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Distribution of arsenic compounds in *Mytilus galloprovincialis* of the Venice lagoon (Italy)

Emanuele Argese*, Cinzia Bettiol, Chiarafrancesca Rigo, Sebastiano Bertini, Silvia Colomban, Pier Francesco Ghetti

Department of Environmental Sciences, Ca' Foscari University, Calle Larga S. Marta 2137, I-30123 Venezia, Italy

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Abstract

Samples of *Mytilus galloprovincialis* collected in different sites of the Venice lagoon (Italy) were investigated for total arsenic concentrations by ICP-AES and for single arsenic species by HPLC-ICP-MS. For this purpose, an analytical procedure for the sensitive and efficient speciation of the arsenic species As(III), As(V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AB), arsenocholine (AC), and four arsenosugars was optimised. The total arsenic and the single arsenic species were determined in both the hepatopancreas (digestive gland) and the remaining soft tissues in order to verify the different arsenic accumulation in the body parts of mussels. Arsenic compounds were extracted from the mussels with a methanol/water mixture; the extracts were evaporated to dryness, redissolved in water, and chromatographed in an anion-exchange column, a Hamilton PRP-X100. Only small quantities or traces of inorganic arsenic were detected in the mussels. The majority of arsenic compounds detected in the extracts were organic species, with a predominance of arsenobetaine and of an arsenosugar. In addition, a greater arsenic accumulation in the digestive glands of mussels was observed.

Keywords: Arsenic; Speciation; HPLC-ICP-MS; *Mytilus galloprovincialis*; Venice lagoon

1. Introduction

In marine ecosystems, arsenic is present in different forms, according to the matrix taken into consideration. In sediments and water arsenic is mainly found in inorganic forms, such as arsenate or arsenite, whereas in marine organisms arsenic mostly appears in organic forms like arsenobetaine and arsenosugars (Cullen and Reimer, 1989; Edmonds and Francesconi, 1992; Geiszinger et al., 2002). The biogeochemical cycle of arsenic in the marine environment is rather complex and many aspects regarding the processes of accumulation and bio-transformation are not fully known and require further investigation. To this aim, it is important to

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* Corresponding author. Tel.: +39 412348602; fax: +39 412348584.

E-mail address: argese@unive.it (E. Argese).

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succeed in identifying and quantifying the single arsenic species in the various environmental matrices by means of suitable methodologies of analysis (Jain and Ali, 2000).

This study is part of a research project concerning the characterisation of arsenic pollution in the Venice lagoon (Italy), with regard to the metabolic processes occurring in this complex ecosystem. This paper reports the preliminary results regarding the development of a speciation procedure for arsenic in biological matrices and its subsequent application to samples of bivalve molluscs (*Mytilus galloprovincialis*) collected in different sites and at different periods of the year in the lagoon. Mussels of the species *M. galloprovincialis* are present in great abundance in the lagoon of Venice. They can be found in most parts of the lagoon, characterised by different levels of pollution; thus, they can represent an ideal bioindicator of water quality. In addition, they have also a commercial importance, since they are farmed in some areas of the lagoon. The study of arsenic speciation in *M. galloprovincialis* can therefore be useful for the assessment of the risk posed to human health.

The analytical approach used is based on the coupling of HPLC with ICP-MS.

The compounds studied are the inorganic species As(III) and As(V) and the organic species monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AB), and arsenocholine (AC); in addition, two arsenosugars were identified and quantified.

Arsenic species and total arsenic were determined in both whole body and in the digestive gland of the mussels, in order to highlight a possible preferential accumulation into this target organ.

2. Experimental

2.1. Reagents

Milli-Q (Millipore) water with a resistivity of 18.2 MΩ cm was used for the preparation of reagents and standards. Pyrex, polyethylene and Teflon containers were treated before use with 0.1 M HNO_3 over 48 h and then washed thoroughly with Milli-Q water. All the reagents used were of analytical grade or better.

The mobile phase used in the HPLC separation was prepared with $NH_4H_2PO_4$ (Suprapur Merk), filtered through a 0.45-μm filter under vacuum and degassed with helium before use.

The stock solutions of arsenic compounds were prepared from As(III) oxide (Aldrich) by dissolution in 0.2% NaOH, whereas As(V) oxide hydrate (Aldrich), dimethylarsinic acid sodium salt $C_2H_6AsO_2Na$ (Sigma), arsenocholine bromide $C_5H_{14}AsBrO$ (Argus Chemicals, Italy), arsenobetaine $C_5H_{11}AsO_2$ (Argus Chemicals, Italy), and disodium methylarsenate $CH_3AsNa_2O_3 \cdot 6H_2O$ (Supelco) were dissolved in water. A freeze-dried extract of the brown alga *Fucus serratus*, containing four arsenosugars (Madsen et al., 2000), was kindly donated by W. Goessler (Karl-Franzens University, Graz); the algal extract was dissolved in Milli-Q water immediately before use.

The analytical methods were tested by analyzing the certified reference materials NRCC DORM-2 (National Research Council of Canada) and NIST SRM 2976 (National Institute of Standards and Technology).

2.2. Study area

The Lagoon of Venice is a wide, shallow, coastal basin, located in north-eastern Italy.

Mussel samples were collected in three different sites: Celestia, Tresse, and S. Nicolò (Fig. 1). The site of Celestia is located near the city of Venice and not far from the island of Murano, where the glass industry is concentrated; it suffers therefore from pollution of both urban and industrial origin. The site of Tresse is situated in the proximity of Porto Marghera, one of the most important industrial districts in Italy, where many chemical and petrochemical plants are operating. The last sampling site (S. Nicolò) was selected as a reference site, near one of the inlets connecting the lagoon to the Adriatic sea, relatively far from pollution sources.

The three sites are characterized by different hydrodynamic conditions and pollution levels. In particular, the site of S. Nicolò is subject to a more intense tidal water exchange, whereas the other sites are less affected by this process and water movement is limited. Moreover, sediments of the site of S.