

# Soil arsenic but not rice arsenic increasing with arsenic in irrigation water in the Punjab plains of Pakistan

Asif Javed · Abida Farooqi · Zakir Ullah Baig · Tyler Ellis · Alexander van Geen

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## Abstract

**Aim** Irrigating rice with groundwater can lead to As accumulation in soil and rice grains. Matched sets of irrigation water, paddy soil, and rice grains were collected to assess the scale of the problem in the Punjab plains of Pakistan.

**Methods** From a total of 60 sites, irrigation water and rice grains as well as 103 soil samples were collected and analyzed in the laboratory. Irrigation water and 660 soil samples were also analyzed in the field using a field kit.

**Results** Concentrations of As in irrigation water ( $65 \pm 32 \mu\text{g/L}$ ) are higher in the floodplain of the Ravi River compared to the Chenab ( $13 \pm 9 \mu\text{g/L}$ ) and Jhelum ( $4 \pm 5 \mu\text{g/L}$ ) rivers, as well as the intervening Rechna ( $6 \pm 6 \mu\text{g/L}$ ) and Chaj doabs ( $0.8 \pm 0.2 \mu\text{g/L}$ ). Area-weighted mean soil As concentrations are  $12 \pm 3 \text{ mg/kg}$  along the

Ravi,  $8.9 \pm 2$  and  $8.1 \pm 2 \text{ mg/kg}$  along the Chenab and Jhelum, respectively, and  $6.2 \pm 0.2 \text{ mg/kg}$  within the Rachna and  $6.1 \pm 0.1 \text{ mg/kg}$  in Chaj doabs. The As content of polished grains export-quality basmati rice of  $0.09 \pm 0.05 \text{ mg/kg}$ , however, is low across the entire area.

**Conclusions** Groundwater irrigation leads to elevated As concentrations in paddy soil of some rice-growing regions of Punjab but does not result in increased uptake of As in basmati rice grains.

**Keywords** Arsenic · Groundwater · Soil · Rice · Punjab

## Introduction

The northern Indus Plain of Pakistan is known as the rice-wheat belt, with rice grown in summer (Kharif) and wheat in winter (Rabi) (Hassan and Bhutta 1996). Pakistan ranks 10th globally in terms of rice production but is the world's 4th largest exporter at 4 million tons of rice per year (FAO 2017). On account of the semi-arid to arid climate of the country, an extensive network of canals was built starting in the nineteenth century to distribute water draining the Himalayas (Greenman et al. 1967). In northern Punjab, growing wheat during winter requires little irrigation (Naheed and Mahmood 2009), but rice requires about 1.6 m of water per season (Erenstein 2009). Supplemental irrigation is typically needed because the summer rains are insufficient. Since the 1960s, the canal irrigation system has gradually been supplanted by pumping groundwater from wells which

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A. Javed · A. Farooqi (✉) · Z. U. Baig  
Environmental Geochemistry Laboratory, Department of Environmental Sciences, Faculty of Biological Sciences, Quaid-i-Azam University, Islamabad, Pakistan  
e-mail: afarooqi@qau.edu.pk

A. Javed  
Department of Earth and Environmental Sciences, Bahria University, Islamabad, Pakistan

T. Ellis · A. van Geen (✉)  
Lamont Doherty Earth Observatory, Columbia University, Palisades, New York, USA  
e-mail: avangeen@ldeo.columbia.edu

57 numbered over half a million by 2000 and most of  
58 which are located in Punjab (Qureshi et al. 2010).

59 Unfortunately, the pumped groundwater can be con-  
60 taminated with arsenic (As) in some parts of the country,  
61 including in northern Punjab which is the country's  
62 main rice growing region and where the present study  
63 was conducted (Farooqi et al. 2007; Javed et al. 2019;  
64 Nickson et al. 2005). Testing of over 30,000 drinking-  
65 water wells across 400 villages of northern Punjab on  
66 both sides of the border between Pakistan and India has  
67 revealed that As concentrations in groundwater are par-  
68 ticularly elevated along the floodplain of the Ravi River,  
69 whereas the Sutlej, Chenab, and Jhelum floodplains are  
70 less affected (van Geen et al. 2019). This could be a  
71 concern for two reasons: the accumulation of As in  
72 paddy soil leading to a reduction in yield and the trans-  
73 location of As to the rice grain resulting in human  
74 exposure.

75 Many studies, most conducted in Bangladesh, have  
76 shown that irrigating with groundwater that is elevated  
77 in As results in the accumulation of As in the upper  
78 ~20 cm of soil (Duxbury et al. 2009; Meharg and  
79 Rahman 2003; Panaullah et al. 2009; Van Geen et al.  
80 2006). A few studies have shown that this accumulation  
81 of As significantly reduces rice production (Hossain  
82 et al. 2008; Huhmann et al. 2017; Panaullah et al.  
83 2009). Most reports have focused instead on the accu-  
84 mulation of As in rice grains, concluding in some cases  
85 that high As concentrations in soil result in increased As  
86 concentrations in the grain (Azad et al. 2009; Khan et al.  
87 2009; Rahaman et al. 2011; Rauf et al. 2011; Williams  
88 et al. 2006; Zhao et al. 2009), with others pointing to less  
89 conclusive results (Panaullah et al. 2009; Stroud et al.  
90 2011; Van Geen et al. 2006). Given the growing evi-  
91 dence of the negative health impacts of exposure to As,  
92 including in early life, As accumulation in rice is a  
93 serious issue (Davis et al. 2012). Considerable attention  
94 therefore continues to be paid to rice varieties that  
95 accumulate less As in the grain (Halder et al. 2012;  
96 Williams et al. 2005), as well as changes in water or soil  
97 management that reduce the uptake of As by the rice  
98 plant (Duxbury and Panaullah 2007; Spanu et al. 2012).

99 Previous reports on rice grown in Pakistan indicate  
100 relatively low As concentration in export-quality  
101 basmati, although these analyses were not paired with  
102 soil As measurements (Adomako et al. 2011; PCRWR  
103 2014; Zavala and Duxbury 2008). In the present study,  
104 we explore the potential relationship between As in  
105 paddy soil and rice grains in a new setting by taking

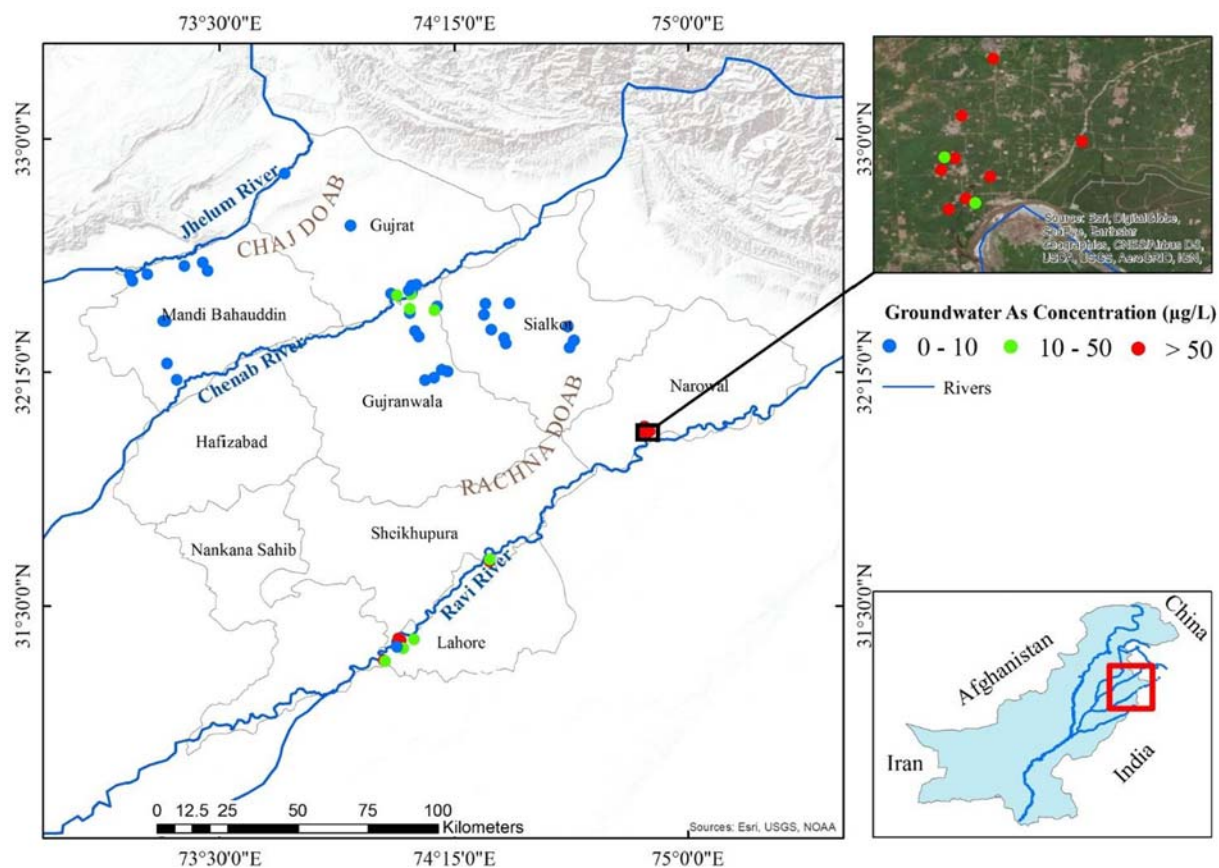
106 advantage of the recently documented difference in  
107 groundwater As levels across different floodplains and  
108 doabs of northern Punjab (van Geen et al. 2019). Along  
109 with irrigation water, transects of surface soil were col-  
110 lected from dozens of fields across the region and paired  
111 with rice samples obtained directly from the farmer  
112 cultivating each field. Motivated by the need for farmers  
113 to know the status of their field, we used a kit to analyze  
114 the As content of irrigation water and paddy soil in the  
115 field for comparison with laboratory measurements.

## 116 Materials and methods

117 The study area lies in northern Punjab ("five rivers") and  
118 is bound by the floodplain of the Jhelum River to the  
119 northwest and the floodplain of the Ravi River to the  
120 southeast (Fig. 1). The floodplain of the Chenab River  
121 divides the region roughly midway into the slightly  
122 elevated Chaj and Rechna doabs, a local word to de-  
123 scribe the land between two rivers.

### 124 Sampling

125 From each of 60 individual rice fields irrigated by a  
126 single well, matched sets of irrigation-well water, and  
127 10 surface soil samples were collected. Water was col-  
128 lected from the irrigation wells without filtration in  
129 20 mL polyethylene scintillation vials with a PolySeal-  
130 lined cap (Wheaton no. 986706) and soil in polyethyl-  
131 ene bags. Ten ~100 g soil samples scooped from the  
132 upper ~1 cm were evenly spaced along the diagonal  
133 across each field originating from the corner closest to  
134 the inlet of the irrigation water to the corner furthest  
135 away (Online Resource Fig. 1). For a subset of 10 fields  
136 in the floodplain of the Ravi River, a locally-made  
137 stainless steel core sampler (diameter 2.5 in., length  
138 70 cm) was used to collect a soil profile to 60 cm depth  
139 in 10-cm intervals. About 1 kg of polished rice sample  
140 of the same 60 fields from the previous season was also  
141 obtained directly from the farmers and stored in poly-  
142 ethylene bags. Given that the harvest from each field  
143 was dried and threshed locally by each farmer, it is  
144 reasonable to assume that rice grains from different parts  
145 of the field had been well mixed and that the sample was  
146 therefore representative. A total of 60 water and 660 soil  
147 tests were conducted in the field using the ITS Econo-  
148 Quick kit (George et al. 2012). The same well water



**Fig. 1** Map of northern Punjab with the 60 study sites and the As content of water sampled from irrigation wells at each site

149 samples and a subset of 103 soil samples were also  
150 analyzed in the laboratory (Online Resource Table 1).

#### 151 Laboratory measurements

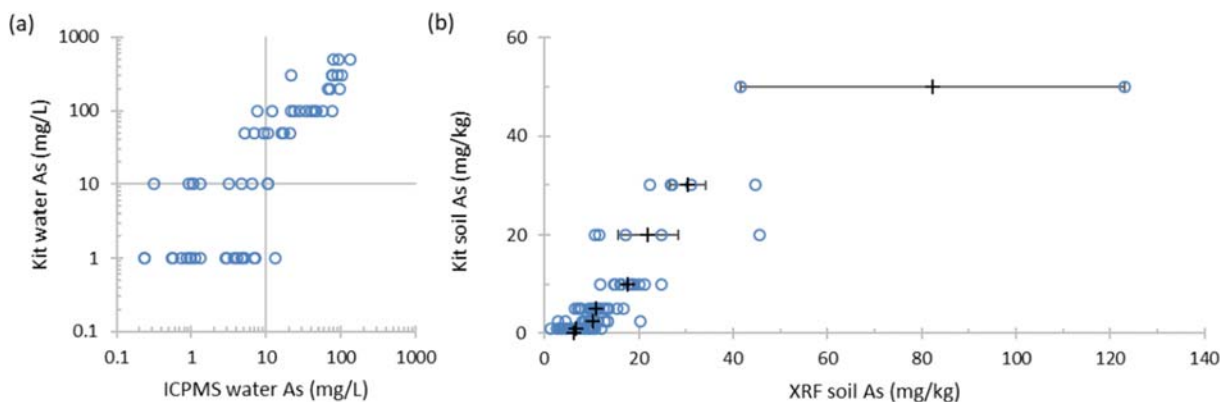
152 Water samples were acidified to 1% high-purity HCl  
153 (Fisher Scientific Optima) at least one week before  
154 analysis by high-resolution inductively-coupled plasma  
155 mass spectrometry (HR ICPMS) on a Thermo-Finnigan  
156 Element2 at Lamont Doherty Earth Observatory  
157 (LDEO) Laboratory of Columbia University, New York,  
158 USA (Cheng et al. 2004). This procedure has previously  
159 been shown to re-dissolve any iron oxides and therefore  
160 As that might have precipitated (Van Geen et al. 2007).  
161 An internal consistency standard containing 430 µg/L  
162 As and reference materials NIST1640a ( $8.08 \pm$   
163  $0.07$  µg/L As) and NIST1643e ( $58.98 \pm 0.7$  µg/L As)  
164 were included with every run to ensure accuracy and  
165 precision of the method within <5%. The detection limit  
166 of the procedure is <0.1 µg/L based on the variability of  
167 the blank.

168 Soil samples collected in polyethylene bags were  
169 sun-dried and homogenized. Out of a total of 660 soil  
170 samples, a subset of 103 samples spanning the range of  
171 As concentrations were analyzed for As using an Innova-  
172 X Delta Premium field X-ray fluorescence spectrometer  
173 in the soil mode for a total counting time of 120 s. All  
174 soil As concentrations were above the detection limit of  
175 the XRF for As of ~3 mg/kg under these conditions. Soil  
176 standards 2709 and 2711 from the National Institute of  
177 Standards and Technology (NIST) were analyzed at the  
178 beginning and end of each of the two sample runs, and  
179 once in the middle of the longer run. The measured  
180 average and standard deviation for NIST 2709 of  $16.9$   
181  $\pm 0.9$  mg/kg ( $n = 5$ ) matched the reference value of  $17.7$   
182  $\pm 0.8$  mg/kg and the measured average and standard  
183 deviation for NIST 2711 was  $105 \pm 4$  mg/kg ( $n = 5$ )  
184 matched the reference value of  $105 \pm 8$  mg/kg.

185 Polished rice grains were washed with deionized (DI)  
186 water and sun dried. Individual 7 g portions of rice were  
187 pulverized with a coffee grinder and transferred to a  
188 200 mL glass beaker. The volume was raised to 70 mL

189	with DI water and 1% HNO <sub>3</sub> . The solution was then	antifoaming agent were added followed by one sachet	236
190	boiled for 20 min using a gas burner. Evaporation was	of sulfamic acid and one tablet of NaBH <sub>4</sub> . The lead	237
191	compensated by adding DI water to raise the volume	acetate filter was used to remove H <sub>2</sub> S and the HgBr <sub>2</sub>	238
192	back to 70 mL, after which the digest solution was	holder for trapping the generated arsine. The sample was	239
193	cooled in a water bath. A portion of each digest was	allowed to react for 20 min, after which the HgBr <sub>2</sub>	240
194	saved in 20 mL polyethylene scintillation vials with a	holder was inserted in the digital reader. The reader	241
195	PolySeal-lined cap (Wheaton no. 986706) and analyzed	was zeroed with a blank filter paper before each mea-	242
196	by HR ICPMS after diluting 5-fold in a 1% HNO <sub>3</sub>	surement. The iAs concentration in rice flour measured	243
197	solution containing a Ge spike for drift correction	for NIST Standard Reference Material 1658b with the	244
198	(Cheng et al. 2004). The remaining 50 mL was saved	Arsenator averaged $0.04 \pm 0.01$ mg/kg ( $n = 3$ ), i.e. only	245
199	for analysis using a different kit (see below). In total,	40% of the certified value of $0.092 \pm 0.01$ mg/kg. For	246
200	rice samples were digested and analyzed in triplicate	this reason, we make no attempt to interpret the average	247
201	from all 60 fields where irrigation water and soil sam-	iAs concentration of $0.023 \pm 0.01$ mg/kg ( $n = 60$ tripli-	248
202	ples were analyzed as well. For quality control, the same	cates) measured in the Punjab rice samples.	249
203	procedure was followed to measure the As content of		
204	rice flour obtained as Standard Reference Material		
205	1568a from NIST. The mean As concentrations of	<b>Results</b>	250
206	$0.28 \pm 0.02$ mg/kg measured by analyzing 3 batches of		
207	SRM 1568b using the above procedure was consistent	Distribution of As in irrigation water	251
208	with its certified value of $0.285 \pm 0.014$ mg/kg.		
209	Field kit measurements		
210	Irrigation water samples were analyzed for As using the	The World Health Organization guideline of 10 µg/L for	252
211	ITS Arsenic Econo-Quick Kit, which relies on the gen-	As in drinking water is not directly relevant to crop	253
212	eration of arsine gas and a strip impregnated with mer-	irrigation but still a useful benchmark. On the basis of	254
213	curic bromide turning from white to yellow, orange, or	laboratory measurements, 31 out of 60 samples of irri-	255
214	brown depending on the level of arsenic (George et al.	gation water contained $\leq 10$ µg/L As, with 27 out of the	256
215	2012). The second of the kit's 3 reagents, an oxidant to	remaining 29 samples containing $\leq 100$ µg/L (Fig. 1).	257
216	suppress potential interference by hydrogen sulfide, was	Concentrations of As in the two remaining irrigation	258
217	not added. Each test strip was matched visually to the	wells, both in the Ravi floodplain, were marginally	259
218	closest of a sequence of colors corresponding to 0, 10,	higher at 102 and 135 µg/L, respectively (Fig. 2a).	260
219	15, 50, 100, 200, 300, 500, and 1000 µg/L As provided	The proportion of wells with $>10$ µg/L As is the highest	261
220	by a reference card supplied with the kit. Paddy soil was	in the Ravi floodplain (17 out of 20 wells), followed by	262
221	also analyzed for easily mobilized As using the ITS	the Chenab floodplain (5/9), the Rechna doab (4/19), the	263
222	Econo-Quick field kit using a modification of the pro-	Jhelum floodplain (1/6), and the Chaj doab (0/6) (On-	264
223	cedure. Using a battery-powered balance, 0.5 g of wet	line Resource Table 2). The floodplain was assumed to	265
224	soil was added to 50 mL of DI water in the kit's reaction	extent 8 km from either side of the river for this study,	266
225	vessel and subsequently handled as a water sample. For	with more distant areas classified as doabs (Greenman	267
226	quality control, water standards containing 50 and	et al. 1967).	268
227	100 µg/L of total As prepared in deionized were ana-	Kit measurements in the field correctly classified	269
228	lyzed each day in the field.	irrigation wells relative to the WHO guideline for 27	270
229	The method of Bralatei et al. 2015 was used in an	out 31 wells containing $\leq 10$ µg/L and 26 out 29 wells	271
230	attempt to measure the inorganic As (iAs) of rice with	containing $>10$ µg/L based on ICPMS measurements.	272
231	only two slight modifications: digesting 7 g of rice in	Nominal kit values over-estimated the actual As con-	273
232	70 mL instead of 5 in 50 mL, and adjusting the volume	centration by a factor of $4 \pm 3$ for As concentrations	274
233	back to 70 mL at the end to avoid the formation of a	$>10$ µg/L (Fig. 2a).	275
234	thick slurry. The 50 mL of saved digest was transferred		
235	to the reaction bottle, after which 2–3 drops of	Distribution of As in paddy soil	276
		Average concentrations of As in soil samples measured	277
		by XRF increase roughly linearly from $6.1 \pm 0.4$ mg/kg	278





**Fig. 2** Comparison of kit measurements in the field with laboratory measurements of (a) well-water As concentrations ( $n = 60$ ) by HR ICP-MS and soil As concentrations ( $n = 103$ ) by XRF

279 for the lowest kit reading of  $0 \mu\text{g/L}$  to  $30 \pm 4 \text{ mg/kg}$  for a  
 280 kit reading of  $300 \mu\text{g/L}$ , which is equivalent to a leach-  
 281 able As concentration of  $\sim 30 \text{ mg/kg}$  in the soil (Fig. 2b).  
 282 The average of  $82 \text{ mg/kg}$  As in soil at the high end for  
 283 the kit reading of  $500 \mu\text{g/L}$ , equivalent to  $50 \text{ mg/kg}$  in  
 284 soil, doesn't follow quite the same trend but is  
 285 constrained by only two samples. Only a fraction of  
 286 the total As is likely to be released by the kit during  
 287 the 10 min reaction time. The almost one-to-one corre-  
 288 spondence between total As measured by XRF and As  
 289 released measured by the kit is therefore serendipitous  
 290 and attributable to the kit overestimating the As concen-  
 291 tration in the soil-water slurry. All kit soil measurements  
 292 displayed and discussed hereon were converted to the  
 293 average As concentration obtained for each kit value by  
 294 XRF (Online Resource Table 3).

295 For lack of a local regulatory standard, the subset of  
 296 soil samples analyzed by XRF are classified relative to  
 297 Japan's threshold of  $15 \text{ mg/kg}$  As for paddy soil (MOE  
 298 2016). For the subset of soil samples analyzed with the  
 299 kit and by XRF, the classification relative to that thresh-  
 300 old ( $0\text{--}15 \text{ mg/kg}$ ) was correct in 81 (88%) out 92 cases  
 301 whereas 11 (12%) were not consistent with XRF mea-  
 302 surements (Online Resource Table 4). All inconsisten-  
 303 cies were underestimates by the kit relative to XRF.  
 304 Converting all the soil measurements to concentrations  
 305 based on XRF show that that 30% ( $n = 200$ ) of soil  
 306 samples from the Ravi, 4% ( $n = 90$ ) from the Chenab,  
 307 and 2% ( $n = 60$ ) from the Jhelum floodplain do not meet  
 308 this standard (Online Resource Table 5). In contrast, all  
 309 150 analyzed soil samples from Rechna and Chaj  
 310 contained  $<15 \text{ mg/kg}$  As. The kit did not detect any soil  
 311 As for three-quarters of the samples from the Rechna doab  
 312 ( $n = 190$ ) and all samples from the Chaj doab ( $n = 90$ ).

313 Most diagonal transects with elevated levels of As in  
 314 soil show higher concentrations recorded closest to the  
 315 current inlet of irrigation water (Fig. 3). For the 10  
 316 profiles close to the inlet in the Ravi floodplain, 22 out  
 317 of 30 intervals in the  $0\text{--}30 \text{ cm}$  depth range contained  
 318  $>15 \text{ mg/kg}$  As whereas only 3 out of 30 intervals in the  
 319  $30\text{--}60 \text{ cm}$  depth range did so (Fig. 4, Online Resource  
 320 Table 6).

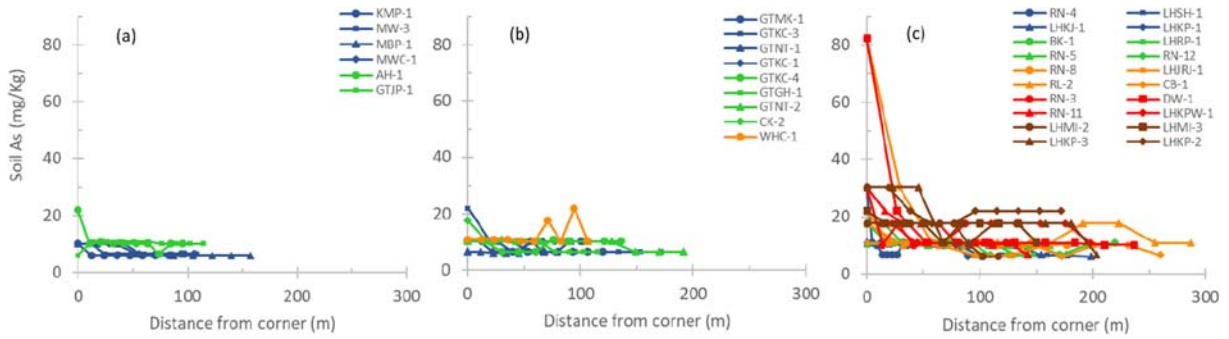
#### Concentration of As in rice grains 321

322 Average concentrations of As in rice based on triplicates  
 323 for 60 samples ranged from  $0.05$  to  $0.28 \text{ mg/kg}$  (Fig. 5).  
 324 Standard deviations for triplicates were  $<0.05 \text{ mg/kg}$   
 325 for 52 out of 60 sets of samples. The concentration of  
 326 As in rice grain averaged over all 60 samples was  $0.09 \pm$   
 327  $0.05 \text{ mg/kg}$  based on all 180 measurements. The lowest  
 328 grain As concentrations of  $0.06 \pm 0.01 \text{ mg/kg}$  (with  
 329 standard error of the mean) were measured in the Jhelum  
 330 flood plain for 6 sets of triplicates and the highest of  
 331  $0.090 \pm 0.01 \text{ mg/kg}$  in the Ravi floodplain for 20 sets of  
 332 triplicates. The 2-standard error intervals of these two  
 333 averages overlap and their difference is therefore not  
 334 statistically significant at the 0.05 level (Online Re-  
 335 source Table 7).

## Discussion 336

### Accumulation of As in soil 337

338 The observed pattern of highest soil As concentrations  
 339 closest to the inlet of the irrigation water has been docu-  
 340 mented previously in Bangladesh and attributed to the



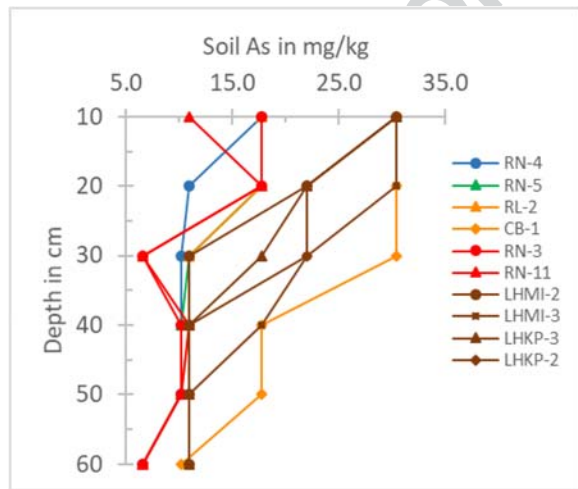
**Fig. 3** Surface soil As concentrations for 10 equidistant points along a diagonal from corner of the field closest to the entry point of irrigation water to the opposite corner of the field in floodplains of the (a) Jhelum, (b) Chenab, (c) and Ravi rivers. Each colored line indicates a specific rice field and the points on the line show the concentrations for every single sample. Soil As concentration were

measured with the ITS Econo-Quick kit in the field and converted to equivalent readings by XRF (Fig. 2 and Online Resource Table 3). The sites are ordered by increasing area-weighted mean soil As and represented by the different color and symbol combinations in sequence of blue<green<orange<red<brown and circles<square<triangles<diamonds based on area-weighted As

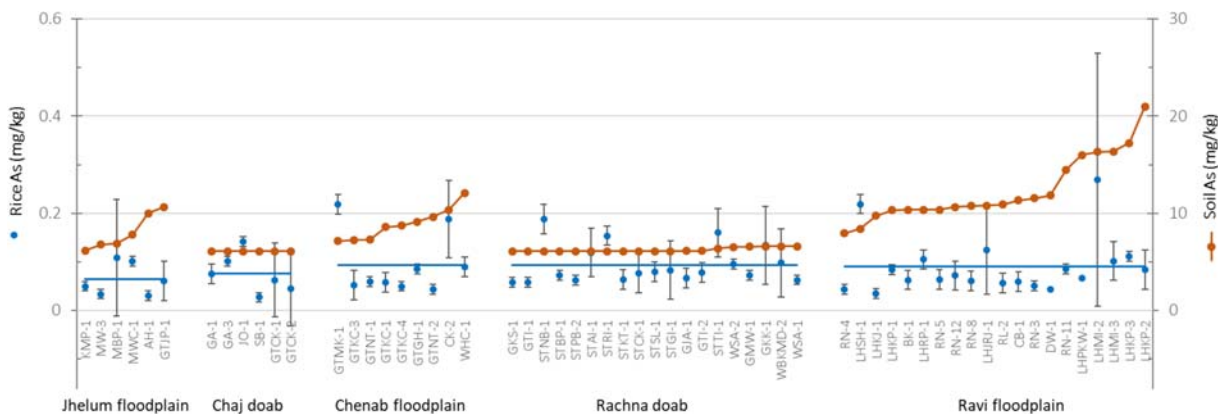
341 co-precipitation of As with iron oxyhydroxides after  
 342 oxidation in contact with air (Dittmar et al. 2007;  
 343 Roberts et al. 2007). A few fields in the Ravi and Chenab  
 344 floodplains where soil As levels are higher away from the  
 345 inlet may indicate that the position of the inlet was moved  
 346 or that the field was reconfigured in the past (Fig. 3). The  
 347 Ravi>Chenab>Jhelum>Rechna>Chaj sequence of geo-  
 348 graphic units based on average soil As content (Fig. 5)  
 349 follows the Ravi>Chenab>Rechna>Jhelum>Chaj se-  
 350 quence based on the proportion of irrigation wells with  
 351 >10 µg/L, with the exception of a switch in order be-  
 352 tween the Jhelum floodplain and the Rechna doab (Fig.  
 353 1). The As content of irrigation water therefore seems to

determine the As content in excess of local background 354  
 for paddy soil across the region. 355

Groundwater has been used for growing rice in the 356  
 region starting in the 1960s (Qureshi et al. 2010). In 357  
 order to relate the duration of irrigation with groundwa- 358  
 ter to the accumulation of As in soil, each diagonal 359  
 transect of soil As measurements was first converted to 360  
 a representative field average by weighing the first 5 361  
 samples by 0.6, 5, 10, 15, and 20%, respectively, and by 362  
 the same weights in reverse order for last 5 samples 363  
 based on simple geometry (Online Resource Fig. 1). 364  
 Subtracting a background concentration of 6 mg/kg As 365  
 and assuming a bulk density of the soil of 1.5 g/cm<sup>3</sup>, an 366  
 excess inventory of As per surface area was calculated 367  
 for each field. Farmers in the study area require an 368  
 average of 1.6 m of water, groundwater and rainfall 369  
 combined, to grow rice each season (Erenstein 2009). 370  
 None of the farmers participating in this study reported 371  
 using canal water to irrigate their rice field, either be- 372  
 cause they were too far away from a canal or because 373  
 canal water did not reach them. Rainfall during the rice 374  
 growing season across the study region between 1981 375  
 and 2010 averaged 0.4 m in the driest southwesterly 376  
 portion of the study area to 0.7 m in the wettest north- 377  
 easterly portion (Bokhari et al. 2017). By difference, the 378  
 quantity of groundwater required in the driest area was 379  
 therefore estimated at 1.2 m (22 sites), in the intermedi- 380  
 ate area at 1.0 m (27), and 0.9 m (11) in the wettest area. 381  
 From these net requirements, the amount of As supplied 382  
 by pumping groundwater for growing rice each year 383  
 was calculated using the As concentrations measured 384  
 for irrigation water in the laboratory. 385



**Fig. 4** Soil As in soil profiles close to the inlet of ten selected fields in Ravi flood plain. The soil As concentration was measured by ITS Econo-Quick field kit and converted based on mean XRF As for each kit bin. (Fig. 2 and Online Resource Table 6)



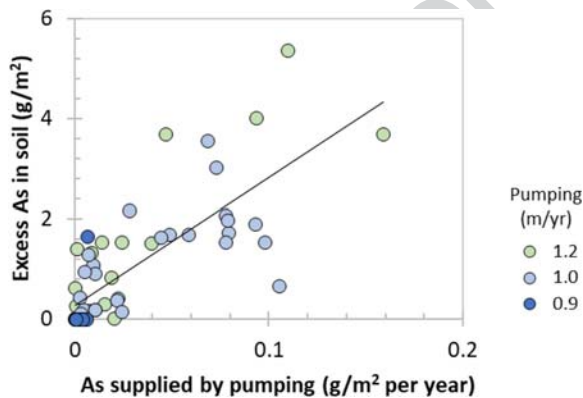
**Fig. 5** Soil and rice As, sorted by soil As, in a geographical sequence from West to East: 1) Jhelum floodplain, 2) Chaj Doab, 3) Chenab floodplain, 4) Rachna Doab, and 5) Ravi floodplain. The blue circles show the mean rice As (mg/kg) of 3 batches in the

same field, the error bars show the standard deviation between the 3 batches, and the blue horizontal line shows the mean rice As of each floodplain/doab

386 The comparison of excess As concentration per sur-  
 387 face area for each field as a function of As supplied per  
 388 surface area each year shows a generally increasing  
 389 trend corresponding to an average duration of irrigation  
 390 with groundwater of  $26 \pm 3$  years (Fig. 6). Assuming the  
 391 growth in the number of irrigation wells in Punjab from  
 392 1960 to 2000 (Qureshi et al. 2010) has continued and  
 393 can be approximated by a linear trend, the average  
 394 irrigation well would have been in use for about three  
 395 decades. The match between these two independent  
 396 estimates confirms that groundwater pumping is the  
 397 main driver of As concentrations in paddy soil of Punjab  
 398 exceeding background levels for the region. The

implication is that continued irrigation of rice paddies  
 with groundwater will result in further increases in As  
 concentrations in paddy soil over broader areas.

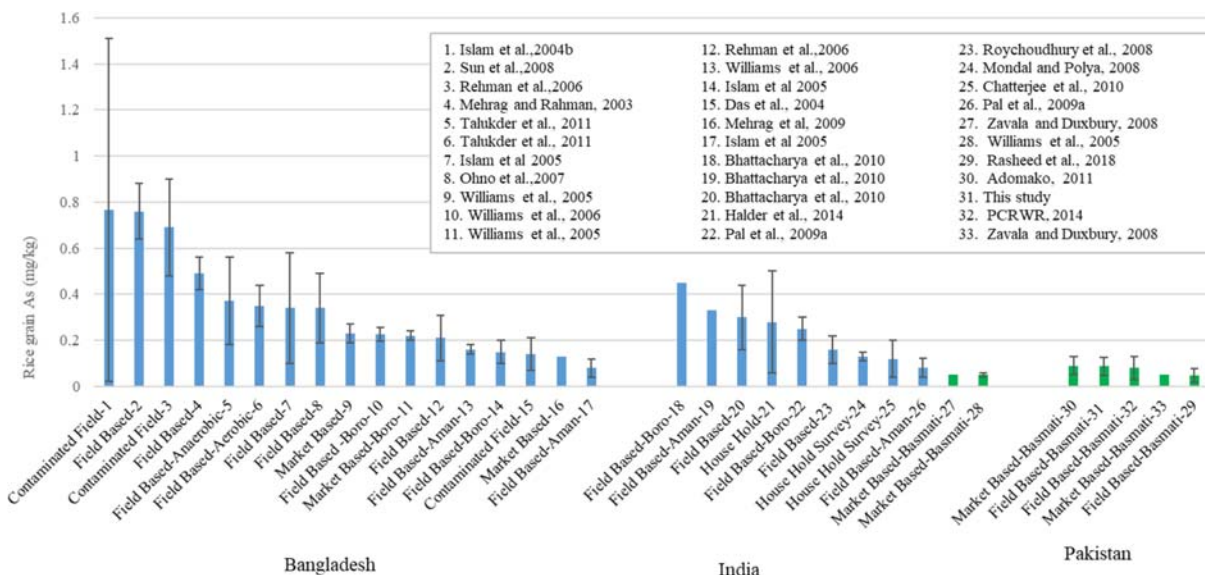
Recent studies of boro rice varieties grown in Ban-  
 gladesh indicate a loss in yield of 0.5–1.0 t/ha from an  
 average of 3 t/ha for a 10 mg/kg increase in soil As  
 (Huhmann et al. 2017; Panaullah et al. 2009). It is  
 unclear to what extent the yield in basmati rice might  
 be similarly sensitive to the build-up of As in paddy soil.  
 The low As content of basmati rice doesn't necessarily  
 mean the variety is less susceptible to yield loss from  
 build-up of As in paddy soil, especially if levels contin-  
 ue to rise. The issue could potentially be addressed with  
 an experimental design similar to that of Huhmann et al.  
 Another approach would be to compare rice yield  
 closest to the irrigation inlet with rice yield furthest  
 away from the inlet, but within the same field in order  
 to keep other factors such as soil type, water manage-  
 ment, fertilizer input, and weeding as similar as possible.



**Fig. 6** Comparison of excess soil As concentrations in 60 study fields of Punjab with the annual As supply from pumping ground-  
 water. Pumping rates were estimated by subtracting Kharif season  
 rainfall divided in three categories (Bokhari et al. 2017) from the  
 total of 1.6 m/yr of water required for growing rice in the region  
 (Erenstein 2009). The slope and intercept of the least-squares  
 regression line for all data combined are  $26 \pm 3$  yr (1-sigma) and  
 $0.3 \pm 0.1$  g/m<sup>2</sup>, respectively

Low As content of basmati rice

The patterns of As in irrigation water and paddy soil are  
 clearly coupled geographically but are not accompanied  
 by any such trend in the As content of rice (Fig. 5). Each  
 of the five geographic units includes a few outliers with  
 a slightly elevated average or a larger standard deviation  
 for As concentrations in rice. The overall average of  
 0.09 mg/kg in total rice As for the region is consistent  
 with 6 previous studies of basmati rice from Pakistan  
 and India (Fig. 7). Studies of other varieties from India  
 and Bangladesh, some market-based and some-field



**Fig. 7** Mean total As concentrations in rice reported by 33 studies conducted in Bangladesh, India and Pakistan. Blue bars combine various varieties, with the exception of basmati, which instead is

shown as green bars. Error bar correspond to one standard deviation for the entire data set where listed or where it could be calculated

based, indicate a consistently higher average As content of rice, with even a few studies showing averages exceeding 0.5 mg/kg As (Fig. 7, Online Resource Table 8). About 40% of rice production in Pakistan is basmati, along with other varieties including IRRI-6, IRRI-9, KS-282, DR-82 and DR-83 that were not analyzed in this study (Memon 2013). Punjab province is the largest producer of basmati rice, whereas long-grain white rice of the IRRI type is grown mostly in Sindh province to the south.

to grain varies and is sensitive to a number of factors including soil As, the variety of rice, and the irrigation regime (Williams et al. 2007). The results reported here confirm the low levels of As in basmati rice regardless of where it is grown. Growing varieties of basmati rice that do not accumulate as much as As could therefore be explored to replace, for instance, the main varieties currently grown in Bangladesh.

A number of studies have suggested that the As content of rice is related to the As content of paddy soil (Azad et al. 2009; Khan et al. 2009; Rahaman et al. 2011; Rauf et al. 2011; Williams et al. 2006; Zhao et al. 2009), however other studies did not observe such a connection (Adomako et al. 2009; Bhattacharya et al. 2010; Panaullah et al. 2009; Stroud et al. 2011; Van Geen et al. 2006). One reason for the inconsistency may be that the efficiency of the transfer of As from soil

Human exposure to as from well water relative to Rice

The new rice data combined with a recent well-water survey conducted across the Punjab plains provide a measure of exposure to As to compare with other rural populations in South Asia (Table 1). According to Akram and Henneberry 2016, rice consumption at 50 g/day is supplanted by wheat, at least in urban areas of Pakistan and, therefore, ten times lower than rice consumption in Bangladesh. In rural Pakistan, however, the consumption of rice may be comparable to Bangladesh (Akram and Henneberry 2016). The As content of wheat flour is generally much lower than in rice (Zhao et al., 2010) and therefore not considered in this analysis. Rasheed et al. 2018 report higher levels of As in wheat grains from Pakistan, but this was prior to milling and therefore not representative of actual intake. A quarter of wells in rural Punjab do not meet the WHO guideline of As in drinking water of 10 µg/L (van Geen et al. 2019) but that proportion

**Table 1** Comparison of intake of As from rice and water (µg/day)

Rice As (mg/kg)	Rice consumption (g/day)		Water As (µg/L)	
	50	500	10	100
0.09	4.5	45	30*	300*
0.30	15	150		

\*for 3 L of water/day30



474 is probably about twice as high in rural Bangladesh (Pfaff  
475 et al. 2017). The daily As intake of a farmer in Punjab from  
476 eating 50–500 g/day of basmati rice and drinking water  
477 from a well that just meets the WHO guideline is therefore  
478 on the order of 34–75 µg/day (Table 1). That figure would  
479 be closer to 450 µg/day for a farmer in Bangladesh eating a  
480 local rice variety that is elevated in As and drinking water  
481 containing 100 µg/L As. Under these two end-member  
482 scenarios, the intake of As from well water is comparable  
483 or dominates the intake from rice (Table 1). Given that, in  
484 addition, exposure through water is all inorganic As where-  
485 as a sizeable fraction of As in rice can be in a less toxic  
486 organic form (Meharg et al. 2009), helping rural popula-  
487 tions of South Asia with access to low As water for  
488 drinking and cooking should remain the highest priority.  
489 Once that goal has been achieved, further reductions in  
490 exposure will be achieved by avoiding rice varieties with a  
491 particularly high As content in both Bangladesh and India,  
492 particularly in areas outside Pakistan where rice dominates  
493 the diet (Fig. 7).

## 494 Conclusion

495 Using matched water, soil, and rice As measurements from  
496 a considerable number of sites distributed across the Pun-  
497 jаб plains of Pakistan, this study confirms that groundwater  
498 pumping is the main contributor of As concentrations in  
499 some paddy soil of Punjab. The contamination of paddy  
500 soil with As is currently limited in the region but is likely to  
501 increase in severity and geographic extent over time. The  
502 accumulation of As in paddy soil of the Punjab plains is  
503 not linked to a measurable increase in the uptake of As in  
504 rice grains of basmati rice. After reducing exposure from  
505 drinking well-water along the Ravi River, the main con-  
506 cern in the region could potentially become the loss in rice  
507 yield resulting from further accumulation of As in soil over  
508 time. This is why the ITS Econo-Quick arsenic kit could  
509 be useful to farmers by helping them determine the As  
510 content of both their irrigation water and their paddy soil.  
511

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525

526

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