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Organic Matter—Solid Phase Interactions Are Critical for Predicting Arsenic Release and Plant Uptake in Bangladesh Paddy Soils

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S *Supporting Information*

ABSTRACT: Agroecological zones within Bangladesh with low levels of arsenic in groundwater and soils produce rice that is high in arsenic with respect to other producing regions of the globe. Little is known about arsenic cycling in these soils and the labile fractions relevant for plant uptake when flooded. Soil porewater dynamics of field soils ($n = 39$) were recreated under standardized laboratory conditions to investigate the mobility and interplay of arsenic, Fe, Si, C, and other elements, in relation to rice grain element composition, using the dynamic sampling technique diffusive gradients in thin films (DGT). Based on a simple model using only labile DGT measured arsenic and dissolved organic carbon (DOC), concentrations of arsenic in Aman (Monsoon season) rice grain were predicted reliably. DOC was the strongest determinant of arsenic solid-solution phase partitioning, while arsenic release to the soil porewater was shown to be decoupled from that of Fe. This study demonstrates the dual importance of organic matter (OM), in terms of enhancing arsenic release from soils, while reducing bioavailability by sequestering arsenic in solution.

■ INTRODUCTION

Producing safe and nutritious foods in ever-greater quantities is a major global priority.[1] Arsenic contamination of food crops threatens this goal, with small, yet prolonged doses of this element via the daily rice meal being a serious public health concern for some parts of Asia.[2] This scenario is epitomised in the Bengal delta, where burdens from rice are significant, and, even for those drinking arsenic elevated water, account for ca. 50% of the total intake.[2] The food security issue is compounded further, as arsenic can perturb rice growth; severely diminishing harvested yields,[3] while simultaneously reducing the concentration of essential mineral nutrients in the grain.[4]

The agricultural lands in parts of south-central Bangladesh have been severely degraded as a consequence of irrigation with arsenic enriched groundwaters used in irrigation of paddy fields.[5] Yet, elevated arsenic in rice grain is a problem not confined to this region or just to soils most greatly impacted by arsenic in irrigation waters. Lu et al.[6] demonstrated that even baseline concentrations (averages between 1.6 and 6.6 μg As g^{-1}, depending on soil type) in Bengal delta soils can be problematic, probably due to naturally high arsenic bioavailability[6,7] combined with rice's highly efficient shoot arsenic assimilation and the effective transfer of this arsenic to the grain when shoot tissue content is low.[8]

Gauging the ability of Bangladesh soils to produce low arsenic rice grain is of paramount importance. Soil porewater and chemical extraction techniques have not proved useful in this task.[7] A holistic approach which has had documented success in monitoring element availability in flooded soils is DGT.[9,10] The DGT measurement integrates a wider range of key soil properties

that impact on release/adsorption than other single measurement approaches.[9] Importantly, it emulates the dominant processes occurring in soils during plant uptake by lowering the solute concentration locally and inducing diffusive supply and release from complexes and the solid phase.[9] Although DGT has not previously been used to investigate arsenic uptake in rice, DGT devices with ferrihydrite as the binding phase have been shown to be effective for measuring both arsenate and arsenite species.[11,12] Laboratory soil measurements by DGT have been shown to be a robust predictor of cationic metal concentrations in field cultivated rice.[10] The DGT measurements outperformed soil solution, acetic acid, and calcium chloride extractions in their capacity to explain rice root and grain metal variability.

Element release from Bangladesh paddy soils is only understood in the general sense, with arsenic mobility in most soils being governed by reductive dissolution of Fe(III) hydroxides, and hence redox conditions and the reactivity of the Fe(III) phases. However, as metal oxides have a strong affinity with OM, due to ligand exchange reactions with COOH and phenol/catechol OH functional groups, they can compete with arsenic for absorption sites.[13−15] Additionally, adsorption affinities can be affected by OM mediated change in redox conditions, thus favoring arsenic transport.[15] OM and dissolved OM-Fe complexes also bind arsenic, which may promote desorption of

arsenic from solid phases by altering soil/solution equilibrium, while simultaneously impacting on bioavailability.[16−18]

OM release in wetland soils during flooding events can be substantial, with OM desorption processes tending to occur faster and in less reducing conditions than Fe(II) release.[19] This is largely because as redox potentials drop, pH has a tendency to increase, due to the consumption of H^+.[20] This changes OM mobility, causing the positive charge at mineral surfaces to weaken while concurrently heightening the electronegativity of organic moieties, resulting in a repulsion of OM and soil.[19] There has been increasing importance placed on OM in determining arsenic behavior within soil environments.[17,18,21] As yet, however, the extent and role that OM plays in arsenic bioavailability in Bangladesh paddies is poorly understood, despite there being the potential for high organic carbon inputs within rooting zones in Bengal delta paddy soils.[22]

The aim of this study was to assess if rice grain arsenic concentrations can be predicted effectively using DGT and to explore the impact of OM on soil arsenic release and grain arsenic concentrations. To achieve this we used a broad selection ($n = 39$) of Bangladesh rice paddy soils and associated rice plants, spanning a range of physiographic soil areas, typified by low total soil arsenic concentrations (i.e., from agronomic zones where irrigation water is low to moderate in arsenic), but with elevated grain arsenic levels.

■ MATERIALS AND METHODS

Field Sites. Seven upazilla (Chandpur, Matlab, Natore, Kahalu, Gouripur, Sripur and Rangpur) encompassing the main rice agroecological zones within Bangladesh were selected for this study[23] (Supporting Information (SI) Figure S8). The sampling campaign ran over two consecutive rice cropping seasons. The first was for Boro rice (pre-monsoon), employing BRRI dhan 28/29 cultivars. The second applied to monsoon season Aman rice using a variety of commonly grown rice cultivars. Plant material and soils were obtained following protocols documented in Adomako et al.[24] Soils were collected when Boro rice was harvested and represented intermediary time points between the two cropping seasons. Soils and grain were air-dried in Bangladesh, prior to transportation to the UK for further processing.

Grain and Soil Sample Preparation and Analysis. Grain was dehusked, oven-dried and whole rice samples (0.2 g) were weighed into 50 mL polyethylene centrifuge tubes and digested with concentrated HNO_3.[4] For soils, 0.1 g of dried and sieved soil (<2 mm) were weighed into 50 mL polyethylene centrifuge tubes, predigested overnight in 2.5 mL of concentrated HNO_3, then mixed with 2.5 mL of H_2O_2 and digested for 90 min at 95 °C using microwave-assisted digestion.[24]

DGT. This study used cylindrical DGT piston devices with an exposure window of 2.54 cm^2. Diffusive gel (0.8 mm) overlaid a 0.4 mm ferrihydrite binding gel prepared by in situ precipitation (SI Figure S1 and S2).

Anaerobic (O−) DGT Assay. Air-dried and 2 mm-sieved soil samples (ca. 50 g, $n = 39$) were wetted to 60% maximum water holding capacity (MWHC) and incubated for two days, as recommended by Zhang et al.[9] They were then transferred into small cylindrical lidded dishes (50 mm × 20.3 mm), raised to 90% MWHC and sealed with parafilm tape for 24 h. The soils (in duplicate) were then placed into purpose built polypropylene chambers (90 mm × 55 mm) (SI Figure S3) that were purged with 99.99% pure argon gas for 10 min. After oxygen had been driven out of the system, the soil/chamber assemblages were randomized and located within sealed gas purging vessels. Each vessel (400 × 300 mm), accommodated four soils, and was individually constructed from heavy gauge polyethylene plastic, featuring two self-sealing rubber septums for the in/outlet gas lines. At all times the vessels were continually purged with argon gas. The resulting positive pressure of each bag was individually monitored and optimized. Soils were conditioned for a period of two weeks, at which point the purging vessels were transferred into a nitrogen filled anaerobic glovebag (94 × 94 × 64 cm) for subsequent deployment of DGT.

Inside the anaerobic glovebag, the soil/chambers were dismantled, and resazurin anaerobic indicator strips (Oxoid) were used to monitor oxygen. All DGT devices were degassed with nitrogen for 24 h in a clean 0.01 M NaCl solution prior to deployment. A detailed record of the diurnal temperatures was achieved with a series of data loggers (StowAway Tidbit). After deployment, soil/DGT/chambers were again placed in the purging vessels and flooded with argon gas for the duration of the experiment (t = ca. 24 hrs). For the retrieval, all chambers were moved back into the anaerobic glovebag. DGT devices were sequentially collected. The ferrihydrite binding gels were removed from the DGT devices, and placed in 1.5 mL PVC tubes containing 1 M HNO_3 for 24 h to elute the bound arsenic before dilution and analysis. After DGT retrieval, soil slurries (ca. 45 cm^3) still contained in the anaerobic glovebag were transferred into 50 mL centrifuge tubes, then spun at 5000g for 15 min to extract the porewater. The resulting soil solutions were then filtered through 13 mm diameter, 0.45 μm polysulfone filters and further divided into batches; one of which was acidified to 0.1 M HNO_3 for metal analysis; another used for DOC measurements.[25] Finally, a subset of the twenty porewaters obtained from the most arsenic problematic floodplain soils were speciated for arsenic. These samples were diluted with a phosphate-EDTA buffer solution (2 mM NaH_2PO_4 and 0.2 mM Na_2EDTA, pH 6.0),[26] prior to freezing and transport to the University of Aberdeen for analysis.

Aerobic (O+) DGT Assay. The standard DGT soil deployment assay was used for a subset of thirty soil samples, ten from each of the three districts (Natore, Rangpur and Gazipur). The selection criteria ensured that the soils had the greatest range of corresponding grain arsenic and porewater DOC concentrations as possible, and reflected a variety of agroecological zones. Apart from the anaerobic soil incubation period, the only major difference from the anaerobic assay was that deployments were conducted in triplicate: hence the starting weight of dry soil was increased to ca. 80 g.

Chemical Analysis. Arsenic detection, speciation and trace metal characterization. ICP-MS (Thermo Elemental X7) was used to determine arsenic in DGT and porewater samples. Grain, irrigation water and soil samples were analyzed using an ICP-MS 7500c (Agilent Technologies). Soil solution matrixes were modified to a final concentration of 2% MeOH. Arsenic in the porewaters was speciated using HPLC-ICP-MS (HP1100 HPLC coupled with ICP-MS 7500c Agilent Technologies).[7] *Major plant nutrients,* Ca, Fe, K, Mg, Mn, P, and Si, were measured using an ICP-OES ICAP 6000 (Thermo Elemental). *Dissolved organic carbon concentration,* [DOC], was quantified in extracted porewater samples using UV absorption on an Agilent 8453 diode array instrument.[25] *Soil pH,* was measured both in extracted porewaters and in a soil: water ratio (1:2.5), after letting the solution equilibrate for 60 min.

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Quality Control. Matrix matched reference materials, spikes and blanks were analyzed with each analytical batch. Arsenic recoveries for NIST 1568a rice flour for the Boro and Aman rice analysis was 92% and 86% respectively. Soil arsenic CRM (NCS ZC73007) recoveries averaged 58%, while accompanying groundwater CRM (BCR CRM 610) recoveries for irrigation water analysis averaged 101%. For DGT and soil porewaters, mean arsenic and Fe recoveries for river water CRM (SLRS-5) were 91% and 99%, respectively. Suwannee river humic acid standards were run every tenth sample and recoveries averaged 101%. Every 10th sample was analyzed in duplicate.

Calculating DGT labile arsenic. DGT labile arsenic ($^{As}C_{DGT}$) was calculated using eq 1.

$$^{As}C_{DGT} = M \times \Delta g / (D \times A \times t) \tag{1}$$

The mass accumulated on the binding gel is M, Δg is the thickness of the diffusive gel layer (0.8 mm) plus the thickness of the filter membrane (0.13 mm), A is the surface area (2.54 cm^2), t is the deployment time and D is the diffusion coefficient of arsenic in the gel. D was calculated using temperature corrected diffusion coefficients for arsenite/arsenate mixtures.[11]

Calculating Effective Arsenic Concentrations from DGT. Effective arsenic concentration ($^{As}C_E$) is calculated from the DGT measurement and includes both the soil solution concentration and an additional term, that represents metal supplied from the solid phase.[9]

The DGT measured concentration in a soil, $^{As}C_{DGT}$ can be converted to $^{As}C_E$ using eq 2

$$^{As}C_E = {}^{As}C_{DGT}/R_{diff} \tag{2}$$

R_{diff} is the ratio of $^{As}C_{DGT}$ to the soil solution concentration when supply to the DGT device is slowly by diffusion. It was calculated using the numerical model of the DGT-soil system DIFS (DGT induced fluxes in soils). Input values were calculated using eqs 3, 4, and 5:

$$P_c = m/V \tag{3}$$

$$\varphi = d_p/(P_c + d_p) \tag{4}$$

$$D_s = D_0/(1 - \ln \varphi^2) \tag{5}$$

The total mass of soil particles is m, V is the pore water volume in a given volume of soil, and d_p is the density of the soil particles, which in this model was assumed to be 2.65 g cm^{-3}. The terms D_s and D_0 are the diffusion coefficient in soil and water, respectively. The ratio (^{As}R) of the DGT measured concentration ($^{As}C_{DGT}$) to the bulk concentration in soil solution ($^{As}C_{sol}$) (see eq 7) reflects the extent to which there is dynamic resupply from the soil solid phase:

$$^{As}K_d = \text{total soil}[As](\mu g \ kg^{-1})/^{As}C_{sol}(\mu g \ L^{-1}) \tag{6}$$

$$^{As}R = {}^{As}C_{DGT}/^{As}C_{sol} \tag{7}$$

Where no resupply from soil to solution occurs ^{As}R is termed R_{diff} because the supply to the DGT is solely by diffusion. The 2D DIFS model[27] was used to calculate the soil specific R_{diff} values.

Statistics. Principle component analysis (PCA), analysis of variance (ANOVA), t tests, multiple regression analysis and correlations were performed using Minitab 15 Statistical Software. PCA analysis utilized 17 multielement characteristics (Al, As, Ca, Cd, Co, Cu, DOC, Fe, K, Mg, Mn, Ni, P, Pb, Se, Si, Zn) obtained from the anaerobic soil porewater.

■ RESULTS AND DISCUSSION

Soil Groupings. By simulating the conditions of a flooded paddy soil within the laboratory under standardized conditions it was possible to observe the variation in metal release trends between the soils. PCA (SI Figure S9) was successful in resolving these differences; 78.5% of the variance was explained by the first and second components, with arsenic concentration the best single element factor of the second component ($R^2 = 0.81, p < 0.001$). Physiomorphic soil origins were unable to resolve fully the PCA analysis groupings, suggesting other factors, such as field management, contribute to the element mobilization trends. The soils from the seven upazilla were, however, successfully classified into three groups based on porewater composition and upazilla: α^{soil}, Meghna river floodplain, comprising of soils from the southeastern upazillas Matlab and Chandpur; β^{soil}, Barind tract soils from Natore and Kahalu, along with old Brahmaputra floodplain soil from Gouripur; χ^{soil}, Madhupur tract soil samples from Sripur and Tista floodplain samples from Rangpur[23] (SI Figure S8).

Grain Arsenic Concentrations. The concentrations of arsenic were higher in Boro rice than the corresponding Aman crop ($^{Paired \ t \ test} \ p < 0.001$). α^{soil} and β^{soil} regions had higher concentrations than χ^{soil} sites: a trend common to both cultivation seasons (Table 1). The average concentration of arsenic in Bangladesh rice is ca. 0.13 $\mu g \ g^{-1}$ dry wt. [2,28,29] Median lifetime cancer risks estimated for a Bengali diet based on cooked rice equivalents of this average were predicted to be higher than the range typically used by the U.S. Environmental Protection Agency as a threshold level.[2] In this investigation, 70, 65, and 42% of the Boro rice from the α^{soil}, β^{soil}, and χ^{soil} groups, respectively, exceeded 0.13 $\mu g \ As \ g^{-1}$, despite arsenic concentrations in the corresponding soil samples being below country norms.[4−6] In the Aman season, 90% of the α^{soil}, 30% of β^{soil} and none of the χ^{soil} produced rice exceeding this level.

Irrigation Water and Paddy Soil Arsenic. Arsenic concentrations in the α^{soil} irrigation water surpassed the other sites (mean =148 $\mu g \ L^{-1}$), and the soils possessed the highest arsenic content (mean = 5.8 $\mu g \ g^{-1}$) (Table 1). In contrast, irrigation water arsenic levels from the remaining two groupings were considerably lower, averaging <10 $\mu g \ L^{-1}$. Soil arsenic concentrations varied, however, with the β^{soil} samples exhibiting a mean of 2.7 $\mu g \ g^{-1}$, while χ^{soil} had ca. half this amount (Table 1).

Porewater Arsenic, R, C$_E$, and DOC Concentrations. Porewater arsenic concentrations were highest in α^{soil} (36 $\mu g \ L^{-1}$), but were also highly variable, and although the mean concentration was greater than for β^{soil}, sample distributions were comparable (Figure 1). During anaerobic incubation, both α^{soil} and β^{soil} had considerably more solution phase arsenic, than χ^{soil} which averaged <10 $\mu g \ As \ L^{-1}$. However, a greater proportion of the total As content present in the χ^{soil} was mobilized to the porewaters (see eq 6), with median $^{As}K_d$ values being ca. 3-fold lower than α^{soil} and slightly less than β^{soil} (Table 1).

The mean R_{diff} value for all the samples was 0.08 $\pm$ 0.004. In none of the anaerobic samples was the resupply of arsenic sequestered by the DGT device sufficient to sustain solution phase concentrations matching that of the initial porewater concentration. However, resupply (i.e., $^{As}R > R_{diff}$) was partially sustained in 90% of the samples (Figure 1). β^{soil} recorded the highest ^{As}R values (Table 1). χ^{soil}, exhibited poor dynamic

Table 1. Grain, Soil and DGT Characteristics[a]

		α^{soil} ($n = 12$)	β^{soil} ($n = 17$)	χ^{soil} ($n = 10$)
		Rice Grain [As]		
[As] Boro	mean	0.18	0.18	0.15
grain	max	0.32	0.45	0.27
(μg g^{-1})	min	0.10	0.02	0.03
[As] Aman	mean	0.17	0.11	0.07
grain	max	0.23	0.25	0.12
(μg g^{-1})	min	0.11	0.03	0.03
		Soil and Water [As]		
[As] soil	mean.	5.8	2.7	1.2
(μg g^{-1})	(stdev.)	(3.0)	(1.0)	(0.5)
irrigation water	mean.	148	5	8
(μg As L^{-1})	(stdev.)	(111)	(9)	(7)
porewater	mean.	36	23	9.2
(μg As L^{-1})	(stdev.)	(38)	(23)	(5)
$^{As}C_E$	mean.	128	103	17
(μg L^{-1})	(stdev.)	(179)	(157)	(14)
$^{As}C_{DGT}$	mean.	10.7	8.4	1.4
(μg L^{-1})	(stdev.)	(15)	(13)	(1)
R	mean.	0.22	0.31	0.15
	(stdev.)	(0.1)	(0.2)	(0.1)
soil [pH]	mean.	6.7	6.3	5.2
	(stdev.)	(0.1)	(0.2)	(0.1)
		OC and $^{As}K_d$		
[DOC]	median	25	69	106
(mg L^{-1})				
^{As}Kd	median	353	130	120
(L kg^{-1})				

[a] Data for porewaters, DGT. DOC, and As Kd were all obtained from anaerobic soils. α^{oil} = Matlab and Chandpur. β^{oil} = Natore, Kahalu and Gouripur. χ^{soil} = Sripur and Rangpur.

release, shown by low ^{As}R values that were consistent with low $^{As}K_d$ values, which indicate a small pool of arsenic available for resupply. The χ^{soil} samples had lower values of $^{As}C_E$ and $^{As}C_{sol}$ than from α^{soil} and β^{soil} (Table 1). The difference was more pronounced for $^{As}C_E$, with concentrations in the α^{soil} and β^{soil} being ca. 6–7 fold higher than the χ^{soil}, due to the poorer contribution from the solid-phase labile pool of χ^{soil}.

DOC concentrations varied significantly between groupings ($^{ANOVA\ on\ ranked\ data}$ $p = 0.001$). χ^{soil} contained the highest DOC, averaging 117 ± 68 mg L^{-1}, with values ranging from 23 to 265 mg L^{-1}. The average DOC concentration in the β^{soil} were ca. one and a half-fold lower than the χ^{soil} samples, yet the range still spanned 175 mg L^{-1}. Considerably less DOC was measured in the α^{soil}; the mean was 33 mg L^{-1}, with 50% of the samples recording values less than 20 mg L^{-1}. A recent study of waters collected from paddy soils in the Bay of Bengal delta found similar concentrations of 57–128 mg L^{-1} ($n = 8$).[22] Total organic soil carbon levels were within ranges reported for Bangladesh paddy soils,[7] yet poorly explained DOC trends ($R^2 = 0.02$, $p = 0.368$). Linkages were apparent though, particularly for fertilizer regime, and cow dung application, with the χ^{soil} average cow manure inputs being nearly five times that of the other groups.

DOC has a strong potential to mobilize arsenic in paddy fields,[21,22] which this study confirms, with increases in porewater arsenic being matched by concurrent rises in DOC. Porewater arsenic when expressed against DOC convincingly segregated the 3 soil groupings. χ^{soil} exhibited the least responsive relationship to rising DOC concentrations, ($^{linear\ regression}$ $R^2 = 0.74$, $p < 0.001$; slope 0.06) (SI Figure S10). However, at the other extreme the α^{soil} was highly responsive ($^{linear\ regression}$ $R^2 = 0.72$, $p < 0.001$; slope 1.47).

Porewater Si also increased with DOC concentration. There was also differentiation based upon soil type, although χ^{soil} as opposed to α^{soil} and β^{soil} samples exhibited a more acute rise in mobilized Si with increasing DOC (SI Figure S10). The relationship between the three soil sources was unified when $^{As}K_d$ was plotted against DOC, (Figure 2) ($^{linear\ regression}$ $R^2 = 0.77$, $p < 0.001$). In all samples, DOC concentrations exceeded that of Fe, with overall mean and median Fe:DOC ratios of 0.18 and 0.17 respectively. When porewater log $^{As}K_d$ was expressed against log porewater Fe, the relationship was significant ($^{linear\ regression}$ $p < 0.001$), but the R^2 was only 0.47, a drop of 30% in comparison with the regressions with DOC, suggesting arsenic mobilization by DOC is partly distinct from Fe(II) release.

Arsenic Speciation of Soil Porewaters. Samples for speciation were specifically selected from the α^{soil} and β^{soil} sites, as these areas possessed the highest soil arsenic concentrations (Table 1). The predominant species was arsenite, in keeping with other studies[7,26,30]. However, there were also appreciable amounts of arsenate, which represented around $^1/_3$ of the total inorganic fraction. Despite DOC influencing arsenite/arsenate interconversion[15], no relationship was found between the percentage of arsenate and DOC concentration ($^{linear\ regression}$ $R^2 = 0.04$, $p = 0.414$). Bangladesh rice grains tend to exhibit only low levels of mono- and dimethyl arsenic (MMA and DMA, respectively) (31), yet soil porewater speciation patterns revealed a relatively high proportion of organic arsenic moieties (26.8%), of which on average half was MMA and half DMA. DOC correlated strongly with total organic arsenic in the porewater ($^{Logged\ Data}$ $R^2 = 0.69$, $p < 0.001$) and unlike regression of total or inorganic arsenic and DOC, unified the 2 soil groups (SI Figure S11). This demonstrates soil source segregation is not originating from differences in organic arsenic mobilization per se; rather it is the variability in arsenite/arsenate release with DOC that is of importance.

Anaerobic (O$^-$) vs Aerobic (O$^+$) conditions. There were a number of critical changes in porewater composition and properties when soils became anaerobic. First, solution phase arsenic pools were considerably larger, with porewater concentrations in O$^+$ soils on average 5-fold less than their O$^-$ counterparts. Yet, this was highly dependent on district origins. For χ^{soil} from Rangpur and Sripur upazillas, arsenic concentrations from the O$^+$ treatments were 81% and 95% lower, respectively, than O$^-$ treatments (Figure 3). Soils from Natore upazilla, however, yielded comparable amounts of arsenic in both the O$^-$ and O$^+$ scenarios. Trends in DOC release were similar to those of arsenic, not just in O$^-$ conditions, as was the case with Fe, but also for O$^+$ conditions (Figure 3). Indeed, when O$^+$ $^{As}K_d$ was plotted against DOC, together with the data for the O$^-$ assays (Figure 2), regressions using the unified data (O$^+$ and O$^-$) were significant ($^{Logged\ Data}$ $R^2 = 0.80$, $p < 0.001$), bridging solid-solution phase partitioning in the different redox treatments.

Predicting Grain Arsenic Concentrations in Rice. In this investigation, attempts to predict Boro rice concentrations based
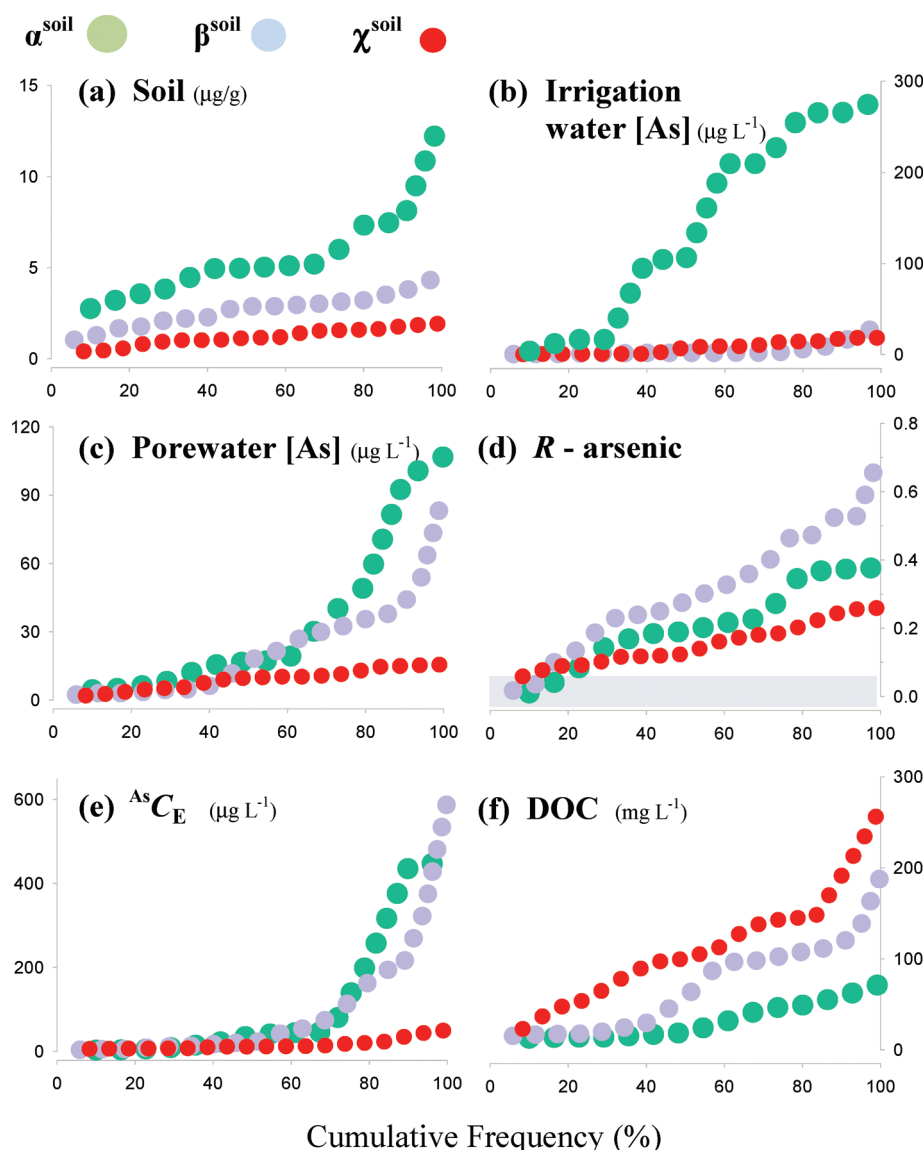
Figure 1. O⁻ porewater summary. Cumulative frequency distribution plots of (a) Soil [As] (b) irrigation water arsenic (c) porewater arsenic (d) R values − gray shading denotes R Diff. That is, no resupply of solutes to the pore water (e) $^{arsenic}C_E$ (f) DOM (O⁻ assay). $n = 39$. Soil groupings: α^{soil}, green dot; β^{soil}, blue dot; χ^{soil}, red dot.

on soil and porewater characteristics (no. of parameters = 21) proved unsuccessful. This finding is explainable, as Boro cultivation using tubewell irrigation inherently creates greater heterogeneity in both arsenic and redox gradients than other cropping practices.[32,33] A full comparison of all the regression combinations resulted in a maximum of only 57% of the variation being explained (SI Table S7), with the best single measurement for determining Boro grain arsenic being the concentration of arsenic in irrigation water ($R^2 = 0.102$; $p < 0.05$). In soils with relatively low soil arsenic contents, as in this study, it is reasonable that the grain arsenic should be affected by arsenic in the irrigation water.

It has been shown previously that arsenic levels in Aman rice reflect those of Boro, but at a lower concentration, with this pattern being most prevalent in areas with severe arsenic problems .[31] Yet, whether this phenomenon occurs at sites with low/marginal soil arsenic concentrations is less certain. In this study, there was no significant correlation between

the arsenic concentration in Boro and Aman rice ($R^2 = 0.16$, $p > 0.05$). Aman rice, where irrigation water is largely sourced from monsoon rains, was a much better candidate for a predictive soil assay. It was initially postulated that porewater Si concentrations would be an important factor, as the inhibitory effect of silicic acid on rice uptake of arsenite has been observed at a molecular level.[34] Silicic acid − arsenic interactions held for α^{soil} and χ^{soil}, with a regression (eq 8) based on porewater Si and $^{As}C_{DGT}$ found to explain grain concentrations well ($R^2 = 0.81$, $p < 0.001$, $n = 22$). Biplots of predicted verses measured grain concentration were highly significantly correlated ($p < 0.001$) with an R^2 of 0.87 (SI Figure S12).

log Aman Grain[As]

$$= -0.562 - (0.340 \times \log \text{porewater[Si]}) + (0.164 \times \log^{As}C_{DGT}))$$

$$(8)$$

However, when the β^{soil} were included in the data set the model failed, indicating variability in the role porewater Si had as a predictor of plant arsenic uptake. In agreement with Khan et al.,[7] arsenic had a positive coefficient, while Si a negative one. There was a slight diminution in model performance when porewater arsenic concentrations were substituted for $^{As}C_{DGT}$. The relationship was still highly significant, but the amount of explained variation fell by 5%. Using $^{As}C_E$ instead of $^{As}C_{DGT}$ had a negligible impact on the model R^2 values. $^{As}C_{DGT}$, was used in preference thereafter because it is a simpler measurement to obtain. An alternative to the $^{As}C_{DGT}$-Si model was found ($R^2 = 0.72$, $p < 0.001$, $n = 32$) (Figure 4) (eq 9), that could reliably predict grain arsenic levels and unify the data set.

log Aman Grain[As]

$$= -0.275 + (0.255 \times \log {}^{As}C_{DGT}) - (0.467 \times \log[DOC]) \quad (9)$$
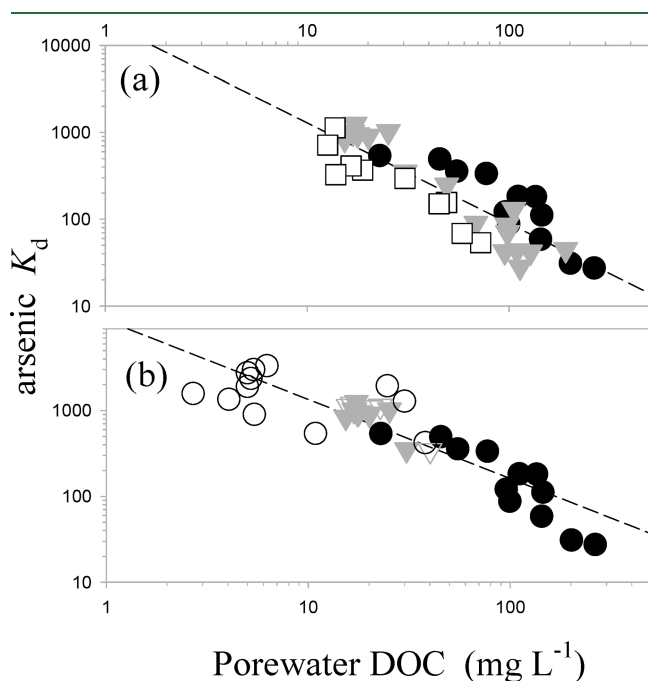
Figure 2. $^{As}K_d$ **versus** [**DOC**] (a) Anaerobic soil assay. Comparison of α^{soil}, β^{soil} and χ^{soil} groupings. $R^2 = 0.77$, $p < 0.001$ ($n = 39$) (b) Comparison of aerobic and aerobic treatments for β^{soil} and χ^{soil}. $R^2 = 0.80$, $p < 0.001$ ($n = 38$). Soil groupings: α^{soil} (O$^-$ = open square), β^{soil} (O$^-$ = inverted gray triangle,O$^+$ = inverted open triangle) χ^{soil} (O$^-$ = filled circle, O$^+$ = open circle).

When $^{As}C_{DGT}$ was replaced by $^{As}C_{sol}$, R^2 fell by 17%. The most important feature of this regression is that the coefficient for DOC was negative, thus appearing to contradict the arsenic mobility trends in the soil solution, in which DOC enhances arsenic release. These findings can be rationalized, however, when arsenic-DOC complexes are considered.[16] Binding of arsenic to DOC or to DOC via an intermediary such as Fe or Al,[17,18] is a plausible explanation for $^{As}C_{DGT}$ outperforming $^{As}C_{sol}$ as a predictor of grain arsenic content, as arsenic complexed species measured in porewater totals would only partially contribute to the DGT measurement. Furthermore, the presence of arsenic-DOC complexes in the porewaters is supported by the speciation analysis, where calculated recoveries ((Σ of As species/total As) $\times$ 100), were negatively correlated with DOC ($^{Logged\ Data}R^2 = 0.60$, $p < 0.001$). This trend was improved further when the difference in pre and post−column arsenic concentrations (total As-Σ sum of As species) was plotted against DOC ($^{Logged\ Data}R^2 = 0.83$, $p < 0.001$) (SI Figure S13).

■ IMPLICATIONS

With total soil arsenic concentrations and chemical extractions unable to predict grain arsenic content in Bangladesh rice,[7,35] new approaches for estimating grain levels, such as the $^{As}C_{DGT}$-DOC model presented in this study are not only a useful land assessment tool, but provide insights into the processes impacting on arsenic uptake. Further work is needed to develop a method that can better integrate irrigation water alongside soil chemical data to improve predictive models for Boro rice. However, ensuring low grain arsenic contents in the Aman crop is also a priority,
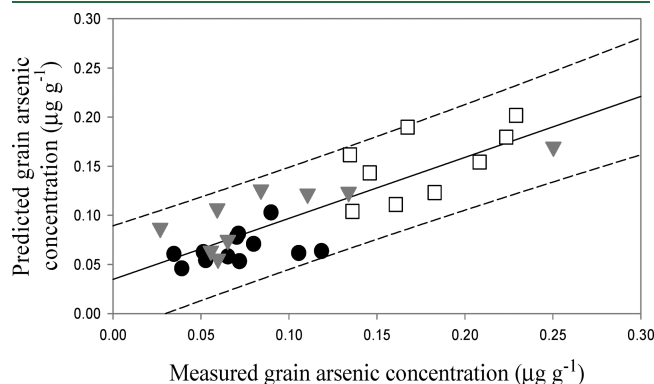

Figure 4. [$^{As}C_{DGT}$] **and** [**DOC**] **model.** Biplot of actual grain arsenic concentration versus predicted grain levels. (- - - -) 95% prediction intervals. (——) = regression ($R^2 = 0.72$, $p < ; 0.001$). Soil groupings: α^{soil}, open square; β^{soil}, inverted gray triangle; χ^{soil}, filled circle.
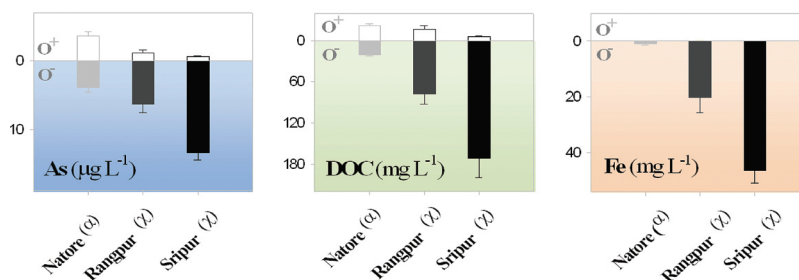

Figure 3. Porewater Arsenic, DOC and Fe Concentrations in Aerobic and Anaerobic Soil Assays. Mean $\pm$ s.e. Natore, $n = 7$. Rangpur = 5. Gazipur = 5. Soil groupings: $\alpha = \alpha^{soil}$. $\chi = \chi^{soil}$.

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especially as it is feared that soils in areas most suitable for high yielding Aman varieties are at particular risk from arsenic accumulation as arsenic removal from receding monsoon floodwaters may be insufficient to offset inputs from dry season irrigation.[30]

Paddy soils even at baseline total arsenic concentrations can produce arsenic elevated grain due to large labile arsenic reservoirs that contribute to a significant resupply flux from the soil to the porewater. Furthermore there is increasing evidence to suggest that the geochemistry of these baseline soils is distinct from those heavily contaminated by arsenic due to irrigation.[35] This manifests principally in a shift away from arsenic release being tied with Fe mobilization into porewaters, to a system far more influenced by DOC dynamics. Chemically and physically DOC species can vary widely among graphical areas.[15] As DOC is derived from decomposed plant and animal products,[17] its composition is influenced strongly by biomass origin and locally active transformation processes.[15] It is perhaps this heterogeneity, not only in total DOC concentration, but also composition, that explains why Bangladesh paddy soils display such a range of arsenic bioavailabilities.

There are also land management implications arising from concomitant DOC and arsenic transport/release. Episodic rewetting of soils, such as those encountered in alternate-wet and drying practices, can impact significantly on carbon mineralization processes accelerating OM decomposition and enhancing DOC concentrations.[36] Poor timing of such cycles during critical periods of grain fill[37] could lead to pulses of DOC and heightened arsenic mobilization, which may in turn contribute to arsenic uptake. Impacting not only on plant bioavailability, As-DOC complexation in OM-enriched zones, such as those encountered around plant roots, are likely also to be important for chemical and biotransformation of arsenic and arsenic cycles in general.

In summary, the relationship between arsenic and DOC warrants greater consideration when trying to produce low arsenic rice.

■ ASSOCIATED CONTENT

ⓢ **Supporting Information.** Eight additional tables and 13 figures as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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