

10th NTES Symposium  
Review

## Arsenic in the human food chain, biotransformation and toxicology – Review focusing on seafood arsenic



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### ABSTRACT

Fish and seafood are main contributors of arsenic (As) in the diet. The dominating arsenical is the organoarsenical arsenobetaine (AB), found particularly in finfish. Algae, blue mussels and other filter feeders contain less AB, but more arsenosugars and relatively more inorganic arsenic (iAs), whereas fatty fish contain more arsenolipids. Other compounds present in smaller amounts in seafood include trimethylarsine oxide (TMAO), trimethylarsoniopropionate (TMAP), dimethylarsenate (DMA), methylarsenate (MA) and sulfur-containing arsenicals. The toxic and carcinogenic arsenical iAs is biotransformed in humans and excreted in urine as the carcinogens dimethylarsinate (DMA) and methylarsonate (MA), producing reactive intermediates in the process. Less is known about the biotransformation of organoarsenicals, but new insight indicates that bioconversion of arsenosugars and arsenolipids in seafood results in urinary excretion of DMA, possibly also producing reactive trivalent arsenic intermediates. Recent findings also indicate that the pre-systematic metabolism by colon microbiota play an important role for human metabolism of arsenicals. Processing of seafood may also result in transformation of arsenicals.

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### Introduction

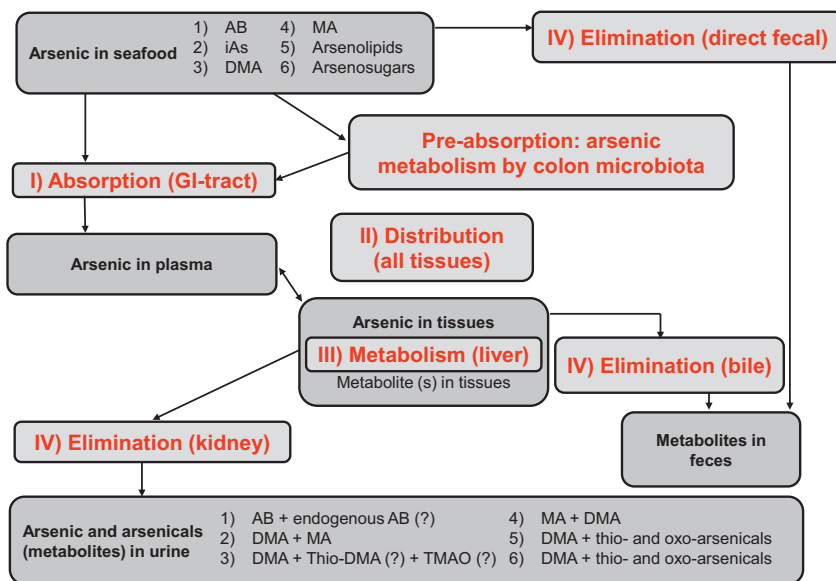
The beneficial effects on health of a diet consisting of a moderate fish and seafood intake are well established [1–3]. On the other hand, fish and seafood may also contain harmful contaminants and

other undesirable substances such as mercury and persistent halogenated compounds, which has resulted in a number of risk-benefit assessments of fish and seafood during the last decade [3–8]. However, the role of arsenic (As) has received attention only in few reports [1,9,10].

Seafood is the major contributor to As in the diet. Although As in seafood mostly occurs as organic As species, occurrence data on As in seafood are usually reported as total arsenic (tAs). However, due to the differences in toxicity among the different arsenicals, there

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**Fig. 1.** Illustration of the absorption, distribution, metabolism and elimination (ADME) of arsenicals from seafood in humans, based on current knowledge. The main arsenicals ingested from seafood and into which arsenical(s) these are metabolized are indicated.

is a need for speciation data to conduct a risk assessment of As ingested from seafood [11]. Furthermore, there is a need to explore whether the arsenicals present in seafood may be converted during food processing to As species of possible health concern. Of additional importance is to examine whether arsenicals ingested with (sea)food may convert into intermediates or As species of toxicological concern by the intestinal microflora or during metabolism in the body. The aim of the present paper is to review what is currently known about the chemistry, metabolism and toxicity of arsenicals in seafood (Fig. 1).

### Chemico-biological characteristics of arsenic

Arsenic is a metalloid with the atomic number 33 and belongs to group 15 in the Periodic Table. The German scholar and alchemist Albertus Magnus (1193–1280) is believed to be the first who isolated As in 1250. Arsenic can exist in four oxidation states:  $-3$ ,  $0$ ,  $+3$  and  $+5$ , the latter state being the dominant one under oxygenated and normal environmental conditions (Table 1). The majority of As species found in organisms and foods are in the pentavalent oxidation state [11,12].

The chemistry of As shows similarities with other elements in the same group of the Periodic Table, i.e. nitrogen and phosphorous. For example, arsenate ( $\text{AsO}_4^{3-}$ ), occurring in seawater together with the structurally similar phosphate ( $\text{PO}_4^{3-}$ ), are indistinguishable to marine algae, hence the uptake of arsenate is high [11]. In addition, the As compound arsenobetaine (AB) (Table 1) has structural similarities to glycine betaine [ $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-$ ], a nitrogen betaine, which is used as an osmolyte by aquatic organisms to maintain osmotic balance under conditions of changing salinity [13]. These structural similarities might explain the high concentrations of inorganic arsenic (iAs) in marine algae and the higher concentrations of AB in marine organisms compared to freshwater organisms.

Arsenic is not considered to be an essential element for humans. Research on the possible essentiality of As is scarce and mostly conducted in the 1970s and 1980s [14]. However, based on animal studies (chickens, hamsters, goats, miniature pigs and rats) indicating that As deprivation results in depressed growth, abnormal reproduction, growth retardation and fragile red blood cells, a few

researchers have hypothesized that As is an essential element for humans at very low dosages [15–17].

### Arsenicals in food

Food is the primary contributor for human As intake for those that are not exposed through occupation or drinking water [12,14,18]. Already at the beginning of the 20th century reports on high concentrations of As in marine organisms were presented [19]. The As concentrations vary widely depending on the food type, growing conditions (type of soil, water, geochemical activity conditions, use of As pesticides) and processing techniques [12]. Most monitoring data are still reported as total As (tAs), thus not differentiating the various arsenicals, although As in foods occurs as a mixture of inorganic and organic species (organoarsenicals) [11].

When chemically quantified, As (V) and As (III) are usually reported together and referred to as the sum of iAs. Foods of terrestrial origin generally contain concentrations of tAs below  $0.02 \text{ mg As/kg wet weight (ww)}$  [20] and therefore have low concentrations of iAs. The exceptions are plants that accumulate As by root uptake from the soil (e.g. the rice plant) [21] or by absorption of airborne As deposited on the leaves, e.g. tea [22]. Cereal and cereal products, and in particular rice and rice based products, have the highest iAs concentrations with  $0.1\text{--}0.4 \text{ mg As/kg dry weight (dw)}$  [11,23,24]. The proportion of iAs of tAs in rice ranges between 10 and 93%, and brown rice seems to have a higher iAs content than white rice, indicating that the As is attached to bran components [25,26]. The iAs in rice is probably present both as As (III) and As (V) [27,28]. Rice may also contain minor amounts of organic As such as DMA (V) [28,29].

Although fish and seafood are the food groups with the highest tAs concentrations, these food groups are generally low in iAs (usually  $<0.2 \text{ mg As/kg dw}$ ) [11,30]. A few exceptions exist, e.g. some marine algae, with hijiki (*Hizikia fusiforme*) having an extremely high iAs concentration (arsenate  $>60 \text{ mg/kg}$ ) [11]. Bivalves, like blue mussels (*Mytilus edulis*), also have relatively high concentrations of iAs with concentrations ranging between  $0.001$  and  $4.5 \text{ mg As/kg}$  [31].

While terrestrial organisms mainly contain As in the form as iAs, most of the As in marine organisms are organoarsenicals with levels between  $1$  and  $100 \text{ mg As/kg ww}$  [11]. Arsenobetaine (AB),

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