Review Article

Arsenic in rice: An emerging challenge in context of food security

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Abstract: Arsenic speciation in food and diet is assessed for human exposure through dietary approaches because arsenic exposure is a critical public health issue all over the world. Globally, rice is a vital commodity for world hunger reduction and vastly important for the survival of the human race. Rice is widely used for the formulation of baby formulas, breakfast cereals, bread, cookies, cakes, rice drinks and other foodstuff. Arsenic is concentrated at a higher rate in rice as compared with other cereal grains and contains more than 85% of total arsenic forms, which poses serious health aliments to human as well as animal life on the planet. In addition, arsenic-contaminated water and soil may induce hazardous effects to humans through the water-soil-plant pathway.

Keywords: rice; arsenic; health threat; food safety; metabolic disorders

1. Introduction

The analysis of the elemental composition of food is an effective approach to establishing a suitable pattern for consuming nutrients as well as identifying their toxic exposure limit. The level of toxicity of any metals present in our daily diet or food cannot be measured from metal concentration. In some regions of Pakistan, for example, the presence of arsenic above the acceptable limit (10 ppb) has been demonstrated in drinking water and thus is a potentially critical concern regarding public health^[1].

2. Arsenic

Arsenic is a pure elemental crystal comprised of different minerals, especially in conjunction with sulfur and other metals. It was first documented by Albert Magnus in 1250 and exists in various allotropes. It is the 53rd most abundant element and makes up 1.5 ppm of the earth's crust. The concentration of arsenic in soil and seawater is 10 ppm and 1.6 ppb, respectively. Arsenic is ubiquitous in the environment as trivalent arsenate and pentavalent arsenate, which are more hazardous irrespective of monomethylarsonate (MMA) as well as dimethyl arsenate (DMA). Arsenic is notoriously poisonous to all living organisms, although a few bacterial species respire arsenic. Geological conditions, genetic factors and manmade activities, such as the increased use of vehicles, the production of smoke, the application of agrochemicals and the deposition of industrial effluents, have led to the contamination of underground water and soil, which ultimately deteriorate agriculture commodities^[2,3].

3. Presence of arsenic in soil, water and plants

Total arsenic (As) concentration varies from 10 ppm to several thousand ppm in the soil according to areas, whereas in terrestrial plants the concentration depends on the soil's As contents and the plant's uptake or accumulation ability. Plants growing on contaminated sites can have up to 1000 ppm As compared with

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uncontaminated plants, which contain 0.2 to 0.4 ppm. The presence of inorganic arsenic is predominantly in terrestrial foods and minorly in marine food^[4].

It is critical to assess the hazards of dietary arsenic. Arsenic, as a toxic metalloid, is present in irrigated water up to a certain safe limit i.e., 10 ug/L and 100 ug/L, as proposed by the United Nations' World Health Organization (WHO) and Food and Agriculture Organization (FAO), respectively. The occurrence of arsenic from natural and artificial processes above the safe level is a serious concern to food security^[5,6].

Arsenic toxicity affects the photosynthesis of plants and ultimately decreases plant growth and yield in promising rice varieties. The plant's roots are the most efficient accumulator of arsenic than rice straw and leaf, where the husks or outer protective coverings contain more arsenic than the rice grains. As the byproduct of the rice milling industry, rice straws are a major agricultural source and are used as the main ingredient in cattle feed. Hence, cattle feed rich in arsenic poses a direct threat to animal life and indirectly affects humans via animal meat, milk and others^[7].

Edible plants are well-recognized sources of As contamination in Asian countries, such as India, Bangladesh and Pakistan, as well as in Latin America, thus posing a health risk to inhabitants. It is obvious that long-term exposure to As intake through water and plants adversely affects the production and quality of food. Cultivation methods, plant composition, morphology, soil physiology and identification of arsenic form are essential factors contributing to As uptake in food^[7].

4. Rice

Agriculture is the major profession among masses around the globe and occupies 37% of land areas. Rice is a staple diet that feeds over half of the world's population. Rice is a water-loving plant and requires groundwater as the irrigated source from its establishment till further operations in the fields. It is one of the major sources of carbohydrates (70%), proteins (6%–9%) and vitamins (1%). Rice grains have strong potential as anti-oxidant, anti-inflammatory and anti-allergic agents and are widely consumed for health promotion and wellbeing. The rice plant has a circular breathing system of taking oxygen in directly through surface leaves to provide oxygen to the stalks and leaves underwater for the growth of the root system, and then releases carbon dioxide into the water. Globally, rice is a vital commodity for world hunger reduction and vastly important for the survival of the human race. Rice consumption among the Asian population has exceeded 100 kg/capita annually. Rice contributes about 50% of the global energy supply to humans. Rice is widely used for the formulation of baby formulas, cakes, rice milk, beverages and other foodstuff for vulnerable groups having metabolic disorders. However, such products may contain As and may enhance the severity of diseases in individuals relying on these food items^[8].

5. Arsenic in foods

Cereal and cereal-based products are chief contributors to arsenic exposure in humans. According to data collected on exposure to the population, arsenic is nominated as a Class I human carcinogen^[9]. Naturally occurring organ arsenic compounds are non-toxic^[10]. Arsenic speciation in food and diet is evaluated and assessed for human exposure through dietary approaches^[11].

5.1. Arsenic in rice

Approximately, 90% of arsenic is present in rice plants in various forms, i.e., As III, As V and DMA. All these forms are responsible for cancer propagation due to specific routes for their entry through silicic and phosphate transporters^[12]. Firstly, arsenic accumulates in rice plants' roots and then moves towards the shoots, leaves and grains due to the formation of phytochelatin complexes between metals and the sequestration within

the cell vacuoles of rice. The anaerobic system of rice cultivation under flooded conditions is one of the major reasons for the higher arsenic concentration of up to ten folds in rice as compared with other cereal grains such as wheat, barley and maize, which grow best in an aerobic environment^[13,14].

It is obvious from previous findings that total As concentration depends on the rice cultivar. Brown rice contains more arsenic as compared with polished rice. The endosperm of rice contains the least amount of arsenic as compared with the bran and husk. Brown rice is a famous food due to its all-natural characteristics and nutritional benefits, but at the same time it is not known to be safe for infant diet. Hence, the quality and safety of designer foods should be wisely monitored before consumption^[15]. It is concluded that only white rice with a lower As content should be incorporated in the manufacturing of baby foods^[16,17].

Arsenic accumulation in food crops has become a serious public health problem. In 2014, CODEX/FAO established a maximum limit for polished rice (0.2 mg/kg). In 2016, CODEX recommended that brown rice or cargo rice (rice without husk only) should not contain more than 0.35mg/kg arsenic. Foods prepared from rice and its flour are gluten-free and alternatively consumed by celiac patients, gluten-intolerant individuals and people suffering from severe allergies as well as lactose intolerance. In the Western population, up to 1% of individuals including children and people of old age (over 65 years) are celiac patients. Celiac disease is an immune-mediated allergy linked with the malabsorption of nutrients and vitamins due to an abnormal response to gluten, which harms the small intestinal lining of children during infancy and adolescence. Rice and its products are the main edible alternative for wheat-based products because of the lack of gluten. Pre-cooked milled rice is commonly used for weaning purposes owing to its bland taste, discoloration, low allergens and high nutrition value^[18].

Twelve rice samples were collected from local markets in Australia for the determination of arsenic via inductively coupled plasma mass spectrometry (ICP-MS). The mean concentrations of As ranged from 0.026 to 0.464 ppm in all rice samples. The variation among As concentrations was due to the differences in geographic origins. American rice contained the highest arsenic (0.25 mg/kg), followed by Thai rice (0.20 mg/kg), Pakistani rice (0.14 mg/kg), Indian rice (0.10 mg/kg) and Egyptian rice (0.09 mg/kg). Some varieties under study contained hazardous concentrations of toxic elements. There is a dire need for concerned authorities to regulate and monitor the arsenic content in paddy fields for the improvement and protection of public health. Millions of subjects are exposed to As toxicity through water in Bangladesh and West Bengal. Skin diseases, cancer risks and potential effects on the development of children have become the basis for arsenic regulation. According to Codex, the maximum permissible limit of 0.2 mg/kg was established for freshly milled rice^[19].

Approximately 75%–90% of arsenic found in the analysis of rice products are inorganic As species. Liquid rice products, including oil, rice milk and vinegar, contained 0.01 to 0.03 ppm of As, which is lower than solid rice products. The reduction in arsenic was probably due to the dilution of rice As with water during processing. Rice milk is used as a beverage in contrast to cow milk, and thus a monotonous intake can lead to an elevated dietary As among subjects.

Arsenic toxicity in irrigated groundwater used for rice cultivation is more prevalent in South and Southeast Asian countries. Asian rice contains the highest fraction of inorganic As species due to its higher toxicity, bioavailability and bioaccessibility. Therefore, Asian rice is considered to be a serious health hazard for the local population, as well as for others who consume rice imported from these regions. A higher level of As was found in rice grains grown in contaminated soil. Cooked rice contains more As concentration if the cooking is done in contaminated water^[20].

and corn grits due to the lower arsenic content^[21].

5.2. Baby foods and arsenic

Rice is the complementary ingredient in many baby foods as well as the first food for American babies. In an internal analysis, 200 rice samples for baby foods were examined for their arsenic contents and compared with substitutes, such as oatmeal. Infants fed with 2 or 3 servings of rice per day were prone to cancer risks twice the acceptable level. It was suggested that babies are only fed rice cereal no more than one serving per

Long-grain rice (8 varieties) and baby foods prepared from rice (n = 10) in the Finland market were evaluated for inorganic and total arsenic contents by using the high-performance liquid chromatography–inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) system. The mean values for inorganic As levels varied from 0.09 to 0.28 mg/kg and 0.11 to 0.13 mg/kg for long-grain rice and baby foods, respectively. The total arsenic concentration ranged from 0.11 to 0.65 mg/kg and 0.02 to 0.29 mg/kg for long-grain rice and baby foods. This indicated that, in each age group, the As intake is quite close to the lowest detection limit in the body, i.e., 3 ug/kg body weight/day, set by the European Food Safety Authority (EFSA)^[22].

week and that parents diversify their child's diet and endorse the consumption of other food made from oat

In another study of US children, it was found that every 1/4th-cup increase in cooked rice consumption enhanced the urinary arsenic concentration by 14 folds. Arsenic toxicity in early life is connected with deprived growth and other harmful consequences, including high blood pressure and kidney malfunction. According to the Food and Drug Administration (FDA), there is no authentic evidence that rice cereal is not superior to other grains as the first solid food^[23]. The total As concentration present initially in rice does not change during processing for the production of rice foods and ultimately reaches the end consumers. There is a need to pay extraordinary attention to infants and kids due to their weak and underdeveloped immune system to arsenic toxicity. Children with celiac disease are more prone to As contamination due to the intake of baby formulas and weaning foods^[24].

In a research study, 103,773 food samples were collected from European countries and analyzed by the EFSA for the estimation of As exposure through food intake. After the analysis, the EU established the maximum legal threshold of As in white rice at 0.2 mg/kg, parboiled rice at 0.25 mg/kg, baby foods at 0.1 mg/kg and wafers, cookies or cakes at 0.30 mg/kg. Furthermore, the FDA also proposed a legal limit of As for infant rice cereals at 0.1 mg/kg. The government of China has set the maximum value for inorganic arsenic in rice at 0.15 mg/kg^[25].

Rice cooking in As-contaminated water increases the complexity of contamination. In some countries, rice fortified with iron, zinc and folate involves no rinsing or water drainage before cooking to prevent nutrient loss. However, in other countries, rice is washed thrice, cooked with plenty of water and then drained, which significantly increases human exposure to As due to the strong binding between rice proteins and inorganic arsenic^[26]. Rice grown in flooded conditions accumulates higher levels of As in grains than other plant species. In a study, it was suggested that the bioavailability of iron and zinc in milled rice grains significantly affects heavy metal contents. Many other researchers are trying to improve the bioavailability of minerals and other staple foods to maintain the nutritional profile and also reduce As accumulation^[27,28].

In a Japanese study, the effects of polishing, cooking and storing on the total As content in rice were evaluated. Total As was reduced to 65% in white rice polished using 10% bran removal, whereas 50% removal of As was observed in brown rice with the bran layer. Moreover, the As level in white rice after washing three times with deionized water decreased to 80% and 75% compared with raw rice without washing. The effect of rinsing on As was quite similar for brown rice. Rice cooked in a low volume of water (2:1 water-to-rice ratio) did not remove As, while brown rice stored for one year exhibited stable As content^[29]. The level of As was

very heterogeneous in rice, ranging from 0.01 to 0.8 ppm, according to the transfer coefficient of As from the grain to the soil of $0.1^{[30]}$.

Rice and bulgur (parboiled wheat product) samples (5 g) were analyzed for arsenic speciation via the HPLC–ICP-MS system, followed by the collection of exposure-related information among participants (14–75 years old) in Turkey. Both samples were dominated with inorganic arsenic, but more concentration was found in rice samples (160 mg/kg) than in bulgur samples (30 mg/kg). For individuals with more consumption of rice, As exposure is higher, resulting in carcinogenic risks. The average rice intake by an individual is 9 and 278 g/day in Europe and Asia, respectively^[31]. Rice cooked in abundant water with the extra water discarded has shown a lower As level than raw rice, while cooking with limited water (steaming) does not affect As concentration. Rice bran and its products contain 10–20 folds of As and hence possess more detrimental effects^[32].

It was reported that As intake through rice was high in some Indian areas because of the presence of arsenic in drinking water, as indicated by the off-flavors developed in rice grains due to significant arsenic content. Rice crops cultivated on soil enriched with arsenic were also a source of arsenic, with more accumulated elevated levels of As than those cultivated in normal soil and water. Rice products from various categories were analyzed for the average As level, which showed that the mean values for arsenic ranged from 0.14 to 0.28 mg/kg for solids foods and 0.12 to 0.47 mg/kg for baby foods due to extensive geographic differences among Indian, EU and US rice.

6. Measurement of arsenic

High-performance liquid chromatography is a versatile and rapid monitoring method for the measurement of total inorganic and organic arsenic in rice. It is further equipped with inductively coupled plasma–mass spectrometry. Various forms of arsenic can be identified and eluted at the same retention time and completely separated via an isocratic elution program set on a reverse-phase column. This is the latest and a reliable analytical procedure for the efficient estimation of arsenic from biological tissues of rice based on the hydride generation–atomic absorption spectrometry. Nowadays, non-chromatographic methods are also introduced for the determination of inorganic arsenic due to ease of working and simplicity^[33,34].

7. Strategies for mitigation of arsenic

The screening of rice cultivars with low As accumulation should be fully implemented with other workable solutions to mitigate the threat. Furthermore, simple recommendations should be revised for rice processing of infant food to significantly reduce As exposure^[35].

Rice grown in unsaturated soils has a lower content of arsenic compared with those cultivated in flooded conditions in Mediterranean climates. Rice production is increased through an efficient water management system. Successive sprinkle irrigation for 7 years decreased total As concentration to one-sixth of its initial value in flooded irrigation (0.55 to 0.09 ppm), whereas one cycle of sprinkle irrigation reduced 0.20 ppm of As. Moreover, both irrigation techniques do not affect crop yields (3000 kg/ha). It was suggested that changes in the water regimes of rice fields seem to be beneficial against excessive arsenic accumulation as well as having a valuable impact on food safety and the conservation of water resources^[36,37].

The best demonstrated technologies for the treatment of sites contaminated with heavy metals are immobilization, soil washing and phytoremediation. Low-cost and sustainable options are required to restore contaminated lands in countries with a greater population index and scarcely available funds to enhance food security. Due to diverse soil chemistry, heavy metals exert low to severe toxic effects on plants according to their concentration in the soil. Arsenic is a metalloid as well as a hazardous element in soil. Arsenic toxicity is assessed on the basis of its impact on plant and human health^[37]. Silica and phosphate fertilization in soil is suggested to decrease the uptake of arsenic through soil and irrigation water to rice plants^[38].

Arsenic accumulation in rice plants can be reduced by modifying specific genes that perform functions such as uptake, transport and detoxification. Therefore, genetic modifications are of much importance for crop improvement in terms of breeding resistant varieties and revealing how these varieties metabolize. By using effective and practical approaches, such as genetic engineering, rice crops with a low arsenic content can be produced. Additionally, other strategies, including methylation and volatilization, have been employed to minimize the exposure of arsenic in rice cultivars because these processes sequester arsenic in plant vacuoles and detoxify plant parts. Some biologically active rice cultivars have a minimum amount of arsenic, i.e., 20–30 folds less than others due to the development of blockage pathways for uptake, translocation and accumulation of this toxic element in rice grains^[14,39].

In a recent Korean symposium, existing techniques for lowering heavy metals were evaluated, as well as their pros and cons in the rice cropping system, paddy soils, rice cultivars and irrigation process. An integrated approach was established that involved a combination of remedial options and the water management system with economically and technologically feasible methods for the mitigation of As levels. Filtration through absorbents (iron-oxide-coated sand) represents an emerging and effective way to treat arsenic-contaminated aqueous solutions without any drawbacks. Important parameters for absorption are pH, contact time, adsorbent dose and initial As concentration. It is suggested that 5g/L of iron-oxide-coated sand could efficiently remove 100 ug/L of arsenic from a solution, and the method is advantageous due to its availability, low cost and better performance^[40].

8. Conclusion

Rice is a major dietary source as well as a staple food for many populations. Rice produced multiple processed foods including syrups, bars, breakfast cereals, cookies and crackers as well as vital component of baby cereals, i.e., first solid food at infancy. Meanwhile, epidemiological studies reported the strong association between rice consumption and human health ailments due to presence of higher arsenic concentrations. Additionally, higher rice intake may increase the risk of certain chronic diseases such as diabetes, cancers, cardiovascular conditions and skin lesions. Thus, it is important to address the health challenges and impacts originated from arsenic ingested food and drinking water especially in remote areas. In future studies should be more focused to measure the arsenic levels in biological specimens to further understand the health effects of dietary arsenic and protect the masses from rice heavy diets.

Conflict of interest

The authors of the article have no conflicts of interest to declare.

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