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Arsenic speciation in rice and risk assessment of inorganic arsenic from Ghentugachhi village of Chakdaha block, Nadia, West Bengal, India

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ABSTRACT

The purpose of the present study was to assess arsenic (As) speciation in rice from West Bengal, India, in order to improve understanding of the health risk posed by arsenic in Indian rice. Rice is a potentially important route of human exposure to arsenic, especially in populations with rice-based diets. However, arsenic toxicity varies greatly with species. Determination of arsenic (As) species in rice is necessary because inorganic As species are more toxic than organic As. Total arsenic was determined by inductively coupled plasma mass spectrometry; arsenite, arsenate, monomethylarsonic acid, and dimethyarsinic acid were quantified by high-performance liquid chromatography- inductively coupled plasma mass spectrometry. The analysis of a rice flour certified reference material (SRM-1568-a) were evaluated for quality assurance. The use of 2M TFA for extraction with an isocratic mobile phase was optimized for extraction and employed for arsenic speciation in rice. The extraction method showed a high recovery of arsenic. Most of the As species in rice were noticed to be inorganic [Arsenite (As-III), Arsenate As-V]. It appeared very clear from the present study that inorganic arsenic shared maximum arsenic load in rice straw while in grains it is considerably low. As species recovered from rice grain and straw are principally As-III and As-V with a little share of DMA and almost non-detectable MMA and As-B. The order of As species in rice grain revealed in this study were As-III (54.5-65.4 %)>As-V(21.2-28.3%)>DMA(5.2%).

Key words: *Speciation, arsenic species, HPLC, ICPMS, rice*

INTRODUCTION

Natural arsenic contamination of groundwater resources is posing a serious threat to the health of millions of people. Out of 20 countries (covering Argentina, Chile, Finland, Hungary, Mexico, Nepal, Taiwan, Bangladesh, India and others) in different parts of the world where groundwater arsenic contamination and human suffering have been reported so far, the magnitude is considered to be the highest in Bangladesh, followed by West Bengal, India (Chowdhury et al., 2000; Chowdhury et al., 2001). The wide spread arsenic contamination in groundwater in different parts of West Bengal, distributed over 111 blocks, located primarily in twelve districts in West Bengal (http://www.soesju.org). Rice is staple food for more than half of the world's population especially in Asian countries (Kim et al., 2011; Sun et al., 2012). Arsenic is a well-known toxic element that has been classified as Category 1 carcinogen by the International Agency for Research on Cancer of the World Health Organization of the United Nations. It accumulates in the human digestive tract and kidneys when contaminated foods are ingested (Das et al., 2004; World Health Organization/International Agency for Research on Cancer 2014). In India, rice is predominantly grown in the Indo-Gangetic plains, on 13.5 mha or 85% of the cultivated land area with ground water as a principal source of irrigation (Samra et al., 2004). Most of the shallow groundwater in southern

Bangladesh and eastern part of West Bengal, India, is geogenicaly contaminated with arsenic (As), exposing more than 40 million people at risk of As in drinking water (World Bank, 2005). Arsenic contamination of water and soil can also adversely affect food safety. Arsenic contaminated groundwater used for drinking purpose is likely the major pathway of human exposure (Gupta et al., 2017). However, food crops, specifically rice, serve as a major source of arsenic being the dietary staple food of half of the world's population (Banerjee et al., 2013). In Asian countries like Bangladesh, India, China, Korea, Taiwan, and Thailand, arsenic intake from rice diet is significantly higher, as rice plants have a special ability to take up arsenic from the soil and water used for irrigation (Ohno et al., 2007). The transfer of arsenic from soil to plant systems is a serious issue that leads to considerable human exposure (Dave et al., 2013). Arsenic exists in the environment in several inorganic and organic forms. In paddy fields, arsenite (AsIII) is the dominant arsenic species, comprising 63% of total arsenic in soil, followed by arsenate (AsV) at 36%, and methylated arsenic species (Abedin et al., 2002). Following root to shoot translocation, arsenic can severely impede plants' growth by arresting biomass accumulation, reducing reproductive capacity through impaired fertility, yield, and fruit production (Garg and Singla, 2011). Toxicity symptoms of rice plants grown in soils (containing >60 mg kg^{-1} total arsenic) include stunted growth, brown spots, and scorching on leaves (Bakhat et al., 2017). The predominance of arsenite over arsenate is the result of reducing conditions in soils due to water submergence that affect the growing plants (Bakhat et al., 2017). Roots are the major part to get exposure and accumulation of arsenic that may affect its elongation and proliferation. Usually, due to translocation in plants, the accumulation of arsenic decreases from root to above ground parts. Under flooding or anaerobic conditions in paddy soils, reductive mobilization of arsenic greatly enhances the bioavailability of arsenic leading to excessive accumulation of this metalloid in rice grain and plant (Meharg and Zhao, 2012).

Arsenite is the predominant species in the submerged soil and microbial transformation of inorganic species to organic form produces considerable quantities of methylated arsenic species dimethylarsinic acid (DMA) and smaller amounts of monomethylarsonic acid (MMA) in the paddy soil (Meharg et al., 2009). This transformation to organic form is beneficial because methylated arsenic species are less toxic than the pentavalent arsenic species. Inorganic arsenic species (AsIII and AsV) are more efficiently taken up by roots than methylated arsenic species (DMA and MMA), but the translocation rate in plant shoot of inorganic arsenic species is much lower than methylated arsenic species. The reduced complex formation of methylated arsenic-species with the ligands (glutathione/ phytochelatin) may be the reason for the better translocation of methylated-arsenic species (Rabb et al., 2007). As-III was found to be the most abundant species in the rice grain, followed by DMA with low concentrations of AsV, MMA, and other two unidentified arsenic species, as suggested by analysis of 121 samples of 12 rice types (Huang et al., 2012). On the other hand, in rice straw, As-V is a predominant species followed by As-III and DMA (Sinha and Bhattacharyya, 2015). A global normal range of 0.08 to 0.2 mg As kg^{-1} has been suggested for rice (Zavala and Duxbury, 2008), but values as high as 0.25 mg As kg^{-1} have been found in rice (Mandal et al., 2007). Daily consumption of 400 g dry wt. of rice containing 0.25 mg As kg^{-1} would provide 100 μg As or 5 times the 20 μg As from consumption of 2 L of water at the acceptable WHO limit of 10 $\mu g\ L^{-1}$ (WHO, 1993).

Besides, rice grain and straw are dominated by arsenite (As- III) and arsenate (As-V), which are more toxic in nature (Juskelis et al., 2013; Sinha and Bhattacharya, 2015). Arsenic occurs in different physicochemical forms or species and the toxicological effects are largely dependent upon the bioavailability of the individual species, rather than the total element concentration (Gomez-Ariza et al., 2001; Gong et al., 2002; Sanz et al., 2007; Khan et al., 2015). The solubility, mobility, bioavailability and hence toxicity of arsenic in soil-crop system depends on its chemical form, primarily the oxidation state. Estimation of total arsenic often leads to either over or under estimation of the crux of toxicity problem due to species-dependent toxicity of the metalloid (As). The inorganic arsenic forms, arsenite and arsenate, are very toxic and have been connected to an increased risk of cancer and cardiovascular disease (Pizarro et al., 2004). The As-III and As-V remained the major arsenic species in most of the grain and straw samples analyzed. It is interesting to note that As-III accounted for the major As species recovered from grains of paddy while As-V dominate in rice straw (Sinha and Bhattacharya, 2015). Among organic arsenic species, monomethylarsonic acid and dimethyarsinic acid are significantly less toxic while arsenobetaine, arsenocholine, and arsenosugars are not toxic (Gong et al., 2002; Liang et al., 2010). Although total arsenic is most often cited as an area of concern, the toxicity is highly dependent on the chemical species in which it occurs. Acute toxicities (LD50) of the organic species monomethyl arsenic acid (MMA) and dimethyl arsenic acid (DMA) range from 700 to 2,600 mg/kg while inorganic arsenate (AsV) and arsenite (AsIII) are as low as 15 to 20 mg/kg. Therefore the actual health concerns over arsenic exposure are highly related to inorganic species (James et al., 2008).

Accurate arsenic speciation is therefore essential to evaluate the impact of arsenic toxicity in rice on human health. Most of As-speciation analytical methods are based on chromatographic separation techniques such as High performance Liquid Chromatography (HPLC) coupled with Atomic Absorption Spectrometry (AAS) and, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The present study was undertaken to determine the different forms of As-species in rice and to provide the percentage of inorganic As/total As and accurate information of human health risk assessment.

Table 1. Validation of total As recoveries from rice through NIST standards.

Sample	Certified value (µg/g)	Observed value (µg/g)
SRM 1568a (rice flour)	290±30	283±8*

*in HNO_3-digest, determined through Perkin Elmer ELAN DRCe-6000 ICP-MS.

MATERIALS AND METHODS

Selected rice grain samples (both aus rice, variety GS-3 and summer rice, variety IET-4786) were collected from farmer's field of village Ghentugachhi (N 23^{0}02'7.1", E88^{0}35'4.8") for speciation study. A microwave digestion system (Multiwave 3000, Anton Par) with a rotor of 48 Teflon digestion vessels was

Table 2. Recoveries of As species from *boro* rice.

Sample	Recovery of Arsenic species in boro rice (µg.kg^{-1})					Sum of Species	Total As (µg.kg^{-1}) (HNO_3- digest)	Species recovery (%)
	As B	As-III	DMA	MMA	As-V			
Grain	nd	750.70	140.50	nd	482.20	1373.40	1461.60	93.97
	nd	516.00	45.60	nd	217.80	779.40	864.00	90.21
	nd	489.00	34.80	nd	267.00	790.80	918.00	86.14
	nd	1223.50	41.50	nd	173.00	1438.00	1542.00	93.26
	nd	589.50	53.00	nd	136.90	779.40	1082.30	72.01
	nd	1040.90	57.20	nd	217.60	1315.70	1180.00	111.50
	nd	768.26 ±301.81 (65.4%)	62.1 ±39.23 (5.28%)	nd	249.08 ±122.48 (21.2%)	1079.45 ±326.85	1174.65 ±278.64	91.18 ±12.79
Straw	nd	865.80	443.00	nd	7600.30	8909.10	8823.00	100.98
	nd	1693.00	367.30	nd	2763.30	4823.60	4739.60	101.77
	nd	586.80	292.80	nd	5073.00	5952.60	6048.00	98.42
	nd	969.00	792.60	194.0	8146.80	10102.80	9684.00	104.32
	nd	577.00	294.70	nd	5080.30	5952.00	6308.00	94.36
	nd	126.00	133.20	nd	6756.60	7015.80	7326.00	95.77
	nd	802.93 ±525.31	387.27 ±223.5	194.00	5903.38 ±1993.3	7125.98 ±2005.45	7154.77 ±1843.06	99.27 ±3.79
Characterization of arsenic sources (STW/PW) and sink (soil) of the experimental site								
STW	nd	278.78	nd	nd	73.10	351.88	320.00	109.96
PW	nd	nd	nd	nd	23.65	23.65	31.50	75.08
SOIL	nd	900.15	nd	nd	13300.70	14200.85	19400.00	73.20

Table 3. Arsenic speciation of selected straw and grain samples of Aus paddy by TFA (@ pH 6.2) extraction through HPLC-ICP-MS.

Sample	Arsenic species					Sum of Species	Total As (ppb) (HNO_3 igestion)	Per cent recovery
	As B (ppb)	As-III (ppb)	DMA (ppb)	MMA (ppb)	As-V (ppb)			
Grain	nd	320.4	113.4	nd	251.4	685.2	669.0	102.4
	nd	284.4	nd	nd	118.8	403.2	390.0	103.4
	nd	288.6	nd	nd	121.9	410.4	434.7	94.4
	nd	328.0	nd	nd	183.3	511.3	743.7	68.8
	nd	307.6	nd	nd	134.7	442.3	557.3	79.4
	nd	314.6	nd	nd	147.2	461.9	585.7	78.9
		307.27 ±17.48 (54.53%)	113.40 (20.12%)	nd	159.55 ±50.69 (28.31%)	485.72 ±105.24	563.40 ±134.78	87.88 ±14.22
Straw	nd	369.0	208.0	nd	3428.5	4005.5	3988.0	100.4
	nd	187.6	nd	nd	2987.4	3175.0	3879.0	81.9
	nd	224.2	nd	nd	2763.0	2987.2	4120.0	72.5
	nd	387.6	202.8	nd	4169.4	4759.8	4836.0	98.4
	nd	106.8	nd	nd	2691.6	2798.4	4398.0	63.6
	nd	328.9		nd	3578.6	3907.5	4587.0	85.2
		267.35 ±111.87	205.4 ±3.68	nd	3269.75 ±565.82	3605.56 ±748.69	4301.33 ±370.47	83.67 ±14.35

used for sample digestion and extraction. Arsenic species were determined in a HPLC-ICP-MS (PerkinElmer ElanDRCe 6000).

All chemicals used were reagent grade. All of the solutions were prepared with Mili-Q (Millipore, Bedford, MA, USA) water. For the speciation studies, standard solution (100mg/l) of As compounds were prepared from: i) arsenite ($NaAsO_2$, Perkin Elmer, USA) ii) arsenate (Na_2HAsO_4, $7H_2O$, Perkin Elmer, USA) iii) monomethyl arsonate($CH_3AsNa_2O_3$, Sigma-Aldrich Corp St. Louis, MO USA) iv) dimethyl arsenate (CH3)2AsO(OH), Sigma) and arsenobetaine (AsB; Sigma). TFA was purchased from Aldrich (St. Louis, MO)

The inorganic (As-III & As-V) and organic (DMA & MMA) arsenic accumulation in rice grain and straw were determined from TFA (@ pH 6.2) extraction.

Sample preparation and digestion

Sample digestion (total As; HNO_3-digest)

About 0.2 g of rice grain or straw sample were weighed into a microwave Teflon vessel and 7 ml of concentrated nitric acid was added to it and left to stand overnight at room temperature. Samples were then digested in a microwave maintained at 200 ^{0}C for 20 minutes. Samples were then cooled and transferred to a 50 ml volumetric flask for total arsenic analysis through Perkin Elmer ELAN DRCe 6000 ICP-MS.

Sample extraction (for As species)

For speciation analysis about 0.2 g of rice grain or straw sample were weighed into a microwave Teflon vessel and 2 ml of 2.0 M TFA was added to it. Samples were then digested in a microwave maintained at 90^{0}C for 20minutes. Samples were then cooled and transferred to a 50 ml volumetric flask for speciation analysis. (Abedin et al., 2002). Total As recoveries from rice were validated by using the Perkin Elmer ELAN DRCe 6000 ICP-MS and compared with the NIST standard SRM 1568a (rice flour); the certified value was 290±30 μgkg^{-1} and the observed value was 283±8 μgkg^{-1}. (Table 1).

Statistical analysis

Data were subjected to analysis of variance (ANOVA) according to the methods(SPSS) and means between treatments were compared by least significant difference (LSD) at $p \leq 0.05$.

RESULTS AND DISCUSSION

The inorganic [*i.e.*, As(III) and As(V)] and organic (*i.e.*, DMA and MMA) arsenic accumulation in rice grain and straw were determined from the TFA (at pH 6.2) extract by using HPLC-ICP-MS (Perkin Elmer ElanDRCe 6000) and the results are given in Table 2 & 3. The HPLC-ICP/MS chromatograms of the speciation analysis of arsenic in rice sample and standard solution are shown in Fig. 1. The recovery of arsenic species through TFA extraction remained at quite satisfactory level (63 to 103 % of total arsenic in aus rice and74.21 to 111.70 per cent of the total arsenic recoveries in summer rice from HNO_3 extract which are quite appreciable for a particular extractant in the backdrop of such recoveries reported by Abedin et al., 2002. The As-III and As-V remained the major arsenic species in most of the grain and straw samples analyzed. It is interesting to note that As-III accounted for the major arsenic species recovered from grains of both transplanted aus rice and boro rice while As-V predominates arsenic recoveries from rice straw. Meharg et al., 2002 also observed that arsenic species in rice straw extracted with TFA are arsenate, arsenite and DMA. The proportion of arsenate, arsenite and DMA were 72-84%, 15-26% and 1-4% respectively.

They showed that rice grain arsenic speciation is dominated by inorganic arsenic and DMA. DMA has been recovered from few grain and straw samples. The inorganic arsenic of grain has been found to increase with increasing levels of total grain arsenic ($R^2 \approx 0.95$).

Sanz et al., 2007 observed that for rice and paddy samples, inorganic arsenic counted up to 70-98% of the total arsenic content, being the major species As (III). The levels of arsenic obtained from straw and soil samples are significantly higher than the background levels, being the major species As (V), thus increasing human exposure to arsenic via the soil-plant-animal-human pathway. It is interesting to note that characterisation of arsenic source-STW and sink -soil (Table 5) did not show any recoveries of organic arsenic, although boro grain and straw accumulates organic arsenic species . The recoveries of such organic species in rice grain and straw may be due to transformation of inorganic arsenic to organic forms in plant body. Organic arsenic species present in field samples of plants may have been taken up from soil solution in that particular form as they can be present in soil through microbial activity; however, it is also possible that plants themselves could potentially transform arsenic species. In a study conducted by Koch et al., no evidence of methylation was found in the surrounding soil and water, and yet a number of plant species contained MMA, DMA, tetramethyl arsonium ion and trimethylarsenium oxide (tetra). The percent recoveries of organic arsenic (out of total arsenic from HNO_3-digest) ranged from as low as 1.82

Table 4. Recoveries of organic As in *boro* rice.

Sample	Inorganic As (µg.kg^{-1}) (As-III + As-V)	Organic As (µg.kg^{-1}) (DMA + MMA + As-B)	Total As (µg.kg^{-1}) (HNO_3- digest)	Per cent oganic As
Grain	1232.90	140.50	1461.60	9.61
	733.80	45.60	864.00	5.28
	756.00	34.80	918.00	3.79
	1396.50	41.50	1542.00	2.69
	726.40	53.00	1082.30	4.90
	1258.50	57.20	1180.00	4.85
	1017.35±310.39 (86.6%)	62.1±39.23	1174.65±278.64	5.18±2.36
Straw	8466.10	443.00	8823.00	5.02
	4456.30	367.30	4739.60	7.75
	5659.80	292.80	6048.00	4.84
	9115.80	987.00	9684.00	10.19
	5657.30	294.70	6308.00	4.67
	6882.60	133.20	7326.00	1.82
	6706.31±1799.54	419.66±296.28	7154.76±1843.05	5.71±2.88

Table 5. Characterization of As in source and sink of the experimental area.

	Total As (µg.kg^{-1})	i- As (µg.kg^{-1}) As-III	As-V	Organic As (µg.kg^{-1}) (DMA + MMA + As-B)
Source (µg.kg^{-1})	320.0	278.78	73.10	nd
Sink (Soil)	19400	900.15	13300.70	nd

nd = Not detected

Table 6. Assessment of risk for dietary exposure to As-contaminated rice.

	i-As conc. (mg.kg^{-1})	Daily rice consump-tion (g)	Weekly i-As ingestion (mg)	% PTWI for an 60 kg Adult
Boro rice	1.01	1564.80*	10.5	1166.67
Aus rice	0.46	1564.80*	5.02	557.77

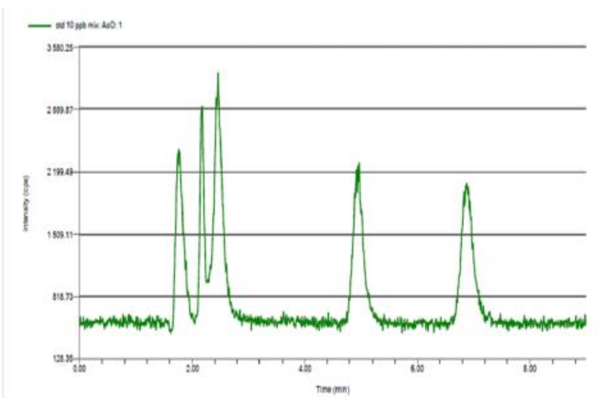
* National Nutrition Monitoring Bureau (NNMB) Diet Survey and Nutritional Status of rural population, 2006 (www.nnmbindia.org).

% to10.19 % (Table 4). Since rice is the main staple food in West Bengal, India, the possibility of arsenic ingestion through consumption of rice by people in the contaminated region cannot be ignored. The maximum daily consumption of the rice by an adult of 60 kg body weight is 1564.80 g (NNMB, 2006) and the maximum inorganic-arsenic accumulation in rice grain (recovered through the present study) is 1.01 mg kg^{-1}. The provisional tolerable weekly intake (PTWI) for inorganic-arsenic (WHO 2000, Safety Evaluation of Certain Food Additives and Contaminants) for a 60 kg adult is 900 µg and the weekly intake of inorganic-arsenic from rice for an adult accounts for 15.35mg, which leads to a risk associated with consumption of arsenic contaminated rice of 1166% of PTWI (Table 6).

CONCLUSION

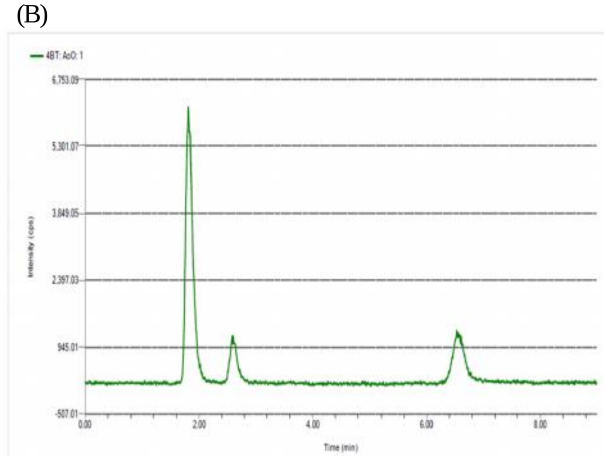
The results indicated that the recoveries of inorganic-arsenic is dominated by As(III) in rice grain and As(V) in rice straw, leading to a toxicity profile that presents more risk as there are higher levels of the more toxic As(III) in the edible portion. Recoveries of organic arsenic species in rice grain and straw without having any organic arsenic in the source and sink in detectable range emerged with possibilities of methylation of inorganic-As in the plant system. The order of arsenic species in rice grain revealed in this study were As-III (54.5 - 65.4 %) > As-V (21.2 - 28.3%) > DMA (5.2%) while in straw the order of As species were As-V > As-III > DMA.

(A)



RT (min)	Analyte	Species	Height (cps)	Area (counts)	Concentration µg/L
1.77	AsO	As-B	1 954.26	19 888.73	10.00
2.18	AsO	As-III	2 442.04	13 396.91	10.00
2.47	AsO	DMA	2 311.70	26 452.47	10.00
4.95	AsO	MMA	1 609.69	21 936.10	10.00
6.88	AsO	As-V	1 554.81	23 610.38	10.00

(B)



RT (min)	Analyte	Species	Height (cps)	Area (counts)	Concentration µg/L
1.82	AsO	As-III	5,855.36	49,585.54	18.79
2.61	AsO	DMA	952.60	8,638.56	2.59
6.54	AsO	As-V	1,004.82	12,707.86	7.98

Fig. 1. HPLC-ICP/MS chromatogram for As speciation in ((A) standard, (B) rice grain sample).

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