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Polychlorinated biphenyls in fish from Black Sea, Bulgaria

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ABSTRACT

Polychlorinated biphenyls (PCBs) were measured in muscle tissue of six marine fish species: sprat (*Sprattus sprattus sulinus*), grey mullet (*Mugil cephalus*), bluefish (*Pomatomus saltatrix*), turbot (*Psetta maxima*), red mullet (*Mullus barbatus*) and garfish (*Belone belone*). Samples were collected from different parts of Bulgarian Black Sea coast. The PCBs were analyzed in order to evaluate the status of pollution in Bulgarian Black Sea coastal area and to assess the dietary intake through fish consumption. The PCBs (including Indicator and dioxin-like PCBs) were determined by capillary gas chromatography system with mass spectrometry detection. Total PCBs were found in all fish species at concentrations ranging between 134.2 ng/g lipid weight (lw) in bluefish and 571.9 ng/g lw in turbot. The sum of the six Indicator PCBs ranged from 100.3 to 453.8 ng/g lw (in bluefish and turbot, respectively). Dioxin – like PCBs were used in order to estimate the toxicity potential (TEQs) of PCB exposure. TEQs of the 6 "dioxin–like" PCB congeners were calculated from 0.04 pg TEQ/g wet weight (ww) (turbot) to 0.14 pg TEQ/g ww (bluefish) and did not exceed the limit of 3 pg TEQ/g ww, according to European Commission. The experimental results for PCBs in fish species from different sampling sites showed no significant differences between the North, Varna and South coast sampling area. The levels of PCBs in marine fish from Bulgarian Black Sea were found lower than those reported from the other regions. Estimated dietary intake of polychlorinated biphenyls through the analysed marine species does not seem to pose a health risk.

1. Introduction

Polychlorinated biphenyls (PCBs) are lipophilic contaminants, very persistent, widely distributed in the environment and can be accumulate in aquatic organisms. PCBs are transported by air all over the world, because they are driven by temperature and their volatility (Gouin et al. 2005). Although these contaminants are present in the water at low levels, they could be bioconcentrate in aquatic organisms and bioaccumulate to the higher levels in the food chain, especially in predatory fish.

The contamination of PCBs is a significant health problem because they can cause several adverse effects to human health and wildlife survival (Falandysz et al. 2004; Fisk, Hobson, & Norstrom, 2001). In biological systems, several of these chemicals are potentially carcinogenic and may cause alterations in endocrine, reproductive and nervous systems (Langer et al. 2003). For these reasons, most countries have restricted the use of PCBs since 1970s. Some of PCBs are classified as dioxin-like PCBs (dl-PCB), they show a similar toxicity as polychlorinated dibenzodioxins and polychlorinated furans. The dl-PCBs are used in order to estimate the toxicity potential of PCB exposure as toxic equivalency (TEQ). TEQ is defined by the sum of the concentration of each dl-PCB congener in a mixture multiplied by its toxic equivalency factors (TEF), developed by the World Health Organization (WHO-TEF) (Van den Berg et al. 2006).

The risk assessment of PCBs in fish for human diet is important and necessary (Binelli & Provini, 2003; Smith & Gangolli, 2002). In most cases, dietary intake is the major source of the total human exposure to PCBs (European Commission, 2000; Smith & Gangolli, 2002). It has been reported that meat, dairy products and fish, makes up more than 90% of the intake of PCBs for the general population (Schecter, Cramer, Boggess, Stanley, & Olson, 1997; Bocio, Domingo, Falcó, & Llobet, 2007; Zhang et al. 2012.)

The objectives of this study were to determine the levels of PCB congeners in six fish species from different sites in the Black Sea along the coast of Bulgaria and to estimate the intake of PCBs through dietary consumption of fish.

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2. Materials and methods

2.1. Sampling and sample preparation

Samples were caught by local professional fishermen by net from 2007 to 2011. The sampling strategy allows covering the entire Bulgarian Black Sea coast and includes three important fishing regions: North (near cape Kaliakra, Krapec and Balchik), Varna Bay and South (Bourgas, Nessebar). The map of the study area is presented on Fig. 1. The sampling campaigns took place during September–November in every year. The samples were transferred immediately to the laboratory in foam boxes filled with ice and were stored in a freezer (−20 °C) until analysis. The fish species were selected according to their characteristic feeding behaviour and importance to human consumption in Bulgaria: sprat (*Sprattus sprattus sulinus*), grey mullet (*Mugil cephalus*), bluefish (*Pomatomus saltatrix*), turbot (*Psetta maxima*), red mullet (*Mullus barbatus*) and garfish (*Belone belone*).

Each sample was prepared from edible tissue of several individuals. The fish tissues were homogenized using a blender; pools of about 300 g were made for every sample. The samples of small species (sprat, red mullet) were comprised 15–20 individuals and samples of bigger species (bluefish, grey mullet, garfish and turbot) contained approximately between 5 and 10 individuals. Number of samples (n) is presented in Table 1. The length and weight of each specimen were measured and they were rinsed with distilled water to remove sand and impurities.

2.2. Analytical methods

Twenty grams of homogenized fish tissue were mixed with 100 g of anhydrous sodium sulfate and was extracted with hexane/dichloromethane (3/1, v/v) in Soxhlet Extractor. Each sample was spiked with internal standards PCB 30 and PCB 204. The solvent was carefully evaporated and the lipid content was determined gravimetrically of an aliquot of the extract (1/5th). The extract was cleaned-up on a glass column (10 × 250 mm) packed with 2 g neutral silica, 4 g acid silica and 2 g neutral silica (Merck KGaA, Darmstadt, Germany). PCBs and DDTs were eluted with 80 ml n-hexane followed by 50 ml n-hexan/dichloromethane (80:20) (Sigma-Aldrich Chemie, Taufkirchen, Germany). The eluates were concentrated to near dryness and reconstituted in 0.5 ml in hexane. One micro liter of purified extract was injected into GC/MS.

Gas chromatographic analysis of PCBs were carried out by GC FOCUS (Thermo Electron Corporation, Austin, Texas, USA) using POLARIS Q Ion Trap mass spectrometer and equipped with an AI

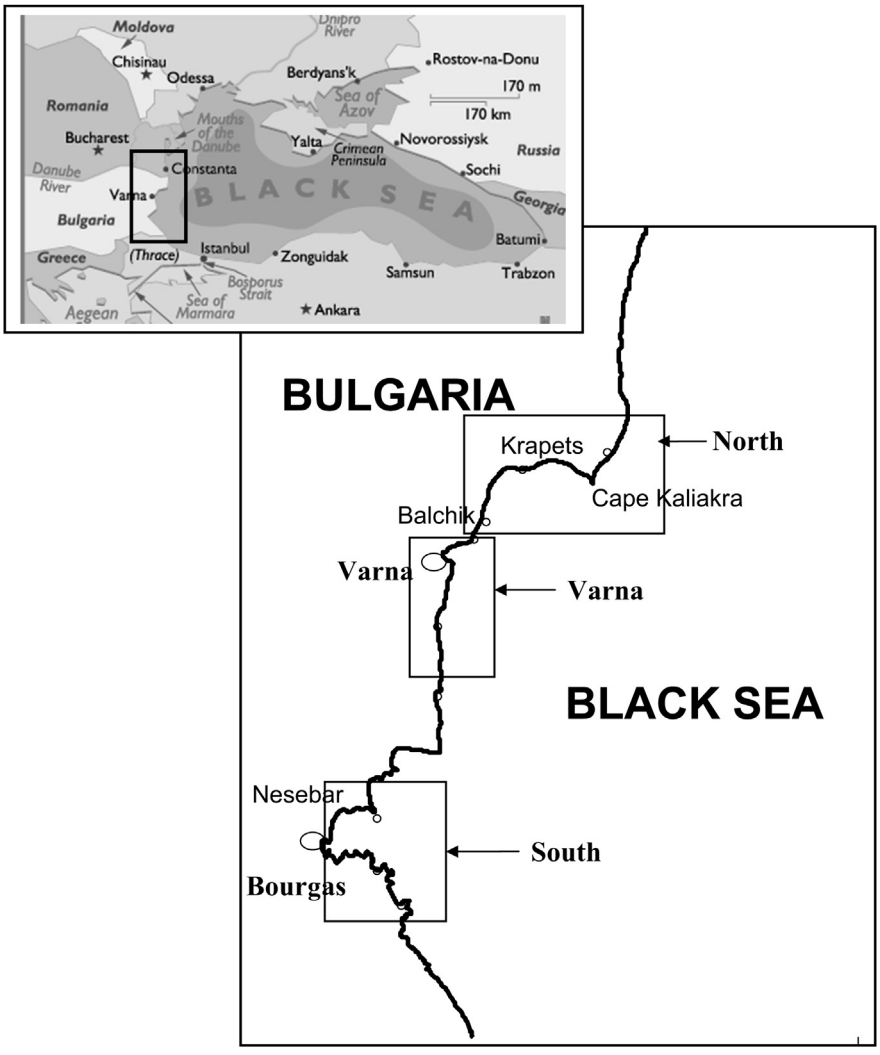

Fig. 1. Black sea map and sampling area.