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

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

3

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26

27 **Abstract**

28

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

45

46 **Introduction**

47

48 Rice is elevated in inorganic arsenic compared to all other dietary staples (Meharg et al.,
49 2009). Flooding of soils, as in paddy cultivation, leads to the mobilization of natural and
50 anthropogenic inorganic arsenic stores in iron oxyhydroxide phases, caused by both the

51 reduction of arsenic and iron under negative soil redox potentials (Meharg and Zhao, 2012).
52 Paddy soils are managed through tilling, fertilization, and surface water and groundwater
53 irrigation, with the latter often elevated in inorganic arsenic throughout large areas of
54 Bangladesh (Huq et al., 2003; Meharg and Rahman, 2003; Roberts et al., 2007; Lu et al.,
55 2009). Furthermore, arsenic can undergo a number of processes within paddy soils that
56 leads to its subsequent loss such as partitioning to monsoonal floodwaters (Dittmar et al.,
57 2007; Saha and Ali, 2007; Dittmar et al., 2010; Roberts et al., 2010), leaching to sub-surfaces
58 (McLaren et al., 2006; Khan et al., 2009; Heikens et al., 2007), and biovolatilization to arsines
59 (Mestrot et al., 2011). Thus, the arsenic loading of any particular paddy soil will be due to
60 geological origin and the subsequent weathering of constituent minerals, and the
61 agronomic management of that sediment (Lu et al., 2009).

62

63 Bangladesh has three major geomorphological units (Brammer, 1996; Huq and Shoaib,
64 2013). These are hill, terrace, and floodplain areas. The hills occupy twelve percent of the
65 country's land area. The uplifted terrace areas are of Pleistocene age and occupy eight
66 percent of the country. The floodplains are of Holocene age and occupy eighty percent of
67 the country. The Holocene floodplains include the piedmont plains, river floodplains, tidal
68 floodplains, and estuarine floodplains. These geomorphological units are related to the
69 parent geological formations, however, they are also characterized by land topography and
70 age of the soil formation through sediment deposition over time (Brammer, 1996).

71

72 To understand and characterise the physiography of the geomorphological areas,
73 Bangladesh is divided into twenty main physiographic regions (FAO/UNDP, 1988). This
74 physiographic classification was based on the parent material in which individual soil types

75 were formed and the landscape on which the soils were developed (FAO/UNDP, 1988).

76 Therefore, the physiographic regions have differences in geology, relief, drainage, age of

77 land formation and pattern of sedimentary deposition. These differences ultimately

78 influence the nature and properties of the soils in the different physiographic regions.

79

80 The biogeochemical cycling of arsenic in soils is strongly affected by other elements. Iron is

81 central due to the strong association between insoluble arsenate and iron(III) oxyhydroxides

82 under aerobic conditions and with the mobilization of iron (II) and arsenite under reducing

83 (that is, paddy) conditions (BGS/DPHE, 2001; Smedley and Kinniburgh, 2002; McArthur et

84 al., 2004; Polizzotto et al., 2005). Manganese oxides also have a similar redox chemistry to

85 iron and are strongly implicated in arsenic immobilization/mobilization during oxic/anoxic

86 cycling of paddy sediments (Smedley and Kinniburgh, 2002; Hasan et al., 2007). Arsenate is

87 a phosphate analogue and, thus, key to competition for binding sites within the soil solid

88 phase, as well as having similar biogeochemical cycling under oxic conditions (Adriano,

89 2001; Meharg and Hartley-Whitaker, 2002; Smith et al., 2002; Lambkin and Alloway, 2003;

90 Stachowicz et al., 2008). Calcium and magnesium immobilize arsenate under oxic

91 conditions, and could also have a role in the biogeochemical cycling of arsenic at a

92 landscape level (Smith et al., 2002; Stachowicz et al., 2008; Fakhreddine et al., 2015).

93

94 Here, we wanted to understand the relationship between soil arsenic and paddy

95 management practice with respect to arsenic loadings in Bangladeshi soils. Cultivation zones

96 of paddy soils (n = 1209) across ten physiographic regions of Bangladesh, from latitude

97 22°06' to 24°53', and longitude 88°20' to 90°59' were sampled and analysed for arsenic and

98 a suite of sixteen other elements (aluminium, calcium, cadmium, cobalt, chromium, copper,

99 iron, lead, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, sodium
100 and zinc). For a subset of soils (n = 235), paired paddy and adjacent non-paddy soils were
101 also collected and characterised. The data were used to address four specific objectives: to
102 assess the impact that geomorphological differences have on soil arsenic at a landscape
103 level; to understand the relationship between the concentration of arsenic in the paddy
104 soils with the concentration of arsenic within the underlying groundwater; to determine if
105 the source of irrigation water impacts on soil arsenic concentrations; and by examining the
106 concentrations of arsenic and other elements in paddy and non-paddy soils, we aimed to
107 understand the impacts that paddy management has on soil elemental concentrations.

108 **Materials and Methods**

109 ***Collection of Soil Samples***

110 A total of 1444 soil samples (topsoil, 0-15 cm from the surface) from paddy fields (n = 1209)
111 and neighboring non-paddy areas (n = 235) were collected from 10 different physiographic
112 regions within 57 sub-districts (upazilas) from 17 districts of Bangladesh (Table S1). Non-
113 paddy soils were defined as the soils where paddy cultivation and groundwater irrigation
114 had not been practiced within known memory of the farmers. The physiographic regions
115 from where the soil samples were collected included Arial Bil (n = 42 paddy and 10 non-
116 paddy soils), Brahmaputra Floodplain (n = 207 paddy and 64 non-paddy soils), Ganges River
117 Floodplain (n = 261 paddy and 58 non-paddy soils), Ganges Tidal Floodplain (n = 47 paddy
118 and 11 non-paddy soils), Gopalganj-Khulna Bils (n = 63 paddy and 8 non-paddy soils),
119 Karatoya-Bangali floodplain (n = 15 paddy soils only), Meghna Estuarine Floodplain (n = 204
120 paddy and 28 non-paddy soils), and Meghna River Floodplain (n = 184 paddy and 26 non-
121 paddy soils) from Holocene floodplains, and Barind Tract (n = 68 paddy and 15 non-paddy
122 soils) and Madhupur Tract (n = 118 paddy and 15 non-paddy soils) from Pleistocene
123 terraces. The source of irrigation water for the paddy soils was recorded (groundwater, n =
124 904; surface water, n = 281; both, n = 24). Only the soils that had a non-mixed irrigation
125 source were used for analyzing the impact of irrigation type on soil arsenic.

126

127 ***Sample Processing and Preparation for Analysis***

128 The soil samples were air-dried and, prior to analysis, the samples were oven dried (80°C ±
129 5°C for 48 h), and finely ground using a ball-mill. The soil digestion procedure followed was
130 described by Adomako et al. (2009). Briefly, 0.1 g of soil was placed in a glass digest tube
131 and 2.5 ml of concentrated nitric acid was added to the tube and left overnight for pre-

132 digestion. Then, 2.5 ml of hydrogen peroxide was added to the sample just before digesting
133 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
134 120°C and, finally, at 140°C for 3 h until the solution was clear. Once cooled, the digested
135 soil samples were transferred into 15 ml polypropylene tubes and each glass tube was
136 thoroughly rinsed 3 times with ultrapure deionized water (Milli-Q 18.2 MΩ). The volumes
137 were made up to 15 ml mark using the same water. To obtain the appropriate dilution for
138 analysis by inductively coupled plasma-mass spectrometer (ICP-MS) and microwave plasma-
139 atomic emission spectrometer (MP-AES), the samples were further diluted to 1 in 10.
140 Calibration standards were prepared from 1000 mg/l multi-element stock solutions (SPEX
141 CertiPrep Reference Material).

142

143 ***Chemical Analysis***

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

155

156 ***Soil Mapping***

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

162

163 ***Statistical Analysis***

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

167

168 **Results and Discussion**

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

175

176 To develop a soil arsenic map of the sampled soils, all paddy soil sampling locations within a
177 10 km² grid were averaged (Fig. 1). Individual locations and sampling densities are shown in
178 Fig. S2. There is a clear north/south divide in paddy arsenic concentrations with much higher
179 concentrations, in general, in the south. The paddy soil arsenic levels reported here (1-88
180 mg/kg, average = 8 mg/kg) are within the ranges reported for previous Bangladesh paddy
181 soil surveys (Huq et al., 2003; Meharg and Rahman, 2003; Lu et al., 2009; Williams et al.,
182 2011; Huq and Shoaib, 2013). The pattern of paddy soil concentrations relate well to
183 groundwater measurements (BGS-DPHE, 2001), again with groundwater elevated in the
184 south, excluding the coastal zone. The exception is the cluster of sampling points in the
185 extreme south-east that have a low soil arsenic concentration and the highest groundwater
186 arsenic concentration. This is probably due to the source of irrigation water used in this
187 south-east region, where the main irrigation method is from surface water rather than
188 groundwater (Fig. S3). When comparing the arsenic concentrations in the paddies that have
189 been irrigated with groundwater and surface water across Bangladesh, there was a
190 significant difference ($F^{ANOVA} = 26.23, p < 0.001$) in the soil arsenic concentration (Fig. 2).
191 Soils irrigated with groundwater had on average an arsenic concentration of 8.5 mg/kg

192 which was significantly higher than the soils irrigated with surface water, which had an
193 average arsenic concentration of 5.7 mg/kg. For the individual physiographic regions, seven
194 of the regions had enough groundwater and surface water irrigated soils (>10) to do
195 comparisons between irrigation method and soil arsenic. There was no significant difference
196 in soil arsenic between the groundwater irrigation and surface water irrigation for four of
197 the seven physiographic regions. For the three other physiographic regions, significant
198 differences in arsenic concentrations were observed between the soils irrigated with
199 groundwater (GWI) and surface water (SWI), with higher arsenic concentrations in the
200 groundwater irrigated soils than in the surface water irrigated soils (for Ganges Tidal
201 Floodplain, $^{ANOVA}F = 5.97$, $p < 0.05$, $n = 28$ (GWI) and 20 (SWI), mean = 14.6 mg/kg (GWI) and
202 8.6 mg/kg (SWI); for Meghna Estuarine Floodplain, $^{ANOVA}F = 14.84$, $p < 0.001$, $n = 69$ (GWI)
203 and 111 (SWI), mean = 8 mg/kg (GWI) and 3.9 mg/kg (SWI); for Meghna River Floodplain,
204 $^{ANOVA}F = 62.06$, $p < 0.001$, $n = 130$ (GWI) and 54 (SWI), mean = 9.4 mg/kg (GWI) and 4.7
205 mg/kg (SWI)). As the samples were collected from different geomorphic regions, these
206 results could be confounded by the underlying geomorphology. However, difference in soil
207 arsenic due to different irrigation techniques appears to be a trend across the country.

208

209 Soil arsenic concentrations across ten different physiographic regions of Bangladesh were
210 compared to see how the concentrations varied between the different regions. Highly
211 significant variations ($^{ANOVA}F = 75.28$, $p < 0.001$ and $^{ANOVA}F = 6.33$, $p < 0.001$, respectively for
212 paddy and non-paddy soils) were observed in soil arsenic concentrations among the ten
213 physiographic regions (Fig. 3 for paddy soils, fig. S4 for non-paddy soils). The Madhupur
214 Tract and the Barind Tract were found to have the lowest arsenic concentrations (0.6-10.3,
215 mean = 3.4 mg/kg, and 0.8-23.4, mean = 2.8 mg/kg, respectively) in the paddy soils, whereas

216 the Ganges River Floodplain (1.6-68, mean = 11 mg/kg) and the Ganges Tidal Floodplain (3-
217 42.5, mean = 13.1 mg/kg) had the highest soil arsenic concentrations. Martin et al. (2014,
218 2015) reported higher concentrations and mobilization of arsenic in the Ganges floodplain
219 soils, due to enhanced influence of the pedoenvironmental properties in the region,
220 compared to that in the Meghna floodplain soils suggesting a complex interaction between
221 soil properties, climate and agricultural management practices in the paddy soil
222 environment in Bangladesh. In the present study the Ganges floodplain soils were classified
223 as Ganges River Floodplain and Ganges Tidal Floodplain, and the Meghna floodplain soils
224 were classified as Meghna River Floodplain and Meghna Estuarine Floodplain, while no
225 significant difference in arsenic concentrations was observed between Ganges River
226 Floodplain and Meghna River Floodplain soils (Fig. 3). Similar observations were also
227 reported for groundwater arsenic concentrations across the different geomorphological
228 units of the country (BGS/DPHE, 2001; Ravenscroft, 2001).

229

230 At a gross level, high and low groundwater arsenic concentration regions are known to be
231 based on physiographic units, with low concentrations of arsenic in groundwaters in the
232 higher altitude Pleistocene terraces, and at high concentrations in Holocene floodplains
233 (BGS/DPHE, 2001; Smedley and Kinniburgh, 2002; Ahmed et al., 2004; Ravenscroft et al.,
234 2005). The explanation for this is that Pleistocene sediments are more highly weathered and
235 leached of arsenic (Ravenscroft, 2001; Ravenscroft et al., 2005). A recent study on the
236 source of arsenic in the Holocene/ Pleistocene sediments from the Terai plain of Nepal (that
237 stratigraphically resemble Bangladeshi sediments) proposed a number of complex processes
238 which can explain the differences in arsenic concentration between Holocene and
239 Pleistocene sediments (Guillot et al., 2015). However, the river systems of Bangladesh

240 actively rework the landscape, giving lenses of soil remobilized and re-deposited,
241 interlayering Holocene and Pleistocene soils (BGS/DPHE, 2001; Polizzotto et al., 2005;
242 Meharg et al., 2006; Guillot et al., 2015). It is also known that differential loss of arsenic
243 occurs from groundwater irrigated paddy soils during the subsequent monsoonal floods
244 through partitioning of soil arsenic into overlaying floodwaters (Dittmar et al., 2007; Saha
245 and Ali, 2007; Dittmar et al., 2010; Roberts et al., 2010).

246

247 To determine the contribution of both natural soil arsenic concentrations and how paddy
248 management practices have contributed towards the current soil arsenic concentration,
249 paired non-paddy and paddy soils from major physiographic units of Bangladesh were
250 analysed (Fig. 4). There was a significant relationship for soil arsenic between the paddy and
251 non-paddy soils (linear regression $R^2 = 0.26$, $p < 0.001$, $n = 235$) (Table S3). The slope of the overall
252 regression (that is, for all soils) is 1.6:1 for paddy:non-paddy, that is, a general increase in
253 arsenic of 60% in paddy cultivated soils. The soils from the floodplains and bils (low-lying
254 floodplain) followed the same pattern as the overall regression regardless if they are from
255 the Brahmaputra, Ganges or Meghna floodplains. Pleistocene terrace soils stand apart and
256 do not follow the overall regression, being both on average lower in arsenic, and having less
257 arsenic accumulation in paddy soils compared to Holocene floodplain soils. A paired t-test of
258 the matching paddy and non-paddy soils for arsenic concentrations within the Pleistocene
259 terrace soils indicated that these soils were significantly different ($p < 0.05$), with the non-
260 paddy soils having elevated arsenic concentrations in comparison to the paddy soils, on an
261 average the non-paddy soils had 19 percent higher arsenic. This indicates that paddy
262 management is not increasing arsenic concentrations in these terrace soils. Pleistocene
263 terrace groundwaters are low in arsenic (Nickson et al., 2000; BGS/DPHE, 2001; Ahmed et

264 al., 2004; Ravenscroft et al., 2005), and thus, irrigation of Pleistocene terrace soils with
265 groundwaters should not lead to elevation in arsenic. As Holocene floodplain groundwaters
266 used in paddy irrigation are elevated in arsenic (Ali et al., 2003; Huq et al., 2003; Meharg
267 and Rahman, 2003; Saha and Ali, 2007; Lu et al., 2009; Huq and Shoaib, 2013), irrigation of
268 paddies with arsenic elevated groundwaters has the potential to lead to build-up in soil
269 arsenic. Arsenic in the non-paddy floodplain soils ranged from 1.8-24.3 mg/kg (mean \pm sd =
270 5.6 ± 2.9 , coefficient of variation = 0.52, n = 205), showing that arsenic is naturally variable
271 in Bangladeshi floodplain soils, with this range being 2-11 mg/kg (mean \pm sd = 3.9 ± 1.8 ,
272 coefficient of variation = 0.46, n = 30) for the Pleistocene terrace soils. This emphasises the
273 inherent variability in natural soil arsenic, but that variability is less on Pleistocene terrace
274 soils. It is the Holocene soils/sediments that are exposed to the active reworking that
275 typifies a dynamic estuarine depositional environment (Sullivan and Aller, 1996; BGS/DPHE,
276 2001; Polizzotto et al., 2005; Meharg et al., 2006; Lu et al., 2009; Guillot et al., 2015), and
277 this may explain the variability. The inherent differences in the sediments of the floodplain
278 basins deposited from different sources over time, differences in arsenic accumulation/
279 release equilibria related to the indigenous soil chemistry, residence time, depth and
280 duration of monsoon flood water, rate of particle dispersion, rate of leaching to subsurface,
281 and biovolatilization to the atmosphere can also contribute to explain the variability of
282 arsenic in the floodplain soils of Bangladesh (McLaren et al., 2006; Huq et al. 2008; Khan et
283 al., 2009; Roberts et al., 2010; Mestrot et al., 2011; Brammer, 2012; Martin et al., 2015). In
284 addition, the diversity and complexity of soils in the floodplains of Bangladesh are
285 influenced by variations in flooding depth within the inundation land types (Brammer 1997;
286 Huq et al., 2008), and hence, the accumulation and release of arsenic in soils vary within the

287 toposequence of a landscape due to variations in relief and soil properties, particularly iron,
288 clay and organic matter contents (Huq et al., 2008; Brammer 2012b; Ahmed et al. 2011).
289
290 Given that different geomorphic regions within the Holocene floodplain and Pleistocene
291 terrace regions follow the same general trends, with the main differences being between
292 floodplain and terrace, further analysis concentrated on floodplain versus terrace
293 comparisons. For the Pleistocene soils, comparing paddy and non-paddy relationships were
294 seen for all elements tested (Fig. 5 and Fig. S7). However, it was only for arsenic that paddy
295 soils moved away from a 1:1 relationship, and groundwater is specifically only elevated in
296 arsenic to any significant extent (BGS/DPHE, 2001) with respect to levels already found in
297 soil, this is further evidence that it is groundwater irrigation *per se*, rather than other
298 aspects of field management, such as fertilizer and manuring practices, that perturb paddy
299 soil arsenic levels compared to non-paddy soils. The depletion in macro-nutrients in
300 Pleistocene sediments, particularly the alkaline earths calcium and magnesium, is most
301 apparent. Arsenic is also positively correlated ($r = 0.3$, $p < 0.001$) with soil pH (Fig. S3?), with
302 low pH caused by low calcium and magnesium concentrations, cross confirming the
303 interplay of soils factors correlated with arsenic. Iron and phosphorus, two elements
304 intimately associated with arsenic's biogeochemical cycles (Fitz and Wenzel, 2002; Smith et
305 al., 2002; Heikens et al., 2007) are also highly depleted in Pleistocene soils. Non-essential
306 aluminium, cadmium, and lead also follow the same trend. It has been demonstrated that
307 pedogenic processes are responsible for the depletion of nutrients within soils over time
308 (Peltzer et al., 2010). Additionally, nutrients can be depleted in soils over shorter periods of
309 time (Chen et al., 2011). Soils that have been under continuous paddy cropping have been
310 shown to be depleted in key macronutrients in a very short period of time, for example,

311 calcium, magnesium, and sodium have been demonstrated to be rapidly lost in paddy soils
312 within 50 years of rice cultivation (Chen et al., 2011).

313

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

328

329 What is also apparent from the plots of elemental concentration against arsenic is that
330 Holocene soils have a much wider range of arsenic concentrations at higher concentrations
331 of the other elements compared to Pleistocene soils, that is, there is much greater inherent
332 variability in arsenic compared to other elements, specifically when other elemental
333 concentrations are high (Fig. 6). This is indicative again that agricultural management
334 practices specifically alter soil arsenic concentrations in Bangladesh. Groundwater for

335 irrigation is the primary source of arsenic to floodplain paddies that are cropped during the
336 dry season and is well known to elevate arsenic in paddy soils (Ali et al., 2003; Huq et al.,
337 2003; Meharg et al., 2003; Dittmar et al., 2007; Saha and Ali, 2007; Huq, 2008; Lu et al.,
338 2009; Ahmed et al., 2011; Huq and Shoaib, 2013). Paddy soils also have differential
339 interaction with monsoonal floods following dry season application of arsenic, with arsenic
340 capable of partitioning from soils into floodwaters (Dittmar et al., 2007; Saha and Ali, 2007;
341 Dittmar et al., 2010; Roberts et al., 2010). As this interaction between floodwater and soil
342 arsenic will be dependent on soil properties and on the dynamics of floodwater patterns for
343 any specific paddy soil, heterogeneity in arsenic removal is expected. As the paddy soils
344 have a higher arsenic concentration compared to the matched non-paddy soils, it would
345 indicate that this process of loss of arsenic from the soils by monsoonal floods is not
346 sufficient to reduce that arsenic concentration in the paddy soils back to the non-paddy soil
347 background concentration.

348

349 When Principle Components Analysis (PCA) is used to look at the interrelationships between
350 arsenic and other elements, the soils cluster into Pleistocene and Holocene using the first
351 and second components (Fig. 7, Table S5). There is some overlap in the middle but this is
352 expected perhaps as the large scales at which physiographic regions are drawn will miss the
353 fine detail on the ground. This is further confounded by the lensing of old soils over new and
354 with the sediment depositional environment also being highly active (Polizzotto et al., 2005;
355 Meharg et al., 2006; Lu et al., 2009; Guillot et al., 2015). The direction of the loadings for the
356 components shows that arsenic trends with most elements, and it is only cadmium and
357 molybdenum that generally differ. The PCA analysis gives further strength to the hypothesis
358 that arsenic is simply associated with less well weathered/ leached sediments, again

359 suggesting it is either due to the geological newness of Holocene sediments or differences
360 between the sources of sediments that gives rise to the arsenic problems in Bangladesh, and
361 elsewhere (Smedley and Kinniburgh, 2002; McArthur et al., 2004; Nickson et al., 2005;
362 Polya et al., 2005; Berg et al., 2007; Mukherjee et al., 2008; Rowland et al., 2008; Winkel et
363 al., 2008; Guillot et al., 2015).

364

365 **Conclusion**

366 ...

367 **Supporting Information**

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

370

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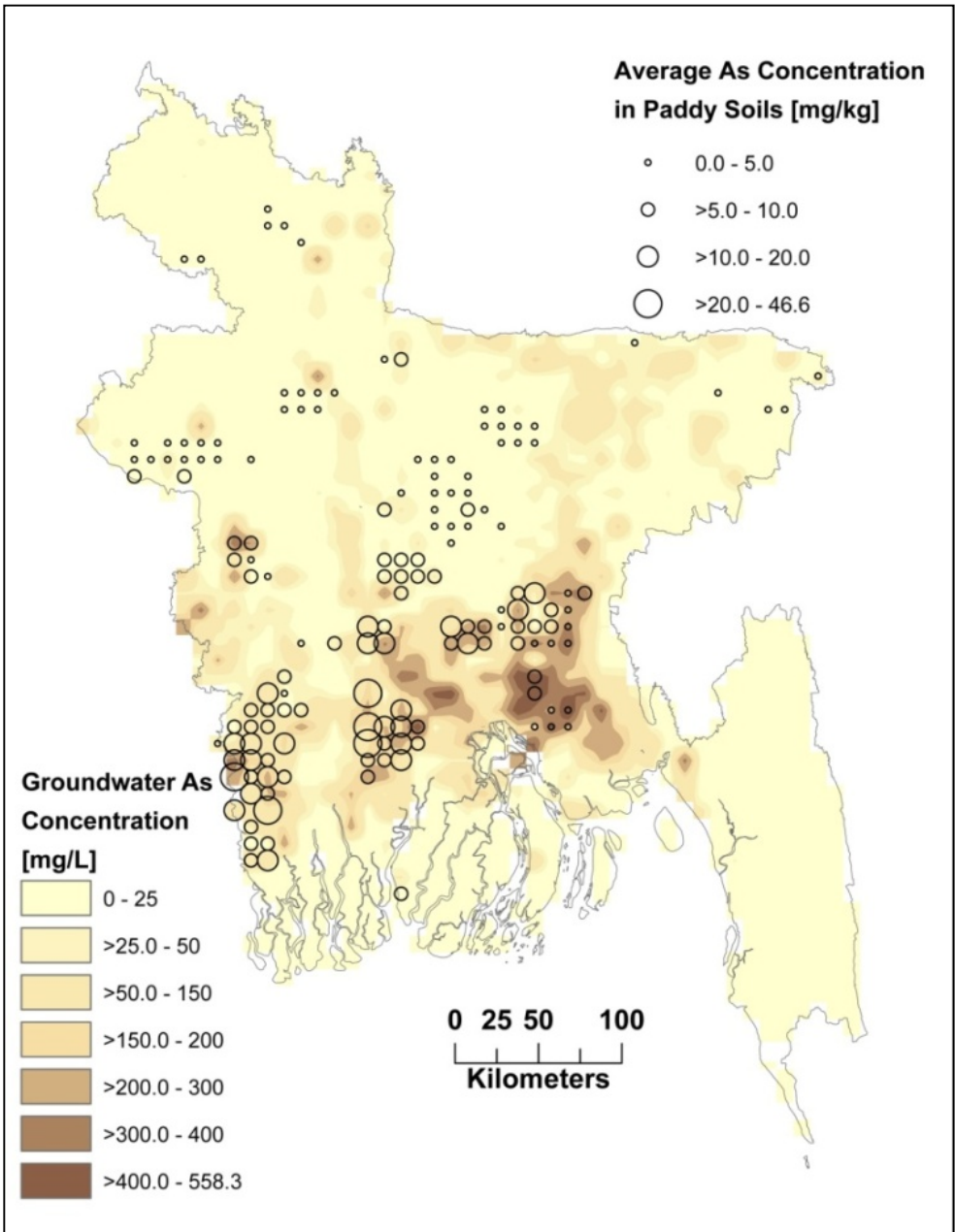
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545 **Fig. 1. Sampling locations grouped per 10 km² and sample location marker scaled to size**
 546 **for average arsenic content of that location for surface soils. The underlying contour map**
 547 **is for groundwater arsenic with data inputted from the BGS/DPHE (2001) arsenic survey.**

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

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

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582 **Fig. 4. Relationships between arsenic in paddy and non-paddy soils from different**
583 **physiographic regions of Bangladesh. The regression line in each graph is the regression**
584 **line for all the data. The fit and line equations are given in table S2.**
585

586

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

590
591 **Fig. 6. Relationships for arsenic versus elements for paddy soils grouped into Holocene**
592 **and Pleistocene. The line on each of the graphs is the regression line for the corresponding**
593 **elements. The fit and line equations are given in table S3.**

595
596 **Fig. 7. PCA of paddy soils classified into Holocene floodplain and Pleistocene terrace along**
597 **with loading plot. The first and second component contributed 54.7 and 10.3 percent,**
598 **respectively, to the variations.**