



Determination of moderately polar arsenolipids and mercury speciation in freshwater fish of the River Elbe (Saxony, Germany)



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ARTICLE INFO

Article history:

Received 9 July 2015

Received in revised form

9 October 2015

Accepted 10 October 2015

Available online 6 November 2015

Keywords:

Element species

Freshwater fish

Metal contamination

Arsenolipids

ABSTRACT

Arsenic and mercury are frequent contaminants in the environment and care must be taken to limit their entrance into the food chain. The toxicity of both elements strongly depends upon their speciation. Total amounts of As and Hg as well as their species were analyzed in muscle and liver of 26 fishes of seven freshwater fish species caught in the River Elbe. The median concentrations of As were 162 $\mu\text{g kg}^{-1}$ w.w. in liver and 92 $\mu\text{g kg}^{-1}$ w.w. in muscle. The median concentrations of total Hg were 241 $\mu\text{g kg}^{-1}$ w.w. in liver and 256 $\mu\text{g kg}^{-1}$ w.w. in muscle. While this level of Hg contamination of the freshwater fish in the River Elbe is significantly lower than 20 years ago, it exceeds the recommended environmental quality standard of 20 $\mu\text{g Hg kg}^{-1}$ w.w. by a factor of 5–50. However, the European maximum level of 500 $\mu\text{g Hg kg}^{-1}$ for fish for human consumption is rarely exceeded. Arsenic-containing fatty acids and hydrocarbons were determined and partially identified in methanolic extracts of the fish by HPLC coupled in parallel to ICP-MS (element specific detection) and ESI-Q-TOF-MS (molecular structure detection). While arsenobetaine was the dominant As species in the fish, six arsenolipids were detected and identified in the extracts of liver tissue in common bream (*Abramis brama*), ide (*Leuciscus idus*), asp (*Aspius aspius*) and northern pike (*Esox lucius*). Four arsenic-containing fatty acids (AsFA) and two arsenic-containing hydrocarbons (AsHC) are reported in freshwater fish for the first time. With respect to mercury the more toxic MeHg^+ was the major species in muscle tissue (>90% of total Hg) while in liver Hg^{2+} and MeHg^+ were of equal importance. The results show the high relevance of element speciation in addition to the determination of total element concentrations to correctly assess the burden of these two elements in fish.

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1. Introduction

Arsenic (As) and mercury (Hg) are well known for their high toxicity to humans and ecosystems. Adsorption, transport, bioaccumulation, metabolism and toxicity of As and Hg highly depend on their speciation in the environment and in organisms (Yin et al., 2013; Francesconi, 2007). The origin and role of arsenic species in seafood was discussed in detail previously (Francesconi, 2010). Most organoarsenic compounds were found in marine organisms e.g. algae or fatty fish with total arsenic concentrations of 5–100 $\mu\text{g g}^{-1}$ dry weight. It is still unclear, whether they are synthesized intentionally or unintentionally. The detoxification of inorganic arsenic

As(V) by formation of methylarsonic acid (MA), dimethylarsinic acid (DMA) and arsenosugars in the brown alga *Fucus serratus* was demonstrated by Geiszinger et al. (2001). Kaise et al. (1985) investigated the influence of inorganic arsenic and arsenobetaine, first identified by Edmonds et al. (1977), on the health of male mice; they showed that the LD_{50} value of arsenobetaine of 10 g/kg was much higher than for As_2O_3 with 34.5 mg/kg. Arsenobetaine was excreted rapidly and unaltered. The different sorption behavior of inorganic arsenic on iron oxides/hydroxides in dependence of pH conditions was described by Dixit and Hering (2003). Also the bioaccessibility and bioavailability of arsenic in soils and biota grown in contaminated soil was strongly influenced by their oxidation state (Yang et al., 2005; Helgesen and Larsen, 1998).

As an example for Hg, cationic methylmercury (MeHg^+), a highly toxic form of Hg, is formed from inorganic Hg(II) in aquatic

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sediments through the action of microorganisms (Kerin et al., 2006).

Aquatic organisms, such as fish, can accumulate As and Hg and reach humans by their diet. Fish is a major food in many parts of the world and therefore, the contamination of fish by As and Hg needs to be controlled.

For total mercury a maximum level (ML) of 500 $\mu\text{g Hg kg}^{-1}$ w.w. (wet weight) is valid for fish in the European Union, except for large predatory fishes like pike, for which a ML of 1000 $\mu\text{g Hg kg}^{-1}$ is set (Commission regulation (EC), 2006). According to EFSA (2012) the major route of exposure of humans to methylmercury is by fish and seafood products. Besides that an environmental quality standard (EQS) related to biota (fish) of 20 $\mu\text{g Hg kg}^{-1}$ w.w. for mercury and its compounds was defined under the Directive of the European Parliament and the Council as regards priority substances in the field of water policy (Directive, 2013/39/EU, 2013).

Because total As concentrations tend to be higher in marine compared to freshwater fish, analyses of As species in freshwater fish have been performed only rarely (Ciardullo et al., 2010; Culioli et al., 2009; Jankong et al., 2007; Schaeffer et al., 2006; Soeroes et al., 2005). Since inorganic water-soluble As species dominate in freshwater fish, these have been in the focus rather than lipid-soluble ones (Arroyo-Abad et al., 2010, 2013; Lischka et al., 2013; Ruiz-Chancho et al., 2012; Sele et al., 2013; Taleshi et al., 2010). Speciation analysis of Hg and As in freshwater fish have been performed – for MeHg^+ – using GC with different detectors like electron capture detection (ECD) (Kenšová et al., 2012; Kružíková et al., 2008), CV-AFS (Kruse and Bartelt, 2008), ICP-MS (Hrenchuk et al., 2012; Rodríguez Martín-Doimeadios et al., 2002; Rüdell et al., 2011), AED (Tutschku et al., 2002; Pereiro and Diaz, 2002) and HPLC with ICP-MS detection for As (Ciardullo et al., 2010; Jankong et al., 2007; Schaeffer et al., 2006; Soeroes et al., 2005).

The aim of this work was to investigate less polar arsenic-containing compounds e.g. As-fatty acids and As-hydrocarbons extracted from freshwater fish samples by HPLC in combination with elemental detection (ICP-MS) and molecular analysis (ESI-MS) simultaneously and to elucidate their chemical structures. The high sensitive GC hyphenated with microwave induced plasma atomic emission detection (AED) was carried out for speciation of Hg^{2+} and MeHg^+ simultaneously.

The use of HPLC-ICP-MS/ESI-MS is a powerful hyphenated technique for the determination and identification of arsenic-containing fatty acids (AsFA) and hydrocarbons (AsHC) in capelin meal (*Mallotus villosus*) (Amayo et al., 2011), herring fillet (*Clupea harengus*) (Lischka et al., 2013) and cod liver (*Gardus morhua*) (Arroyo-Abad et al., 2013, 2014) and is here applied for the trace analysis of freshwater fish.

The River Elbe is one of the largest European rivers with a length of 1094 km and a drainage area of 148,268 km^2 (FGG Elbe, 2004–15). During the last century significant amounts of metals and metalloids like mercury and arsenic originating from anthropogenic and geogenic sources have been accumulated in its sediments. Metals and metalloids in sediments may be taken up by aquatic organisms like crustacean or fish (Baborowski et al., 2012; Overesch et al., 2007). Therefore, the aim of this investigation was to study the presence of more hydrophobic As species (AsFA and AsHC) and of Hg species in muscle and liver tissues of several freshwater fish from the River Elbe by HPLC-ICP-MS/ESI-Q-TOF-MS, and by GC-AED, respectively.

2. Material and methods

2.1. Chemicals and reagents

All the solutions were prepared with Milli-Q water

(18.2 M Ω cm). Standard solutions of arsenic acid (As^{V}), methylarsonic acid (MA), dimethylarsinic acid (DMA) and arsenobetaine (AB) (BCR 626) were prepared for the identification of the water-soluble arsenic species. For the quantification of arsenolipids in the extract, solutions of AB in the range of 10.3–206 $\mu\text{g L}^{-1}$ of AB were prepared and used for calibration in the flow injection mode (FIA-ICP-MS) and by means of HPLC-ICP-MS/ESI-MS. With this ubiquitous calibration curve that has the same response for all mono-arsenic compounds the concentration of AsFA and AsHC were calculated. The retention time dependent response factors caused by the methanol gradient were determined previously (Arroyo-Abad et al., 2013). As^{V} was obtained from Fluka (Buchs, Switzerland); MA was obtained from Luxembourg Industries (Pamol) LTD (Rehovot, Israel), and DMA was obtained from Sigma (St. Louis MO, USA); methanol (HPLC grade) and formic acid (analytical grade) were purchased from Merck (Darmstadt, Germany). For mercury speciation the following standard compounds were used: methylmercury chloride (1 g Hg L^{-1}) in water (Alfa Aesar), mercury (II) nitrate monohydrate (1 g Hg L^{-1}) in 10% nitric acid (Merck). For derivatization of MeHg^+ and Hg^{2+} sodium tetrapropylborate in tetrahydrofuran (Merseburger Spezialchemikalien, Schkopau, Germany) was applied. The extraction of mercury species from fish was performed with HNO_3 (suprapure) (Merck, Darmstadt, Germany).

2.2. Fish sampling

The fish species namely common bream (*Abramis brama*), common nase (*Chondrostoma nasus*), ide (*Leuciscus idus*), asp (*Aspius aspius*), chub (*Squalius cephalus*), common barbel (*Barbus barbus*) and northern pike (*Esox lucius*) were caught by electro-fishing at selected sites of the River Elbe in Saxony, Germany in autumn 2012 (Fig. 1). The fishes were dissected, muscle and liver homogenized and frozen at -20°C immediately.

For the determination of total concentration of As and Hg aliquots (ca. 0.2 g) of homogenized liver and muscle tissues of the fish was digested with concentrated $\text{HNO}_3/\text{H}_2\text{O}_2$ (10:1, v/v) in the microwave (Anton Paar Multiwave, Perkin Elmer).

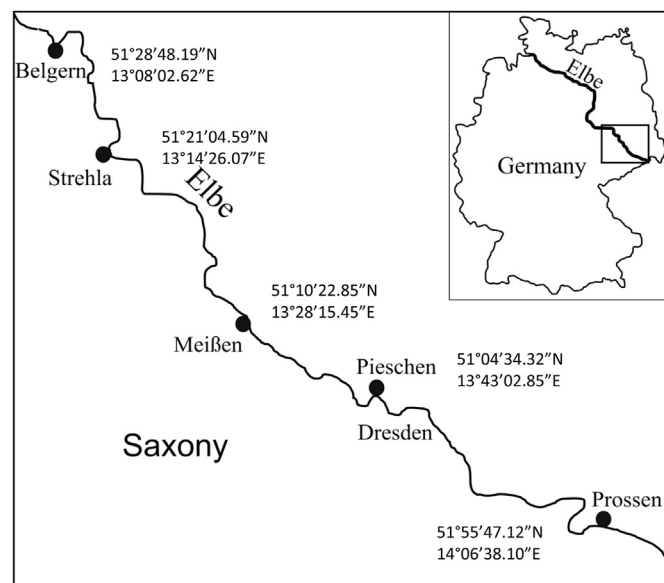


Fig. 1. Sampling sites along the River Elbe in Saxony, Germany (year 2012).

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