Arsenic Dynamics in Porewater of an Intermittently Irrigated Paddy Field in Bangladesh

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Supplementary Information
(9 pages, 7 figures)

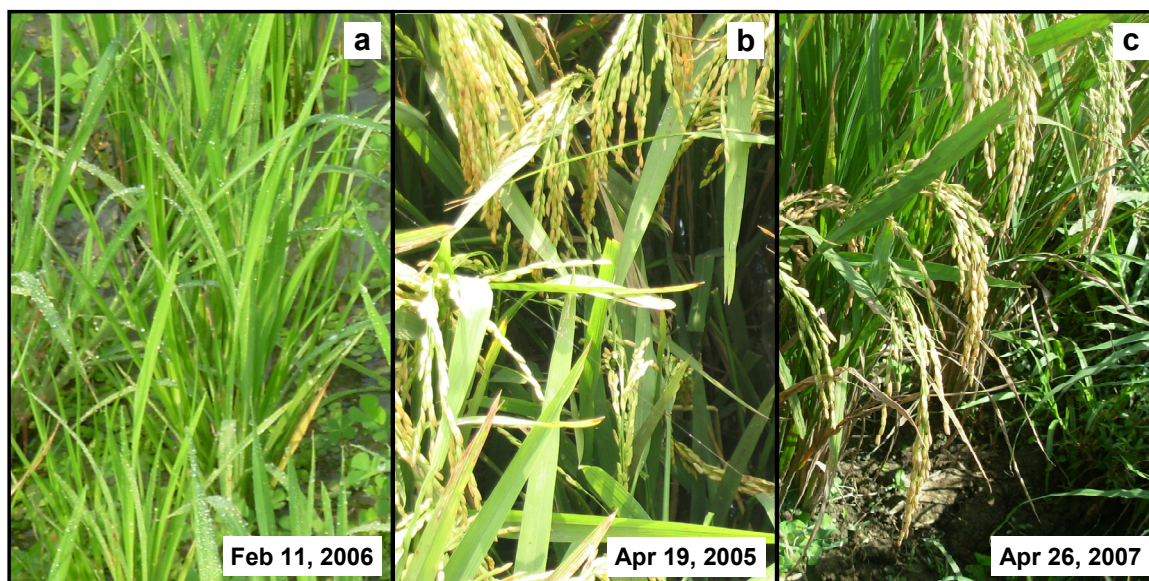## 1. Rice growth stages during porewater sampler deployment

Figure S1 Rice growth stages at times of porewater sampler deployment. (**a**) Vegetative stage (February 2006); (**b** & **c**) Grain-filling stage (April 2005 & 2007). The pictures were taken on the days on which the porewater samplers were recollected.

2. Details of porewater sampler deployment

The porewater samplers, described in detail in *(1)*, contain horizontal rows of 5-6 cylindrical cells of 2.5 mL volume filled with high purity deionized water (Millipore, 18 MΩ cm) and covered by 0.2-μm polysulfone membranes (Pall, USA). The samplers were assembled and deoxygenated for at least 72 hours *(1)* and transported to the field in oxygen-impermeable aluminium-coated polyethylene bags (Isco, Switzerland). Upon retrieval from the soil, samplers were rinsed with low conductivity bottled water (Fresh Water, Bangladesh, 73 μS cm-1) and sampled within 2-3 hours using syringes to extract the soil solution from the sampler cells. In April 2007, sampling was carried out under N_2-atmosphere as described in *(1)*. Mixed samples from each row were divided into three subsamples added to pre-acidified polyethylene vials (pH 2, HCl) (i) directly, (ii) after 0.2-μm filtration, and (iii) after filtration through a 0.2-μm filter combined with a modified As speciation cartridge *(2)*.

3. Colloid formation within porewater samplers and presence of brown precipitates
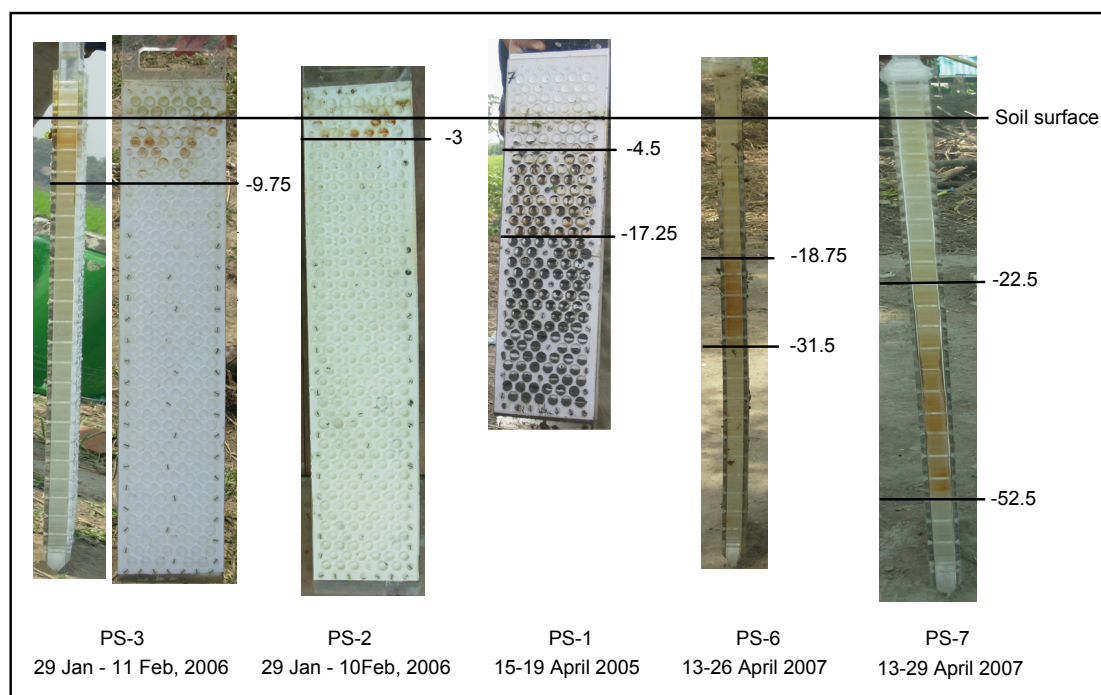

Figure S2 Porewater samplers deployed during the irrigation season showing depth ranges (in cm) in which brown precipitates formed in situ. The photographs shown were taken immediately upon retrieval of the samplers from the soil (PS-1, 6 & 7), or after the samplers had been rinsed to remove soil particles (PS-2 & 3; precipitates already visible prior to rinsing).

Since sampler cells were covered by 0.2 μm-membranes, discrepancies between unfiltered and filtered samples indicate the formation of colloids within the sampler. Sampling of the porewater profilers, which required between 2-3 hours each time, was carried out under ambient atmosphere in all cases except April 2007. The presence of Fe colloids in sampler cells is therefore not exclusively attributable to colloid formation during sampler deployment, but also reflects Fe^{II} oxidation, leading to Fe^{III}(hydr)oxide formation, due to oxygen diffusion across the sampler membranes during the sampling process. By contrast, the brown precipitates visible on the membranes and inside the sampler chambers upon sampler retrieval (Figure S2) identify depth ranges in which Fe^{III}(hydr)oxide particles formed in situ. We therefore utilize the presence of brown coloration rather than the presence of a colloidal Fe fraction in porewater samples to identify depth ranges in which Fe^{II} oxidation occurred while the samplers were in the soil.

Since the formation of Fe colloids can also affect the speciation of other elements, we base our discussion of porewater profiles mainly on total element contents, but utilize speciation data in the case of As and Mn. We justify these exceptions in the following.

Due to partial oxidation of As^{III} by reactive intermediates formed in the reaction of Fe^{II} with oxygen *(3)*, Fe oxidation also impacts As speciation. Our data may therefore slightly underestimate the As^{III}/As^{III+V} ratio in porewater. However, the extent of As^{III} oxidation expected does not affect the trends described *(4)*. Likewise, our data may slightly underestimate the fraction of dissolved porewater As, due to As sorption to Fe colloids during the sampling process. Considering the high P/As-ratios measured in porewater, the effect on As speciation is however likely to be negligible *(4)*.

Mn concentrations measured in unfiltered and filtered porewater samples coincided within measurement error, indicating that Mn was exclusively present as dissolved species in the sampler cells. Mn speciation changes related to Fe oxidation during the sampling process could therefore be excluded.

4. Porewater profiles in Field I, inlet corner, in April 2005 and April 29, 2007

Figure S3 Porewater profiles obtained near the irrigation inlet of field I on 19 April 2005 (Sampler PS-1, (**a-e**)) and 29 April 2007 (Sampler PS-7, (**f-j**)). (**a**, **e**) As(tot), As(diss) and As^{III}(diss); (**b**, **f**) Fe(tot) and S(tot); (**c**, **g**) Mn(tot) and P(tot); (**d**, **h**) Ca(tot) and Si(tot). The plow pan is indicated by a hatched bar and the depth ranges in which brown precipitates were visible are shaded in brown.

Whilst the porewater samplers were in general deployed over a period of ~2 weeks (12-16 days), sampler PS-1, deployed in April 2005, remained in situ for only 5 days. Consistent with the shorter period of deployment the brown coloration on the membrane of this sampler was less intense than in the case of the other samplers (compare Figure S2). The presence of brown coloration on the April 2005 sampler should be interpreted with caution. The samplers deployed in April 2007 also displayed a slight brown coloration in the depth range above the plow pan, which was however much less pronounced than the distinct band of brown precipitates observed at greater depth (Figure S2). The slight brown color observed between 4.5 and 16.5 cm depth on the April 2005 sampler may reflect oxidation of freshly infiltrating irrigation water (as probably also occurred in the April 2007 samplers) rather than a shift from a reducing to an oxidizing soil regime in this depth range. The porewater profiles obtained in April 2005 reveal that an oxidizing soil regime prevailed above the plow pan in mid-April 2005.

5.   Lateral heterogeneity

5.1. Molar ratios of As/Fe, P/Fe and As^{III}/Si in porewater at the near inlet and far corner location
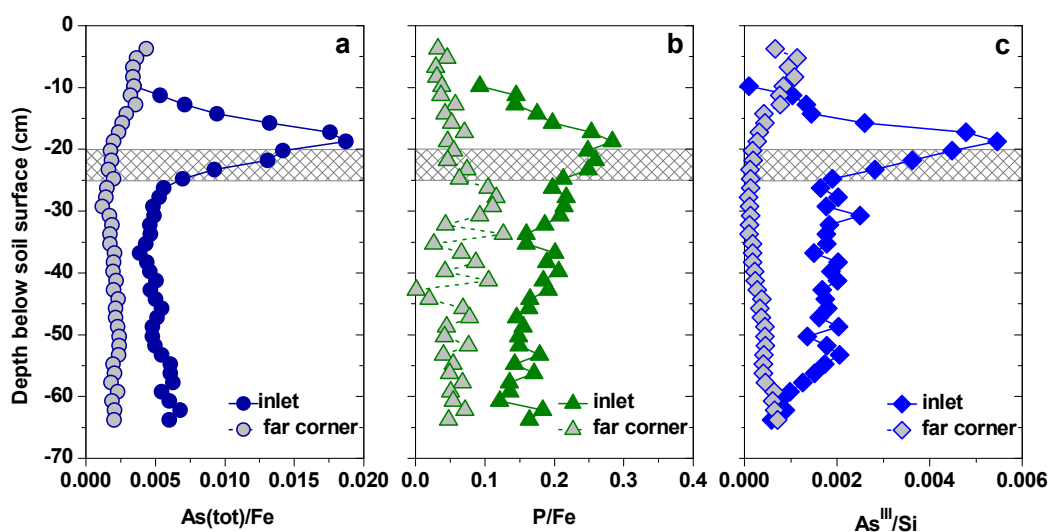

Figure S4 Comparison of molar ratios in soil porewater obtained in the vicinity of the irrigation inlet and in the far field corner. The samplers were retrieved on February 11, 2006 (PS-3, inlet location) and February 10, 2006 (PS-2, far corner), respectively. (**a**) As/Fe; (**b**) P/Fe; (**c**) As^{III}/Si. Data points from the top centimeters of soil in which the samplers displayed brown precipitates were excluded.

5.2. Molar ratios of As/Si in rice straw and grain along a transect across the study field
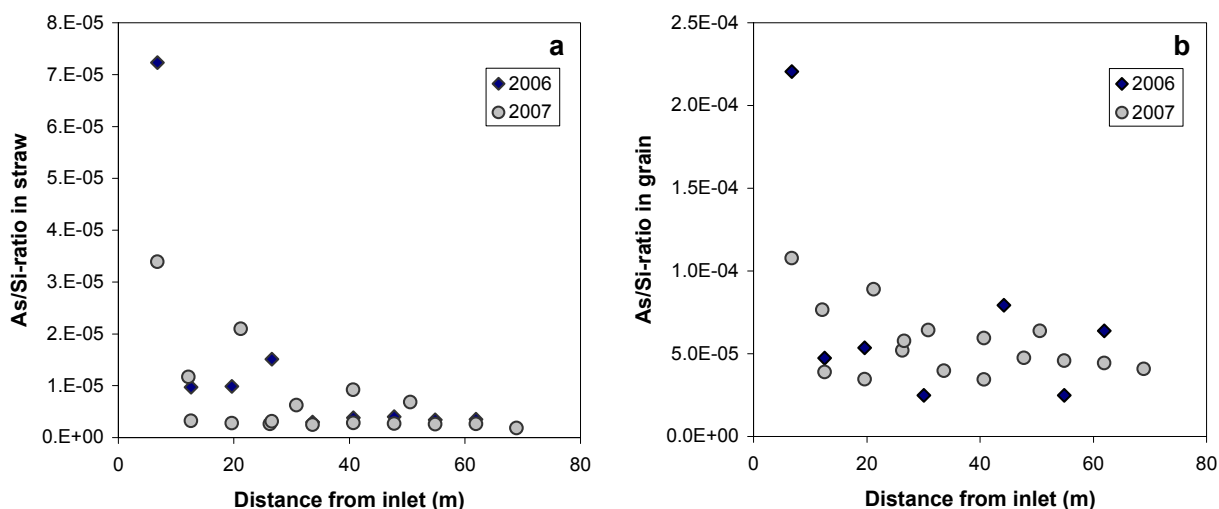

Figure S5 As/Si ratios in straw (**a**) and grain (**b**) of rice plants sampled along a transect across field I in May 2006 and 2007 *(5)*, plotted versus distance from the irrigation inlet. As and Si contents in straw were determined from samples collected at 9 points in 2006 (no replicates), and in samples from 16 points (13 points: 4 As replicates, no Si replicates; 3 points: 4x4 As replicates, 4 Si replicates) in 2007. As and Si contents in grain were determined from samples collected at 9 points in 2006; As contents were determined for each point separately, whereas for Si analysis, samples from 4 points were pooled into 2 groups comprising 2 points each (distance between grouped sampling points 7 m). In 2007, As and Si contents in grain were determined in 16 points (13 points: 4 As replicates, no Si replicates; 3 points: 4x4 As replicates, 4 Si replicates). Where applicable (points with sample replicates), average As and Si values were used to calculate As/Si ratios. Si grain contents determined in pooled samples (2006) were related to average As grain contents from the pooled sample locations and plotted versus the average distance of the pooled points from the inlet.

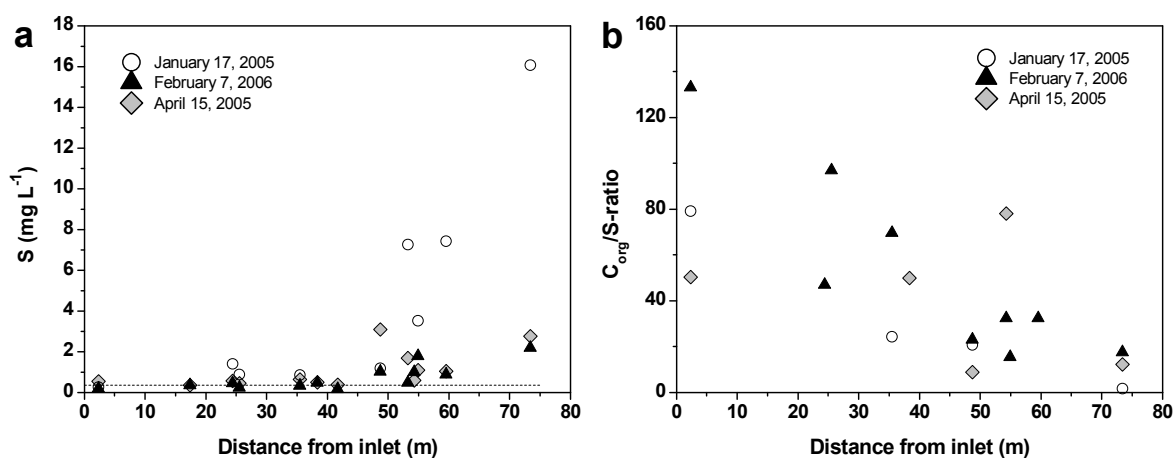## 5.3. Lateral S distribution in irrigation water on the study field

Figure S6 (**a**) Total S concentrations in field water sampled on the study field shortly after irrigation events in January 2005, February 2006 and April 2005 plotted as a function of distance from the irrigation inlet. For comparison, the dotted line shows S concentrations in the irrigation well water. (**b**) C_{org}/S-ratios in field water after the same irrigation events. The decrease in C_{org}/S-ratios with increasing distance from the inlet shows an overproportional increase of S concentrations with respect to organic carbon. This demonstrates that the S present in irrigation water was not primarily constituted by organic S and was therefore most likely sulfate.

6. Porewater dynamics below the plow pan

Elevated Fe and Mn concentrations in the porewater, and the presence of As^{III} as the predominant As species, revealed reducing conditions at varying depths below the plow pan (Figures 2 & S3). The samplers deployed in February 2006 and April 2005 suggest that conditions were reducing from the plow pan down to the maximum depth sampled (65 and 40 cm, for February and April, respectively). Toward the end of the growing season O_2 penetrated to below the plow pan, as evidenced by the presence of brown precipitates in the samplers deployed in April 2007 (Figure S2), and reducing conditions were found at greater depth (Figure 2 & S3). The porewater data obtained below the plow pan need to be interpreted with caution, however. Insertion of the porewater samplers may have injured the plow pan and given rise to preferential flow along the outside of the samplers in the sub-plow pan depth range. This may have created locally saturated and therefore reducing conditions in an otherwise oxidized soil matrix. Preferential flow along the samplers could also account for the discrepancy between the porewater As concentrations we measured below the plow pan, and the lower As concentrations reported from the sub-plow pan depth range of a neighboring field *(6)*.

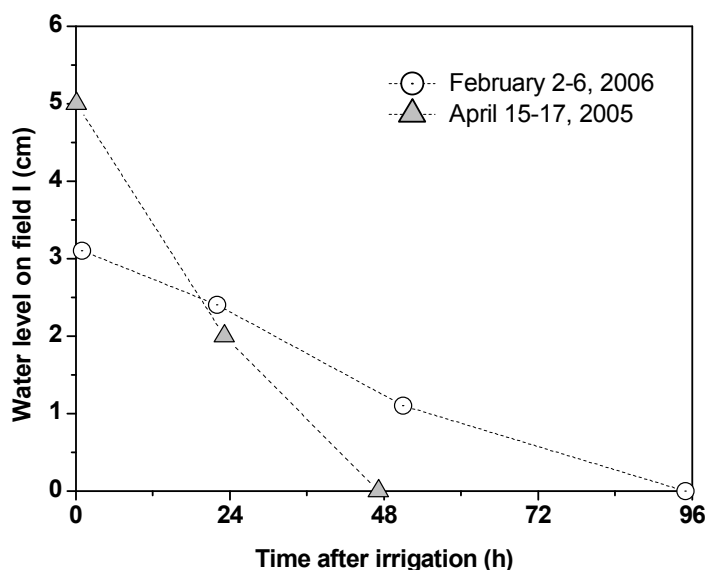## 7. Water level decrease after irrigation events

Figure S7 Water level decrease on field I after single irrigation events in February 2006 and April 2005. Water level was monitored in the corner of field I close to the irrigation inlet. Irrigation events lasted 2.5 hours in February and 3 hours in April 2005. There was no rainfall during February 2-6, 2006 or April 15-17, 2005 (as recorded at Bhagyakul Meteorological Station, 7 km southwest of the field site). Although more irrigation water was applied in April, water level decreased more rapidly than in February. After an irrigation event on April 14, 2007, the soil surface was exposed to air within 24 hours after irrigation (water level on field immediately after irrigation not recorded).

8. Estimation of vertical As translocation by infiltration

At the inlet-near location, porewater As concentrations just above the plow pan were around 390 ± 43 μg L^{-1} in February (average±standard error of concentrations measured between 15.75 and 20.25 cm depth). We assumed this As concentration to be representative of the period during which reducing conditions prevailed in the bottom part of the soil above the plow pan. For this time period, we estimated daily As loss via infiltration across the plow pan by multiplying the measured porewater As concentrations with the infiltration rate of 0.35 ± 0.1 cm d^{-1} derived in a rice paddy adjacent to our study field *(7)*. The infiltration rate was determined at the beginning of the irrigation season and represents the sum of matrix infiltration and preferential flow *(7)*. We assume that immediately above the plow pan, conditions were reducing and As was released over the initial two thirds of the irrigation season. This represents a rough estimate which is supported by porewater data collected at 30 cm depth in the neighboring field studied by Neumann et al., 2010 *(6)*. This data suggest that soil redox conditions just below the plow pan remained reducing until the beginning of April. We thus estimate that over the irrigation season 110 ± 40 mg m^{-2} As were lost from the 10-25 cm segment by infiltration. In the 10-25 cm depth interval, soil As contents did not display a

pronounced spatial gradient across the field (unpublished data). For the purpose of the rough infiltration loss estimate, we therefore assumed As mobilization, and hence translocation to depth by infiltration determined near the inlet to be representative of the entire field.

9. References

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