LEVELS OF ORGANOHALOGENATED POLLUTANTS (PCBs, OCPs AND PBDEs) IN BIOTA FROM THE DANUBE DELTA, ROMANIA

A. Covaci[1], A. Gheorghe[1], O. Hulea[2], P. Schepens[1]

[1]Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium
[2]Laboratory of Hydrobiology, Danube Delta National Institute, Tulcea, Romania

Introduction

Danube Delta is the largest wetland from Europe (580,000 ha), situated in the S-E of Romania and at N-W of the Black Sea. The Danube river flows through many European countries, receiving discharges of agricultural, industrial, and urban effluent. At its mouth is the vast wetland system that constitutes the Danube Delta. The delta wetlands perform many important functions contributing to the economical and physical health of the area, not least of which is a part of a filtering system for pollutants. Data about the current contamination status of the lower Danube River and Danube Delta are very scarce. For heavy metals, it was shown (1) that the pollution loading in the mussels collected from the Danube Delta are relatively high (at least for Pb) and that the contaminant loads varied 5-10 fold between sampling sites. For organic pollutants, no systematic measurements are done in water and fish and thus, no data are available in the literature. Sediments collected in 1994 from the Danube Delta (2) did not contain measurable concentrations (< 5 ng/g dw) of polychlorinated biphenyls (PCBs). Unfortunately, no measurements of pesticides, the main organochlorine contaminants in Romania (3), were done at that time. In 2000, PCBs and organochlorine pesticides (OCPs) were measured in sediments collected at the mouth of the Danube Delta (4) and it was found that the high concentrations associated with the Danube indicate that the river is a major source of contamination to the Black Sea. In another study, PCBs and OCPs were measured in bird's eggs collected in 1997 from the Danube Delta (5). It was found that DDTs are the main contaminants in all samples and that PCB concentrations are not as low as it might have been thought. Organohalogenated compounds have been found in a wide range of environmental media and biota because of their lipophilic properties, persistence in the environment and potential for magnification in the food chain.

This study aims to evaluate the occurrence of important organic contaminants, such as organochlorine pesticides (DDTs, HCHs and HCB), PCBs and polybrominated diphenyl ethers (PBDEs), in biota (invertebrates, different species of fish and cormorant tissues) collected from the Danube Delta.

Methods

Samples

Zooplancton and chironomids (*Chironomus plumosus*) were collected from 3 different locations (Merhei, Rosu and Razim) and were dried at room temperature prior analysis. 33 individual fishes (Table 1) were obtained from 3 different locations (Matita, Caraorman and Enisala). The samples were of variable age (2-7 yrs), both females and males, with whole body weights ranging from 90 g to 1.3 kg. Liver and muscle tissues were collected from 4 cormorants (*Phalacrocorax carbo)* caught in 2 different locations (canal Papadia and japsa Marcova). All samples were collected beginning of August 2001, except for birds and zooplancton collected end August 2001 and mid September 2001, respectively. The samples were wrapped in polyethylene bags and frozen immediately at –20 ^{o}C.

Sample preparation

The fish samples were thawed, filleted, skinned and the epaxial muscle homogenized before being subdivided into portions of approximately 100 grams. The portions were stored in tightly sealed polythene recipients and frozen at -20 °C, prior to analysis

Analysis

The following compounds were included: hexachlorobenzene (HCB), α-, ß- and γ-HCH hexachlorocyclohexane isomers (the sum expressed as HCHs), o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT (the sum expressed as DDTs), 18 PCB congeners (IUPAC no: 28, 52, 74, 99, 101, 105, 110, 118, 128, 138, 153, 156, 170, 180, 183, 187, 194, 199) and 7 PBDEs congeners (n°: 28, 47, 99, 100, 153, 154, 183). The method used for the determination of selected POPs in animal tissues has been previously described and validated (6) and briefly presented below. All dried zooplankton or invertebrates, 10 g of muscle for fish and 5 g of muscle or liver for birds were homogenised with anhydrous Na_2SO_4, spiked with internal standards (e-HCH, PCB 46 and 143, PBB 80, 103 and 155) and extracted for 2h by hot Soxhlet with 100 ml hexane:acetone (3:1). After lipid determination, the extract was purified on acidified silica. After elution with 15 ml hexane and 10 ml dichloromethane, the cleaned extract was concentrated to approximately 80 µl.

PCB and OCP determination

One µl of extract was injected in pulsed splitless mode into a GC-µECD equipped with a 50m x 0.22mm x 0.25mm, HT-8 capillary column. Method limits of determination for individual compounds ranged between 0.5-1 ng/g lipids. Recoveries of internal standards ranged between 75 and 85 %.

PBDE determination

One µl of extract was injected in cold splitless mode into a GC/NCI-MS equipped with a 10m x 0.10 x 0.10 µm, HT-8 capillary column. The MS was operated in the negative chemical ionisation in SIM mode (ions: 79 and 81). Method limit of determination ranged between 0.1 and 0.2 ng/g lipids for individual PBDE congeners.

Quality Control

The procedure was validated through regular analysis of procedural blanks, certified material CRM 350 (PCBs and OCPs in mackerel oil) and through successful participation to Quasimeme interlaboratory tests (PCB/OCPs determination in sediment and fish).

Results and discussion

Concentrations of HCB, HCHs, DDTs, PCBs and PBDEs measured in chironomids, zooplancton, different fish species and birds from Danube Delta are given in Table 1. It can be observed that organochlorine pesticides, particularly DDTs, are the main contaminants in all samples. PCBs were also found at relatively high levels, while HCB and PBDE concentrations were low.

Concentrations of pollutants in fish samples varied greatly between species and per location and they are closely related to feed intake and pattern. However, no clear trend in the concentrations of pollutants could be observed from benthic to piscivorous species. The lipid percentage was relatively low, varying between 0.2 and 2.0 %. For lean fish (fat percent < 2 %), seasonal fluctuations in fat content are noticeable, especially before and during the spawning period, when they draw on their reserves of fat and protein.

DDTs were the main contaminants also in muscle and liver from cormorants with concentrations of all pollutants being 2 fold higher for specimens collected from japsa Marcova location. PCBs concentrations were high and dominated by the hexa- and hepta-PCB congeners, while the ß-HCH was the dominant HCH isomer. For HCB, HCHs and PCBs, the concentrations were higher in liver, while levels of DDTs were higher in the muscle of birds.

For invertebrates, which serve as food for many species of fishes, concentrations of HCHs were similar with concentrations of DDT. These organisms provide an important link in the transfer of disolved and particle bound persistent pollutants to higher level in the aquatic food web.

Table 1.. Concentrations of organohalogenated pollutants (ng/g lipids) determined in fish, birds and invertebrates from Danube Delta

Sample		Species	Location	N	HCB	Σ **HCHs**	Σ **DDTs**	Σ **PCBs**	Σ **PBDEs**
Fish	B	Tench (*Tinca tinca*)	***Mat***	2	3.3	142.3	654.3	192.8	ND
			Car	1	9.3	188.2	603.2	204.2	4.0
		Bream (*Abramis brama*)	**Car**	2	33.1	276.8	2962.2	544.3	4.1
			Eni	1	5.0	186.3	613.7	170.7	0.7
	H	Gibel carp	**Mat**	2	4.7	179.8	214.7	89.5	0.8
		(*Carasius auratus gibelio*)	**Car**	2	6.1	152.7	370.0	83.9	3.0
			Eni	2	6.1	318.7	999.3	232.8	4.4
	O	Rudd	**Mat**	2	3.1	150.1	180.2	52.5	1.9
		(*Scardinius erythrophthalmus*)	**Car**	1	7.7	172.4	178.4	56.0	0.4
		Carp (*Cyprinus carpio*)	**Mat**	2	57.3	209.1	2846.5	1209.1	14.3
		White bream (*Blicca bjoerkna*)	**Mat**	2	15.7	160.4	675.5	354.5	2.0
		Roach (*Rutilus rutilus*)	**Eni**	2	6.9	201.0	846.0	500.9	1.9
	P	Wels (*Silurus glanis*)	**Mat**	1	10.2	133.4	684.3	223.2	3.2
			Car	2	17.0	211.9	728.8	239.7	5.5
			Eni	2	6.6	147.2	1628.5	401.0	8.3
		Pikeperch (*Stizostedion lucioperca*)	**Eni**	2	8.1	136.6	4829.0	1239.9	2.2
		Pike (*Exos lucius*)	**Mat**	2	10.1	56.3	591.5	163.1	7.6
			Car	1	1.6	129.1	423.8	140.5	3.8
		Perch (*Perca fluviatilis*)	***Car***	2	17.4	153.2	918.2	302.4	2.8
Birds	Cormorant	Muscle	**Pap**	2	67.0	181.0	1970.8	622.8	2.6
		(*Phalacrocorax carbo*)	**Mar**	2	174.6	357.7	4977.2	2231.0	6.9
		Liver	**Pap**	2	72.6	210.5	1632.5	714.4	NA
			Mar	2	199.0	503.4	3708.3	2969.3	NA
Invertebrates		Chironomids*	**Mer**		0.4	63.6	37.6	10.2	ND
		(*Chironomus plumosus*)	**Ro**		ND	82.7	38.7	8.9	ND
			Rz		0.4	29.4	25.7	9.6	ND
		Zooplancton*	**Mer**		0.5	53.8	25.9	63.2	1.0
			Ro		ND	33.7	37.3	23.6	7.2
			Rz		ND	38.6	99.0	13.2	1.9

*concentrations expressed as ng/g dry weight; B – benthic; H– herbivorous; O – omnivorous; P – piscivorous; Mat – Matita; Car – Caraorman; Eni – Enisala; Mer – Merhei; Ro – Rosu; Rz – Razim; Pap – canal Papadia; Mar – japsa Marcova;

For fishes collected from the same location (Matita), it could be seen that carp (with an omnivorous feeding pattern) contained the highest load of pollutants (Figure 1). Piscivorous fish (wels and pike) contained similar levels with another omnivorous fish (white bream). Benthic and herbivorus fishes (except tench) contained lower concentrations of contaminants.

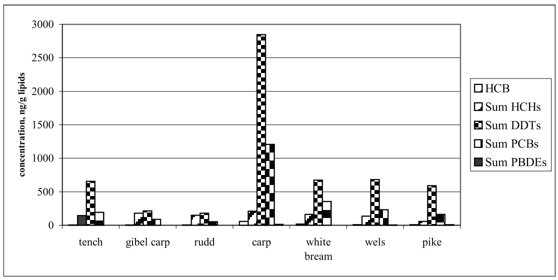

Figure 1. Profiles of organohalogenated pollutants in different fish species from Matita location.

For gibel carp collected in all three locations, it can be seen that for all contaminants, there was an increasing trend to Enisala location (Figure 2). The same trend was also observed for PCBs, DDTs and PBDEs in wels.

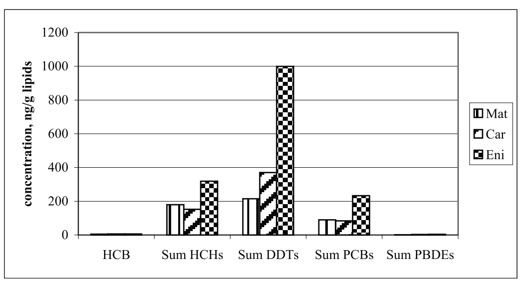

Figure 2. Profiles of organohalogenated pollutants in gibel carp from different locations.

The presence, for the first time reported here, of PCBs and PBDEs in biota from Danube Delta, together with relatively high concentrations of OCPs, indicates a need for continuous monitoring of biotic and abiotic compartments of this particular environment.

References

1. Jamil A, Lajtha K, Radan S, Ruzsa G, Cristofor S, Postolache C (1999) Hydrobiologia 392, 143-158.
2. Winkels HJ, Kroonenberg SB, Lychagin MY, Marin G, Rusakov GV, Kasimov NS (1998) Appl Geochem 13, 581-591.
3. Covaci A, Hura C, Schepens P (2001) Sci Total Environ 280, 143-152.
4. Fillmann G, Readman JW, Tolosa I, Bartocci J, Villeneuve JP, Cattini C, Mee LD (2002) Mar Pollut Bull 44, 122-133.
5. Aurigi S, Focardi S, Hulea D, Renzoni A (2000) Environ Pollut 109, 61-67.
6. Covaci A, Ryan JJ, Schepens P (2002) Chemosphere 47(2), 207-217.