Governing Controls of Sulfur On Arsenic Uptake By Rice in Paddy Soil

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Background
Arsenic (As) uptake in rice from contaminated soil and irrigation water is currently being highlighted as an important exposure pathway for humans to this potent toxin. Sulfur (S) has a high affinity for arsenic, both in minerals and organic molecules, and the addition of excess S can decrease the uptake of As, concentration and translocation of As in rice. However, the exact mechanisms behind these effects are not fully understood.

Aim and approach
We combine monitoring and observation of bulk effects with in-depth analyses of microscale processes in the rice rhizosphere, intending to elucidate the governing controls of sulfur on arsenic mobility, uptake and translocation in the paddy rice system with and without organic amendments, as conceptualized in Fig. 1.

Materials & Methods

Material
Two Cambodian paddy soils (Table 1)
Four organic amendments plus gypsum (Table 2)

Experiments
Pot trials with/without rice plants
Batch reactors

Analytical methodology
Solids – XRF, XAS, NMR
Solution – ICP, IC, HPLC-ICP-MS, TOC, Spectrophotometry
Rhizosphere - μXAS, SEM, TXM, Microsensors
Microbiology - Isothermal microcalorimetry, Pyrosequencing

Results – solubility coupled to microbial reductive dissolution
Dried rice straw and charred rice straw increased the rate of As release from soil K in a batch experiment (Fig. 2). The effect was most prominent with the dried straw, due to an almost 5.5 times higher C addition.

However...
• The charred straw treatment had not reached equilibrium by the end of the batch experiment (after 65 days).
• The microbial activity (Fig. 3) was lower with charred straw, even when the application rate was adjusted to add the same amount of C, suggesting that the differences can be attributed to C chemistry rather than amount.

Conclusions and future
The addition of S in the form of gypsum alone had a very limited effect on the release of As from flooded soil without plants (Fig. 2). The addition of organic matter alone promoted As release (Fig. 3). What happens when the two are combined? What happens when plants are added to the system?

Further investigations:
• Pot trial with rice, organic amendments and/or gypsum – bulk effects
• Batch experiments with char and gypsum combined
• Rhizosphere chemistry mapping
• Detailed soil solution As speciation
• Amendment chemical characterization
• Microbial metabolism – thermodynamics, functional presence

References
3 Hu et al. (2007) Environ. Pollut., 147, 387-393

Results – solid phase speciation
Flooding caused arsenic reduction in both soils and increased the relative contribution from As(III) species from 30% to 51% and 19% to 53% in soil P and K respectively (Fig. 4a). Although the flooding also increased the contribution from sulfides to the total sulfur speciation (Fig. 4b), the fitting of the As XANES spectra did not indicate any formation of As-S species after 53 days of flooding.

Materials

Table 1. Soil properties

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<thead>
<tr>
<th>Texture</th>
<th>Sandy/Clay</th>
<th>Organic carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil K</td>
<td>6.15</td>
<td>2.16</td>
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<tr>
<td>Soil P</td>
<td>5.19</td>
<td>1.98</td>
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</table>

Table 2. Amendment total element concentration

<table>
<thead>
<tr>
<th>Amendment total element concentration</th>
<th>Dry</th>
<th>Chilled</th>
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<th>Sulfide (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (mg/g)</td>
<td>0.14</td>
<td>0.17</td>
<td></td>
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<tr>
<td>As (μg/g)</td>
<td>11</td>
<td>6.6</td>
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<td></td>
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<tr>
<td>S (μg/g)</td>
<td>30</td>
<td>30</td>
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<td></td>
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<tr>
<td>C (%)</td>
<td>2.1</td>
<td>2.3</td>
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<tr>
<td>N (%)</td>
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Figure 1. Conceptual model of the rhizosphere processes potentially affected by sulfur addition.

Figure 2. Arsenic and iron dissolutions/precipitations (% of total element in soil, i.e., 35 μg As/g soil, 45 mg Fe/g soil) in batch reactors with 4 g of soil K, flooded with 125 ml TRIS buffer (10 mM, pH 7.0), amended with dry or charred rice straw or un-amended. All vials were sealed immediately after flooding. Two application rates were used for the organic amendments in the microcalorimetry measurements (Fig. 3a): 1 – same amount of 5 (7 μg C/g soil, as in batch experiment), 2 – same amount of C (9 mg C/g soil).

Figure 3. Microbial activity, estimated by: a) heat output (μg C/g soil) using isothermal microcalorimetry and b) O2 depletion (CO2 production) using in situ optical spot sensors, in 4 g of dry soil K, flooded with 125 ml TRIS buffer (10 mM, pH 7.0), amended with dry or charred rice straw or un-amended. All vials were sealed immediately after flooding. Two application rates were used for the organic amendments in the microcalorimetry measurements (Fig. 3a): 1 – same amount of 5 (7 μg C/g soil, as in batch experiment), 2 – same amount of C (9 mg C/g soil).

Figure 4. Arsenic (a) and sulfur (b) speciation in soils P and K before (0) and after (2) 53 days of flooding with DI water in unplanted pots amended with 2% dried rice straw.