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1 **Arsenic in Peruvian rice cultivated in the major rice growing region of Tumbes river**  
2 **basin**

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14  
15 **Abstract**

16 Arsenic (As) exposure from surface and groundwater in Peru is being recognised as a  
17 potential threat but there are limited studies on As in the food-chain and none on As in  
18 Peruvian rice. In this study, we have determined the As content in rice cultivated in the  
19 Tumbes river basin located in the northern province of Peru, an area known for extensive rice  
20 cultivation. We collected rice and soil samples from agricultural fields, soil was collected  
21 using grid sampling technique while rice was collected from the heaps of harvested crop  
22 placed across the fields. The average total As concentration in rice was  $167.94 \pm 71 \mu\text{g kg}^{-1}$   
23 ( $n=29$ ; range 68.39-345.31  $\mu\text{g kg}^{-1}$ ). While the rice As levels were not highly elevated, the As  
24 content of few samples ( $n=7$ ) greater than 200  $\mu\text{g kg}^{-1}$  could contribute negatively to human

25 health upon chronic exposure. Average concentration of As in soil was  $8.63 \pm 7.8 \text{ mg kg}^{-1}$   
26 ( $n=30$ ) and soil to grain transfer factor was  $0.025 \pm 0.018$  for 12 matched samples. Compared  
27 to our previous pilot study in 2006 (samples collected from the same agricultural fields but  
28 not from exact locations) there was a 41% decrease in As soil concentration in this study.  
29 Rice samples collected in 2006 ( $n=5$ ) had a mean concentration of  $420 \pm 109 \text{ } \mu\text{g kg}^{-1}$ . Our  
30 data provides a baseline of rice grain As concentrations in Peruvian province of Tumbes and  
31 warrants further studies on factors affecting uptake of As by the rice varieties cultivated in  
32 Peru and any potential human health risks.

33 **Key words:** arsenic; rice; soil; Tumbes river basin; Peru; Latin America

## 34 **1. Introduction**

35 Arsenic (As) has emerged as a major global health concern in the last few decades due to its  
36 serious impact on human health. Though the problem of As contamination has been well  
37 studied in some of the Latin American countries which have a long history of widespread As  
38 contamination, this is not so true for Peru. While As exposure in Peru, was first reported in  
39 the Ilo valley in 1970 (Bundschuh et al., 2012a) there are very few studies on As exposure in  
40 Andean river basins and none, to best of our knowledge on As contamination of the northern  
41 coastal region of Peru - the Tumbes river basin.

42 It was once roughly estimated that 250,000 Peruvian were exposed to As (McClintock et al.,  
43 2012) but there is no systematic exposure or health risk assessment. In most areas, As is  
44 predominantly released due to mining activities or natural weathering and transported by the  
45 river. These river waters are predominantly used for irrigation apart from drinking purposes  
46 (Bundschuh et al., 2012b). In a 2014 study, 77% of the ground drinking water samples  
47 collected from twelve districts of Peru ( $n=151$ ) were found to exceed the WHO  
48 recommended limit of  $10 \text{ } \mu\text{g L}^{-1}$  with maximum recorded As concentration of  $193.1 \text{ } \mu\text{g L}^{-1}$

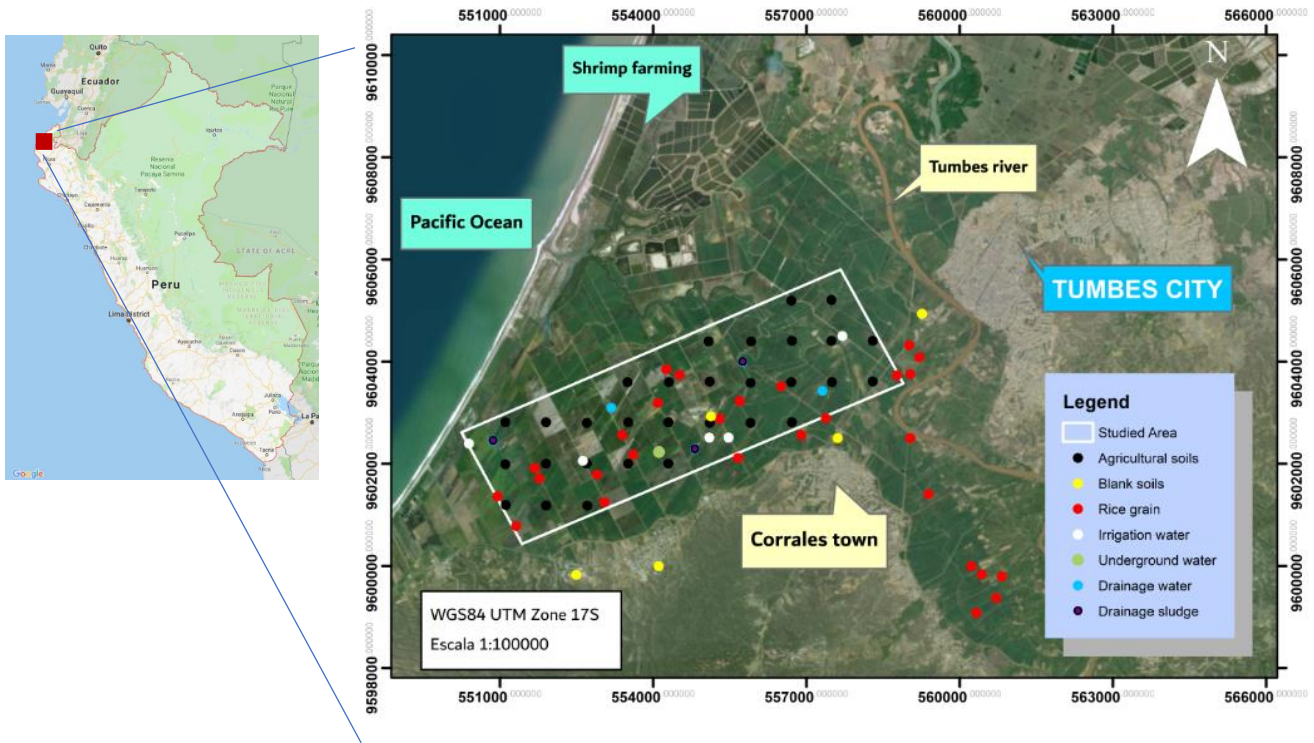
49 (George et al., 2014). Peruvian National Authority of Water found As concentrations  
50 reaching up to 1174  $\mu\text{g L}^{-1}$  in filtered water of Tumbes river between 2011 - 2016 (Silva,  
51 2018) flowing from Ecuadorian provinces (where it is called Puyango river) into Tumbes  
52 district of Peru. But Tumbes was not among the twelve districts surveyed in the George et al.  
53 (2014) study. In a recent study, the majority of the water and sediment samples collected  
54 from the Puyango-Tumbes river had elevated concentrations of As along with mercury (Hg),  
55 cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) exceeding the Canadian Council of  
56 Ministers of the Environment thresholds for the Protection of Aquatic Life (Marshall et al.,  
57 2018). Puyango-Tumbes river is the only available water source in the semi-arid region of  
58 northern Peru (Marshall et al., 2018) and similar to other Peruvian river basins, the main  
59 source of irrigation and drinking water.

60 The Puyango-Tumbes river basin encompasses a large diverse land area (90,000 ha in  
61 Tumbes) essentially devoted to agriculture, where more than 6000 farmers are engaged in  
62 cultivation, predominantly of rice along with banana, corn and other fruits (Marshall et al.,  
63 2018). The Tumbes river is an important source of water for irrigation, hence pollutants  
64 discharged from mining and other activities in the upper course of the river (Puyango in  
65 Ecuador) including As, pose a significant health risk to those consuming food, cultivated in  
66 these lands. Compared to other crops, rice has a high ability to absorb As from the soil,  
67 making it the most contaminated cereal (Meharg and Zhao, 2012) and consumption of rice is  
68 a well-established route of As exposure (Mondal and Polya, 2008; Mondal et al., 2010).  
69 Agriculture being an important part of the economy in Tumbes, with one of the dominant  
70 crops being rice, assessment of As in rice cultivated in Tumbes river basin is of significance.  
71 Moreover, unlike other Latin American countries, little is known about the As in food-chain  
72 of Peru (Bundschuh et al., 2012b) and none about rice. In this study we have determined the  
73 As content in rice cultivated in the Tumbes river basin of Peru and compared the findings

74 with a preliminary pilot data collected by us in 2006 (Bermejo and Cruz, 2006). We have also  
75 estimated As and other potentially toxic elements present in the agricultural soil and  
76 irrigation water of Tumbes river basin and calculated the transfer factor between soil and the  
77 grain.

78 **2. Methods**

79  
80  
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82



83 **Figure 1:** Sampling location for all the different samples collected

84 **2.1 Sample collection and analysis:**

85 Figure 1 shows the sampling site for this study within the paddy cultivation fields covering  
86 2100 ha in Tumbes river basin located in the northern province of Peru. Rice samples (n=29)  
87 were collected from the heaps of harvested crop placed across the agricultural field from  
88 locations shown in Figure 1. All the samples (husked rice and grain separated), were washed,  
89 dried, grinded to powder using a porcelain mortar to avoid contamination and then stored in  
90 zip-lock bags.

91 Agricultural soil samples (n=30) were collected by grid sampling technique overlaying a  
92 rectangular grid of 8088 m by 2600 m over the rice fields as shown in Figure 1. A single soil  
93 core of 30 cm square and 30 cm deep was collected at a grid spacing distance of 800 m over  
94 30 different locations (Figure 1). The pH, redox potential (Eh) and textural properties  
95 (content of lime, clay and sand) were analysed for all agricultural soil samples. Both pH and  
96 Eh were measured using potentiometer (Inolab pH 7310 WTW (Merck, Germany)) after  
97 making a soil suspension (5 g of the agricultural soil was mixed with 50 mL of water,  
98 agitated for 30 minutes and then left for 1 h before vacuum filtration) while the soil texture  
99 was measured by hydrometer method. The soil (roughly 2 kg) were homogenised, sieved  
100 through ASTM N° 100 (150 µm), oven dried at 80 °C and stored in zip-lock bags. In order to  
101 compare the content of As and potentially toxic elements in samples of agricultural soils  
102 inside the paddy fields with those outside the paddy fields, control (blank) samples (n=5)  
103 were taken (two were taken from the hills covered by dry forest close to the agricultural  
104 fields; one from similar agricultural area but outside the paddy fields; one from a local area  
105 close to the river near the Corrales town: and one sample was taken inside the studied area,  
106 but from a location in between the paddy fields). These samples were collected,  
107 homogenised, dried and stored similar to the agricultural soils. Samples of irrigation (n=5)  
108 and drainage water (the water coming out of the paddy field; n=5) along with the ground  
109 water (n=1) were taken from the study area. 20 mL of the water samples were taken from the  
110 source and filtered using a 20 mL syringe filter fitted with Whatman 41 filter paper, and then  
111 acidified using 0.2 mL of concentrated nitric acid (65% vol). Drainage sludge samples were  
112 collected (n=3) from the drainage system while sampling the drainage water and then they  
113 were dried, grinded and sieved following the same protocol as for the agricultural soils.

114 Rice and soil samples were analysed at The University of Newcastle, Australia following the  
115 established protocols. Briefly, rice samples were digested for the analysis of total As and

116 other elements based on the protocol of Roychowdhury et al. (2002) while a microwave  
117 assisted digestion system (model: MARS 5, CEM) was used for the digestion of soil using  
118 the USEPA 3051A method (USEPA, 2007). Determination of As and other trace metals (Cd,  
119 Cu, Pb, Zn, antimony (Sb), barium (Ba), boron (B), cobalt (Co), chromium (Cr), manganese  
120 (Mn), selenium (Se), Strontium (Sr) and vanadium (V)) was carried out with an Agilent 7900  
121 (Agilent Technologies, Tokyo, Japan) inductively coupled plasma mass spectrometer (ICP-  
122 MS) coupled with an autosampler (Agilent Technologies). Major elements such as calcium  
123 (Ca), magnesium (Mg), sodium (Na), aluminium (Al), iron (Fe) were analyzed using the dual  
124 view (Axial and radial) inductively coupled plasma emission spectrometer (ICP-OES,  
125 PerkinElmer Avio 200, USA). CRM, blanks, duplicates, and continuing calibration  
126 verification (CCV) were included in each batch throughout the elemental analysis. Standard  
127 reference materials (SRM) from the National Institute of Standards and Technology (NIST),  
128 USA (Rice flour (SRM 1568b) and Montana soil (SRM 2711a)) were used. Water samples  
129 were analyzed at the University of Salford using ICP-OES Varian 720-ES (California, USA).

## 130 ***2.2 Data analysis:***

131 Data was analyzed using Microsoft Excel and Stata 11.2 for descriptive statistics and for  
132 independent t-test. The multivariate principal component analysis (PCA) technique was  
133 applied to the soil data, in order to explore the grouping of elements according to their  
134 similarities and the analysis was performed using Stata 11.2. The spatial distribution of  
135 elements in soil for the study area was developed using Surfer 18 (Golden Software,  
136 Colorado, EEUU). The grids used as bases to build contour maps were done using  
137 interpolation with the kriging method (no data was assigned outside convex hull of data).  
138 Based on these grids, the contour maps for every element were developed. The transfer factor  
139 between soil and grain ( $TF_{\text{grain/soil}} = \text{concentration in grain} / \text{concentration in soil}$ ) was

140 determined by matching the rice samples (n=12) to the nearest soil sample within the grid  
 141 (Figure 1).

### 142 3. Results and discussion

#### 143 3.1 Quality control

144 Mean total recoveries (n=5) from both rice and soil SRMs were within the range of 80-120%  
 145 confirming accuracy of rice and soil digestion and analysis (Table 1). In each batch CCV  
 146 recoveries were between 92-115% for all elements.

147 **Table 1:** Percentage recovery of As and other elements in NIST SRMs (n=5 for both rice and  
 148 soil)

149

Elements	NIST SRM 1568b (Rice flour)			NIST SRM 2711a (Montana soil)		
	Certified values	Measured values	Recovery (%)	Certified values	Measured values	Recovery (%)
As ( $\mu\text{g kg}^{-1}$ )	285 $\pm$ 14	261 $\pm$ 5.6	92	107,000 $\pm$ 5000	99,000 $\pm$ 4000	92
V ( $\mu\text{g kg}^{-1}$ )	-			80,700 $\pm$ 5700	69,000 $\pm$ 3100	85
Cr ( $\mu\text{g kg}^{-1}$ )	-			52,300 $\pm$ 2900	41,000 $\pm$ 3000	78
Co ( $\mu\text{g kg}^{-1}$ ) <sup>a</sup>	17.7 $\pm$ 0.05	15.2 $\pm$ 1.44	86	9890 $\pm$ 180	9300 $\pm$ 910	94
Ni ( $\mu\text{g kg}^{-1}$ )	-			21,700 $\pm$ 700	19,100 $\pm$ 2300	88
Se ( $\mu\text{g kg}^{-1}$ )	365 $\pm$ 29	347 $\pm$ 18	95	2000	4000	
Cd ( $\mu\text{g kg}^{-1}$ )	22.4 $\pm$ 1.3	21.9 $\pm$ 2.9	98	54,100 $\pm$ 500	47,000 $\pm$ 1065	86
Sb ( $\mu\text{g kg}^{-1}$ )	-			23,800 $\pm$ 1400	19,000 $\pm$ 457	80
Pb ( $\mu\text{g kg}^{-1}$ ) <sup>a</sup>	8 $\pm$ 3	52 $\pm$ 2.5		0.140 $\pm$ 0.001 <sup>b</sup>	0.144 $\pm$ 0.16	102
Mn (mg kg <sup>-1</sup> )	19.2 $\pm$ 1.8	16.8 $\pm$ 2.9	88	675,000 $\pm$ 18,000	589,000 $\pm$ 3600	87
Cu (mg kg <sup>-1</sup> )	2.35 $\pm$ 0.16	2.11 $\pm$ 0.07	89	140,000 $\pm$ 2000	121,000 $\pm$ 2000	86
Zn (mg kg <sup>-1</sup> )	19.42 $\pm$ 0.26	17.36 $\pm$ 0.14	89	414,000 $\pm$ 11,000	385,000 $\pm$ 4900	93
Al (mg kg <sup>-1</sup> )	4.21 $\pm$ 0.34	3.80 $\pm$ 1.21	90	6.72 $\pm$ 0.06 <sup>b</sup>	5.10 $\pm$ 0.07	76
Ca (mg kg <sup>-1</sup> )	118.4 $\pm$ 3.1	116.2 $\pm$ 4.0	98	2.42 $\pm$ 0.06 <sup>b</sup>	1.93 $\pm$ 0.02	79.7
Fe (mg kg <sup>-1</sup> )	7.42 $\pm$ 0.44	6.24 $\pm$ 0.25	84	2.82 $\pm$ 0.04 <sup>b</sup>	2.51 $\pm$ 0.06	89
K (mg kg <sup>-1</sup> )	1282 $\pm$ 11	1129 $\pm$ 23	88	2.53 $\pm$ 0.10 <sup>b</sup>	2.37 $\pm$ 0.01	94
Mg (mg kg <sup>-1</sup> )	559 $\pm$ 10	462 $\pm$ 9	83	1.07 $\pm$ 0.06 <sup>b</sup>	0.95 $\pm$ 0.01	89
Ba (mg kg <sup>-1</sup> )	-			730,000 $\pm$ 15,000	572,000 $\pm$ 14,300	78
Na (mg kg <sup>-1</sup> )	6.74 $\pm$ 0.19	29.1 $\pm$ 4.7		1.2 $\pm$ 0.01 <sup>b</sup>	0.7 $\pm$ 0.06	58
Sr (mg kg <sup>-1</sup> )	-			242,000 $\pm$ 10,000	235,000 $\pm$ 3800	97

150 <sup>a</sup>Reference values, <sup>b</sup>concentration in percentage



### 151 **3.2 Arsenic in Peruvian rice**

152 This is the first study reporting As concentrations in rice cultivated in Peru (Table 2). When  
153 compared with other Latin American countries, the average total As concentration in 29 rice  
154 samples  $167.94 \pm 71 \mu\text{g kg}^{-1}$  (range 68.39-345.31  $\mu\text{g kg}^{-1}$ ) was higher than reported  
155 concentrations in rice cultivated in Guayas and Los Ríos provinces of Ecuador ( $125 \pm 44 \mu\text{g}$   
156  $\text{kg}^{-1}$  in Guayas;  $42 \pm 33 \mu\text{g kg}^{-1}$  from Los Ríos and  $67 \pm 29 \mu\text{g kg}^{-1}$  from the market) (Otero et  
157 al., 2016) but similar to total As in Brazilian husked rice from Santa Catarina ( $157 \pm 108 \mu\text{g}$   
158  $\text{kg}^{-1}$ ; 70-427  $\mu\text{g kg}^{-1}$ ); while lower than the concentrations in rice from Rio Grande do Sul  
159 ( $235 \pm 157 \mu\text{g kg}^{-1}$ ; 20-630  $\mu\text{g kg}^{-1}$ ) (Kato et al., 2019). In a review, Bundschuh et al.  
160 (2012b)(based on the published results of Juarez-Soto's MSc thesis) summarised As  
161 concentrations in food chain, other than rice and reported As in edible plants collected from  
162 Rímac river, Carapongo in Peru in the range of 51-121  $\mu\text{g kg}^{-1}$ ; 33-512  $\mu\text{g kg}^{-1}$  and 40-193  
163  $\mu\text{g kg}^{-1}$  by wet weight in radish, lettuce and beet respectively.

164 While the maximum total As recorded was 345.31  $\mu\text{g kg}^{-1}$ , 7 out of 29 rice samples had total  
165 As greater than 200  $\mu\text{g kg}^{-1}$ . The Joint FAO-WHO Codex Alimentarius Commission in July  
166 2014 established a maximum level of 200  $\mu\text{g kg}^{-1}$  for inorganic As in polished rice (EFSA,  
167 2014) but in a population based study, Banerjee et al. (2013) reported elevated genotoxic  
168 effects in a population from West Bengal, India, consuming cooked rice with total As greater  
169 than 200  $\mu\text{g kg}^{-1}$ . While inorganic As content of rice depends on the rice variety and can be  
170 up to 90% of total As (Rahman et al., 2014), As in cooked rice depends on the cooking  
171 method (Rahman et al., 2006; Mwale et al., 2018). In Peru, rice is often cooked with  
172 vegetable oil, garlic, salt and limited water (water to rice ratio less than 2:1) which is then  
173 evaporated to dryness. Removal of As on cooking with uncontaminated water is least when  
174 rice is cooked with limited water and the water is evaporated (Mwale et al., 2018). Based on  
175 total annual per capita rice consumption of 51.6  $\text{kg person}^{-1}$  in coastal areas of Peru (INEI,

2012), amount of rice consumed per day would be approximately 141.37 g. Considering inorganic As content of the rice to be 80%, as observed in Ecuadorian rice by Otero et al. (2016), for an average weight of 70 kg person, consuming rice cultivated in Tumbes river basin (average total As in rice of  $168 \mu\text{g kg}^{-1}$ ) the ADI (average daily intake) of inorganic As would be  $0.27 \mu\text{g (kg bw)}^{-1} \text{d}^{-1}$ , but the maximum intake could reach up to  $0.56 \mu\text{g (kg bw)}^{-1} \text{d}^{-1}$  (based on maximum As concentration of  $345 \mu\text{g kg}^{-1}$  in rice). This estimated ADI is safe considering the European Food Safety Authority recommended range of inorganic As exposure of  $0.3\text{-}8 \mu\text{g (kg bw)}^{-1} \text{d}^{-1}$  based on 1% increased incidence in lung, skin and bladder cancer and skin lesions ((Mondal et al. (2019) from Cubadda et al. (2017)). But further studies addressing As speciation in Peruvian rice, As in cooked rice, accurate rice intake by the local population and risk perception of As exposure from rice intake (Mondal et al., 2019) can elucidate the increased health risk, if any due to As in Peruvian rice.

**Table 2:** Total As and concentrations of other elements in rice grains (n=29) collected from agricultural fields of Tumbes river basin in Peru.

Elements	Average $\pm$ Std. Dev	Median	Range	Spearman rho <sup>a</sup>
As ( $\mu\text{g kg}^{-1}$ )	$167.94 \pm 71.00$	164.79	345.31-68.39	
V ( $\mu\text{g kg}^{-1}$ )	$50.15 \pm 36.68$	42.14	204.77-11.34	0.4355**
Cr ( $\mu\text{g kg}^{-1}$ )	$150.94 \pm 163.00$	119.20	746.46-0.25	0.3655
Co ( $\mu\text{g kg}^{-1}$ )	$16.42 \pm 10.21$	13.79	42.51-5.44	0.2576
Ni ( $\mu\text{g kg}^{-1}$ )	$0.54 \pm 1.56$	0.25	8.66-0.25	-0.4813**
Se ( $\mu\text{g kg}^{-1}$ )	$85.12 \pm 48.24$	81.32	183.55-15.02	-0.6340**
Cd ( $\mu\text{g kg}^{-1}$ )	$327.20 \pm 395.66$	146.99	1550.05-41.36	-0.5187**
Sb ( $\mu\text{g kg}^{-1}$ )	$32.91 \pm 60.76$	8.71	239.01-3.24	0.4670**
Pb ( $\mu\text{g kg}^{-1}$ )	$86.07 \pm 54.38$	71.21	275.50-36.94	0.4670**
Mn(mg $\text{kg}^{-1}$ )	$19.51 \pm 5.55$	19.29	31.15-10.00	-0.1089
Cu (mg $\text{kg}^{-1}$ )	$4.01 \pm 1.25$	3.79	8.07-2.31	-0.4315**
Zn (mg $\text{kg}^{-1}$ )	$12.91 \pm 2.19$	12.39	19.98-10.68	-0.5921**
Al (mg $\text{kg}^{-1}$ )	$9.48 \pm 15.51$	4.77	78.74-0.03	0.3345

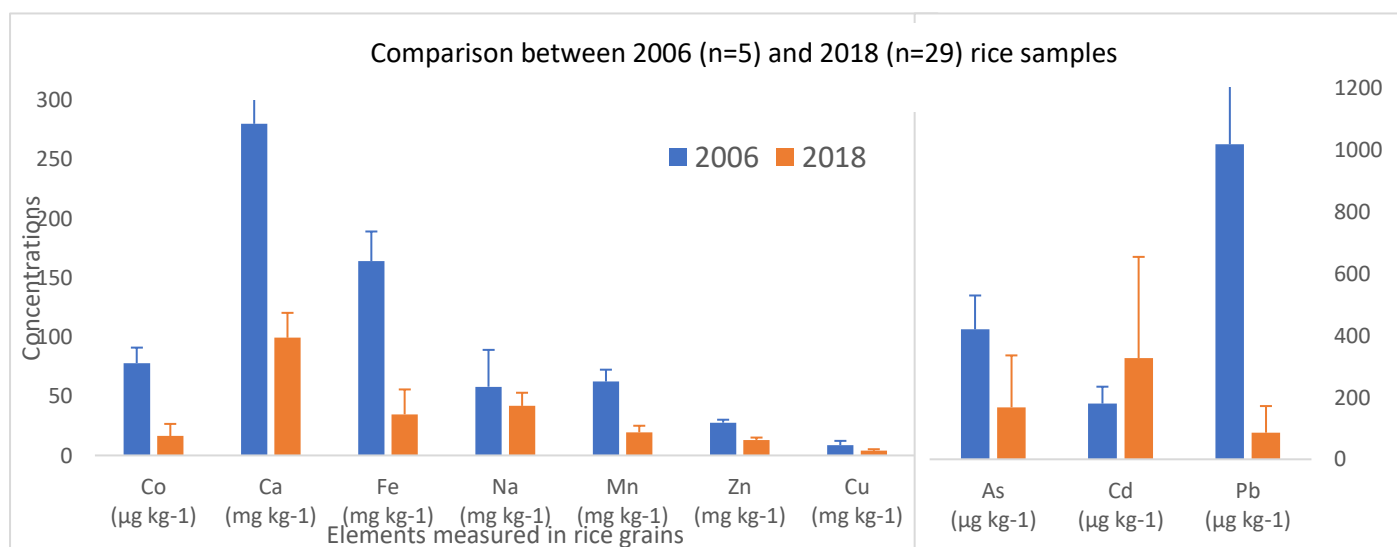
Ca (mg kg <sup>-1</sup> )	99.36 ± 21.03	99.86	142.64-67.67	0.2980
Fe (mg kg <sup>-1</sup> )	34.66 ± 21.07	29.64	121.79-12.74	0.4168**
K (mg kg <sup>-1</sup> )	1859.33 ± 540.04	1639.14	3568.77-1095.80	0.2300
Mg (mg kg <sup>-1</sup> )	806.88 ± 267.81	719.65	1531.50-414.75	0.2310
Ba (mg kg <sup>-1</sup> )	0.51 ± 0.22	0.49	1.18-0.20	0.0458
Na (mg kg <sup>-1</sup> )	41.83 ± 11.11	39.87	80.26-29.17	0.0586
Sr (mg kg <sup>-1</sup> )	0.31 ± 0.11	0.28	0.63-0.16	0.4182**
B (mg kg <sup>-1</sup> )	1.05 ± 0.31	0.90	1.64-0.63	0.3197

190 <sup>a</sup>Spearman's rank correlation coefficient between As and other elements; \*\* significance level (p  
191 <0.05)

### 192 3.3 Comparison between 2006 and 2018 study

193 Rice production in Peru is on the rise, for example, between 2006 and 2017 both rice  
194 production and area harvested for paddy cultivation increased by 29 and 23% respectively  
195 (based on data published by FAOSTAT (FAO, 2019)). In 2006, authors (Bermejo and Cruz,  
196 2006) had collected five rice samples from the same agricultural fields and As content (420 ±  
197 109 µg kg<sup>-1</sup>; n=5) measured using ICP-MS at a private Canadian laboratory (ACME Lab,  
198 along with other elements) was found to be significantly higher (based on two-sample t-test)  
199 compared to this study (Figure 2 and 4).

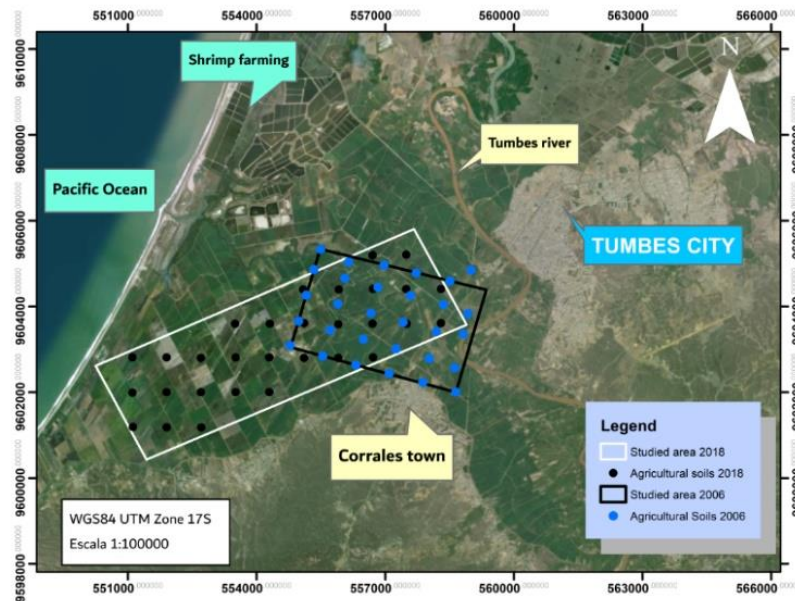
200



201 **Figure 2:** Comparison of analysed elements in rice grains collected between 2006 and 2018

202 This could be due to the difference in sample size, exact location of cultivation within the  
203 agricultural field, method of cultivation, rice variety and seasonal variation apart from change  
204 in As concentrations of the agricultural soil. Indeed, we find a significant (based on two-  
205 sample t-test) decrease (by 41%) in As concentration in agricultural soil samples collected  
206 between 2006 (n=30) and 2018 (Table 3). Furthermore, the control soil samples (n=5) also  
207 had reduced concentrations ( $6.09 \pm 5.73 \text{ mg kg}^{-1}$  in 2018 compared to  $14.06 \pm 11.75$  in 2006).  
208 Apart from possible reduction in soil As over time this difference could be due to difference  
209 in exact location of soil collection between the two surveys (as shown in Figure 3; the soil  
210 sampling locations in 2006 in comparison to 2018) and difference in analytical procedures.  
211 Plausible explanation for this observed reduction in soil As over time might also include a)  
212 periodic flooding of Tumbes river which was more often in 2006 compared to recent times  
213 resulting in increased deposition of As and other contaminants due to their presence in river  
214 water (Marshall et al., 2018); b) increased crop cycle for rice cultivation between 2006 to  
215 2018 resulting in higher uptake of As by the rice plants; c) change in cultivation method with  
216 recent practice allowing weed proliferation which might accumulate As from soil; and d)  
217 increased accumulation of As back into the soil due to burning of the rice agricultural  
218 residues in the fields as was followed back in time over increased use of fodder for animal  
219 feed in recent times, but further studies are needed to investigate the observed reduction. The  
220 irrigation water collected in this study had higher As ( $16.40 \pm 8.41 \mu\text{g L}^{-1}$ , n=5) compared to  
221 2006 ( $10.40 \pm 10.30 \mu\text{g L}^{-1}$ , n=5) so as the drainage sludge but not the drainage water (Figure  
222 4). The increase of As concentration in irrigation water could be an artefact of increased  
223 mining activities. As noted by Marshall et al. (2018), the upper Puyango Tumbes river basin  
224 includes the mining district of Portovelo with 87 gold processing centres and in their study  
225 conducted in 2012-14, authors reported high concentrations of total As along with Cd, Cu, Pb  
226 and Zn in the river water even up to 160 km downstream from the discharge point. Indeed,

227 among all the elements it was only for Cd and Pb that we didn't find a significant difference  
 228 in soil concentrations between this study and 2006 samples, perhaps indicating Cd and Pb  
 229 contamination due to mining activities remaining the same overtime. Mean soil As of  $8.63 \pm$   
 230  $7.8$  observed in this study was higher than Guayas and Los Ríos provinces of Ecuador ( $4.48 \pm$   
 231  $3 \text{ mg kg}^{-1}$ ) in Otero et al. (2016) study. Also, As in irrigation water was less than  $10 \mu\text{g L}^{-1}$  in  
 232 Ecuador compared to  $16.40 \mu\text{g L}^{-1}$  observed in this study.



233

234 **Figure 3:** Sampling location for agricultural soil samples collected in 2006 (Bermejo and  
 235 Cruz, 2006) as compared to 2018

236 **Table 3:** Concentrations of arsenic and of other elements in agricultural soil samples of  
 237 Tumbes river basin

Elements	Agricultural soils 2006 (n=30)	Agricultural soils 2018 (n=30)	Percentage decrease <sup>a</sup>
	Mean $\pm$ Std. Dev	Mean $\pm$ Std. Dev	
As ( $\text{mg kg}^{-1}$ )	$14.73 \pm 5.56$	$8.63 \pm 7.8$	41.41%
Cd ( $\text{mg kg}^{-1}$ )	$0.97 \pm 0.26$	$0.89 \pm 0.5$	8.25% <sup>b</sup>
Co ( $\text{mg kg}^{-1}$ )	$14.82 \pm 1.13$	$3.91 \pm 0.78$	73.62%
Cr ( $\text{mg kg}^{-1}$ )	$24.8 \pm 3.14$	$6.32 \pm 1.18$	74.52%
Cu ( $\text{mg kg}^{-1}$ )	$57.18 \pm 17.44$	$18.95 \pm 14.27$	66.86%
Mn ( $\text{mg kg}^{-1}$ )	$490.17 \pm 125.63$	$165.89 \pm 62.89$	66.16%

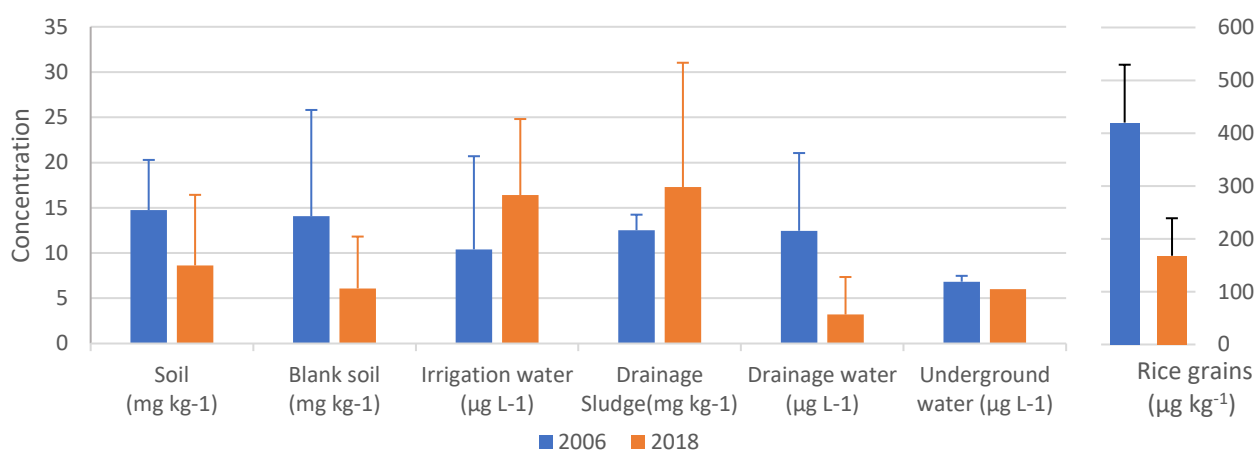
Mo (mg kg <sup>-1</sup> )	1.38 ± 0.3	1.09 ± 0.41	21.01%
Ni (mg kg <sup>-1</sup> )	22.26 ± 3.48	2.63 ± 0.76	88.19%
Pb (mg kg <sup>-1</sup> )	37.65 ± 19.39	40.95 ± 38.26	-8.76% <sup>b</sup>
Zn (mg kg <sup>-1</sup> )	137.4 ± 26.67	43.33 ± 20.99	68.46%
Al (%)	2.12 ± 0.27	1.67 ± 0.37	21.23%
Ca (%)	0.47 ± 0.12	0.75 ± 0.52	-59.57%
Fe (%)	3.42 ± 0.3	3.02 ± 0.44	11.70%
K (%)	0.21 ± 0.04	0.17 ± 0.05	19.05%
Mg (%)	0.62 ± 0.07	0.55 ± 0.08	11.29%
Na (%)	0.03 ± 0.02	0.04 ± 0.04	-33.33% <sup>b</sup>

238 <sup>a</sup> Percentage decrease between 2006 and 2018, negative value shows an increase

239 <sup>b</sup> No significant difference between 2006 and 2018 concentrations based on two-sample t-test  
 240 (unequal variance)

241

Comparison of arsenic concentration in different media between  
 2006 and 2018



242

243 **Figure 4:** Comparison of arsenic concentrations in different media collected in 2006 and  
 244 2018

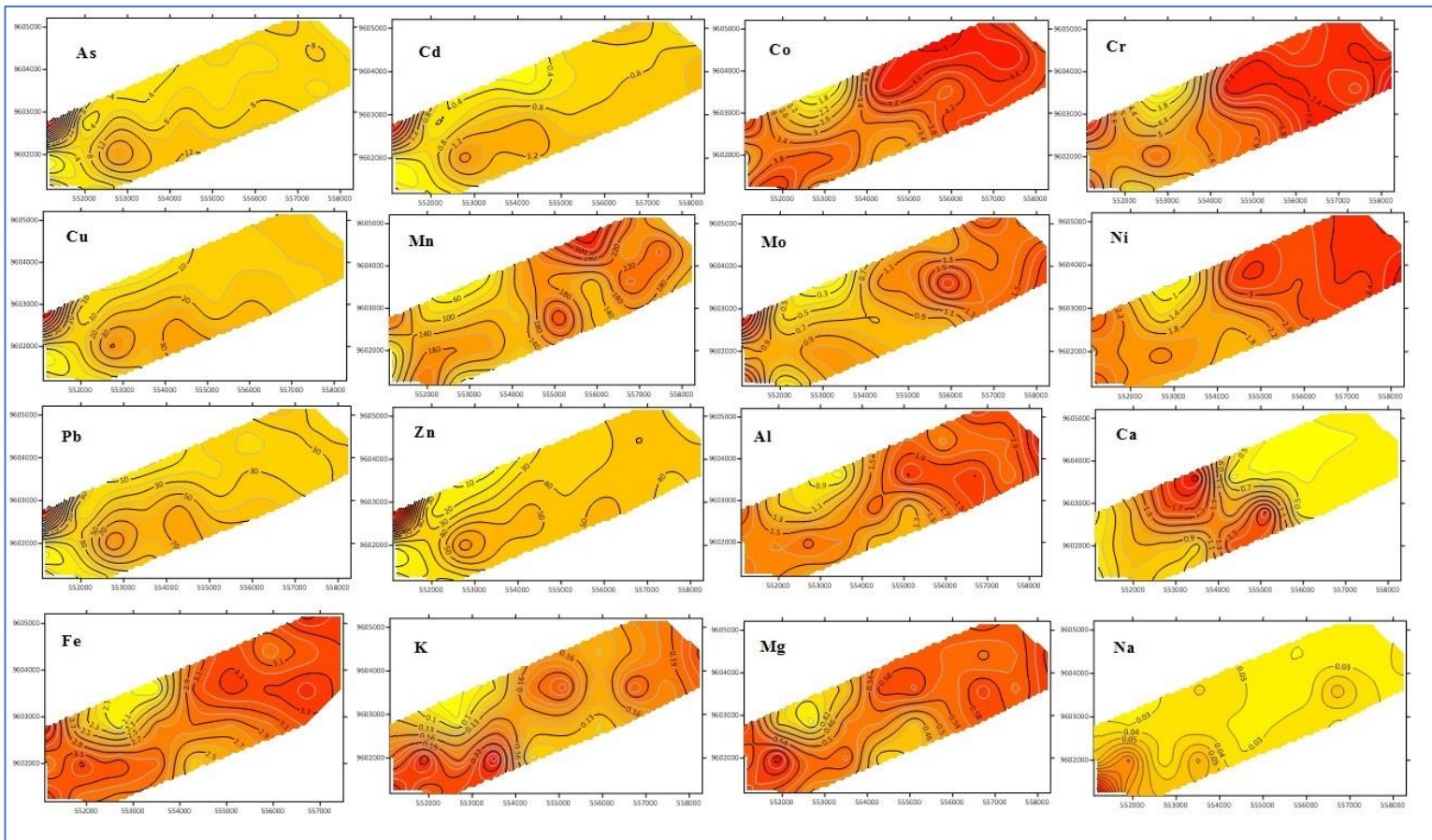
### 245 **3.4 Arsenic and other elements in the agricultural soil of Tumbes river basin**

246 The contour maps of the study area are displayed in Figure 5 showing the areas with higher  
 247 concentration of the elements in red colour and the areas with lower concentrations in yellow.

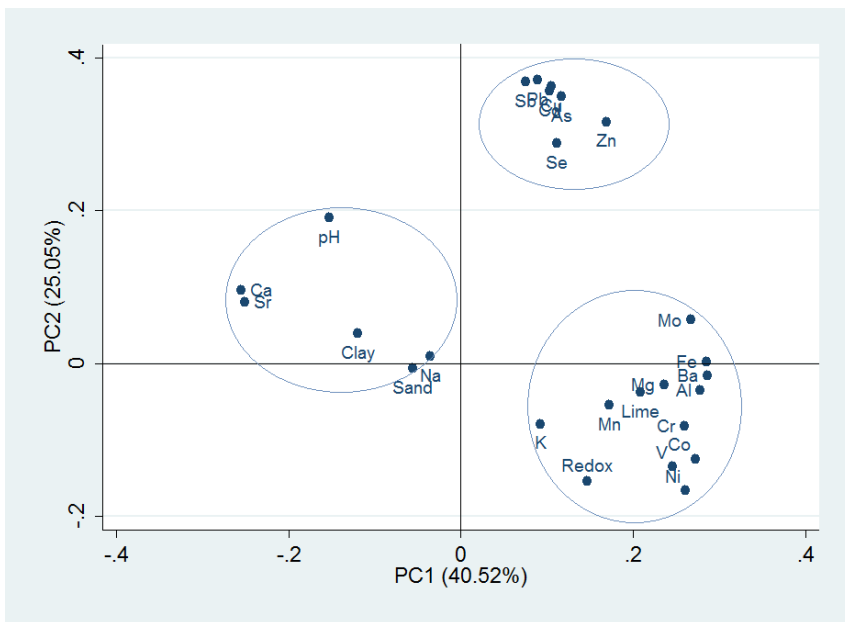
248 Concentrations of As along with Cd and Pb are found to be higher towards the coastline and  
 249 as apparent from the maps, As is significantly correlated with Cd, Pb, Zn and Cu (with

250 Spearman rho of 0.731, 0.8861, 0.8056, and 0.8994 respectively (p<0.05)).

251 While, except for Cd, Pb and Na, a significant decrease in elemental concentrations of both  
252 trace and major elements in soil between 2006 and 2018 was noted (Table 3), none of the  
253 potentially toxic elements had mean concentrations (both in 2006 and 2018) above the limit  
254 specified by the Peruvian Ministry of Environment which stated 50 mg kg<sup>-1</sup>, 1.4 mg kg<sup>-1</sup> and  
255 70 mg kg<sup>-1</sup> as safe limit for As, Cd and Pb respectively for agricultural soil (MINAM, 2018).  
256 But with maximum concentration recorded of 3.06 mg kg<sup>-1</sup> in this 2018 study, four samples  
257 had Cd greater than the safe limit, and two of the Pb soil exceeded the limit with maximum  
258 concentration recorded 212.4 mg kg<sup>-1</sup>. Though soil As was positively correlated with Cd and  
259 Pb, rice As was positively correlated with Pb but negatively correlated with Cd (Table 2).  
260 When PCA was applied to the soil data to explore similarities in behaviour of the elements,  
261 first two principle components extracted (Figure 6), explained approximately 65% (PC1:  
262 40.52%; PC2 25.05%) of the information contained in the initial variables while the five  
263 components together explained more than 90% of the variability observed. It is visible from  
264 Figure 6 that As was not associated with the soil properties including texture, pH and redox  
265 potential and was more associated with elements such as Pb, Cd, Zn, Se and Sb. Further  
266 studies looking at interrelationship of uptake of elements by rice depending on the variety  
267 cultivated in this area along with soil proprieties, will explain potential combined hazard and  
268 health risk, if any, from Peruvian rice consumption.



270 **Figure 5:** Geochemical distribution map of trace and major elements in the surveyed  
 271 agricultural field area in Tumbes river basin



272  
 273 **Figure 6:** Principal component analysis diagram for average elemental concentrations and  
 274 other parameters measured in soil samples of agricultural fields in Tumbes river basin



275 **3.5 Transfer of potentially toxic elements in rice grain**

276 Based on the ratios of heavy metal concentration in rice grains over 12 matched soil samples,  
 277 the transfer factors TF<sub>grain/soil</sub> were calculated (Table 4). The average TF<sub>grain/soil</sub> had the  
 278 trend Cd > Zn > Cu > Mn > Cr > As > Co > Pb which was similar to previous studies (Zeng et al.,  
 279 2015; Lu et al., 2018; Mao et al., 2019) and As transfer ratio of 0.025 ± 0.018 is similar to the  
 280 study in Yangtze river delta in China (0.020 ± 0.001; Mao et al. (2019)).

281 **Table 4:** Transfer factor of potentially toxic elements in rice grain (n=12, matched paired  
 282 samples)

Sample	As	Cd	Co	Cu	Cr	Mn	Pb	Zn
GA15-SA28	0.0154	0.1386	0.0057	0.1814	0.0000	0.1433	0.0022	0.3417
GA13-SA26	0.0512	0.1884	0.0106	0.3325	0.0337	0.1003	0.0080	0.3728
GA11-SA22	0.0627	0.1668	0.0103	0.3484	0.1637	0.1851	0.0138	0.5287
GA18-SA23	0.0048	0.0891	0.0031	0.1087	0.0012	0.0640	0.0007	0.1888
GA09-SA21	0.0102	1.3479	0.0041	0.3219	0.0117	0.1119	0.0018	0.2782
GA10-SA20	0.0325	0.0944	0.0021	0.1393	0.0001	0.0911	0.0013	0.2674
GA08-SA17	0.0092	0.3785	0.0030	0.2122	0.0000	1.3185	0.0008	0.2957
GA16-SA18	0.0238	0.7196	0.0013	0.3042	0.0064	0.1143	0.0017	0.3272
GA17-SA18	0.0150	0.1532	0.0020	0.2297	0.0062	0.1157	0.0019	0.3383
GA03-SA09	0.0200	0.1709	0.0021	0.2544	0.0276	0.0977	0.0019	0.2753
GA02-SA08	0.0397	0.2425	0.0031	0.2704	0.0024	0.0415	0.0079	0.2416
GA06-SA15	0.0199	1.4360	0.0057	0.3725	0.0596	0.0799	0.0036	0.4352
Mean ±SD	0.025 ± 0.018	0.427 ± 0.483	0.004 ± 0.003	0.256 ± 0.084	0.026 ± 0.047	0.205 ± 0.352	0.004 ± 0.004	0.324 ± 0.091
Range	0.005- 0.063	0.089- 1.436	0.001- 0.011	0.109- 0.373	0.000- 0.164	0.042- 1.318	0.001- 0.014	0.189- 0.529

283

284 **Conclusions**

285 This study confirms the presence of As in Peruvian rice produced in a major paddy  
 286 cultivation area of Tumbes river basin in northern Peru. While the grain As levels were not  
 287 highly elevated, the As content of few samples (n=7) greater than 200 µg kg<sup>-1</sup> arguably could

288 contribute negatively to human health upon chronic exposure. In addition, our data provides a  
289 baseline of grain-As concentrations in a country and in particular a province where  
290 appreciable agricultural intensification has taken place. Since Peruvian rice production is on a  
291 steep rise, this results demand for further comprehensive investigation covering all rice  
292 cultivation areas in Peru. Arsenic TF grain/soil observed in this study was similar to previous  
293 studies in other countries, hence further studies should address potential factors including  
294 different rice genotypes affecting uptake of As by the rice plant. It was worth noting that we  
295 found a substantial decrease in As content in rice collected in this study when compared to  
296 samples collected from same agricultural fields in 2006 along with significant decrease in soil  
297 As content. But compared to 2006 study, there was a rise in As concentration in the irrigation  
298 water which comes from Tumbes river, and this could be attributed to increased mining  
299 activities in the upper Puyango-Tumbes river basin which includes the mining district of  
300 Portovelo. Further studies should focus on As induced health risks in Tumbes river basin  
301 attributed to arsenic exposure not only from drinking water which is often collected from the  
302 river but also from rice, cultivated and consumed locally. Besides, presence of inorganic As  
303 in different genotypes as well as As bioaccessibility study from rice varieties cultivated in  
304 Peru could help understand the actual scenario of contamination as well as realistic exposure  
305 and risk assessment.

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313 **Competing interests**

314 The authors declare that they have no competing/conflicting interests.

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