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POLYCHLORINATED BIPHENYLS AND ORGANOCHLORINE PESTICIDES IN BLACK MUSSEL AND GOBY FROM BLACK SEA, BULGARIA

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SUMMARY

Concentrations of persistent organic pollutants including polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were measured in two marine species: black mussel (*Mytilus galloprovincialis*) and goby (*Neogobius cephalarges*). Samples were collected from Lake Varna and Varna Bay in the period of 2004 - 2005 in order to evaluate the status, spatial distribution and potential sources of pollution in these areas. The mussel, one of the most widely used bioindicators of persistent organic pollutants, has been used to monitor PCBs and DDTs contamination trends in Lake Varna and Varna Bay. Black sea gobies are non-migratory species and feed mainly with benthic organisms. Average PCB concentration in mussels were found 28.7 ng/g fat. Total PCB concentrations in goby varied in the range of 21.3 and 71.5 ng/g fat. Concentration in black mussel were found 28.7 ng/g fat for total DDTs. Average DDTs concentration in goby were measured 2116 ng/g fat. The levels of PCBs and DDTs in black mussels and goby from the Lake Varna and Varna Bay were comparable with those found in other marine ecosystems.

Key words: polychlorinated biphenyls, organochlorine pesticides, fish, Black Sea, Bulgaria

INTRODUCTION

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are among the most dangerous pollutants because of their high liposolubility and tendency to bioaccumulate along the food chain. As a consequence, they are widespread in the biotic compartment of the environment (11). Even at lower concentration the pesticides eases the human immune system, while higher concentration of persistent organic pollutions have possible mutagenic and carcinogenic effects of humans.

The north-western part of the Black Sea receives a number of landbased sources of pollution (i.e. the Danube, Dniepr and Dniestr rivers) and the Danube River is an important source of organochlorine substances, as it flows through several regions with intensive agriculture and industrial activities (9).

Pesticides and polychlorinated biphenyls are found in various parts of the environment in quite small concentrations, but they accumulate and thus become a threat to human health and life (11). PCBs and OCPs were measured in sediments collected in 2000 year from the mouth of the Danube Delta and it was found that the Danube River is a potential source of contamination to the Black Sea (3,4,7).

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Mussels and fish are an excellent indicator for pollution in aquatic ecosystems, where trace contaminants are difficult to analyze directly. The concentration of PCBs were found much higher in mussels compared to that of the sediments due to the fact that the mussels are filter feeders and have the ability to bioconcentrate pollutants in their tissues at very high levels (9,13). Fish consumption is the main source of human exposure to different environmental contaminants like PCBs and DDTs. Black sea gobies are non-migratory species and feed mainly with benthic organisms

There are only few data available on residue concentrations of OCPs in mussel and fish from the Bulgarian coast of the Black Sea (12).

The aim of this study is to assess the status of polychlorinated biphenyls and organochlorine pesticides contamination in mussels and goby samples from Bulgarian Black Sea coast - Varna Bay and from Lake Varna.

MATERIALS AND METHODS

Black mussel (*Mytilus galloprovincialis*) and goby (*Neogobius cephalarges*) were collected from Lake Varna and Varna Bay in the period of 2004 - 2005. Samples were immediately transferred to the laboratory in foam boxes filled with ice and were stored in a freezer (-18^{o}C) until analysis.

Edible tissues of fish and mussels were homogenized and sub-samples of 10 g were taken from it for extraction. The

PCBs and DDTs were extracted with hexane / dichloromethane (3/1; v:v) in Soxhlet apparatus, and then the extracts were purified by column chromatography.

The PCBs and DDTs were analyzed by a Perkin Elmer Autosystem XL gas chromatograph equipped with an electron capture detector. A Restek Rtx-5 capillary column (60 m length, 0.25 mm ID, 0.25 μm film thickness) was used for separation of organochlorines. The experimental conditions were as follows: split/splitless injector temperature - 250oC, detector temperature - 310°C, oven temperature - 120°C for 1 min, then programmed at a rate of 2°C/min to 320°C and hold 15 min. Helium was used as the carrier gas. Pure reference standard solutions (Dr. Ehrenstorfer) were used for instrument calibration, recovery determination, and quantification. Measured compounds are: 14 PCB congeners (IUPAC No 28, 31, 52, 77, 101, 105, 118, 126, 128, 138, 153, 156, 169, 180), p,p'-DDT, p,p'-DDD and p,p'-DDE.

RESULTS AND DISCUSSION

Table 1. Lipid content (%) and concentrations of individual PCBs congeners (ng/g fat) in black mussel and goby

	Mussel		Goby		
	2005		2004		2005
	Varna bay	Lake Varna	Varna bay	Lake Varna	Varna bay
Lipids %	3.3	2.8	3.4	6.0	1.4
PCB 28*	nd	2.5	nd	nd	0.2
PCB 31	nd	0.8	3.8	8.1	nd
PCB 52*	nd	22.2	nd	nd	nd
PCB 77	nd	nd	16.9	nd	nd
PCB 101*	9.7	3.6	1.9	nd	23.4
PCB 105	nd	nd	nd	nd	nd
PCB 118*	nd	nd	nd	13.2	nd
PCB 126	nd	8.0	nd	nd	nd
PCB 128	nd	nd	1.5	nd	nd
PCB 138*	nd	10.6	nd	nd	42.3
PCB 153*	nd	nd	nd	nd	5.6
PCB 156	nd	nd	16.4	nd	nd
PCB 169	nd	nd	nd	nd	nd
PCB 180*	nd	nd	nd	nd	nd
Total PCBs (ng/g fat)	9.7	47.7	40.5	21.3	71.5
Total PCBs* (ng/g fat)	9.7	46.9	1.9	nd	65.9

** Indicator PCBs, nd – not detection*

PCBs levels

Concentrations of 14 individual PCBs congeners found in mussels and goby, average of duplicate measurements, are present in Table 1. For monitoring of PCB burden, fish and mussel samples are analyzed usually for seven indicator PCBs (IUPAC № 28, 52, 101,118, 138, 153, 180). They are defined by WHO as important for evaluating the risk to human health.

The most abundant PCB congeners in mussels were the indicator PCBs constituting almost 100% of the total amount of PCBs. The PCB pattern found in mussels showed a predominance of PCB 52 followed by PCB 138 and PCB 101 for indicator PCBs. The predominance of hexachlorinated PCBs in mussels, especially PCB 153 and PCB 138, has been reported by several authors for different coastal areas in the Mediterranean (8,13) and in the Adriatic Sea (1,10). The levels found in present study are in accordance with the results of mussel from the northern Adriatic Sea (1.3-18.5 ng/g fresh weight based) determined by Bayarri, S. et al. (1). Our results indicate that PCB contamination of mussels were found higher than results in mussels of the Mid-Black Sea Coast of Turkey, where no PCB were detected in any samples (6). Okay O.S. et al. were measured levels of PCBs in mussels of the Istanbul strait, Turkey during the period of January-February 2007 and their results ranged from 1026 to 35 983 pg g^{-1} wet weight (9).

Total PCB concentrations in goby varied in the range of 21.3 and 71.5 ng/g fat (Table 1). PCB 138 was the major contaminant PCB congener. PCB 153 and PCB 138 were also predominant congeners in fish species from the Mediterranean (8) and in fish from Marmara Sea (2). In general, our results indicate that PCB contamination of goby from the Black Sea - region of Varna city is much lower compared to the results from Marmara Sea, where average concentrations (sum of seven PCB congeners) were found 297.7 ng/g fat (2).

In mussels total PCB concentrations from the Varna Bay (9.7 ng/g fat) were found lower than those from the Lake Varna (47.7 ng/g fat). The different distribution of PCBs congeners in mussels and goby reflected their feeding behaviour.

DDT and its metabolites

Concentrations of DDE, DDD and DDT found in the sample studied, average of duplicate measurements, are present in Table 2.

p,p'-DDE was the major organochlorine contaminant in all samples. DDE concentration found in mussels of the present study were 6.3 ng/g wet weight and this is in accordance with the concentration levels of mussel from the northern Adriatic Sea (1.6-3 ng/g fresh weight) determined by Bayarri, S. et al. (1) Nasso B. et al. studied the blue mussels from the Gulf of Naples, Southern Italy and they were measured levels of DDTs (sum of p,p'-DDT, p,p'-DDD and p,p'-DDE) in the range 32.1-308.8 ng/g lipid weight (8). Our results showed the similar concentration levels of DDTs in mussel samples from Black Sea.

The mussel samples taken from Lake Varna showed that the results regarding DDTs contamination are higher than those from Varna Bay.
Levels of DDTs in goby from the Varna bay and Lake Varna (see Table 2) were found slightly higher than levels measured in the same fish species from neighbor seas - Marmara Sea, Adriatic Sea, Mediterranean sea and Belgian North Sea (2,5,14).

Table 2. Concentrations of DDT and its metabolites (ng/g fat) in black mussel and goby

	Mussel		Goby		
	2005		2004		2005
	Varna bay	Lake Varna	Varna bay	Lake Varna	Varna bay
p,p'- DDE	192.3	222.9	1219.1	254.4	3309.0
p,p'- DDD	nd	124.8	510.5	37.5	699.3
p,p'- DDT	nd	75.2	318.9	nd	nd
Total DDTs (ng/g fat)	192.3	422.9	2048.5	291.9	4009.3

nd – not detection

Goby, sampled from coastal waters of Varna bay, was found to contain average concentration 3029 ng/g fat DDTs, while goby sampled from Lake Varna contained 291.9 ng/g fat. The higher levels of DDTs may be due to the wastewater outfalls of the Varna city and due to the high number of ships which use the area for mooring. The differences in feeding preferences and lipid content of mussel and goby justify the large range of observed DDTs levels (307.6 and 2116 ng/g fat for mussel and goby, respectively).
In all tested samples, the residues were found in the order of DDE > DDD > DDT and this is in agreement with the results of other authors (3,7). DDT was presented mainly in the form of its metabolites p,p'-DDE and p,p'-DDD. This suggests that recently these pesticides have not been used in agriculture after their ban. DDTs profiles in goby and mussel were measured as follows 76% p,p'-DDE, 18% p,p'-DDD and 5% p,p'-DDT. The prevailing DDE presence, compared to DDT (high DDE/DDT ratio), suggested that the biotransformation rate of pollutants was very efficacious in fish and mussels.

CONCLUSIONS

PCBs and DDTs were found in all analyzed samples. Our results indicate that PCBs contamination of goby from the Lake Varna is lower compared to the results from Varna Bay. In mussels total PCB concentrations from the Varna Bay were lower than those from the Lake Varna.
DDTs were the predominant organohalogenated contaminants in all species, with the p,p- DDE contributing to more than 75% to the total DDTs. In all samples DDT was present mainly in the form of its metabolites pp'- DDE and p,p'-DDD, suggesting previous contamination.
In general, levels of PCBs and DDTs in mussels and goby from the Varna bay and Lake Varna were found comparable or slightly higher than levels measured in the same marine species from neighbor seas - Marmara Sea and Mediterranean Sea.
The experimental data present initial investigations from a profound study of PCBs and DDTs in fish and seafood from Black Sea.

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REFERENCES

1. Bayarri, S., Baldassarri, L.T., Iacovella, N., Ferrara, F., di Domenico, A. PCDDs, PCFDs, PCBs and DDE in edible marine species from the Adriatic Sea. *Chemosphere* **43**, 2001, 601-610.
2. Coelhan M, Stroheimer J, Barlas H. Organochlorine levels in edible fish from the Marmara Sea, Turkey. *Environ Int* **32**, 2006, 775-780.
3. Covaci A, Gheorghe A, Hulea O, Schepens P. Levels and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediments and biota from the Danube Delta, Romania. *Environ Poll* **140**, 2006, 136-149
4. Fillmann, G., Readman, J.W., Tolosa, I., Bartocci, J., Villenueve, J.-P., Cattini, C., Mee, L.D. Persistent organochlorine residues in sediments from the Black Sea, *Mar. Poll. Bull.*, 44, 2002, 122.
5. Kalyoncu L., Agca I., Aktumsek A., Some organochlorine pesticide residues in fish species in Konya, Turkey. *Chemosphere* **74**, 2009, 885-889
6. Kurt P., Ozkoc H. A survey to determine levels of chlorinated pesticides and PCBs in mussels and seawater from the Mid-Black Sea Coast of Turkey. *Mar. Poll. Bull.* **48** (2004) 1076-1083
7. Maldonado C., Bayona J.M. Organochlorine compounds in the north-western Black Sea water: distribution and water column process. *Estuar Coast Shelf Sci*, **54**, 2002, 527-540.
8. Naso B, Perrone D, Ferrante MC, Bilancione M, Lucidano A. Persistent organic pollutants in edible marine species from the Gulf of Naples, southern Italy. *Sci Total Environ*, **343**, 2005, 83-95
9. Okay O.S., Karacik B., Serden Basak, Henkelmann B., Bernhöft S., Schramm K.W. PCB and PCDD/F in sediments and mussels of the Istanbul strait (Turkey). *Chemosphere* **76**, 2009, 159-166
10. Perugini M, Cavaliere M, Giammarino A, Mazzone P, Olivieri V, Amorena M. Levels of polychlorinated biphenyls and organochlorine pesticides in some edible marine organisms from the Central Adriatic Sea. *Chemosphere*, **57**, 2004, 391-400

11. Smith, A.G., Gangoli, S.D., Organochlorine chemicals in seafood: occurrence and health concerns. *Food Chem. Toxicol.* **40**, 2002, 767-779
12. Stoichev T., Makedonski L., Trifonova T., Stancheva M., Ribarova F., DDT in fish from the Bulgarian region of the Black Sea. *Chem. and Ecology*, Vol.**23**, No. 3, 2007, 191-200
13. Villeneuve J.P., Carvalho F.P., Fowler S.W., Cattini C., Levels and trends of PCBs, chlorinated pesticides and petroleum hydrocarbons in mussels from the NW Mediterranean coast: comparison of concentrations in 1973/1974 and 1988/1989. *Sci Total Environ* **237/238**, 1999, 57-65
14. Voorspoels S., Covaci A., Maervoet J., De Meester I., Schepens P., Levels and profiles of PCBs and OCPs in marine benthic species from the Belgian North Sea and the Western Scheldt Estuary. *Mar. Poll. Bull.* **49**, 2004, 393-404