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Determination of heavy metals in selected black sea fish species

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ABSTRACT

Heavy metals can be accumulated by marine organisms thought a variety of pathways, including respiration, adsorption and ingestion. The levels of heavy metals are known to increase drastically in marine environment through mainly anthropogenic activities. Fish are good indicators for the long term monitoring of metal accumulation in the marine environment. The aim of this study was to determine the levels of Cd, As, Hg, Pb, Zn and Cu in edible part and gill of seven most consumed Bulgarian fish species collected from north-east coast of Black Sea. These fish species are sprat (*Sprattus sprattus sulinus*), Mediterranean horse mackerel (*Trachurus mediterraneus ponticus*), Black sea gobies (*Neogobius melanostromus*), shad (*Alosa pontica*), Atlantic bonito (*Sarda sarda*), bluefish (*Pomatomus saltatrix*) and grey mullet (*Mugil cephalus*). The fish samples were collected during 2010. The analytical determination of As, Cd, Pb, Zn and Cu were performed by using flame and graphite furnace atomic absorption spectrometry after microwave digestion procedure. The total mercury determination was determined using a direct mercury analyzer (DMA-80). The metal concentration of analyzed elements was highest in the gill for all fish species. The maximum metal concentration was measured for Cu (1.40 mg kg^{-1} w.w), Zn (11 mg kg^{-1} w.w) and Pb (0.08 mg kg^{-1} w.w) in muscle tissues of shad and sprat. The edible part of horse mackerel has the maximum value for Hg (0.12 mg kg^{-1} w.w) while Atlantic bonito predominantly accumulates As (1.10 mg kg^{-1} w.w). The analytical results obtained from this study were compared within acceptable limits for human consumption set by various health institutions.

1. Introduction

Heavy metals in marine systems are a global problem, since continuous exposure of marine organisms to their low concentrations may result in bioaccumulation, and subsequent transfer to man through the food web (Mendil et al., 2005). Heavy metals in the marine environment may originate from either natural or anthropogenic sources. Although trace metals are normal constituents of the marine environment, and some of them are essential to marine organisms, all metals are toxic above some threshold level (Kljaković- Gašpić, Herceg-Romanic, Kožul, & Veža, 2010).

A fundamental characteristic of trace metals is their lack of biodegradability (Mendil et al., 2005). Once introduced into the aquatic environment, trace metals are redistributed throughout the water column, deposited or accumulated in sediments and consumed by biota (Kljaković- Gašpić et al., 2010). Heavy metals can be classified as potentially toxic (arsenic, cadmium, lead, mercury, nickel, etc.), probably essential (vanadium, cobalt) and essential (copper, zinc, iron, manganese, selenium) (Munoz-Olivas & Camara, 2001; Tuzen & Soylak, 2007). Fishes are good indicators for the long term monitoring of metal accumulation in the marine environment (Türkmen, Türkmen, & Tepe, 2007).

The Black Sea is the world's largest natural anoxic water basin below 180 m in depth. It is a closed sea with a very high degree of isolation from the world's oceans, but it receives freshwater inputs from some of the largest rivers in Europe; the Danube, the Dniester, and the Dnieper (Stoichev, Makedonski, Trifonova, Stancheva, & Ribarova, 2007). For this reason, Black Sea is considered one of the most polluted seas in the world, and the increasing concentration of nutrients in recent years have led to a higher degree of eutrophication. The fishery yield has declined dramatically, and the tourism industry in the region of Bulgarian coast of Black Sea also suffers from serious pollution of the Black Sea. Therefore, numerous studies have been carried out on metal accumulation in different fish species in the parts of Black Sea (Al-Sayed, Al-Saad, Madany, & Al-Hooti, 1996; Türkmen et al., 2007).

There are limited data about heavy metals pollution of the Bulgarian Black Sea coast for the last twenty years (Görür, Keser,

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Akçay, & Dizman, 2012). Therefore, the aim of this study were to determine the levels of cadmium, mercury, copper, zinc, arsenic and lead in edible parts and gills of seven most consumed Bulgarian fish species collected from the coast of Black Sea, Bulgaria so as to assess their human exposure through diet.

2. Experimental

2.1. Sampling and sample treatment

Samples of fish were randomly acquired in local fishermen from cities across the coastal waters of Bulgarian Black Sea. All the fish species were sampled from February to November 2010. These sampling sites of two regions of Bulgarian Black Sea coast were Balchik (North) and Nessebar (South) (Fig. 1).

The seven species (44 samples) included in this study are shown in Table 1.

Total length and weight of the sample brought to laboratory on ice after collection were measured to the nearest millimeter and gram before dissection. For small species (i.e. sprat and horse mackerel), the entire edible part of each individual was included for preparation of composite sample. However, for bigger species (i.e. gray mullet, bluefish, goby, bonito and shad) fillets of edible part of each individual were collected separately from the gill samples and included in the respective composite samples. Approximately 1.0 g sample of muscle or gills from each fish were dissected, washed with distilled water, weighted, packed in polyethylene bags and stored at −18 °C until chemical analysis.

2.2. Reagents and standard solutions

All solutions were prepared with analytical reagent grade chemicals and ultra-pure water (18 MΩ cm) generated by purified distilled water with a Millipore Milli-Q Gradient A-10 water purification system (Bedford, MA). .

HNO_3 was of superb quality was purchased from Fluka (Buchs, Switzerland). All the plastic and glassware were cleaned by soaking in 2 M HNO_3 for 48 h, and rinsed five times with distilled water, and then five times with deionized water prior to use. The stock standard solutions of Cd and Pb 1000 μg mL^{-1} were Merck (Darmstadt, Germany) in 2% v/v HNO_3 and were used for preparation calibration standards.

A DORM-2 (NRCC, Ottawa) certified dogfish tissue was used as the calibration verification standard. Recoveries between 90.5 and 108% were accepted to validate the calibration.

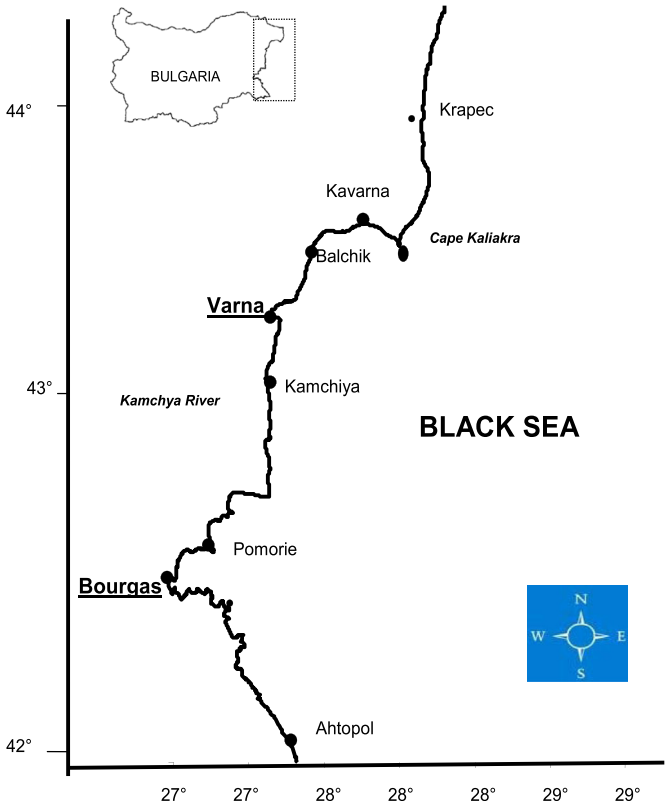

Fig. 1. The map of sampling locations.

2.3. Sample digestion

Fish samples (whole fish body, fish fillets or gills) are thoroughly washed with Milli-Q water. The fish specimens were dissected and samples of fish fillets quickly removed and washed again with Milli-Q water. Each fish filletes (approximately 0.0 g) were analyzed after homogenization in small mixer. To assess the total metal contents, microwave assisted acid digestion procedure was carried out using the parameters in Table 2:

Multiwave™ 3000 Microwave Sample Preparation System (PerkinElmer/Anton-Paar) delivering a maximum power and temperature of 800 W and 300 °C, respectively, and internal temperature control, was used to assist the acid digestion process. Reactors were subjected to microwave energy at 800 W in five stages shown in Table 3:

2.4. Instrumental

The samples were digested with nitric acid followed up by appropriate spectroscopic determination.

Determination of Cu and Zn: Flame atomic absorption spectrometric (FAAS) measurements were carried out on a Perkin Elmer (Norwalk, CT, USA) Zeeman 1100 B spectrometer (Überlingen, Germany) with an air/acetylene flame. The instrumental parameters were optimized in order to obtain maximum signal-to-noise ratio.

Determination of As, Cd, and Pb: Electrothermal atomic absorption spectrometric (ETAAS) measurements were carried out on a Perkin Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace (Table 4). Pyrolytic graphite-coated graphite tubes with integrated platforms were used as atomizers. The spectral bandpass, the wavelengths and instrumental parameters used were as recommended by the manufacture. Only peak areas were used for qualification. Pd as $(NH_4)_2PdCl_4$ was used as modifier for ETAAS measurements of As and Cd.

Determination of Hg was performed by Milestone DMA-80 direct Mercury Analyzer. The sample size was between 0.020 and 0.0060 g, with drying temperature at 300 °C for 60 s, decomposition time for180 s and waiting time of 60 s.

2.5. Statistical analysis

The whole data were subjected to a statistical analysis. Student's-test was employed to estimate the significance of values.

3. Results and discussion

Levels of heavy metal in the muscle of fish species from coastal waters of Bulgarian Black Sea are shown in Table 5. The summarized results of this study are expressed as means (mg kg^{-1}) wet weight (w.w).

Cadmium levels in analyzed fish species were below