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

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Abstract

Arsenic (As) exposure from surface and groundwater in Peru is being recognised as a potential threat but there are limited studies on As in the food-chain and none on As in Peruvian rice. In this study, we have determined the As content in rice cultivated in the Tumbes river basin located in the northern province of Peru, an area known for extensive rice cultivation. We collected rice and soil samples from agricultural fields, soil was collected using grid sampling technique while rice was collected from the heaps of harvested crop placed across the fields. The average total As concentration in rice was 167.94 ± 71 µg kg^{-1} (n=29; range 68.39-345.31 µg kg^{-1}). While the rice As levels were not highly elevated, the As content of few samples (n=7) greater than 200 µg kg^{-1} could contribute negatively to human health upon chronic exposure. Average concentration of As in soil was 8.63 ± 7.8 mg kg^{-1} (n=30) and soil to grain transfer factor was 0.025 ± 0.018 for 12 matched samples. Compared to our previous pilot study in 2006 (samples collected from the same agricultural fields but not from exact locations) there was a 41% decrease in As soil concentration in this study. Rice samples collected in 2006 (n=5) had a mean concentration of 420 ± 109 µg kg^{-1}. Our data provides a baseline of rice grain As concentrations in Peruvian province of Tumbes and warrants further studies on factors affecting uptake of As by the rice varieties cultivated in Peru and any potential human health risks.

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

1. Introduction

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

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

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

The Puyango-Tumbes river basin encompasses a large diverse land area (90,000 ha in Tumbes) essentially devoted to agriculture, where more than 6000 farmers are engaged in cultivation, predominantly of rice along with banana, corn and other fruits (Marshall et al., 2018). The Tumbes river is an important source of water for irrigation, hence pollutants discharged from mining and other activities in the upper course of the river (Puyango in Ecuador) including As, pose a significant health risk to those consuming food, cultivated in these lands. Compared to other crops, rice has a high ability to absorb As from the soil, making it the most contaminated cereal (Meharg and Zhao, 2012) and consumption of rice is a well-established route of As exposure (Mondal and Polya, 2008; Mondal et al., 2010). Agriculture being an important part of the economy in Tumbes, with one of the dominant crops being rice, assessment of As is rice cultivated in Tumbes river basin is of significance. Moreover, unlike other Latin American countries, little is known about the As in food-chain of Peru (Bundschuh et al., 2012b) and none about rice. In this study we have determined the As content in rice cultivated in the Tumbes river basin of Peru and compared the findings with a preliminary pilot data collected by us in 2006 (Bermejo and Cruz, 2006). We have also estimated As and other potentially toxic elements present in the agricultural soil and irrigation water of Tumbes river basin and calculated the transfer factor between soil and the grain.

2. Methods

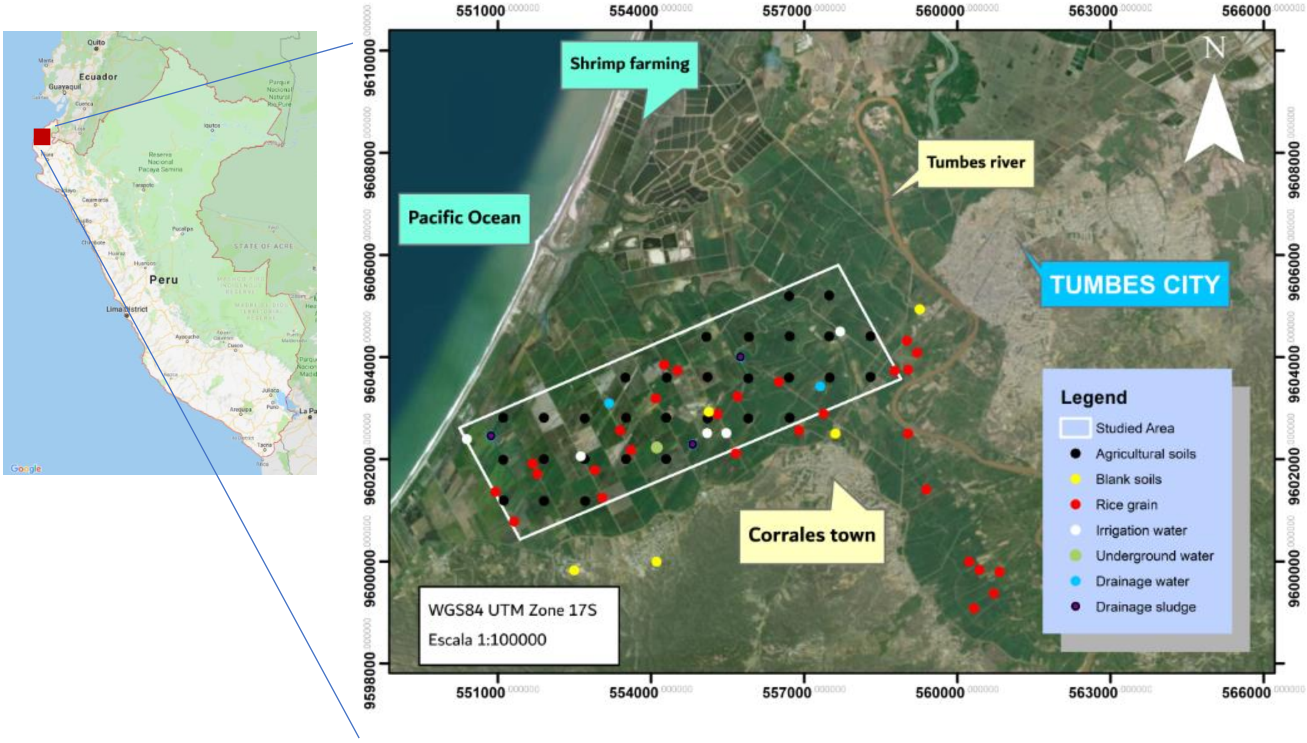

Figure 1: Sampling location for all the different samples collected

2.1 Sample collection and analysis:

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

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

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

2.2 Data analysis:

Data was analyzed using Microsoft Excel and Stata 11.2 for descriptive statistics and for independent t-test. The multivariate principal component analysis (PCA) technique was applied to the soil data, in order to explore the grouping of elements according to their similarities and the analysis was performed using Stata 11.2. The spatial distribution of elements in soil for the study area was developed using Surfer 18 (Golden Software, Colorado, EEUU). The grids used as bases to build contour maps were done using interpolation with the kriging method (no data was assigned outside convex hull of data). Based on these grids, the contour maps for every element were developed. The transfer factor between soil and grain (TFgrain/soil = concentration in grain/concentration is soil) was determined by matching the rice samples (n=12) to the nearest soil sample within the grid (Figure 1).

3. Results and discussion

3.1 Quality control

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

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

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

[a]Reference values, [b]concentration in percentage

3.2 Arsenic in Peruvian rice

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

While the maximum total As recorded was 345.31 µg kg^{-1}, 7 out of 29 rice samples had total As greater than 200 µg kg^{-1}. The Joint FAO-WHO Codex Alimentarius Commission in July 2014 established a maximum level of 200 µg kg^{-1} for inorganic As in polished rice (EFSA, 2014) but in a population based study, Banerjee et al. (2013) reported elevated genotoxic effects in a population from West Bengal, India, consuming cooked rice with total As greater than 200 µg kg^{-1}. While inorganic As content of rice depends on the rice variety and can be up to 90% of total As (Rahman et al., 2014), As in cooked rice depends on the cooking method (Rahman et al., 2006; Mwale et al., 2018). In Peru, rice is often cooked with vegetable oil, garlic, salt and limited water (water to rice ratio less than 2:1) which is then evaporated to dryness. Removal of As on cooking with uncontaminated water is least when rice is cooked with limited water and the water is evaporated (Mwale et al., 2018). Based on total annual per capita rice consumption of 51.6 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 µg kg^{-1}) the ADI (average daily intake) of inorganic As would be 0.27 µg (kg bw)$^{-1}$ d^{-1}, but the maximum intake could reach up to 0.56 µg (kg bw)$^{-1}$ d^{-1} (based on maximum As concentration of 345 µg kg^{-1} in rice). This estimated ADI is safe considering the European Food Safety Authority recommended range of inorganic As exposure of 0.3-8 µg (kg bw)$^{-1}$ 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 ± Std. Dev	Median	Range	Spearman rho[a]
As (µg kg^{-1})	167.94 ± 71.00	164.79	345.31-68.39	
V (µg kg^{-1})	50.15 ± 36.68	42.14	204.77-11.34	0.4355**
Cr (µg kg^{-1})	150.94 ± 163.00	119.20	746.46-0.25	0.3655
Co (µg kg^{-1})	16.42 ± 10.21	13.79	42.51-5.44	0.2576
Ni (µg kg^{-1})	0.54 ± 1.56	0.25	8.66-0.25	-0.4813**
Se (µg kg^{-1})	85.12 ± 48.24	81.32	183.55-15.02	-0.6340**
Cd (µg kg^{-1})	327.20 ± 395.66	146.99	1550.05-41.36	-0.5187**
Sb (µg kg^{-1})	32.91 ± 60.76	8.71	239.01-3.24	0.4670**
Pb (µg kg^{-1})	86.07 ± 54.38	71.21	275.50-36.94	0.4670**
Mn(mg kg^{-1})	19.51 ± 5.55	19.29	31.15-10.00	-0.1089
Cu (mg kg^{-1})	4.01 ± 1.25	3.79	8.07-2.31	-0.4315**
Zn (mg kg^{-1})	12.91 ± 2.19	12.39	19.98-10.68	-0.5921**
Al (mg kg^{-1})	9.48 ± 15.51	4.77	78.74-0.03	0.3345

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

[a] Spearman's rank correlation coefficient between As and other elements; ** significance level ($p < 0.05$)

3.3 Comparison between 2006 and 2018 study

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

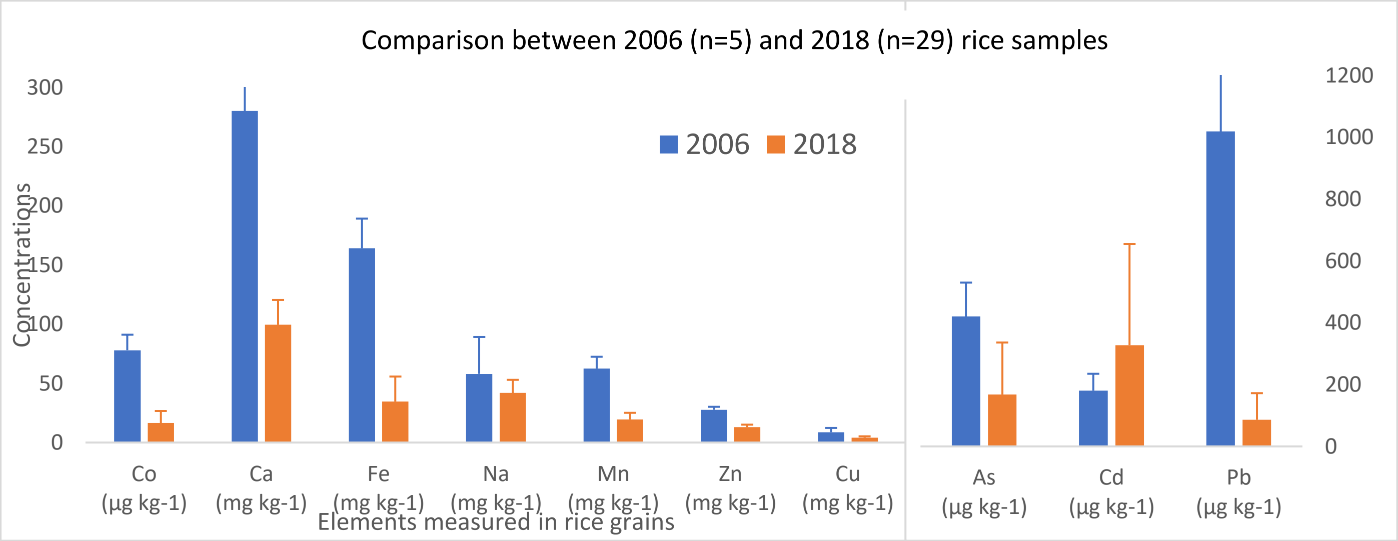

Figure 2: Comparison of analysed elements in rice grains collected between 2006 and 2018

This could be due to the difference in sample size, exact location of cultivation within the agricultural field, method of cultivation, rice variety and seasonal variation apart from change is As concentrations of the agricultural soil. Indeed, we find a significant (based on two-sample t-test) decrease (by 41%) in As concentration in agricultural soil samples collected between 2006 (n=30) and 2018 (Table 3). Furthermore, the control soil samples (n=5) also had reduced concentrations (6.09 ± 5.73 mg kg^{-1} in 2018 compared to 14.06 ± 11.75 in 2006). Apart from possible reduction in soil As over time this difference could be due to difference in exact location of soil collection between the two surveys (as shown in Figure 3; the soil sampling locations in 2006 in comparison to 2018) and difference in analytical procedures. Plausible explanation for this observed reduction in soil As over time might also include a) periodic flooding of Tumbes river which was more often in 2006 compared to recent times resulting in increased deposition of As and other contaminants due to their presence in river water (Marshall et al., 2018); b) increased crop cycle for rice cultivation between 2006 to 2018 resulting in higher uptake of As by the rice plants; c) change in cultivation method with recent practice allowing weed proliferation which might accumulate As from soil; and d) increased accumulation of As back into the soil due to burning of the rice agricultural residues in the fields as was followed back in time over increased use of fodder for animal feed in recent times, but further studies are needed to investigate the observed reduction. The irrigation water collected in this study had higher As (16.40 ± 8.41 µg L^{-1}, n=5) compared to 2006 (10.40 ± 10.30 µg L^{-1}, n=5) so as the drainage sludge but not the drainage water (Figure 4). The increase of As concentration in irrigation water could be an artefact of increased mining activities. As noted by Marshall et al. (2018), the upper Puyango Tumbes river basin includes the mining district of Portovelo with 87 gold processing centres and in their study conducted in 2012-14, authors reported high concentrations of total As along with Cd, Cu, Pb and Zn in the river water even up to 160 km downstream from the discharge point. Indeed, among all the elements it was only for Cd and Pb that we didn't find a significant difference in soil concentrations between this study and 2006 samples, perhaps indicating Cd and Pb contamination due to mining activities remaining the same overtime. Mean soil As of 8.63 ± 7.8 observed in this study was higher than Guayas and Los Ríos provinces of Ecuador (4.48 ± 3 mg kg^{-1}) in Otero et al. (2016) study. Also, As in irrigation water was less than 10 µg L^{-1} in Ecuador compared to 16.40 µg L^{-1} observed in this study.

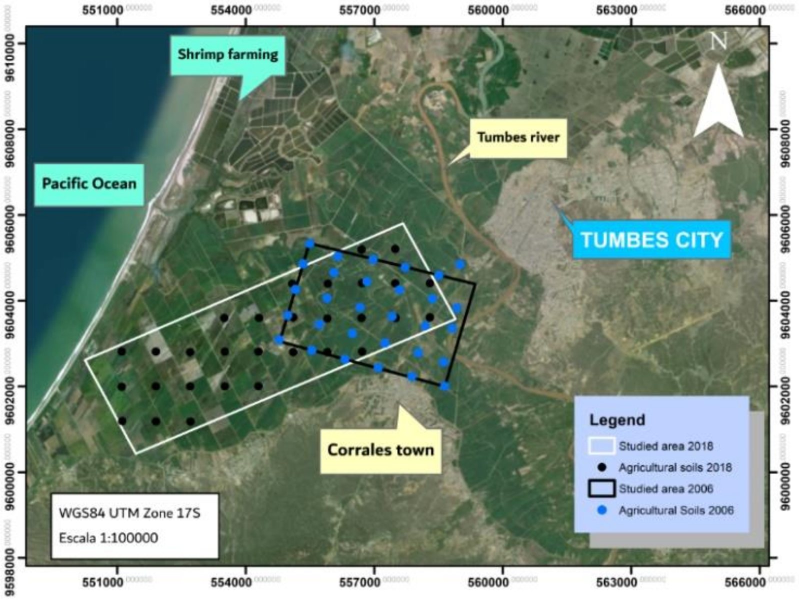

Figure 3: Sampling location for agricultural soil samples collected in 2006 (Bermejo and Cruz, 2006) as compared to 2018

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

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

Mo (mg kg^{-1})	1.38 ± 0.3	1.09 ± 0.41	21.01%
Ni (mg kg^{-1})	22.26 ± 3.48	2.63 ± 0.76	88.19%
Pb (mg kg^{-1})	37.65 ± 19.39	40.95 ± 38.26	-8.76% [b]
Zn (mg kg^{-1})	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% [b]

[a] Percentage decrease between 2006 and 2018, negative value shows an increase

[b] No significant difference between 2006 and 2018 concentrations based on two-sample t-test (unequal variance)

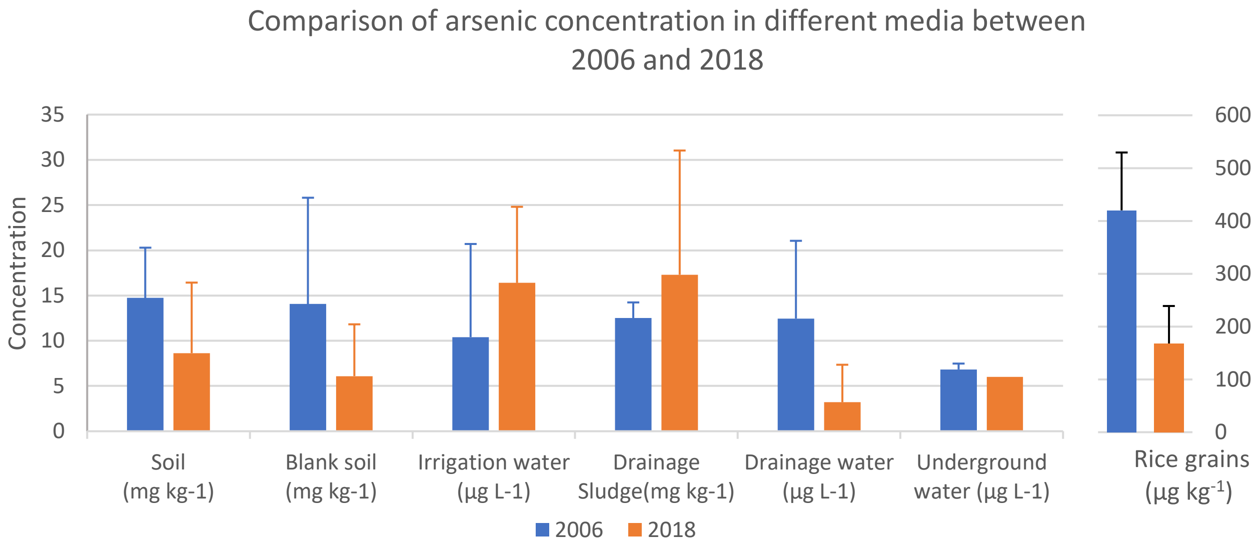

Figure 4: Comparison of arsenic concentrations in different media collected in 2006 and 2018

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

The contour maps of the study area are displayed in Figure 5 showing the areas with higher concentration of the elements in red colour and the areas with lower concentrations in yellow. Concentrations of As along with Cd and Pb are found to be higher towards the coastline and as apparent from the maps, As is significantly correlated with Cd, Pb, Zn and Cu (with Spearman rho of 0.731, 0.8861, 0.8056, and 0.8994 respectively (p<0.05)).

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

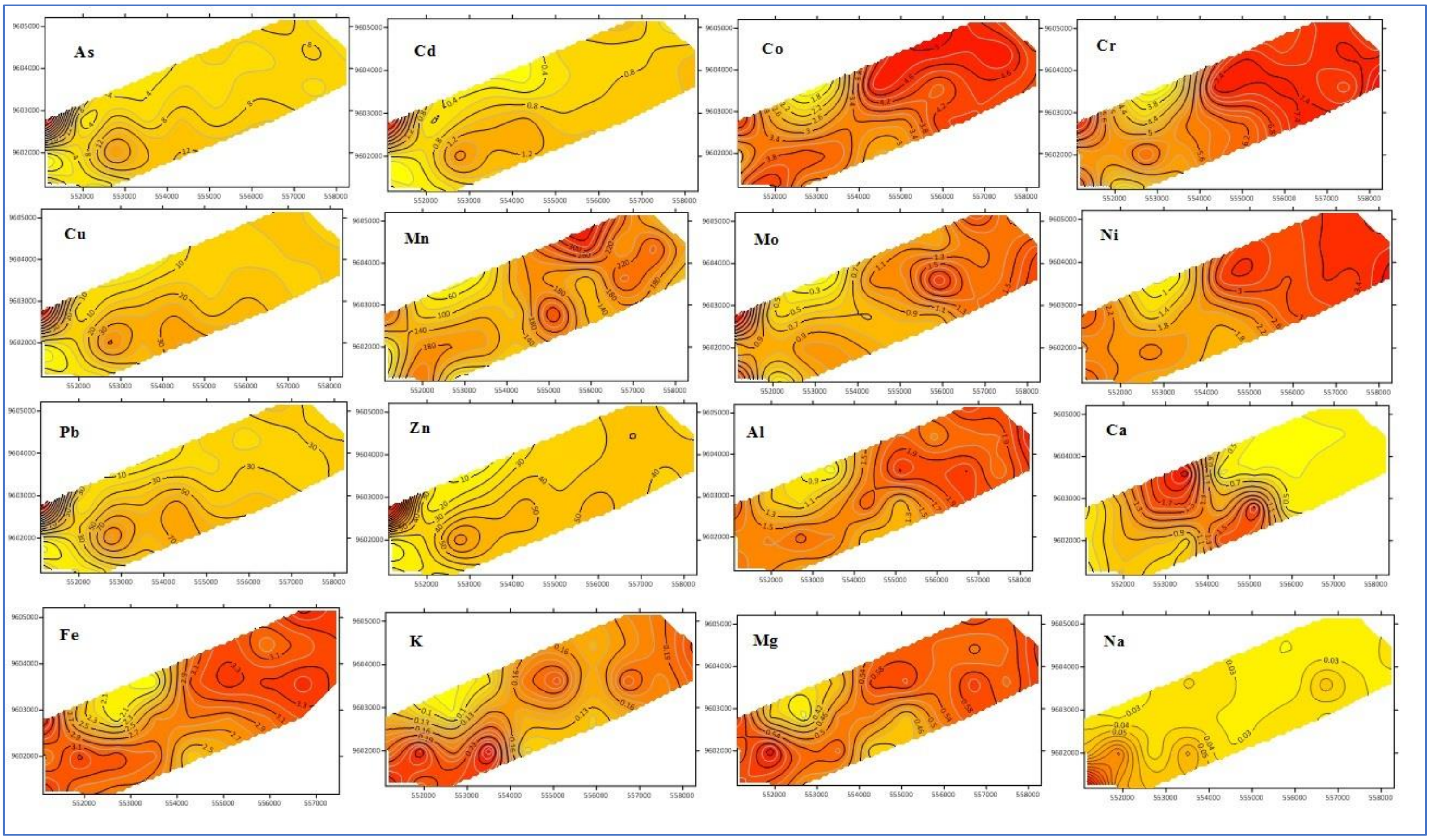

Figure 5: Geochemical distribution map of trace and major elements in the surveyed agricultural field area in Tumbes river basin

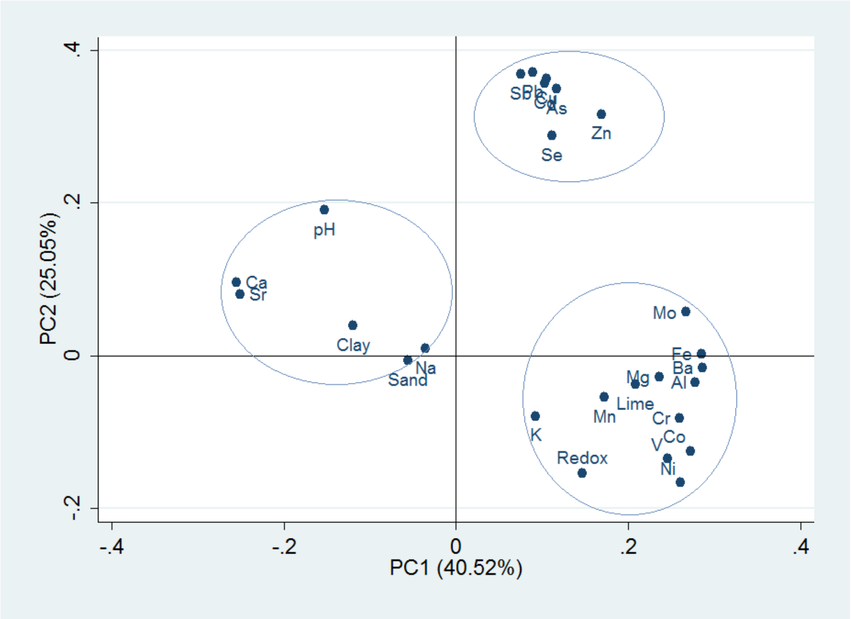

Figure 6: Principal component analysis diagram for average elemental concentrations and other parameters measured in soil samples of agricultural fields in Tumbes river basin

3.5 Transfer of potentially toxic elements in rice grain

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

Table 4: Transfer factor of potentially toxic elements in rice grain (n=12, matched paired 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

Conclusions

This study confirms the presence of As in Peruvian rice produced in a major paddy cultivation area of Tumbes river basin in northern Peru. While the grain As levels were not highly elevated, the As content of few samples (n=7) greater than 200 µg kg^{-1} arguably could contribute negatively to human health upon chronic exposure. In addition, our data provides a baseline of grain-As concentrations in a country and in particular a province where appreciable agricultural intensification has taken place. Since Peruvian rice production is on a steep rise, this results demand for further comprehensive investigation covering all rice cultivation areas in Peru. Arsenic TF grain/soil observed is this study was similar to previous studies in other countries, hence further studies should address potential factors including different rice genotypes affecting uptake of As by the rice plant. It was worth noting that we found a substantial decrease in As content in rice collected in this study when compared to samples collected from same agricultural fields in 2006 along with significant decrease in soil As content. But compared to 2006 study, there was a rise in As concentration in the irrigation water which comes from Tumbes river, and this could be attributed to increased mining activities in the upper Puyango-Tumbes river basin which includes the mining district of Portovelo. Further studies should focus of As induced health risks in Tumbes river basin attributed to arsenic exposure not only from drinking water which is often collected from the river but also from rice, cultivated and consumed locally. Besides, presence of inorganic As in different genotypes as well as As bioaccessibility study from rice varieties cultivated in Peru could help understand the actual scenario of contamination as well as realistic exposure and risk assessment.

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Competing interests

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

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