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Distribution of persistent organic pollutants (POPs) in cultured mussels from the Croatian coast of the Adriatic Sea

Snježana Herceg-Romanić [a], Zorana Kljaković-Gašpić [a,*], Darija Klinčić [a], Ivana Ujević [b]

[a] Institute for Medical Research and Occupational Health, Ksaverska c. 2, PO Box 291, 10001 Zagreb, Croatia
[b] Institute of Oceanography and Fisheries, PO Box 500, 21000 Split, Croatia

HIGHLIGHTS

- OCPs and PCB congeners were determined in edible tissue of cultivated mussels.
- Contaminants profiles in mussels are seasonally dependent.
- The results are discussed in the light of maximum levels permitted by European Union.
- Contaminant levels do not show evidence of risk for consumers.

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ABSTRACT

In this study we investigated the distribution of 7 organochlorine pesticides (OCPs) and 17 polychlorinated biphenyl (PCBs) congeners in the edible tissue of the blue mussels (*Mytilus galloprovincialis*) collected at 15 shellfish breeding farms and 1 harvesting area along the Croatian Adriatic coast. All analyzed OCPs were found in all samples (0.011–1.47 ng g^{-1} w.wt.). Concentrations of PCB congeners in positive samples ranged between 0.007 and 7.66 ng g^{-1} w.wt. The most abundant compounds were γ-HCH, PCB-138 and PCB-153. Overall levels of PCBs and OCPs were in the lower end of the concentration ranges reported in literature. Significant differences of all contaminants were recorded between seasons, with higher values in the warmer part of the year. Results of the evaluation of the risks to human health associated with consumption of the mussels containing organic contaminants suggest that the levels of these compounds in mussels do not pose any threat for consumers of cultivated mussels.

Introduction

Recently, a lot of attention has been devoted to the analysis of various essential elements and toxic contaminants in seafood in order to limit exposure of consumers to contaminants while maximizing the benefits of seafood consumption. Seafood has clear nutritional benefits as it provides high quality protein, minerals, essential trace elements, fat-soluble vitamins (Vitamin D) and essential fatty acids (James, 2013). However, seafood is also known to accumulate certain contaminants, such as toxic metals and persistent organic pollutants (POPs), which can have harmful effects on human health and development (James, 2013).

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), which belong to group of POPs, have received much attention due to their persistent nature, bioaccumulation, long-range environmental transport and toxicity to wildlife and humans. Although the production and usage of these compounds in most industrialized countries were banned in the early 1970s, they persist in all parts of the environment because they are resistant to environmental degradation (Ritter et al., 1995). Consequently, although PCBs and OCPs levels in the environment are steadily declining (Albaigés et al., 2011; UNEP/MAP, 2012), they continue to bioaccumulate in human and animal tissues and bio-magnify in food chains, and may have potentially significant impacts on human health and the environment (Ritter et al., 1995). Given that the predominant route of exposure of general population to POPs is through the diet, especially through consummation of fish and seafood products, European Commission (EC) included them in the EU Priority Pollutants List (EC Decision, 2001). Also, maximum permissible levels of dioxin-like PCBs and sum of indicator PCBs have

* Corresponding author. Tel.: +385 1 4673188; fax: +385 1 4673303.
E-mail address: zorana.kljakovic-gaspic@imi.hr (Z. Kljaković-Gašpić).

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recently been set by the Croatian Government (MHRC, 2012) to limit dietary exposure of consumers to PCBs.

The Mediterranean blue mussel (*Mytilus galloprovincialis*) is the most widespread shellfish species in the Adriatic Sea and the Mediterranean Sea and is important component of seafood dishes in various Mediterranean cuisines. Shellfish farming is widespread in Croatia along its entire coastline. Croatian shellfish industry, with its production of 515 tons of oysters and other shellfish (mostly blue mussels) per year (Croatian Bureau of Statistics, 2013), is small when compared to the other Mediterranean countries, but Croatia has a high natural and environmental potential for aquaculture expansion. Future development of this sector is directly dependent on an increase in the EU market. In accordance with EU Directives, 25 sampling sites from shellfish breeding and harvesting areas along the Croatian coast of the Adriatic Sea are included in continuous monitoring of shellfish quality (sanitary quality, heavy metals, biotoxins, Benzo[*a*]pyrene) and seawater quality (phytoplankton composition) (MARC, 2013) since July 2000 to ensure that contaminant concentrations are within the safe limits for consumers. However, very little information is available in the literature about contamination of these cultured mussels with trace organic contaminants. Rare information are mostly limited to the area of the Mali Ston Bay (Kožul et al., 2008, 2009), which is the most important shellfish farming area in Croatia with more than one hundred years long tradition. Therefore, there is a wide interest in increasing information on PCBs and OCPs contamination levels in the different shellfish production areas.

The aim of this study was to investigate the spatial and seasonal distribution of 7 OCPs and 17 PCB congeners in the edible tissue of the cultured mussels *M. galloprovincialis* collected at 15 shellfish breeding farms and 1 harvesting area along the middle and south Croatian Adriatic coast, and to estimate associated health risk for people consuming shellfish from this area. Furthermore, obtained values can be used to fill in the database of levels of organic contaminants in seafood, which can be used for future risk assessment of the Croatian population.

2. Materials and methods

2.1. Sampling procedures

Mussels for PCB and OCP analysis were collected at 15 breeding farms and 1 harvesting area (location 8) along the Croatian coast (Supplementary information, Table S1; Fig. S1) in January and July 2010. Mussels were collected from the plastic boat. At each sampling site 2–3 kg of mussels of similar shell length were collected from the long-lines, both from the surface and the middle of the rope, placed in plastic bags and transported to the laboratory. Collected shellfish were of commercial size. Mussels were scrubbed with a brush to remove adhering detritus, washed with seawater, and whole soft tissue of mussels was dissected to prepare composite sample. Tissue was homogenized using laboratory blender, and 50–100 g of the homogenate was taken and freeze dried for organic contaminants analysis. Water content in soft tissues varied between 81.3% and 90.0% (Supplementary information, Table S1). The gut content of mussels was not depurated prior to analysis.

2.2. Organochlorine determination

Trace organic contaminants in composite samples were analyzed using a procedure similar to (Storelli et al., 2008). Details of the procedure were published previously (Kljaković-Gašpić et al., 2010). Briefly, lyophilisate was cold extracted with *n*-hexane and cleaned up with sulphuric acid. Before gas chromatography, the residues were dissolved in 1.0 mL of *n*-hexane. The simultaneous analysis was performed on high resolution gas chromatographs CLARUS 500 on two capillary columns (Restek, Bellefonte, PS, SAD): 60 m × 0.25 mm × 0.25 μm (Rtx-5) and 30 m × 0.25 mm × 0.25 μm (Rtx-1701), with nitrogen as a carrier gas (purity: 5.5 for ECD). Temperature program was following: 100 °C (1 min), ramp 1: 4 °C per min to 110 °C (5 min), and ramp 2: 15 °C per min to 240 °C (50 min). Temperature of injector was 250 °C and of electron capture detector (^{63}Ni) was 270 °C. The recovery and reproducibility experiments were performed by spiking of real samples. Composite mussel sample was thoroughly mixed and homogenized, and divided into two sets each containing seven aliquots. In each set, known amount of all analyzed compounds (between 1.18 and 11.09 ng g^{-1} d.wt., depending on the compounds) was added to five aliquots before extraction, while two aliquots were used as 'blanks'. The recoveries of PCBs and OCPs, as ratios between measured and theoretical value, were calculated after subtracting the mean levels of two non-spiked aliquots from the spiked ones. The recoveries for the PCBs and OCPs (N = 10) ranged from 60% to 93% (RSD = 6–25%) and from 54% to 82% (RSD = 7–20%), respectively. The detection limits for the analyzed compounds were 0.06 ng g^{-1} d.wt. for PCBs and 0.07 ng g^{-1} d.wt. for OCPs, and were calculated as the average of all analysis, based on signal-to-noise ratio and recovery of compounds. Concentrations of all analyzed compounds in reagent blanks, which were used to indicate laboratory contamination, were below the detection limit. Performance of the used analytical procedure was validated through participation in inter-laboratory comparison on OCPs and PCBs organized by the International Atomic Energy Agency–Marine Environment Laboratory (IAEA–MEL), and produced data were in the acceptable range (Villeneuve et al., 2006).

In prepared extracts seventeen PCB congeners [PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180, PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, PCB-170, PCB-189, PCB-60, and PCB-74 (numbered according to IUPAC)] and seven OCPs [hexachlorobenzene (HCB), α-HCH, β-HCH, γ-HCH (α-, β-, γ-hexachlorocyclohexanes), 1,1-dichloro-2,2-di(4-chlorophenyl)ethylene (DDE), 1,1-dichloro-2,2-di(4-chlorophenyl)ethane (DDD) and 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (DDT)] were analyzed. All the results (obtained on dry wet basis because we analyzed lyophilized samples) were recalculated to wet weight basis (Table 1; Fig. 1) for easier understanding.

2.3. Data analysis

Data analysis was performed using STATISTICA (data analysis software system), version 12 (StatSoft, Inc., 2012). Because of the skewed distribution of all measured parameters, the results are presented with range, the 25th, the 50th (median), and the 75th percentile values (Table 1). Based on the examination of normal scores plots of residuals, most of biological variables and contaminant concentration data were transformed to achieve normality prior to statistical analysis. Of all variables, only γ-HCH values were normally distributed. Inverse transformation was performed on HCB data, while natural log-transformations achieved best normal approximation for remaining organic contaminants. All data were plotted in a north-to-south direction to examine the spatial pattern (Fig. 1). Wilcoxon matched pairs test was used to test for differences of POPs levels between two seasons.

2.4. Environmental health risk

PCBs are a group of 209 different congeners which are usually divided into two groups according to their toxicological properties: