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Arsenic dynamics in paddy soil under traditional manuring practices in Bangladesh

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Abstract

Fertilization with organic matter (farm yard manure and/or rice straw) is thought to enhance arsenic (As) mobilization into soil porewaters, with subsequent As assimilation by rice roots leading to enhanced translocation to grain. Here, interlinked experiments (field manuring and soil batch culture) were conducted to find the effect of organic matter at a field application rate practiced in Bangladesh (5 t/ha) on As mobilization in soil for paddies impacted by As contaminated groundwater irrigation, a widespread phenomenon in Bangladesh where the experiments were conducted. Total As concentration in a paddy soil (Sonargaon) ranged from 21.9 to 8.1 mg/kg down the soil profile and strongly correlated with TOC content. Arsenic, Fe, Mn, and DOC release into soil solution, and As speciation, are intimately linked to OM

amendment, soil depth and temporal variation. Organic matter amendments lead to increased mobilization of As into both soil porewaters and standing surface waters. The As speciation in the porewater was dominated by inorganic As (As_i) (arsenite and arsenate), with traces amounts of methylated species (DMA^V and MMA^V) only being found with OM amendment. It was noted in field trials that OM fertilization greatly enhanced As mobility to surface waters, which may have major implications for the fate of As in paddy agronomic ecosystems.

Key words: Arsenic speciation; OM amendment; rice straw; farmyard manure; dissolve organic carbon

Capsule: Organic matter fertilization greatly enhances As mobility to surface waters: major implications for fate of As in paddy agronomic ecosystems

Highlights

- ✓ We investigated the effects of paddy soil manuring on the mobilization of As in porewater.
- ✓ Arsenic concentrations down the soil profile is strongly correlated with total organic carbon.
- ✓ Paddy pore and surface water As concentrations were associated with iron, manganese and dissolved organic carbon.
- ✓ The arsenic speciation in paddy soil porewater was dependent on the organic amendments.

Introduction

Rice is naturally elevated in arsenic (As) in many regions of Bangladesh (Meharg and Rahman, 2003; Meharg et al., 2009), and exacerbated further in some regions due to the practise of irrigating rice with As elevated groundwater (Meharg and Rahman, 2003; Norra et al., 2005). Rice is the major dietary source of As for the population having rice as the staple food. Meharg et al. (2009) reported that 22 per 10,000 Bangladeshis are on the risk of cancer from rice consumption. It is, therefore, imperative to reduce the As content of Bangladeshi rice grain. However, there are other challenges to rice cultivation in Bangladesh. The use of non-sustainable chemical fertilizers, particularly urea, while stripping organic resources from agricultural environments for cattle (rice straw) and fuel (cattle dung), and cropping 2 - 4 times a year (BBS 2018), leads to soil fertility depletion with respect to nutrient and organic matter (OM) status (Jahiruddin and Satter 2010).

Bangladesh soils are poor in OM status due to its sub-tropical climate and very limited biomass recycling; about 45% of the net cultivable area of Bangladesh has <1% OM (BARC, 2018). Sustainable use of OM in the form of rice straw and farm yard manure (FYM) may have considerable benefits. FYM is rich in N (0.5 %) and P (0.2 %), and other nutrients (Ram et al., 2014) and a good means of soil rejuvenation (Jeptoo et al., 2013). It can also be applied as a mulch to reduce water loss from evaporation and to suppress weeds and eventually increase soil OM status (Jahiruddin and Satter, 2010). If reduced water technologies are introduced into Bangladesh, such as Alternate Wetting and Drying (AWD), then the water loss and weed suppression properties of rice mulching may come to the fore. However, OM amendments may have a key role in As mobilization in paddies (Williams et al., 2011; Mestrot et al., 2011; Jia et al., 2013; Norton et al., 2013, Chen et al., 2017, Qiao et al., 2019), and OM amendments may lead to enhanced As release into paddy pore waters, resulting in

enhanced As assimilation by the plant. The role of OM amendment in As mobilization is primarily due to microbial utilization of OM decreasing redox potential which leads to As dissolution from iron oxyhydroxide (Islam et al., 2004, Arao et al., 2011, Qiao et al., 2019, He et al., 2020). Organic C may donate electron during anaerobic microbial respiration and reduce iron (III) and arsenate (V) may be reduced into Fe (II) and arsenite respectively, thereby mobilized into porewater. Also, OM may desorb some As species from soil surface exchange sites (Redman et al., 2002), and OM may form complex As species (Williams et al., 2011; Sharma et al., 2011; Hossain et al., 2012). Therefore, the objective of present study was to investigate the dynamics of As and other biogeochemically interrelated elements viz. dissolved organic carbon (DOC), iron (Fe), Manganese (Mn) in paddy pore and surface waters, following rice straw and FYM amendment practised in Bangladesh.

Materials and Methods

Experiments

Field trial

A Bangladeshi (Sonargaon, 23.66°N, 90.6°E) field experiment was conducted immediately prior to transplanting boro (monsoon season) rice. The field had been submerged since the previous monsoon (July). The plot had >10 y of only cropping boro rice using groundwater irrigation, and remained under flood water for most of the time. A 0.18 acre plot was selected for the experiment. Undisturbed soil cores of up to 30 cm were initially collected from the plot in triplicate using a soil corer and sliced into 5 cm segments and also, bulk soils were collected from 0 - 15 cm depth for batch and incubation experiments. All samples initially air dried.

Nine subplots were laid out and traditionally bunded with clay banks to restrict plot-to-plot water movement. The experiment was laid out in a randomized complete block design having 3 treatments (control, FYM (0.7 ± 0.1 mg/kg As) amendment and rice straw (1.8 ± 0.1 mg/kg As) amendment) with 3 replicates per treatment. OM amendments were selected based on local practice and application rate (5 t/ha) was selected based on Bangladesh Agricultural Research Council (BARC) recommendation (BARC, 2018). OM was collected from a local farmer and mixed thoroughly with top soil, and kept undisturbed for 10 d. Rhizon samplers (Rhizosphere Research Products, Dolderstraat, JG Wageningen, The Netherlands) were inserted vertically into the ground to collect porewater from 0 - 5 and 5 - 15 cm depth from the plots (Mestrot et al., 2011). Flooded condition within the plots was maintained with supplemental irrigation with surface water, with special attention to avoid overflowing. After 10 d of OM amendments porewater and surface water were collected from the plots. Tubewell waters used for drinking were also sampled from the surrounding area to supplement

irrigation water data in the area (Table SI-1). The installation depth data of the tubewell was collected from the owner. All the water samples were 0.45 μm filtered (Econofilter, Agilent Technologies, Germany). Water samples were divided into 2 subsamples; one of which was acidified to 1% HNO_3 and 5 mM EDTA and kept in the dark; the other was not amended and was used for DOC analysis, while tubewell waters were not analysed for DOC (Hossain et al., 2012). All the water samples were kept in a cool box in the field. The samples were sent to the University of Aberdeen and stored in the freezer before chemical analysis.

Batch mobilization experiments

An incubation experiment was conducted with bulk soil collected from Sonargaon (0 - 15 cm depth). Air-dried soil (0.4 g) was placed in Whatman VectaSpin micro centrifuge tubes with 0.45 μm filter inserts. The filter assemblies were then amended where appropriate with 0.002 g of ball milled (Retsch, Germany) OM (FYM and rice straw) and 0.6 mL ultrapure water (18.2 $\text{M}\Omega\cdot\text{cm}$ water (Milli-Q[®])) was added. Enough tubes were prepared for destructive sampling at 3, 10, 24, 52 and 108 d in triplicate for each treatment, and the whole experimental design duplicated to allow separate samplings for DOC determination and for elemental analysis, and As speciation determination. The tubes were incubated at 26 °C in Sanyo growth cabinets in the dark at the University of Aberdeen, UK. For sampling, the tubes were centrifuged at 10,173 x g for 10 min and centrifugate collected in the outer tube. This soil porewater extract was then diluted as per requirement for analysis and stored at -20° C. Samples for As speciation and DOC analysis were preserved as described above for porewater.

A further batch experiment was conducted to determine how FYM and rice straw derived DOC mobilized As abiotically in a short term (2 h) desorption experiment. To prepare soluble

FYM and rice straw derived organic extract 0.5 g soil and 25 g oven dried FYM or rice straw were placed in a jar and incubated with 1 L Milli-Q water for 10 d. Following incubation OM extract was 0.45 μm filtered. Then 5 g air dried Sonargaon paddy soil (0 - 15 cm depth) was placed in a 50 mL falcon tube with 3 treatments of either 10 mL Milli-Q water, FYM extract (FYM) and rice straw extract (Straw). The tubes were then shaken for 2 h in a rotary shaker (Model-SK71, JE10 TECH, KOREA) at 200 rpm. After incubation, tubes were centrifuged at 1720 x g for 10 min and the supernatant carefully decanted into 50 mL tube. The supernatants were filtered using a 0.45 μm filter. The samples were run for As speciation on the same day, and for total As analysis samples were stored in the dark at 5 °C before analysis.

Chemical analysis

Soil preparation

All soil samples were oven dried until a constant weight was achieved and then ground and sieved (2 mm). Soils were digested following Hossain et al. (2012) where subsamples of approximately 100 mg soil digested with concentrated HNO_3 and H_2O_2 at 140 °C on a block digester with soil CRM (NCS-ZC-73007) as the reference material. For HNO_3 acid dissolution each digestion batch had a spike, a blank and a CRM as part of quality control. Finally, the digested samples were suitably diluted with Milli-Q[®] water.

Total elemental analysis

Total As (m/z 75) and Rhodium (Rh) (m/z 103) analyses in water and digest samples were determined by ICP-MS (Agilent technologies 7500, Tokyo, Japan); the instrument was tuned for the monitoring of m/z 75 (As) and m/z 77, and 82 (Selenium) (m/z 77 and m/z 78 while collision cell was used) to check ArCl interferences. Rhodium (10 $\mu\text{g/L}$) was run as internal standard. Standards were prepared from 1000 mg/L ICP-MS grade multi-element stock

solutions with appropriate ranges (0 - 300 $\mu\text{g/L}$). Corrections were not required for polyatomic $\text{Ar}^{40}\text{Cl}^{35}$ interferences on m/z 75 (Hossain et al., 2012). Total Fe and Mn analyses in water and digest samples were conducted by flame-atomic absorption spectrophotometry (Perkin Elmer AAnalyst 300), calibrated with appropriate standards and change in sensitivity of the instrument checked every 12 samples. Ball milled soils were analyzed for total organic carbon (TOC) by flash combustion method (NA 1500 Series 2, Fisons Instruments, UK).

As speciation analysis

Arsenic speciation in porewater and surface water was analysed by anion exchange HPLC coupled with ICP-MS. The mobile phase used for anion-exchange chromatography consisted of 6.66 mM ammonium hydro phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and 6.66 mM ammonium nitrate (NH_4NO_3), and adjusted to a pH of 6.2 using 3 % ammonia (Heitkemper 2001; Norton et al., 2013). Retention time for the As species was adjusted using a species mix comprising standards of 10 $\mu\text{g/L}$ arsenite, dimethylarsinic acid (DMA^{V}), monomethylarsonic acid (MMA^{V}) and arsenate. Chromatographic peaks of the samples were integrated with species mix and their concentration determined using a calibration equation developed from appropriate standards of DMA^{V} (0, 1.0, 2.5, 5.0, 10.0, 15.0 and 20.0 $\mu\text{g/L}$). Rhodium (10 $\mu\text{g/L}$) was run as internal standard.

Mechanical analysis

A subset of sections from each core profile was selected for particle size analysis. Sediment (25 g) was mixed with 1 L of deionized water with 5 mL dispersant (mixture of sodium polyphosphate and sodium carbonate, buffered at pH 8.3). A hydrometer (g/L. T: 68 °F Zeal, Soil Hydrometer No.2/7243 ASTM. 152H, 0 - 60) was inserted into the suspension and readings were recorded at 46 s, 6 min 51 s, 76 min and 11.5 h with corresponding temperature

(°C) reading to determine particles within the equivalent spherical diameter (e.s.d.) ranges of 2000 - 60 µm (sand), 60 - 20 µm (coarse silt), 20 - 6 µm (medium silt), 6 - 2 µm (fine silt) and < 2 µm (clay), respectively (BSI 1975).

Statistical analysis

Statistical analyses were performed using the statistical software Minitab v.17 (State College PA) and significance reported at $\alpha < 0.05$. The figures were produced using SigmaPlot v.14 (Systat Software Inc., CA). Assumptions of normality of all data were tested using the Anderson-Darling test in Minitab.

Results and Discussion

Field experiment

The analysis of total As in soil CRM (NCS-ZC-73007) gave a recovery of $94 \pm 3 \%$ ($n = 5$). Total As concentration in the Sonargaon paddy soil decreased from 21.9 to 8.1 mg/kg down the profile. Norton et al. (2009) reported As concentration in their experimental site which was very close to our field trial at Sonargaon to be 10.3 ± 2.2 mg/kg in surface soil (0 - 15 cm depth) analyzing 24 samples across the trial area. Topsoil (0 - 15 cm depth) As concentration (20.1 ± 0.9 mg/kg) was more than double of subsoil (15 - 30 cm depth) As concentration (8.8 ± 0.4 mg/kg) keeping with the findings of other reports (Hossain et al., 2012; Norra et al., 2005). The area is irrigated by As contaminated water from shallow tubewells; we could not sample groundwater as the experiment was conducted pre boro season when irrigation tubewells have not yet been reinstalled. Drinking (tubewell) water sampling in the surrounding area gave a high As concentration in groundwater (275 ± 84 μ g/L, $n = 9$) (Table SI 1). Norton et al. (2009) reported an irrigation tubewell As concentration of 331 ± 13 μ g/L in their nearby experimental site. Rice cultivation forms a hard impermeable pan, limiting downward water movement contaminated with As below the layer. Down the core, As content in rice paddy soil was found strongly correlated with TOC content (Figure 1). A sharp decline in total As and TOC down the core was observed at 0 - 15 cm depth and thereafter the trends approached a plateau for both the elements. Elevated As concentration in water used for irrigation over the last decade may have caused As build up in top soil by adsorption of As to the soil for its affinity to metal oxides/hydroxides (Meharg and Rahman 2003; Norra et al., 2005). Particle size analysis did not show significant change down the cores (Figure 1); this is probably due to rice fields being puddled (wetland ploughing) before every crop cultivated therein causing homogeneous soil texture.

The concentration of DOC and total As in porewater at 2 different soil depths (0 - 5 and 5 - 15 cm) and surface water as a function of the 2 different types of OM amendment (FYM and rice straw) shown in Figure 2. Porewater and surface water were collected after 10 d of uninterrupted flooded condition in the plots irrigated with surface water ($10 \pm 0.4 \mu\text{g/L}$ As) when needed. Two-way analysis of variance (TW-ANOVA) showed that the OM treatments had significantly ($F = 13.05$; $P = 0.001$) higher porewater DOC, but that sampling depth and depth*treatment were not significant. No change in surface water DOC was apparent with OM treatments. FYM amendment produced twice as much DOC ($34 \pm 6.0 \text{ mg/L}$) compared to control plots ($17 \pm 1.8 \text{ mg/L}$) and rice straw amendment generated $24 \pm 1.8 \text{ mg/L}$ DOC in porewater. In FYM treated plots, production of DOC was higher at 0 - 5 cm depth compared to 5 - 15 cm depth, while in rice straw amended plots the DOC generation was higher at 5 - 15 cm depth compared to 0 - 5 cm depth. FYM is low in C:N ratio (Ram et al., 2014), whereas rice straw has high C:N ratio (Chivenge et al., 2019). The C:N ratio of an OM is a good indication of its quality; with high C:N ratio refer to low OM quality as well as a slow rate of biodegradation, while low C:N ratio represents improved quality as well as faster biodegradation (Chivenge et al., 2019). Yan et al. (2020) stated that pig manure Dissolved Organic Matter (DOM) having more labile C mobilized more arsenic, whereas rice straw DOM containing more aromatic compounds mobilized less As. Porewater As concentration also increased with OM amendment, the highest As mobilization at 0 - 5 cm depth observed in FYM amended plots ($557 \pm 25 \mu\text{g/L}$) followed by rice straw amendment ($502 \pm 80 \mu\text{g/L}$) then non-amended control plots ($340 \pm 45 \mu\text{g/L}$) and at 5 - 15 cm depth the highest As mobilization was observed in rice straw amended plots ($585 \pm 75 \mu\text{g/L}$), followed by FYM amendment ($440 \pm 116 \mu\text{g/L}$), then non-amended plots ($421 \pm 154 \mu\text{g/L}$). Arsenic concentration in porewater showed a little increase with soil depth. This is due to the mixing of the OM amendments with the soil upto 15 cm depth (plough pan) as well as higher reduced

condition with increasing soil depth in the flooded paddy soil. Akter et al. (2018) described that soil redox potential decreases with soil depth in paddy soil from their experiments in four locations in Bangladesh. Organic amendments further reduced the soil micro-environment and mobilized more As in porewater. As mobilization between the soil depths followed the same trend as observed for DOC; higher As mobilization at 0 - 5 compared to 5 - 15 cm depth in FYM treated plots whereas higher As mobilization at 5 - 15 cm depth compared to 0 - 5 cm depth in the rice straw treated plots. Qiao et al. (2020) also reported that type of biodegradable OM has good correlations with As mobilization in porewater. Nakamura and Katou (2011) also reported higher As concentrations in porewater at 12.5 cm depth compared to 2.5 cm depth even under prolonged submergence in paddy soil. Roberts et al. (2011) reported porewater As concentration up to 500 $\mu\text{g/L}$ from their field study in Munshiganj, Bangladesh. Porewater Fe concentration was found significantly affected by OM amendment ($F = 6.83$; $P = 0.012$) and sampling depth ($F = 7.4$; $P = 0.02$), but the interaction term (OM amendment* sampling depth) was not significant. The 2 different types of OM amended in the experiment did not show an appreciable difference in releasing Fe into porewater; 19 ± 3 and 22 ± 5 mg/L Fe in FYM and rice straw amendment, respectively (Figure 3). Higher Fe concentrations were observed at 0 - 5 cm depth (20.6 ± 3 mg/L) compared to at 5 - 15 cm depth (12.5 ± 3 mg/L) when porewater Fe averaged across 3 treatments. Mn concentration in porewater in rice fields, was found significantly affected by OM amendment ($F = 6.94$; $P = 0.011$) though type of OM did not show much variation in Mn mobilization. With the flooding initiation As is mobilized into porewater by reductive dissolution of iron oxyhydroxide mineral, and arsenate reduction to more mobile arsenite (Norton et al., 2013, Xu et al., 2008; Masscheleyn 1991).

The As speciation in porewater was dominated by inorganic As (As_i) (arsenite and arsenate), with traces amounts of methylated species (DMA^V and MMA^V) only found with OM

273 amendment (Figure 4). Arsenite + cationic As (as the chromatography method cannot exclude
 274 the presence of positive charged species eluting at the same time as arsenite) denoted as
 275 arsenite hereafter was not significantly affected by OM amendment ($F = 3.74$; $P = 0.055$), but
 276 rice straw amendment produced higher arsenite mobilization compared to control and FYM
 277 amendment. However, arsenate concentration in porewater was significantly influenced by
 278 OM treatments ($F = 5.54$; $P = 0.02$) with FYM resulting in the highest mobilization, followed
 279 by rice straw. Among the 2 inorganic As species FYM amendment caused arsenate
 280 mobilization ($332 \pm 50 \mu\text{g/L}$) more than arsenite ($149 \pm 43 \mu\text{g/L}$) in contrast to rice straw
 281 amendment mobilizing 302 ± 33 and $208 \pm 22 \mu\text{g/L}$ arsenite and arsenate, respectively (mean
 282 between depths). Schaller et al. (2018) also reported that, readily biodegradable OM induce
 283 comparatively lower redox potential in the paddy soil pore water which stimulates As
 284 mobilization. Arsenic mobilization and speciation is generally microbial metabolism
 285 dependent, microbial reduction of oxidized quinones from humic DOM initiates in Fe(III)
 286 reduction, contributing to arsenate mobilization in the system (Chen et al., 2017). Aqueous
 287 arsenite reoxidation can take place microbially resulting in higher arsenate in paddy porewater
 288 (Cullen and Reimer, 1989); DOC also influences arsenite/arsenate interconversion (Redman
 289 et al., 2002). FYM generated more methylated species compared to rice straw amendment at 0
 290 - 5 cm depth whereas, at 5 - 15 cm depth methylated species were below LOD or similar to
 291 the level as found in control plot, indicating that DMA^{V} was formed as a result of OM
 292 amendment, in agreement with Arao et al. (2011). Stroud et al. (2011) and Xu et al. (2008)
 293 reported negligible amount of organic As in porewater under flooded conditions even without
 294 OM amendment. On average across treatments surface water in the plots were found 37-fold
 295 lower in As concentration compared to porewater in the 0 - 15 cm layer, and surface water As
 296 in FYM amended plot ($24 \pm 4.5 \mu\text{g/L}$) was found more than double the As concentrations in
 297 non-amended control ($10.0 \pm 0.8 \mu\text{g/L}$) and rice straw amended plots ($11 \pm 0.5 \mu\text{g/L}$); effect

of FYM amendment was statistically significant ($F = 8.51$; $P = 0.018$) in As transfer from porewater to surface water. Roberts et al. (2010) found that diffusion of As in soil porewaters to surface waters was a major loss mechanism of As from soil, and it appears that this process is exacerbated by FYM amendment, thus such amendments could be beneficial in reducing As build up in soils. Although As levels were ~40-fold lower in surface waters, this does not reflect that once in more oxic surface waters that As will precipitate (Roberts et al., 2007), or that surface water is subject to drainage and, hence, removal (Roberts et al., 2010).

Batch experiments

A batch experiment using soil and OM from Sonargaon was conducted to investigate the As mobilization, along with DOC in soil porewater to support porewater geochemistry in the field trial in Sonargaon. Results are presented in Figure 5 and 6 show that As and DOC release into soil solution, and As speciation, are intimately linked to OM amendment. FYM and rice straw amendment had a significant role in mobilizing As ($F = 16.62$; $P < 0.001$), but OM type was not significant. The highest As mobilization was found in rice straw amended cells ($295 \pm 68 \mu\text{g/L}$), 3-fold higher than As mobilization for control ($98 \pm 34 \mu\text{g/L}$), while the FYM amendment had an As porewater concentration of $231 \pm 59 \mu\text{g/L}$. The similar trend of As mobilization was also observed in the field trial. There was a strong temporal variation in As mobilization ($F = 37.8$; $P < 0.001$), with the treatment*day term also significant ($F = 4.23$; $P = 0.002$). Among the five sampling points, day 3 and 10 are significantly higher than the later periods (24, 52 and 108 d). OM amendment in the batch experiment also had a significant role on porewater DOC ($F = 29.64$; $P < 0.001$), with the 2 types of OM used resulting in identical DOC. Sampling time also showed a prominent influence in DOC release into soil solution ($F = 103.46$; $P < 0.001$), and treatment*time interaction also significant ($F = 7.69$; $P < 0.001$). DOC production was greatest earlier in the experiment. Regression analysis

(Figure SI-1) found that DOC and As in soil solutions were correlated ($r = 0.795$, $n = 45$; $P < 0.001$). A similar finding on the role of OM on DOC and As porewater concentrations has been previously illustrated (Jia et al., 2013; Williams et al., 2011; Mestrot et al., 2011). DOC is generally negatively charged, it may compete with arsenate for the adsorption sites on the soil colloidal surface and facilitates arsenate desorption into the soil solution (Mohapatra et al., 2007, Yan et al., 2020). Again, DOC has positively charged amino groups on the surface that can combine with negatively charged As ions and thereby As is mobilized into soil solution (Yan et al., 2020, Williams et al., 2011). Further, the arsenate mobilized into soil solution is reduced into arsenite through reductive dissolution where DOC plays the major role by donating electron (Islam et al., 2004, Arao et al., 2011, Qiao et al., 2019, He et al., 2020).

Porewater samples at 3 and 10 d samples were measured for As speciation. Arsenite was found predominant at 3 d (Figure 6), in keeping with porewater data from other reports (Xu et al., 2008; Williams et al., 2011; Masscheleyn 1991). However, at 10 d porewater in OM amended cells was dominated by arsenate, perhaps due to DOC influencing arsenite/arsenate interconversion (Redman et al., 2002) and microbial reoxidation of aqueous arsenite (Cullen and Reimer, 1989). OM amendment also caused enhanced porewater concentrations of methylated species (Williams et al., 2011; Mestrot et al., 2011), DMA^V accounting for ~10% of species, with MMA^V accounting for ~2.5%. The 2 different types of OM did not show significant variation in porewater As species.

A short-term (2 h) desorption experiment was carried out to investigate the effect of DOC generated from FYM and rice straw on As mobilization. Artificially generated DOC desorbed a significantly higher ($F = 114$; $P < 0.001$) amount of total As compared to distilled water

(Figure 7). The highest desorption of total As ($181 \pm 4.1 \mu\text{g/kg}$) was found with FYM-DOC, significantly higher than for control and rice straw-DOC treated soil. Arsenate was predominant among the four As species analysed, accounting 47% of species sum. As for total As, arsenate mobilization was also found highest with FYM-DOC ($77 \pm 2.8 \mu\text{g/kg}$), which was significantly higher than control ($22 \pm 3.6 \mu\text{g/kg}$) and rice straw-DOC ($8 \pm 1.5 \mu\text{g/kg}$) treated soil ($F = 177$; $P < 0.001$). Moreover, arsenate desorption by rice straw-DOC treated soil was significantly lower than arsenate desorbed using ultrapure water indicating some re-adsorption of arsenate or interconversion of arsenate/arsenite (Redman et al., 2002), as discussed for porewater and batch experiment As speciation. The arsenite accounts for 38% of species sum. Treatment effect was not significant ($F = 3.7$; $P = 0.089$) on arsenite mobilization from soil with the highest desorption observed in rice straw-DOC ($33 \pm 2.0 \mu\text{g/kg}$) followed by FYM-DOC ($29 \pm 2.8 \mu\text{g/kg}$), while ultrapure water mobilized the lowest arsenite ($23 \pm 2.8 \mu\text{g/kg}$). FYM-DOC mobilized an appreciable amount of DMA^{V} (18% of species sum), but very little MMA^{V} (3% of species sum). DMA^{V} and MMA^{V} mobilization in control treatment were below LOD, showing that DOC directly desorbed these species from the solid phase. FYM-DOC mobilized 11-fold higher DMA^{V} compared to rice straw-DOC (Figure 7). However, no variation in MMA^{V} mobilization was noticed between the two types of DOC used in the experiment. OM amendment may increase the microbial activity and thereby the inorganic As metabolism into organic As species. OM mediated organic As in porewater in Bangladesh soils is also reported from Williams et al. (2011) and Mestrot et al. (2011). Moreover, organic manuring in paddy soils may produce arsines, the volatile As species (William et al., 2011, Yan et al., 2020).

Conclusion:

Arsenic contaminated paddy field fertilization with organic matter (farm yard manure and/or rice straw) increases As mobilization in porewater and subsequent As assimilation in rice grain. Down the soil profile, As content is strongly correlated with TOC content. Arsenic, Fe, Mn, and DOC release into soil solution, and As speciation, are intimately linked to OM amendment, soil depth and temporal variation. Arsenic speciation in paddy soil porewater is also dependent on the organic amendments which have been observed in all the three interlinked studies. Organic matter fertilization greatly enhanced As mobility to surface waters, which may have major implications for the fate of As in paddy agronomic ecosystems.

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References

- Akter, M., Derooa, H., De Graved, E., Alboome, T. V., Kader, M. A., Pierreuxa, S., Begum, M. A., Boeck, P., Sleutel, S. 2018. Link between paddy soil mineral nitrogen release and iron and manganese reduction examined in a rice pot growth experiment. *Geoderma*, 326, 9-21.
- Arao, T., Kawasaki, A., Baba, K., Matsumoto, S. 2011. Effects of arsenic compound amendment on arsenic speciation in rice grain. *Environ. Sci. Technol.* 45, 1291-1297.
- BARC (Bangladesh Agricultural Research Council). 2018. *Fertilizer Recommendation Guide*. BARC Soils Pub. No. 45. Bangladesh Agril. Res. Coun. Dhaka, Bangladesh.

- BBS (Bangladesh Bureau of Statistics). 2018. The Year Book of Agricultural Statistics of Bangladesh. Stat. Div. Minis. Planning, Govt. Peoples Repub. Bangladesh, Dhaka
- BSI (British Standards Institution). 1975. *Methods of test for soils for civil engineering purposes*. British Standard 1377. Brit. Stan. Inst., London.
- Chen, Z., Wang, Y., Jiang, X., Fu, D., Xia, D., Wang, H., Dong, G., Li, Q. 2017. Dual roles of AQDS as electron shuttles for microbes and dissolved organic matter involved in arsenic and iron mobilization in the arsenic-rich sediment. *Sci. Total Environ.* 574, 1684–1694.
- Cullen, W. R., Reimer, K. J. 1989. Arsenic Speciation in the Environment. *Chemical Reviews*, 89(4), 713-764.
- He, S., Wang, X., Zheng, C., Yan, L., Li, L., Huang, R., Wang, H. 2020. Enhanced arsenic depletion by rice plant from flooded paddy soil with soluble organic fertilizer application. *Chemosphere*, 252, 126521.
- Heitkemper, D. T., Vela, N. P., Stewart, K. R., Westphal, C. S. 2001. Determination of total and speciated arsenic in rice by ion chromatography and inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* 16, 299-306.
- Hossain, M., Williams, P. N., Mestrot, A., Norton, G. J., Deacon, C. M., Meharg, A. A. 2012. Spatial heterogeneity and kinetic regulation of arsenic dynamics in mangrove sediments: the Sundarbans, Bangladesh. *Environ. Sci. Technol.* 46(16), 8645-8652.
- Islam, F. S., Gault, A. G., Boothman, C., Polya, D. A., Charnock, J. M., Chatterjee, D., Lloyd, J. R. 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature* 430, 68-71.

- 418 Jahiruddin, M., Satter, M. A. 2010. Final report: *Agricultural research priority: Vision-*
 419 *2030 and beyond*. Sub-sector: Land and soil resource management. Bangladesh
 420 Agricultural Research Council (BARC), Dhaka, Bangladesh.
 421 <http://www.barc.gov.bd/documents/Final-Prof.Jahir.pdf>.
- 422 Jeptoo, A., Aguyoh, J. N., Saidi, M. 2013. Improving Carrot Yield and Quality through
 423 the Use of Bio-Slurry Manure. SAR 2(1), 164-172.
- 424 Jia, Y., Sun, G. X., Huang, H., Zhu, Y. G. 2013. Biogas slurry application elevated arsenic
 425 accumulation in rice plant through increased arsenic release and methylation in paddy
 426 soil. Plant Soil 365, 387–396.
- 427 Masscheleyn, P. H., Delaune, R. D., Patrick, W. H. 1991. Effect of redox potential and pH
 428 on arsenic speciation and solubility in a contaminated soil. Environ. Sci. Technol. 25,
 429 1414-1419.
- 430 Meharg, A. A., Rahman, M. M. 2003. Arsenic contamination of Bangladesh paddy field
 431 soils: implications for rice contribution to arsenic consumption. Environ. Sci. Technol. 37,
 432 229-34.
- 433 Meharg, A. A., Williams, P. N., Adomako, E., Lawgali, Y. Y., Deacon, C. M., Villada,
 434 A., Cambell, R. C. J., Sun, G., Zhu, Y. G., Feldmann, J., Raab, A., Zhao, F. J., Islam, M.
 435 R., Hossain, S., Yanai, J. 2009. Geographical variation in total and inorganic arsenic
 436 content of polished (white) rice. Environ. Sci. Technol. 43, 1612-1617.
- 437 Mestrot, A., Feldmann, J., Krupp, E. M., Hossain, M., Roman-Ross, G., Meharg, A. A.
 438 2011. Field fluxes and speciation of arsines emanating from soils. Environ. Sci. Technol.
 439 45, 1798-1804.

- Mohapatra, D., Mishra, D., Rout, M., Chaudhury, G. R. 2007. Adsorption kinetics of natural dissolved organic matter and its impact on arsenic(V) leachability from arsenic loaded ferrihydrite and Al-ferrihydrite. *J. Environ. Sci. Heal. A.* 42, 81-88.
- Nakamura, K., and Katou, H. 2012. Arsenic and cadmium solubilization and immobilization in paddy soils in response to alternate submergence and drainage, In: H. M. Selim(Eds), *Competitive sorption and transport of heavy metals in soils and geological media*, CRC Press, 379-404.
- Norra, S., Berner, Z. A., Agarwala, P., Wagner, F., Chandrasekharam, D., Stuben, D. 2005. Impact of irrigation with As rich groundwater on soil and crops: a geochemical case study in West Bengal Delta Plain, India. *Appl. Geochem.* 20, 1890-906.
- Norton, G. J., Islam, M. R., Deacon, C. M., Zhao, F. J., Stroud, J. L., McGrath, S. P., Islam, S., Jahiruddin, M., Feldmann, J., Price, A. H., Meharg, A. A. 2009. Identification of low inorganic and total grain arsenic rice cultivars from Bangladesh. *Environ. Sci. Technol.* 43, 6070-6075.
- Norton, G. J., Adomako, E. E., Deacon, C. M., Carey, A. M., Price, A. H., Meharg, A. A. 2013. Effect of organic matter amendment, arsenic amendment and water management regime on rice grain arsenic species. *Environ. Pollut.* 177, 38-47.
- Qiao, J., Li, X., Li, F., Liu, T., Young, L. Y., Huang, W., Sun, K., Tong, H., Hu, M. 2019. Humic Substances Facilitate Arsenic Reduction and Release in Flooded Paddy Soil. *Environ. Sci. Technol.* 53, 5034-5042.
- Qiao, W., Guo, H., He, C., Shi, Q., Xiu, W., Zhao, B. 2020. Molecular evidence of arsenic mobility linked to biodegradable organic matter. *Environ. Sci. Technol.* 54, 12, 7280-7290.

- Redman, A. D., Macalady, D. L., Ahmann, D. 2002. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* 36, 2889-2896.
- Ram, M., Davari, M. R., Sharma, S. N. 2014. Direct, residual and cumulative effects of organic manures and biofertilizers on yields, NPK uptake, grain quality and economics of wheat (*Triticum aestivum* L.) under organic farming of rice-wheat cropping system JOS, 9(1), 16-30.
- Roberts, L. C., Hug, S. J., Dittmar, J., Voegelin, A., Saha, G. C., Ali, M. A., Badruzzaman, A. B. M., Kretzschmar, R. 2007. Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladesh: 1. Irrigation water. *Environ. Sci. Technol.* 41, 5960-5966.
- Roberts, L. C., Hug, S. J., Dittmar, J., Voegelin, A., Kretzschmar, R., Wehrli, B., Cirpka, O. A., Saha, G. C., Ali, M. A., Badruzzaman, A. B. M. 2010. Arsenic release from paddy soils during monsoon flooding. *Nat. Geosci.* 3, 53-59.
- Roberts, L. C., Hug, S. J., Voegelin, A., Dittmar, J., Kretzschmar, R., Wehrli, B., Saha, G. C., Badruzzaman, A. B. M., Ali, M. A. 2011. Arsenic dynamics in porewater of an intermittently irrigated paddy field in Bangladesh. *Environ. Sci. Technol.* 45, 971-976.
- Schaller, J., Wang, J., Islam, M. R., Planer-Friedrich, B. 2018. Black carbon yields highest nutrient and lowest arsenic release when using rice residuals in paddy soils. *Scientific Reports.* 8:17004
- Sharma, P., Rolle, M., Kocar, B., Fendorf, S., Kappler, A. 2011. Influence of natural organic matter on arsenic transport and retention. *Environ. Sci. Technol.* 45, 546-553.

- Chivenge, P., Rubianes, F., Chin, D. V., Thach, T. V., Khang, V. T., Romasanta, R. R., Hung, N. V., Trinh, M. V. 2019. "Chapter: Rice Straw Incorporation Influences Nutrient Cycling and Soil Organic Matter". Gummert, M., Hung, N. V., Chivenge, P., Douthwaite, B. (Ed.) *Sustainable Rice Straw Management*, Springer Open Publication, November 2019. P 131-144.
- Stroud, J. L., Norton, G. J., Islam, M. R., Dasgupta, T., White, R. P., Price, A., Meharg, A. A., McGrath, S. P., Zhao, F. J. 2011. The dynamics of arsenic in four paddy fields in the Bengal delta. *Environ. Pollut.* 159, 947-953.
- Williams, P. N., Zhang, H., Davison, W., Meharg, A. A., Hossain, M., Norton, G. J., Brammer, H., Islam, M. R. 2011. Organic matter- solid phase interactions are critical for predicting arsenic release and plant uptake in Bangladesh paddy soils. *Environ. Sci. Technol.* 45, 6080-6087.
- Xu, X. Y., McGrath, S. P., Meharg, A. A., Zhao, F.J. 2008. Growing rice aerobically markedly decreases arsenic accumulation. *Environ. Sci. Technol.* 42, 5574-5579.
- Yan, M., Zeng, X., Wang, J., Meharg, A. A., Meharg, C., Tang, X., Zhang, L., Bai, L., Zhang, J., Su, S. 2020. Dissolved Organic Matter Differentially Influences Arsenic Methylation and Volatilization in Paddy Soils. *J. Hazard. Mater.* 388, 121795.

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Highlights

- ✓ We investigated the effects of paddy soil manuring on the mobilization of As in porewater.
- ✓ Arsenic concentrations down the soil profile is strongly correlated with total organic carbon.
- ✓ Paddy pore and surface water As concentrations were associated with iron, manganese and dissolved organic carbon.
- ✓ The arsenic speciation in paddy soil porewater was dependent on the organic amendments.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: