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[1]. Sulfur (S) has a high affinity for arsenic, both in minerals and organic molecules, and the addition of excess S can decrease the uptake[2,3], concentration[2,4] and translocation[2,4] 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.

Table 1. Soil properties

	Soil K	Soil P
Texture	Sandy Clay Loam	
pH	6.13	5.39
Totals		
As (µg/g)	15	11
Fe (mg/g)	45	44
S (µg/g)	330	363
C (%)	1.3	1.6
N (%)	0.14	0.17
Oxalate extractable		
As (µg/g)	11	6.6
Fe (mg/g)	21	24

Table 2. Amendment total element concentration

	Dry Husks	Charred Husks	Dry Straw	Charred Straw	Gypsum ($CaSO_4$)
C (%)	37	49	37	15	-
N (%)	0.2	0.4	0.9	0.6	-
S (µg/g)	26	21	192	422	18%
As (µg/g)	0.02	0.08	0.06	1.5	-

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

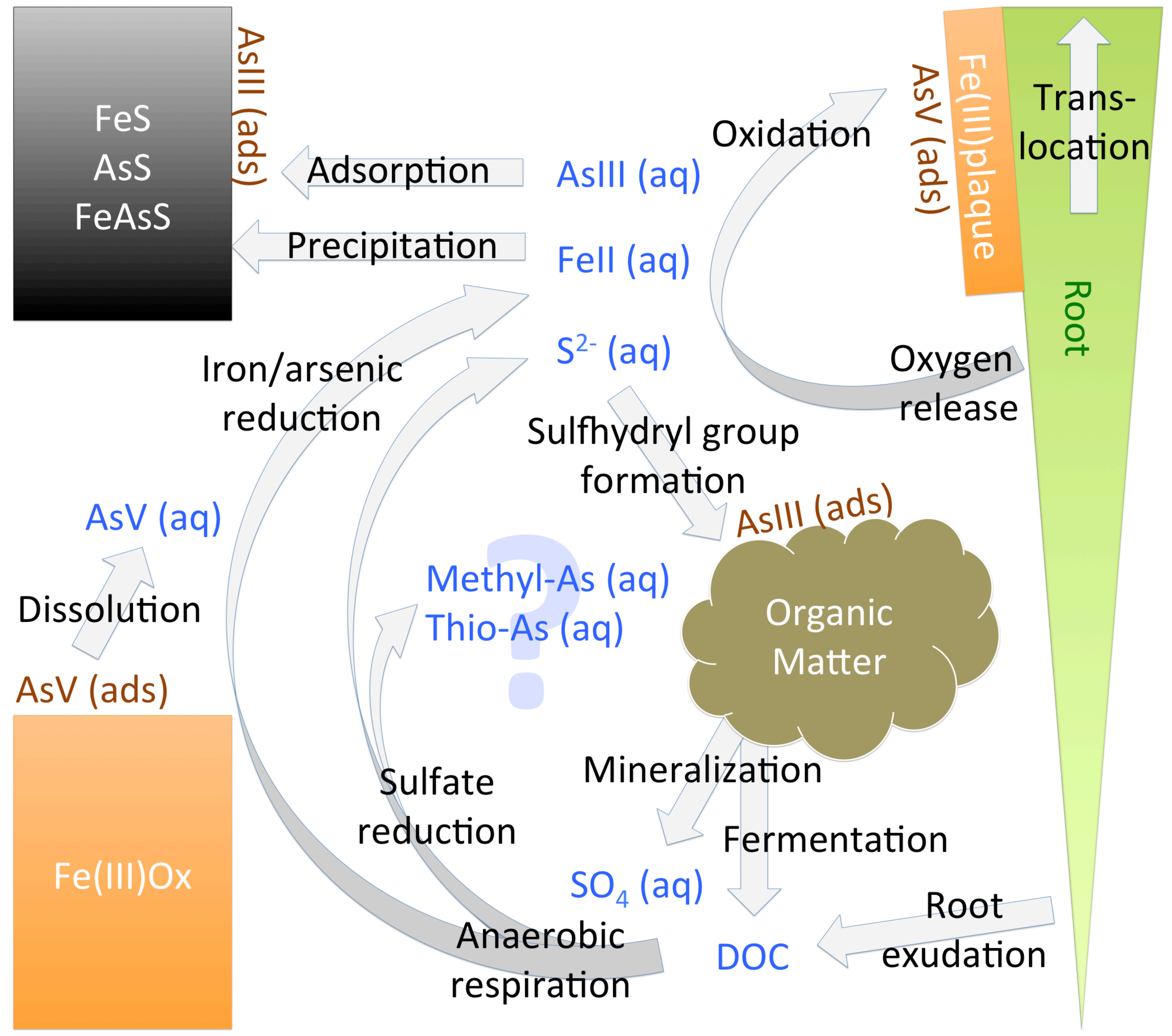
Analytical methodology

Solids – XRF, XAS, NMR

Solution - ICP, IC, HPLC-ICP-MS, TOC, Spectrophotometry

Rhizosphere - µXAS, SEM, TXM, Microsensors

Microbiology - Isothermal microcalorimetry, Pyrosequencing



Solubility/Soil mobility	*Aqueous speciation*	*Mobility in planta*
Sulfide precipitation/ adsorption	Increased methylation	Detoxification by S-compounds
Organic sulfide adsorption (on sulfhydryl groups)	Thioarsenic species formation	Increased retention in roots
Increased iron plaque		

Figure 1. Conceptual model of the rhizosphere processes potentially affected by sulfur addition.

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

[1] *Halder et al.* (2012) Environ. Sci. Technol., 46, 4142–4148

[2] *Fan et al.* (2013) Plant Soil Environ., 59, 169-174

[3] *Hu et al.* (2007) Environ. Pollution, 147, 387-393

[4] *Zhang et al.* (2011) Environ. Exp. Bot., 72, 34–40

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.

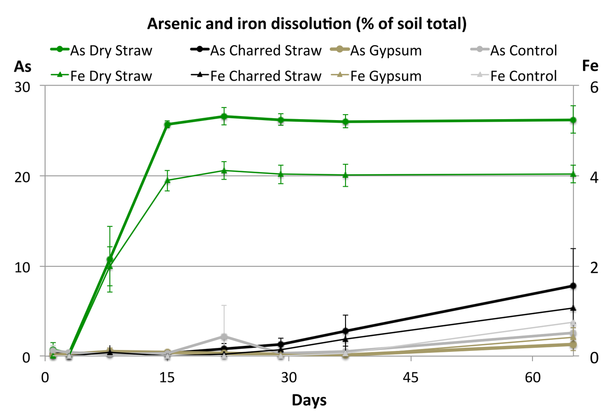


Figure 2. Arsenic and iron dissolution/ desorption rates (% of total element in soil, i.e. 15 µg As/g soil, 45 mg Fe/g soil) in batch reactors with 4 g of soil K, flooded with 125 ml TRIS buffer (10 mM, pH 7.0), amended with 4% dried or 2% charred rice straw, gypsum or unamended. The amendment additions were set to 7.7 µg S added per g soil. All vials were sealed immediately after flooding and placed on a shaker in a dark incubator (25 C). Each sampling withdrew a proportional (soil:solution) sample of 15 ml.

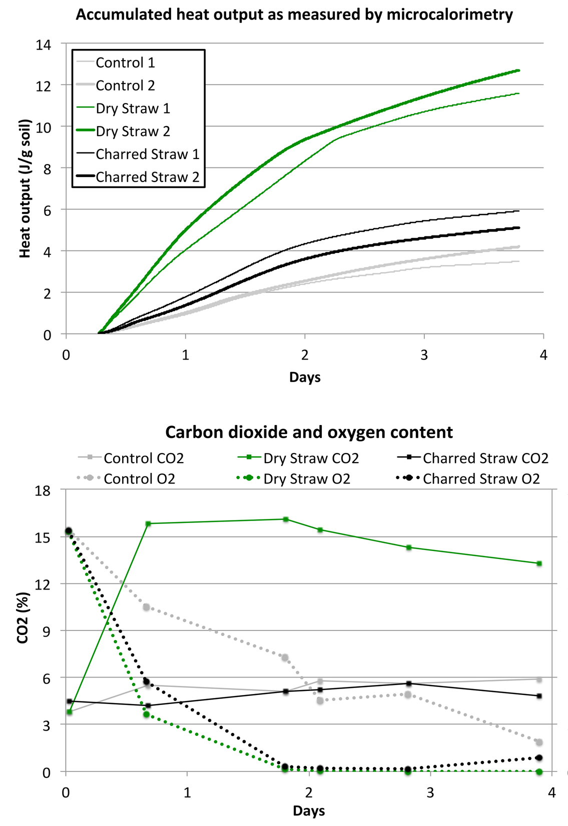


Figure 3. Microbial activity, estimated by a) heat output (J/g soil) (using isothermal micro-calorimetry) and b) O_2 depletion/CO_2 production (using *in situ* optical spot sensors), in 4 g of dry soil K, flooded with 15 ml TRIS buffer (10 mM, pH 7.0), amended with dried or charred rice straw or un-amended. 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 S (7.7 µg S/g soil, as in batch experiment), 2 – same amount of C (9 mg C/g soil).

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.

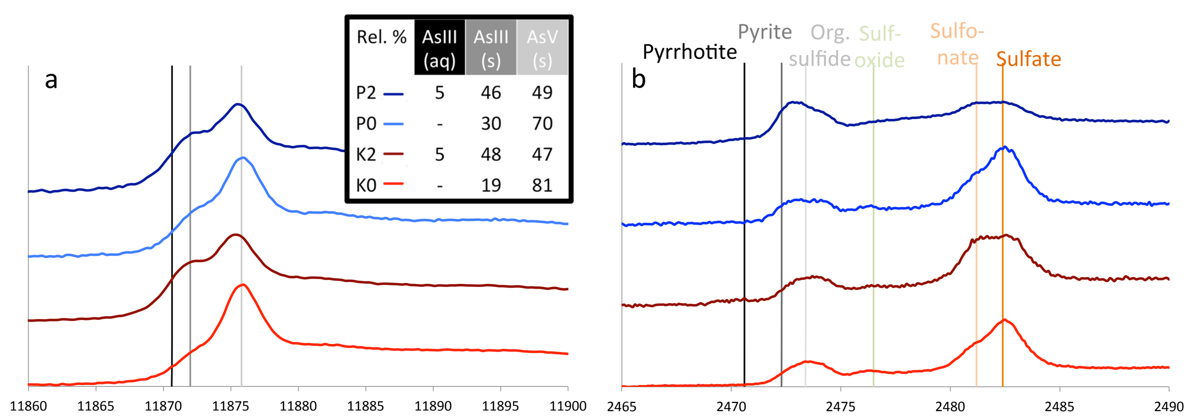


Figure 4. Arsenic (a) and sulfur (b) speciation in soils P and K before (0) and after (2) 53 days of flooding with DI water in unplanted pots amended with 1% dried rice straw.