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Accumulation, Distribution, and Speciation of Arsenic in Wheat Grain

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Food can be an important source of inorganic As for human intake. Recent studies have focused on rice, while little information is available on As accumulation, distribution, and speciation in wheat, which is the second most important food grain cereal. Grain samples of 26 wheat cultivars grown in five field trials located in productive farming regions in Europe were therefore analyzed for As concentration and speciation. Grain from four trials contained low concentrations of total As (7.7 ± 5.4 μg kg^{-1}), reflecting low levels of As in the soils (1.3−11 mg kg^{-1}). In contrast, at one of the trial sites the As level in the soil was greater (29 mg kg^{-1}), and much higher As concentrations (69 ± 17 μg kg^{-1}) were present in the wheat grain. Milling of wheat grain into bran and white flour fraction showed the concentration of As in the bran, with a 3.8−4.7-fold higher As concentration than in the white flour. Two methods (a phosphate buffer solution and 1% HNO_3) were used to extract As species from wholemeal, bran, and white flour of wheat, with average extraction efficiencies of 65% and 88%, respectively. Only inorganic As was found in the extracts, with no methylated As being detected. The contribution of wheat to human intake of inorganic As is small for wheat crops grown in uncontaminated soils but becomes significant for those grown in soils with elevated As. In the latter case, milling can be used to reduce the As concentration in the white flour.

Introduction

Arsenic (As) is an environmental and food-chain contaminant, and inorganic As is a class-one carcinogen (*1, 2*). The Joint FAO/WHO Expert Committee on Food Additives (JECFA) recommended a provisional tolerable weekly intake (PTWI) of inorganic As of 15 μg kg^{-1} body weight, equivalent to 150 μg per day for a 70 kg person (*3*). However, a recent report commissioned by the European Food Safety Authority (ESFA) concluded "that the PTWI of 15 μg kg^{-1} body weight established by the JECFA is no longer appropriate as data had shown that inorganic As causes cancer of the lung and urinary bladder in addition to skin, and that a range of adverse effects had been reported at exposures lower than those reviewed by the JECFA" (*4*). ESFA (*4*) recommended that dietary exposure to inorganic As should be reduced and called for more data of As speciation in different food commodities to support dietary exposure assessment.

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Drinking water and foodstuffs are the two main sources of inorganic As (*5, 6*). In a rice-based diet, rice contributes substantially to the human intake of inorganic As, constituting the major exposure route for populations not exposed to As-contaminated drinking water (*7, 8*). For this reason, As accumulation in rice and the underlying mechanisms have attracted much attention in recent years (*9*). Wheat is an important staple food with a worldwide total production similar to that of rice (*10*). Average European adults consume about 0.25 kg of cereals and cereal products per day, with wheat-based products being the main component (*11*). However, there is little information about As accumulation, distribution, and speciation in this important cereal. Williams et al. (*12*) showed that the As transfer factor from soil to grain (the ratio of As concentration in grain to that in soil) was, on average, 10-fold higher in rice (0.04) than wheat (0.004). This is partly due to enhanced As bioavailability in the flooded soil conditions in rice paddy fields (*13*−*15*). In addition, wheat also accumulated less As in shoots than rice when plants were supplied with either arsenite or arsenate in hydroponic culture (*16*). This difference was attributed to arsenite, the main form of As transported in rice xylem sap, sharing the Si transport pathway which is highly expressed in rice (*17*). There are only a few reports in the literature of As concentrations in field-grown wheat grain. A survey of 84 field-grown wheat in The Netherlands showed a range of 5−285 μg As kg^{-1} grain fresh weigh with a mean of 45 μg kg^{-1} (*18*). Wheat grain produced from a field experiment in England with a soil total As of 12 mg kg^{-1} contained 2−17 μg As kg^{-1} (*19*), while the average As concentration in wheat grain grown in the U.S. was reported as 20 μg kg^{-1} (*20*). Higher concentrations (>100 μg As kg^{-1}) were reported in grain collected from As-contaminated sites (*12, 21*). However, the distribution of As in the grain and its speciation in flour are not known. This information is needed to assess the potential risk of As intake from consumption of wheat.

The objective of the present study was to determine As concentration, distribution, and speciation in wheat grain from field-grown crops. Grain samples were obtained from wheat variety trials located in productive arable farming areas not previously known to have As contamination in four European countries.

Materials and Methods

Grain Samples. Twenty-six cultivars (see the Supporting Information, SI Table S1 for the list) of winter wheat (*Triticum aestivum*) were grown at one site in 2006 (Martonvásár, Hungary) and four sites in 2007 (Martonvásár, Hungary; Woolpit, UK; Choryn, Poland; Clermont Ferrand, France). Different fields were used for the trials at the Martonvásár, Hungary, in the two years. These cultivars represent diverse geographic origins and genetic diversity (*22*). Each line was sown in two replicate plots of 2 m long with six rows spaced at a distance of 20 cm. Crop protection and fertilization were performed according to local practices (*23*). Wheat grain was harvested at crop maturity, and the samples from the two replicate plots were combined. Milling was carried out using a Perten Laboratory Mill 3100 (with 0.5 mm sieve) to produce wholemeal. A subset of samples were milled into bran and white flour fractions using a Brabender Quadrumat Junior Mill. Soil samples were also collected from the plow depth (0−15 cm) in each field. Samples were stored at −20 °C prior to analysis.

Analysis. Wholemeal flour, bran, or white flour samples (0.5 g) were digested with high purity HNO_3 and H_2O_2 in a microwave digestor as described previously (*19*). The con-

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TABLE 1. pH and the Concentrations of Total and Ammonium Phosphate-Extractable As in Soils from the Five Sites Used To Grow Wheat (Mean ± SD, $n = 4$)

trial site/season	pH	total As (mg/kg)	extractable As (μg/kg)
Martonvásár, Hungary, 2006	8.1 ± 0.08	9.0 ± 0.4	68.3 ± 4.3
Martonvásár, Hungary, 2007	7.6 ± 0.02	10.7 ± 0.05	73.3 ± 4.6
Choryn, Poland, 2007	6.0 ± 0.12	1.3 ± 1.2	44.0 ± 8.3
Clermont Ferrand, France, 2007	8.2 ± 0.04	28.5 ± 1.2	706.3 ± 82.7
Woolpit, UK, 2007	8.0 ± 0.24	8.3 ± 3.4	122.8 ± 8.8

centrations of As were determined using inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500ce, Agilent Technologies, Palo Alto, CA, U.S.A.) (*19*). Blank and a certified reference material (CRM; NIST 1568a rice flour) were included in each digestion batch for quality assurance. Repeated analysis ($n = 9$) of the CRM NIST 1568a gave a mean value (±SD) of 281 ± 11 μg As kg^{-1}, which is in good agreement with the certified values of 290 ± 30 μg As kg^{-1}. The detection limit (3 × SD of the blank) was 2 μg As kg^{-1}.

Soil total As was determined using ICP-MS following aqua regia digestion. Soil adsorbed As was extracted with 0.05 M $NH_4H_2PO_4$ (5 g of soil in 25 mL of solution) for 16 h (*24, 25*).

Arsenic speciation was determined in selected wholemeal, bran, and white flour samples. Two extraction methods were used. In the first method, samples (0.5 g) were extracted with a 10 mL phosphate buffer solution (2 mM NaH_2PO_4 and 0.2 mM Na_2-EDTA, pH 6.0) for 1 h under sonication. In the second method, samples (0.5 g) were extracted with 10 mL of 1% HNO_3 in a microwave digester at 100 °C according to Sun et al. (*26*). The extracts were filtered through 0.2 μm filter prior to As speciation analysis using HPLC-ICP-MS (Agilent LC1100 series and Agilent ICP-MS 7500ce, Agilent Technologies, Santa Clara, CA, U.S.A.). The volume of the sample injected was 50 μL. Arsenic species (arsenite, arsenate, dimethylarsinic acid (DMA), and monomethylarsonic acid (MMA)) were separated by an anion-exchange column (Hamilton PRP X-100; Reno, NV, U.S.A.) with a mobile phase containing 6.6 mM $NH_4H_2PO_4$ and 6.6 mM NH_4NO_3 (pH 6.3), run isocratically at 0.65 mL min^{-1}. An internal standard (Ge) was mixed continuously with the postcolumn solution through a peristaltic pump before being delivered to a concentric nebulizer and a water-jacketed cyclonic spray chamber of the ICP-MS. Signals at m/z 75 (As) and 72 (Ge) were collected with a dwell time of 500 ms and at m/z 35 (Cl) of 100 ms. Possible polyatomic interference of $^{40}Ar^{35}Cl$ on m/z 75 was eliminated by the Agilent Octopole Reaction System operating in the helium gas mode; this was demonstrated by no m/z 75 signal where the ^{35}Cl peak appeared in the chromatogram. The As signal was normalized by the Ge signal to correct any signal drift during the analysis. Peaks were identified by comparisons with the retention times of standard compounds. Arsenic species in the samples were quantified by external calibration curves with peak areas. The detection limit (defined as 3:1 signal-to-noise ratio in the HPLC-ICP-MS chromatogram) for arsenite, arsenate, DMA, and MMA were 6.4, 7.6, 6.6, and 8.8 μg kg^{-1}, respectively. The rice flour CRM (NIST 1568a) was included in the As speciation analysis, with the results obtained comparable to those reported previously (*14, 26*). The recoveries for the spike of arsenite, arsenate, DMA, and MMA added to three wheat or rice flour samples were 87−93% (SI, Table S2).

Results and Discussion

Soil As Concentration. Total As concentration in the soils from the five experimental sites varies from 1.3 to 28.5 mg kg^{-1} (Table 1). The soil from Clermont Ferrand, France, has a substantially elevated As concentration, exceeding the levels generally found in uncontaminated soils (<10 mg kg^{-1}) (*28*). The source of this elevated As may be geogenic in nature, as there are no obvious sources of anthropogenic contamination at the site. Ammonium phosphate is used to extract specifically adsorbed arsenate from soil (*24*), which gives an indication of As bioavailability to plants (*25*). This reagent extracted 0.7−3.3% of the total As in the soils (Table 1). The soil from the French site again showed a much higher level of adsorbed As than the other four soils.

Arsenic Concentration in Wheat Grain. Figure 1 shows a box-plot of grain As concentrations in 26 wheat cultivars grown in the five field trials. Grain from the sites in Hungary, Poland, and UK, where soil As concentrations were low (Table 1), had low levels of As (0−24 μg kg^{-1}), with 6% of the samples being below the detection limit (2 μg kg^{-1}). The mean As concentrations (±SD) were 6 ± 3, 9 ± 4, 13 ± 3, and 3 ± 2 μg kg^{-1} for the trials in Hungary 2006, Hungary 2007, Poland 2007, and UK 2007, respectively. In contrast, grain produced

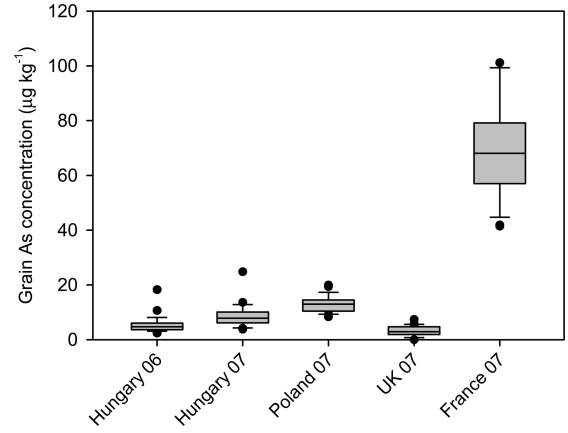

FIGURE 1. Boxplot of As concentration in wholegrain samples of 26 wheat cultivars grown in five field trials. The box represents 25th−75th percentile, the whiskers 10th−90th percentile, and closed circles any data outside the 10th−90th percentile. The horizontal line inside the box indicates the median.

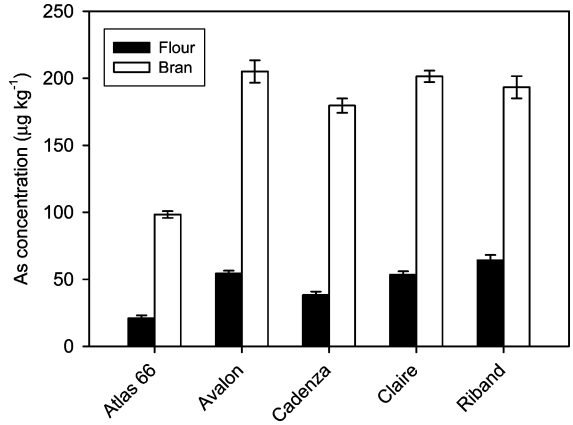

FIGURE 2. Distribution of As in bran and white flour of five wheat cultivars grown in Clermont Ferrand, France, 2007 (mean ± SD, $n = 3$).

TABLE 2. Arsenic Speciation in Grain and Flour Samples from Five Wheat Cultivars Grown at Clermont Ferrand, France, 2007 (Mean ± SD, $n = 2$)

			As concentration (μg kg^{-1})		As species (%)		
cultivar	sample	extraction method	As(III)	As(V)	As(III)	As(V)	recovery (%)[a]
Clair	whole meal	PBS[b]	41.6 ± 2.8	18.0 ± 6.8	70 ± 9.4	30 ± 9.4	59 ± 4.1
Riband	whole meal	PBS	55.9 ± 3.0	6.6 ± 7.3	90 ± 11.0	10 ± 11.0	64 ± 4.4
Avalon	whole meal	PBS	39.6 ± 0.3	22.1 ± 4.6	64 ± 4.6	36 ± 4.6	61 ± 4.9
Atlas-66	whole meal	PBS	28.4 ± 5.1	9.6 ± 4.2	75 ± 11.8	26 ± 11.8	75 ± 1.6
Cadenza	whole meal	PBS	37.9 ± 0.0	6.4 ± 9.0	87 ± 17.8	13 ± 17.8	67 ± 13.5
Clair	bran	HNO_3[c]	73.9 ± 5.6	78.8 ± 1.2	48 ± 1.5	52 ± 1.5	76 ± 3.4
	white flour		29.3 ± 0.6	20.9 ± 3.0	59 ± 3.0	42 ± 3.0	94 ± 6.7
Riband	bran	HNO_3[c]	43.2 ± 3.0	66.2 ± 10.4	40 ± 2.1	60 ± 2.1	57 ± 6.9
	white flour		45.4 ± 0.9	22.2 ± 3.1	67 ± 2.7	33 ± 2.7	105 ± 6.2
Avalon	bran	HNO_3[c]	111.8 ± 25.8	102.0 ± 6.9	52 ± 4.1	48 ± 4.1	104 ± 16.0
	white flour		29.6 ± 3.0	20.1 ± 1.3	60 ± 4.0	41 ± 4.0	92 ± 3.1
Atlas-66	bran	HNO_3[c]	34.3 ± 17.2	50.7 ± 1.0	39 ± 12.7	61 ± 12.7	87 ± 16.4
	white flour		21.4 ± 2.4	24.4 ± 1.4	47 ± 4.2	53 ± 4.2	218 ± 4.5
Cadenza	bran	HNO_3[c]	55.5 ± 8.0	54.1 ± 8.1	51 ± 0.1	49 ± 0.1	61 ± 9.0
	white flour		23.6 ± 1.2	19.8 ± 4.0	55 ± 6.2	45 ± 6.2	113 ± 7.4

[a] Sum of As species determined by HPLC-ICP-MS divided by total As concentration by acid digestion and ICP-MS determination. [b] Phosphate buffer solution (2 mM NaH_2PO_4 and 0.2 mM Na_2-EDTA, pH 6.0) + sonication. [c] 1% HNO_3 + microwave extraction at 100 °C.

at the French site had much higher concentrations of As (41−101 μg kg^{-1}, mean 69 ± 17 μg kg^{-1}). It is clear that the high soil concentration of As at the French site had led to increased As accumulation in wheat grain. The soil to grain As transfer factor varies from 0.0004 to 0.01 (mean 0.003) among the five trials. This range is within that reported by Williams et al. (*12*) for wheat (0.000−0.024, mean 0.004). Our data are generally comparable to those reported elsewhere (*18*−*20*). Based on a survey of paired soil-crop samples in the UK including many high As soils, Williams et al. (*12*) showed that As concentration in wheat grain increased with soil As concentration in a log−log linear fashion. The majority of the grain samples from uncontaminated soils (<10 mg As kg^{-1} soil) had <50 μg As kg^{-1} in grain, although a number of samples from As contaminated sites contained >100 μg As kg^{-1} in grain. Plotting the data of grain As versus soil As concentrations in the present study (SI, Figure S1) shows that the high grain As in the French site was associated with a high As concentration in the soil; however, in the low As soils the relationship was poor and not improved using the phosphate-extractable As.

Pooling the data together and treating the sites as replicates in analysis of variance (ANOVA) showed that the 26 wheat cultivars differed significantly in grain Fe and Zn concentrations (*23*). However, this was not the case for grain As, with cultivar differences being insignificant. This probably results from the large site-to-site variation, which masks any genotypic variation in grain As accumulation.

Arsenic Distribution in Wheat Grain. Grain samples of the five wheat cultivars grown in the high As French site were milled into the white flour (endosperm) and bran fractions (comprising mainly pericarp, aleurone, and embryo). The concentration of As in the bran fraction (98−205 μg kg^{-1}) was 3.8−4.7-fold higher than that in the white flour fraction (21−54 μg As kg^{-1}) (Figure 2). Thus, although the bran fraction accounted for only 23−29% of the total grain weight, it contained 53−65% of the total As in grain. This pattern shows that As is concentrated in the outer layer of wheat grain, and, as a result, milling can be used to produce white flour which has a lower concentration of As than the whole grain. There is little information of the As distribution pattern in wheat grain, although it has been shown that rice bran has 10−20-fold higher As concentration than polished rice (*26*). X-ray fluorescence and Nano-SIMS mapping have shown that As accumulates in the outer layers of rice grain, corresponding to the ovary vascular trace and subaleurone cells (*28, 29*). Further investigation is needed to reveal the precise cellular localization of As in wheat grain.

Arsenic Speciation in Wheat Grain. The five cultivars from the trial at the French site were selected for As speciation analysis (Table 2); the As concentrations in the grain samples from other sites being too low to allow the reliable determination of As species. Grain wholemeal was first extracted with a phosphate buffer solution (PBS) that was similar to the eluant solution used in HPLC separation of As species. This mild extraction with the inclusion of EDTA helps to preserve the As species in the extracts (*30*). The recovery of As species by the PBS extraction and HPLC-ICP-MS procedure was 59−75% (mean 65%) of the total As determined following acid (HNO_3/H_2O_2) digestion. Only inorganic As was detected in the extracts with no traces of methylated As species (Figure 3). Furthermore, the majority (64−90%) of the extracted As was arsenite, with the remainder being arsenate (Table 2).

Sun et al. (*26*) used microwave-assisted extraction with 1% HNO_3 to extract As species from rice flour and bran, achieving a recovery of As species of 70−90%. The method is efficient at extracting both inorganic and methylated As (*26*). This method was therefore used to extract the bran and white flour fractions of wheat from the French trial. The recovery of As species varied from 57 to 218% (Table 2). The anomalously high recovery from the white flour of the cultivar Atlas-66 (218%) was probably related to the low concentration of As in this sample (total As concentration =21 μg kg^{-1}, compared with 50−205 μg kg^{-1} in other samples). When the sample of Atlas 66 was excluded the recovery was 57−113% (mean 88%). Again, only inorganic As species were detected in the bran or white flour extracts, with the percentages of arsenite and arsenate being approximately equal. The higher proportion of arsenate in these extracts than in the PBS extraction was probably due to some oxidation of arsenite to arsenate during the microwave-assisted extraction with HNO_3; for this reason Sun et al. (*26*) presented only the sum of arsenite and arsenate as inorganic As. The PBS extraction is considered to be more effective than the HNO_3 extraction in preserving the in situ ratio of the two inorganic As species.

Our results show no evidence of methylated As species in wheat wholemeal flour, bran, or white flour. There is little information of As speciation in wheat grain or flour in the literature. Schoof et al. (*5*) reported mean values for total As and inorganic As of 39 and 11 μg kg^{-1}, respectively, in four wholemeal wheat flour samples collected in Texas, U.S.A.; however, it is not clear whether the difference between the

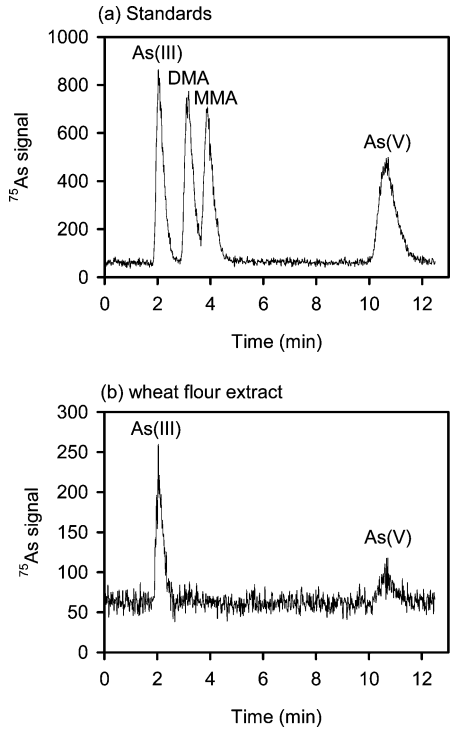

FIGURE 3. Arsenic speciation in wholemeal wheat extracted with a phosphate buffer solution: (a) standards of As species (10 μg L^{-1}) and (b) wholemeal wheat extract (cultivar Clair).

amounts of total and inorganic As was due to incomplete extraction of the As species for analysis or the presence of organic As. In rice grain, both inorganic As and methylated As species are present, with inorganic As (mainly arsenite) accounting for between 10% and 90% of the total As and the remainder being mainly DMA (*7, 31*). However, very little methylated As was found in the grain when rice was grown under aerobic conditions in greenhouse experiments (*14, 15*). The DMA present in rice grain may be taken up from soil, where it is present as a result of microbial or algal methylation of As or as residues from previous use of methylated As pesticides. There is also some evidence that microbial methylation of As in soil is enhanced by flooding of soil and the inputs of organic matter (*32*). This would explain the greatly diminished accumulation of methylated As in aerobic rice grain, and possibly also the absence of methylated As in wheat grain found in the present study because the wheat was grown in aerobic soils. Whether plants are able to methylate As remains controversial (*9*).

Implications for Human Intake of As. Assuming a daily consumption of 0.25 kg (0.225 kg dry weight assuming 90% dry matter) of wheat products per adult (*11, 33*) and using mean values of grain As at each site, the intake of inorganic As would be 0.7−2.9 μg per day for the wheat produced in the four trials at the low As sites (Hungary, Poland, and UK). For the high As French site, the intake would increase to 16 μg per day for wholemeal wheat and to 10 μg per day for white flour. For comparison, daily dietary intake of inorganic As from all food sources is estimated to range from 5 to 14 μg per day in the U.S. and Canada (*34*), and for average European consumers, intake of inorganic As from food and drinking water ranges from 9 to 39 μg per day for a 70 kg person (*4*). Another comparison is the intake of inorganic As from food with that from drinking water. The current WHO guideline is set at 10 μg L^{-1}, and a daily consumption of 1.5 L water at this concentration would give 15 μg As. Thus, intake of inorganic As from consumption of wholemeal wheat produced at the French site would be comparable to that from drinking water at the WHO guideline. The above calculations suggest that the contribution of wheat to human intake of inorganic As is small for wheat crops grown in uncontaminated soils but becomes significant for those grown in soils with elevated As.

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Supporting Information Available

List of wheat cultivars and breeding lines used in this study, recoveries of As species spikes, and the relationships between wheat grain As and soil As concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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