

Assessment of Potential Human Exposure to Arsenic in Imported and Locally Produced Rice in Kenya

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Abstract

Rice (*Oryza sativa*) is a potential dietary source of toxic arsenic. Rice accumulates ten times higher inorganic arsenic, a human carcinogen than other grains. It is one of the most consumed food crop not only in Kenya but worldwide. Human exposure to arsenic is of great concern. There is need for continual analysis of arsenic in rice. The main purpose for the study was to determine the content of arsenic in locally produced and imported rice. Locally produced rice was sampled from Ahero and Mwea Irrigation schemes, Kenya. The varieties of imported rice from Thailand, Pakistani and India were sampled from market outlets in Nairobi County, Kenya. The analysis was done using Hydride Generation Atomic Absorption Spectrometry (HG-AAS). The results showed that arsenic content in Kenyan ordinary grain (Sindano) and Basmati (Pishori) rice gave an average of 0.059043 ± 0.04 and 0.037124 ± 0.03 mg/kg respectively. Arsenic content in imported Basmati rice from Thailand, Pakistan and India showed average means of 0.1259 ± 0.01 , 0.0746 ± 0.01 and 0.062167 ± 0.02 respectively. Arsenic content in the imported Sindano variety from Thailand, Pakistan and India 0.15266 ± 0.02 , 0.175 ± 0.02 and 0.088372 ± 0.02 mg/kg respectively. Basmati rice from Thailand had significantly higher levels of arsenic than Basmati rice from Kenya. There was significant difference ($P < 0.05$) in arsenic content of locally produced rice from the imported rice ($P < 0.05$). However, there was no significant difference in levels of arsenic in the locally produced Sindano and Pishori rice varieties ($P > 0.05$). The levels were found to be below the WHO recommended levels of 1.0 mg/kg.

Keywords: Arsenic; Hydride Generation Atomic Absorption spectrometry (HG-AAS); Rice

Introduction

Arsenic (As) has been graded among the most carcinogenic element [1]. It occurs in the environment in various oxidation states such as, arsenate (+5); arsenite (+3); arsenic metal (0); arsine (-3) [2]. Arsenic compounds (Figure 1) occur both in organic and inorganic forms with inorganic form being quite toxic.

Due to its high solubility property in water, bioavailability of arsenic in rice is quite alarming since the crop is grown under anaerobic conditions [3]. Existence of Arsenic in the environment has been brought about by its natural occurrence and man activities. It is a major constituent in more than 100 minerals [4]. Those human activities that contribute highly to Arsenic in the environment are: application of arsenical fertilizers, manures especially from poultry and pork, burning of coal, mining processes and treatment of wood with chromate copper arsenate which eventually leaches into the environment [5,6].

Human exposure to arsenic occurs through water and food intake, and to a smaller extent absorption through the skin [7]. The time of exposure might lead to acute or chronic effects. In addition to being carcinogenic, arsenic is related to other adverse diseases such as

diabetes, neurotoxicity, skin lesions (Plate 1) and hyperpigmentation [8]. Arsenic in oxidation states III and V are able to get through the rice using the silicon and phosphate transporters [9-11]. In the anaerobic environment, arsenate is reduced to arsenite which is more toxic.

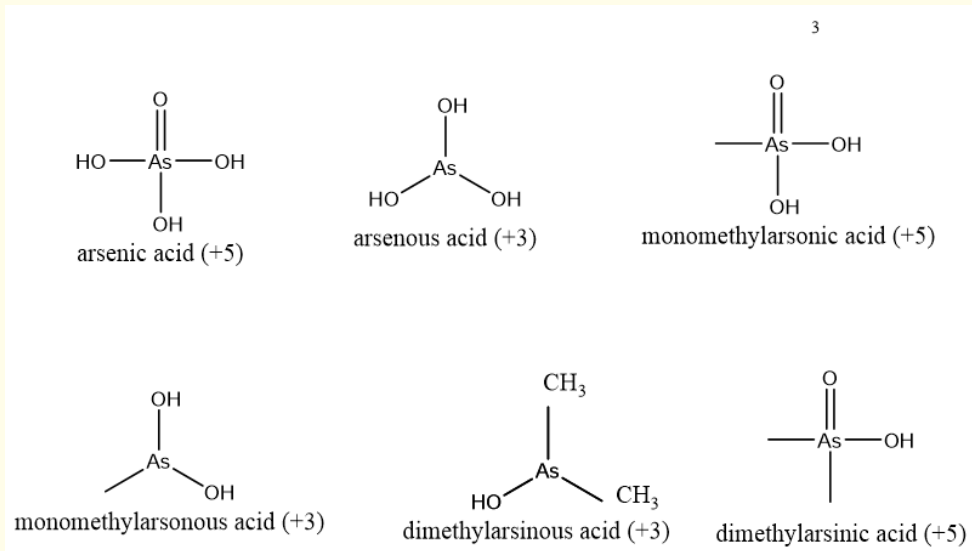


Figure 1: Arsenic compounds.



Plate 1: Skin lesions [8].

Arsenic has been analyzed in different types of crops such as barley, wheat, maize and pulse from different countries around the world [2,12]. Thailand being the main exporter of rice to many countries, arsenic levels have been analyzed on some of its rice varieties such as Jasmine, Sticky and white rice and their concentrations have been reported to be 0.125 ± 0.03 , 0.124 ± 0.0214 and 0.136 ± 0.0439 mg/kg respectively [13].

Rice is the third most important staple food from maize and wheat in Kenya. Kenya produces between 40,000 to 80,000 metric tons against the demand of 300,000 metric tons. The deficit is imported [14].

Aim of the Study

The aim of this study was to analyze the levels of arsenic in Sindano (IR-2793) and Pishori rice grown in Kenya and compare the levels with those in imported rice from Thailand, Pakistan and India.

Materials and Methods

Chemicals

The chemicals and the reagents used were of analytical grade. Concentrated hydrochloric acid, concentrated nitric acid, arsenic trioxide, sodium hydroxide, concentrated sulphuric acid, perchloric acid, sodium borohydride and sodium iodide were procured from Merck chemicals (Darmstadt, Germany) and Sigma Aldrich (St. Louis, MO).

Sample collection

Local rice samples were collected from Ahero and Mwea irrigation schemes whose maps are shown in figure 2 while the imported rice varies were sampled from Ngara, Eastleigh, Githurai and Kenyatta market outlets in Nairobi County, Kenya.

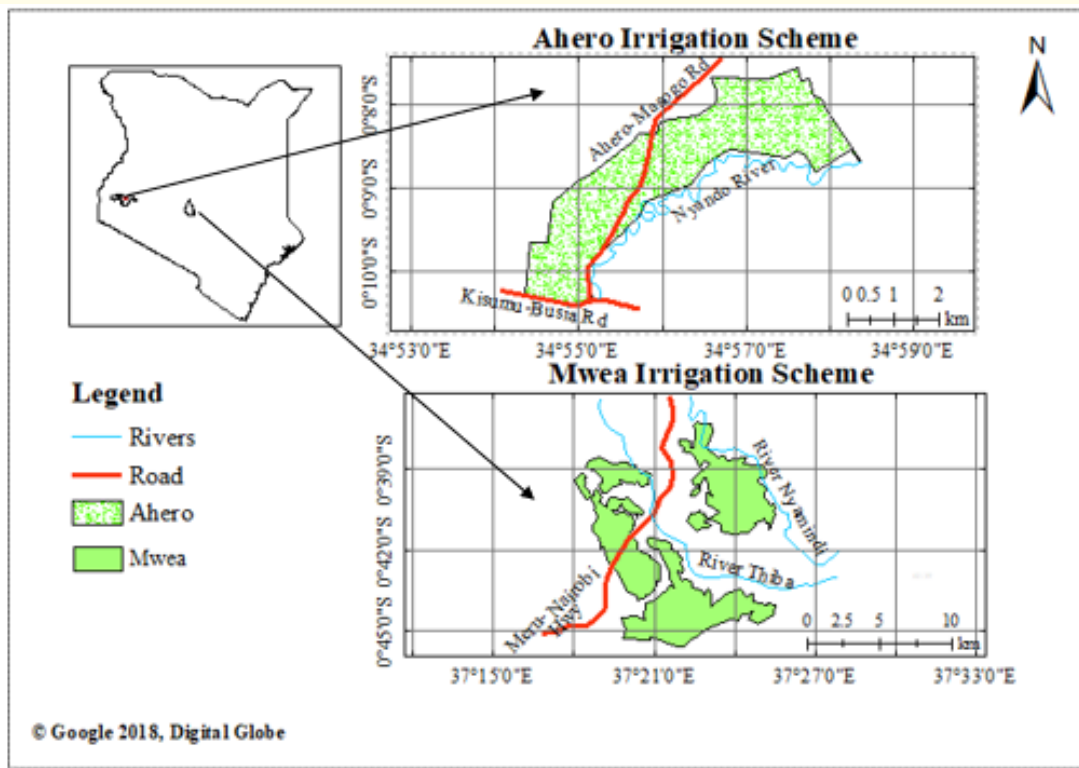


Figure 2: Maps showing location of Ahero and Mwea irrigation schemes.

Sample preparation

Rice samples were ground into powder using grinder and passed through a 2 mm sieve into a plastic container. The pulverized material was then oven dried for 10 hours at a temperature of 100°C and cooled in a desiccator.

Digestion of the samples

Rice digestion was performed following the wet digestion procedure [15] with slight modifications. 1g of sample was weighed on analytical balance and then placed into a 50 ml beaker. 5 ml of a mixture of nitric acid, sulphuric acid and perchloric acid in a ratio of 6:3:1 was added and stirred thoroughly then left to stand for about 8 minutes. Thereafter, the mixture was placed on a hot plate at a temp of 70° - 120°C for 8 minutes generating brown fumes of nitrogen (IV) oxide that were driven off, then cooled at room temperature. Subsequently, 20 ml of 5% HCl was added to the cooled sample. It was reheated for another 15 minutes at a temperature of 75°C. The digested sample was left to cool at room temperature then filtered through a Whatmann filter paper No.42 into 100 ml volumetric flask to obtain a clear solution. The solution was then topped up to the mark with deionized water and kept until use.

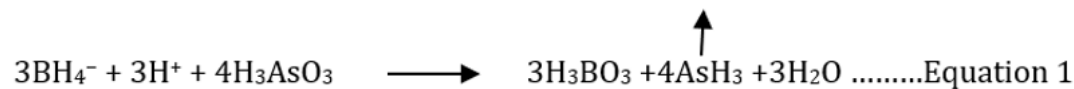
Hydride generation atomic absorption spectrophotometer (HGAAS)

Analysis of all the samples for arsenic content was done using Shimadzu Atomic Absorption Spectrophotometer (Model AA-6200 Germany), incorporated with Hydride Vapour Generator (HVG).

The conditions comprised: a quartz cell path length at 16 cm, 90.7 cm internal diameter, electro thermal heating cell temperature of 900°C, carrier gas argon flow rate of 50 - 100 ml/min, the reducing agent sodium borohydride (0.2% w/v) in 0.5% (w/v) sodium hydroxide solution at a flow rate of 5 to 7 ml/min and HCl flow rate of 9 to 11 ml/min.

Sample analysis

The sample solutions were treated sodium borohydride/hydrochloric acid for reduction of arsenate (+5) to arsenite (+3). Subsequently, generation of volatile arsine hydride is as indicated in equation 1.



The arsine hydride is then transported to the quartz cell by means of argon gas as a carrier gas. The hydrides are then converted to gaseous metal atoms in the heated quartz cell. Arsenic metal atom absorbs at a wavelength of 193.7 nm and at operated at a slit width of 0.7 nm of the HGAAS.

Preparation of arsenic standard stock solution

Arsenic standard stock solution of 100 mg/kg was prepared using 0.0132 g of arsenic (III) oxide which was diluted with 0.5M HCl in 100 ml volumetric flask. 2.5g sodium hydroxide was used to solubilize arsenic (III) Oxide.

Standard working solutions of 1 ng/g, 2 ng/g, 4 ng/g, 8 ng/g, 12 ng/g, 16 ng/g and 20 ng/g were prepared by serial dilution of the stock solution using ultra-pure water. The standards were then read in a HG-AAS and a calibration curve of a good linearity was obtained (R² = 0.9991) as shown on figure 3.

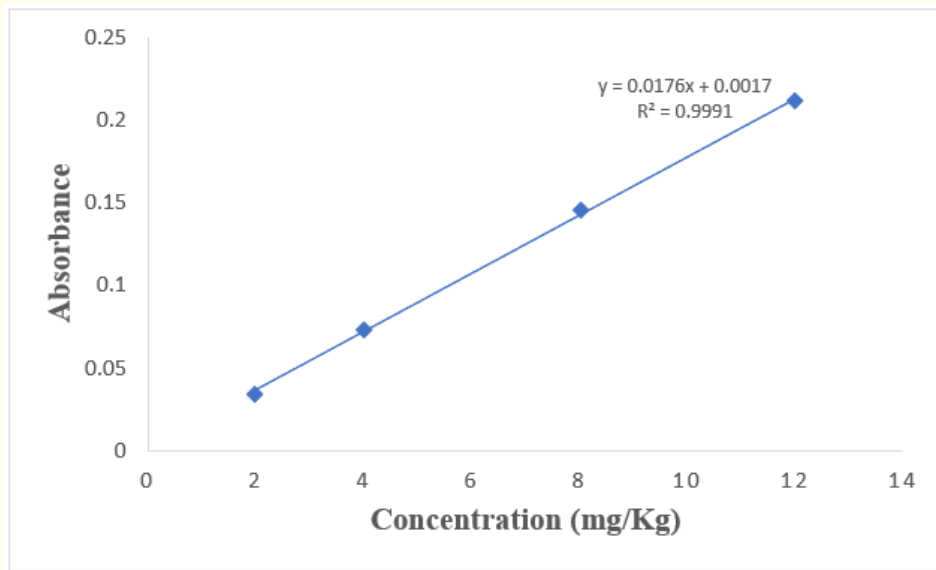


Figure 3: Arsenic calibration curve.

Method validation

The accuracy for the determination of total arsenic in rice samples fortified with arsenic mixture at four concentrations was assessed as a percentage recovery. The % recovery was calculated as per the method by [16] as shown below.

$$\%R = \frac{\text{Spiked Sample Conc} - \text{Unspiked Sample Conc}}{\text{Spike Concentration}} \times 100$$

Where, R=Recovery

The precision of the method was expressed as a relative standard deviation (%RSD):

$$\%RSD = (SD/X) \times 100 \text{ where SD and X represent standard deviation and mean respectively.}$$

The calculated values are given in table 1.

Sample	Recovered concentration (mg/kg)	% Recovery	% RSD
I	0.0388 ± 0.001	98	2.5
II	0.0412 ± 0.001	101	2
III	0.0458 ± 0.002	105	4
IV	0.0486 ± 0.002	98	4

Table 1: % recovery and % RSD.

The percentage recoveries obtained were close to 100% hence the method was accurate for quantification of As levels in the three types of test samples [13]. The % RSD values were below 5%, an indication good precision.

Statistical analyses

The data was expressed as mean of three times experiment (n = 3) ± SD (standard deviation).

The means of arsenic content in rice grains were compared between two sets of values using one- way ANOVA by Turkey’s HSD test. All the statistical analysis was done with SPSS version 21 software.

Results and Discussion

The arsenic content in the locally produced Sindano and Pishori rice is shown in table 2 and 3.

Sample ID	Arsenic concentration (mg/kg)
KS1	0.0142 ± 0.001 ^b
KS2	0.1072 ± 0.010 ^b
KS3	0.0337 ± 0.000 ^b
KS4	0.0662 ± 0.010 ^a
KS5	0.0039 ± 0.000 ^b
KS6	0.1563 ± 0.010 ^a
KS7	0.02197 ± 0.00 ^b
KS8	0.0942 ± 0.001 ^a
KS9	0.0377 ± 0.000 ^b
KS10	0.0631 ± 0.000 ^a
KS11	0.1327 ± 0.000 ^a
KS12	0.1354 ± 0.010 ^a
KS13	0.0283 ± 0.000 ^{ab}
KS14	0.0665 ± 0.010 ^{ab}
KS15	0.0437 ± 0.000 ^{ab}
Overall Mean	0.0590 ± 0.040

Table 2: Arsenic concentration (mg/kg) in Sindano rice (IR-2793).

Means ± SD followed by same letters, a, b, are not significantly different at 95% confidence level.

Sample ID stands for sample identification.

Sample ID	Arsenic concentration (mg/kg)
KP1	0.0047 ± 0.000 ^b
KP2	0.0665 ± 0.000 ^a
KP3	0.0102 ± 0.001 ^b
KP4	0.0381 ± 0.000 ^b
KP5	0.0304 ± 0.000 ^b
KP6	0.0039 ± 0.000 ^b
KP7	0.0772 ± 0.010 ^a
KP8	0.0609 ± 0.000 ^a
KP9	0.0097 ± 0.000 ^b
KP10	0.0306 ± 0.001 ^b

KP11	0.0035 ± 0.001 ^b
KP12	0.1354 ± 0.010 ^a
KP13	0.0051 ± 0.001 ^b
KP14	0.0662 ± 0.000 ^a
KP15	0.0105 ± 0.000 ^b
Overall Mean	0.0371 ± 0.030

Table 3: Arsenic concentration (mg/kg) in Pishori rice.

Means ± SD followed by same letters are not significantly different at 95% confidence level.

Sample ID stands for sample identification and KP for Kenyan Pishori rice samples.

The arsenic levels of Sindano (IR-2393) rice ranged from 0.00397 ± 0.00 to 0.156325 ± 0.01 mg/kg with an overall mean of 0.059043 ± 0.04 mg/kg and a median of 0.0437 (mg/kg). Arsenic content in Pishori rice variety ranged from 0.003543 to 0.135377 mg/kg with an overall mean of 0.037124 ± 0.03 mg/kg. Arsenic concentration in SindanoR-2393) and Pishori (Basmati) rice varieties were not significantly different (P > 0.05). This could be attributed to same soil chemical factors which may not be significantly different [17]. The range and the mean of Arsenic content in Pishori (aromatic) rice had a similar trend with levels of Arsenic content in aromatic Basmati rice from Sylheti region in Bangladesh, which ranged between 0.0101 to 0.125 mg/kg with a mean of 0.048 ± 0.043 mg/Kg [18]. According to studies done in India, different rice varieties exhibited different levels of arsenic accumulation [7]. However, rice of different varieties in Thailand exhibited no significant difference in levels of arsenic [13].

Arsenic levels in the imported rice

The levels of Arsenic content in sampled Sindano and Basmati rice imported from India are given in table 4.

Sindano Variety		Basmati Variety	
Sample ID	As Conc (mg/kg)	Sample ID	As conc (mg/kg)
IS1	0.136 ± 0.010 ^b	IB1	0.025 ± 0.001 ^b
IS2	0.133 ± 0.005 ^b	IB2	0.078 ± 0.000 ^a
IS3	0.136 ± 0.001 ^b	IB3	0.072 ± 0.002 ^a
IS4	0.081 ± 0.001 ^a	IB4	0.048 ± 0.000 ^b
IS5	0.080 ± 0.000 ^a	IB5	0.010 ± 0.0001 ^b
IS6	0.071 ± 0.001 ^a	IB6	0.060 ± 0.000 ^a
IS7	0.077 ± 0.002 ^a	IB7	0.089 ± 0.002 ^a
IS8	0.078 ± 0.003 ^a	IB8	0.062 ± 0.001 ^a
IS9	0.080 ± 0.001 ^a	IB9	0.066 ± 0.003 ^a
IS10	0.080 ± 0.002 ^a	IB10	0.072 ± 0.000 ^a
IS11	0.054 ± 0.000 ^a	IB11	0.086 ± 0.003 ^a
IS12	0.0536 ± 0.00 ^a	IB12	0.078 ± 0.000 ^a
Overall Mean	0.088372 ± 0.02	Overall Mean	0.062167 ± 0.02

Table 4: Arsenic concentration (mg/kg) in imported Indian rice to Kenya.

Means ± SD with same letters are not significantly at 95% confidence level.

Sample ID stands for either Sindano or basmati rice samples

Arsenic concentration in Sindano rice from India ranged between 0.136 ± 0.001 and 0.0536 ± 0.000 mg/kg with an overall mean of 0.0883 ± 0.02 mg/kg while the concentration in Basmati rice ranged from 0.010 ± 0.0001 to 0.089 ± 0.002 mg/kg with an average of 0.0621 ± 0.02 mg/kg. There was no significant difference in the levels of arsenic in Sindano rice from India and locally produced Sindano (IR-2793) rice ($P > 0.05$). The locally produced Basmati (Pishori) rice had significantly lower levels of arsenic than Basmati rice from India ($P < 0.05$).

Similarly, the arsenic concentration in Sindano rice imported from Thailand and Pakistani was 0.153 ± 0.02 mg/kg ($N = 25$) and 0.175 ± 0.02 mg/kg ($N = 21$) respectively, while arsenic content in Basmati rice from the two countries was 0.126 ± 0.01 mg/kg ($N = 25$) and 0.0746 ± 0.01 mg/kg ($N = 23$) respectively. The Arsenic concentration in imported Sindano rice from Pakistan was significantly higher than Sindano rice from India ($P > 0.05$). These levels were significantly higher than the locally produced Sindano (IR-2793) and Pishori rice ($P > 0.05$).

Figure 4 shows the comparison of Arsenic levels in Sindano and basmati rice varieties produced in Kenya and imported from India, Pakistan and Thailand. The Arsenic in the locally produced Sindano rice was significantly lower than the imported Sindano rice from Pakistan and Thailand. The levels of arsenic in Kenyan Basmati (Pishori) rice was significantly lower than the imported Basmati rice from the three countries.

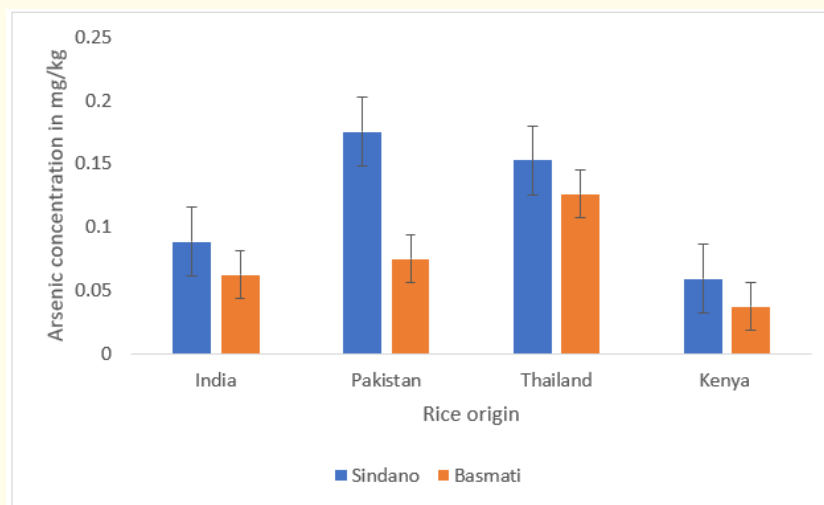


Figure 4: Arsenic concentration in imported and the Kenyan rice.

Conclusion

The Arsenic content in the locally produced Sindano (IR-2793) and Basmati (Pishori) rice was 0.0590 ± 0.04 and 0.0371 ± 0.03 mg/kg respectively. The levels were below the WHO recommended level in rice grains of 1.0 mg/kg. The Basmati rice variety from India, Pakistan and Thailand had mean arsenic levels of 0.0622 ± 0.02 , 0.0746 ± 0.01 and 0.126 ± 0.01 mg/kg respectively. These levels were also below the WHO safe limits. The arsenic content in Basmati rice from Thailand was significantly higher than in Kenyan aromatic Pishori rice. Though the levels were within the WHO recommended arsenic levels in rice grains there is need for continual analysis of Arsenic in rice due to seasonal variations.

Conflicts of Interest

The authors declare no conflict of interest.

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