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Stability of arsenic compounds in seafood samples during processing and storage by freezing

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ABSTRACT

In this study, the stability of arsenic compounds in fresh and frozen samples of raw, boiled and fried Atlantic cod (*Gadhus morhua*), Atlantic salmon (*Salmo salar*) and blue mussel (*Mytilus edulis*) were examined. Results show that the total arsenic concentrations of the fresh Atlantic cod and Atlantic salmon samples were not different from the frozen samples within the same seafood type. For blue mussel, the total arsenic concentration decreased significantly after storage. Inorganic arsenic was found only in blue mussels and, importantly, no significant increase of inorganic arsenic was observed after processing or after storage by freezing. The content of tetramethylarsonium ion was generally low in all samples types, but increased significantly in all fried samples of both fresh and frozen seafood. Upon storage by freezing, the arsenobetaine content was reduced significantly, but only in the samples of blue mussels.

1. Introduction

Seafood contains nutrients associated with various beneficial health effects and is regarded as an important part of a healthy diet. In the Norwegian guidelines for food and nutrition, an increased intake of fish and other seafood is particularly recommended (Norwegian Ministries, 2007). Seafood is a good source of proteins, omega-3 fatty acids, vitamin D, vitamin B_{12}, selenium and iodine (Alexander et al., 2007). Nevertheless, seafood also contributes substantially to dietary arsenic, which is one of the trace elements of concern in relation to food safety (Francesconi, 2007). A wide range of arsenic compounds, including inorganic arsenic, has been reported in marine organisms. Table 1 shows a selection of some of the chemical forms of arsenic typically found in seafood. The inorganic arsenic compounds, arsenate (As(V)) and arsenite (As(III)), are toxic and carcinogenic, whereas the methylated species methylarsonate (MA), dimethylarsinate (DMA) and tetramethylarsonium ion (TETRA) are less toxic. In the recent Scientific Opinion on Arsenic in Food, the European Food Safety Authority (EFSA) set a range of benchmark dose lower confidence limit ($BMDL_{01}$) values between 0.3 and 8 μg/kg bodyweight (bw) per day (EFSA, 2009). The $BMDL_{01}$ values were identified for lung, skin and bladder cancer, as well as skin lesions, with the lowest values being found for lung cancers (EFSA, 2009). The estimated dietary exposures to inorganic arsenic, for average and high level consumers in Europe, are within the range of $BMDL_{01}$ (EFSA, 2009). The Joint FAO/WHO Committee on Food Additives (JECFA) also recently re-evaluated arsenic (WHO, 2010). A benchmark dose lower confidence limit for a 0.5% increased incidence of lung cancer ($BMDL_{0.5}$), from epidemiological studies, was determined to be 3.0 (range 2–7) μg/kg bw per day of inorganic arsenic. The Committee withdrew the previous provisional tolerable weekly intake (PTWI) of 15 μg/kg bw set for inorganic arsenic. Mean dietary exposures to inorganic arsenic ranged from 0.1 to 3.0 μg/kg bw per day in the United States of America (USA) and various European and Asian countries. JECFA noted that more accurate information on the inorganic arsenic content of foods, as they are consumed, is needed to improve assessments of dietary exposures of inorganic arsenic species. The predominant arsenic compound in seafood, arsenobetaine (AB), which is excreted unchanged, is considered non-toxic (Borak & Hosgood, 2007). Other arsenic compounds usually found in

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Table 1
Acronyms and chemical formulae of the arsenic compounds included in the present study. For simplicity the compounds are depicted in their fully deprotonated form. Nomenclature is as proposed by Francesconi and Kuehnelt (2004).

Acronym	Arsenic compounds	Formula
As(V)	Arsenate	$As(O^-)_3$
As(III)	Arsenite	$O{=}As(O^-)_3$
MA	Methylarsonate	$CH_3AsO(O^-)_2$
DMA	Dimethylarsinate	$(CH_3)_2AsO(O^-)$
TMAO	Trimethylarsine oxide	$(CH_3)_3AsO$
TETRA	Tetramethylarsonium ion	$(CH_3)_4As^+$
AB	Arsenobetaine	$(CH_3)_3As^+CH_2COO^-$
TMAP	Trimethylarsoniopropionate	$(CH_3)_3As^+CH_2CH_2COO^-$
AC	Arsenocholine	$(CH_3)_3As^+CH_2CH_2O^-$
DMAA	Dimethylarsinoylacetate	$(CH_3)_2(O)AsCH_2COO^-$
DMAP	Dimethylarsinoylpropionate	$(CH_3)_2(O)AsCH_2CH_2COO^-$

seafood are arsenocholine (AC), trimethylarsoniopropionate (TMAP), trimethylarsine oxide (TMAO) and arsenosugars; the latter are particularly found in marine algae.

The consumption of fish and other seafoods in Norway is high, compared with many other countries (Alexander et al., 2007). Atlantic cod, Atlantic salmon and blue mussels are examples of commonly consumed seafoods in Norway. While arsenic in seafood is usually determined as total arsenic, the primary importance, from a food safety point of view, is the amount of inorganic arsenic in seafood.

Although total arsenic content in the fillet of Atlantic cod varies by several orders of magnitude with concentrations from 0.4 to 220 mg As/kg wet weight (Julshamn, Lundebye, Heggstad, Berntssen, & Bøe, 2004; NIFES), the amount of inorganic arsenic in fillets of cod usually constitutes <1% of total arsenic or <0.01 mg/kg wet weight (Amran, Lagarde, Leroy, & Maier, 1997; Sloth, Larsen, & Julshamn, 2005a). In fillets of farmed Atlantic salmon, total arsenic concentration typically ranges from 0.6 to 4.8 mg/kg wet weight (Julshamn et al., 2004; NIFES) and inorganic arsenic is only found in trace amounts (Sloth et al., 2005a). AB is the predominant form of arsenic in fish fillets (Francesconi & Kuehnelt, 2002). Blue mussels, harvested from various locations along the Norwegian coastline, show concentrations of total arsenic ranging from 1.2 to 13.8 mg As/kg wet weight (Sloth & Julshamn, 2008). In addition to high concentrations of AB and DMA, are arsenosugars, significant arsenicals in blue mussels (Larsen, 1995). In most studies, only relatively low concentrations (<0.1 mg As/kg) of inorganic arsenic in blue mussels have been reported (Francesconi & Kuehnelt, 2002; Munõz et al., 2000; Sörös, Bodó, Fodor, & Morabito, 2003). However, unusually high levels of inorganic arsenic were recently reported in blue mussels from certain locations in Norway (Sloth & Julshamn, 2008). The inorganic arsenic fraction increased with increasing contents of total arsenic, and concentrations as high as 5.8 mg As/kg wet weight of inorganic arsenic, corresponding to 42% of the total arsenic present, were reported (Sloth & Julshamn, 2008). Numerous other studies have also determined arsenic species in raw samples of seafood and they report results similar to those described above (De Gieter et al., 2002; Hirata, Toshimitsu, & Aihara, 2006; Li et al., 2003; Sloth, Larsen, & Julshamn, 2003; Súñer et al., 2002).

Seafood is stored and/or processed (freezing, drying, salting) and is usually consumed after processing, e.g. fried or boiled. Storing and processing of seafood may potentially alter the concentration and/or speciation pattern of arsenic compounds. Consequently, from a food safety point of view, it is important to study the impact of processing on arsenic compounds in seafoods (Devesa, Velez, & Montoro, 2008).

Previous studies on the effect of cooking on total arsenic content in seafood report both decreases and increases of total arsenic concentrations (Dabeka et al., 1993; Devesa et al., 2001a; Ersoy, Yanar, Kücükgülmez, & Celik, 2006). These changes might be due to changes in water content during cooking. Devesa and coworkers (2001b) also found increases in the concentrations of DMA for sardines and bivalves and of TETRA for anchovy, Atlantic horse mackerel, sardine and meagrim after cooking. Cooking procedures (i.e. heat treatment) appear to transform some of the arsenicals present in seafood. As discussed thoroughly by Devesa and colleagues (2008) heat treatment leads to a decarboxylation of AB, forming TETRA, while inorganic arsenic and DMA may be formed by degradation of other arsenic species present. Another study (Devesa et al., 2001b) indicated that, at temperatures between 150 and 190 °C, a partial decomposition of AB to TMAO and/or TETRA was achieved.

Although some information on the effect of storage and processing on arsenic compounds has become available in recent years, there is still inadequate information on the stability of arsenicals in seafood, in particular the impact of storage by freezing. In the present study, we therefore investigate the stability of arsenic compounds in Atlantic cod, Atlantic salmon and blue mussels during storage by freezing and further processing.

2. Material and methods

2.1. Sample collection and preparation

The study included two different species of fish, Atlantic cod (*Gadus morhua,* L.), as a representative of a lean fish species (⩽1% fat in the fillet) and Atlantic salmon (*Salmo salar,* L.), as a representative of a fatty fish species (>10% fat in the fillet), and one type of shellfish, blue mussel (*Mytilus edulis,* L.). The three different types of seafood were purchased at the fish market in Bergen, Norway in May, 2007. Each of the fish weighed ~3.5 kg. The head, tail and intestines were removed from the fish ($n = 3$ for each species) and each fish fillet was divided into nine sub samples of ~150–200 g. Each blue mussel sample ($n = 2$) consisted of 1 kg of blue mussels and was divided into nine subsamples, consisting of 10 specimens each. The total arsenic content and the arsenic compounds were determined in fresh and frozen (stored for one and three months, at −20 °C, respectively) samples of raw, boiled (boiling water (100 °C; seafood was simmered for 10 min) and fried seafood (applied temperature of ~140 °C for 10 min). The processing (Fig. 1) was carried out using a household ceramic electric cooker, a stainless steel cooking pan (diameter 20 cm) and an aluminium frying pan covered with Teflon (diameter 28 cm). Samples ($n = 24$) of the boiling water from the cooking procedure were also included in the study. All seafood samples were freeze-dried to constant weight and subsequently homogenised to a fine pow-

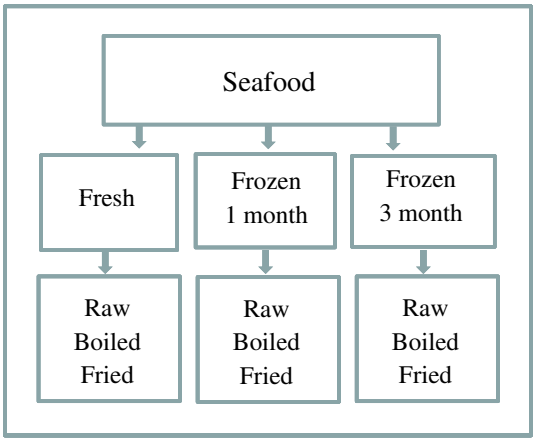

Fig. 1. Schematic overview of sample processing.