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Total and inorganic arsenic levels in some marine organisms from Izmir Bay (Eastern Aegean Sea): A risk assessment

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HIGHLIGHTS

- Arsenic compounds in marine biota were evaluated from Izmir Bay.
- Mean TAs levels in *M. barbatus* were 6 times higher than *D. Annularis* and mussel.
- Inorganic arsenic occurred as a minor fraction.
- Based on results, the risk of As intake by eating fish is low in the Bay.

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ABSTRACT

The arsenic compounds in marine biota were evaluated from Izmir Bay (Eastern Aegean) and found that inorganic arsenic occurred as a minor fraction. No information is available on the annual variations of arsenic in important edible biota species from Izmir Bay. Fish and mussel samples were taken from different regions of Izmir Bay between 2009 and 2011 ($n = 854$ individual specimens). The average percentages of inorganic arsenic to total arsenic for all biota samples were 3.43 ± 3.38% with a range of 0.11–11.8%. The importance of speciation analysis for arsenic is supported by our work, because arsenic is ubiquitous in the ecosystem, and flexible toxicity of arsenic is based on chemical form. The average total As levels in *Mullus barbatus* were 6 times higher than *Diplodus annularis* and *Mytilus galloprovincialis*. This study also revealed that spatial variation influenced the arsenic levels in the fish samples and the highest concentrations of arsenic were found in Gediz site. Our study showed that estimated daily intakes of arsenic via consumption of flesh fish and shell fish were below the $BMDL_{0.5}$ values established by FAO/WHO.

1. Introduction

Arsenic is a ubiquitous element, introduced to the environment from natural and anthropogenic sources (Sloth et al., 2005). It is one of the most toxic elements and has serious effects on plants, animals and human health (Munoz and Palmero, 2000). Arsenic is present in many chemical forms that differ with regard to their physical, chemical and biological specifications and have very different toxicities (Devesa et al., 2008).

Humans are exposed to arsenic (As) from several sources such as food, water, air and soil. Most foods contain both organic and inorganic forms of As and the inorganic compounds are generally considered to be more toxic. Although fish and mollusc are major contributors to dietary As among seafood consumers, over 90% of the As in seafood is generally organic rather than inorganic. Thus, it is important to know the relative levels of several As species in fish and mollusc when estimating risks from seafood consumption. Some marine organisms can accumulate arsenic from ~2 $\mu g l^{-1}$ that is the typical level in seawater to in some instances several hundreds of $\mu g\, g^{-1}$ (dry weight) (Francesconi and Edmonds, 1994). The World Health Organisation has established a toxicological reference value of 15 $\mu g\, kg^{-1}$ body weight per week for human intake of inorganic arsenic (WHO, 1998).

Toxic and non-toxic fractions of arsenic compounds are determined by analysing of inorganic and organic arsenic species in biological samples for human health risk assessments. In this study, inorganic and total arsenic (TAs) levels were analysed in marine biota and found that inorganic arsenic levels generally as a minor fraction, far below the levels of prevailing assumptions often used in risk assessments when only TAs is analysed.

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Izmir Bay (Eastern Aegean Sea) is one of the biggest natural inlets of the Mediterranean Sea whose shoreline is dominated by Izmir Metropolitan Municipality. Izmir is an important industrial, commercial and cultural focal point. Industrial activities cover a large range of industries including food processing, paint, tanneries, textile, chemicals and petroleum refining. The Bay of Izmir has a total surface area of over 500 km^2, a water capacity of 11.5 billion m^3, and a total length of 64 km. The Gediz River, which flows to the northern part of the bay, is the second biggest river in the western part of Turkey and this river is one of the major sources of anthropogenic input into the outer part of the Bay. Most of the industries in Izmir are located in the inner part of the bay.

A large number of studies have been carried out on the physical, chemical and biological oceanography of Izmir Bay during the last *ca.* 25 years, however no data are available from the published literatures monitoring and discussing arsenic levels in the marine biota from the Eastern Aegean coast.

The objective of this study was firstly to measure total and inorganic arsenic; secondly to monitor spatio-temporal variations in muscle tissues of different marine species (*Mytilus galloprovincialis, Mullus barbatus, Diplodus annularis*) taken from Izmir Bay; and also to assess potential risks for arsenic contamination in seafood samples collected from Izmir Bay. The benchmark dose lower confidence limit for a 0.5% increased incidence of lung cancer in human ($BMDL_{0.5}$) of inorganic As were also evaluated by the consumption of muscle tissues of fish species for possible human health risks.

2. Material and methods

Samples were collected from different parts of Izmir Bay (Gediz, Uzunada, Hekimada, Gulbahce, Yenikale, Pasaport) in 2009–2012 at six locations during *R/V* K. Piri Reis Cruise in Izmir Bay (Fig. 1). A total of 557 individuals of marine biota species ($N = 229$ for *M. barbatus*, $N = 168$ for *D. annularis*, $N = 160$ for *M. galloprovincialis*) were collected by trawling and hand from Izmir Bay. The muscle tissue of the samples was removed in the field using surgical sheets, acid-washed lancet, wrapped in aluminum foil and preserved at −20 °C until analysis.

The samples were freeze-dried and passed through a precleaned grinder to produce a consistent tissue homogenate. Arsenic concentrations were measured in the whole soft tissues of biota. In the laboratory, approximately 0.5 g of biota muscle was digested with 5:1 HNO_3:$HClO_4$ in microwave digestion system (UNEP, 1982). The final solutions were then diluted to the final volume with double distilled water and TAs concentrations were measured in ICP-MS. Accuracy of ICP-MS and validity of the processes tested with a reference material (NIST). The arsenic values obtained for the analysis of triplicates of the reference sample (certified; observed values ± standard deviation) were given as: reference 0.20 ± 0.01 mg kg^{-1}dry weight; found 0.194 ± 0.008 mg kg^{-1} dry weight.

For the determination of inorganic arsenic the modified method of Sloth and Julshamn (2008) was applied in this study (Pétursdóttir, 2010). Approximately 0.2 g of biota sample was accurately weighed and put in a glass tube along with 10 ml of the alkaline solution (3.05 g L^{-1} NaOH) for determination of inorganic arsenic. The temperature was slowly increased and held at 50 °C and 75 °C for two min before allowing the temperature to rise to the final temperature of 85 °C at which it was held for 4 min. The samples were centrifuged at 3500 rpm for 10 min before the supernatants were removed and the remains discarded. Hydrogen peroxide (H_2O_2) is a well known oxidising agent. To make ensure that all arsenite was oxidized to arsenate 0.1 ml of 30% hydrogen peroxide was added to 0.9 ml of the extracted sample and allowed to react overnight. The samples were centrifuged for 5 min at 13 000 rpm before analysis on the ICP-MS.

Pearson's Product-Moment Correlation test was used to check for significant relationships between arsenic and species length and the level of significant was set at $p < 0.05$ using STATISTICA for Windows, Release 8.0. One-way analysis of variance (ANOVA) was utilised to investigate effect of species, sampling area and annual variations in total As and inorganic arsenic concentrations in biota from Izmir Bay. Post hoc Tukey HSD test was applied to determine statistically significant differences ($p < 0.05$) following ANOVA.

3. Results and discussion

3.1. Arsenic concentrations

The results of total arsenic concentrations are shown in Table 1 and expressed as wet weight basis (ww, μg g^{-1}). As presented in Table 1 the highest arsenic concentration belonged to *M. barbatus* by 22.1 μg g^{-1}. Then, sorting from maximum to minimum arsenic levels, the fish and shellfishes were ordered as follows: *M. barbatus* > *M. galloprovincialis* > *D. annularis*. The minimum arsenic concentration was found in *D. annularis* by 1.4 μg g^{-1}. These results

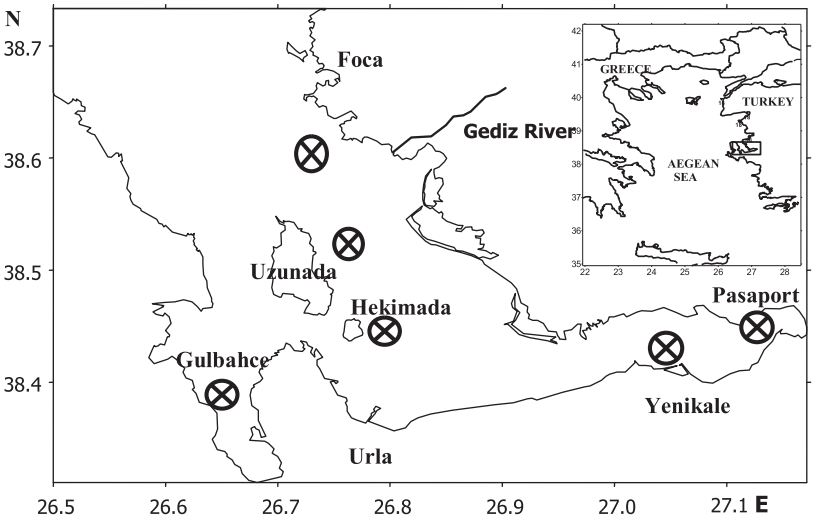

Fig. 1. Sampling areas (circle with cross) in Izmir Bay.