Review

Presence of arsenic in agricultural products from arsenic-endemic areas and strategies to reduce arsenic intake in rural villages

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About 100 million rural people in Asia are exposed to arsenic (As)-polluted drinking water and agricultural products. Total and inorganic arsenic (t-As and i-As) intake mainly depend on the quality of drinking and cooking waters, and amounts of seafood and rice consumed. The main problems occur in countries with poor water quality where the population depends on rice for their diet, and their t-As and i-As intake is high as a result of growing and cooking rice in contaminated water. Workable solutions to remove As from water and breeding rice cultivars with low As accumulation are being sought. In the meantime, simple recommendations for processing and cooking foods will help to reduce As intake. For instance, cooking using high volumes of As-free water may be a cheap way of reducing As exposure in rural populations. It is necessary to consider the effects of cooking and processing on t-As and i-As to obtain a realistic view of the risks associated with intake of As in As-endemic areas.

Keywords: Cooking / Drinking water / Inorganic arsenic / Rice / Seafood

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1 Introduction

The countries with the highest daily intake of total arsenic (t-As) are Spain and Japan followed by India and France, as shown in Fig. 1 [1–12]. Reviewing the scientific literature, there are several papers stating that the world's two most significant cases of As contamination where the population suffers the most are located in Asia, particularly in Bangladesh and West Bengal in India [13, 14] At this point, the reader cannot be sure about what makes the cases in Bangladesh and India different and more special to those in Spain or Japan, for instance. The answer to this initial question is quite clear: the speciation of As which is related to the different sources of As. In general, As from seafood is organic (o-As) while As from drinking water and vegetables is inorganic (i-As). Therefore, dietary As can be categorized by As species (*e.g*. organic *vs*. inorganic) and by source (seafood *vs*. vegetables, mainly rice) [15].

2 As endemic areas and As sources

In evaluating the significance of exposures to i-As, it is important to consider the range of background exposures. Because As occurs naturally in the environment and is present in most food, As exposure is a typical part of everyday life. Drinking water and diet are generally the most significant sources of background exposure [16].

At this point, it is interesting to distinguish among three different situations. The first is represented by Spain (but could also be represented by Japan), where seafood is the main source of As in the diet, and theoretically “nontoxic” o-As is the predominant As form. The second is represented by Chile, where drinking water is the main source although vegetables also contribute to the daily intake. The third example is West Bengal (India), where cooked rice plays an important role together with drinking water.

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Abbreviations: **As,** arsenic; **DMA,** dimethylarsinic acid; **i-As,** inorganic arsenic; **MA,** monomethylarsonic acid; **o-As,** organic arsenic; **PTWI,** provisional tolerable weekly intake; **t-As,** total arsenic; **TDI,** tolerable daily intake; **ww,** wet weight

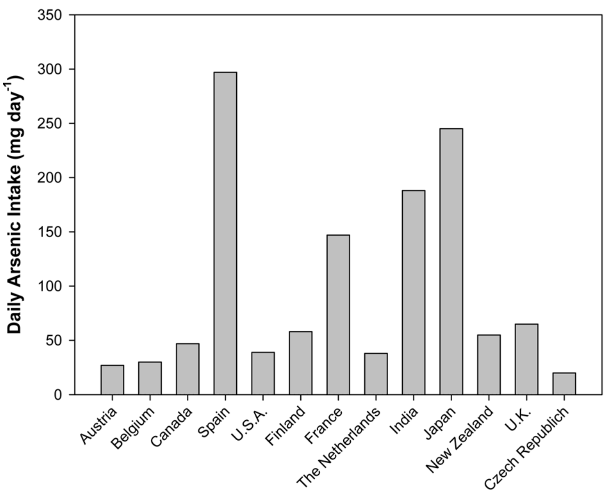

Figure 1. Daily As intake around the world.

2.1 Spain: Seafood

In 1990 the Health Department of the Basque Government started a total diet study. Its purpose was to provide estimates of the average intake of constituents of concern, including heavy metals and metalloids [17]. Between1990 and1995, the average intake of t-As in the Basque Country was 297 μg/day which was higher than estimated in all other countries in the literature, including Japan (280 μg/day) [17]. The main food group contributing to the As intake was the fish and seafood group (96%). Of the remaining composites, only the alcoholic beverages group contained measurable levels of As, with a mean concentration level of 4 μg/kg compared to the 3217 μg/kg of fish [17].

As seafood is an important part of the Spanish diet (and other Mediterranean countries); trace elements from fish contribute significantly to trace element intake of the Spanish consumer [17].

Results from As speciation of Basque seafood and fish indicated that 84–100% of the As was present as arsenobetaine and the maximum i-As detected was 5% of t-As, which only accounts for 10% of the provisional tolerable weekly intake (PTWI) for i-As (15 μg/wk/kg weight) [18].

More recently, in our laboratory (Universidad Miguel Hernández, Spain) the i-As content of commercial Spanish canned and frozen seafood and fish samples was quantified and found that only 8.0 and 5.7% of the t-As was present as i-As in canned seafood and frozen fish, respectively (data not published). These recent results come from the Valencian Community (south-eastern Spain) and agree with those previously obtained in the Basque country.

The vast majority of As in fish and seafood is in the form of arsenobetaine, a compound that is essentially inert, nontoxic, and excreted without transformation. Until a few years ago, it was generally admitted that the quantities of monomethylarsonic acid (MA) and i-As were sufficiently small to mitigate concerns about their possible adverse effects in seafood eaters [19]. However, Borak and Hosgood [15] concluded that because the ingestion of seafood may lead to the generation of metabolites such as dimethylarsinic acid [DMA(V)] from decomposition of initial arsenosugars and arsenolipids involved in As-induced carcinogenesis, it is worthwhile to consider the potential role of dietary seafood in long-term cancer risk.

To summarize, in Spain the main source of As in the diet is sea products (seafood and fish). Total As intake is well above that of most countries; however, i-As intake accounts for only approximately 10% of the PTWI. Although t-As is high, exposure to this metalloid appears not to pose appreciable risk to human health because most of the As is present as nontoxic o-As.

2.2 Chile: Drinking water

Díaz *et al*. [20] studied the contribution of water, bread, and vegetables to the dietary intake of As in a rural village in northern Chile. Because of geological factors, the Second Region in Chile presents an environment with high As concentrations. In this region, concentrations of As reaching 1099 mg/kg have been detected in the soil, and levels attaining 11.25 mg/L have been found in aquifers [21]. Díaz *et al*. [20] studied foodstuffs in two different periods, in which the water used by the population for drinking and cooking purposes contained 0.572 (first period) or 0.041 μg/mL (second period). The food studied contributed 5% (first period) or 30% (second period) to the t-As intake. Their final conclusion was that the significance of the intake of As from food increases as the concentration of As in water decreases. This shows that failure to consider the contribution of food intake of t-As and i-As could introduce a substantial bias into the estimation of risks for the population of As-endemic areas [20]. In the first period, the FAO/WHO reference intake was exceeded by all of the persons interviewed while in the second period, the reference intake was only exceeded by persons interviewed aged between 13 and 15 years. The mean daily t-As and i-As intakes were 1400 μg As/day from the water and food consumption and only 66 μg As/day coming from the analyzed vegetables and bread [20]. If it is assumed that As is present in drinking water mainly in the inorganic forms, *i.e.* arsenite and/or arsenate, the As intake estimated in this study shows that the daily i-As intake represents between 82 and 99% of the daily t-As intake.

In a later study carried out by Muñoz *et al*. [22] the dietary intake of As by the population nation capital Santiago was estimated as being 77 μg/day using a total diet study. The fish and shellfish group had the highest contents of As, 1351 ng/g. This second study reported in an industrial and developed city is closer to that previously reported in Spain than in the Second Region of Chile, because drinking water was not a key food item in this case.Summarizing, in the As-affected and rural parts of Chile the main source of As in the diet was drinking water, with i-As intake accounting for as much as 82–99% of the daily t-As intake. Both the t-As and i-As intakes depend mainly on the As concentration in the water used for drinking and cooking. The FAO/WHO reference intake was exceeded by many of those interviewed, especially those under 15 years of age.

2.3 India: Drinking water and cooked rice

The Bengal delta is one of the most fertile places in the world, replenished with nutritious sediments each year by the mighty flood water of the monsoon season. The Green Revolution in India transformed the agriculture into intensive, expanding production from one to four crops *per* year, in order to feed the growing population. These areas are mostly groundwater-dependent: the environmental conditions are optimum for the release of As to groundwater by oxidation of pyrite, reduction of ferric iron hydroxides to ferrous iron, or by over-application of phosphate fertilizer to surface soils [23, 24]. In addition, the West Bengal population depends on groundwater as the surface water is heavily contaminated with microorganisms and causes millions of deaths each year through water-borne diseases [25].

In West Bengal it is reported that about 6 million people from 2600 villages in 74 As-affected blocks are at risk: for instance 9.8% of the 86 000 people examined are suffering from As burden [26].

Nickson *et al*. [27] tested As concentration in 132 262 government-installed hand-pumps in 8 districts and 25.5% of the samples were found to contain As at concentrations greater than 50 μg As/L and 57.9% at concentrations greater than 10 μg As/L.

As-contaminated groundwater is not just used for drinking but is also widely used for irrigation of crops, and particularly for the staple food paddy rice (*Oryza sativa*) If As levels build up in paddy soils, it can lead to elevated As in rice grain, and the amount of As ingested by inhabitants of this region could be considerably more than previously thought [28].

The studies carried out by Roychowdhury *et al*. [9] in the Murshidabad district (West Bengal) provided data for t-As intake from water and food. It was estimated to be 4.5 times greater than the tolerable daily intake (TDI) and contributions from food (rice, vegetables, and spices) represented 27% of the daily t-As intake.

As a consequence of long periods of exposure to such high level of As intake, people suffer from damage to the skin, kidney, brain, heart, and circulation; miscarriages and stillbirth also seem to increase whereas bladder and lung cancer are the major killers. Besides, social problems arise from As-related diseases, for example, marriages are annulled and people with arsenicosis are avoided. In some areas, panic sets in. With so many likely to fall ill, a huge burden is placed on family units and their land [24].

Summarizing, in the As-affected parts of India the main sources of As in the diet are (i) drinking water from tube wells and (ii) foodstuff such as cooked rice and vegetables and both have given rise to high As daily intake resulting in serious health diseases and social problems.

3 As in agricultural products: Grains, vegetables, and fruits

From now on, the present review will focus on grains, vegetables, and fruits because the other two main pathways of As ingestion by humans, namely drinking water, [26, 29–32] and seafood [15, 17, 18] have already been studied in detail elsewhere.

As is found at low concentrations in surface and groundwaters. However, high As concentrations have been reported round the world, for instance West Bengal (India), Bangladesh, Vietnam, Argentina, Chile, Thailand, *etc*. [26] (see Section 2). Epidemiological studies have proved that chronic exposure to As through drinking water is associated with detectably increased risk of several noncancer diseases (*e.g.* hyperkeratosis, pigmentation changes, cardiovascular diseases, hypertension, and respiratory, neurological, liver, and kidney disorders, as well as diabetes mellitus) [32–35]. For instance, Mazumder *et al*. [36] investigated As-associated skin lesions of keratosis and hyperpigmentation in West Bengal and found a clear relationship among these diseases and the As concentration in drinking water. Besides, i-As is a well-documented potent human carcinogen, causing cancer in skin, lungs, urinary bladder, kidney, and perhaps liver [32].

Seafood is the main pathway of As ingestion in many cities and countries around the world, for instance Spain, Japan, and USA. As is ubiquitous in open ocean seawater, with levels ranging from 1–2 μg/L [15, 32, 37]. As accumulates in seafood following a sequence which starts with phytoplankton and is followed by marine animals eating algae. In marine animals, the predominant form of As is arsenobetaine, but also in other species MA, DMA, trimethyl arsine oxide, arsenocholine, arsenosugars, and i-As could be found but in very low concentrations [15]. Finally, it is important to mention that t-As and As species in seafood consumed by humans will differ according to which, particular tissues are consumed and how they are cooked [15].

After summarizing the basics of drinking water and seafood, the review focuses on grains, vegetables, and fruits. All possible pathways of As ingestion in rural areas of India, Bangladesh, and similar areas around the world have been illustrated in Fig. 2, which is a modification of the scheme proposed by Mondal and Polya [38].

Arsenicals have been used in agriculture as pesticides or plant defoliants for many years. Organic arsenicals have

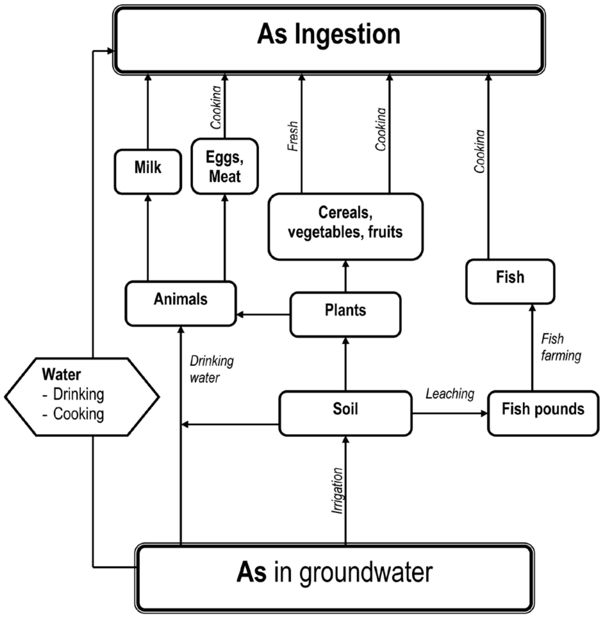

Figure 2. Possible pathways of As ingestion in rural populations of India and Bangladesh.

largely replaced inorganic forms as selective or general herbicides. They are applied at much lower rates than the inorganic arsenicals thus reducing the problems associated with As accumulations in agricultural and horticultural soils [39]. However, a legacy of contaminated orchard soils has been left behind due to the extensive use of inorganic forms in the past; this is of great importance because residues from the application of these compounds can produce phytotoxic effects long after application has ceased. Similar problems can be caused by the use of As-polluted groundwater for irrigation purposes in India and Bangladesh. Soils and sediments have been referred to as heavy metals and trace element "sinks", however, what they really do is to convert a short-term problem, through adsorption onto clays and Fe and Mn oxides or precipitation of insoluble sulfides under oxidizing or reducing redox conditions, respectively, into a long-term risk, because some day the soil conditions will change and the toxic species of As will become more available. Therefore, precautions must always be taken when working with polluted soils even if the sink mechanism of soils and sediments seems to be solving current pollution hazards.

As is not essential for plants and appears not to be involved in specific metabolic reactions when available at low concentration. At higher concentrations, however, As has been reported to interfere with metabolic processes and to inhibit plant growth, sometimes leading to death because of the toxicity of the As taken up.

As uptake by plants is controlled by a large number of factors including the As chemical form, species concentrations, soil pH, Eh and draining conditions, the amount of organic matter, seasonal effects, plant species, and chemical factors operating on the soil as phosphorus fertilizer addition [40]. For instance, Signes-Pastor *et al*. [23] reported that soluble As increased with the addition of P-fertilizers to the soil suspension.

3.1 As uptake, transport, and distribution in plants

In general the highest residues of As are found in plant roots (*e.g*., potatoes, carrots, radishes, turnips), with intermediate values in the vegetative top growth (*e.g*., spinach and grasses) with edible seeds and fruits containing the lowest levels of As [40].

Carbonell-Barrachina *et al*. [40], Burló *et al*. [41], and Lario *et al*. [42] studied As uptake by turnip, tomato, and beans, respectively. These authors used soil-less culture conditions, four As species (arsenite, arsenate, MA, DMA, and three As concentrations (1.0, 2.0, and 5.0 mg/L)). These studies showed that the As concentration in plants increased significantly with increasing concentrations in the nutrient solution. Turnip plants accumulated As mainly in the root system (75% of the t-As) and only relatively low quantities (25%) were transported to shoots. In general, it could be stated that a higher As accumulation in the root system resulted in a higher tolerance to this metalloid, as found in tomato and turnip. Higher upward transportation, mainly of o-As, resulted in sensitive plants, as found in the case of beans. Furthermore, a significant difference between As concentration in the outer root skin (adsorption) and in the inner root (absorption) was shown, with As accumulating mainly in the root skin. In this way, clear recommendations for consumers of potatoes, carrots, radishes, and turnips can be established; roots and tubers have to be washed and peeled before its consumption.

Even though rice is a grain and this type of plants are not expected to accumulate high As concentrations, ranging from 0.03 to 1.83 mg As/kg [38, 43–48]. Signes *et al*. [14] studied the As content of vegetables from West Bengal and reported that the highest As concentrations were found in rice, ranging from 0.12 to 0.50 mg As/kg. The main reason for the high As accumulation in rice is its cultivation: rice is cultivated in As-contaminated soils under anaerobic conditions, at which As is highly available for plant uptake [46, 49].

3.2 Accumulation of total As

As uptake by edible vegetables from polluted soil transforms them into an important source of As to the human food chain and therefore it is important to determine As concentration in these foodstuffs [40].

There are several studies on t-As concentrations in food, mainly vegetables. Roychowdury *et al*. [50] analyzed t-As in food coming from an As-affected area of Murshidabad district in West Bengal (Jalangi and Domkal blocks) (Table 1). The mean t-As concentration, in Jalangi block, for the

Table 1. Concentration of total As (μg/kg dry weight) in different foods from West Bengal (India).

Samples	Place	t-As (μg/kg)	References
VEGETABLES	Jalangi block, Murshidabad district	92.2	[50]
Potato skin		526	
CEREALS AND BAKERY		137	
Cooked rice		330	
SPICES		81	
Coriander		334	
VEGETABLES	Domkal block, Murshidabad district	121	[50]
Brinjal		560	
CEREALS AND BAKERY		225	
Cooked rice		378	
SPICES		161	
Turmeric powder		23	
VEGETABLES	North 24-Parganas	75	[51]
Radish		167	
CEREALS		339	
Paddy rice		496	
Boiled rice		469	
SPICES		90	
Ginger mango		214	

food sorted as vegetables was 92.2 μg As/kg, with potato skin showing the highest concentration of the group, 526 μg As/kg; for cereal and bakery goods the mean value was 137 μg As/kg and the highest concentration was found in cooked rice as 330 μg As/kg; finally, for spices the mean was 81 As/kg and coriander showed the highest t-As concentration, 334 μg As/kg. On the other hand, the mean t-As concentration, in Domkal block, for food sorted as vegetables was 121 μg As/kg and brinjal showed the highest concentration of the group, 560 μg As/kg; for cereal and bakery goods the mean was 225 μg As/kg and the highest concentration was found again in cooked rice, 378 μg As/kg; the mean for spices was 161 μg As/kg and turmeric powder showed the highest concentration, 233 μg As/kg.

Signes-Pastor *et al*. [51] analyzed t-As in agricultural products from West Bengal (north 24-Parganas district): vegetables, cereals, and spice (Table 1). The vegetable group presented a mean of 75 μg As/kg, with radish having the highest t-As concentration, 167 μg As/kg. The mean t-As concentration for the cereal group was 339 μg As/kg, with paddy and boiled rice showing the highest concentrations, 496 and 469 μg As/kg, respectively. Finally, the mean t-As concentration for the spice group was 90 μg As/kg and ginger mango showed the highest concentration, 214 μg As/kg.

Signes *et al*. [52] reported that the most popular types of commercial rice from West Bengal (paddy, atab, and boiled) had t-As concentrations as high as 550, 339, and 507 μg/kg respectively. Farid *et al*. [53] reported t-As in different vegetables irrigated with As-contaminated water: amaranth 572 μg/kg, saishim (china shark) 539 μg/kg, red amaranth 321 μg/kg, stem amaranth (katua data) 284 μg/kg, Indian spinach 189 μg/kg, chilli 112 μg/kg, and potatoes 103 μg/kg.

3.3 Accumulation of inorganic As

Whereas not all As species are toxic, the most toxic species are the inorganic forms. Additionally, i-As has been assigned to Group I of human carcinogens by the International Agency for Research on Cancer because there is sufficient evidence, from epidemiological studies, to support a causal association between i-As and cancer [54]. As big differences exist in the toxicity of the different As species, it is very important to analyze both t-As and As speciation in food in order to obtain real information about the potential toxicity of the food under study.

It is important to mention that data cited below were derived by a variety of analytical methods used in numerous laboratories over a period of decades; caution must be used when comparing such results across studies. This is why data presented in this review is always provided together with the extraction method.

There should be an official method to carry out As speciation studies and directly compare results from different studies. For instance, Baba *et al*. [55] compared different methods to carry out As speciation and concluded that As extraction from rice grains and straw with 68% HNO_3 was a better extraction method than water, 50% CH_3OH, or TFA, although the extraction with TFA was also quite good. The overall recovery for the proposed extraction methods (68% HNO_3 and TFA) were 96.9 and 97.3% for rice, respectively, and 80.1 and 51.8% for straw, respectively.

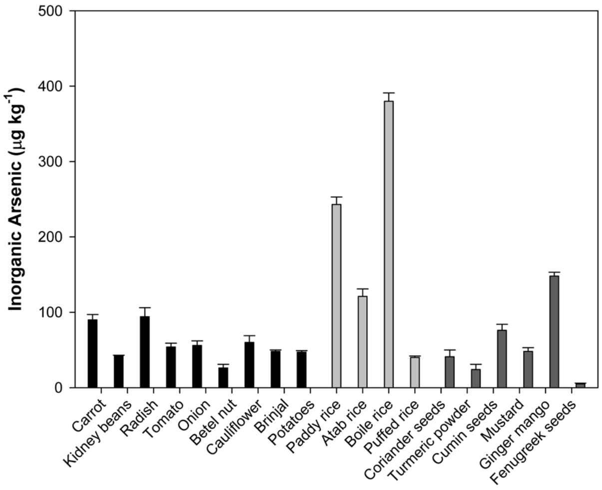

Figure 3. Concentration of inorganic As (µg/kg dry weight) in different foods from West Bengal (India); black bars: vegetables; clear grey bars: cereals; dark grey bars: spices.

Signes-Pastor *et al.* [51] analyzed As species in raw food collected from farms and local markets of Kasimpur, a rural village of West Bengal. These authors used HPLC-HG-AFS after As extraction with 2 mol/L TFA. The raw food samples were classified into three different groups: vegetables (carrot, kidney beans, radish, onion, betel nut, cauliflower, aubergine, and potatoes), grains (paddy rice, atab rice, boiled rice, and puffed rice) and spices (coriander seeds, turmeric powder, cumin seeds, mustard, ginger mango, and fenugreek seeds) (Fig. 3). The As species studied were arsenite, DMA, MA, and arsenate. These analyses demonstrated that As was mainly present as i-As forms, basically arsenite because arsenate was not detected in any of the studied samples. Only a few samples had a low percentage of i-As, for instance, fenugreek seeds (18%), paddy rice (50%), atab rice (44%), and puffed rice (33%). All other samples presented i-As percentages above 50%. Puffed rice showed the lowest percentage of i-As of all the types of rice grains studied, perhaps due to its manufacturing process. Boiled rice, however, had a high percentage of i-As because the water used to cook it usually had a high concentration of i-As. The i-As and t-As ranged from 26 to 94 µg/kg and from 26 to 154 µg/kg, respectively, in vegetables; from 40 to 380 µg/kg and from 120 to 488 µg/kg, respectively, in grains; and finally, from 5 to 148 µg/kg and from 28 to 208 µg/kg, respectively, in spices (Fig. 3).

Meharg *et al.* [56] studied As speciation in brown and white rice samples obtained from Bangladesh, United States, and China. Total As concentration in all rice samples ranged from 0.28 to 0.61 mg/kg, with the brown rice from Bangladesh having the highest As concentration. As speciation was performed by HPLC-ICP-MS after As extraction with 2 M TFA and the main species detected were DMA and inorganic forms which represented between 39 and 57% of the t-As. In general, brown rice showed higher As content than white rice, which could be related with the As distribution in the rice grain (highest accumulation in the bran).

4 Food processing and cooking

Food is usually cooked before eating (Fig. 2) and this process may alter the As concentration in final ready-to-eat foods, depending on whether As-contaminated water is used or not. It is necessary to consider the effect of processing and cooking on t-As and arsenical species to obtain a realistic view of the risk associated with food intake around the world [57].

In many As-contaminated rural villages of India and Bangladesh the residents depend heavily on rice for their intake of calories (70% of the total). Therefore, there is no doubt that rice is the most important food for the inhabitants of these rural areas and deserves a detailed study. In previous sections it has been shown that rice, cultivated in polluted soil and irrigated with As-polluted groundwater, has high levels of t-As but this level could change as a consequence of dehusking and cooking processes.

4.1 Rice processing

Signes *et al.* [52] studied the two most popular dehusking procedures in India: (i) dry dehusking process and (ii) wet dehusking process, from which "atab rice" and "boiled rice" are obtained, respectively. In general, dehusking of paddy rice (373 µg/kg) significantly reduced the As concentration of rice (mean value of 311 µg/kg). This reduction in the t-As concentration was related to the high As content of the husk (1000 µg/kg); thus, it is not recommended to use rice husk for feeding animals.

"Atab rice," obtained only by mechanically dehusking paddy rice, presented significantly lower t-As concentration (290 µg/kg) than "boiled rice" (332 µg/kg), which was first soaked in water, boiled lightly, and finally mechanically dehusked. In this study, As-polluted water, 40 µg/L, was used for all purposes (soaking and boiling). Thus the final recommendation of Signes *et al.* [52] was to use the dry method if As-free water is not available. However, if villagers are forced to use the wet process, they could decrease the t-As concentration in the final boiled rice by discarding the soaking water and using new water for the further light boiling. Of course, if As-free water is available, part of the initial As present in the paddy rice will migrate to the soaking and boiling waters. Unfortunately, this type of water is not available in many areas of India and Bangladesh.

It may be noted, finally, that boiling rice in harvested rainwater or even plain surface water would reduce As intake even further. People will tend to shy away from this possibility, however, because they associate this water with water-borne diseases even though boiling removes this risk theoretically. The social and health aspects of this option are certainly worthy of further research however.

4.2 Rice cooking

The three most common methods of cooking rice in India are called: (i) traditional; (ii) intermediate; and (iii) contemporary. In the *traditional method*, rice is washed until washings become clear, the washings are discarded, and rice is boiled in excess water until cooked; finally, the remaining water is discarded. Rice cooked following the *intermediate method* is washed as above but is boiled with less water until no water is left to be discarded. Finally, in the *contemporary method* unwashed rice is boiled with low water volume until no water is left to discard [58]. Signes *et al*. [14] and Signes-Pastor *et al*. [51] simulated these three cooking methods in their laboratory and found significant differences in t-As concentrations in the final ready-to-eat cooked rice. The As concentrations were 258, 365, and 387 μg/kg (mean values of atab and boiled rices) for the traditional, intermediate, and contemporary methods, respectively, when water spiked with As until 40 μg As/L and atab rice (185 μg As/kg) and boiled rice (315 μg As/kg) were used. Therefore, the use of the traditional method of rice cooking (using high volumes of water for washing and cooking the rice) is finally recommended; this method significantly reduces the quantity of i-As ingested by the population. A previous study by Sengupta *et al*. [58] also agreed with this recommendation. These authors cooked rice using low-As water (<3 μg As/L) using traditional and modern methods and found that the traditional method (washed until clear; cooked with rice/water ratio of 1:6; discarded excess water) removed up to 57% of the As from the initial rice containing 203–540 μg As/kg. Approximately half of the As was lost in the washed water and the other half in the discarded water.

At the same time, Signes *et al*. [59] simulated cooking of rice with different levels of As species in the cooking waters. The variables under study were: (i) four As species (arsenite, arsenate, MA, and DMA) and (ii) three t-As concentrations (50, 250, and 500 μg As/L). The results showed that the As concentration in cooked rice was always higher than that in the raw rice and ranged from 227 to 1642 μg As/kg. Mondal and Polya [38] reported values of As in cooked rice of 170 μg As/kg (during two household surveys in Nadia district of West Bengal), Smith *et al*. [60] of 350 μg As/kg for a Bangladesh household survey, Bae *et al*. [61] of 270 μg As/kg for a Bangladesh onsite survey, Rahman *et al*. [62] of 320 μg As/kg for a Bangladesh field survey and Roychowdhury *et al*. [50] of 370 μg As/kg for a West Bengal household survey in Murshidabad district of West Bengal. Perhaps, the lower t-As concentrations reported in these later studies were due to the use of cooking water with low-As contents or even free-As water.

In addition, Signes *et al*. [59] showed that the cooking rice did not change the As speciation in rice. This could be because the temperature of rice cooking, around 100°C is lower than required for these changes to take place. Van Elteren and Slejokovec [63] studied the effect of high temperature on aqueous standards of various species of As and concluded that temperatures above 150°C were required to find significant changes in the As speciation of cooked rice. A later study carried out by Devesa *et al*. [57] agreed with this statement and concluded that these high temperatures can be attained in some cooking treatments in which the surface of the food is in direct contact with the heat source (grilling, frying, or baking) and reaches temperatures close to 250°C.

Further research is still needed to investigate alternative cooking procedures to reduce As concentrations in cooked rice and other foods. Of course, if cooking water containing low levels of As or free of it can be provided to villagers, even if the initial rice is still contaminated with As, cooked items will have an As concentration lower than expected due to migration of some of the As to the cooking water. Finally, the information about the significant increase caused by cooking of rice with As-polluted water should be used by regulatory organizations to set limits in the cooked items rather than in raw products.

5 As intake in As-endemic areas

The parameter most commonly used for the evaluation of arsenic risk assessment in the PTWI establish by FAO/WHO is 15 μg i-As/wk/kg body weight [64]. The PTWI value can be transformed into the TDI of i-As as follows: TDI = PTWI/7 days = 127 μg i-As/day for adult, if we assume that adults in West Bengal have a mean body weight of approximately 58 kg.

5.1 Intake of total As

Roychowdury *et al*. [50] estimated the daily As intake for the villagers of Jalangi and Domkal blocks (West Bengal). In these blocks, rice and vegetables are the main food for the villagers, both foodstuffs being eaten three times *per* day (breakfast, lunch, and dinner). Adults (male and female) and children (around 10 years of age) normally eat 750 and 400 g of rice (wet weight, ww) *per* day. Adults and children eat 500 and 300 g vegetables (ww) *per* day and the vegetables are usually cooked with spices. The intake of spices (ww) for adult and children is approximately 10 and 5 g *per* day, respectively. The villagers occasionally eat fish (once *per* week), egg (once *per* week), and meat (once a month). With all these data the estimated daily dietary intake of As from foodstuff was for adults, both male and females (171 and 189 μg respectively) and children (92 and 102 μg) in Jalangi and Domkal blocks, respectively. As rice is the main source of As intake, it contributed about 92–94% and 91–93% to the total As intake from food composites (rice, vegetables, and spices) by adults and children in Jalangi and Domkal blocks, respectively.

Ohno *et al*. [29] estimated the As intake of 18 families living in one block of a rural village in an As-affected district of Bangladesh *via* drinking water and food, including cooking water. The mean of the t-As intakes by male and female subjects were 180 and 96 μg As/day, and the range for all 18 respondents was 43–490 μg As/day. The average contributions to the total As intake were: drinking water 13%, liquid food 4.4%, cooked rice 56%, solid food 11%, and cereals 16%. As intake *via* drinking water was not high despite the highly contaminated groundwater in the survey area because many families had changed their drinking water sources to less contaminated ones. Instead, cooked rice contributed mostly to the daily As intake because some households were still using contaminated water for cooking which led to an increase in As intake. Consequently, it seems evident that communication of the risks associated with using As-contaminated water for cooking purposes might help in significantly reducing As intake by villagers but the active participation of the community in the implementation of the recommendations is needed.

5.2 Intake of inorganic As

In order to have a more realistic risk evaluation, the daily intake of As should be based on data from i-As, the most toxic group of species (arsenite and arsenate).

Signes-Pastor *et al*. [51] estimated the daily i-As intake in Kasimpur, a rural village of West Bengal. The daily As intake was estimated using data of the consumption of water (1760 mL/day), rice (385 g/day), and vegetables (205 g/day); the remaining foodstuffs (fruits, poultry meat, fish, eggs, bakery products, and spices) only represented 95 g/day and were not considered in the estimation to simplify the mathematical study. The results showed that the contribution of rice to the total As intake ranged from between 46 and 60% and the contribution of vegetables was only around 1%, mainly because of their high water content (approximately 90%).

The food analyses and the food questionnaires administered led Signes-Pastor *et al*. [51] to establish a daily intake of i-As of 170 μg/day, which was above the TDI of 150 μg i-As/day. The experimental daily intake of i-As can increase up to 251 μg i-As/day when food is abundant and the amount of food ingested increases. These estimations were made using data from raw products; as described previously in this review, most of the cooking processes used in As-endemic areas, such as India, entail a significant increase in the i-As concentration and consequently an increase in the toxicological risk for the exposed population.

Kile *et al*. [65] studied the dietary As exposure in Bangladesh. Median daily t-As intake was 48 μg t-As/day from food and 4 μg t-As/day from drinking water (mean concentration of 1.6 μg/L). On average, 82% of the As found in their food samples were in the inorganic forms. This study was a clear example of how important food becomes in studying the dietary intake of As when As concentration in drinking water is below the 10 μg/L drinking water standard of WHO.

Results reported here clearly demonstrated the importance of food as a source of t-As and i-As and that this source should never be forgotten in populations depending heavily on vegetables (mainly rice) for their diets. It is highly recommended that the intake of As should be evaluated on the basis of the product as ingested by the consumer and not from raw products.

6 Strategies to reduce As intake in endemic areas

6.1 Long-term strategies

Fundamental solutions to the high As intake in As-endemic areas such as India and Bangladesh are to reduce As in drinking water and rice. To reducing the As concentration in rice, the only option is to reduce the uptake of As by rice plants. It is not cost effective to remediate paddy fields in poor countries such as India and Bangladesh, so the only solution is to breed rice with a low As uptake, upward translocation, and consequently low As accumulation in the rice grains.

For the drinking water, there are two different options: (i) finding new sources or (ii) removing As from groundwater. Surface water is abundant in India and Bangladesh but unavailable as a solution due to waterborne diseases. Rainwater storage carries the same risks and tends not to suffice during the dry season. Therefore, research for solutions focuses mainly on deep wells (with safe water but questionable sustainability), post-extraction treatment, and pre-extraction (*in situ*) treatment of the shallow groundwater.

Although these options receive much attention nowadays (*e.g*. www.insituarsenic.org), much time will be needed to implement them. It is therefore highly relevant to have a number of no-threshold options that can be implemented by anybody anytime.

6.2 Short-term strategies

After careful study of all the information available in the scientific literature dealing with As presence in agricultural products (grains, vegetables, and fruits) the three solutions proposed are:

(i) It has been demonstrated that As accumulates mainly in the skins of roots and tubers, therefore washing and peeling of potatoes, carrots, radishes, and turnips should be compulsory.

(ii) In those places where only As-polluted water is available, the exclusively mechanical dehusking of paddy rice is recommended; this method provides the consumer with the so-called “atab rice.” Besides, the traditional method of cooking rice is recommended. This method uses high volumes of water for washing and boiling the rice.

(iii) In those places where As-free water is available, the paddy rice could be dehusked using the wet system leading to “boiled rice”; a significant reduction in the initial As content of paddy rice will be obtained. Finally, the traditional method of cooking rice is also recommended under these circumstances.

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7 References

[1] Pfannhauser, W., Pechanek, U., The contamination of food in Austria by toxic heavy metals, *Lebensm. Ernaehr.* 1977, *30*, 88 – 92.

[2] Robberecht, H., Cauwenbergh, R., Bosscher, D., Cornelis, R., Deelstra, H., Daily dietary total arsenic intake in Belgium using duplicate portion sampling and elemental content of various food stuff, *Eur. Food Res. Technol.* 2002, *241*, 27 – 32.

[3] Dabeka, R. W., Mckenzie, A. D., Lacroix, G. M. A., Bowe, S. *et al*., Survey of arsenic in total diet food composites and estimation of the dietary intake of arsenic by Canadian adults and children, *J. AOAC Int.* 1993, *76*, 14 – 25.

[4] González-Moreno, M. J., Urieta-Guijarro, L., Macho-Eiras, M. L., Azpiri-Luzar, M., *Vigilancia de la Contaminación Química de los Alimentos en la Comunidad Aautónoma del País Vasco 1990 – 1995*, Servicio Central de publicaciones del Gobierno Vasco, Vitoria-Gasteiz 1997.

[5] Gunderson, E. L., FDA total diet study, July 1986-April 1991, dietary intakes of pesticides, selected elements, and other chemicals, *J. AOAC Int.* 1995, *78*, 1353 – 1363.

[6] Varo, P., Koivistoinen, P., Mineral element composition of finish foods. XII. General discussion and nutrition evaluation, *Acta Agric. Scandinavaca* 1980, 161 – 164.

[7] Noel, L., Leblanc, J. C., Guerin, T., Determination of several elements in duplicate meals from catering establishment using closed vessel microwave digestión with inductively coupled plasma mass spectrometry detection: estimation of daily dietary intake, *Food Addit. Contam.* 2003, *20*, 44 – 56.

[8] Van-Dokkum, W., De-Vos, R. H., Muys, T., Wesstra, J. A., Minerals and trace elements in total diets in The Netherlands, *British. J. Nutr.* 1989, *61*, 7 – 15.

[9] Roychowdhury, T., Tokunaga, H., Ando, M., Survey of arsenic and other heavy metals in food composites and drinking water and estimation of dietary intake by the villages from arsenic affected area of West Bengal, India, *Sci. Total Environ.* 2003, *308*, 15 – 35.

[10] Devesa, V., Macho, M. L., Jalón, M., Urieta, I. *et al*., Arsenic cooked seafood products: study on the effect of cooking on total and inorganic arsenic contents, *J. Agric. Food. Chem.* 2001, *49*, 4132 – 4140.

[11] Dick, G. L., Hughes, J. T., Mitchell, J. W., Davidson, F., Survey of trace elements and pesticides residues in the New Zeland diet, *N. Z. J. Sci.* 1978, *21*, 57 – 69.

[12] Ysart, G., Miller, P., Croasdale, M., Crews, H. *et al*., 1997 U. K. total diet study dietary exposures to aluminium, arsenic, cadmium, chromium, cooper, lead, nickel, selenium, tin and zinc, *Food Addit. Contam.* 2000, *17*, 775 – 786.

[13] Rahman, M. M., Mandal, B. K., Chowdhury, T. R., Sengupta, M. K. *et al*., Arsenic groundwater contamination and sufferings of people in North 24-Parganas, one of the nine arsenic affected districts of West Bengal, India, *J. Environ. Sci. Health A* 2003, *38*, 25 – 59.

[14] Signes, A., Mitra, K., Burló, F., Carbonell-Barrachina, A. A., Effect of cooking method and rice type on arsenic concentration in cooked rice and the estimation of arsenic dietary intake in a rural village in West Bengal, India, *Food Addit. Contam.* 2008, *11*, 1345 – 1352.

[15] Borak, J., Hosgood, H. D., Seafood arsenic: implications for human risk assessment, *Regul. Toxicol. Pharmacol*. 2007, *47*, 204 – 212.

[16] Schoof, R. A., Yost, L. J., Eickhoff, J., Crecelius, E. A. *et al*., A market basket survey of inorganic arsenic in food, *Food Chem. Toxicol.* 1999, *37*, 839 – 846.

[17] Urieta, I., Jalón, M., Eguileor, I., Food surveillance in the Basque Country (Spain). II. Estimation for the dietary intake of organochlorine pesticides, heavy metals, arsenic, aflatoxin M_1, iron and zinc trough the total diet study, 1990/1991, *Food Addit. Contam.* 1996, *13*, 29 – 52.

[18] Jalón González-Moreno, M., Urieta Guijarro I., Macho Eiras, M. L., Azpiri Luzar, M., *Survey of Chemical Contamination of Foods in the Autonomic Community of the Basque Country 1990 – 1995 (In Spanish)*. Servicio de Publicaciones del Gobierno Vasco, Vitoria-Gasteiz, Spain 1997.

[19] Donohue, J. M., Abernathy, C. O., in: Chappell, W. R., Abernathy, C. O., Calderon, R. L. (Eds.), *Arsenic Exposure and Health Effects*, Elsevier Science, Amsterdam 1999, pp. 89 – 98.

[20] Díaz, O. P., Leyton, I., Nuñez, N., Devesa, V. *et al*., Contribution of water, bread, and vegetables (raw and cooked) to dietary intake of inorganic arsenic in a rural village of Northern Chile, *J. Agric. Food Chem.* 2004, *52*, 1773 – 1779.

[21] Muñoz, O., Diaz, O. P., Leyton, I., Nuñez, N. *et al*., Vegetables collected in the cultivated Andean area of Northern Chile: total and inorganic arsenic contents in raw vegetables, *J. Agric. Food Chem.* 2002, *50*, 642 – 647.

[22] Muñoz, O., Bastias, J. M., Araya, M., Morales, A. *et al*., Estimation of the dietary intake of cadmium, lead, Mercury, and arsenic by the population of Santiago (Chile) using a total diet study, *Food Chem. Toxicol.* 2005, *43*, 1647 – 1655.

[23] Signes-Pastor, A., Burló, F., Mitra, K., Carbonell-Barrachina, A. A., Arsenic biogeochemistry as affected by phosphorus fertilizar addition, redox potencial and pH in West Bengal (India) soil, *Geoderma* 2007, *137*, 504 – 510.

[24] Meharg, A. A., *Venomous Earth. How Arsenic Caused the World's Worst Mass Poisoning*, Macmillan, Basingstoke, Hampshire 2005.

[25] Drury, S., *Water and Well-being: Arsenic in Bangladesh*, The Open University, Milton Keynes 2007.

[26] Mandal, B. K., Suzuki, K. T., Arsenic round the world: a review, *Talanta* 2002, *58*, 201 – 235.

[27] Nickson, R., Sengupta, C., Mitra, P., Dave, S. N. *et al*., Current knowledge on the distribution of arsenic in groundwater in five states of India, *J. Environ. Sci. Health* 2007, *42*, 1707–1718.

[28] Meharg, A. A., Rhaman, M. D. M., Arsenic contamination of Bangladesh paddy field soils: implications for rice contribution to arsenic consumption, *Environ. Sci. Technol.* 2003, *37*, 229–234.

[29] Ohno, K., Yanase, T., Matsuo, Y., Kimura, T. *et al*., Arsenic intake via water and food by a population living in an arsenic-affected area of Bangladesh, *Sci. Total Environ.* 2007, *381*, 68–76.

[30] Cantor, K. P., Lubin, J. H., Arsenic, internal cancers, and issues in inference from studies of low-level exposures in human populations, *Toxicol. Appl. Pharmacol.* 2007, *222*, 252–257.

[31] WHO, *Environmental Health Criteria 18: Arsenic*, World Health Organization, Geneva 1981.

[32] WHO, *Enviornmental Health Criteria 2 24: Arsenic and Arsenic Compounds*, World Health Organization, Geneva 2001.

[33] Vahter, M., Health effects of early life exposure to arsenic, *Basic Clin. Pharmacol. Toxicol.* 2008, *102*, 204–211.

[34] IARC, *Some Drinking Water Disinfectants and Contaminants, Including Arsenic*, Vol. 84, International Agency for Research on Cancer, Lyon 2004.

[35] NRC, *Arsenic in Drinking Water: 2001 Update*, National Academy Press, Washington DC 2001.

[36] Mazumder, D. N. G., Haque, R., Ghosh, N., De, B. K. *et al*., Arsenic levels in drinking water and the prevalence of skin lesions in West Bengal, India, *Int. J. Epidemiol.* 1998, *27*, 871–877.

[37] Francesconi, K. A., Edmonds, J. S., Arsenic species in marine samples, *Croactica Chemica Acta* 1998, *71*, 343–359.

[38] Mondal, D., Polya, D. A., Rice is a major exposure route for arsenic in Chakdaha block, Nadia district, West Bengal, India: a probabilistic risk assessment, *App. Geochem.* 2008, *23*, 2987–2998.

[39] Carbonell-Barrachina, A. A., Burló, F., Valero, D., Martínez-Romero, D., Martínez-Sánchez, F., Environmental factors affecting arsenic incorporation in fruits and horticultural products, *Recent Res. Devel. Agric. Food Chem.* 2000, *4*, 95–121.

[40] Carbonell-Barrachina, A. A., Burló, F., Valero, D., López, E. *et al*., Arsenic toxicity and accumulation in turnip as affected by arsenic Chemicals speciation, *J. Agri. Food Chem.* 1999, *47*, 2288–2294.

[41] Burló, F., Guijarro, I., Carbonell-Barrachina, A. A., Valero, D., Martinez-Sánchez, F.,Arsenic species: effects on and accumulation by tomato plants, *J. Agric. Food Chem.* 1999, *47*, 1247–1253.

[42] Lario, Y., Burló, F., Aracil, P., Martínez-Romero, D. *et al*., Methylarsonic and dimethylarsinic acids toxicity and total arsenic accumulation in edible bush beans, *Phaseolus vulgaris*, *Food Addit. Contam.* 2002, *19*, 417–426.

[43] Abedin, M. J., Cotter-Howells, J., Meharg, A. A., Arsenic uptake and accumulation in rice (*Oryza sativa* L.) irrigated with contaminated water, *Plant Soil* 2002, *240*, 311–319.

[44] Abedin, M. J., Cresser, M. S., Meharg, A. A., Feldmann, J., Cotter-Howells, J., Arsenic accumulation and metabolism in rice (*Oryza sativa* L.), *Environ. Sci. Technol.* 2002, *36*, 962–968.

[45] Heitkemper, D. T., Vela, N. P., Stewart, K. R., Westphal, C. S., Determination of total and specited arsenic in rice by ion chromatography and inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 2001, *16*, 299–306.

[46] Meharg, A. A., Arsenic in rice – understanding a new disaster for South-East Asia, *Trends Plant Sci.* 2004, *9*, 415–417.

[47] Schoof, R. A., Yost, L. J., Crecelius, E., Irgolic, K. *et al*., Dietary arsenic intake in Taiwanese districts with elevated arsenic in drinking water, *Human Ecol. Risk Assess.* 1998, *4*, 117–135.

[48] Williams, P. N., Price, A. H., Raab, A., Hossain, S. A. *et al*., Variation in arsenic speciation and concentration in paddy rice related to dietary exposure, *Environ. Sci. Technol.* 2005, *39*, 5531–5540.

[49] Carbonell-Barrachina, A. A., Aarabi, M., DeLaune, R. D., Gambrell, R. P., Patrick, W. H., Jr., The influence of arsenic chemical form and concentration on Spartina patens and Spartina alterniflora growth an tissue arsenic concentration, *Plant Soil* 1998, *198*, 33–43.

[50] Roychowdury, T., Uchino, T., Tokunaga, H., Ando, M., Survey of arsenic in food composites form an arsenic-affected area of West Bengal, India, *Food Chem. Toxicol.* 2002, *40*, 1611–1621.

[51] Signes-Pastor, A. J., Mitra, K., Hobbes, M., Burló, F. *et al*., Arsenic speciation in food and estimation of the dietary intake of inorganic arsenic in a rural village of West Bengal, India, *J. Agric. Food Chem.* 2008, *56*, 9469–9474.

[52] Signes, A., Mitra, K., Burló, F., Carbonell-Barrachina, A. A., Effect of two different rice dehusking procedures on total arsenic concentration in rice, *Eur. Food Res. Technol.* 2008, *226*, 561–567.

[53] Farid, A. T., Roy, K. C., Hossain, K. M., Sen, R., *A study of arsenic contamination irrigation water and its carried over effect on vegetable*, Proceedings of the International Symposium of Fate of Arsenic in the Environmental, Dhaka, Bangladesh 2003, pp. 113–121.

[54] Tsuda, T., Babazono, A., Ogawa, T., Hamada, H. *et al*., Inorganic arsenic: a dangerous enigma for mankind, *Appl. Organomet. Chem.* 1992, *6*, 306–322.

[55] Baba, K., Arao, T., Maejima, Y., Watenabe, E. *et al*., Arsenic speciation in rice and soil containing related compounds of chemicals warfare agents, *Anal. Chem.* 2008, *80*, 5768–5775.

[56] Meharg, A. A., Lombi, E., Williams, P. N., Scheckel, K. G. *et al*., Speciation and localization of arsenic in white and brown rice grain, *Environ. Sci. Technol.* 2008, *42*, 1051–1057.

[57] Devesa, V., Vélez, D., Montoro, R., Effect of thermal treatments on arsenic species contents in food, *Food Chem. Toxicol.* 2008, *46*, 1–8.

[58] Sengupta, M. K., Hossain, M. A., Mukherjee, A., Ahamed, S. *et al*., Arsenic burden of cooked rice: traditional and modern methods, *Food Chem. Toxicol.* 2006, *44*, 1832–1829.

[59] Signes, A., Mitra, K., Burló, F., Carbonell-Barrachina, A. A., Contribution of water and cooked rice to an estimation of dietary intake of inorganic arsenic in a rural village of West Bengal, India, *Food Addit. Contam.* 2008, *25*, 41–50.

[60] Smith, A. H., Lee, R., Heitkemper, D. T., Cafferky, K. D. *et al*., Inorganic arsenic in cooked rice and vegetable from Bangladeshi households, *Sci. Total Environ.* 2006, *370*, 294–301.

[61] Bae, M., Watanabe, C., Inaoka, T., Sekiyama, M. *et al*., Arsenic in cooked rice in Bangladesh, *Lancet* 2002, *360*, 1839–1840.

[62] Rahman, M. A., Hasegawa, H., Rahman, M. A., Rahman, M. M., Miah, M. A. M., Influence of cooking method on arsenic retention in cooked rice related to dietary exposure, *Sci. Total Environ.* 2006, *370*, 51–60.

[63] van Elteren, J. T., Slejkovec, Z., Ion-exchange separation of eight arsenic compounds by high-performance liquid chromatography-UV decomposition-hydride generation-atomic fluorescence spectrometry and stability test for food treatment procedures, *J. Chromatogr.* 1997, *789*, 339–340.

[64] WHO, *Evaluation of Certain Food additives and Contaminants*, *33rd Report of the Joint FAO/WHO Expert Committee on Food Additives*, Technical Report Series 776, WHO, Geneva 1989.

[65] Kile, M. L., Houseman, E. A., Breton, C. V., Smith, T. *et al.*, Dietary arsenic exposure in Bangladesh, *Environ. Health Perspect.* 2007, *115*, 889–893.