Food Chemistry 112 (2009) 520–524

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Accumulation of arsenic in different fresh water fish species – potential contribution to high arsenic intakes

Abdul Qadir Shah, Tasneem Gul Kazi *, Muhammad Balal Arain, Muhammad Khan Jamali, Hassan Imran Afridi, Nusrat Jalbani, Jamil Ahmed Baig, Ghulam Abbas Kandhro

National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

ARTICLE INFO

Article history:
Received 20 November 2007
Received in revised form 28 May 2008
Accepted 28 May 2008

Keywords:
Fish species
Arsenic
Muscles
Bioaccumulation factor
Atomic absorption spectrometry
Daily dietary intake

ABSTRACT

The aim of the study was to evaluate total arsenic (As) in five tissues (gills, mouthpiece, intestine, liver and muscles) of 10 fish species caught from As contaminated Manchar Lake (26°3′N: 67°6′E) Sindh Pakistan during 2006–2007. The total As concentration was determined by hydride generation atomic absorption spectrometry (HG-AAS), prior to microwave assisted acid digestion. The certified reference material DORM-2 (dogfish muscle) was used to check the quality control of the technique. The good agreement with the certified value at 95% confidence limit confirmed the validity of As determination method. The limit of detection (LOD) and limit of quantitation (LOQ) of As were 0.034 and 0.11 μg/g, respectively.

The As concentration ranges in different tissues were obtained as: gills (1.01–10.4), mouth pieces (1.01–18.6), intestine (1.01–11.2), liver (3.51–10.9) and in muscles (2.12–15.2) μg/g on dried basis. The bioaccumulation factor (BAF) for As in fish muscles were found in two ranges (4.88–7.2) and (17.6–35.3). The contribution of the daily intake of As, based on the consumption of 250 g fresh fish muscles per day was found in the range of 0.1–0.76 μg, higher than WHO tolerable limit.

1. Introduction

Contamination of aquatic ecosystems (e.g. lakes, rivers and underground water) with As has been receiving worldwide attention and has become a challenge for world scientists (Bhattacharya, Jacks, Ahmed, Routh, & Khan, 2002). The effect of As exposure on human health was observed in population of south and southeastern Asia, particularly in Bangladesh, India and Taiwan (Al Rmalli, Haris, Harrington, & Ayub, 2005; Das et al., 2004; Hall et al., 2006; Lin & Liao, 2008).

In different areas of Pakistan, people are facing the As related severe public health disaster like India and other neighboring countries. In Pakistan As concentration was high in ground and surface water used as a drinking water (Shrestha, 2002). In Sindh province, 16–36% of population has been exposed to As contaminated water with over 10–50 ppb (Ahmad, Kahlown, Tahir, & Rashid, 2004). Manchar Lake (Sindh, Pakistan) is a biggest Asian Lake and main source of water for domestic, irrigation and fishing purposes. The Main Nara Valley Drain is a most important source of As enrichment in this lake, as reported in our previous work (Arain et al., 2008).

Arsenic exposure has been related to the appearance of some types of cancer. Arsenic is a known carcinogen in humans, causing lung, liver, skin and bladder cancer (Kapaj, Peterson, Liber, & Bhattacharya, 2006).

The most serious sources of As pollution include emissions and wastewater of the ore mining and processing industry, dye manufacture facilities, tanneries, thermal power plants, and application of certain insecticides, herbicides and pesticides (Sarkar & Datta, 2004).

Water pollution leads to fish contaminated with toxic metals, from many sources, e.g. industrial and domestic waste water, natural runoff and contributory rivers (Marcursen, Holm, Ha, & Dalgard, 2007; Rashed, 2001). Arsenic has a considerable tendency to accumulate in bottom sediments (Smedley & Kinniburgh, 2002). Essentially, fish assimilate metals (also As) by ingestion of particulate material suspended in water, ingestion of food, ion-exchange of dissolved metals across lipophilic membranes, e.g., the gills, and adsorption on tissue and membrane surfaces. Metal distribution between the different tissues depends on the mode of exposure, i.e., dietary and/or aqueous exposure, and can serve as a pollution indicator (Alam et al., 2002). The bioaccumulation of metals is therefore an index of the pollution status of the relevant water body and is a useful tool studying the biological role of the

* Corresponding author. Tel.: +92 022 2771379; fax: +92 022 2771560.
E-mail addresses: aqshah07@yahoo.com (A.Q. Shah), tgkazi@yahoo.com (T.G. Kazi), bilal_ku2004@yahoo.com (M.B. Arain), mkhanjamali@yahoo.com (M.K. Jamali), hassanimranafridi@yahoo.com (H.I. Afridi), nusratjalbani_21@yahoo.com (N. Jalbani), jab_mughal@yahoo.com (J.A. Baig), gakandhro@yahoo.com (G.A. Kandhro).

0308-8146/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2008.05.095

metals present at elevated levels in aquatic organisms, especially fish (Tariq, Jaffor, & Ashraf, 1991).

In order to determine the total As concentration in different fish tissues, it is imperative to assure complete mineralization of the samples, unless using non-destructive technique (Jalbani et al., 2007).

In recent years, microwave digestion processes have been used, owing to the advantages of this technique, which include speed of digestion and less possibility of contamination during the process (Soylak, Tuzen, Narin, & Sari, 2004). Different techniques have been used for As determination at trace levels, such as electrothermal atomic absorption spectrometry (ETAAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma mass spectrometry (ICP-MS) (Gong, Xiufen, Mingsheng, Corinna, & Le Chris, 2002). The generation of hydride is one of the most important procedure for the determination of As (Moretto & Cadore, 2004).

The aim of the present study is to determine the total As concentration in gill, mouth piece, intestine, liver and muscle tissues of 10 edible fish species, collected from As contaminated Manchar Lake, Pakistan. All fish species are edible and local people (75% fishermen) used daily, while these fishes are frequently used in their diet in other parts of Pakistan especially in Sindh. The fish tissues (dry basis) were acid digested by microwave oven. Quality control was assured by the analysis of samples, reagent blank, procedural blanks and standard reference material. The estimated daily intake (EDI) of As by adults consuming different understudied fish species were also evaluated for possible human health risks.

2. Experimental

2.1. Sample collection

The 10 different fish species were sampled in December 2006–May 2007 by professional fishermen from different stations, located at both ends of Manchar Lake, scientific and common names are reported in Table 1. These fishes were differ according to their eating habits (*Mirgala, Thaila, Seenghara, Bam* and *Gonia* were *omnivorous*, whereas *Calbasu, Reba, Gullio, Dayo, Rahu* belongs to the herbivorous group Has-Schon, Bogut, & Strelec, 2006).

All fish species were collected at sizes 20–45 cm with weight range 750–1500 g and assigned individual identification numbers. At the end of each sampling effort, all the samples were wrapped in plastic bags, placed in polyethylene bags, held in an ice box, and refrigerated at −4 °C until further treatment. In first step, the fishes were dissected and separated gills, mouthpiece, intestine, liver and muscles. The livers were separated from gallbladders while intestines were cleaned by squeezing out the contents, making a longitudinal incision and scraping and blotting to remove As-containing food particles and feces. All tissues were washed with physiological saline and deionized water repeatedly and were stored in rewashed polyethylene bottles at −20 °C till further analysis and preparation.

2.2. Analytical

Ultra pure water, obtained from an ELGA lab water system (Bucks, UK) was used throughout the experiment. Concentrated HCl, HNO_3 and H_2O_2 were analytical reagent grade from Merck (Darmstadt, Germany) and were checked for possible trace contamination. Calibrations were prepared for each analytical session using certified stock standard solution of As 1000 ppm, Fluka Kamica (Bushs, Switzerland). Appropriate dilutions were made from this solution with 0.1 M HCl whenever necessary. The methods were validated by certified reference material, NRCC DORM-2 (dogfish Muscle) from the National Research Council of Canada (Ottawa, Ontario Canada).

All glassware and polyethylene bottles were thoroughly washed and then soaked overnight in 5 M HNO_3, thoroughly rinsed with distilled and deionized water before use. Solution of sodium tetrahydroborate was prepared by dissolving $NaBH_4$ powder Acros Organics (New Jersey, USA) in 0.05 M KOH.

Total As determined by Perkin–Elmer A Analyst 700 atomic absorption spectrometer equipped with a deuterium background corrector and a MHS-15 hydride generation system, Perkin–Elmer Corp., Perkin–Elmer (Shelton, CT, USA). The operating parameters for working of As hollow cathode lamp were set as recommended by the manufacturer. Milestone Microwave System (Bergamo, Italy) was used for samples digestion.

2.3. Digestion methods

2.3.1. Conventional wet acid digestion method (CAD)

Replicate six samples of (0.2 g) of CRM (DORM-2) and triplicate 1.2 g sub samples of different tissues of each fish species ($n = 20$) were directly weighed into Pyrex flasks separately. Added 5 ml of a freshly prepared mixture of concentrated HNO_3–H_2O_2 (2:1, v/v) and kept for 10 min at room temperature, then the content of flasks were heated on an electric hot plate at 60–70 °C for 2–3 h until clear, transparent digests were obtained. Final solutions were made up to 10 ml with 0.1 M HCl. The final solutions were collected in polyethylene flasks and kept at 4 °C until further analysis. As was determined by hydride generation AAS. Blank digestions were also carried out.

2.3.2. Microwave acid digestion method (MAD)

A microwave assisted digestion procedure was carried out in order to achieve a shorter digestion time. About 0.2 g replicates six samples of CRM, while 0.2 g triplicate (dry weight) of different tis-

Table 1
Estimation of arsenic in different parts of fish species by microwave assisted and conventional acid digestion methods (μg/g) on dried basis ($n = 100$)

Scientific name with common name	Gills	Mouth piece	Intestine	Liver	Muscles
Labeo calbasu (Calbasu)	9.7 ± 0.5[a] (10.1 ± 0.5)	18.2 ± 0.5 (18.6 ± 0.3)	8.9 ± 0.74 (9.6 ± 0.71)	5.6 ± 0.04 (6.1 ± 0.31)	9.1 ± 0.9 (9.3 ± 0.1)
Cirrhinus mrigala (Mrigala)	1.1 ± 0.13 (1.4 ± 0.15)	1.0 ± 0.13 (1.3 ± 0.13)	6.9 ± 0.22 (7.3 ± 0.31)	8.3 ± 0.11 (8.8 ± 0.05)	2.0 ± 0.11 (2.2 ± 0.21)
Cirrhinus reba (Reba)	0.79 ± 0.06 (1.1 ± 0.13)	1.0 ± 0.07 (1.2 ± 0.13)	6.5 ± 0.05 (7.3 ± 0.31)	9.3 ± 0.05 (9.7 ± 0.03)	2.6 ± 0.09 (2.7 ± 0.11)
Mystus gullio (Gullio)	7.6 ± 0.5 (8.0 ± 1.3)	10.1 ± 1.3 (11.0 ± 1.5)	9.9 ± 1.3 (10.3 ± 1.1)	4.8 ± 0.12 (5.3 ± 0.08)	8.2 ± 1.4 (8.6 ± 1.2)
Catla catla (Thaila)	6.5 ± 0.5 (7.7 ± 1.1)	14.6 ± 0.90 (15.1 ± 0.81)	10.4 ± 1.1 (11.0 ± 0.9)	3.5 ± 0.21 (3.9 ± 0.18)	14.8 ± 0.80 (15.2 ± 0.25)
Mystus seenghara (Senghara)	10.6 ± 0.14 (11.0 ± 0.21)	12.0 ± 0.9 (12.5 ± 0.2)	9.9 ± 0.81 (10.6 ± 0.78)	4.4 ± 0.07 (5.0 ± 0.13)	12.0 ± 0.37 (12.1 ± 0.37)
Mastacembelus armatus (Bam)	0.86 ± 0.04 (1.2 ± 0.05)	1.5 ± 0.14 (1.9 ± 0.15)	0.58 ± 0.11 (1.0 ± 0.21)	8.8 ± 0.13 (9.4 ± 0.05)	3.0 ± 0.06 (3.1 ± 0.09)
Tilapia mossambicus (Dayo)	1.4 ± 0.14 (2.1 ± 0.15)	1.7 ± 0.15 (2.1 ± 0.21)	1.8 ± 0.11 (2.5 ± 0.12)	9.0 ± 0.03 (9.6 ± 0.14)	2.3 ± 0.21 (2.4 ± 0.30)
Labeo rohita (Rahu)	9.8 ± 0.41 (10.4 ± 0.51)	11.0 ± 0.51 (11.4 ± 0.68)	10.9 ± 0.41 (11.2 ± 0.37)	8.5 ± 0.04 (9.0 ± 0.11)	7.3 ± 0.30 (7.6 ± 0.31)
Labeo gonius (Gonia)	4.0 ± 0.11 (4.4 ± 0.51)	2.1 ± 0.15 (2.5 ± 0.20)	3.7 ± 0.11 (4.1 ± 0.12)	10.1 ± 0.05 (10.9 ± 0.12)	2.0 ± 0.26 (2.1 ± 0.31)

Key = [a]conventional digestion method.
Values in parenthesis obtained by microwave digestion method.