Total Concentration of Arsenic in Commercial Infant/Toddler Food: A Preliminary Study in Libya

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Abstract. Infant/toddler food (ITF) contamination with As is a severe issue of concern due to the fact that food is the second leading source of As after drinking water in the aspect of toxicity induced by nutrition. This study aimed to perform a preliminary assessment of As contamination in commercially available ITF in Libya, thus revealing possible exposure of consumers to As. ITF samples were purchased at supermarkets and were divided as follows: i) ITF containing cereal mixture (ITF-mix); ii) ITF containing wheat (ITF-wheat); and iii) ITF containing rice (ITF-rice). The total concentration of As was detected after wet digestion using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The highest mean concentration of As was detected for ITF-rice in comparison to other ITF samples. Sources of As in food are both, natural and human-induced; the main source of ITF contamination with As could be industrial food processing, manufacturing and storage, as well as cultivation specifics of crops. The study revealed the significance of monitoring or supervision over food safety, especially regarding ITF as these products are intended for the most vulnerable groups of consumers.

Keywords: Child nutrition, food contamination, heavy metal pollution

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1 Introduction

Besides the range of essential trace elements (such as Co, Cr, I, Li, Mo, Se, V) required for the human organism in tiny quantities (μg d⁻¹), non-essential trace elements such as Cd, As, Al, Hg, Pb and others also may be transferred into food affecting its quality [1]. If contaminated food is consumed for a long time, adverse health effects may occur.

Arsenic (As) is quite abundant in the environment, and even a relatively low amount of it can cause an undesirable impact on human health after the trans-dermal contact, ingestion, or inhalation [2–5]. Toxicity of various As compounds is distinctive. The highest arsenic toxicity levels (if ingested) can be attributed to the inorganic forms: As(III) and As(V), while the organic compounds are assessed as less toxic [5, 6]. For instance, arsenobetaine and arsenocholine are low-toxic organic As compounds, mostly found in seafood and some fish species. These compounds, if ingested with food, are rapidly excreted by the urinary system within 1 d to 2 d, while inorganic As compounds, if ingested, are metabolized in the liver and excreted only within 1 wk to 3 wk [7, 6, 2]. The studies have revealed that rice is a significant source of inorganic As in human nutrition, apart from drinking water, especially in Asia [8, 7, 4, 5]. A range of studies related to the investigation of As impact on human health has led to the inclusion of inorganic As among the carcinogenic substances with chronic exposure. Adverse health effects induced by As ingestion (or contact) involves affected fertility, risk of congenital disabilities resulting in the impaired mental development of children. Fetus, infants and toddlers are highly vulnerable even to a tiny concentration of As, and chronic exposure of As may induce the risk of infant morbidity and lung diseases such as bronchiectasis and lung cancer. Furthermore, As may elevate the risk of other types of cancer (prostate, bladder, or skin) and various diseases (e.g., diabetes, hypertension). The main population groups that are subjected to As contamination are inhabitants of the areas with a high geochemical background of As [8–12, 6].

Drinking water, followed by food, are the primary sources of As. In many regions worldwide, contamination of groundwater is a problem inducing chain-type reaction of potentially toxic element transfer from environmental media (soil and water) to locally produced food [13, 14, 2, 4]. The sources of human-induced As pollution are agriculture and industry, mainly such activities as application of pesticides and contaminated water for crop irrigation, as well as mining [15, 12, 5]. As has been found in various food commodities and beverages, thus, emphasizing the concern of possible chronic exposure [15–19, 8, 12], indicating that surveillance (e.g., market basket surveys or food safety monitoring programs) has the crucial role in the detection of food chain contamination and estimation of a possible hazard. The studies have revealed that some food commodities may contain higher amounts of As than others, e.g., considerably high As contamination is found in fish (concentration of As above 1 mg kg⁻¹), but meat, cereal products and bakery products usually are not as much contaminated (As level do not exceed 0.03 mg kg⁻¹) [20].

Specifics of food intended for infants and toddlers (4 mo to 2 yr old) involve the manufacturing of products that are easy to chew, swallow and digest. Up to the age of 6 mo, breastfeeding is primarily recommended in all societies, and it is one of the oldest practices for feeding babies, especially significant for the first months of newborns’ life. However, it is reported that on average less than 35 % of infants worldwide are fed solely by mother’s breast milk at age 0 mo to 6 mo. This number is higher for developing countries (about 40 %), while in the USA only 13 % and in the EU only 3 % of 6 mo old infants are breastfed [21, 3]. Regular intake of essential elements, minerals and vitamins is vital for the human organism, especially in childhood when growth and development are rapid. Therefore, the element entity in the diet should be balanced, but any contamination of ITF is unacceptable and may expose to poisoning risk a large group of consumers [3, 6].
Not with standing, in the past, the cases of As contamination were documented. One of the most screaming incidents occurred in Japan, in 1955, robbing more than a hundred infants’ lives who were fed with As-contaminated dry milk powder as well as several hundreds of children were subjected to neurotoxic effects and various health disorders during their lifetime. The source of As was a low purity Na₂HPO₄ or DSP added to the milk powder as a stabilizer [22].

Economic development and social revolution that Libya withstood like other countries of the Middle East has resulted in changes in day-to-day habits of the population, including infant feeding, i.e., breast milk is more frequently substituted by infant formulas and commercially available ITF is more frequently fed to children than raw food commodities. This is primarily attributed to urban areas where mothers with elevated socioeconomic ranks switch early from infant breastfeeding to bottle-feeding, e.g., mixed feeding of children was practised by most mothers in different subgroups (up to 79 %) starting from 4 mo after the children birth [23, 24].

Regarding the situation in Libya, the report on additional food given to children at the Al-Fateh Pediatric Hospital, in Benghazi (the second largest city of Libya), besides breast milk, cow’s milk powder and ITF has been prepared [25]. The conclusion was that 38.4 % of infants younger than 6 mo were additionally fed with supplementary foods. Further, 17.9 % of those younger than 3 mo were given additional food, 65.4 % of those aged 3 mo to 5 mo, 82.5 % of those aged 6 mo to 9 mo and 97.5 % of those aged 10 mo to 12 mo [25].

This study aimed to perform a preliminary assessment of As contamination in commercially available ITF in Libya, thus revealing possible exposure of consumers to As.

2 Materials and methods

2.1 Sampling of ITF and sample preparation

ITF samples containing wheat, rice and mixed cereals were obtained in at supermarkets in Sabha, Tripoli, and Benghazi cities (Libya). In total, 36 ITF samples were purchased. Collected ITF samples were divided as follows: i) ITF containing cereal mixture (ITF-mix, n = 7); ii) ITF containing rice (ITF-rice, n = 11); iii) ITF containing wheat (ITF-wheat, n = 18), according to the product labels taking into account the country of production. Before the analysis, the samples were dried in an oven at 90 °C for 48 h. Analytical sample preparation was performed according to previously developed methodology [26, 11] and involved wet digestion using 2mL HNO₃ (70 % w v⁻¹) and H₂O₂ (30 % w v⁻¹) on a dry mass of a sample 0.2 g (using reagents (Aristar) of analytical grade). Microwave digester Mars5 (CEM Corp) was used for sample mineralization at following operating mode: i) 10 min at 55 °C; ii) 10 min at 75 °C; and iii) 30 min at 95 °C (at a maximal pressure 500 psi —1 psi = 6.89 kPa). Each sample was prepared in triplicate. After the process of digestion, an internal standard 0.5 μL of indium solution (1 mg L⁻¹) was added to sample solutions, as well as ultra-pure deionized water (18 MΩ specific resistance; millipore) was filled up to 50 mL.

2.2 Quantitative analysis

Quantitative determination of As in ITF samples was performed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS — PerkinElmer Optima 5300 DV, Canada). The analytical procedure for total As determination was performed as described in previous studies [11, 26]. Accuracy of the applied analytical method was ensured by the analysis of blank samples for each batch of samples, as well using certified reference material (rice
flour, SRM 1568a, NIST). The precision of analytical performance was assessed as acceptable (Table 1).

Table 1. Analysis of the reference material rice flour SRM 1 568a (n = 5) using ICP-MS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference (mg kg⁻¹)</th>
<th>Mean detected (mg kg⁻¹)</th>
<th>Recovery (%)</th>
<th>LOD (μg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.29 ± 0.03</td>
<td>0.22 ± 0.03</td>
<td>76</td>
<td>0.02</td>
</tr>
<tr>
<td>Se</td>
<td>0.38 ± 0.04</td>
<td>0.27 ± 0.01</td>
<td>72</td>
<td>0.03</td>
</tr>
</tbody>
</table>

2.3 Data statistical assessment

Data statistical analysis was performed by using extended MS Excel data analysis tool QI Macros, involving the application of ANOVA test.

3 Results and discussion

3.1 Results

3.1.1 Total concentration of As in ITF-mix

The average total concentration of As in analyzed samples of ITF-mix was 0.16 mg kg⁻¹. ITF-mix produced in Turkey contained a higher concentration of As than ITF-mix produced in Libya (Table 2). However, according to ANOVA, the concentration of As in various ITF-mix samples was not significant (P = 0.34).

Table 2. The total concentration of As in ITF-mix.

<table>
<thead>
<tr>
<th>Number</th>
<th>Country of origin (number of samples)</th>
<th>Concentration (mg kg⁻¹)</th>
<th>Mean/median</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Libya (n = 3)</td>
<td>0.05 to 0.17 (0.03)</td>
<td>0.11</td>
</tr>
<tr>
<td>2.</td>
<td>Turkey (n = 2)</td>
<td>0.19 to 0.27 (0.04)</td>
<td>0.23</td>
</tr>
<tr>
<td>3.</td>
<td>France (n = 1)</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>4.</td>
<td>Egypt (n = 1)</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>5.</td>
<td>On average (n = 7)</td>
<td>0.05 to 0.27 (0.04)</td>
<td>0.16</td>
</tr>
</tbody>
</table>

3.1.2 Total concentration of As in ITF-wheat

Higher values of total As were detected for ITF-wheat originating from Egypt, following by Tunisia; but in all ITF-wheat samples the total concentration of As varied from 0.04 mg kg⁻¹ to 0.33 mg kg⁻¹ (Table 3).

Table 3. The total concentration of As in ITF-wheat.

<table>
<thead>
<tr>
<th>Number</th>
<th>Country of origin (number of samples)</th>
<th>Concentration (mg kg⁻¹)</th>
<th>Mean/median</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Turkey (n = 8)</td>
<td>0.04 to 0.25 (0.03)</td>
<td>0.14 / 0.16</td>
</tr>
<tr>
<td>2.</td>
<td>Oman (n = 4)</td>
<td>0.09 to 0.22 (0.03)</td>
<td>0.16 / 0.17</td>
</tr>
<tr>
<td>3.</td>
<td>Egypt (n = 3)</td>
<td>0.29 to 0.33 (0.01)</td>
<td>0.32 / 0.33</td>
</tr>
<tr>
<td>4.</td>
<td>Germany (n = 2)</td>
<td>0.08 to 0.14 (0.03)</td>
<td>0.11</td>
</tr>
<tr>
<td>5.</td>
<td>Tunisia (n = 1)</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>6.</td>
<td>On average (n = 18)</td>
<td>0.04 to 0.33 (0.03)</td>
<td>0.19</td>
</tr>
</tbody>
</table>
The detected concentration of As in ITF-wheat from Germany was three times lower than in the products from Egypt. According to ANOVA, the differences in the concentration of As in ITF-wheat can be assessed as statistically significant \((P < 0.004)\), regarding the samples which were sufficient for the test.

### 3.1.3 Total concentration of As in ITF-rice

The higher total concentration of As in ITF-rice was detected for samples originating from France and Turkey (Table 4), but ANOVA test revealed that the difference among the countries of origin was not significant \((P = 0.72)\).

<table>
<thead>
<tr>
<th>Number</th>
<th>Country of origin (number of samples)</th>
<th>Concentration (mg kg(^{-1}))</th>
<th>Mean/median</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Turkey (n = 7)</td>
<td>0.15 to 0.35 (0.03)</td>
<td>0.22 / 0.21</td>
</tr>
<tr>
<td>2.</td>
<td>France (n = 3)</td>
<td>0.15 to 0.39 (0.07)</td>
<td>0.24 / 0.20</td>
</tr>
<tr>
<td>3.</td>
<td>Libya (n = 1)</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>4.</td>
<td>On average (n = 11)</td>
<td>0.15 to 0.39 (0.05)</td>
<td>0.21 / 0.19</td>
</tr>
</tbody>
</table>

### 3.2 Discussion

Overall data assessment revealed that the concentration of As in the samples of ITF-mix produced in Turkey was comparable to ITF-rice of the same origin (Figure 1). On the contrary, the mean concentration of As in ITF-mix produced in Egypt was by 50 % lower than the concentration of As in ITF-wheat from Egypt. It was also found that the concentration of As in different types of ITF from the same country of production was not uniform. For instance, the concentration of As in ITF-wheat originating from Turkey was by about 36 % lower than in ITF-rice from the same country.

**Fig. 1.** Levels of As in commercial ITF samples of various origin collected in Libya (excluding the countries with the insufficient number of samples).
Although, the information on As concentration in wheat-containing ITF is poor, detected concentration of As in ITF-wheat in Libya could be assessed as quite high if compared to other studies: the total concentration of As in wheat-containing ITF samples collected in Spain did not exceed 0.02 mg kg\(^{-1}\) [27], but the concentration of As in similar products (mainly containing semolina and spelt flour) in Sweden was much lower (0.003 mg kg\(^{-1}\)) [21]. Furthermore, cereal-based ITF might be more abundant in potentially harmful elements (such as Cd, As, Sb) than milk-based ITF [21]. Statistical analysis revealed significant differences among the countries of origin for ITF-wheat, indicating that the process of raw commodities processing or other steps of industrial food production may become a source of potentially toxic elements. However, other factors are not excluded (e.g., transfer of As by food additives and supplements, mixing of raw material from various producers, inappropriate materials used for processing and storage) [28, 1].

Involvement of rice-containing ITF in children daily nutrition is substantiated by its nutritional and organoleptic properties such as high content of carbohydrates, low content of allergens, absence of gluten and specific taste [6, 7]. However, obtained data revealed that on the average concentration of As was higher for ITF-rice in comparison to other tested ITF samples. This finding is not surprising as many other studies have indicated a similar tendency – more significant contamination of rice versus other cereals [4, 6, 7, 12]. Firstly, this fact can be associated with higher accumulation efficiency of As transferred from soil and water to rice plants and grains. Secondly, the type of rice, degree of grain purity, as well as the geographical location of cultivation, are of importance. For example, the studies indicate that lower As contamination has been detected for basmati rice cultivated in the regions of India with a low geochemical background of As. However, rice cultivated in the USA and Spain contained a higher amount of As [29, 4, 11, 12]. The average concentration of As in the USA rice markets was reported 0.30 mg kg\(^{-1}\) [12]. However, the differences in the concentration of As in raw rice can be quite significant, e.g., rice cultivated in the USA may contain up to five times greater concentration of total As than rice produced in India [7].

Furthermore, cultivation mode is of importance as the transfer of As from substrate (soil and water) at anaerobic conditions into crops (such as rice) occurs more intensively than for conventionally grown cereals (wheat and barley) [30, 7]. In this case, speciation of As also can be taken into account as, for example, arsenate (As(V)-containing compound) dominates in aerobic soils, but As(III)-containing arsenite is predominant at anaerobic conditions [31] as element speciation is of great importance within toxicological assessment and bioavailability. The study carried out in the UK revealed that the most considerable part (75 % to 90 %) of As compounds in ITF are of inorganic forms [29], thus, emphasizing the control of As content as an issue of concern. Bioavailability of As in rice-based products may reach 90 %, that means very high exposure risk to consumers if the content of As in a food commodity is high. Therefore, regarding children, daily consumption of only 20 g that corresponds to four teaspoons of contaminated rice-containing food may result in exceeding the maximum permitted inorganic As levels [7]. In many countries of Asia, daily nutrition consists of rice-based food for both adults and children; thus, strict controlling measures must be implemented to ensure ITF safety.

4 Conclusions

This preliminary study on detection of the total concentration of As in commercial infant/toddler food available in Libya has revealed that rice-containing ITF is more abundant in As than other kinds of ITF and in comparison with similar studies performed in other countries. It should be remarked that the number of samples for some ITF was
insufficient for an in-depth food contamination survey; therefore, broader, and deeper investigation is needed in this field. Sources of As in food are both natural and human-induced; the main source of ITF contamination with As could be food industrial processing, manufacturing and storage, as well as cultivation of crops.

The study revealed the significance of monitoring or supervision over food safety, especially regarding ITF as these products are intended for the most vulnerable groups of consumers. Derived data are useful for daily intake assessment for infants and toddlers.

With sadness, the authors report Yogo Adhi Nugroho, one of the authors of this manuscript, passed away after a fight against COVID-19. The authors sincerely appreciate his enthusiasm and dedication to the writing of this manuscript.

References