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Arsenic Limits Trace Mineral Nutrition (Selenium, Zinc, and Nickel) in Bangladesh Rice Grain

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A reconnaissance of 23 paddy fields, from three Bangladesh districts, encompassing a total of 230 soil and rice plant samples was conducted to identify the extent to which trace element characteristics in soils and irrigation waters are reflected by the harvested rice crop. Field sites were located on two soil physiographic units with distinctly different As soil baseline and groundwater concentrations. For arsenic (As), both straw and grain trends closely fitted patterns observed for the soils and water. Grain concentration characteristics for selenium (Se), zinc (Zn), and nickel (Ni), however, were markedly different. Regressions of shoot and grain As against grain Se, Zn, and Ni were highly significant ($P < 0.001$), exhibiting a pronounced decline in grain trace-nutrient quality with increasing As content. To validate this further, a pot experiment cultivar screening trial, involving commonly cultivated high yielding variety (HYV) rice grown alongside two U.S. rice varieties characterized as being As tolerant and susceptible, was conducted on an As-amended uniform soil. Findings from the trial confirmed that As perturbed grain metal(loid) balances, resulting in severe yield reductions in addition to constraining the levels of Se, Zn, and Ni in the grain.

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Introduction

Human exposure to inorganic arsenic (As_i), a class 1, nonthreshold carcinogen, for nonindustrially exposed cohorts, is primarily from food and water (*1*−*4*). Attributed to high arsenic (As) mobility in flooded paddy soils, As_i levels in rice, generally, exceed those found in other common cereals by an order of magnitude (*2, 5*). This makes those on rice subsistence diets particular prone to high As_i intakes (*1, 2*). The problem is compounded in regions, such as the Bengal Delta, where farmers are reliant on As elevated waters to irrigate their crops. Modeled excess cancer risks from As exposure from rice alone for Bangladeshi consumers on typical diets, are 22-fold higher than upper risk goals mandated by the U.S. Environmental Protection Agency (EPA) (*2*).

When coexisting with malnutrition and micrometerutrient deficiencies are present, the onset of arsenicosis or other As-related illnesses may be aggravated further (*6*−*9*). Selenium (Se) and zinc (Zn) are both micrometerutrients generally found lacking in polished rice, posing a serious problem for those reliant on rice as their dietary mainstay (*10, 11*). Indeed 15% of the world's population are estimated to be Se-deficient (*12*), with there being considerable overlap with those also having to contend with high As exposures (*13*). Being a vital component of glutathione peroxidase, Se is a requirement for antioxidant system function (*12*). It is, however, its specific antagonistic relationship with As, that makes enhancing dietary intakes of this element so attractive (*13*). Glutathione dependent formation of the seleno-bis(S-glutathionyl) arsinium ion in erythrocytes, facilitates the transfer of As from blood to bile, and subsequent excretion (*13, 14*), with increased Se concentrations in urine having been associated with greater rates of As loss (*15*). Findings from a case-cohort study in the groundwater elevated district of Narayanganj, Bangladesh highlights this further, with the risk of developing skin lesions, an early manifestation of As poisoning, being reduced by up to 50% in those with higher blood Se concentrations (*7*). In China, comparable scenarios exist; with Se deficiency being significantly correlated with cutaneous abnormalities in As exposed subpopulations (*8*).

Zn is the principal micrometerutrient constraining crop production (*16*), yet it is also a prevalent human nutrient deficiency affecting up to 33% of the global populace (*17*). The associated health impacts of Zn insufficiency range from stunting, infertility, reduced immunocompetence, and neurobehavioral impairment, while a continued dietary supply must be ensured as storage rates within the body are transient (*18*). The supportive ability of Zn in human As-disease remission is still unclear, although there are a number of studies that suggest it to be a putative therapeutic (*19, 20*). Inadequate Zn, along with low intakes of niacin, Fe and dietary protein has also been linked to a reduction in in vivo As methylation capacity, a risk factor associated with As exposure (*9*). Nickel deficiency is less common than for Se and Zn, however Ni remains an essential element for a number of mammalian species. In deprivation scenarios it has been implicated as a cause of stunting, in addition to impairing the absorption of other trace nutrients such as Fe, Zn, and copper (*21*).

In Bangladesh not only does rice contribute up to approximately 80% of energy intake (*22*), it can be the principal source of protein and micrometerutrients (*23*). For example, in a study of 156 households in Bangladesh, rice supplied 66% of the dietary Zn for children aged between 2 and 10 years (*24*). Rice, however, exhibits a particular

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vulnerability to As, with elevated exposures disrupting rice carbohydrate metabolism, impairing photosynthetic function, and altering nutrient balances (*25*−*29*). Yet its impact on rice grain quality, in terms of essential trace elements such as Se and Zn requires further clarification. Identifying or characterizing grain nutrient trends, within Bangladesh, is stifled by the country's highly diverse and heterogeneous soil and groundwater irrigation systems that reflect the major shifts in river system flows and tectonic movements in the area. Furthermore, experimental findings must also consider smaller scale variation in addition to differences in hydrology and regional soils. Even within villages or individual paddy fields, soil and water properties can range considerably, before human-use differences, field leveling and cultivation practices are taken into account (*30*).

To test whether As can impact the general mineral nutrition of rice, a range of soils and concomitant rice plants (shoot and grain) were collected in both As groundwater impacted and nonimpacted regions of Bangladesh. To validate observations from the field, and to minimize variability attributed to differences in soils and cultivation practice, a pot experiment trial was established using a uniform soil amended with As and rice cultivars commonly grown in Bangladesh.

Materials and Methods

Field Rice. As detailed in Lu et al. (*31*), 23 rice paddy fields were selected for study; four in Faridpur, a district with elevated As in tubewell accessed groundwater; nine in Gazipur with low groundwater arsenic; and 10 in Jessore with intermediate water contamination (see the Supporting Information (SI)). From each field, 10 rice plants were obtained to account for intrafield variation in soil/water characteristics. In total 230 paired soil/plant samples were obtained.

Lying on the Holocene sediments of the Ganges alluvium plain, the soils within the district of Faridpur and Jessore are naturally rich in weathered material, especially minerals such a biotite and plagioclase. Originating principally from the Himalayas, this region also bears a signature associated with the peninsular Indian shield and from eroding terrace soils (*32*): typical background levels for As are between 5 and 10 μg g topsoil $^{-1}$ (*31, 33, 34*). Gazipur soils in contrast are older, highly weathered and constitute part of the Madhupur tract; a terrace formed prior to Bangladesh's inclusion into the Himalayan drainage system (*32*). Commonly this terrace contains only around 1−2 μg As g top soil^{-1} (*31*). With grain export from rice shoots found to plateau when soil concentrations exceed 5 μg As g^{-1} in Bangladesh paddy soils, it is efficient shoot assimilation and subsequent transfer to the grain at low shoot concentrations that is a major source of As to rice consuming populations, not just the highly enriched grains resulting from the irrigation of rice with As elevated waters that are of concern (*5, 31, 35*). With this in mind, sites were principally selected based on whether paddies resided on either the Pleistocene terrace or Holocene tract.

Samples were harvested upon grain maturity in May 2006 (between 120 and 140 days after seed sowing), with planting taking place in the previous winter, which is typical of dry season cultivation practices. The dominant cultivar planted was a high yielding variety called, BRRIdhan 29, although in Jessore district BRRIdhan 28 was more prevalent. These varieties were specifically selected because they are widely cultivated throughout Bangladesh.

Pot Experiment Trials. Rice cultivars utilized in this study included BR's 1−3, 6, 8, 9, 12, and 14−19 in addition to the BRRIdhan's 28, 29, 35, 36, and 45, and represent the dominant HYV's planted during the boro season. In addition, two rice varieties characterized as As tolerant (Nortai) and susceptible (Dawn) were also included as a comparison to the Bangladesh rice (*27*). Soils were treated with 10 or 20 mg As kg^{-1} (on a soil basis) sodium arsenate and a control nonspiked soil was also maintained. Further information pertaining to the pot experiment setup can be found in the SI.

Plant Sample Preparation. This was in accordance with Adomako et al. (*35*). Raw rice samples were washed with ultrapure water (18.2 Ω) and then all grains (field and pot) were oven-dried (70 °C) until a constant weight was reached. All husks were removed and the grains powdered mechanically. Standard digestion and analysis methodologies were adapted from Williams et al. (*5*). Sample digestion batches were accompanied by analytical blanks, certified reference material (Rice flour NIST 1568a or GBW 10010) and blank spikes. For samples found to be below the limit of detection (LOD) an arbitrary value of 50% LOD was used. All data presented in this study are expressed on a dry weight basis.

Soil Sample Preparation. Soils were processed as described in Lu et al. (*31*) and Adomako et al. (*35*), further details are provided in the SI. For total digestion, 0.100 g of soil was weighed into 50 mL polypropylene digest tubes and 2 mL of concentrated nitric acid added and left to imbibe overnight. Soil NCS ZC 73007 certified reference material (CRM), an agricultural farming soil was also included, with one CRM in each digest batch of forty. Samples were then heated in a microwave accelerated reaction system (CEM, Mars 5, CEM Corp., Matthews, NC). The temperature was raised to 55 °C (held 10 min) then 75 °C (held 10 min), finally to 95 °C for 30 min and allowed to cool to room temperature. Subsequently, 500 μL of 100 μg L^{-1} indium solution was added as internal standard. Samples were then diluted to a mass of 50.000 g with ultrapure deionized water (Mill-Q 18.2 MΩ).

Total Element Detection. 7500 series ICP-MS (Agilent Technologies, Toyoko, Japan) was used to quantify elemental composition of soils and rice shoot and grains. Elements of focus were Ti (m/z 49), Mn (m/z 55), Ni (m/z 60), Zn (m/z 64, 66, 67, 68), As (m/z 75), Se (m/z 77, 78, 82) and In (m/z 115). The following m/z 77, 78, 82 were measured in order to identify polyatomic $Ar^{40}Cl^{35}$ interferences on m/z 75. Corrections for interference from $Ar^{40}Cl^{35}$ were not found to be necessary. Samples were randomized prior to analysis. Standards were run after every set of 20 samples. CRM recoveries were in good agreement with certified values. Recoveries for rice flour CRMs were As, 122 ± 25%; Se 104 ± 27%, Zn 122 ± 32%. The combined blank spike recoveries for As, Se, Zn, and Ni were 94 ± 32%. Combined recoveries for soil digestion were 98 ± 32%.

Results

Field Survey. *Soils.* Holocene tract soils contained more As than the Pleistocene terraces ($P < 0.001^{\text{Mann−Whitney}}$), yet there were still significant differences between each of the individual district soils ($P < 0.001^{\text{ANOVA}}$). In Gazipur the mean As content was 0.99 ± 0.29 μg g^{-1} ($n = 90$), while Faridpur levels were approximately an order of magnitude higher at 9.76 ± 2.36 μg g^{-1} ($n = 40$). Marginally lower As concentrations were observed in Jessore, with sites averaging 7.37 ± 4.9 μg As g^{-1}, (n = 100) (Table 1).

There was a clear demarcation in the trace mineral composition of Pleistocene terrace soils compared with those from the Holocene tract, with significant variation in Se ($P = 0.005^{\text{Mann−Whitney}}$), Zn ($P < 0.001^{\text{Mann−Whitney}}$) and Ni ($P < 0.001^{\text{Mann−Whitney}}$). All districts exhibited distinctive Zn and Ni concentrations ($P < 0.001^{\text{ANOVA}}$), although, only Gazipur and Faridpur were found to vary significantly with respect to Se ($P < 0.001^{\text{Mann−Whitney}}$). Average levels of Se in Gazipur soils were 0.37 ± 0.27 μg g^{-1}, while mean levels for Jessore and Faridpur were 0.49 ± 0.26 and 0.45 ± 0.27 μg g^{-1}, respectively (Table 1). Global soil Se concentrations typically range between 0.01 and 2.00 μg g^{-1} with a world average of 0.40 μg g^{-1} (*36*). However, common levels for rice paddies

TABLE 1. Field Trial. Summary of As, Se, Ni, and Zn in Soils and Rice from Gazipur, Jessore, and Faridpur. Mean Averages Are Presented, Parentheses Denotes the Standard Error

		As		Se		Ni		Zn	
		(mg kg^{-1})		(mg kg^{-1})		(mg kg^{-1})		(mg kg^{-1}	
GAZIPUR (n = 90)	grain	0.26	(0.06)	0.12	(0.08)	0.68	(0.34)	16.85	(2.04)
	shoot	0.36	(0.22)	0.11	(0.06)	0.61	(0.26)	45.54	(14.81)
	soil	0.99	(0.29)	0.37	(0.27)	7.16	(1.68)	17.49	(3.94)
>JESSORE (n = 100)	grain	0.35	(0.09)	0.05	(0.03)	0.40	(0.37)	13.01	(2.57)
	shoot	1.57	(1.72)	0.06	(0.04)	0.59	(0.38)	21.09	(9.03)
	soil	7.37	(4.90)	0.49	(0.26)	27.45	(6.66)	73.63	(17.30)
FARIDPUR (n = 40)	grain	0.42	(0.12)	0.06	(0.03)	0.26	(0.08)	14.94	(2.07)
	shoot	2.60	(1.83)	0.08	(0.04)	0.60	(0.43)	24.35	(9.04)
	soil	9.76	(2.36)	0.45	(0.27)	40.70	(2.40)	96.92	(24.09)

and rhizospheres are far less well-defined, with Se tending to accumulate in waterlogged as opposed to well drained soils (*36*). Ahson et al. (*37*) tested floodplain agricultural soils from Faridpur and found them to range from 0.57 to 1.37 μg g^{-1}, which is comparable with this study.

For most soils, the critical Zn deficiency threshold is ~10 μg g^{-1}, yet the demand for Zn in rice paddy soils can be greater as bioaccessible pools are constrained under reducing conditions and high bicarbonate concentrations (*17*). Arable soils generally range from 10 to 300 μg Zn g^{-1}, with a baseline of around 60 μg Zn g^{-1} (*17*); in the Bengal delta, levels of between 19 and 92 μg Zn g^{-1} are commonplace (*38*). In this study, soils from Jessore and Faridpur averaged 74 $\pm$ 17 and 97 $\pm$ 24 μg Zn g^{-1}, respectively (Table 1). In contrast, though were the samples from Gazipur, recording a mean of 17 $\pm$ 4 μg g^{-1}, with 16% found to contain 12 μg Zn g^{-1} or less (Table 1). Half the world's rice paddies are potentially lacking in Zn, with Zn deficient soils amounting for ~70% of the total arable land in some countries, such as is the case in Pakistan. In Bangladesh the level is ~23% or equivalent to 2 million hectares (*17*).

Bangladesh topsoils typically vary from 8 to 92 μg Ni g^{-1} (*38*). Ahson et al. (*37*), reported mean Ni levels in Faridpur paddy soils to be 48.9 μg Zn g^{-1}, which is in good agreement with the average for Faridpur found in this study of 40.7 $\pm$ 2.4 μg Ni g^{-1}. Jessore levels, 27.45 $\pm$ 2.4 μg Ni g^{-1} (Table 1), compare favorably with sites at Tahirpur, Nijhuri, and Tippera, which lie to the north of Jessore across the river Padma (*38*). Paddies from Gazipur were Ni deplete, and nearly 6-fold lower than the global average of ~40 μg Ni g^{-1} (*39*), concurring with previous measurements from Chandra town (9 μg Ni g^{-1}), which is also located within the Madhupur tract (*38*).

Shoot. Similar to the soils, shoot As concentrations from the Holocene tract and Pleistocene terrace differed significantly ($P < 0.001$ $^{t\ \mathrm{test}}$), furthermore district baselines were also clearly defined ($P < 0.001$ $^{\mathrm{ANOVA}}$). Mean shoot As concentrations were the lowest in Gazipur (0.36 $\pm$ 1.7 μg As g^{-1}; Table 1), Faridpur averages were the highest (2.60 $\pm$ 1.83 μg As g^{-1}), and the most elevated sample originated from Jessore, which mirrors the soils data well.

Trace-nutrient concentrations in rice shoot were in contradiction to trends found in soils. Far from reflecting the limited levels of Se, Zn, and Ni in paddies from Gazipur, rice shoot concentrations surpassed those of both Jessore and Faridpur districts where total soil levels indicate replete conditions (Table 1). The Se and Zn content in shoots from Gazipur were around 2-fold higher than the levels measured in Jessore plants, with all districts differing significantly from each other ($P < 0.001^{\mathrm{ANOVA}}$). Variation in shoot Ni concentrations between the 3 districts was only marginal ($P = 0.196$ $^{\mathrm{ANOVA}}$). This follows a very different pattern from that observed for the soils, which revealed soil Ni to have the greatest relative difference between districts compared to any other elements tested (Table 1).

Grain. Faridpur rice grains were the most elevated in As, with a reported mean of 0.42 $\pm$ 0.12 μg As g^{-1}, and ~20% of the samples found to contain more than 0.50 μg As g^{-1}. Although milling reduces the As content in Bangladesh wholegrain by ~20% (*40*), polished rice would still contain elevated levels of As, of which the predominant form would be As_i (*27*). The average level of As in Jessore rice was 0.35 $\pm$ 0.09 μg g^{-1}, which is still appreciably high (*2*), whereas the mean for Gazipur rice was 0.26 $\pm$ 0.06 μg As g^{-1}; although 23% of the samples still exceeded 0.30 μg As g^{-1}. Based simply on a conversion from wholegrain to polished rice, and assuming the main form of As is inorganic (*27*), around 94% of the samples analyzed could potentially exceed Chinese maximum contaminant levels for a rice based diet (*3, 41*).

Average levels of Se in the grains and shoots were analogous and followed similar trends, with Gazipur rice containing more than twice that of grains from Jessore and Faridpur (Table 1). Biplots of Se shoot concentrations against grain revealed a robust 1:1 transfer relationship (SI Figure S1). Compared with calculated global baselines for Se in polished rice, and accounting for a reduction in Se associated with milling, the rice grains from Jessore and Faridpur would fall below the world baseline; an average concentration that still may not be sufficient to provide the recommended daily allowance of Se, especially on a diet principally composed of rice and vegetables (*11*). When grain Se was plotted against both shoot and grain As levels a number of highly significant relationships were apparent (Figure 1), with there being a clear association between increasing plant tissue As and a concurrent drop in grain Se (Figure 1). Grain Se concentrations fell by ~0.24 μg g^{-1} over a range of As shoot levels that spanned ~12 μg g^{-1}. To the authors' knowledge this is the first instance that this has been documented.

Despite considerable concentration differences in shoot Zn between districts, less variation was observed between their associated grains. The Gazipur mean was 17.49 $\pm$ 0.06 μg As g^{-1}, whereas Jessore and Faridpur averaged 13.01 $\pm$ 2.57 and 14.94 $\pm$ 2.07 μg As g^{-1}, respectively (Table 1). Far from being abundant in Zn, levels in wholegrains from Jessore and Faridpur, fall below country baselines of 16 μg Zn g^{-1} for white rice (*42*), even before losses associated with polishing are accounted for (*43*). Although less well-defined than for Se, grain Zn concentrations appear perturbed as both shoot and grain As rose, as illustrated in Figure 1.

Average levels of Ni in Gazipur rice (0.68 $\pm$ 0.34 μg g^{-1}) were 2.6-fold higher than observed for Faridpur (0.26 $\pm$ 0.08 μg g^{-1}), which was the largest relative difference seen for all the elements surveyed, this is despite the similarity in shoot Ni concentrations from all sites. Correlations of shoot As

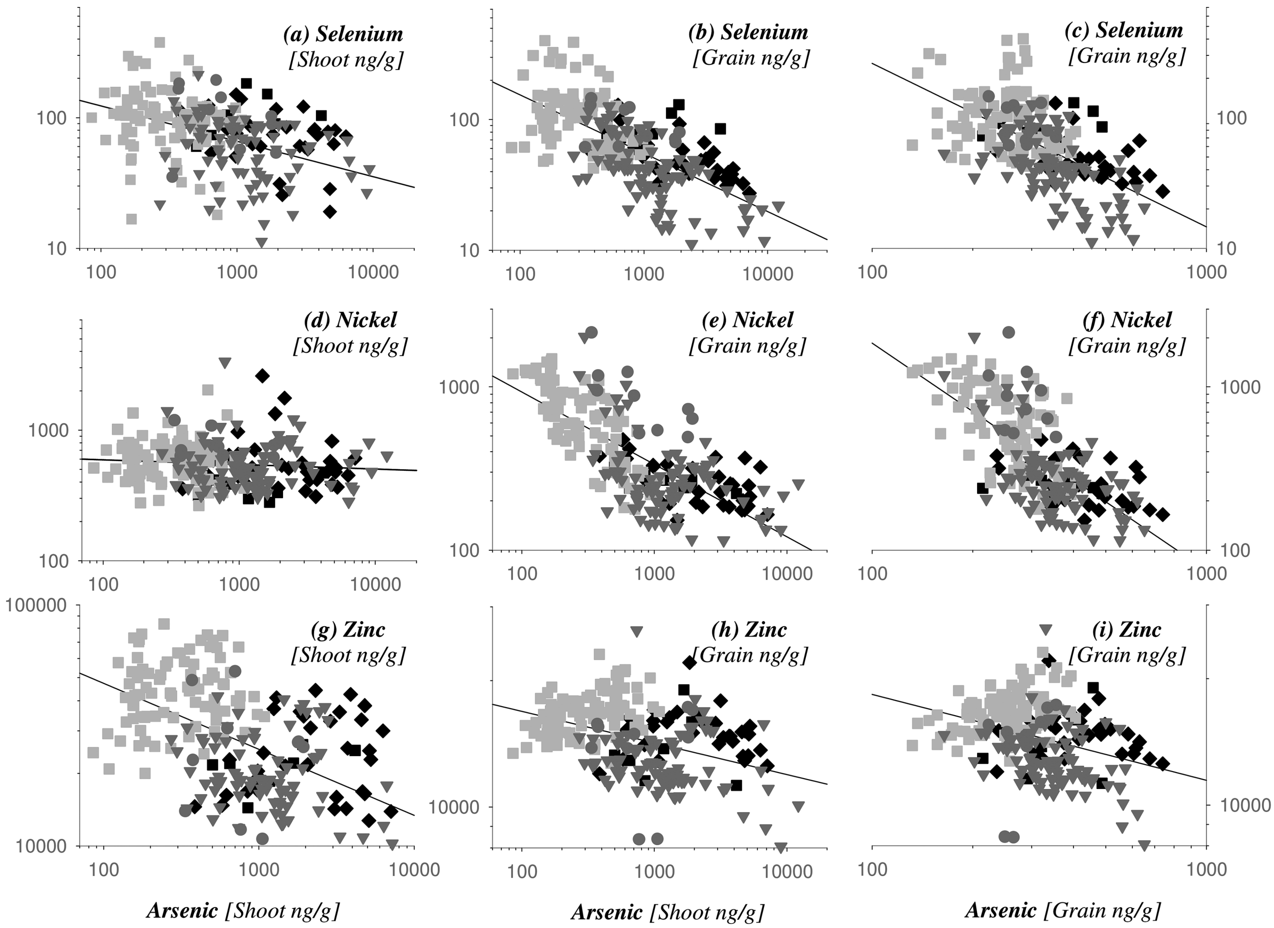

FIGURE 1. Biplots of shoot and grain As concentration against grain As, Se, Zn and Ni. All correlations, except for (d) shoot As vs shoot Ni, were highly significant $p < 0.000$. (a) $r^2 = 0.15$. (b) $r^2 = 0.46$. (c) $r^2 = 0.16$. (d) $r^2 = 0.74$. (e) $r^2 = 0.52$. (f) $r^2 = 0.48$. (g) $r^2 = 0.30$. (h) $r^2 = 0.16$. (h) $r^2 = 0.11$. ■ =GAZIPUR, BR29 ($n = 90$); ◆ = FARIDPUR, BR29 ($n = 40$); ● = JESSORE BR29 ($n = 10$); ▼ = JESSORE BR28 ($n = 90$).

against shoot Ni were notable as no relationship was detected, which contrasts with that of Se and Zn (Figure 1). Grain Ni variation is likely impacted by in planta physiological differences, as the issue cannot be one of bioavailability, and genotypic variation was controlled to a large extent. Biplots of shoot and grain As against grain Ni were highly significant ($P < 0.001$) with grain Ni concentrations in rice varying by ~1 $\mu g\ g^{-1}$ across the span of shoot As levels (Figure 1). For Se, Zn, and Ni, correlations of shoot As against grain micrometerutrient content were the strongest. The reason why grain to grain relationships are not more clearly defined could be because suppression of shoot to grain As transfer at higher shoot As concentrations is likely to obscure trends somewhat, if not matched by similar mechanisms for Se, Zn, or Ni transfer (*5*).

Pot Experiment. Applications of As, significantly impacted rice growth (Figure 2, SI Tables S4 and S7). Rice yields, especially, were dramatically impaired upon amendment of soils with As. The average grain weights derived from all the cultivars decreased 33 and 58% respectively, compared to the control, with each successive As dose (SI Table S4). Significant differences in aerial biomass, filled grain panicles and tiller number were noted between Bangladesh cultivars ($P < 0.001^{GLM}$), in addition to cultivar x arsenic interactions ($P < 0.001^{GLM}$). Grain reductions were highly pronounced in the As-sensitive cultivar Dawn, where average yields fell by 68 and 81% over the two As treatments, respectively. In comparison the BRRIdhan rices 28 and 29 were more resilient deceasing by only ~25% and between ~40 and 55%. Other growth parameters, including 1000-grain weight, number of unfilled grains, panicle length and plant height remained relatively unchanged (Figure 2).

Rice grains responded mimetically to the augmentation of soil As, with an average increase in grain content of 139 and 235% respectively, for all cultivars, in both the 10 and 20 $\mu g\ g^{-1}$ spiked soils (Figure 2 and SI Table S4). Cultivar, soil As amendment and the interaction between the two, were significant ($P < 0.001^{GLM}$). Grains were found to be As elevated in all but the control soil, with seven cultivars accumulating more than 1.00 μg As g^{-1} in the grain (SI Table S6). Despite the impact of As on grain yield the As content of Dawn was within the range found for the rest of the Bangladesh rice (SI Table S6). BRRIdhan 29 closely matched the average of all the rice (Figure 2). Although grains were more elevated than observed in the field, it is common practice to dry paddies during grain maturation, resulting in more aerobic conditions and substantial reductions in grain As content (*44*). In this study, pots remained inundated/flooded until grain maturity to enable sufficient As uptake to observe the response in trace-nutrients.

Amending the experimental soils with As impacted grain trace element nutrition greatly (Figure 2). Levels of Se, Ni, Zn, and Mn all significantly declined ($P < 0.001^{GLM}$) as grain As levels rose. For Se, Zn, and Mn, the 10 μg As g^{-1} spikes invoked a ~20% drop in average grain content, whereas for Ni there was a change of ~40%. Further As enhancement caused Se, Ni and Mn levels to fall to ~30% of their control, and sent Ni concentrations plummeting to 64% (SI Table S4). Considering the already pronounced decrease in grain biomass, any bolstering of element levels due to there being

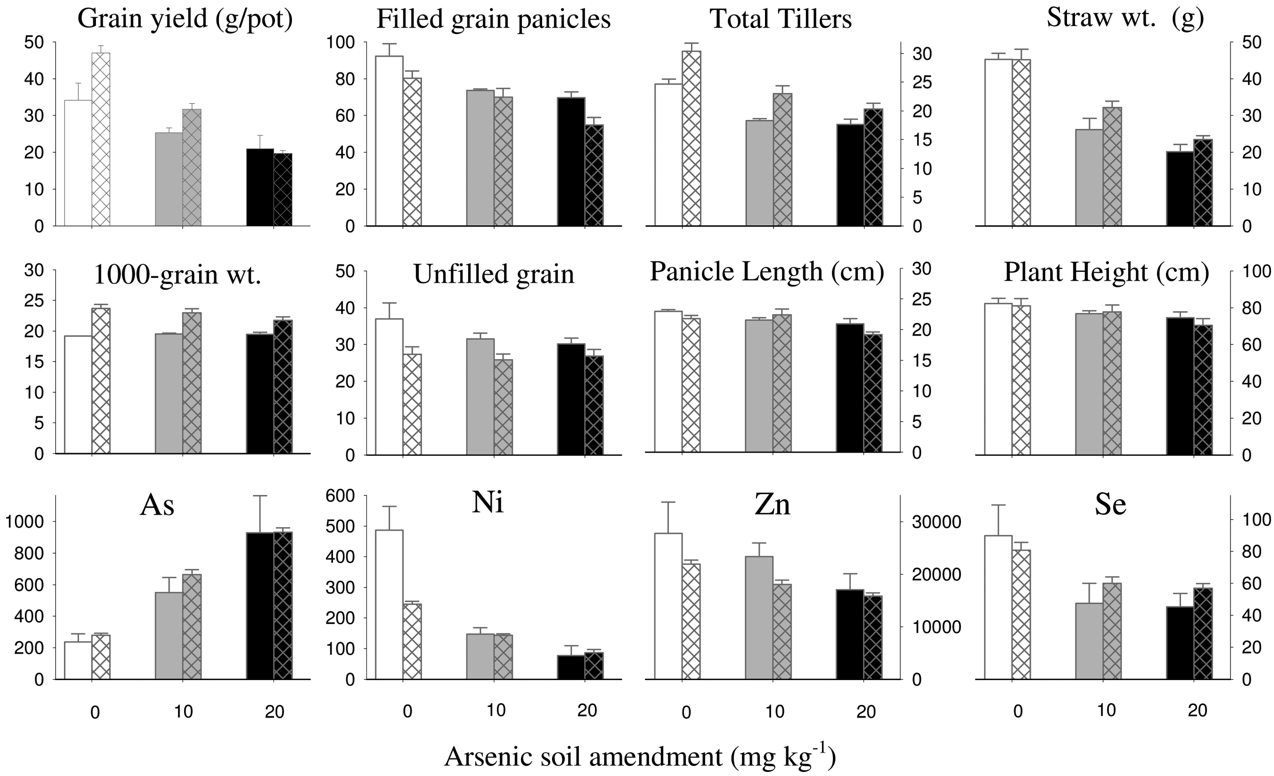

FIGURE 2. ***Pot Experiment Trials*****. Impacts of arsenic amendments on grain element composition and plant growth. Mean + s.e. Greyscale solid bars = BRRI dhan 29. Cross-hatched bars = Average from all cultivars. Grain As, Ni, Zn, and Se concentrations are in ng g^{-1}.**

less grain per plant did little to offset As induced physiological changes in trace element translocation.

Genotype was an important variable in determining trace-mineral nutrient content of rice upon As exposure ($P < 0.001^{GLM}$, see SI Table S8), with there being significant arsenic x cultivar interactions for grain Ni ($P = 0.007^{GLM}$) and Mn ($P < 0.001^{GLM}$), but not for Se ($P = 0.775^{GLM}$) or Zn ($P = 0.472^{GLM}$). BRRIdhan 29, followed the trends found for the other cultivars, displaying marginally greater resilience to Zn accumulation when exposed to As and less to Se (Figure 2).

Discussion

Findings from this study show a significant decline in essential trace elements in rice with increased in planta As concentrations. These results have perhaps the greatest implications for infants consuming nutrient jejune rice, concomitantly elevated in As. Rice, being the principal complementary food during weaning; can play a greater role in the diets of Bangladeshi infants in comparison to other countries. In the Bengal Delta rates of exclusive breastfeeding in early life fail to exceed 13%, with rice based porridges accounting for much of the deficit (*45*). If maternal diets are also Se and Zn constrained, even supplementation with milk may still result in a nutrient shortfall. To compound the problem, the extent of As damage in early development is difficult to discern/diagnose with health consequences often only manifesting in later years (*6*) or acting indirectly to compromise immune responses predisposing individuals to a myriad of health concerns including respiratory infections such as influenza (*46*). Worryingly, evidence of faltering arsenic methylation pathways, an indication of increased bladder cancer risk, are starting to be observed in Bangladeshi infants less than one year old; a state attributed in part to increases in dietary As exposure (*47*).

Understanding element specific impacts on metal(loid) uptake, assimilation and redistribution within rice presents enormous challenges. Take for example the process of grain filling, over 269 genes may play a functional role, but how and at what concentration As induces phenotypic changes is not well-defined (*48*). The situation is further complicated by the interconversion of metal(loid) species and their species specific uptake, translocation and interaction characteristics (*49*). What is apparent, however, is that As has a negative influence on plant metabolism at much lower concentrations than can be detected by comparing general growth features alone (*50*). The implications are, therefore, that even at geogenic soil baseline concentrations in Bangladesh, there is sufficient uptake of As by rice to stifle grain nutrient balances. Tackling, human Se and Zn micrometerutrient deficiencies by considering the role As plays not just in impacting directly on health when ingested via the daily rice meal, but on its impacts on rice micrometerutrient content in the grain, is a fresh way to approach an established and entrenched problem.

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Supporting Information Available

Pot experiment setup, yields, grain and irrigation water metal(loid) concentrations, further data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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