Occurrence and Partitioning of Cadmium, Arsenic and Lead in Mine Impacted Paddy Rice: Hunan, China

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Paddy rice has been likened to *nictiana* sp in its ability to scavenge cadmium (Cd) from soil, whereas arsenic (As) accumulation is commonly an order of magnitude higher than in other cereal crops. In areas such as those found in parts of Hunan province in south central China, base-metal mining activities and rice farming coexist. Therefore there is a considerable likelihood that lead (Pb), in addition to Cd and As, will accumulate in rice grown in parts of this region above levels suitable for human consumption. To test this hypothesis, a widespread provincial survey of rice from mine spoilt paddies ($n = 100$), in addition to a follow-up market grain survey ($n = 122$) conducted in mine impacted areas was undertaken to determine the safety of local rice supply networks. Furthermore, a specific Cd, As, and Pb biogeochemical survey of paddy soil and rice was conducted within southern China, targeting sites impacted by mining of varying intensities to calibrate rice metal(loid) transfer models and transfer factors that can be used to predict tissue loading. Results revealed a number of highly significant correlations between shoot, husk, bran, and endosperm rice tissue fractions and that rice from mining areas was enriched in Cd, As, and Pb. Sixty-five, 50, and 34% of all the mine-impacted field rice was predicted to fail national food standards for Cd, As, and Pb, respectively. Although, not as elevated as the grains from the mine-impacted field survey, it was demonstrated that metal(loid) tainted rice was entering food supply chains intended for direct human consumption.

Introduction

Human exposure to arsenic (As), cadmium (Cd), and lead (Pb) via the daily rice staple is a concern in some regions,

especially within Asia, in areas where farming and mining coexist (1–5). Inorganic As (As_i), a proven group 1 carcinogen (6), is associated with a plethora of insidious diseases affecting fertility in addition to cardiovascular and neurological function (6). Similarly to As, Cd has been linked to pathologies including diabetes, cancers, and high blood pressure (6–8), although it is principally a cumulative nephrotoxicant, that is poorly eliminated by the body with prolonged exposure resulting in renal dysfunction (4, 7). In the case of Pb there is no known no-effect level, and like Cd it can cause kidney failure at both acute and chronic exposures in addition to impacting on cognitive function (9). To safeguard dietary exposure to these metal(loid)s maximum contaminant levels (MCLs) have been set for rice. Surprisingly though, only a small number of countries have an MCL for As_i . In China the upper limit for As_i in rice is 150 ng g^{-1} (10). Cadmium and Pb regulations are more widely endorsed globally, with the Chinese safety thresholds for rice being 200 ng g^{-1} for both metals, respectively (10).

China has the highest global grain production (11), and with advances in agricultural sciences has maintained grain sufficiency for its 1.3 billion people (12), producing over 184 million tonnes of paddy rice annually; this is despite considerable pressures on water and arable land resources. In parallel with other major rice producing nations, the majority of rice cultivation within China is concentrated in specific key areas. Hunan province (south central China) lies in one such prominent rice producing area, with a largely rural population upward of 65 million, a semitropical climate, and large annual rainfall; it can propagate over 4000 ha of rice (13). Although the cultivation epicenter lies in the north, at the start of the Yangtze river floodplain, rice paddy farming is found throughout the region. The province is also regarded as the heartland of Chinese nonferrous mining. A number of studies have documented severe impacts within Hunan on rice agroecosystems as a result of mining and metal processing activities (3, 14, 15), although as yet how extensive the problem is has been poorly defined. In particular the safety of local food supply chains in mine-impacted areas has not been adequately addressed.

Soil to plant, and in planta transfer of metal(loid)s is key to risk assessment of mine-impacted rice paddies in China, not just for rice endosperm (polished white rice) but also for straw, husk, and bran. With end uses of these harvested residues as fertilizers, animal feed, building material, and fuel, they play an important role in metal(loid) cycling within arable land systems with resulting consequences for human exposure. Although it is not practical or economically viable to characterize all plant components in widespread rice surveys, developing predictions of likely metal(loid) levels in plant tissue fractions is crucial.

Here we present an extensive province-wide survey of rice from mine impacted areas conducted to determine grain suitability as a constituent of either human or animal diets, by comparing concentrations with national MCLs. In addition, a detailed Cd, As, and Pb biogeochemical assessment of rice paddies was undertaken to identify important commonalities in metal(loid) transfer and to calibrate models for predicting elemental partitioning in rice.

Materials and Methods

Survey of Mine Impacted Grain and Market Sourced Rice. Heterogeneity is a prominent feature of rural rice distribution networks within Hunan, with the point source nature of many contaminant pathways, small scale milling practices, and with many areas still largely reliant on local farmers to supply

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their rice needs, determining metal(loid) exposure for the hominid is problematic. In this study, it is those with the highest potential risk from the consumption of Cd, As, and Pb tainted rice that are considered, i.e., those in the vicinity of major mining operations where there is a priori knowledge of severe land degradation (16).

Wholegrain rice, from 100 paddies adjacent to large mining operations, comprised of a composite sample derived from three plants per paddy, were collected. With obvious pollutant source traceability to mine activities these samples allow the extent of rice contamination within Hunan to be gauged in addition to providing information on potential hot spot areas. In total, 12 sites from a variety of different districts were sampled. Four of the areas had prominent lead (Pb) and zinc (Zn) mining concerns: Yizhang (*Chenzhou*) ($n = 6$), Changningshi (*Hengyang*) ($n = 11$), Linxiangshi (*Yueyang*) ($n = 12$), and Shizhuyuan (*Chenzhou*) ($n = 13$). Two more sites (Qingshuitangqu (*Zhuzhou*), $n = 10$; Daoxian (*Yongzhou*), $n = 11$) were within busy metal smelting zones, while the rest represented arable lands close to manganese (Yuetangqu (*Xiangtan*), $n = 7$), arsenic (Shimenxian (*Changde*), $n = 13$), gold (Heshanqu (*Yiyang*), $n = 10$), and antimony (Lengshuijiangshi (*Loudi*), $n = 7$) mining operations. To ascertain the potential threat of contamination in the local food supply in these mine impacted areas, 122 polished rice samples intended for direct human consumption were sourced from local shops, markets, and farmers. Ten samples of rice obtained from markets within Hunan, but that were grown outside of the province, were analyzed as a comparison.

Characterization of Metal(loid) Partitioning in Chinese Rice. Four cultivated zones in south-central China with very different soil contaminant loading characteristics were selected (16). A representative value for each zone was obtained by sampling at least five paddy fields in each area. Quadruple paired rice grain, shoot, and soil (0–12 cm depth/10–20 g) subsamples, based on strategies adapted from Williams et al. (17) were obtained from each paddy site. Grain, shoot, and root/soil sections were separated in the field. A section of shoot (first 10 cm of the culm to root base) was discarded to minimize errors associated with soil contamination. In each case the soil collected was directly from under the sampled plants and represented an amalgamation of both rhizosphere and bulk soil.

The most seriously contaminated site, Shuikoushan (Changningshi, Hengyang) in south central Hunan, is located in a prolific lead (Pb) and zinc (Zn) mining belt. Rice production in this area has been significantly reduced in recent years due to human health concerns. The arable lands in and around the northeastern Hunanese site of Qingshuitangqu (Zhuzhou) are subject to a potential contamination risk from the numerous smelteries found in this area. The paddies sampled were in an active agricultural zone bordered by metal processing industries, which supplied grain and vegetables to the nearby city. Two control sites were targeted, one within the Hunan Agricultural University (Furongqu, Changsha), and another from the Yangtze River Delta; both were considered free from mining activities although geogenic levels of Cd, As, and Pb were expected to be different.

Plant and Soil Sample Preparation and Analysis. Standard multielement methodologies for determining metal(loid) concentrations in soil and rice were adapted from Zhu et al. (3), Williams et al. (17), and Sun et al. (18) and used throughout; for the the readers convenience, these have been reproduced in the Supporting Information (SI). Readily labile pools of Cd, As, and Pb from paddy soil-derived dust, corresponding to exchangeable acid and water soluble soil fractions, were estimated by extraction at room temperature of 1.000 g of soil with 40 mL of 0.11 mol⁻¹ acetic acid adapted from Rauret et al. (19). Total element detection was achieved

using an Agilent 7500a ICP-MS, operated with a babington nebulizer (3). All soil and plant tissue Cd, As, and Pb concentrations are given on a dry weight basis.

Quality Control. The limits of detection for plant digestions ranged between 0.001 and 0.1 $\mu\text{g Cd L}^{-1}$, 0.001 and 0.1 $\mu\text{g As L}^{-1}$, and 0.018 and 0.3 $\mu\text{g Pb L}^{-1}$. Limits of detection for soil digests and extractions ranged between 0.04 and 0.1 $\mu\text{g Cd L}^{-1}$, 0.001 and 0.19 $\mu\text{g As L}^{-1}$, and 2.0 and 2.2 $\mu\text{g Pb L}^{-1}$. Certified reference materials (CRM) 10010 Chinese rice flour and GBW 07405 and 07401 Chinese soils were used to validate the analysis. The average rice flour CRM recovery for Cd ranged from 91 to 103%, whereas for As and Pb it was 107 and 73%, respectively. Average recoveries for both soil CRM's ranged from 69 to 100%, 97 to 100%, and 98 to 105% for Cd, As, and Pb, respectively. Cumulative totals of metal(loid) levels in endosperm and bran fractions were compared with paired wholegrain concentrations. The average recovery ((bran + endosperm/wholegrain) $\times$ 100), $\pm$ SE, was $99 \pm 14\%$, $101 \pm 9\%$, and $104 \pm 14\%$, for Cd, As, and Pb, respectively ($n = 35$). Further details for spike recoveries, calibration standards, sample duplication, and chemicals used can be found in the SI.

Results

Grain Survey (a). The field rice most elevated by Cd, determined from average concentrations, was from Changningshi (*Hengyang*) followed by Qingshuitangqu (*Zhuzhou*) > Yuetangqu (*Xiangtan*) > Lengshuijiangshi (*Loudi*), with median levels in wholegrain rice collected from the Changningshi site being 2272 ng Cd g⁻¹. The large disparity between mean and median values in Cd grain contents reflects the wide variation in Cd contamination even within a small area. Mean and median As wholegrain levels were similar. Based on median As levels the highest grain averages were found in Shimenxian (*Changde*) > Lengshuijiangshi (*Loudi*) > Yizhang (*Chenzhou*) > Shizhuyuan (*Chenzhou*) (Table 1). The highest median Pb grain levels were found at sites in Hengyang and Chenzhou. Both these locations were actively mined for Pb and Zn.

Levels of grain intended for human consumption were generally lower than for the field survey (Table 1). Rice grain median values for Cd ranged from 55 ng Cd g⁻¹ for rice grown outside the province to 332 ng Cd g⁻¹ in eastern Hunan. For As, the lowest averages were found in northern Hunan areas, whereas grain concentrations in the Chenzhou region were found to reach up to 723 ng As g⁻¹. Lead was generally low, i.e., < 100 ng Pb g⁻¹; however, a few samples recorded levels of ~1000 ng Pb g⁻¹ or higher.

Biogeochemical Partitioning (b). *Soil. Cadmium.* The mean total soil Cd levels in the four different sample sites varied ~140 fold, from 0.26 to 37 $\mu\text{g g}^{-1}$. The highest recorded soil Cd concentration was 99 $\mu\text{g g}^{-1}$; although uncommon, cultivated paddy soils in southern Asia have been found to reach up to 284 $\mu\text{g g}^{-1}$ (2). In arable soils not severely contaminated by anthropogenic activities such as mining, smelting, or from inputs of Cd tainted fertilizers, global levels should range between 0.1 and 2 $\mu\text{g Cd g}^{-1}$ (20). Of the total amount of Cd in the Chinese soils, on average 52% of the Cd in Hunan and 19% of the Yangtze River Delta soils was shown to be labile following weak acid extraction, with levels at Shuikoushan found to be an order of magnitude higher than the global background for total Cd.

Arsenic. At each successive site (Yangtze River Delta, Furongqu, Qingshuitangqu, Shuikoushan), mean total soil As concentrations increased around 3–4 fold, ranging from 6 to 253 $\mu\text{g g}^{-1}$. The highest recorded soil was 321 $\mu\text{g As g}^{-1}$; equally elevated levels have been documented in mining-impacted agricultural land in southwest England (17). Yangtze River Delta mean levels matched similarly low concentrations found in paddy soils from the east coast province of Fujian

TABLE 1. Median and 95th Percentile Concentrations of Cd, As, and Pb in Endosperm Grain Fractions from Mining Districts in Hunan Province, China^a

			endosperm Cd (ng/g)		endosperm As (ng/g)		endosperm Pb (ng/g)		n	mining activity
location			market	field	market	field	market	field	market/field	
north	Heshanqu	median	122	304	126	224	67	51	5/10	Au
	Yiyang	95th	309	658	161	585	69	158		
	Linxiangshi	median	123	251	107	196	64	94	13/12	Pb and Zn
	Yueyang	95th	276	871	248	348	164	240		
	Shimenxian	median	69	84	142	262	68	82	12/13	As
	Changde	95th	107	817	211	483	88	197		
middle	Changningshi	median	330	1963	229	233	76	784	20/11	Pb and Zn
	Hengyang	95th	2808	2706	428	483	2177	197		
	Lengshuijiangshi	median		555		260		107	1/7	Sb
	Loudi	95th		1351		302		235		
south	Shizhuyuan	median	189*	50	232*	244	16*	329	10/13	Pb and Zn
	Chenzhou	95th	351*	2757	723*	359	621*	537		
	Yizhang	median	189*	32	232*	256	16*	171	10/6	Pb and Zn
	Chenzhou	95th	351*	1243	723*	493	621*	329		
	Daoxian	median	76	71	189	153	109	104	37/11	Smeltery
	Yongzhou	95th	384	212	355	251	721	329		
east	Qingshuitangqu	median	334	999	218	163	207	166	2/10	Smeltery
	Zhuzhou	95th	336	2492	253	233	261	495		
	Yuetangqu	median	211	694	243	205	24	147	5/7	Mn
	Xiangtan	95th	1567	2644	448	501	1780	288		
west	Huaihua	median	56		143		67		3/	
	Huaihua	95th	74		147		67			
	Non-Hunan	median	55		196		16		10/	
		95th	183		266		68			

^a Field rice endosperm levels have been predicted from wholegrain concentrations, based on linear regressions (Fig 1.).

*combined market rice catchment. A more comprehensive summary of rice metal(loid) levels is presented in the Supporting Information, including addition data from middle Hunan. Data is expressed on a dry weight basis.

($6\mu\text{g g}^{-1}$) (21), whereas the Furongqu average was comparable to a control site ($18.9\mu\text{g g}^{-1}$) used in the Hunan study reported by Liao et al. (15). In Hunan soils only 0.52% of the total As was readily labile, whereas in the Yangtze River Delta soils, 1.21% of the total As was deemed mobile.

Lead. Average Pb concentrations from Shuikoushan soils were 77 times higher than those reported for the Yangtze River Delta, with $3576\mu\text{g g}^{-1}$ being the maximum concentration for an individual paddy. Chinese environmental quality standards for Pb in arable soils are set at $250\mu\text{g g}^{-1}$ (16). In both the Pb enriched sites (Qingshuitangqu, Shuikoushan), proportional release of Pb was greater than the control sites, with Pb levels at Shuikoushan reaching 14% of the total.

Shoot. Cadmium levels in all Hunan straw samples obtained in this biogeochemical survey were found to be highly elevated in comparison to those from the Yangtze River Delta. The Shuikoushan site was the most enriched with average levels of $25\,802\text{ ng Cd g}^{-1}$. In addition to high levels of Cd, the straw from Qingshuitangqu and Shuikoushan was elevated in both As and Pb, while levels in the control sites were comparable. Average levels of As from Shuikoushan reached $35\,417\text{ ng As g}^{-1}$. In both contaminated sites, straw concentrations reflected only $15 \pm 4\%$ of corresponding total soil levels. Although not speciated here, studies suggest that almost all the As found in rice straw is As₅ (22, 23). Levels up to $20\,000\text{ ng As g}^{-1}$ in shoot from commercially grown rice in the French Carmargue have been previously documented (17). Lead levels in shoot from Shuikoushan averaged $192\,466\text{ ng g}^{-1}$; although high, shoot concentrations were 93% lower than paired soils, a trend that was a feature of all sites.

Husk. There was a 36-fold difference in mean Cd concentrations between Furongqu and Shuikoushan, with

all of the husk failing national animal feed hygiene standards of 1000 ng Cd g^{-1} (see SI) in both Qingshuitangqu and Shuikoushan sites. Arsenic levels in rice husk were similarly high with average levels from Shuikoushan reaching nearly $11\,000\text{ ng As g}^{-1}$, with all husk from Qingshuitangqu and Shuikoushan found unsuitable for animal consumption. Pb too, was found to be problematic with mean levels of $20\,776$ and $87\,140\text{ ng Pb g}^{-1}$ for the Qingshuitangqu and Shuikoushan sites, respectively.

Bran. The levels of Cd in bran fractions were found to be on average 2.2 ± 0.5 times higher than their corresponding endosperm, a trend which was maintained throughout several orders of magnitude in grain Cd, with polishing reducing wholegrain Cd content by $\sim 12\%$. No significant difference (general linear model [GLM], $p = 0.633$) in the percentage of wholegrain Cd lost by removing the bran was observed between the Hunan rice (Furongqu, Qingshuitangqu, Shuikoushan). The Yangtze River Delta site was found to differ, with the variation being largely attributed to the low concentrations of Cd found in the associated grain fractions.

Bran As levels were highly elevated in the Hunan collected rice, reaching up to 4074 ng As g^{-1} . Similar concentrations were reported in an As speciation study of Hunan sourced grain (18). Speciation studies of rice bran show the principal species are As₃ (18, 24). A significant difference (GLM, $p = 0.001$) in the relative proportion of total wholegrain As assimilated in the bran was observed when all the sample sites were considered. When Shuikoushan was removed from the data set, however, no significant difference (GLM, $p = 0.444$) was observed between the Yangtze River Delta, Furongqu, and Qingshuitangqu sites. Bran from the Shuikoushan accumulated around $\sim 60\%$ of the total As found in

FIGURE 1. South-central Chinese rice aerial biomass transfer relationships for cadmium, arsenic and lead. Biplots of Cd, As, and Pb in rice plant tissue. All correlations were statistically significant ($p < 0.0001$). Biplot labels (top) denote x-axis first, followed by y-axis. r^2 (a) 0.96, (b) 0.96, (c) 0.94 [linear] 0.97 [hyperbola], (d) 0.88 [linear] 0.95 [hyperbola], (e) 0.99, (f) 0.95, (g) 0.86, (h) 0.81, (i) 0.52, (j) 0.94, (k) 0.94, (l) 0.80, (m) 0.90, (n) 0.70, (o) 0.87.

the wholegrain, which contrasted with the two control sites where only around ~40% was assimilated, whereas Qingshuitangqu bran was marginally higher averaging 54%. Bangladesh rice has been reported to store only ~20% of the wholegrain As in the bran (18, 25).

A significant difference (GLM, $p = 0.001$) was found between bran Pb: endosperm Pb ratios between the Hunan sites. In both Qingshuitangqu and Shuikoushan, ~75% of the all the wholegrain Pb was stored within the bran, whereas for Furongqu and Yangtze River Delta the values were 50 and 64%, respectively. Although still high, with maximum recorded levels of 11 377 ng Pb g⁻¹, the concentrations found in bran from Hunan were much lower than corresponding husk levels. The relative proportions of Cd, As, and Pb in bran and endosperm are important when milling is considered.

Endosperm (Polished Rice). The highest Cd levels were found at the Shuikoushan site, with an average value of 3174 ± 429 ng g⁻¹. Levels at Qingshuitangqu were less elevated but still high at 1053 ± 452 ng g⁻¹, whereas Furongqu and the Yangtze River Delta were much lower at 281 ± 314 and 5 ± 7 ng g⁻¹, respectively. Total levels of As did not vary greatly between the three Hunan sites, with an overall mean of 227 ± 69 ng g⁻¹. The average from the Yangtze River Delta was roughly 50% lower at 99 ± 27 ng g⁻¹. Only the Shuikoushan site had highly elevated endosperm levels of Pb, at 612 ± 69 ng g⁻¹. When compared to national standards 80 and 33% of the rice from Hunan (Furongqu, Qingshuitangqu, Shuikoushan) failed to meet MCLs for Cd and Pb, respectively. Estimated As_i, derived from total As (3) revealed 7% of the Hunan samples would exceed the MCL for As_i in rice.

Cd, As, and Pb Plant Transfer Dynamics. Soil-Shoot. Median Cd soil-shoot transfer factors (TFs) based on total soil concentrations ranged from 0.25 to 0.95 with no discernible trend found between sites. Soil-shoot TFs from soil to shoot as high as ca. 15 have been observed in Cd-accumulating rice grown in pot experiment conditions (26).

Average soil-shoot TFs of As for the Yangtze River Delta closely matched those of the French Carmargue (17), whereas proportional transfer decreased with increasing total soil As levels and mining impact intensity. Shuikoushan exhibited the lowest transfer at 0.14. There was little difference between sites in Pb TFs. Factors ranged from between 2 and 15 fold less than either Cd or As.

Shoot-Husk. Highly significant ($p < 0.0001$) positive correlations were found for Cd ($r^2 = 0.96$), As ($r^2 = 0.96$), and Pb ($r^2 = 0.94$) (Figure 1). With average shoot-husk transfer factors (TFs) being similar for As and Cd at 0.3, whereas Pb exhibited a slightly higher value at 0.5.

Husk-Bran. A correlation of husk and bran Cd levels was also highly significant ($p < 0.001$; $r^2 = 96\%$) closely following a 1:1 relationship throughout the biplot, indicative of possibly similar tissue loading (Figure 1). Lead TFs were ~10-fold less than reported for Cd, however, the regression was still linear and the correlation highly significant. In contrast to the shoot-husk relationship, proportional translocation of As from husk to bran was curtailed at high husk As levels in excess of 4000 ng g⁻¹ (Figure 1). A similar phenomenon in rice wholegrains was documented in Williams et al. (17) when shoot became elevated in As. It therefore appears that bran and endosperm As transfer is distinct from that of husk, with husk being more closely associated with shoot.

Shoot-Bran. For both Cd and Pb, strong correlations ($p < 0.0001$) were found between shoot and bran with r^2 values of 0.94 and 0.90, respectively (Figure 1). For As, a nonlinear hyperbola model ($f = a - b/(1 + cx)^{1/d}$) best explained the data ($p < 0.0001$; $r^2 = 0.81$), exhibiting the same trend as for husk-bran. Shoot-bran TFs for Pb were around 5-fold lower than for corresponding Cd levels at 0.07, contrasting with shoot-husk in which Pb transfer was greater than Cd.

Shoot-Endosperm. TFs were highest for Cd averaging 0.12, which is 4.5 times higher than found for As and ~40 times higher than for Pb. Biplots of shoot and endosperm Cd and Pb produced significant correlations ($p < 0.001$, Cd $r^2 = 0.81$, Pb $r^2 = 0.81$), whereas As followed trends observed in shoot-

bran and husk-bran (Figure 1). The transfer of Pb from shoot to endosperm is proportionally very small (with a TF of 0.003), exhibiting a linear relationship with endosperm and a highly significant correlation. In a comparable survey of As in EU and U.S. rice, median shoot-wholegrain TFs averaged 0.05 for 72 samples (17). This is approximately double the Chinese shoot-endosperm TFs average, and in excellent agreement with overall median shoot-wholegrain TFs found in this study that were 0.04. Intriguingly though, when the same EU and U.S. data set was compared with Bangladesh grown rice, shoot to grain transfer was significantly higher in the Bengal delta plants (27).

Validation. To assess the shoot-wholegrain transfer models derived from the metal(loid) biogeochemical assessment, data from 29 rice plants grown in Guangdong (adjacent province to Hunan) and analyzed at the University of Aberdeen using ICP-MS (unpublished data) were used as a comparison, see SI. Wholegrain levels of Cd, As, and Pb were successfully predicted from straw concentrations using the Hunan models; correlations between actual and predicted concentrations were all significant with r^2 values of 0.98 (Cd), 0.83 (As), and 0.65 (Pb). Median recoveries of predicted against actual values were 113.3, 100.1, 100.1% for Cd, As, and Pb, respectively.

Predicted levels of endosperm As, derived from the Hunan calibration model using solely wholegrain concentrations were in excellent agreement with those reported in Sun et al. (18) for Hunan rice, yielding recoveries of 83 and 93% for rice CH1A and CH2G, respectively. Similarly for Cd, in 24 paired wholegrain/endosperm rice obtained from Hunan (data from PhD thesis, in prep) correlations between predicted and actual grain Cd were highly significant ($p < 0.001$; $r^2 = 0.97$) with a gradient of 1.06. Although, modeled levels of Pb in rice were not validated they were within ranges reported for rice grown in mine impacted paddies in northern Guangdong (5).

Discussion

Grain Survey (a). There is increasing evidence from this and other studies (3, 14–16, 28) that Cd-, As-, and Pb-tainted paddy soils and rice within Hunan are a common problem in the vicinity of old or currently active large scale mining or ore processing facilities, with mine waste runoff or overspill tainted irrigation water, heavy rainfall induced sediment redistribution, and atmospheric deposition resulting from ore smelting, all contributing to localized land degradation (14, 15). With the proliferation of industrial mining, only two regions in Hunan, remain relatively undeveloped, these are the Dongting lake area in the north and the western border, a stretch of land encompassing Shaoyang, Xiangxi, and Zhangjiajie districts.

With wholegrain rice accounting for ~50% of total animal feed grain consumption in Hunan (29), 78% of the rice collected from the field met national livestock fodder MCLs for feed, whereas it is predicted that only 26 and 1% of the bran and husk, respectively, fell within safety limits. It is worth noting that these levels were for washed rice, typically animal food would be unwashed. Using biplots of wholegrain and endosperm metal(loid) levels (Figure 1) in conjunction with estimates of As_i (3), to predict the levels in the grain after polishing, the same data set was assessed for its suitability for human consumption. It was predicted that 65, 50, and 34% of all the mine impacted field rice would fail national food standards for Cd, As, and Pb, respectively. Although it didn't necessarily concur that grains elevated in one metal(loid) were also high in others. Considering, therefore, that exceeding any MCL warrants the grain unfit for human consumption only 15 out of 100 samples were predicted to be within MCLs for As, Cd, and Pb.

The vast majority of rice consumed in China conforms to national safety standards, which are some of the most stringent globally, for example a survey of 269 polished rice/endosperm samples collected in 31 districts encompassing six provinces recorded mean Cd and Pb levels of 81.4 ± 65 ng g⁻¹ and 113 ± 65 ng g⁻¹, respectively (30). While the predicted grain As_i averages for market rice, collected from 11 provinces ($n = 230$) were all under 150 ng g⁻¹ (3). This aside though, a small percentage of contaminated grains are finding avenues into local markets and supply networks in the vicinity of mines. In general, areas found to have the highest metal(loid) levels in the field rice matched those in the local market survey. By using rough geographical classification categories for Hunan and considering MCLs, 17% of the northern ($n = 30$), 45% ($n = 47$) of the southern, 64% ($n = 25$) of the midlands and 86% ($n = 7$) of the eastern rice were predicted to not be suitable for human consumption. While all the samples from the west of Hunan and those obtained from local Hunanese markets but that were imported from other provinces, i.e., considered to have originated from nonmetal mining areas, were deemed compliant with Cd, As_i , and Pb safety levels.

Biogeochemical Partitioning (b). A number of remarkably clear trends and plant loading commonalities were apparent despite extensive genotypic and environmental variability (Figure 1). The principal sink for metal(loid)s were soil matrixes, however, accumulation in the aerial biomass (i.e., harvested component) was significant representing higher concentrations than labile soil fractions in many instances. Severely elevated levels of Cd, As, and Pb were a common feature of rice shoots (straw) at all the mine impacted sites, while even background concentrations in Hunan rice appeared higher than other provinces (3, 30).

The extent and frequency of elevated levels of endosperm Cd, was the major human dietary exposure concern. In the mine impacted sites average shoot Cd and As concentrations were similar. Distinct differences were observed, though, in shoot to grain transfer and grain loading characteristics, with shoot-endosperm TFs being 4.5 times higher for Cd than As. The suppression of proportional As transfer from shoot to grain, at high As exposures was demonstrated again to be an important factor in curtailing grain As levels (17). Although, not as pronounced a similar phenomenon appears to in affect for Cd shoot-endosperm transfer when plants are very highly Cd elevated. However, Cd shoot-bran and husk-bran relationships do not follow those of As. The role of bran as the final interface before endosperm was also crucial, especially for the plants growing in the most heavily contaminated sites. The enormous propensity for Chinese rice to assimilate Pb and As in the bran was validated here, with bran As content being on average 10-fold higher than corresponding endosperm levels. This was not a situation reciprocated for Cd, though, with wholegrain Cd concentrations decreasing only marginally upon milling.

Typically Pb concentrations are not high in most plants (20). Seldom do maximum levels in animal feeds exceed 2000 ng Pb g⁻¹ (31), yet levels approaching 2 orders of magnitude higher were observed during this investigation as potential animal fodder. With root mediated Pb uptake and transfer unlikely, a direct pathway from soil-shoot/husk is probable. Indeed, with potentially extractable pools of Pb found to range from 50 000 to 392 000 ng g⁻¹ in impacted sites, some leaching of Pb from dust and particulate material depositing on the rice is almost assured.

Being a key deposition site for dust borne contaminants, husk is an effective Pb scavenger, shown to have a high capacity to adsorb Pb from aqueous solutions (32). It also, however, shares a close proximity to bran layers, so transfer to wholegrains is tenable. When biplots of husk Pb against relative titanium (Ti, is commonly used to ascertain soil

contamination, see Williams et al. (17)) were considered correlations proved significant, (Pb, $r^2 = 93$; $p < 0.0001$). While wholegrain Pb levels also exhibited a positive relationship (Pb, $r^2 = 23$; $p < 0.0001$) albeit a much weaker one, supportive of dust/husk/bran Pb lead fluxes in these severely contaminated sites. In addition to Pb, husk As, and Cd levels correlated significantly with Ti ($p < 0.0001$, Cd, $r^2 = 91$; As, $r^2 = 93$), with Cd wholegrain not found to share a correlation with Ti, while As was ($p < 0.0001$, Cd, $r^2 = 57\%$). Although only circumstantial at the present, this could explain the high proportions of wholegrain As found in bran at the Shuikoushan site.

In conclusion, a series of striking transfer dynamics highlighted the vulnerability of rice to accumulate elevated levels of Cd, As, and Pb in mine impacted areas. Milling/polishing rice was shown to dramatically reduce grain As and Pb, but the effect was only marginal for Cd. Two clear Cd, As, Pb exposure pathways, in the form of market rice and animal feed, in mine impacted areas within Hunan province have been identified. Mitigation strategies to curtail body metal(loid) burdens need careful tailoring to meet the needs of impacted communities, and this requires further determination of dose and potential effects to better quantify the risk in exposed populations.

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Supporting Information Available

Chemical lists, analytical methodologies, quality control and further data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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