caused by spikelet sterility, which is a common symptom of As-induced "straighthead" disease in rice (*25, 26*). Straw biomass was not affected by the watering regimes, but there was a small but significant decrease ($P < 0.05$) in the +arsenite treatment compared to that in the control or +arsenate treatment.

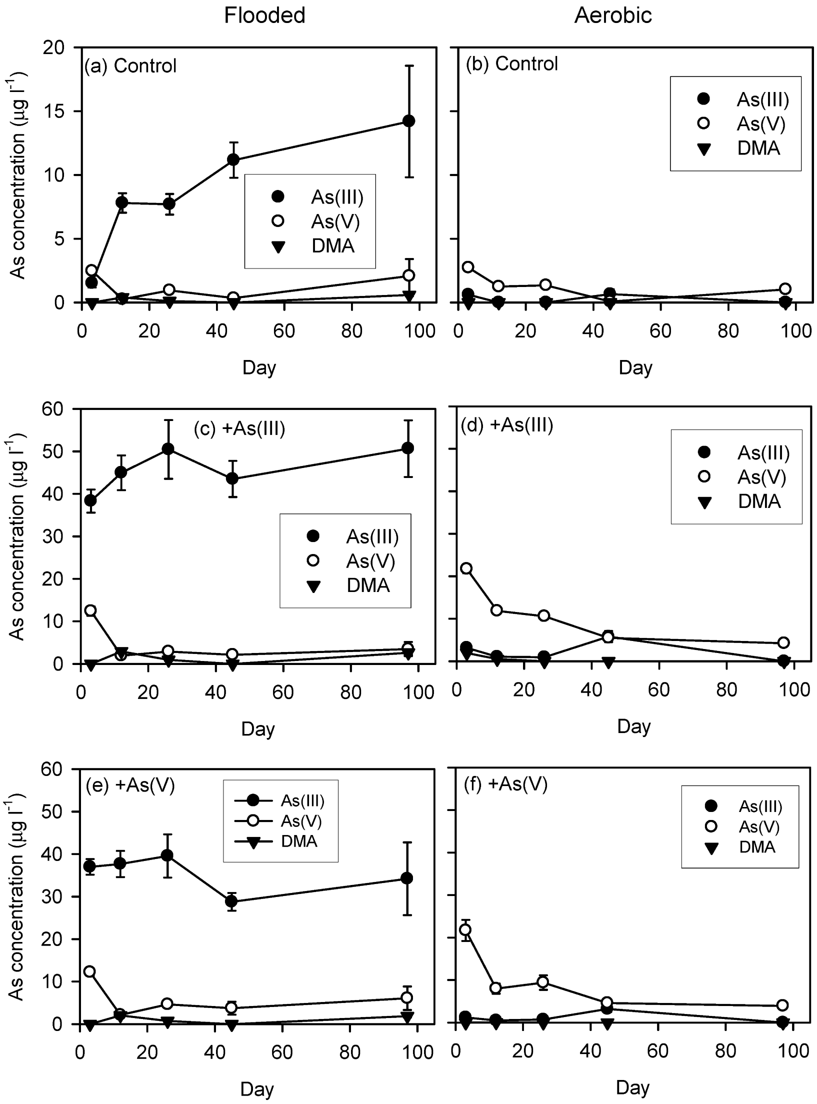

FIGURE 1. Dynamics of As speciation in the soil solution under flooded (a, c, e) or aerobic (b, d, f) conditions in the control treatment (a, b), +arsenite treatment (c, d), and +arsenate treatment (e, f). Data are means ± SE ($n = 4$).

Arsenic Concentrations in Plants. At maturity, As concentration followed the order of straw > husk > grain. Arsenic concentrations in different rice tissues were all markedly higher ($P < 0.001$) in the flooded treatments than in the aerobic treatments (Figure 2). In the unpolished grain and husk, the As concentration was 10−15-fold higher in the flooded than in the aerobic treatment, and in straw the difference was 7−35 fold with the largest differences occurring in the control treatment. Addition of arsenite or arsenate to soil increased As concentrations in straw, husk, and grain significantly ($P < 0.001$); in the unpolished grain the increase was 70−95% and 115−153% in the aerobic and flooded treatments, respectively. When all data from both the flooded and aerobic treatments were plotted together, there was a linear relationship between the As concentration in the rice shoots at the stem extension stage and that in the grain at maturity (SI, Figure S8a), whereas the relationship between the concentrations of As in grain and straw at maturity appeared to approach a plateau at the high concentration range (SI, Figure S8b).

Arsenic Speciation in Grain. There was good agreement between the total As concentrations in grain determined by acid digestion and ICP-MS measurement and the sum of all As species determined by HPLC-ICP-MS following TFA extraction (SI, Figure S9). Inorganic As (arsenite and arsenate) accounted for 20−100% of the sum of all As species, with the rest being DMA (Figure 3a). MMA was not detected in the grain samples. Grain samples from the aerobic treatment contained 91−100% inorganic As, compared with only 20−44% from the flooded treatment. The difference in the percentage of inorganic As between the flooded and aerobic treatments was highly significant ($P < 0.001$). Even though grain from the flooded treatment had a smaller percentage of inorganic As, the concentration of inorganic As was still 2.6−2.9-fold higher in the grain from the flooded treatment than in those from the aerobic treatment (Figure 3).

When data from both aerobic and flooded rice were plotted together, it can be seen that the concentration of inorganic As increased with increasing total As much less than that of DMA; the slope of the linear regression line for the latter was approximately 5 times higher than that for the former (Figure 3b). Furthermore, the percentage of inorganic As in total As in rice grain decreased exponentially with the total As concentration (SI, Figure 10).

Discussion

Because roots take up As mainly from the soil solution, the concentration and speciation of As in the soil solution should reflect its bioavailability to plant roots. The present study demonstrates a rapid and marked mobilization of As as arsenite in the soil solution under flooded conditions (Figure

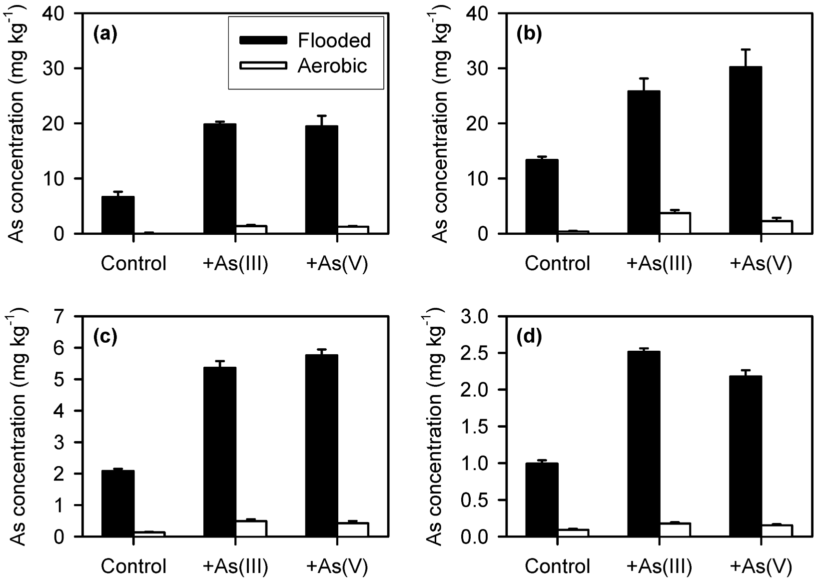

FIGURE 2. Arsenic concentrations in different rice tissues as affected by water management regimes and As treatments: (a) rice shoots at stem extension; (b) rice straw at maturity; (c) rice husk at maturity and (d) rice grain (unpolished) at maturity. Data are means $+$SE ($n = 4$). Note the different axis scales used.

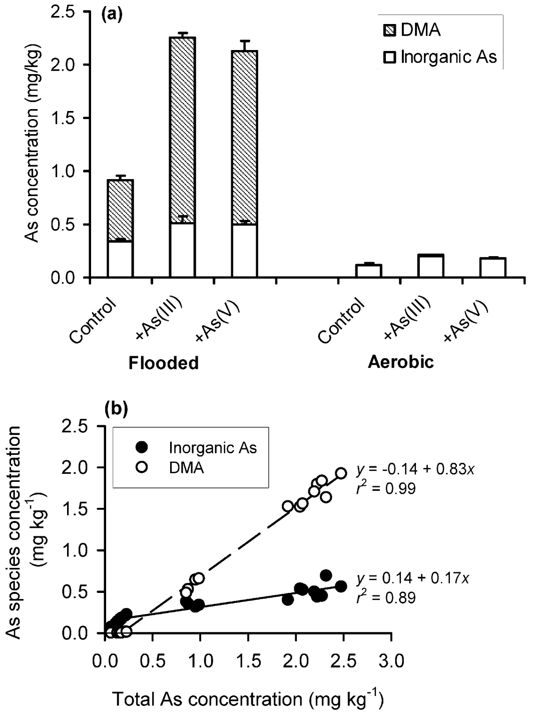

FIGURE 3. (a) Arsenic speciation in rice grain as influenced by water management regimes and As treatments. Data are means $+$SE ($n = 4$). (b) Relationship between the concentrations of inorganic As or DMA and total grain As.

1). During the period of active rice growth (days 12−97), the As concentration in the soil solution was 7−16 and 4−13 times higher under the flooded than under the aerobic conditions from the control and +As treatments, respectively. Similarly, Masscheleyn et al. (*27*) reported a 13-fold increase in soluble As for a heavily contaminated soil (total As 555 mg kg^{-1}) following the change in the soil Eh from 500 to −200 mV. Previous studies have shown that two mechanisms are involved in the mobilization of As when a soil is flooded: (i) reduction of arsenate to arsenite which then desorbs from the adsorption surfaces of iron oxyhydroxides into the solution phase, and (ii) reductive dissolution of iron oxyhydroxides, which releases the adsorbed or coprecipitated As to the solution (*27–29*). A rapid mobilization of Fe in the soil solution after flooding in our experiment suggests that the second mechanism is likely to be important. Because arsenite can be taken up as efficiently as arsenate by rice roots (*30*), the soil solution data (Figure 1) indicate that As bioavailability to rice is much enhanced under flooded conditions.

The primary form of As taken up by flooded paddy rice is not known. This question is important, because arsenite and arsenate are taken up into plant roots by different mechanisms (*31*) and, therefore, the targets for breeding low As accumulating rice would be different. The As speciation data in the soil solutions suggest that arsenite would be the main form of As taken up by flooded rice, and arsenate the main form taken up for aerobic rice. This is consistent with the finding that addition of phosphate, which is expected to inhibit the uptake of arsenate but not arsenite, had no significant effect on As accumulation by flooded rice in pot experiments (*32*). Rice roots release oxygen to the rhizosphere, resulting in the oxidation of ferrous iron and the formation of the iron plaque on the root surface, which has a substantial capacity to retain As. Much of the adsorbed As on the rice iron plaque appears to be arsenate (*33*), although both arsenate and arsenite were found to be present in association with the iron plaque of the wetland plant *Typha latifolia* (*34*). Arsenite in the rhizosphere of flooded rice may be oxidized to arsenate by the oxygen released from the roots, although oxygenation of arsenite is kinetically slow (*35*). The oxidized species, arsenate, is much more strongly adsorbed by the iron plaque than arsenite (*36*); consequently, arsenite that remains unoxidized in the rhizosphere solution may be more readily taken up by rice roots. The lack of a significant correlation between the amount of iron plaque formed and As accumulation by different rice genotypes (*33*) suggests that the ability of roots to take up arsenite and/or root to shoot translocation may be the critical steps controlling As accumulation in flooded rice.

Our study demonstrates a dramatic effect of watering regimes on As accumulation in the shoots and grain of rice, with the grain of the flooded rice containing >10-fold more total As than that from the aerobic rice (Figure 2). Previously, Marin et al. (*37*) reported an increasing accumulation of As in rice roots with decreasing redox potential in a soil suspension. They detected little As accumulation in rice shoots grown in non-As amended soil, presumably because their analytical technique (ICP-OES) was not sensitive enough. The total As concentrations in the grain samples from the flooded treatment in our experiment were very high, approximately 1 mg kg^{-1} in the control and 2.2−2.5 mg kg^{-1} in the As-amended treatments. Such high levels of grain As concentration have been reported before. For example, Meharg and Rahman (*6*) reported total grain As of 1.7−1.8 mg kg^{-1} in some samples from a field survey in Bangladesh where soils contained 15−27 mg kg^{-1} total As (comparable with 15 mg kg^{-1} in the soil used in our study). Wang et al. (*38*) reported 0.43−2.9 mg kg^{-1} total As in rice samples from a mining-impacted area in Hunan, China. The grain samples in our study were unpolished, and so would also have a higher As concentration than the polished counterparts (*39*). Our data show that soil flooding causes As mobilization in soil, resulting in a much elevated As accumulation in flooded rice. Chemical transformation in soil is, therefore, the dominant reason for a greatly enhanced As assimilation in paddy rice compared with other cereals such as wheat and barley (*19*). In support of this conclusion, earlier studies showed that As-induced "straighthead" symptoms in rice were found to occur only under flooded conditions, and not in rice grown under aerobic conditions (*25, 26*).

Flooded and aerobic treatments also produced dramatic differences in As speciation in grain (Figure 3a). Grain of aerobically grown rice contained As almost exclusively as inorganic As, whereas in flooded rice grain DMA accounted for a majority of the total As. It is generally considered that methylated species are less toxic to humans than inorganic As (*13*). Increased methylation of As in grain of flooded rice alleviates to a certain extent the problem of excessive As accumulation. Nevertheless, the concentration of inorganic As in the flooded rice grain was still more than double that in the aerobic rice grain. The proportion of inorganic As in total As decreased with increasing total As concentration, while the percentage of DMA increased (Figure 3b). This relationship is similar to that reported recently for a number of market rice samples (*39*). A recent greenhouse study showed a high percentage of DMA (85−94%) in rice grain with a high level of total As (1.25 mg kg^{-1}) (*40*). Since our data were for a single genotype grown under the same climatic conditions, the relationship implies that methylation of As in rice may be a response to increased As loading in grain. This hypothesis awaits further investigation. Based on the relationship between inorganic As or DMA with total As, Zavalta et al. (*11*) proposed to classify rice grain into the inorganic As or DMA type. They speculated that As speciation in rice grain is under genetic, rather than environmental, control. However, our results demonstrate that As speciation in rice grain can be strongly influenced by the environmental conditions such as watering regime and As bioavailability in soil.

In conclusion, our study has revealed that soil chemical transformations occurring under the flooded conditions are the main reason for the much enhanced As accumulation in paddy rice. The results are significant in that they point to the direction for practical mitigation measures through manipulation of soil redox potential during rice growth. For example, midseason draining of water, just before flowering, has been shown to be an effective measure to reduce the As-induced "straighthead" disease in rice (*25, 26*). Further field trials should be carried out to test if this measure can decrease As accumulation in rice grain. Similarly, a recent study has shown that a rice-growing system of raised beds and furrows resulted in a higher soil redox potential and a significantly lower accumulation of As in straw and grain compared with the conventional flooding system (*3*). "Aerobic rice" has been developed as a new cultivation method to save water use (*41*). This system involves growing specific aerobic rice cultivars in nonflooded conditions with supplemental irrigation. It would be interesting to investigate whether the aerobic rice cultivation system decreases As accumulation in grain.

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Supporting Information Available

One table and ten figures. This information is available free of charge via the Internet at http://pubs.acs.org.

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