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Global Geographical Variation in Elemental and Arsenic Species Concentration in Paddy Rice Grain Identifies a Close Association of Essential Elements Copper, Selenium and Molybdenum with Cadmium

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Abstract

Despite the centrality of staple grains for human well-being, both as a source of nutrients and of toxic ions, there is little understanding of where and how elements vary, and if there are particular elements that correlate. Here, for shop bought polished (white) rice, we comprehensively characterized trace (arsenic species, cadmium, copper, iron, manganese, molybdenum, rubidium and zinc) and macro-nutrients (calcium, chlorine, potassium, phosphorus and sulphur) for grain purchased in 18 countries, across four continents, a total of 1045 samples. This was to investigate if there were any major differences between geographic location and elemental content, and to observe if there were any patterns in elemental distribution. Greatest variation in the median was observed for the non-essential rubidium (15-fold) and arsenic species (fivefold). Rubidium was the highest in the Americas, lowest in Europe, while inorganic arsenic (iAs) and dimethylarsonic acid (DMA) were low for Africa and high in the South American and European continents. The highest concentrations of cadmium were found in Asian samples, and lowest in South America, with variation within these regions. At the extremes of individual counties, China had fivefold higher concentrations than the global median, while Tanzania was fourfold lower than this value. Calcium, potassium, molybdenum and phosphorus were the highest in European and lowest in African grain, though the fold-differences were relatively low, ~ 0.2 , while iron was the highest in African grain and lowest in European, Asian and South American grain, with a ~ twofold difference. Selenium was also higher in Africa versus other regions, and copper, manganese and zinc were the highest in American grain. Factor analysis showed that copper, cadmium, molybdenum, rubidium and selenium were strongly associated together, and these element's factor loadings were diametrically opposed to less tightly associated calcium, chlorine, manganese, potassium, phosphorus and sulphur. Stepwise additions linear region analysis was performed on log-transformed concentrations to investigate cadmium associations in more detail. Selenium was the greatest predictor of cadmium concentration, followed by molybdenum, accounting for over 50% of the contribution to the adjusted R². Arsenic species were only weakly correlated with other elements. The implications for these findings with respect to dietary nutrition are discussed. Vietnamese rice was notable in being deficient in macro- and micro-nutrients while also being elevated in cadmium at a median of 0.02 mg/kg, with China though still having a median that is ~ 2.5-fold this concentration. These Chinese concentrations are of particular concern as the 75th percentile for China is 0.1 mg/kg, a value that triggers regulatory action for rice products.

Keywords Arsenic · Cadmium · Mineral nutrition · Rice

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Introduction

Hidden hunger is one of the greatest issues facing society globally, defined as where food delivers adequate calories but is deficient in essential nutrients (Gashu et al. 2021). This is nowhere so prominent than in subsistence diets that rely on polished grains, where milling grains, unfortunately, removes a substantial portion of nutrients present in wholegrain (Rahman et al. 2019). Grain mineral nutrition varies due to soil conditions and cultivation and fertilization practice (Nyachoti et al. 2021; Gashu et al. 2021; Welsh and Graham 2004; White and Broadley 2005), and to crop genetics (Cobb et al. 2021; Huang et al. 2015; Norton et al. 2014). Maximizing grain nutrient density, to deliver as great a quantity of each essential element as feasible, given that bioavailability in the gut is also an issue for elements such as iron (Hoekenga et al. 2011), is a major goal for those wishing to improve human health (Gashu et al. 2021; Rahman et al. 2019).

Food security, supplying a population sufficient quantities of nutritionally balanced foods, has to be combined with food safety, minimizing exposure to toxic compounds. White rice is particularly problematic in both regards as it is not overly nutrient dense, while at the same time being widely elevated, ~ tenfold compared to other grains, in cadmium and arsenic (Rahman et al. 2019). There is evidence that for certain elements such as arsenic (Williams et al. 2007), cadmium (Nan et al. 2002) and selenium (Zhu et al. 2009) that rice grain concentration is linked to the concentration in the soils in which they are grown. These elements tend to act as analogues of essential nutrients, phosphate and silicic acid for arsenic, dependant on whether arsenic is speciated as arsenate or arsenite, respectively (Meharg and Meharg 2015), nutrient divalent metal cations for cadmium (Schaaf et al. 2004), and sulphur for selenium (Zhu et al. 2009). The same is the case for nonessential rubidium, an analogue of essential potassium (Oliferuk et al. 2017). Most nutrient elements are thought to be in homeostasis with plant tissues, given that plant cells have quite stringent requirements for optimum functioning, and all elements/ions can be considered as stressors if outside those optimum activities in cells (Clemens 2001; Ernst et al. 2008; Meharg 1993). Some nutrients can be stored in excess through cellular sub-localization, or the formation of compounds/complexes suitable for storage. Phosphorus, an essential but generally poorly available in soils, undergoes both these storage strategies under luxury uptake, though plants rapidly downregulate phosphate assimilation if leaf tissue becomes too high (Chiou et al. 2006). Quantitative trait loci analysis, also indicates for some elements, notably cadmium, lead, selenium, zinc, that grain accumulation is under genetic control in rice

(Cobb et al. 2021; Huang et al. 2015; Norton et al. 2014). Given these complexities, for food security and safety mitigation strategies, it is important to know how elemental concentrations vary regionally for foods, Deficiency or toxicity mitigation for a specific region may include soil fertilization, water management, food supplementation or high grain nutrient directed breed strategies, i.e. food fortification of biofortification (Welsh and Graham 2004; White and Broadley 2005).

Global and regional assessments of grain mineral nutrition tend to focus on food fraud, using elemental analysis to try and identify geographical origin (Ariyama et al. 2012; Chung et al. 2018); or geo-nutrition, relating crop grain element concentrations to region of origin (Adomako et al. 2011; Gashu et al. 2021), with a number of studies also focusing on dietary consequences of grain elemental content (Gashu et al. 2021; Joy et al. 2017; Nyachoti et al. 2021). These studies generally use inductively coupled plasma-mass spectrometry (ICP-MS), and this has led to a better characterization of micro-elemental quantification, to which ICP-MS is suited, as compared to macro-elements that are generally too elevated in grains for adequate ICP-MS quantification, with the exception of phosphorus. Of particular interest with respect to ICP-MS quantification are arsenic and cadmium which are of concern in rice but too low to be measured by other techniques such as X-ray fluorescence (XRF) (Rahman et al. 2019). Furthermore, arsenic in rice grain is speciated as iAs (the sum of arsenate and arsenite) and DMA, and it is iAs that is regulated not DMA, yet DMA can constitute up to ~ 50% of grain speciation in some regions, and chromatography interfaced to ICP-MS is required to speciate grain arsenic (Rahman et al. 2019). XRF is better suited to macro-element analysis and is becoming more established in characterizing foods, given that issues with external calibration of XRF need to be overcome by using an appropriate range of Certified Reference Materials (CRMs) (Oliveira et al. 2020; Rahman et al. 2019). Also, for arsenic in particular, there is a need to speciate as toxicity and regulation are driven by iAs content, yet rice grain can have highly variable concentrations of dimethylarsonic acid (DMA) (Adomako et al. 2011; Carey et al. 2020). Here, we report macro- and micro-elemental, along with arsenic species, concentrations of market white rice, chosen to reflect direct dietary consumption of 1045 samples, collected across 18 countries from four major rice growing continents; Africa, South America, Asia and Europe. Rice was analysed by ICP-MS, ion chromatography (IC)-ICP-MS (to ascertain arsenic species concentrations) and XRF. Data were interpreted to examine commonalities in elemental and species patterns, and to identify specific deficiency/toxicity issues for given regions/countries.

Materials and Methods

The sampling strategies are outlined in the publications Carey et al. (2020) and Shi et al. (2020). In brief, polished (white) rice was obtained from 18 countries, and 4 continents, from retail outlets so as to best characterize consumer exposure. In total 1045 samples are reported here, a subset from the 1180 reported in Carey et al. (2020) on arsenic speciation, and 2270 from Shi et al. (2020) on cadmium. The current dataset only reports samples where additional XRF characterization has been conducted, leading to reduced sample coverage, in both number and in countries assessed.

As noted in Carey et al. (2020), the type of market basket survey conducted here has its limitations due to the fact that multiple people conducted the survey, with multiple sampling objectives, with each country sampled having differing geographical size, and the surveyors having differing geographical reaches within a given country. Furthermore, some countries only have one rice season per annum, others have multiple, and there is often within country variation on number of seasons based on geographical setting. Also, genetic variation in rice occurs at the subspecies level (Aus, Japonica, Indica and hybrid etc.), and there is considerable cultivar variation within these subspecies. Markets may directly source rice from neighbouring farmers, or at the other extreme, source rice from larger mills that can operate on a regional scale. The nature of variation in rice sourcing will lead to heterogeneity in retail supply. The data presented here does not include retail outlet type, genetic information, seasonal information, etc., and this must be born in mind in interpreting this study. For a global sampling campaign to include such detail, and the subsequent increase in sample size to account for these multiple variables, were well beyond the resources of this current investigation. However, the utility of the sampling approach used here can be validated by comparison with local studies where details of interest are recorded. Examples of more detailed studies cross-referenced to the current investigation in the discussion are country-specific surveys of grain (Adomako et al. 2011; Joy et al. 2017; Williams et al. 2009); and the role of genetic variation (Huang et al. 2015; Norton et al. 2010, 2012, 2014), with respect to rice grain mineral nutrition.

Methodologies for the well-established rice inorganic analysis that we use here are have been published already. A concise overview of the analysis is now presented. Rice samples were freeze dried (Christ Alpha1-4LD) and milled (PM100 Ball Mill, Retsch, Germany) and subsampled for ICP-MS (Thermo Scientific iCap Q), both for arsenic speciation (interfaced with in chromatography, IC), and elemental totals, and for XRF (Nex CG, Rigaku, Japan). ICP-MS and IC-ICP-MS protocols are described in detail in Carey et al. (2020) and Shi et al. (2020), and XRF protocols in Rahman et al. (2019). Certified Reference Material (CRM) rice flour, NIST 1568b, was included in all batches of samples for both elemental totals (ICP-MS and XRF) and for arsenic speciation, and it is certified for both a range of elemental totals and for arsenic speciation. Total elemental analysis was conducted by weighing ~ 100 mg of sample, accurately, into 50 ml polypropylene (PP) tubes, and then adding 2 ml of conc. Aristar nitric acid. The PP tubes were then left to stand for 24 h. Before initiating digestion, 2 ml of undiluted hydrogen peroxide (reagent grade) was pipetted in, then microwaved digested (Mars CEM), using programmes detailed in Carey et al. (2020). Samples were cooled to room temperature on completion of microwaving, and diluted to 30 ml with double distilled deionized water. The protocol for arsenic speciation was identical except that except that 10 ml of one percent nitric acid was used for as the extractant instead of concentrated nitric acid. Prior to IC-ICP-MS speciation, 7 µl of hydrogen peroxide added to 700 µl of the extraction, to convert arsenite to arsenate for subsequent IC chromatography, as arsenite elutes at the solvent front.

ICP-MS analysis was calibrated using eight standards, including one blank. Multi-Element 2 (SPEX CLMS-2 Multi-Element Solution 2, matrix: five percent nitric acid) and Multi-Element 4 (SPEX CLMS-4 Multi-Element Solution 4, matrix: water/Tr-HF) were used to make up all standards in a range of 0–100 μ g/l in one percent nitric acid. Rhodium internal standard (Fluka Analytical rhodium internal ICP-MS standard) was added to all standards and all samples also at ten μ g/l. For IC-ICP-MS, authentic samples of arsenate, monomethylarsonic acid (MMA) and DMA were used to determine retention times, and the calibration was conducted on DMA. XRF (Rigaku NEX CG) was performed on the ball-milled samples to determine elements that are either problematic on non-determinable by ICP-MS (see Table 1).

Only elements with certified quantification for rice flour CRM NIST 1568b were reported. Reported elements were within the range of 67–109% recovery, with CRM recoveries and Limits of Detection (LoD) for ICP-MS techniques, and Detection Limits (DL), for XRF as this method has an internal calibration, are given in Table 1. As a range of elements can be quantified by both ICP-MS and XRF, and for these elements, the technique with the best recovery of NIST rice flour CRM NIST 1568b was selected for reporting, with the technique used for reported analysis also listed in Table 1.

Statistical analysis considered the data both as grouped by continent or as grouped by country. As the datasets are not normally distributed, Kruskal–Wallis test used to compare medians and stepwise linear regression to look at relationships between elements was conducted in SPSS v.27, and

Element/species	Certified value (mg/kg)	Recorded value (mg/kg)	SEM	Recovery (%)	LoD (mg/kg)	DL (mg/kg)	Instrumentation	N
DMA	0.180	0.181	0.005	100	0.002	_	IC-ICP-MS	78
MMA	0.012	0.010	0.000	87	0.002	_	IC-ICP-MS	78
iAs	0.092	0.091	0.001	99	0.002	_	IC-ICP-MS	78
Sum As sp.	0.284	0.282	0.005	99	0.002	_	IC-ICP-MS	78
As	0.285	0.228	0.004	80	0.001	_	ICP-MS	56
Ca	118	116	2	98	_	7.22	XRF	143
Cd	0.022	0.023	0.001	104	0.004	_	ICP-MS	56
Cl	301	232	3	77	_	0.323	XRF	143
Cu	2.35	1.84	0.05	78	0.043	_	ICP-MS	56
Fe	7.42	5.79	0.18	78	0.938	_	ICP-MS	56
Κ	1282	1061	12	83	_	4.67	XRF	143
Mn	19.2	21.0	0.3	109	_	3.35	XRF	143
Мо	1.45	1.42	0.01	98	0.149	_	ICP-MS	56
Р	1530	1325	11	87	_	6.7	XRF	143
Rb	6.20	5.82	0.03	94	_	0.294	XRF	143
S	1200	984	8	82	_	2.14	XRF	143
Se	0.365	0.245	0.006	67	0.087	_	ICP-MS	56
Zn	19.4	17.4	0.2	89	-	0.595	XRF	143

 Table 1
 Certified reference materials (CRM) recoveries by ICP-MS and XRF for rice flour NIST 1568b

Limits of detection (LoD) are given for IC-ICP-MS and ICP-MS as they are externally calibrated, and as detection limits (DL) for XRF as this method has an internal calibration

principal component analysis (PCA) and Spearman's rank correlation were conducted using GraphPad Prism v.9.

Results

Medians, 25th and 75th percentiles, are presented for elements and species by continent in Fig. 1. Kruskal-Wallis analysis was used to investigate differences in medians between the four regions. For all elements and species presented here, all were significantly different between continents, all at P < 0.001, with the exception of Mn (P = 0.002) and Zn (P = 0.032). Greatest variation in the median was observed for the non-essential rubidium, being the highest in the Americas, lowest in Europe, with a 15-fold difference. Arsenic species, iAs and DMA, were the next most variable in their medians with both species being low in Africa and high in the South American and European continents, with a~fivefold difference, while iAs was relatively high in Asia, but DMA low. Cadmium had a different profile, being the highest in Asia and lowest in South America. A range of macro-nutrient elements, calcium, potassium, molybdenum and phosphorus, were the highest in European, and lowest in African grain, though the fold-differences were relatively low, ~0.2. Conversely, iron was high in African grain and lowest in European, Asian and South American grain, ~twofold difference. Chloride was also high in African and Asian grain, as compared to American and European. Selenium was also higher in Africa versus other regions. Copper, manganese and zinc were the highest in American grain, though there was relatively good homeostasis in concentrations across the continents. Sulphur was also found to have a similar homeostasis.

Presentation of medians for individual countries are given in Table 2, and country medians as a percentage of overall mean of country medians in Fig. 2. Kruskal-Wallis analysis found that all counties differed in their median, all at P < 0.0001 with the exception of zinc where P = 0.046. Tanzania is particularly low in iAs DMA, cadmium and rubidium, but high in chloride. Mali is low in selenium, along with Argentina, Paraguay, Uruguay South Korea, Indonesia and Spain. There is a fourfold difference in selenium concentrations for countries across the globe. For some countries there are notable high or low concentrations for particular elements. South Korea is high in calcium compared to all other countries, while Vietnam is particularly low in this element. Cadmium is specifically highly elevated in China, while other Asian countries also tend to be high in this element, ~ 500% higher than the global mean. Chloride is elevated in Chile, phosphorus in Sri Lanka, and sulphur in Bangladesh. Bangladesh is specifically low in zinc, with a median 70% of that of the overall country medians, but high in iron at 200% of the median (Fig. 2). Countries with notably low macro- and **Fig. 1** Boxplots of Median (central line), 25 and 75th (outer box), 5 and 95th (whiskers) and outliers for each element by continental region: green, Africa; light blue, South America; yellow, S.E. Asia; dark blue, Europe



micro-nutrient elements are South Korea for copper, Chile and Sri Lanka for sulphur, zinc in Uruguay and Argentina, and particularly low zinc for Bangladesh, with almost half the concentration of this element compared to other countries. Vietnam is notable as it is deficient in calcium, iron, potassium, manganese and molybdenum, and no other country matches this broad pattern of macro- and micronutrient deficiencies (Fig. 2). For Africa, a depletion in arsenic species is apparent, as is elevation in selenium (Tanzania and Ivory Coast) and iron (universally) (Fig. 2). There is a specific elevation in Ivory Coast grain cadmium relative to other African countries (Fig. 2). What distinguishes American countries, with the exception of Bolivia, from other regions of the world are that they vary from moderate to highly elevated DMA, ~ 300%, and are relatively depleted in selenium especially in Argentina, Paraguay and Uruguay. Asian countries tend to be elevated in cadmium, but interestingly not South Korea. European

Table 2 Medians and 25 and 75th percentiles for each element by country with units reported in mg/kg dry wt

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		iAs			DMA			Ca		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Median	25th	75th	Median	25th	75th	Median	25th	75th
$\begin{split} \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Tanzania	0.009	0.0275	0.0055	0.003	0.008	0.002	39.8	47.3	36
Mair 0.0666 0.0897 0.0192 0.013 40.1 47.6 37.8 Daivia 0.0724 0.0984 0.045 0.149 0.03 40.1 47.6 37.8 Bazil 0.0684 0.0994 0.0521 0.032 0.047 0.009 52.2 60.7 36.3 Brazil 0.0684 0.0716 0.0599 0.113 0.141 0.019 41.4 58.4 34 Chile 0.0679 0.0877 0.0614 0.105 0.13 0.066 43.1 63.2 39.2 China 0.0823 0.0946 0.072 0.025 0.033 0.011 79.9 95.5 65.9 Banglacksh 0.116 0.192 0.004 0.001 43.8 66.8 34.9 Indonesia 0.0252 0.033 0.014 29.3 56.8 25.8 Bayai 0.0641 0.0566 0.022 0.036 0.022 58.8 33.7 Tarkeno	Ivory Coast	0.0492	0.0747	0.0142	0.013	0.019	0.004	42.8	51.1	35.1
$\begin{split} \begin{array}{c c c c c c c c c c c c c c c c c c c $	Mali	0.0696	0.089	0.0193	0.032	0.04	0.013	46.3	57.7	40.9
Boliva 0.0724 0.0899 0.0521 0.032 0.047 0.009 52.2 60.7 53.3 Brazil 0.0684 0.0716 0.059 0.113 0.141 0.081 53.4 76.7 45.4 Paraguy 0.1074 0.133 0.0954 0.086 0.12 0.05 39.6 55.6 34.8 Ureguay 0.0679 0.087 0.0614 0.105 0.13 0.061 3.1 63.2 39.2 Chian 0.0823 0.0946 0.072 0.025 0.033 0.019 51.1 61.3 41.2 South Korea 0.0325 0.0510 0.0152 0.028 0.037 0.011 3.9 58.8 36.8 Victman 0.052 0.053 0.012 0.036 0.021 0.036 0.22 58.8 36.8 254.8 37.7 Victman 0.0621 0.084 0.062 0.033 0.061 0.021 0.036 0.027 58.8 4	Argentina	0.0614	0.0867	0.0488	0.045	0.149	0.03	40.1	47.6	37.8
Brazil 0.668 0.079 0.0484 0.071 0.105 0.019 41.4 58.4 34 Chile 0.0634 0.0716 0.0599 0.113 0.141 0.081 53.4 76.7 45.4 Paraguay 0.0679 0.087 0.064 0.105 0.13 0.066 43.1 63.2 39.2 China 0.0639 0.0812 0.0552 0.016 0.019 0.011 79.9 99.5 65.9 Bangladesh 0.1116 0.1502 0.0794 0.028 0.037 0.013 55.2 67.3 37.9 St Lanka 0.0325 0.0551 0.0152 0.034 0.007 0.011 43.9 58.8 36.6 Vietnam 0.0621 0.0484 0.049 0.059 0.092 0.035 52.2 58.9 47.8 Spain 0.0621 0.0484 0.0490 0.054 0.092 0.033 51.8 2.12 58.4 43.2 Ta	Bolivia	0.0724	0.0984	0.0521	0.032	0.047	0.009	52.2	60.7	36.3
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Brazil	0.0688	0.0899	0.0484	0.071	0.105	0.019	41.4	58.4	34
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Chile	0.0634	0.0716	0.0599	0.113	0.141	0.081	53.4	76.7	45.4
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Paraguay	0.1074	0.1393	0.0954	0.086	0.12	0.05	39.6	55.6	34.8
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Uruguay	0.0679	0.087	0.0614	0.105	0.13	0.066	43.1	63.2	39.2
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	China	0.0823	0.0946	0.072	0.025	0.033	0.019	51.1	61.3	41.2
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	South Korea	0.0639	0.0812	0.0552	0.016	0.019	0.011	79.9	99.5	65.9
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Bangladesh	0.1116	0.1502	0.0794	0.028	0.037	0.013	55.2	67.3	37.9
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Sri Lanka	0.0355	0.0543	0.0234	0.002	0.006	0.001	43.8	66.8	34.9
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Indonesia	0.0325	0.0501	0.0152	0.004	0.007	0.001	43.9	58.8	36
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Vietnam	0.0679	0.0852	0.0556	0.025	0.033	0.018	29.3	36.8	25.8
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Italy	0.0943	0.1151	0.0706	0.059	0.092	0.036	52.2	58.9	47.8
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Spain	0.0621	0.084	0.0469	0.054	0.092	0.023	40.3	54.8	33.7
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Turkey	0.0757	0.0904	0.0682	0.033	0.065	0.027	50.8	58.4	42.4
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		Cl			Cd			Cu		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		Median	25th	75th	Median	25th	75th	Median	25th	75th
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Tanzania	234	274	187	0.0049	0.0049	0.0049	1.74	2.07	1.47
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ivory Coast	183	201	159	0.0217	0.0347	0.0176	1.83	2.18	1.51
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mali	135	156	123	0.0172	0.0238	0.0049	1.98	2.28	1.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Argentina	126	139	113	0.0049	0.012	0.0049	1.95	2.11	1.83
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Bolivia	115	182	100	0.023	0.0697	0.0049	2.45	2.85	2.19
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Brazil	142	164	125	0.0122	0.0175	0.0049	2.21	3.02	1.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Chile	275	304	253	0.0049	0.0049	0.0049	1.94	2.23	1.9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Paraguay	168	187	142	0.0049	0.0049	0.0049	2.41	2.54	2.32
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Uruguay	154	178	122	0.0049	0.0082	0.0049	1.7	1.73	1.39
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	China	218	237	190	0.0539	0.118	0.0103	1.98	2.31	1.78
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	South Korea	170	194	145	0.0154	0.0242	0.0116	1.38	1.7	1.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Bangladesh	175	202	151	0.0247	0.0432	0.017	1.56	1.93	1.41
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Sri Lanka	173	219	135	0.0285	0.0588	0.0168	2.24	2.85	1.65
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Indonesia	223	259	194	0.0208	0.0337	0.0114	1.59	1.81	1.25
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Vietnam	186	214	155	0.019	0.0345	0.0134	1.72	2.27	1.23
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Italy	142	157	130	0.0261	0.0343	0.0154	2.07	2.27	1.54
Spin 170 171 154 6.6049 6.6060 6.6049 1.12 2.61 1.54 Turkey 186 206 162 0.0049 0.0126 0.0049 2.03 2.44 1.65 Fe K Median 25th 75th Median 25th 75th Median 25th 75th Tanzania 6.52 8.58 5.27 812 910 744 12.5 14.15 10.75 Ivory Coast 7.79 15.37 5.72 777 863 690 9.16 10.75 7.8 Mali 7.64 11.44 6.52 926 1443 597 11.75 14.25 7.86 Argentina 4.02 4.49 3.62 832 928 787 10.46 11.15 9.49 Bolivia 3.75 5.49 3.19 581 800 511 10.85 16.83 9.79	Spain	176	191	154	0.0049	0.0401	0.0049	1.72	2.03	1.72
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Turkey	186	206	162	0.0049	0.0126	0.0049	2.03	2.01	1.51
Median25th75thMedian25th75thMedian25th75thTanzania6.528.585.2781291074412.514.1510.75Ivory Coast7.7915.375.727778636909.1610.757.8Mali7.6411.446.52926144359711.7514.257.86Argentina4.024.493.6283292878710.4611.159.49Bolivia3.755.493.1958180051110.8516.839.79		Fe	200	102	K	0.0120	0.0049	Mn	2.11	
Tanzania 6.52 8.58 5.27 812 910 744 12.5 14.15 10.75 Ivory Coast 7.79 15.37 5.72 777 863 690 9.16 10.75 7.8 Mali 7.64 11.44 6.52 926 1443 597 11.75 14.25 7.86 Argentina 4.02 4.49 3.62 832 928 787 10.46 11.15 9.49 Bolivia 3.75 5.49 3.19 581 800 511 10.85 16.83 9.79		Median	25th	75th	Median	25th	75th	Median	25th	75th
Ivory Coast7.7915.375.727778636909.1610.757.8Mali7.6411.446.52926144359711.7514.257.86Argentina4.024.493.6283292878710.4611.159.49Bolivia3.755.493.1958180051110.8516.839.79	Tanzania	6.52	8.58	5.27	812	910	744	12.5	14.15	10.75
Mali 7.64 11.44 6.52 926 1443 597 11.75 14.25 7.86 Argentina 4.02 4.49 3.62 832 928 787 10.46 11.15 9.49 Bolivia 3.75 5.49 3.19 581 800 511 10.85 16.83 9.79	Ivory Coast	7.79	15.37	5.72	777	863	690	9.16	10.75	7.8
Argentina 4.02 4.49 3.62 832 928 787 10.46 11.15 9.49 Bolivia 3.75 5.49 3.19 581 800 511 10.85 16.83 9.79	Mali	7.64	11.44	6.52	926	1443	597	11.75	14.25	7.86
Bolivia 3.75 5.49 3.19 581 800 511 10.85 16.83 9.79	Argentina	4.02	4.49	3.62	832	928	787	10.46	11.15	9.49
	Bolivia	3.75	5.49	3.19	581	800	511	10.85	16.83	9.79
Brazil 4.28 5.78 3.78 797 1258 579 12.25 15.4 10.53	Brazil	4.28	5.78	3.78	797	1258	579	12.25	15.4	10.53

Table 2 (continued)

	Fe			K	K			Mn		
	Median	25th	75th	Median	25th	75th	Median	25th	75th	
Chile	4.43	5.55	3.02	1010	1860	908	12.6	23.35	9.99	
Paraguay	4.54	6.21	4.13	592	677	531	10.6	11.8	9.71	
Uruguay	4.32	4.54	4.08	793	1190	665	12	13.15	9	
China	4.5	5.22	3.84	670	859	599	12.65	14.53	10.63	
South Korea	5.53	7.32	4.74	1050	1370	908	16	21.78	13.38	
Bangladesh	7.9	11.72	6.18	1160	1488	1098	8.62	12.25	1.68	
Sri Lanka	5.69	7.44	4.6	1125	1378	978	10.8	14.98	9.32	
Indonesia	4.5	6.66	4.09	748	838	632	10.85	13.6	9.37	
Vietnam	3.74	4.12	3.41	560	690	493	9.17	10	8.14	
Italy	4.63	5.05	4.21	991	1160	870	11.8	13.93	10.08	
Spain	4.43	4.71	3.98	816	947	748	9.58	11.93	7.75	
Turkey	3.68	4.05	3.11	811	921	737	10.07	11.93	8.63	
	Мо			Р			Rb			
	Median	25th	75th	Median	25th	75th	Median	25th	75th	
Tanzania	0.536	0.621	0.379	842	932	791	2.07	5.53	1.101	
Ivory Coast	0.463	0.669	0.385	799	929	704	4.148	5.875	2.278	
Mali	0.61	0.784	0.398	850	1171	624	7.034	11.152	3.531	
Argentina	0.549	0.558	0.43	1014	1106	902	2.365	6.182	1.096	
Bolivia	0.737	0.917	0.597	681	734	614	1.085	1.707	0.743	
Brazil	0.595	0.714	0.493	1112	1702	850	7.011	12.133	4.753	
Chile	0.552	0.569	0.509	805	1784	744	9.52	21.794	7.886	
Paraguay	0.699	0.739	0.607	785	837	723	6.61	8.098	4.308	
Uruguay	0.459	0.565	0.402	703	815	679	7.677	9.767	4.853	
China	0.529	0.634	0.446	685	762	637	3.256	4.405	2.604	
South Korea	0.452	0.505	0.405	898	1204	800	2.881	3.991	1.966	
Bangladesh	0.595	0.814	0.51	969	1109	848	8.982	11.948	6.598	
Sri Lanka	0.579	0.75	0.441	1408	1880	1106	6.178	10.633	3.221	
Indonesia	0.484	0.573	0.411	794	963	682	3.293	5.157	2.279	
Vietnam	0.425	0.553	0.336	707	999	578	3.751	5.784	1.98	
Italy	0.782	0.988	0.625	1321	1474	1186	0.761	1.127	0.487	
Spain	0.351	0.4	0.315	1022	1098	915	0.723	1.527	0.461	
Turkey	0.519	0.623	0.458	842	916	772	0.818	1.222	0.597	
	S			Se	Se			Zn		
	Median	25th	75th	Median	25th	75th	Median	25th	75th	
Tanzania	861	980	794	0.0354	0.0602	0.0235	9.88	11.10	9.01	
Ivory Coast	837	892	774	0.0441	0.0653	0.0216	10.26	11.48	8.81	
Mali	731	810	696	0.016	0.0277	0.0103	10.78	11.51	6.88	
Argentina	799	834	794	0.0103	0.016	0.0103	8.22	9.06	7.53	
Bolivia	793	945	737	0.0214	0.0353	0.0103	11.28	13.46	10.28	
Brazil	786	842	725	0.0238	0.0359	0.0103	11.98	14.66	9.36	
Chile	680	742	644	0.0333	0.0356	0.0276	11.37	13.89	10.96	
Paraguav	784	816	752	0.0103	0.0103	0.0103	11.80	12.47	10.70	
Uruguav	778	855	751	0.0103	0.0179	0.0103	7.91	9.11	6.62	
China	880	942	829	0.0226	0.0354	0.0103	11.66	12.35	11.37	
South Korea	809	877	740	0.0103	0.0103	0.0103	9.52	11.22	8.81	
Bangladesh	1015	1093	944	0.0275	0.0357	0.0217	5.92	8.18	4.41	
			~ • •							

Table 2 (continued)

	S			Se	Se			Zn		
	Median	25th	75th	Median	25th	75th	Median	25th	75th	
Sri Lanka	712	788	664	0.0412	0.0651	0.0267	11.03	13.26	8.18	
Indonesia	911	1020	856	0.0103	0.0227	0.0103	10.45	11.41	9.23	
Vietnam	890	952	842	0.0234	0.037	0.0103	12.39	14.59	11.03	
Italy	839	888	777	0.0366	0.0429	0.0305	10.05	11.83	8.52	
Spain	862	905	810	0.0103	0.0103	0.0103	9.15	10.27	7.79	
Turkey	780	837	726	0.0271	0.0354	0.0103	10.19	11.10	8.88	



Fig. 2 Country medians expressed as a percentage relative to the mean of all countries for each element, plotted by continent

rice was high in DMA and low in rubidium, and Italy was relatively high in cadmium. Turkish rice was notably low, $\sim 50\%$, in selenium.

PCA and associated factor analysis for the entire data set are presented in Fig. 3. The PCA score means by country are given with the individual scores due to the high data density. The factor loadings analysis showed that copper, cadmium, molybdenum, rubidium and selenium were strongly associated together, and these element's factor loadings were diametrically opposed to less tightly associated calcium, chlorine, manganese, potassium phosphorus and sulphur, with similar strengths of loadings. iAs and zinc were also associated, but less strongly, with this latter cluster. Iron and DMA had factor loadings close to the origin, suggesting that there were not closely associated with any other elements. Element/species pairs that might be thought to be associated with other are diametrically opposed such as copper and zinc (elevated concentrations of both derived from the same pollutant sources); iAs and cadmium (again being derived in elevated concentrations in soil through pollutant



Fig. 3 Factor loading plot for the principal component analysis (PCA) overlain with PCA scores means by country

sources, such as atmospheric deposition of contamination caused by base and precious mining and smelting activities, fossil fuel burning etc.); and the physiological analogues sulphur and selenium. However, potassium and phosphorus factor loadings were similar in direction and strength, which may relate to the fact that these two elements are commonly fertilized together. The American countries, with the exception of Chile, were associated with the copper, cadmium, molybdenum, rubidium and selenium factor loadings, but the countries of other continents were dispersed around the plot, though the nearby countries of Mali and Ivory Coast differed considerably in cadmium content. Vietnam, in particular, has a mean PCA score to the right of the graph but near to the X-axis. This shows, again, that Vietnamese grains are generally nutrient deficient, as shown by plots of the country value of each element expressed as a percentage of the median of country medians given in Table 2 and percentages of medians in Fig. 3.

To validate/cross-reference the PCA factor loading observations for cadmium, log-transformed elemental concentrations underwent stepwise additions linear regression

Table 3 Stepwise regression analysis of log cadmium grain concentrations verses the log transformed other elements quantified

Model	R	R Square	Adjusted <i>R</i> square	SE of the estimate	Sign
A					
Se	.274 ^a	0.075	0.074	0.41024	< 0.0001
Se, Mo	.325 ^b	0.106	0.104	0.40364	< 0.0001
Se, Mo, DMA	.388°	0.151	0.148	0.39350	< 0.0001
Se, Mo, DMA, iAs	.454 ^d	0.206	0.203	0.38062	< 0.0001
Se, Mo, DMA, iAs, Cl	.477 ^e	0.228	0.224	0.37559	< 0.0001
Se, Mo, DMA, iAs, Cl, S	.493 ^f	0.243	0.239	0.37193	< 0.0001
Se, Mo, DMA, iAs, Cl, S, Cu	.506 ^g	0.256	0.251	0.36895	< 0.0001
Se, Mo, DMA, iAs, Cl, S, Cu, P	.516 ^h	0.266	0.260	0.36675	< 0.0001
Se, Mo, DMA, iAs, Cl, S, Cu, P, Zn	.521 ⁱ	0.272	0.265	0.36546	< 0.0001
Se, Mo, DMA, iAs, Cl, S, Cu, P, Zn, Rb	.526 ^j	0.277	0.270	0.36437	< 0.0001
	Beta		Т		Sign
B					
Constant			- 3.694		< 0.001
Se	0.163		5.507		< 0.001
Мо	0.141		4.536		< 0.001
DMA	- 0.564		- 13.289		< 0.001
iAs	0.453		10.724		< 0.001
Cl	- 0.203		- 6.876		< 0.001
S	0.122		4.138		< 0.001
Cu	0.117		3.895		< 0.001
Р	- 0.124		- 4.289		< 0.001
Zn	0.097		3.269		0.001
Rb	0.074		2.680		0.007

Section A shows the R^2 and the significance of each model, while B shows the slopes (Beta) and significance for the model containing all elements in the final model

with log cadmium concentration as the dependent variable (Table 3). Selenium was the greatest predictor of cadmium, followed by molybdenum, accounting for over 50% of the contribution to the adjusted R^2 . Log iAs in stepwise linear regression was highly correlated with log DMA with an adjusted R^2 of 0.556, but not with other elements. When log DMA was removed as a predictor, the next highest correlating parameter was log molybdenum with an adjusted R^2 of 0.029 (data not tabulated).

Figure 4 shows the correlation matrix for the log transformed concentration dataset to enable further comparisons of all elements/species against each other. Besides the strong positive correlation between iAs and DMA, there was also a very strong relationship between potassium and phosphorus (Spearman's R of 0.799). This strong association between potassium and phosphorus is also seen for the factor analysis (Fig. 3). Also notable from the Spearman's rank correlation is that chlorine is negatively correlated with a suite of elements/species including arsenic species, cadmium, copper, molybdenum, phosphorus and rubidium.

Discussion

Plant nutrition is dependent on soil availability and concentration, and plant physiological regulation as determined by genetics (Cobb et al. 2021; Norton et al. 2014). It is considered that most essential elements and ions are in homeostasis for plant tissues in general, and in grain specifically, as outside an individual ion/element's concentration range, the plant will either be in deficiency or toxicity (Bohnert et al. 2006). One essential element that does not appear under



Fig.4 Spearman's rank correlation matrix of log-transformed elements for rice grain concentrations. The scale to the right of the graph is the *R*-value for analysis

tight physiological control, with grain concentration being closely related to soil concentrations is selenium (Zhu et al. 2009). This is thought to be because selenium species are analogues of the much more abundant sulphur, and with sulphur ameliorating selenium species toxicity (Zhu et al. 2009). Non-essential elements/ions also enter grain as analogues of essential nutrients, such as arsenate, a phosphate analogue (Meharg 1993); arsenite, a silicic acid analogue (Meharg and Meharg 2015); rubidium, a potassium analogue (Oliferuk et al. 2017); and cadmium an analogue of a range of divalent cations (Nan et al. 2002). Thus, a key finding here is that the essential elements copper, molybdenum and selenium are tightly associated with non-essential cadmium and rubidium. Hypotheses regarding the relationship between cadmium with copper, molybdenum, rubidium and selenium are now considered.

Copper and selenium can be elevated in soils due to anthropogenic processes, such as mineral smelting and processing and coal burning, where selenium soil pollution actually supplements plants as it is deficient in most soils (Zhu et al. 2009). As noted, selenium can be very variable in plant tissues, while copper is under tight plant homeostasis due its essentiality in a range of cellular functions and due to its toxicity (Clemens 2001). Contrastingly to copper, a divalent metal ion that is also an environmental contaminant, divalent cadmium is also a widely dispersed pollutant that can reach concentrations in grain that cause human health concerns in a wide range of agricultural settings, yet is highly variable in grain (Hu et al. 2016; Nan et al. 2002; Shi et al. 2020). Rubidium differs yet again, being a monovalent ion, and is thought to be preferentially mobilized into plants under acidic soil conditions where soil available potassium is low (Drobner and Tyler 1998). Molybdenum chemistry in soils and plants is complex, with molybdate thought to be a sulphate analogue, and is assimilated by plants more readily at higher pHs due to reduced binding adsorption to amorphous oxides, while sulphur addition also decreased molybdenum assimilation (McGrath et al. 2010). In the context of the close assimilation of the group of elements found to cluster here (cadmium with copper, molybdenum, rubidium and selenium), cadmium is most studied (Hu et al. 2015, 2016; Shi et al. 2020). Cadmium is assimilated under more aerobic conditions of rice cultivation (Hu et al. 2015) and this may be a clue as to why other elements are associated with cadmium, i.e. it could be hypothesized that more aerobic conditions are needed to mobilize these elements in paddy soils effectively. This supposition remains to be tested.

Cadmium, in both soils and plants, is readily complexed by sulphur (Ernst et al. 2008). High grain cadmium is diametrically opposed to high grain sulphur for factor loading plots, and thus when sulphur is high in plants it can be postulated that translocation of cadmium to grain is low as cadmium complexation with sulphur groups of phytochelatins (PCs) are sequestered in the vacuole, retarding their translocation to the plant (Ernst et al. 2008). It is sulphide immobilization under reduced redox conditions that causes cadmium to have poor soil availability under flooded paddy conditions (de Livera et al. 2011; Rinklebe et al. 2016), again emphasizing the intimate link between cadmium and sulphur highlighted in this current study. This sulphur association may also explain grain copper concentrations, with copper like cadmium having a high affinity for sulphur (Ernst et al. 2008; Hartley-Whitaker et al. 2001). Notably, selenium is a sulphur analogue (Zhu et al. 2009). For selenium, the ratio of selenium to sulphur increases, maybe as the plant tries to mine plant sulphur, inadvertently assimilating more selenium, i.e. that selenium may be increased in grain under sulphur deficiency. The same could be argued for rubidium and potassium, i.e. that rubidium is enhanced in grain when potassium is deficient, as rubidium is orthogonal to potassium with respect to its grain PCA factor loading plot. Molybdenum is assimilated through plant roots as molybdate (Baxter et al. 2008), an anion that is thought to interact strongly with sulphate (McGrath et al. 2010), i.e. it is postulated that molybdate is a sulphate analogue. Molybdenum is assimilated into grain when sulphur is low, according to PCA analysis, suggesting that under plant sulphur deficiency conditions that molybdenum is more readily assimilated and translocated. Interestingly, Williams et al. (2009) found that grain zinc and selenium was negatively correlated with grain arsenic for field sites across Bangladesh. Thus elemental toxicity, arsenic in this case, is impacting grain nutritional composition. For the current study, Bangladesh had the highest grain arsenic of this survey and the lowest zinc, supporting this finding, but the selenium grain concentration was median.

The global distribution of arsenic species in polished grain has been previously studied for this data-set (Carey et al. 2020). What is new here is the understanding that both iAs and DMA are not intimately linked to other elements with respect to co-location in grain. Arsenic species mobilization is strongly driven by soil redox, linked to the dissolution of iron plaque and to the microbial methylation of iAs (Meharg and Zhao 2012). It is notable that grain iron is also not strongly linked to other elements in this current investigation. It appears that other factors, such as potential pollution impact and weathering of soils, have a greater influence on grain arsenic species than co-element nutrition of plant or soils, given that arsenic species can also act as phosphate and silicic acid analogues in both soils and plants (Meharg and Zhao 2012). For example, it is the low pollutant impacted and heavy weathered soils of African and Asian southern hemispheres that are low in grain arsenic species in this current study.

With respect to genetic variation in grain elemental content, Norton et al. (2010) investigating 17 elements in grain through ICP-MS quantification found for an indica-japonica cross that there were 41 QTLs. QTLs for iron, molybdenum, selenium and zinc, in particular, were suggested to be suitably strong to be targets for improving grain concentrations through marker assisted selection. Huang et al. (2015) reported genetic variation in cadmium, iron, lead, selenium, and zinc, for wholegrain rice using Chinese association mapping accessions. Genome-wide association mapping found a strong genotype*environment interaction for loci associated with elements in whole grain rice grown at four locations across the globe, but variation was found for arsenic, copper, molybdenum and zinc (Norton et al. 2014), indicating weak genetic links between the elements. Genetic variation was found to be a large determining factor for grain arsenic concentrations across four field sites globally, Bangladesh, China, India and N. America (Norton et al. 2010). Association mapping has identified root and shoot transporters for cadmium and molybdenum, but these are on different loci and are for different putative transporters (Cobb et al. 2021). Thus, rice genetics, particularly between *japonica* and *indica* groups (Huang et al. 2015; Norton et al. 2010), could be an important source of variation in rice's global grain supply chain, but this needs to be systematically investigated in order to validate.

The data sets reported here enable rice from different regions to be grouped as deficient in particular nutrients. The key country with respect to globally mineral nutrient deficiency in the grain was Vietnam as its grain was particularly deficient in a suite of macro- and micro-nutrients, while also being relatively elevated in cadmium. These deficiencies in grain elemental nutrients suggest that Vietnamese soils may be generally deficient in nutrients. This may be due to a range of factors such as over cropping as many Vietnamese paddies have multiple harvests per year (Ba et al. 2016). Soil acidification is widespread in S.E. Asia due to over use of mineral nitrogen fertilizers (Xie et al. 2019), and acidification will lead to issues with nutrient leaching and availability. Straw biomass is widely burnt in Vietnam leading to poor organic waste-stream recycling, including animal manures produced through straw consumption (Hung et al. 2019; Watanabe et al. 2019). The health consequences for the Vietnamese population for having rice low in nutrient density but high in toxicants needs assessing, given that it is a subsistence rice economy with high rates of per capital consumption (Hung et al. 2019; Watanabe et al. 2017). Another notable health concern is Bangladesh that has high iAs, high cadmium and low zinc, given that zinc is vital in enzymatic roles that are key to the general health of the population (Williams et al. 2009). The low selenium content of rice is of concern for a range of South American countries, and for Spain, South Korea and Indonesia, because selenium

deficiency is implicated in a wide range of disease outcomes at a population level (Zhu et al. 2009).

The research findings of this current study provide the basis to start to redress dietary deficiencies in populations that have rice as a subsistence diet. This could be through changing agronomic practices or ensuring key nutrients reach the diet through other food groups. The underlying rice grain nutrient deficiencies reported here require further epidemiological studies to investigate human consequences, and agronomic investigations with respect to how to mitigate against deficiencies through soil management and rice breeding.

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Data availability Will be issued on reasonable request.

Declarations

Conflict of interest None.

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