# Arsenic in the Bangladesh soils related to physiographic region, paddy management, and micro- and macro- element status

# Arsenic in the Bangladesh soils related to physiographic region, paddy management, and mirco- and macro- elemental status

M. Tanvir A. Chowdhury[1, 2], Claire M. Deacon[1], Gerrad D. Jones[3], S.M. Imamul Huq[2], Paul N. Williams[4], A.F.M. Manzurul Hoque[5], Lenny H.E. Winkel[6], Adam H. Price[1], Gareth J. Norton[1*], and Andrew A. Meharg[4*]

[1]Institute of Biological and Environmental Sciences, University of Aberdeen, Cruickshank Building, St. Machar Drive,Aberdeen, AB24 3UU, U.K.

[2]Department of Soil, Water and Environment, University of Dhaka, Dhaka-1000, Bangladesh

[3]Eawag: Swiss Federal Institute of Aquatic Science and Technology, Ueberlandstrasse 133, P.O. Box 611, CH-8600 Duebendorf, Switzerland

[4]Institute for Global Food Security, Queen's University Belfast, David Keir Building, Malone Road, Belfast BT9 5BN, Northern Ireland, U.K.

[5]Soil Resource Development Institute (SRDI), Khamar Bari Road, Dhaka 1215, Bangladesh

[6]Swiss Federal Institute of Technology (ETH), Institute of Biogeochemistry and Pollutant Dynamics,ETH Zurich, CH-8092 Zurich, Switzerland

Corresponding authors

[*]**Andrew A. Meharg**
Tel: +44 (0)28 9097 5413; fax: +44 (0) 28 90976513; e-mail: aa.meharg@qub.ac.uk

[*] **Gareth J. Norton**
Tel: 44 (0)1224272409; fax: +44 (0)1224272396; e-mail: g.norton@abdn.ac.uk

## Abstract

While the impact of arsenic in irrigated agriculture has become a major environmental concern in Bangladesh, to date there is still a limited understanding of arsenic in Bangladeshi paddy soils at a landscape scale. A soil survey was conducted across ten different physiographic regions of Bangladesh, which encompassed six types of geomorphology (Bil, Brahmaputra floodplain, Ganges floodplain, Meghna floodplain, Karatoya-Bangali floodplain and Pleistocene terrace). A total of 1209 paddy soils and 235 matched non-paddy soils were collected. The source of irrigation water (groundwater and surface water) was also recorded. The concentrations of arsenic and sixteen other elements were determined in the soil samples. The concentration of arsenic was higher in paddy soils compared to non-paddy soils, with soils irrigated with groundwater being higher in arsenic than those irrigated with surface water. There was a clear difference between the Holocene floodplains and the Pleistocene terrace, with Holocene floodplains being higher in arsenic and other elements. The results suggest that arsenic is most likely associated with less well weathered/leached soils, suggesting it is either due to the geological newness of Holocene sediments or differences between the sources of sediments, which gives rise to the arsenic problems in Bangladeshi soils.

## Introduction

Rice is elevated in inorganic arsenic compared to all other dietary staples (Meharg et al., 2009). Flooding of soils, as in paddy cultivation, leads to the mobilization of natural and anthropogenic inorganic arsenic stores in iron oxyhydroxide phases, caused by both the reduction of arsenic and iron under negative soil redox potentials (Meharg and Zhao, 2012). Paddy soils are managed through tilling, fertilization, and surface water and groundwater irrigation, with the latter often elevated in inorganic arsenic throughout large areas of Bangladesh (Huq et al., 2003; Meharg and Rahman, 2003; Roberts et al., 2007; Lu et al., 2009). Furthermore, arsenic can undergo a number of processes within paddy soils that leads to its subsequent loss such as partitioning to monsoonal floodwaters (Dittmar et al., 2007; Saha and Ali, 2007; Dittmar et al., 2010; Roberts et al., 2010), leaching to sub-surfaces (McLaren et al., 2006; Khan et al., 2009; Heikens et al., 2007), and biovolatilization to arsines (Mestrot et al., 2011). Thus, the arsenic loading of any particular paddy soil will be due to geological origin and the subsequent weathering of constituent minerals, and the agronomic management of that sediment (Lu et al., 2009).

Bangladesh has three major geomorphological units (Brammer, 1996; Huq and Shoaib, 2013). These are hill, terrace, and floodplain areas. The hills occupy twelve percent of the country's land area. The uplifted terrace areas are of Pleistocene age and occupy eight percent of the country. The floodplains are of Holocene age and occupy eighty percent of the country. The Holocene floodplains include the piedmont plains, river floodplains, tidal floodplains, and estuarine floodplains. These geomorphological units are related to the parent geological formations, however, they are also characterized by land topography and age of the soil formation through sediment deposition over time (Brammer, 1996).

To understand and characterise the physiography of the geomorphological areas, Bangladesh is divided into twenty main physiographic regions (FAO/UNDP, 1988). This physiographic classification was based on the parent material in which individual soil types were formed and the landscape on which the soils were developed (FAO/UNDP, 1988). Therefore, the physiographic regions have differences in geology, relief, drainage, age of land formation and pattern of sedimentary deposition. These differences ultimately influence the nature and properties of the soils in the different physiographic regions.

The biogeochemical cycling of arsenic in soils is strongly affected by other elements. Iron is central due to the strong association between insoluble arsenate and iron(III) oxyhydroxides under aerobic conditions and with the mobilization of iron (II) and arsenite under reducing (that is, paddy) conditions (BGS/DPHE, 2001; Smedley and Kinniburgh, 2002; McArthur et al., 2004; Polizzotto et al., 2005). Manganese oxides also have a similar redox chemistry to iron and are strongly implicated in arsenic immobilization/mobilization during oxic/anoxic cycling of paddy sediments (Smedley and Kinniburgh, 2002; Hasan et al., 2007). Arsenate is a phosphate analogue and, thus, key to competition for binding sites within the soil solid phase, as well as having similar biogeochemical cycling under oxic conditions (Adriano, 2001; Meharg and Hartley-Whitaker, 2002; Smith et al., 2002; Lambkin and Alloway, 2003; Stachowicz et al., 2008). Calcium and magnesium immobilize arsenate under oxic conditions, and could also have a role in the biogeochemical cycling of arsenic at a landscape level (Smith et al., 2002; Stachowicz et al., 2008; Fakhreddine et al., 2015).

Here, we wanted to understand the relationship between soil arsenic and paddy management practice with respect to arsenic loadings in Bangladeshi soils. Cultivation zones of paddy soils (n = 1209) across ten physiographic regions of Bangladesh, from latitude 22°06' to 24°53', and longitude 88°20' to 90°59' were sampled and analysed for arsenic and a suite of sixteen other elements (aluminium, calcium, cadmium, cobalt, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, sodium and zinc). For a subset of soils (n = 235), paired paddy and adjacent non-paddy soils were also collected and characterised. The data were used to address four specific objectives: to assess the impact that geomorphological differences have on soil arsenic at a landscape level; to understand the relationship between the concentration of arsenic in the paddy soils with the concertation of arsenic within the underlying groundwater; to determine if the source of irrigation water impacts on soil arsenic concentrations; and by examining the concentrations of arsenic and other elements in paddy and non-paddy soils, we aimed to understand the impacts that paddy management has on soil elemental concentrations.

## Materials and Methods

### *Collection of Soil Samples*

A total of 1444 soil samples (topsoil, 0-15 cm from the surface) from paddy fields (n = 1209) and neighboring non-paddy areas (n = 235) were collected from 10 different physiographic regions within 57 sub-districts (upazilas) from 17 districts of Bangladesh (Table S1). Non-paddy soils were defined as the soils where paddy cultivation and groundwater irrigation had not been practiced within known memory of the farmers. The physiographic regions from where the soil samples were collected included Arial Bil (n = 42 paddy and 10 non-paddy soils), Brahmaputra Floodplain (n = 207 paddy and 64 non-paddy soils), Ganges River Floodplain (n = 261 paddy and 58 non-paddy soils), Ganges Tidal Floodplain (n = 47 paddy and 11 non-paddy soils), Gopalganj-Khulna Bils (n = 63 paddy and 8 non-paddy soils), Karatoya-Bangali floodplain (n = 15 paddy soils only), Meghna Estuarine Floodplain (n = 204 paddy and 28 non-paddy soils), and Meghna River Floodplain (n = 184 paddy and 26 non-paddy soils) from Holocene floodplains, and Barind Tract (n = 68 paddy and 15 non-paddy soils) and Madhupur Tract (n = 118 paddy and 15 non-paddy soils) from Pleistocene terraces. The source of irrigation water for the paddy soils was recorded (groundwater, n = 904; surface water, n = 281; both, n = 24). Only the soils that had a non-mixed irrigation source were used for analyzing the impact of irrigation type on soil arsenic.

### *Sample Processing and Preparation for Analysis*

The soil samples were air-dried and, prior to analysis, the samples were oven dried (80°C ± 5°C for 48 h), and finely ground using a ball-mill. The soil digestion procedure followed was described by Adomako et al. (2009). Briefly, 0.1 g of soil was placed in a glass digest tube and 2.5 ml of concentrated nitric acid was added to the tube and left overnight for predigestion. Then, 2.5 ml of hydrogen peroxide was added to the sample just before digesting and the sample was heated on the block digester for 1 h at 80°C, for 1 h at 100°C, for 1 h at 120°C and, finally, at 140°C for 3 h until the solution was clear. Once cooled, the digested soil samples were transferred into 15 ml polypropylene tubes and each glass tube was thoroughly rinsed 3 times with ultrapure deionized water (Milli-Q 18.2 MΩ). The volumes were made up to 15 ml mark using the same water. To obtain the appropriate dilution for analysis by inductively coupled plasma-mass spectrometer (ICP-MS) and microwave plasma-atomic emission spectrometer (MP-AES), the samples were further diluted to 1 in 10. Calibration standards were prepared from 1000 mg/l multi-element stock solutions (SPEX CertiPrep Reference Material).

***Chemical Analysis***

The pH of the soil samples were measured at a soil:water (deionized water) ratio of 1:2.5 (Huq and Alam, 2005). The ICP-MS (Agilent Technologies 7500c, Japan) was used to determine the total concentrations of arsenic, cadmium, cobalt, copper, chromium, lead, manganese, molybdenum, nickel, phosphorus, and zinc in the soil digests and the MP-AES (Agilent Technologies 4100 Series, USA) was used to determine the total concentrations of aluminum, calcium, iron, magnesium, potassium, and sodium in the soil digests. In each batch of digestion, ten percent of the total number of samples were selected randomly for duplicate analysis (n =172). Every batch of samples consisted of 33 randomly selected soil samples, 4 duplicates, 1 blank, and 1 soil CRM (certified reference material) (NCS ZC 73007, China National Analysis Center for Iron and Steel), which were randomized prior to analytical analysis.

***Soil Mapping***

The data used to perform the mapping of arsenic in paddy soils across Bangladesh included the 1209 paddy soils analyzed in this study as well as 395 soil arsenic concentrations from previous studies (Williams et al., 2011; Lu et al., 2009; Islam et al., 2012). ArcGIS v.10.2 (Esri) was used to create and analyze groundwater and soil arsenic map. The groundwater arsenic data were obtained from BGS/DPHE (2001).

***Statistical Analysis***

All statistical analyses were performed using the statistical software Minitab v.16 (State College PA) and SigmaPlot v.13 (Systat Software Inc., CA). The data were checked for normality and were transformed prior to statistical analysis where appropriate.

## Results and Discussion

In order to verify the accuracy of the analytical methods as well as the quality of the data, percent recoveries of the elements in CRM and relationships between the element concentrations in the samples and in the duplicates (ten percent of the total number of samples) were calculated and the average recoveries (in percentages) of the elements in the CRMs and the results of the duplicate analysis are presented in Table S2 and Fig. S1, respectively.

To develop a soil arsenic map of the sampled soils, all paddy soil sampling locations within a 10 $km^2$ grid were averaged (Fig. 1). Individual locations and sampling densities are shown in Fig. S2. There is a clear north/south divide in paddy arsenic concentrations with much higher concentrations, in general, in the south. The paddy soil arsenic levels reported here (1-88 mg/kg, average = 8 mg/kg) are within the ranges reported for previous Bangladesh paddy soil surveys (Huq et al., 2003; Meharg and Rahman, 2003; Lu et al., 2009; Williams et al., 2011; Huq and Shoaib, 2013). The pattern of paddy soil concentrations relate well to groundwater measurements (BGS-DPHE, 2001), again with groundwater elevated in the south, excluding the coastal zone. The exception is the cluster of sampling points in the extreme south-east that have a low soil arsenic concentration and the highest groundwater arsenic concentration. This is probably due to the source of irrigation water used in this south-east region, where the main irrigation method is from surface water rather than groundwater (Fig. S3). When comparing the arsenic concentrations in the paddies that have been irrigated with groundwater and surface water across Bangladesh, there was a significant difference ($^{ANOVA}F = 26.23$, $p < 0.001$) in the soil arsenic concentration (Fig. 2). Soils irrigated with groundwater had on average an arsenic concentration of 8.5 mg/kg which was significantly higher than the soils irrigated with surface water, which had an average arsenic concentration of 5.7 mg/kg. For the individual physiographic regions, seven of the regions had enough groundwater and surface water irrigated soils (>10) to do comparisons between irrigation method and soil arsenic. There was no significant difference in soil arsenic between the groundwater irrigation and surface water irrigation for four of the seven physiographic regions. For the three other physiographic regions, significant differences in arsenic concentrations were observed between the soils irrigated with groundwater (GWI) and surface water (SWI), with higher arsenic concentrations in the groundwater irrigated soils than in the surface water irrigated soils (for Ganges Tidal Floodplain, $^{ANOVA}F = 5.97$, $p < 0.05$, n = 28 (GWI) and 20 (SWI), mean = 14.6 mg/kg (GWI) and 8.6 mg/kg (SWI); for Meghna Estuarine Floodplain, $^{ANOVA}F = 14.84$, $p < 0.001$, n = 69 (GWI) and 111 (SWI), mean = 8 mg/kg (GWI) and 3.9 mg/kg (SWI); for Meghna River Floodplain, $^{ANOVA}F = 62.06$, $p < 0.001$, n = 130 (GWI) and 54 (SWI), mean = 9.4 mg/kg (GWI) and 4.7 mg/kg (SWI)). As the samples were collected from different geomorphic regions, these results could be confounded by the underlying geomorphology. However, difference in soil arsenic due to different irrigation techniques appears to be a trend across the country.

Soil arsenic concentrations across ten different physiographic regions of Bangladesh were compared to see how the concentrations varied between the different regions. Highly significant variations ($^{ANOVA}F = 75.28$, $p < 0.001$ and $^{ANOVA}F = 6.33$, $p < 0.001$, respectively for paddy and non-paddy soils) were observed in soil arsenic concentrations among the ten physiographic regions (Fig. 3 for paddy soils, fig. S4 for non-paddy soils). The Madhupur Tract and the Barind Tract were found to have the lowest arsenic concentrations (0.6-10.3, mean = 3.4 mg/kg, and 0.8-23.4, mean = 2.8 mg/kg, respectively) in the paddy soils, whereas the Ganges River Floodplain (1.6-68, mean = 11 mg/kg) and the Ganges Tidal Floodplain (3-42.5, mean = 13.1 mg/kg) had the highest soil arsenic concentrations. Martin et al. (2014, 2015) reported higher concentrations and mobilization of arsenic in the Ganges floodplain soils, due to enhanced influence of the pedoenvironmental properties in the region, compared to that in the Meghna floodplain soils suggesting a complex interaction between soil properties, climate and agricultural management practices in the paddy soil environment in Bangladesh. In the present study the Ganges floodplain soils were classified as Ganges River Floodplain and Ganges Tidal Floodplain, and the Meghna floodplain soils were classified as Meghna River Floodplain and Meghna Estuarine Floodplain, while no significant difference in arsenic concentrations was observed between Ganges River Floodplain and Meghna River Floodplain soils (Fig. 3). Similar observations were also reported for groundwater arsenic concentrations across the different geomorphological units of the country (BGS/DPHE, 2001; Ravenscroft, 2001).

At a gross level, high and low groundwater arsenic concentration regions are known to be based on physiographic units, with low concentrations of arsenic in groundwaters in the higher altitude Pleistocene terraces, and at high concentrations in Holocene floodplains (BGS/DPHE, 2001; Smedley and Kinniburgh, 2002; Ahmed et al., 2004; Ravenscroft et al., 2005). The explanation for this is that Pleistocene sediments are more highly weathered and leached of arsenic (Ravenscroft, 2001; Ravenscroft et al., 2005). A recent study on the source of arsenic in the Holocene/ Pleistocene sediments from the Terai plain of Nepal (that stratigraphically resemble Bangladeshi sediments) proposed a number of complex processes which can explain the differences in arsenic concentration between Holocene and Pleistocene sediments (Guillot et al., 2015). However, the river systems of Bangladesh actively rework the landscape, giving lenses of soil remobilized and re-deposited, interlayering Holocene and Pleistocene soils (BGS/DPHE, 2001; Polizzotto et al., 2005; Meharg et al., 2006; Guillot et al., 2015). It is also known that differential loss of arsenic occurs from groundwater irrigated paddy soils during the subsequent monsoonal floods through partitioning of soil arsenic into overlaying floodwaters (Dittmar et al., 2007; Saha and Ali, 2007; Dittmar et al., 2010; Roberts et al., 2010).

To determine the contribution of both natural soil arsenic concentrations and how paddy management practices have contributed towards the current soil arsenic concentration, paired non-paddy and paddy soils from major physiographic units of Bangladesh were analysed (Fig. 4). There was a significant relationship for soil arsenic between the paddy and non-paddy soils ($^{\text{linear regression}}R^2 = 0.26$, $p < 0.001$, $n = 235$) (Table S3). The slope of the overall regression (that is, for all soils) is 1.6:1 for paddy:non-paddy, that is, a general increase in arsenic of 60% in paddy cultivated soils. The soils form the floodplains and bils (low-lying floodplain) followed the same pattern as the overall regression regardless if they are from the Brahmaputra, Ganges or Meghna floodplains. Pleistocene terrace soils stand apart and do not follow the overall regression, being both on average lower in arsenic, and having less arsenic accumulation in paddy soils compared to Holocene floodplain soils. A paired t-test of the matching paddy and non-paddy soils for arsenic concentrations within the Pleistocene terrace soils indicated that these soils were significantly different ($p < 0.05$), with the non-paddy soils having elevated arsenic concentrations in comparison to the paddy soils, on an average the non-paddy soils had 19 percent higher arsenic. This indicates that paddy management is not increasing arsenic concentrations in these terrace soils. Pleistocene terrace groundwaters are low in arsenic (Nickson et al., 2000; BGS/DPHE, 2001; Ahmed et al., 2004; Ravenscroft et al., 2005), and thus, irrigation of Pleistocene terrace soils with groundwaters should not lead to elevation in arsenic. As Holocene floodplain groundwaters used in paddy irrigation are elevated in arsenic (Ali et al., 2003; Huq et al., 2003; Meharg and Rahman, 2003; Saha and Ali, 2007; Lu et al., 2009; Huq and Shoaib, 2013), irrigation of paddies with arsenic elevated groundwaters has the potential to lead to build-up in soil arsenic. Arsenic in the non-paddy floodplain soils ranged from 1.8-24.3 mg/kg (mean ± sd = 5.6 ± 2.9, coefficient of variation = 0.52, n = 205), showing that arsenic is naturally variable in Bangladeshi floodplain soils, with this range being 2-11 mg/kg (mean ± sd = 3.9 ± 1.8, coefficient of variation = 0.46, n = 30) for the Pleistocene terrace soils. This emphasises the inherent variability in natural soil arsenic, but that variability is less on Pleistocene terrace soils. It is the Holocene soils/sediments that are exposed to the active reworking that typifies a dynamic estuarine depositional environment (Sullivan and Aller, 1996; BGS/DPHE, 2001; Polizzotto et al., 2005; Meharg et al., 2006; Lu et al., 2009; Guillot et al., 2015), and this may explain the variability. The inherent differences in the sediments of the floodplain basins deposited from different sources over time, differences in arsenic accumulation/ release equilibria related to the indigenous soil chemistry, residence time, depth and duration of monsoon flood water, rate of particle dispersion, rate of leaching to subsurface, and biovolatilization to the atmosphere can also contribute to explain the variability of arsenic in the floodplain soils of Bangladesh (McLaren et al., 2006; Huq et al. 2008; Khan et al., 2009; Roberts et al., 2010; Mestrot et al., 2011; Brammer, 2012; Martin et al., 2015). In addition, the diversity and complexity of soils in the floodplains of Bangladesh are influenced by variations in flooding depth within the inundation land types (Brammer 1997; Huq et al., 2008), and hence, the accumulation and release of arsenic in soils vary within the toposequence of a landscape due to variations in relief and soil properties, particularly iron, clay and organic matter contents (Huq et al., 2008; Brammer 2012b; Ahmed et al. 2011).

Given that different geomorphic regions within the Holocene floodplain and Pleistocene terrace regions follow the same general trends, with the main differences being between floodplain and terrace, further analysis concentrated on floodplain versus terrace comparisons. For the Pleistocene soils, comparing paddy and non-paddy relationships were seen for all elements tested (Fig. 5 and Fig. S?). However, it was only for arsenic that paddy soils moved away from a 1:1 relationship, and groundwater is specifically only elevated in arsenic to any significant extent (BGS/DPHE, 2001) with respect to levels already found in soil, this is further evidence that it is groundwater irrigation *per se*, rather than other aspects of field management, such as fertilizer and manuring practices, that perturb paddy soil arsenic levels compared to non-paddy soils. The depletion in macro-nutrients in Pleistocene sediments, particularly the alkaline earths calcium and magnesium, is most apparent. Arsenic is also positively correlated ($r = 0.3$, $p < 0.001$) with soil pH (Fig. S3?), with low pH caused by low calcium and magnesium concentrations, cross confirming the interplay of soils factors correlated with arsenic. Iron and phosphorus, two elements intimately associated with arsenic's biogeochemical cycles (Fitz and Wenzel, 2002; Smith et al., 2002; Heikens et al., 2007) are also highly depleted in Pleistocene soils. Non-essential aluminium, cadmium, and lead also follow the same trend. It has been demonstrated that pedogenic processes are responsible for the depletion of nutrients within soils over time (Peltzer et al., 2010). Additionally, nutrients can be depleted in soils over shorter periods of time (Chen et al., 2011). Soils that have been under continuous paddy cropping have been shown to be depleted in key macronutrients in a very short period of time, for example, calcium, magnesium, and sodium have been demonstrated to be rapidly lost in paddy soils within 50 years of rice cultivation (Chen et al., 2011).

The wider characterization of Bangladeshi paddy soils, where elemental concentration is plotted against corresponding arsenic concentration (Fig. 6), shows the same trend as the paired paddy – non-paddy samples with Pleistocene depleted in all elements tested as compared to Holocene, with those being high in arsenic also, in general, being high in the corresponding elements (Table S4 and Fig. S?). This indicates again that Pleistocene soils are less sustainable than Holocene with respect to their elemental nutritional qualities. It is off concern that rice grains low in arsenic may be lower in nutrients as well. This subject area is not well investigated except where it was shown that in a Bangladeshi context that on arsenic enriched groundwater irrigated paddies that enhanced grain arsenic had, in general, suppression of micro-nutrient levels in rice grain (Williams et al., 2009; Norton et al., 2010). Unfortunately, there appears to be two global processes that regulate arsenic in grain, low nutrient soils have low arsenic, and high arsenic inhibits grain nutrient levels. This warrants further study in Bangladesh, namely by wide survey of grain versus soil associations for the primary mineral nutrients of human health importance.

What is also apparent from the plots of elemental concentration against arsenic is that Holocene soils have a much wider range of arsenic concentrations at higher concentrations of the other elements compared to Pleistocene soils, that is, there is much greater inherent variability in arsenic compared to other elements, specifically when other elemental concentrations are high (Fig. 6). This is indicative again that agricultural management practices specifically alter soil arsenic concentrations in Bangladesh. Groundwater for irrigation is the primary source of arsenic to floodplain paddies that are cropped during the dry season and is well known to elevate arsenic in paddy soils (Ali et al., 2003; Huq et al., 2003; Meharg et al., 2003; Dittmar et al., 2007; Saha and Ali, 2007; Huq, 2008; Lu et al., 2009; Ahmed et al., 2011; Huq and Shoaib, 2013). Paddy soils also have differential interaction with monsoonal floods following dry season application of arsenic, with arsenic capable of partitioning from soils into floodwaters (Dittmar et al., 2007; Saha and Ali, 2007; Dittmar et al., 2010; Roberts et al., 2010). As this interaction between floodwater and soil arsenic will be dependent on soil properties and on the dynamics of floodwater patterns for any specific paddy soil, heterogeneity in arsenic removal is expected. As the paddy soils have a higher arsenic concentration compared to the matched non-paddy soils, it would indicate that this process of loss of arsenic form the soils by monsoonal floods is not sufficient to reduce that arsenic concentration in the paddy soils back to the non-paddy soil background concentration.

When Principle Components Analysis (PCA) is used to look at the interrelationships between arsenic and other elements, the soils cluster into Pleistocene and Holocene using the first and second components (Fig. 7, Table S5). There is some overlap in the middle but this is expected perhaps as the large scales at which physiographic regions are drawn will miss the fine detail on the ground. This is further confounded by the lensing of old soils over new and with the sediment depositional environment also being highly active (Polizzotto et al., 2005; Meharg et al., 2006; Lu et al., 2009; Guillot et al., 2015). The direction of the loadings for the components shows that arsenic trends with most elements, and it is only cadmium and molybdenum that generally differ. The PCA analysis gives further strength to the hypothesis that arsenic is simply associated with less well weathered/ leached sediments, again suggesting it is either due to the geological newness of Holocene sediments or differences between the sources of sediments that gives rise to the arsenic problems in Bangladesh, and elsewhere (Smedley and Kinniburgh, 2002; McArthur et al., 2004; Nickson et al., 2005; Polya et al., 2005; Berg et al., 2007; Mukherjee et al., 2008; Rowland et al., 2008; Winkel et al., 2008; Guillot et al., 2015).

**Conclusion**

....

**Supporting Information**

Four additional tables and four figures as noted in the text. This material is available free of charge via the Internet.

**Acknowledgement**

This work was done as part of a doctoral fellowship plan funded by the Commonwealth Scholarship Commission in the UK. We gratefully acknowledge the Computer and GIS Unit of Bangladesh Agricultural Research Council (BARC) for providing GIS files for soil mapping. The soil samples were imported into the UK under import license IMP/SOIL/6/2013 issued by Science and Advice for Scottish Agriculture. L.H.E.W. and G.D.J. acknowledge funding by the Swiss National Science Foundation (SNF PP00P2_133619; PP00P2_163747).

**References**

Adomako, E.E., Solaiman, A.R.M., Williams, P.N., Deacon, C., Rahman, G.K.M.M., Meharg, A.A. 2009. Enhanced transfer of arsenic to grain for Bangladesh grown rice compared to US and EU. Environ. Int. 35, 476–479.

Adriano, D.C., 2001. *Trace Elements in the Terrestrial Environment*. Springer, New York.

Ahmed, K.M., Bhattacharya, P., Hasana, M.A., Akhter, S.H., Alam, S.M.M., Bhuyian, M.A.H., Imam, M.B., Khan, A.A., Sracek, O. 2004. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. Appl. Geochem. 19, 181–200.

Ahmed, Z.U., Panaullah, G.M., DeGloria, S.D., Duxbury, J.M. 2011. Factors affecting paddy soil arsenic concentration in Bangladesh: Prediction and uncertainty of geostatistical risk mapping. Sci. Tot. Environ. 412–413, 324–335.

Ali, M.A., Badruzzaman, A.B.M., Jalil, M.A., Hossain, M.D., Ahmed, M.F., Masud, A.A., Kamruzzaman, M., Rahman, M.A. 2003. Arsenic in plant-soil environment in Bangladesh, in: Ahmed, M.F., Ali, M.A., Adeel, Z. (Eds.), Fate of Arsenic in the Environment. ITN Centre: Bangladesh University of Engineering and Technology, Dhaka, pp. 85–112.

Berg, M., Stengel, C., Trang, P.T.K., Viet, P.H., Sampson, M.L., Leng, M., Samreth, S., Fredericks, D. 2007. Magnitude of arsenic pollution in the Mekong and Red River Deltas — Cambodia and Vietnam. Sci. Tot. Environ. 372, 413–425.

BGS/DPHE (British Geological Survey/ Bangladesh Department for Public Health Engineering), 2001. *Arsenic contamination of groundwater in Bangladesh*, Final Report. Kinniburgh, D.G. and Smedley, P.L. (Eds.), British Geological Survey Report WC/00/19. BGS, Keyworth, Vol. 2.

Brammer, H., 1996. The Geography of the Soils of Bangladesh. The University Press Ltd., Dhaka.

Brammer, H., 2012. *The Physical Geography of Bangladesh*. The University Press Ltd., Dhaka.

Chen, L.-M., Zhang, G.-L., Effland, W.R. 2011. Soil characteristic response times and pedogenic thresholds during the 1000-Year evolution of a paddy soil chronosequence. Soil Sci. Soc. Am. J. 75, 1807–1820.

Dittmar, J., Voegelin, A., Roberts, L., Hug, S.J., 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. 2. Paddy soil. Environ. Sci. Technol. 41, 5967–5972.

Dittmar, J., Voegelin, A., Roberts, L.C., Hug, S.J., Saha, G.C., Ali, M.A., Badruzzaman, A.B.M., Kretzschmar, R. 2010. Arsenic accumulation in a paddy field in Bangladesh: Seasonal dynamics and trends over a three-year monitoring period. Environ. Sci. Technol. 44 (8), 2925–2931.

FAO/UNDP (Food and Agriculture Organization/ United Nations Development Programme), 1988. Land resources appraisal of Bangladesh for agricultural development, Report 2: Agroecological Regions of Bangladesh. Report prepared for the Government of the People's Republic of Bangladesh by the Food and Agriculture Organization of United Nations, United Nations Development Programme, BGD/81/035, Technical report 2.

Fakhreddine, S., Dittmar, J., Phipps, D., Dadakis, J., Fendorf, S., 2015. Geochemical triggers of arsenic mobilization during managed aquifer recharge. Environ. Sci. Technol. 49 (13), 7802–7809.

Fitz, W.J., Wenzel, W.W. 2002. Arsenic transformations in the soil-rhizosphere plant system: fundamentals and potential application to phytoremediation. J. Biotechnol. 99, 259–278.

Guillot, S., Garçon, M., Weinman, B., Gajurel, A., Tisserand, D., France-Lanord, C., van Geen, A., Chakraborty, S., Huyghe, P., Upreti, B.N., Charlet, L. 2015. Origin of arsenic in Late Pleistocene to Holocene sediments in the Nawalparasi district (Terai, Nepal). Environ. Earth Sci. 74, 2571–2593.

Hasan, M.A., Ahmed, K.M., Sracek, O., Bhattacharya, P., von Brömssen, M., Broms, S., Fogelström, J., Mazumder, M.L., Jacks, G. 2007. Arsenic in shallow groundwater of Bangladesh: investigations from three different physiographic settings. Hydrogeol. J. 15, 1507–1522.

Heikens, A., Panaullah, G.M., Meharg, A.A. 2007. Arsenic behaviour from groundwater and soil to crops: Impacts on agriculture and food safety. Rev. Environ. Contam. Toxicol. 189, 43–87.

Huq, S.M.I., 2008. Fate of arsenic in irrigation water and its potential impacts on food chain, in: Ahuja, S. (Ed.), Arsenic Contamination of Groundwater: Mechanism, Analysis, and Remediation. Wiley, Hoboken, pp. 23–49.

Huq, S. M. I.; Alam, M. D. *A Hand Book on Analyses of Soil, Plant, and Water*; Bangladesh Australia Center for Environmental Research: University of Dhaka, Dhaka, Bangladesh, 2005.

Huq, S.M.I., Shoaib, J.U.M. 2013. *The Soils of Bangladesh*, world soils book series. Springer, Dordrecht.

Huq, S.M.I., Rahman, A., Sultana, N., Naidu, R. 2003. Extent and severity of arsenic contamination in soils of Bangladesh, in: Ahmed, M.F., Ali, M.A., Adeel, Z. (Eds.), Fate of Arsenic in the Environment. ITN Centre: Bangladesh University of Engineering and Technology, Dhaka, pp. 69–84.

Islam, M.R., Brammer, H., Rahman, G.K.M.M., Raab, A. 2012. Arsenic in rice grown in low-arsenic environments in Bangladesh. Water Qual. Expo. Health 4(4), 197–208.

Khan, M.A., Islam, M.R., Panaullah, G.M., Duxbury, J.M., Jahiruddin, M., Loeppert, R.H. 2009. Fate of irrigation-water arsenic in rice soils of Bangladesh. Plant and Soil 322 (1), 263–277.

Lambkin, D. C.; Alloway, B. J. 2003. Arsenate-induced phosphate release from soils and its effect on plant phosphorus. *Water Air Soil Pollut*. *144*, 41–56.

Lu, Y.; Adomako, E. E.; Solaiman, A. R. M.; Islam, M. R.; Deacon, C.; Williams, P.N.; Rahman, G. K. M. M.; Meharg A. A. 2009. Baseline soil variation is a major factor in arsenic accumulation in Bengal Delta paddy rice. *Environ. Sci. Technol. 43*, 1724–1729.

Martin, M., Bonifacio, E., Jakeer Hossain, K.M., Imamul Huq, S.M., Barberis, E., 2014. Arsenic fixation and mobilization in the soils of the Ganges and Meghna floodplains. Impact of pedoenvironmental properties. Geoderma 228–229, 132–141.

Martin, M., Stanchi, S., Hossain, K.M.J., Imamul Huq, S.M., Barberis, E., 2015. Potential phosphorus and arsenic mobilization from Bangladesh soils by particle dispersion. Sci. Tot. Environ. 53629, 973–980.

McArthur, J. M.; Banerjee, D. M.; Hudson-Edwards, K. A.; Mishra, R.; Purohit, R.; Ravenscroft, P.; Cronin, A.; Howarth, R. J.; Chatterjee, A.; Talukder, T.; Lowry, L.; Houghton, S.; Chadha, D. K. 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Appl. Geochem. 19*, 1255−1293.

McLaren, R. G.; et al. Fate of arsenic in the soil environment. In *Managing Arsenic in the Environment: From Soil to Human Health*; Naidu, R., Smith, E., Qwens, G., Bhattacharya, P., Nadebaum, P. Eds.; CSIRO Publishing: Collingwood 2006; pp 157−182.

Meharg, A.A., Hartley-Whitaker, J. 2002. Arsenic uptake and metabolism in arsenic resistant and non-resistant plant species. New Phytol. 154, 29–43.

Meharg, A.A., Rahman, M. 2003. Arsenic contamination of Bangladesh paddy field soils: Implications for rice contribution to arsenic consumption. Environ. Sci. Technol. 37 (2), 229−234.

Meharg, A.A., Scrimgeour, C., Hossain, S.A., Fuller, K., Cruickshank, K., Williams, P.N., Kinniburgh, D.G. 2006. Co-deposition of organic carbon and arsenic in Bengal Delta aquifers. Environ. Sci. Technol. 40, 4928−4935.

Meharg, A.A., Zhao, F.J. 2012. Arsenic & Rice. Springer, Netherlands.

Meharg, A.A., Williams, P.N., Adomako, E., Lawgali, Y.Y., Deacon, C., Villada, A., Cambell, R.C.J., Sun, G., Zhu, Y.-G., Feldmann, J., Raab, A., Zhao, F.-J., Islam, R., Hossain, S., Yanai, J. 2009. Geographical variation in total and inorganic arsenic content of polished (white) rice. Environ. Sci. Technol. 43, 1612-1617.

Mestrot, A., Feldmann, J., Krupp, E.M., Hossain, M., Roman-Ross, G., Meharg, A.A. 2011. Field fluxes and speciation of arsines emanating from soils. Environ. Sci. Technol. 45, 1798−1804.

Mukherjee, A., Bhattacharya, P., Savage, K., Foster, A., Bunschuh, J. 2008. Distribution of geogenic arsenic in hydrologic systems: controls and challenges. J. Contam. Hydrol. 99, 1–7.

Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G., Ahmed, K.M. 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Appl. Geochem. 15, 403−413.

Nickson, R.T., McArthur, J.M., Shrestha, B., Kyaw-Myint, T.O., Lowry, D. 2005. Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan. Appl. Geochem. 20, 55−68.

Norton, G.J., Dasgupta, T., Islam, M.R., Islam, S., Zhao, F.-J., Stroud, J.L., McGrath, S.P., Feldmann, J., Price, A.H., Meharg, A.A. 2010. Arsenic influence on cultivar variation in grain trace-element nutrient content in Bengal Delta grown rice. Environ. Sci. Technol. 44, 8284−8288.

Peltzer, D.A., Wardle, D.A., Allison, V.J., Baisden, W.T., Bardgett, R.D., Chadwick, O.A., Condron, L.M., Parfitt, R.L., Porder, S., Richardson, S.J., Turner, B.L., Vitousek, P.M., Walker, J., Walker, L.R. 2010. Understanding ecosystem retrogression. Ecol. Monogr. 80(4), 509−529.

Polizzotto, M.L., Harvey, C.F., Sutton, S.R., Fendorf, S. 2005. Processes conductive to the release and transport of arsenic into aquifers of Bangladesh. PNAS 102, 18819−18823.

Polya, D.A., Gault, A.G., Diebe, N., Feldman, P., Rosenboom, J.W., Gilligan, E., Fredericks, D., Milton, A.H., Sampson, M., Roland, H.A.L., Lythgoe, P.R., Jones, J.C., Middleton, C., Cooke, D. A. 2005. Arsenic hazard in shallow Cambodian groundwaters. Mineral. Mag. 69, 807−823.

Ravenscroft, P. 2001. Distribution of groundwater arsenic in Bangladesh related to geology, in: Jacks, G., Bhattacharya, P., Khan, A.A. (Eds.), Groundwater Arsenic Contamination in the Bengal Delta Plains of Bangladesh. Proceedings of the KTH-Dhaka University Seminar, University of Dhaka, Bangladesh. KTH Special Publication, TRITA-AMI Report 3084, pp. 41–56.

Ravenscroft, P., Burgess, W.G., Ahmed, K.M., Burren, M., Perrin, J. 2005. Arsenic in groundwater of the Bengal Basin, Bangladesh: Distribution, field relations, and hydrogeological setting. Hydrogeol. J. 13 (5-6), 727–751.

Roberts, L.C., Hug, S.J., Dittmar, J., Voegelin, A., Kretzschmar, R., Saha, G.C., Ali, M.A., Badruzzaman, A.B.M. 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 (1), 53–59.

Rowland, H.A.L., Gault, A.G., Lythgoe, P., Polya, D.A. 2008. Geochemistry of aquifer sediments and arsenic-rich groundwaters from Kandal Province, Cambodia. Appl. Geochem. 23, 3029–3046.

Saha, G.C., Ali, M.A. 2007. Dynamics of arsenic in agricultural soils irrigated with arsenic contaminated groundwater in Bangladesh. Sci. Tot. Environ. 379 (2-3), 180–189.

Smedley, P.L., Kinniburgh, D.G. 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Smith, E., Naidu, R., Alston, A.M. 2002. Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. J. Environ. Qual. 31 (2), 557–563.

Stachowicz, M., Hiemstra, T., van Riemsdijk, W.H. 2008. Multi-competitive interaction of As(III) and As(V) oxyanions with $Ca^{2+}$, $Mg^{2+}$, $PO_4^{3-}$, and $CO_3^{2-}$ ions on goethite. J. Colloid Interface Sci. 320 (2), 400–414.

Sullivan, K.A., Aller, R.C. 1996. Diagenetic cycling of arsenic inAmazonshelf sediments. Geochim. Cosmochim. Acta 60, 1465–1477.

Williams, P.N., Islam, S., Islam, R., Jahiruddin, M., Adomako, E., Soliaman, A.R.M., Rahman, G.K.M.M., Lu, Y., Deacon, C., Zhu, Y.-G., Meharg, A.A. 2009. Arsenic limits trace mineral nutrition (Selenium, Zinc, and Nickel) in Bangladesh rice grain. Environ. Sci. Technol. 43, 8430–8436.

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.

Winkel, L., Berg, M., Amini, M., Hug, S.J., Johnson, C.A. 2008. Predicting groundwater arsenic contamination in Southeast Asia from surface parameters. Nat. Geosci. 1, 536–542.

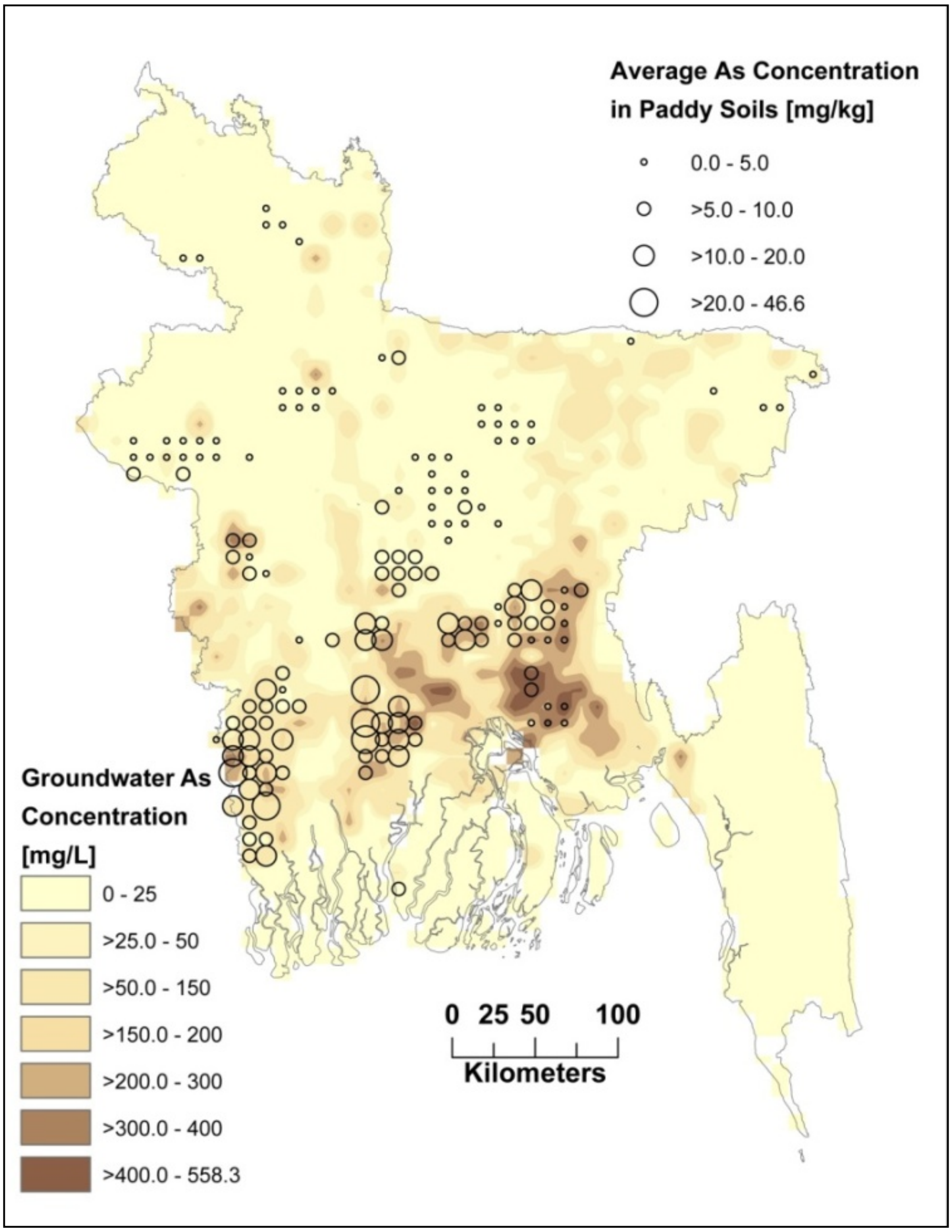


**Fig. 1. Sampling locations grouped per 10 km$^2$ and sample location marker scaled to size for average arsenic content of that location for surface soils. The underlying contour map is for groundwater arsenic with data inputted from the BGS/DPHE (2001) arsenic survey.**

**Fig. 2. Box and whisker plot showing concentrations of arsenic in paddy soils irrigated with groundwater and surface water. The boxplots indicate the lower and upper quartile (box), the median (solid line), the mean (dashed line), the 10th and 90th percentiles (whiskers) and the 5th and 95th percentiles (circles).**

**Fig. 3:** Arsenic concentrations in the paddy soils from different physiographic regions. The numbers of samples (n) at each of the physiographic regions are given within the parentheses. Tukey's *post hoc* analysis was performed with one-way analysis of variance to compare pair-wise the means of arsenic concentrations at each of the physiographic regions to show which regions had significant differences in soil arsenic. Regions that share the same letter (A–E) are not significantly different. The letters indicate Tukey groupings for the physiographic regions with respect to their mean soil arsenic concentrations.

**Fig. 4. Relationships between arsenic in paddy and non-paddy soils from different physiographic regions of Bangladesh. The regression line in each graph is the regression line for all the data. The fit and line equations are given in table S2.**

**Fig. 5. Paddy versus non-paddy elemental relationships with soils classified as Holocene and Pleistocene. The line on each of the graphs is the regression line for each of the elements. The fit and line equations are given in table S2.**

**Fig. 6. Relationships for arsenic versus elements for paddy soils grouped into Holocene and Pleistocene. The line on each of the graphs is the regression line for the corresponding elements. The fit and line equations are given in table S3.**

**Fig. 7. PCA of paddy soils classified into Holocene floodplain and Pleistocene terrace along with loading plot. The first and second component contributed 54.7 and 10.3 percent, respectively, to the variations.**