Arsenic (As) can accumulate in the edible parts of crops and can thus enter the food chain, posing a risk to human health (Zhao et al. 2010). Recently, phytoremediation (Jankong et al. 2007), chemical immobilization (Sun et al. 2015) and leaching (Tokunaga and Hakuta 2002) have been used in the remediation of agricultural farmlands. In the long-term, these techniques accrue huge economic costs, time requirements and risk over-remediation, which can negatively affect soil texture and fertility, making these processes unsuitable to meet the demands of agricultural production. Substitution planting with crops capable of low-As uptake has been regarded as a highly efficient measure to reduce or avoid As accumulation in agricultural products (Requejo and Tena 2014). However, to the best of our knowledge, there has been no proper way to categorize crops as low-As or high-As-accumulating until now. While working toward such a categorization technique, the bio-concentration factor (BCF) of As and the stabil...
ity of As accumulated among crop types or cultivars should be considered as factors of significant priority.

Maize (Zea mays L.) is the most cultivated economic cereal in the world and constitutes a staple food for humans in most developing countries of Latin America, Africa, and Asia (Rosas-Castor et al. 2014a). Previous studies have shown concerns about the risks of As accumulation in maize (Gulz et al. 2005, Liu et al. 2012, Zhao et al. 2018). Maize has a lower BCF for soil As compared to rice and leafy vegetables (Xiao et al. 2009). However, comparisons between the abilities of different maize cultivars to accumulate As and studies of the stability of accumulated As among different cultivars are rare. Furthermore, it is still debatable whether maize is a suitable substitute for other crops with high As accumulation when planting in As-contaminated farmlands. For example, Ding et al. (2011) found that maize showed low As accumulation in its grain and was suitable for growing in As-contaminated soils. Fu et al. (2016) also reported that the As concentration in maize grains was far below the national food safety standard for maize in China, and the As exposure risk to humans could be reduced by choosing maize as a substitute in As-contaminated farmlands. However, Ruiz et al. (2017) considered that maize had high bioaccumulation and high exposure risks to As in high-As soils. Queirolo et al. (2000) also considered that the grain As concentration of some maize cultivars exceeded the safe limit and could pose potential threats to human health. Some chemical inactivators are recommended to be applied to As-contaminated farmlands to reduce As uptake by maize (Requejo and Tena 2012).

In this study, pot and field experiments, outdoor investigations, and analysis of literature data were conducted to reveal the As accumulation ability of maize and the accumulated As stability among maize cultivars. The objectives were as follows: (I) to identify the differences in grain As accumulation among maize cultivars under different soil As levels; (II) to assess the overall situation regarding As accumulation in maize grain around the world; and (III) to understand the reason for the low grain As accumulation in maize. This will help safely utilize As-contaminated farmlands via substitution planting with maize in the future.

MATERIAL AND METHODS

Pot experiment: Grain As in maize grown in soils with different As concentration. A pot experiment was conducted in order to better understand the accumulation response of grain As to soil As. Three As-contaminated soils with total As of 55.8 (soil 1), 146.8 (soil 2) and 238.8 mg/kg (soil 3) were collected from the farmlands surrounding the Shimen realgar mining area, Hunan province, China. According to the Soil Environmental Quality: risk control standard for soil contamination of agricultural land released in China (GB 15618–2018), the As concentration in soil 1 and 2 was 1.4 and 3.7 times higher than the risk screening value of soil As (40 mg/kg, 5.5 < soil pH ≤ 6.5), respectively. The As concentration in soil 3 was 1.6 times higher than the risk intervention value of soil As (150 mg/kg, 5.5 < soil pH 6.5). The physico-chemical properties of these soils are presented in Table 1.

Six maize cultivars were planted in each experimental soil with four replicates for each cultivar. Plastic pots with an inner diameter of 30 cm and a height of 35 cm were loaded with 20 kg As-contaminated soils passed through a 2 mm sieve. The base fertilizers NH₄Cl (200 mg N/kg dry soil), KH₂PO₄ (52 mg P/kg dry soil) and KCl (166 mg K/kg dry soil) were applied before planting. Six seeds were planted and only one seedling in each pot was left to grow. The soil moisture was controlled at 70% field capacity during the experiment. Soil available As and grain As were analysed after cultivation for 104 days post sowing.

Table 1. Physicochemical properties of the experimental soils

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Soil 1</th>
<th>Soil 2</th>
<th>Soil 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total N</td>
<td>g/kg</td>
<td>1.46</td>
<td>2.01</td>
<td>1.16</td>
</tr>
<tr>
<td>Total P</td>
<td>g/kg</td>
<td>1.12</td>
<td>0.88</td>
<td>1.23</td>
</tr>
<tr>
<td>Total K</td>
<td>g/kg</td>
<td>13.2</td>
<td>21.3</td>
<td>19.3</td>
</tr>
<tr>
<td>Organic carbon</td>
<td>g/kg</td>
<td>7.31</td>
<td>10.90</td>
<td>12.88</td>
</tr>
<tr>
<td>Total As</td>
<td>mg/kg</td>
<td>55.8</td>
<td>146.8</td>
<td>238.8</td>
</tr>
<tr>
<td>Available As</td>
<td>mg/kg</td>
<td>1.2</td>
<td>2.8</td>
<td>8.1</td>
</tr>
<tr>
<td>Available Fe</td>
<td>mg/kg</td>
<td>75.3</td>
<td>122.5</td>
<td>105.7</td>
</tr>
<tr>
<td>Available Mn</td>
<td>mg/kg</td>
<td>59.8</td>
<td>80.3</td>
<td>77.2</td>
</tr>
<tr>
<td>Available Al</td>
<td>mg/kg</td>
<td>1.50</td>
<td>3.01</td>
<td>2.88</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>5.92</td>
<td>6.12</td>
<td>5.65</td>
</tr>
<tr>
<td>CEC</td>
<td>cmol/</td>
<td>10.3</td>
<td>11.7</td>
<td>12.0</td>
</tr>
<tr>
<td>Sand (2–0.05 mm)</td>
<td></td>
<td>37.61</td>
<td>32.47</td>
<td>35.68</td>
</tr>
<tr>
<td>Silt (0.05–0.002 mm)</td>
<td>%</td>
<td>38.32</td>
<td>41.32</td>
<td>40.74</td>
</tr>
<tr>
<td>Clay (&lt; 0.002 mm)</td>
<td></td>
<td>24.07</td>
<td>26.21</td>
<td>23.58</td>
</tr>
</tbody>
</table>

CEC – cation-exchange capacity
Field experiment: Grain As concentration and the stability of accumulated As among cultivars. A field experiment was conducted in the Shimen realgar mining area, Hunan province of China, in order to further understand As accumulation in maize and the stability of accumulated As among cultivars. Soil total As and available As concentration was 245.4 (1.6 times higher than the As risk intervention value of 150 mg/kg, 5.5 < soil pH ≤ 6.5) and 8.6 mg/kg, respectively, soil pH was 5.7 and soil organic matter concentration was 24.7 g/kg. Three maize types including 18 cultivars (5 normal maize, 5 sweet maize, and 8 waxy maize) were planted (Table 2). Each plot area measured 5 × 4 m². There were three replicates for each cultivar and the plots were completely randomized. Two outer rows of maize plants around each plot

Table 2. Arsenic (As) concentrations in different parts of the 18 maize cultivars and the As transfer coefficients among different maize parts.

<table>
<thead>
<tr>
<th>Maize type</th>
<th>Maize cultivar</th>
<th>Grain As (mg/kg)</th>
<th>Shoot As (mg/kg)</th>
<th>Root As (mg/kg)</th>
<th>Soil total As (mg/kg)</th>
<th>Soil available As (mg/kg)</th>
<th>Grain/ shoot</th>
<th>Shoot/ root</th>
<th>Root/ soil As</th>
<th>Grain/ root</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal maize</td>
<td>CY1</td>
<td>0.052 ± 0.002</td>
<td>1.742 ± 0.126</td>
<td>22.096 ± 2.426</td>
<td>241.067 ± 2.329</td>
<td>7.870 ± 0.111</td>
<td>0.031</td>
<td>0.810</td>
<td>2.803</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>ZY999</td>
<td>0.054 ± 0.003</td>
<td>3.005 ± 0.639</td>
<td>22.702 ± 3.354</td>
<td>230.210 ± 0.906</td>
<td>8.280 ± 0.197</td>
<td>0.021</td>
<td>0.140</td>
<td>2.738</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>BDY6</td>
<td>0.055 ± 0.000</td>
<td>3.485 ± 0.591</td>
<td>25.095 ± 0.544</td>
<td>237.987 ± 1.663</td>
<td>7.860 ± 0.322</td>
<td>0.017</td>
<td>0.140</td>
<td>3.199</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>JS888</td>
<td>0.053 ± 0.006</td>
<td>1.689 ± 0.331</td>
<td>23.989 ± 3.353</td>
<td>232.160 ± 4.388</td>
<td>8.357 ± 0.394</td>
<td>0.037</td>
<td>0.076</td>
<td>2.851</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>JY506</td>
<td>0.053 ± 0.003</td>
<td>2.112 ± 0.223</td>
<td>21.059 ± 4.509</td>
<td>238.327 ± 4.376</td>
<td>8.080 ± 0.231</td>
<td>0.026</td>
<td>0.106</td>
<td>2.617</td>
<td>0.003</td>
</tr>
<tr>
<td>Sweet maize</td>
<td>LSCR</td>
<td>0.055 ± 0.003</td>
<td>1.888 ± 0.074</td>
<td>22.745 ± 0.335</td>
<td>236.583 ± 1.155</td>
<td>7.680 ± 0.361</td>
<td>0.029</td>
<td>0.083</td>
<td>2.974</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>XW</td>
<td>0.152 ± 0.003</td>
<td>2.182 ± 0.394</td>
<td>22.133 ± 2.137</td>
<td>236.347 ± 4.031</td>
<td>7.650 ± 0.200</td>
<td>0.075</td>
<td>0.097</td>
<td>2.883</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>SSMY</td>
<td>0.119 ± 0.006</td>
<td>0.946 ± 0.220</td>
<td>11.880 ± 0.706</td>
<td>235.433 ± 3.147</td>
<td>7.787 ± 0.237</td>
<td>0.144</td>
<td>0.082</td>
<td>1.527</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>TY4</td>
<td>0.115 ± 0.003</td>
<td>2.023 ± 0.356</td>
<td>18.900 ± 0.409</td>
<td>236.800 ± 3.577</td>
<td>8.047 ± 0.346</td>
<td>0.062</td>
<td>0.123</td>
<td>2.392</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>DMZ</td>
<td>0.081 ± 0.009</td>
<td>1.987 ± 0.120</td>
<td>12.685 ± 0.114</td>
<td>230.563 ± 1.469</td>
<td>7.577 ± 0.179</td>
<td>0.041</td>
<td>0.156</td>
<td>1.675</td>
<td>0.006</td>
</tr>
<tr>
<td>Waxy maize</td>
<td>ZN2</td>
<td>0.058 ± 0.007</td>
<td>2.077 ± 0.585</td>
<td>16.763 ± 2.721</td>
<td>232.677 ± 4.017</td>
<td>8.080 ± 0.183</td>
<td>0.032</td>
<td>0.120</td>
<td>2.092</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>JN628</td>
<td>0.049 ± 0.003</td>
<td>2.293 ± 0.579</td>
<td>18.582 ± 0.407</td>
<td>232.873 ± 3.893</td>
<td>7.820 ± 0.350</td>
<td>0.026</td>
<td>0.124</td>
<td>2.382</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>N2000</td>
<td>0.049 ± 0.003</td>
<td>1.557 ± 0.409</td>
<td>20.469 ± 0.714</td>
<td>241.147 ± 1.268</td>
<td>8.233 ± 0.162</td>
<td>0.035</td>
<td>0.076</td>
<td>2.487</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>ZHCN2008</td>
<td>0.063 ± 0.002</td>
<td>1.968 ± 0.265</td>
<td>19.158 ± 2.867</td>
<td>235.273 ± 1.268</td>
<td>8.340 ± 0.162</td>
<td>0.033</td>
<td>0.103</td>
<td>2.293</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>ZKHXN23</td>
<td>0.063 ± 0.005</td>
<td>2.108 ± 0.537</td>
<td>18.637 ± 3.803</td>
<td>237.887 ± 4.290</td>
<td>8.197 ± 0.156</td>
<td>0.034</td>
<td>0.124</td>
<td>2.276</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>ZCNT8</td>
<td>0.052 ± 0.006</td>
<td>1.122 ± 0.302</td>
<td>19.981 ± 0.493</td>
<td>232.410 ± 3.067</td>
<td>8.540 ± 0.150</td>
<td>0.051</td>
<td>0.056</td>
<td>2.342</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>ZNB18</td>
<td>0.061 ± 0.005</td>
<td>1.801 ± 0.038</td>
<td>18.024 ± 3.799</td>
<td>238.010 ± 4.298</td>
<td>8.437 ± 0.124</td>
<td>0.034</td>
<td>0.112</td>
<td>2.124</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>CJHN</td>
<td>0.057 ± 0.006</td>
<td>0.971 ± 0.303</td>
<td>14.523 ± 2.517</td>
<td>231.863 ± 5.888</td>
<td>8.467 ± 0.264</td>
<td>0.078</td>
<td>0.077</td>
<td>1.701</td>
<td>0.004</td>
</tr>
</tbody>
</table>
were used as protection to eliminate marginal effects and prevent cross pollination. Planting density and field management followed the local customs of maize production. Fertilizers were applied with 11 000 kg/ha organic fertilizer, 190 kg N/ha, 31 kg P/ha and 66 kg K/ha, respectively.

After cultivation for 125 days, five maize strains were randomly chosen from each plot. Subsequently, the roots, shoots and grains were separately sampled and then the same maize tissues were mixed. Simultaneously, five soil samples were collected from the root zones of the sampled maize and then mixed thoroughly. Soil total and available As, as well as plant As were analysed. The available bio-concentration factor (aBCF) was calculated as the ratio of grain As to soil available As (Yang et al. 2016).

**Outdoor investigation of As accumulation in maize grain.** The outdoor investigation was conducted in the Shimen realgar mine area in order to further assess As accumulation in maize. The local farmland soil is a red soil derived from Quaternary red clay. Due to the smelting and the unreasonable disposal of realgar slag, the surrounding farmland soil was contaminated with As (Wu et al. 2017). Based on their soil As distribution characteristics, the 54 maize fields surrounding the Shimen realgar mine were selected. Five strains of maize grain samples were collected from each sampling point and correspondingly, five soil samples from the root zones of the sampled maize were collected. The As concentration of grain and soil available As was analysed.

**Literature analysis of worldwide grain As data.** In order to further understand As accumulation in maize grain cultivation worldwide, 34 available reports from the literature concerning grain As were collected. These publications were chosen based on whether they reported the data of maize grain As from pot or field experiments.

**Sample analysis.** Maize samples were digested using HNO$_3$ and H$_2$O$_2$ (v:v = 3:1) (Mallick et al. 2011). Soil available As was extracted using 0.5 mol/L NaHCO$_3$ (NaHCO$_3$ and soil, v:v = 2.5:1) (Woolson et al. 1971). Soil total As was digested using the mixed acid method (HNO$_3$, HClO$_4$, and HF; v:v:v = 5:1:2) (Wang et al. 2015). Arsenic concentration was determined via hydride generation using an atomic fluorescence spectrometer (HG-AFS, AFS-9120, Titan Instruments, Beijing, China). The certified reference materials GBW07429 (21.7 mg/kg) for soil and GBW10012 (Corn flour, 0.028 mg/kg) for plants (Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences), were used as the quality control during As analysis and their recovery rates were 92.7% and 95.3%, respectively.

**Statistical analyses.** The data were analysed using the SPSS 22.0 (IBM Corporation, Armonk, USA), Excel 2016 (Microsoft Corporation, Redmond, USA) and Origin 9.0 (OriginLab Corporation, Northampton, USA). A one-way ANOVA was conducted using the data from all treatments by least significant difference (LSD). Significance was identified when $P < 0.05$. The data are expressed as means ± standard errors (SE).
RESULTS

The grain As of maize grown in soils with different As concentrations. Significant differences were observed in maize grain As concentration between plants grown in soils with different As concentrations (Figure 1). When the soil total As concentration was 55.8, 146.8, and 238.8 mg/kg, soil available As was 1.2, 2.8 and 8.1 mg/kg, respectively, and grain As concentration was 0.02–0.03, 0.03–0.05 and 0.03–0.07 mg/kg, respectively. Generally, grain As concentration was significantly lower than the safe limit for maize in China (0.50 mg/kg), even though soil As concentration was 1.6 times higher than the risk intervention value (150 mg/kg).

Grain As concentration and the stability of accumulated As among maize cultivars. Significant differences in grain As among the different maize cultivars were observed (Figure 2a, Table 2). The grain As concentration of all maize cultivars was significantly lower than the acceptable limit in China (0.50 mg/kg). The grain As concentration of the 18 maize cultivars ranged from 0.05 (waxy maize, cvs. JN628 and N2000, normal maize cv. BDY6) to 0.15 mg/kg (sweet maize cv. XW) (Table 2). Sweet maize showed the strongest ability to accumulate As

![Figure 2](https://doi.org/10.17221/155/2019-PSE)
with an average grain As of 0.10 mg/kg and aBCF of 0.013, relative to waxy (grain As = 0.06 mg/kg, aBCF = 0.007) and normal maize (grain As = 0.05 mg/kg, aBCF = 0.007) (Figure 2). The coefficients of variation (CV) for grain As (35.6%) or aBCF levels (35.5%) of different sweet maize cultivars were the highest among all cultivars. Comparatively, the waxy and normal maize cultivars accumulated less grain As and had higher accumulated As stabilities. Additionally, it was found that, for each cultivar, grain yields in our experiment matched the average grain yields of local farmers: 8835 kg/ha (calculated based on maize production in a 20 m² plot area) in normal maize, 7875 kg/ha in waxy maize and 7320 kg/ha in sweet maize.

Arsenic transfer between different tissues in maize. Significant differences in shoot and root As between maize cultivars were observed (Table 2). The normal maize cv. BDY6 had the highest shoot (3.5 mg/kg) and root As (25.1 mg/kg), while the sweet maize cv. SSMY had the lowest shoot (0.9 mg/kg) and root As (11.9 mg/kg). Comparatively, the As concentration in different maize tissues decreased in the order of root > shoot > grain. Root As concentration was typically 2.4–79.9 times higher than shoot As and 69.5–693.7 times higher than grain As. The As transfer coefficients decreased in the order of soil to root > root to shoot > shoot to grain > root to grain. Interestingly, the normal maize cv. BDY6 had simultaneously the lowest grain As and the highest root and shoot As.

Principal component analysis (PCA) was used to explore the contribution of As transfer among different maize tissues to grain As concentration (Figure 3). From PC1 (explaining 58.5% of total variance), the As transfer from shoot to grain (X1) and from root to grain (X2) contributed the most to grain As (Y). From PC2 (explaining 22.8% of total variance), X2 and the As transfer from soil to root (X4) contributed the most to grain As (Y). The As transfer from root to shoot (X3) contributed less to grain As. Furthermore, a stepwise regression model, \( Y = 14.881 \times X2 + 0.026 \times X3 - 0.052 \) was successfully fitted \( (P < 0.01, n = 54) \), through which it could be easily observed that As compartmentalization in the roots and low transfer to the above ground parts of maize was the reason for low grain As.

Arsenic accumulation in maize grain based on the outdoor investigations and literature analyses. The grain As concentration observed in the outdoor investigation was significantly lower than the acceptable As limit in China (Figure 4). The soil total and available As concentration ranged between 16.1–377.5 and 0.02–8.45 mg/kg, respectively. The observed grain As ranged from 0.014–0.075 mg/kg, 2.8–15% of the upper acceptable limit for grain As. Further, the relationship between soil available As (X) and grain As (Y) was examined (Figure 4). The power function curve fitted according to the equation \( Y = 0.0368 \times X^{0.1569} \) \( (R^2 = 0.5577, P < 0.01, n = 54) \) had a better fit than the linear curve \( (R^2 = 0.4761) \).
This indicated that the ability of maize grain to accumulate As reaches a maximum value regardless of further increases in available soil As.

Further, the 142 available samples for grain As were collected from the corresponding 34 reports from literature. The grain As concentrations of 140 samples fell into the range of 0.004–0.35 mg/kg (Figure 5), which were significantly lower than the acceptable limit in China. The grain As values of 141 samples were below the acceptable limit of As in maize in Australia (1.0 mg/kg), New Zealand (1.0 mg/kg), and the WHO limit (0.70 mg/kg). All grain As concentration was considerably lower than the limit in Switzerland (4.0 mg/kg).

DISCUSSION

In this study, the pot and field experiments, outdoor investigations, and analyses of literature data indicated...
that grain As of maize was far below the acceptable limit in China, and thus, maize could be recommended for planting in As-contaminated farmlands. In the study area, rice grain can accumulate inorganic As at the concentration of 0.09–0.57 mg/kg (grain water content < 13% of grain weight), while leaf vegetables commonly accumulate As at concentrations of 0.02–0.96 mg/kg fresh weight (data not published, the As limits for rice (water content < 13% of grain weight) and leaf vegetables (fresh weight) in China are 0.2 and 0.5 mg/kg, respectively). Comparatively, using maize as a substitute for rice or leaf vegetables in As-contaminated farmland can avoid the over-accumulation of As in the edible parts of the crop, ensuring As levels do not exceed dangerous levels. Furthermore, grain As varied among different maize cultivars. Sweet maize exhibited the highest As accumulation risk in its grain and low accumulated As stability among all its cultivars. The planting of normal and waxy maize prior to sweet maize in As-contaminated farmlands is strongly recommended.

Rosas-Castor et al. (2014b) also reported significant differences between the As transfer efficiencies of different maize tissues. Generally, As transfer coefficients for maize were in the order of soil to root > root to shoot > shoot to grain (Liu 2008). Maize root was regarded as the primary tissue for As accumulation (Ci et al. 2012). In this study, As compartmentalization by the root and low transfer to the above ground part of maize was regarded the main reason for low grain As. However, little information regarding the mechanism of As sequestration and upward transfer by maize root has been available until now. Maize immobilizes As in the root mainly by iron oxide plaques and thiol ligands, thereby preventing the upward migration of As in maize plants (Parsons et al. 2008). The first internode of the maize plants might greatly limit the upward migration of arsenic as its concentration in the first internodes underground was about 4.2-fold higher than that in the lower stalk (Ci et al. 2012).

Economic benefits should also be taken into consideration before and after implementing the substitution planting. Comparatively, maize cultivation is less economically beneficial than planting of other crops such as rice and vegetables, especially in the south of China. However, maize straw can be used as an energy source (Bani et al. 2019) or feed for livestock, which could compensate the losses resulting from substitution planting to some extent. Nevertheless, a new way to implement the coordination of agricultural production and ensure soil remediation by As removal could be achieved by planting special maize cultivars such as cv. BDY6, which simultaneously had the lowest grain As and the highest root and shoot As. In the future, special economic compensatory measures should be implemented to incite the safe reuse of As-contaminated farmlands via alternative planting using maize.

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REFERENCES


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