

Research Article

Dietary exposure to total and toxic arsenic in Belgium: Importance of arsenic speciation in North Sea fish

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Total and toxic (sum of As(III), As(V), monomethylarsenic (MMA), and dimethylarsenic (DMA)) As concentrations were assessed in 19 respectively 4 different fish and shellfish species from the North Sea. Following results were obtained: (i) for fish an average total As concentration of 12.8 µg/g ww and a P90 value of 30.6 µg/g ww; (ii) for shellfish an average total As concentration of 21.6 µg/g ww and a P90 value of 40.0 µg/g ww; (iii) for fish an average toxic As concentration of 0.132 µg/g ww and a P90 value of 0.232 µg/g ww; (iv) for shellfish an average toxic As concentration of 0.198 µg/g ww and a P90 value of 0.263 µg/g ww. For the Belgian consumer the average daily intake of total arsenic from fish, shellfish, fruit, and soft drinks (the main food carriers of As in Belgium) amounts to 285 µg/day with more than 95% coming from fish and shellfish, while for a high level consumer it amounts to 649 µg/day, more than twice the average value. Using the same daily consumption pattern for the selected food products as for total As, we find that the average daily intake of toxic As amounts to 5.8 µg/day, with a 50% contribution of fish and shellfish and the high level intake to 9.5 µg/day. When considering the FOA/WHO Expert Committee's recommendation for inorganic As intake of 2 µg/kg bw/day or 140 µg/day for a 70 kg person, the toxic dose in Belgium is thus an order of magnitude lower.

Keywords: Arsenic / Dietary intake / North Sea / Seafood / Toxic

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1 Introduction

Humans are exposed to many sources of As (food, water, soil, and air), but exposure *via* diet is by far the most important one and the major source of As in the human diet is seafood (with the exception of areas with an endemic high drinking water contamination). Considerable differences in daily intake rates of total As can be found in the literature; e.g., 56 µg/day in the US [1] but 458.5 µg/day in Tarragona,

Spain. [2] Variations in the amount of seafood in the diet of the studied populations are probably the major cause of the observed differences. However, in some specific cases other food products, especially for populations preferentially consuming those foodstuffs, can also have a large influence on the daily As intake rate. Al Rmali *et al.* [3] made a survey of As in foodstuffs on sale in the UK and imported from Bangladesh and observed that the As levels in vegetables from the UK were between two and three times lower than those found in vegetables imported from Bangladesh. Williams *et al.* [4] reported elevated levels of As in South Central US processed rice compared to California. Yet the number of dietary studies making a distinction between on the one hand total and on the other hand toxic/inorganic As levels is very limited. The daily intake rates for toxic/inorganic As vary between 4.8 µg/day (Canada [5]), 5.6 µg/day (UK, [6]), 8.3 µg/day (US [5]) and 56

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Abbreviations: AB, arsenobetaine; AFM, atomic fluorescence spectrometer; DMA, dimethylarsenic; HG, hydride generator; MMA, monomethylarsenic; PTWI, provisional tolerable weekly intake; TDI, tolerable daily intake

µg/day (Bangladesh [7]). The Bangladesh situation is an atypical example of exposure to As: in fact the daily intake rate of total As (68 µg/day) is only slightly higher than that of toxic/inorganic As. The high inorganic As concentrations in the soil and aquatic system, including drinking water, result in high inorganic As levels in foodstuffs (about 82% of the total As in food was in the inorganic form) and a high exposure to the population.

This paper describes our total and toxic As levels observed in North Sea fish and shellfish as well as literature results on the levels in fruit and soft drinks, which are other major As carriers. In addition, knowing the contamination levels of As in these food products together with their daily consumption rates, daily As intake rates in the human body could be calculated. These values are representative for average and high level (P90–90% percentile) Belgian consumers.

1.1 As in marine organisms

Arsenic levels of marine organisms are generally much higher than those of terrestrial organisms. Even more, amongst marine organisms, it is fish, crustaceans, and mollusks that contain the highest As concentrations. The amounts of As that fish accumulate directly from the water is nevertheless supposed to be very limited, but instead, they are believed to accumulate As mainly *via* diet. Indeed, a number of other elements (*e.g.*, Hg) are also translocated through the food chain and thus an important question with regard to toxicity of As relates to the ability of organisms to concentrate As.

1.2 Origin and chemical forms of As in fish and shellfish

Total As concentrations reported in phytoplankton and algae are markedly higher than those in water or sediments from the same study area. The brown macroalgae *Fucus spiralis* accumulates four times more arsenate (H_3AsO_4) than arsenite (H_3AsO_3) from equivalent concentrations in seawater [8]. Indeed, the close relation between the chemical properties of As and phosphorus tends to cause dissolved arsenate to be taken up together with phosphate and its accumulation via the cellular phosphate transport system. Microorganisms are thus able to accumulate substantial amounts of As and this pathway is undoubtedly an important introduction of As in aquatic food webs.

Nevertheless, microorganisms do not accumulate As to an unlimited extent. Several studies observed toxicity effects, already at this level of the food chain [9, 10]. In the scope of biomagnification, it would be logical that the accumulation of As *versus* its level in water would be even more pronounced higher up the food chain. Certainly, for mollusks and crustaceans as well as for fish, diet is a far more important source of As than water [11]. However, in prac-

tice biomagnification of As, higher up the food chain, is not perceived.

Also for fish, differences in As content could not be explained only by looking at their diet. De Gieter *et al.* [12] concluded that fish species that feed primarily on larger fish contain less As than species that feed on benthic organisms and smaller fish. However, these authors also observed differences in As content between fish species that basically have the same feeding patterns; brill for example, appeared to contain less As than megrim.

Whereas in the water column, As is present as arsenite, arsenate, and in minor amounts as monomethylarsenic (MMA) and dimethylarsenic (DMA); arsenobetaine (AB) is the major As form in marine animals, arsenosugars in marine algae. The characterization of the different arsenicals, their abundance, and the pathways of their synthesis in marine life become progressively elucidated (*e.g.* [13, 14]).

1.3 As concentrations in fish and shellfish

In fish, mollusks, and crustaceans, large variations in As contamination, both inter- as intraspecies, are observed all over the world. What exactly causes these differences is not quite well understood, but it can be hypothesized that they are related to: (i) differences in diet; (ii) differences in the form of ingested arsenic; (iii) seasonal changes, and (iv) the geographical area. Langston [15] reported a contamination of the mollusk *Srobicularia plana*, at the southwestern coast of UK and related the elevated As levels to contamination of the sediment. It seemed that seasonal variations, together with phytoplanktonic activity that changed the chemical form of dissolved As in the water column, influenced the accumulation of As by the mollusks greatly. An extensive study of fish inhabiting the French coastal waters, also indicated significant differences from one sampling area to another; for example, the As concentrations in samples of flounder ranged from 8.2 to 41.1 mg/kg dw; in samples of dogfish from 72 to 230 mg/kg dw [16]. These variations appeared to be only explainable by local or seasonal variations in food source. Another dataset of this study showed a correlation between As level and the fish's length, but this correlation did not appear to be statistically significant. The observed increases in As concentration could be more easily explained by differences in diet between juvenile and adult fish.

The levels of As contamination of seafood could at first sight pose a serious threat to human health upon consumption. However, this would only be the case if the As present, would all be in a toxic form. Schoof and Yager [17] compiled available data of total As, inorganic As, MMA, and DMA from marine seafood and found that 3% of the total As was inorganic at the 75th percentile of the dataset. In addition, they also reported that DMA should not contribute substantially to potential health risks from As in seafood and that MMA was seldom detected.

As a direct result, assessments of only the total As concentrations in fish, cannot provide information about potential health impacts. For this purpose, knowledge of speciation is an absolute prerequisite.

2 Materials and methods

2.1 Fish and shellfish samples

In 1997 and 1998 about 300 samples of 25 different sea fish and 4 shellfish and crustacean species were randomly picked out of the catch of the day, at the fish markets of Zeebrugge and Nieuwpoort. The fishes had been caught by trawling in different areas of the North Sea and the English Channel. Information about this area was supplied by the fishermen of the according boats. Table 1 lists all species investigated. Prior to analysis, the subsamples were weighed, deepfrozen, lyophilized, weighed again to determine the water content, and manually homogenized. Each collected fish and shellfish was regarded upon as an individual sample, except for the shrimps (mixture of five individuals).

2.2 Total arsenic in fish

The samples were dissolved and oxidized by a mixture of HNO_3 and H_2O_2 in a microwave oven (CEM Microdigest 2000), under controlled pressure. Lyophilized, homogenized sample (0.1–0.2 g) was weighed in a Teflon digestion bomb. Sub-boiled HNO_3 (6 mL, 65%, Merck) was added to the sample and the bombs were firmly closed and put in the microwave oven to digest. After cooling down, 1 mL H_2O_2 (27% p.a., Merck) was added to the solution and the Teflon bombs were placed back into the microwave for a second digestion. The mineralized samples were diluted to 50 mL with Milli-Q water and stored in decontaminated HDPE bottles. The digests were analyzed for total As by Inductively Coupled Plasma-MS (VG PlasmaQuadII), using In, Re, Ru, and Bi as internal standards. Certified reference materials, DORM-2 (Dogfish muscle), DOLT-2 (Dogfish liver), and TORT-2 (Lobster hepatopancreas) of the National Research Council of Canada as well as blanks were included in every digestion batch and submitted to the same digestion and analytical procedure as the samples. For the certified materials average recoveries of 108% (TORT-2), 114% (DORM-2), and 102% (DOLT-2) were found.

2.3 Toxic arsenic in fish

The goal was to find an analytical procedure allowing to distinguish between (i) the nontoxic fraction, which consists mainly of AB and to a lesser extent of arsenocholine (AC) and tetramethylarsonium ion (TeMA) and (ii) the toxic species, *i.e.*, inorganic arsenic – arsenite (As(III)) and arsenate (As(V)) – on the one hand, and organic arsenic

compounds – MMA and DMA – on the other hand. In aquatic solution the analysis of the inorganic and methylated As species is rather routine (*e.g.*, a general discussion of analytical speciation methods of As in aquatic samples can be found in Leermakers *et al.* [18]).

However, the speciation in biota is more complex. The fish sample was mineralized in the same way as for the total As determinations. During the digestion all “labile” As compounds present in fish tissue are oxidized. Stable compounds such as AB and AC only liberate As under very stringent conditions (high temperatures and/or very strong oxidants) and remain unchanged during the mineralization procedure used here. Additionally, AB, AC, and TeMA do not form volatile hydrides, contrarily to As(III), As(V), MMA, and DMA, which we further call the toxic As fraction.

The mineralized samples were measured using a hydride generator (HG) coupled to an atomic fluorescence spectrometer (AFS) (PS Analytical Excalibur). The more labile As compounds were reduced to As (III) prior to analyses, by a mixture of HCL (30% v/v), KI (1% w/v), and ascorbic acid (0.2% w/v). The solution was pumped into a gas–liquid separator and mixed with NaBH_4 (1.3% w/v solution in 0.1 M NaOH) to form arsenic hydrides. The arsines were purged from the solution using an argon carrier stream and detected by atomic fluorescence. The LOD of this method, calculated as three times the SD of a blank injected ten times, divided by the sensitivity, was 0.1 $\mu\text{g/L}$, or converted to tissue material, 0.005 mg/kg ww. The method was tested on the same certified materials as mentioned above. The average toxic As fraction equaled 6.9% for TORT-2, 1.3% for DORM-2 and 3.3% for DOLT-2. Spikes of AB to these reference material digests did not show any increase in measured concentrations. These findings correspond to similar speciation studies carried out by Goessler *et al.* [19] and Karadjova *et al.* [20].

2.4 Accuracy tests

An additional check was carried out on the certified materials, using strong-anion exchange HPLC-HG-AFS, with a mobile phase of 20 mM $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ at pH 6.0. Consequently, as the four compounds (As(III), As(V), DMA, and MMA) we considered as the toxic As fraction, are neutral or in anionic form at this pH, a qualitative and quantitative separation and detection of these compounds can be obtained. Extraction of the certified materials was done by ultrasonication and centrifugation in a mixture of methanol and Milli-Q water (1:1). The results of this experiment are summarized in Table 2. They were in a reasonable agreement with the toxic As fractions discussed in this paper. These findings confirmed that DMA is the only of the four toxic arsenicals present in a detectable amount in DORM-2. It accounted for 1.1% of the total As content in this reference material. This method was further evaluated by partic-

Table 1. Speciation of the toxic As fraction for reference materials

Reference material	HG-AFS			HPLC-HG-AFS			Sum
	Certified total	Toxic fraction	As(III)	DMA (mg As per kg)	MMA	As(V)	
ORM-2	18.0	0.25	<DL	0.20	<DL	<DL	0.20
DOLT-2	16.6	0.54	<DL	0.84	0.035	<DL	0.88
TORT-2	21.6	1.6	<DL	0.83	0.056	0.32	1.2

Detection limits are 0.0015 mg/kg for As(III) and MMA, 0.0020 mg/kg for DMA and 0.0030 mg/kg for As(V).

ipation in an intercalibration organized by BCR and set up for the development of new certified biological material for As.

3 Results and discussion

Unfortunately, up till now, most studies focused on the development of analytical techniques to accurately speciate As compounds in fish, instead of focusing on their effective assessment. Our data of total As levels and the abundance of toxic As substances in marine organisms from the North Sea are listed in Table 1, providing evidence for the relatively small amounts of toxic arsenicals in seafood. In fish, the concentrations of inorganic and other toxic As compounds generally stay below 5% of the total As content. In a review article about As [21], they reported that fish, fruits and vegetables primarily contain organic As compounds while less than 10% of the total As exists in the inorganic form. Also Schoof and Yager [17], reviewing all data available on the speciation of As in seafood, came to the same conclusion.

3.1 Levels of As in food products and intake rates for the Belgian population

Dietary exposures to total arsenic have been estimated for average and high level adult consumers in a number of countries such as US and Canada [5], UK [6], France [22]. From these studies it appears that fish and fish products (especially from marine origin) are a major route of total arsenic accumulation in humans. To determine the importance of fish and shellfish as As carriers in the food basket of the Belgian population we calculated the daily As intake from fish, shellfish, and mollusks, fruit, and soft drinks which represent more than 80% of the daily intake in France, where food products and diet are comparable with those in Belgium.

The total As concentrations, average and P90, in fish and shellfish are the average of our measurements in 19 respectively 4 different species of the North Sea (Table 1). Our results compare very well with those obtained by Luten *et al.* [23], who analyzed total As levels in 13 North Sea fish

Table 2. Total and toxic As levels in North Sea fish and shellfish

Species	N	Total As (mg/ kg ww)	Range	% Toxic	Toxic As (mg/ kg ww)
<i>Fish</i>					
Dogfish	20	40.70	21–64	0.59	0.240
Thornback Ray	20	20.20	6.2–36	0.84	0.170
Conger	1	2.37		1.18	0.028
Atlantic Cod	5	5.10	3.1–7	1.33	0.068
Saithe	5	3.60	1.8–5.7	1.33	0.048
Pouting	5	4.10	2.5–5.4	2.20	0.090
Whiting	5	4.90	4.0–6.5	1.37	0.067
Ling	5	3.40	2.1–8.5	2.00	0.068
Angler	20	8.50	4.1–13.7	0.93	0.079
European Sea-bass	1	1.10		4.00	0.044
Dab	13	10.20	6.5–21	1.86	0.190
European Plaice	17	13.80	7.7–26	1.30	0.180
Lemon Sole	20	39.70	14.9–76	0.58	0.230
Common Sole	16	14.50	4.1–49	1.45	0.210
Sand Sole	9	13.70	4.1–35	1.53	0.210
Witch	5	28.30	9.4–49	0.85	0.240
Megrim	6	9.70	3.8–12.8	1.34	0.130
Brill	5	2.00	1.4–2.9	2.50	0.050
Turbot	1	17.90		0.89	0.160
average		12.83		1.03 ^{b)}	0.132
STD		12.01			0.075
P90		30.58			0.232
<i>Mollusks and crustaceans</i>					
Great Scallop	27	1.86	0.99–3.61	0.75	0.200
Whelks	4	40.50	16.5–66	0.32	0.130
Common Shrimp	5 ^{a)}	5.20		3.27	0.170
Edible Crab	2	38.70	37–41	0.75	0.290
average		21.57		0.92 ^{b)}	0.198
STD		20.88			0.068
P90		39.96			0.263

a) Mixture of five individuals.

b) Calculated from the average total and toxic As concentrations.

species of which 12 were the same as in our study. Their average As concentration amounted to $17.4 \pm 21.7 \mu\text{g/g ww}$, ours to $12.8 \pm 12.0 \mu\text{g/g ww}$. The average concentrations in fruit and soft drinks are $76 \mu\text{g/g ww}$ and $17 \mu\text{g/g ww}$, respectively [22]. The daily consumption of fish and shellfish from marine origin, fruit, and soft drinks

Table 3. Daily intake rates of total and toxic As for the Belgian diet

Food product	Total As Average ($\mu\text{g/day}$)	Total As P90 ($\mu\text{g/day}$)	Toxic As average ($\mu\text{g/day}$)	Toxic As P90 ($\mu\text{g/day}$)
Sea fish	189	449	1.94	3.41
Shellfish	86	160	0.79	1.05
Fruit	8 ^{a)}	33.7 ^{a)}	1.95 ^{b)}	
Soft drinks	2.3 ^{a)}	6.1 ^{a)}	1.16 ^{c)}	
TOTAL	285	649	5.84	9.49^{d)}

a) From ref. [22].

b) According to the data of ref. [26], 45.5% of total As in fruit is inorganic.

c) For soft drinks we assumed that half of the total As burden was toxic.

d) The P90 value was estimated from the sea fish and shellfish P90 values and the fact that these two sources contributed to 50% of the average daily intake rate of toxic As.

by the Belgian population is reported by Bilau *et al.* [24] and the Belgian Food Consumption Enquiry (in dutch, <http://www.iph.fgov.be/EPIDEMIO/epinl/foodnl/table04.htm>): fish (14.7 g/day), shellfish (4 g/day), fruit (105 g/day), and soft drinks (136 g/day). The daily intake rate for each of the four selected food products is calculated as the product of the average total As level in the food product (in $\mu\text{g/g}$) multiplied by the daily consumption of that food product (in g/day). For high level consumers, the average total As levels are replaced by the P90 ones. This is done to get an idea of the daily intake for consumers that eat preferentially seafood and fruit species with a high As content (e.g., dogfish or lemon sole). The high level values for fruit and soft drinks are also obtained from Leblanc *et al.* [22]. Results are shown in Table 3.

The average daily intake amounts to 285 $\mu\text{g/day}$ (more than 95% comes from fish and shellfish), the high level to 649 $\mu\text{g/day}$, more than twice the average. Compared to other countries we find higher intake rates (average value – P90 value), especially for the average value: our results (285–649 $\mu\text{g/day}$), UK (88–489 $\mu\text{g/day}$; [6]), France (62–163 $\mu\text{g/day}$ [22]), Japan (182 $\mu\text{g/day}$ [25]), US (56 $\mu\text{g/day}$ [1]), Tarragona-Spain (459 $\mu\text{g/day}$ [2]), Bangladesh (68 $\mu\text{g/day}$ [7]). The relatively higher intake rates of total As by the Belgian population has two origins: (i) the consumption of relatively important quantities of seafood and (ii) the North Sea is still one of the most contaminated coastal seas.

Total arsenic levels are, however, not a good indicator for estimating health risks, because of the low toxicity of AB and arsenosugars, major As fractions in marine organisms and algae. In Table 1 the toxic As fractions we measured in North Sea fish and shellfish are also shown. For fruit and soft drinks in Europe, no ready available data about the toxic As fractions were found. According to Schoof *et al.* [26], about 25% of the total As contamination in fruit in the US is in the toxic form. For soft drinks, the toxic As frac-

tions depends on the soft drink concentrate and the local water used for dilution. For further calculations, we assumed that half of the As burden in soft drinks is in the toxic form. To determine the daily uptake of toxic As, the same daily consumption pattern and calculation method is used as for total As hereabove. We find that the average daily intake of toxic As amounts to 5.8 $\mu\text{g/day}$, with a 50% contribution of fish and shellfish and the high level intake to 9.5 $\mu\text{g/day}$, assuming that fish and shellfish also contribute for about 50% since we have no P90 data for toxic As in fruit and soft drinks. Compared to other countries we find similar results except that in Bangladesh the daily intake of toxic/inorganic As is much higher due to the fact that almost all of the As in food is in the inorganic form: our results (5.8–9.5 $\mu\text{g/day}$), Canada (4.8–12.7 $\mu\text{g/day}$ [5]), US (8.3–14 $\mu\text{g/day}$ [5]), UK (5.6–9.1 $\mu\text{g/day}$ [6]), Bangladesh (56 $\mu\text{g/day}$ [7]).

3.2 Toxicity

Some authors suggest that, at low concentrations, As might be an essential element for organisms [27]. These studies imply that As plays a physiological role in the methionine metabolism. On the contrary, the toxicity of As has been sufficiently documented over the centuries. According to Vega *et al.* [28], the toxicity of arsenicals decrease in the order, inorganic arsenite or As(III) > DMA > MMA > inorganic arsenate or As(V). Arsenite's toxicity is amongst others believed to arise from reaction with sulfhydryl groups. The compound would thus inhibit sulfhydryl enzymes necessary for the cellular metabolism. Arsenate may replace phosphate in the ATP/ADP mechanism and thus inhibit the oxidative phosphorylation. Arsenic compounds are also described as antagonistic to the essential trace elements iodine and selenium [29]. Toxicity arising from ingestion of inorganic As, is believed to manifest itself in systemic effects involving the skin, the cardiovascular and the neurological system. Additionally, the IARC [30] concluded that there is enough evidence to associate the exposure to inorganic As with skin, lung, and bladder cancer and classified As as a so-called “group 1 carcinogen” to humans. DMA is equally shown to induce organ specific lesions in the lungs of mice, rats and humans [31]. The same authors also mention dose-dependent increases in urinary bladder tumors upon lifetime exposure to DMA from diet or drinking water. DMA is believed to act either as a cancer promoter or as a complete carcinogen in different animals and it is genotoxic. MMA(III), a biotransformant of inorganic arsenic, is up to 26 times more toxic than inorganic arsenite in Chang human hepatocytes [32]. According to Lin *et al.* [33], MMA(III) is over 100 times more potent than inorganic As(III) as an *in vitro* inhibitor of thioredoxin reductase. Another recent *in vitro* study showed that MMA(III) was more cytotoxic to human cells (hepatocytes, epidermal keratinocytes, and bronchial epithelial cells),

compared to inorganic As(III) and As(V) [34]. The authors concluded that high methylation capacity did not protect these cells from the acute toxicity of trivalent arsenicals.

Fortunately, the vast majority of arsenic in fish and seafood is in the forms of AB, a compound that is essentially inert, non-toxic, and excreted without transformation [35]. There have been only limited studies of arsenosugar toxicity. In mammalian cells, a synthesized arsenosugar was not cytotoxic at micromolar levels, but a more recent study compared the *in vitro* toxicity of two synthetic arsenosugars, one trivalent and the other pentavalent [36]. The trivalent sugar was positive for cytotoxicity and DNA nicking at concentrations of about 500–600 μM , but inactive for *Salmonella* mutagenicity.

The quantities of inorganic arsenic and MMA found in seafood are sufficiently small to mitigate concerns about their possible adverse effects in seafood eaters [37]. On the other hand, DMA and arsenosugars in seafood pose at least theoretical risks. An issue is whether the quantity of DMA contained in ingested seafood or derived from arsenosugars in ingested seaweed and mollusks is sufficient to cause such carcinogenic or genotoxic effects. Based on conservative dose estimates and the likelihood that arsenic's carcinogenic mechanisms follow sublinear dose–response curves, Borak and Hosgood [35] estimated a margin of exposure of at least 10^3 – 10^4 between carcinogenic doses used in rodent studies and those expected after human consumption of large quantities of seafood.

3.3 Legal limits

Legal limits regarding arsenic exposure have been progressively improved according to increased knowledge about (i) the speciation of As compounds and (ii) the bioavailability of the toxic As species. Since major calamities involving As in drinking water in Bangladesh and West Bengal, several reports and committees have focused on setting or adjusting maximum permissible concentrations for drinking water. Next to drinking water, most attention was paid to fish and seafood since they are common food products and may contain high As levels. Initially, norms in fish were only established for total As concentrations, while studies on the speciation and bioavailability of inorganic As in fish and other foodstuffs were not given high priority. In 1967, 50 $\mu\text{g}/\text{kg}$ body weight was enforced as the tolerable daily intake (TDI) of As, but this norm dates back from before epidemiological studies indicated that inorganic As might be carcinogenic to man. Therefore, the Joint FAO/WHO Expert Committee [38, 39] set a limit of 0.1 mg/kg ww for inorganic As in fish and seafood and arrived at an updated provisional TDI, specific for inorganic As, of 2 μg inorganic As *per kg* bw, thus a provisional tolerable weekly intake (PTWI) of 0.015 mg inorganic As *per kg* bw.

Besides drinking water and seafood, consumption of other foodstuffs such as for example rice and seaweed must

also be considered in assessments of arsenic health risk, especially for regular consumers of those food products (e.g., Japanese population). Arsenic is present in rice grain mainly as inorganic arsenic. After cooking, inorganic arsenic contents increase significantly and simulated gastrointestinal digestion show that the bioaccessibility of inorganic arsenic reached 63–99% [40]. The bioaccessible inorganic As in raw seaweed (54.0–66.5%) also increases after cooking (78.3–84.4%), a fact that is considered to be of interest because this is the usual form in which this seaweed is ingested [41]. In addition, speciation of the inorganic As in the bioaccessible fraction revealed a different arsenic(III)/arsenic(V) relationship in the product when raw or cooked. However, rice and seaweed are actually not important for the dietary exposure to total and toxic As in Belgium.

The average As intake by the Belgian population amounts to 5.8 $\mu\text{g}/\text{day}$ (9.5 $\mu\text{g}/\text{day}$ for the high level consumer). Expressed per kg of body weight and assuming an average person of 70 kg these values become 0.08 $\mu\text{g}/\text{kg}$ bw/day (0.14 $\mu\text{g}/\text{kg}$ bw/day for a high level consumer). When considering the FAO/WHO Expert Committee's PTWI for inorganic As of 2 $\mu\text{g}/\text{kg}$ bw/day, the toxic dose is thus not met.

Conversely, this PTWI can produce either permitted amounts of seafood consumption, or permitted levels of contamination. To arrive at the level of concern described as PTWI, the same person of 70 kg, would daily have to ingest 140 μg inorganic As. Considering 150 g portions of fish, the inorganic As content of the fish would have to be 0.93 mg/kg ww. This concentration level is several times higher than the average of 0.13 (0.20) mg/kg ww encountered in fish (shellfish).

4 Concluding remarks

Fish and shellfish are by far the major sources of total As intake by the Belgian population. They represent more than 90% of the daily intake of total As (around 285 $\mu\text{g}/\text{day}$), fruit and soft drinks ranked in third and fourth place. However, most of the As compounds present in fish and shellfish (essentially AB) are not toxic or have a very low toxicity. Therefore, intake rates of toxic As compounds by the Belgian population have been estimated. These values amount to 5.8 $\mu\text{g}/\text{day}$ for an average consumer and 9.5 $\mu\text{g}/\text{day}$ for a high level consumer. They are much lower than the TDI of 140 $\mu\text{g}/\text{day}$ (for a 70 kg person) set by the Joint FAO/WHO Expert Committee in 1989 [39] and are comparable to toxic As intake rates observed in US, Canada and UK.

The authors have declared no conflict of interest.

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