Oceanological and Hydrobiological Studies
Vol. XXXIV, Supplement 1

Institute of Oceanography (239-248) University of Gdańsk
2005

Research Article

CONTAMINATION BY PERSISTENT ORGANIC POLLUTANTS OF INVASIVE SPECIES FROM THE BALTIC SEA REGION

GRAŻYNA SAPOTA[1*], ANNA SZANIAWSKA[2], MONIKA NORMANT[2]

[1]*Institute of Meteorology and Water Management, Maritime Branch*
ul. Waszyngtona 42, 81-342 Gdynia, Poland
*e-mail: *Grazyna.Sapota@imgw.pl*

[2]*University of Gdańsk, Institute of Oceanography*
Al. M. Piłsudskiego 46, 81-378 Gdynia, Poland

Key words: POPs, *Neogobius melanostomus, Eriocheir sinensis, Orconectes limosus,* the Baltic Sea

Abstract

The aim of this work was to establish the level of pollution by selected POPs (seven PCBs, DDT and its metabolites, HCH isomers, HCB) of the invasive species from the Gulf of Gdańsk and the Vistula Lagoon. The investigated species were the round goby (*Neogobius melanostomus* – fish originating from the Ponto-Caspian region), the Chinese mitten crab (*Eriocheir sinensis* from China), and the American crayfish (*Orconectes limosus* from North America). These species belong to different systematic groups and originate from various parts of the world. The levels of toxic substances were analyzed in the muscle tissue of the fish and the whole body of the crustaceans using capillary gas chromatography (GC). The level of POPs determined in the round goby was very low, despite high lipid concentration. The average values of ΣHCH, ΣDDT, and ΣPCBs in the muscle tissue of the round goby were 6 ng g^{-1} l.w., 187 ng g^{-1} l.w. and 391 ng g^{-1} l.w., respectively. The average values of ΣHCH, ΣDDT, and ΣPCBs in the analyzed crustaceans were: for the American crayfish - 6 ng g^{-1} l.w., 58 ng g^{-1} l.w., and 100 ng g^{-1} l.w; for the Chinese mitten crab - 20 ng g^{-1} l.w., 163 ng g^{-1} l.w. and 289 ng g^{-1} l.w.

INTRODUCTION

The Baltic Sea is the world's second largest body of brackish water, after the Black Sea. The geological history of the Baltic and its low salinity result in a unique mixture of freshwater, brackish water, and marine organisms (Segerstrale 1957, Walentinus *et al.* 1991). The osmotic stress of low salinity means that many marine and freshwater species cannot survive and reproduce. Thus, the Baltic Sea is also unique in having an extremely low diversity of species (Voipio 1981, Elmgren *et al.* 1997). However, the Baltic Sea is inhabited by new, non-indigenous species, the number of which has been increasing in recent years (Burba 1996, Duris 1999, Strużyński and Śmietana 1999, Skóra and Rzeźnik 2001). The species that do survive in the Baltic are under osmotic stress and are thought to be more susceptible to the effects of environmental perturbation, including pollutants with toxic compounds (Elmgren 1984, Tedengren and Kautsky 1986, Elmgren *et al.* 1997). Toxic substances (*e.g.*, persistent organic pollutants) encompass many different and various groups of man-made chemicals. These include, among others, PCBs, HCH isomers, HCB, and DDT and its metabolites. Persistent organic pollutants are a group of chemicals that is very resistant to natural breakdown processes and therefore extremely stable and long-lived. POPs are also highly toxic and build up (bioaccumulate) in the fatty tissues of animals and humans. Many POPs which pollute the environment become incorporated into food webs. Organism age, lipid content in the tissues, the means of feeding, and the actual position held by an organism in the food chain are the deciding factors of the potential pollution level by toxic substances of a given species and individual organisms (Breitholtz *et al.* 2001). Toxic substances can be transferred from one organism to another not only in the food chain, but also within the same species from one generation to the next (Geyer *et al.* 1994, Kamrin and Ringer 1994). Consequently, the Baltic Sea and its biota became highly polluted and even today levels of POPs remain comparatively high (Fitzmaurice 1993). The invasive species are highly tolerant to changes in environmental conditions. The species selected for analysis belong to different systematic groups and come from various parts of the world. It is expected that the results of the investigations will be interesting and useful in characterizing the Baltic Sea environment. The toxic substances which were identified in the American crayfish (*O. limosus*) and the Chinese mitten crab (*E. sinensis*) might have been accumulated in the marine environment or earlier in the river environment, because this species can live in both fresh and brackish water.

MATERIALS AND METHODS

Study Site Description

The samples were taken from three sampling stations (Fig. 1). Two stations were located in the Gulf of Gdańsk (near the Gdynia and Hel harbors), and one station was located in the Vistula Lagoon (near the Nogat River mouth).

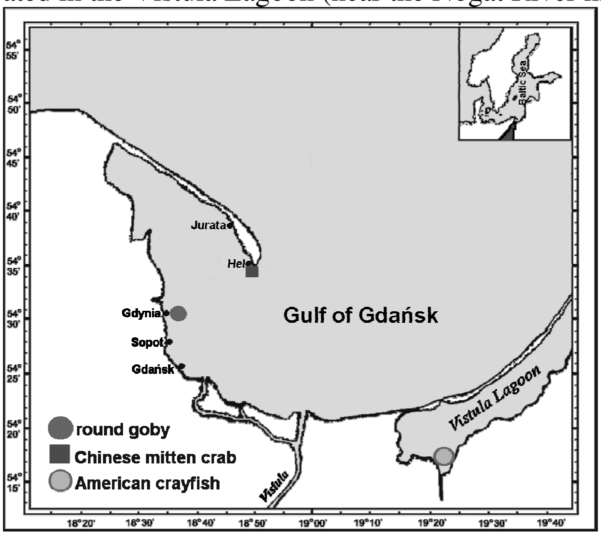

Fig. 1. Sampling station locations

Table 1

Sampling circumstances and average length, dry matter content, and lipid content of the investigated species.

Species	Sampling date	Sampling locations	Sampling tool	Number of organisms	Analyzed tissue	Average length (cm)	Average dry matter content (%)	Average lipid content (%)
Chinese mitten crab	July to September 1999	Hel harbor	fyke net	17 males	whole organism	4.7 ±0.5	42.9 ±6.4	4.2 ±1.2
American crayfish	August to October 2001	Vistula Lagoon	fyke net	9 females 15 males	whole organism	9.7 ±0.4 9.7 ±0.3	37.6 ±2.5 36.7 ±1.4	6.3 ±1.3 5.5 ±1.0
Round goby	March to December 2001	Gdynia harbor	fyke net	25 females 23 males	muscle tissue	11.8 ±3.1 10.5 ±1.9	28.6 ±4.5 30.2 ±4.9	5.7 ±2.1 5.6 ±2.5

Biological Analysis

All samples for analyses were collected with fyke nets. The size and the sex of each organism were determined (Table 1). The right side dorso-lateral muscles of the round goby specimens were taken as the sample. The length and width of the specimens of American crayfish and Chinese mitten crabs were measured using a slide caliper, and their sex was determined from the structure of their abdomen. The muscle tissue of fish and whole crustaceans were freeze-dried using a freeze dry system. The dry weight percentage of each sample was determined. The dried samples were then homogenized in a vibrating powder mill.

Table 2

Average values of the analyzed POPs in the investigated species.

Species	Sex*	ΣHCH (ng g^{-1} l.w.)	ΣDDT (ng g^{-1} l.w.)	ΣPCBs (ng g^{-1} l.w.)
Chinese mitten crab	M	20	163	289
American crayfish	F	5	54	95
	M	7	62	105
Round goby	F	8	197	396
	M	4	176	386

*M – male, F - female

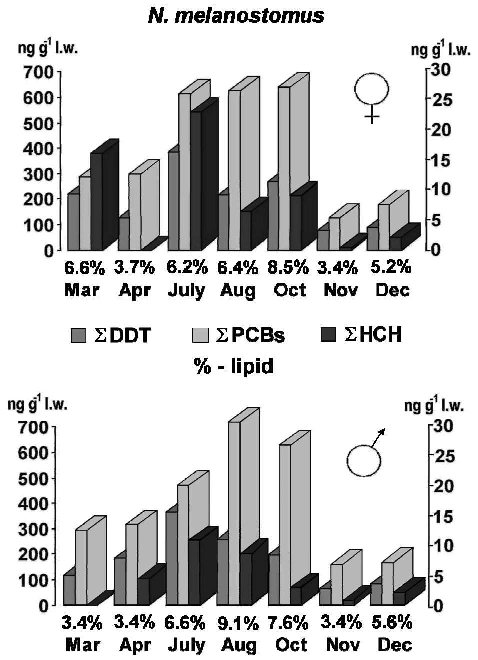

Fig. 2. Seasonal changes in POP concentrations in round goby muscles (ΣHCH - right scale).

Capillary Gas Chromatography

The freeze-dried sub-samples were Soxhlet-extracted in a mixture of hexane and acetone (1:2 vol.). Prior to the extraction, internal standards (CB 65 and CB 207) were added to the solvent (Dannenberger and Lertz 1996). The extracts were purified on a column containing two layers (with K_2CO_3 and H_2SO_4) of silica gel, eluted with dichloromethane /hexane (5:95). The elute was then evaporated and dissolved in isooctane and analyzed by capillary gas chromatography with an electron capture detector (GC – ECD) (Bremle *et al.* 1995, Sapota 1997, 2002). Multilevel calibration was applied for quantification. The QUASIMEME test material was used as a reference material. The concentrations of seven PCBs (IUPAC No. 28, 52, 101, 118, 138, 156, 180), DDT and its

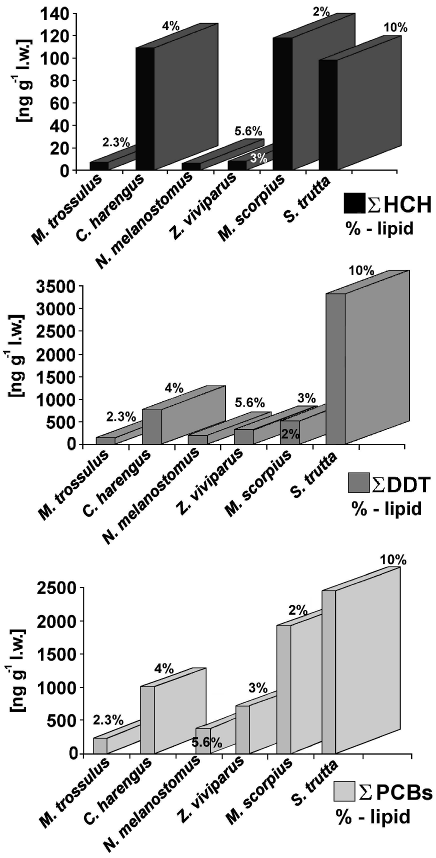

Fig. 3. Levels of POPs in round goby (present work) and various species of fish and blue mussel from the Baltic Sea (Sapota 2004).

metabolites, HCH isomers (α, β, γ) and HCB were determined in the muscle tissue of fish and the whole bodies of the crustaceans. The values were expressed in ng g^{-1} on a lipid weight (l.w.) basis. Limits of detection (LoD) were calculated as the concentration of analyzed substances in carrier gas that gave a signal two times larger than the noise level (Rödel and Wölm 1982). The LoD of HCH isomers and HCB was 10^{-4} ng s^{-1}. The LoD of DDT and its metabolites and PCBs was 10^{-3} ng s^{-1}. The lipid content was determined as the extractable lipid.

RESULTS

The average values of length, dry weight, and lipid weight of the investigated species are shown in Table 1. The average lipid content determined in the round goby was similar in the muscle tissue of males and females. In the American crayfish, the average lipid concentration of the bodies was quite a bit higher in females than in males (Table 1). The average values of ΣHCH, ΣDDT, and ΣPCBs in the investigated species are presented in Table 2. Among DDT and its metabolites, *p,p'*-DDE dominated. In total PCBs, CB 138 and CB 153 dominated. Seasonal changes in the levels of the analyzed contaminants in round goby muscles were detected (Fig. 2). POP concentrations varied seasonally with fat content and increased during the summer and decreased during fall and winter. In comparison with other species of fish from the Gulf of Gdańsk and the southern Baltic Sea (Olsson *et al.* 2002), the level of POPs determined in the round goby was very low, despite high lipid concentrations (Fig. 3). The average values of ΣHCH, ΣDDT, and ΣPCBs in the American crayfish females were lower than in the males (Table 2). Among DDT and its

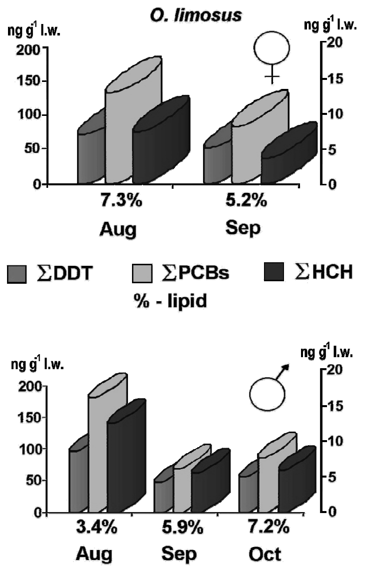

Fig. 4. Changes in concentrations of POPs in American crayfish (ΣHCH - right scale).

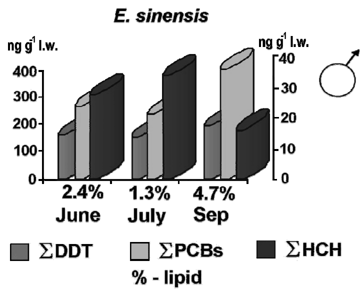

Fig. 5. Changes in concentrations of POPs in Chinese mitten crabs (ΣHCH - right scale).

metabolites, *p,p'*-DDE dominated. Of the selected PCBs, CB 138 and CB 153 dominated. Temporal changes in the levels of the measured POPs were noted in the analyzed crustaceans (Figs. 4 and 5). The concentrations of POPs established in the analyzed crustaceans were comparable with other species of crustaceans from the Gulf of Gdańsk (*O. limosus* with *Crangon crangon* and *E. sinensis* with *Saduria entomon*) (Fig. 6) (Olsson *et al.* 2002, Sapota 2004). The pattern of the analyzed POPs, with the clear predominance of PCBs, was similar in the three analyzed species. This pattern is characteristic for benthic organisms and bottom-feeding fish (Sapota 2002) (Fig. 7).

DISCUSSION

In comparison with other fish species from the Gulf of Gdańsk and the southern Baltic Sea (Olsson *et al.* 2002), the level of POPs determined in the round goby was very low despite high lipid concentrations (Fig. 3). Maybe the long period of batch spawning influenced this (Skóra and Rzeźnik 2001), as organisms can detoxify during reproduction (Larsson *et al.* 1991). The lipid composition can also affect the accumulation of POPs (Larsson *et al.* 1991, Geyer *et al.* 1994). The level of POPs in round goby muscle is similar to that in blue mussel from the same region (Fig. 3). Round gobies from the Gulf of Gdańsk consume mostly blue mussels (Skóra and Rzeźnik 2001). Some pollutants (*e.g.*, POPs) may occur at even higher concentrations in zooplankton or benthic invertebrates than in the fish that feed on them (Breitholtz *et al.* 2001). Olsson *et al.* (2002) confirm that the concentrations of DDT, PCBs, or

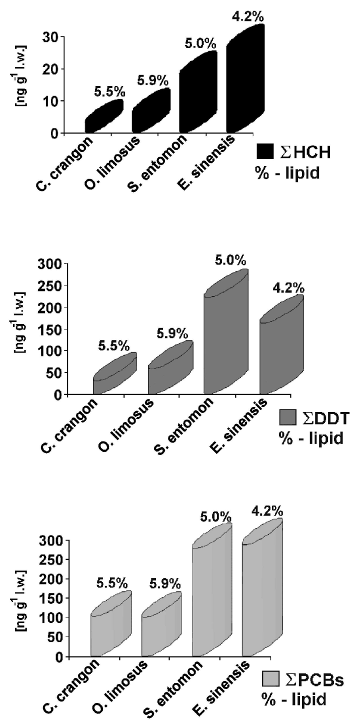

Fig. 6. Levels of POPs in the American crayfish, Chinese mitten crabs (present work), and other crustaceans from the Baltic Sea (Olsson *et al.* 2002, Sapota 2004).

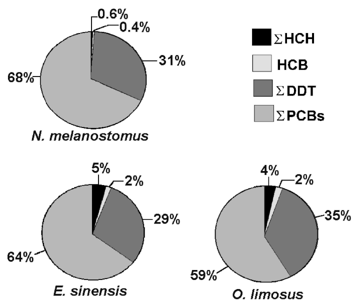

Fig. 7. Pattern (%) of analyzed POPs in the investigated species.

HCHs in fish (*e.g.*, planktivorous *Clupea harengus* or piscivorous *Perca fluviatilis*) are often quite similar to those found in benthic organisms (*M. trossulus, S. entomon*). The American crayfish, which is well known for its ability to survive in water of poor quality, accumulates POPs in smaller concentrations than the Chinese mitten crab, which is sensitive to water pollution. Perhaps sampling station location also has an influence on the pollution levels of the Chinese mitten crab. The highest PCB concentrations in benthic organisms appear in areas with the heaviest industrial pollution, such as harbors (Lee *et al.* 1996a). The Chinese mitten crab spends the majority of its life in rivers, which can transport pollutants to the marine environment. All of the crustacean specimens analyzed in the current work were adult and were probably several years old. Organism age is one of the decisive factors in the potential pollution levels of toxic substances in a given species and in individual organisms (Breitholtz *et al.* 2001). The Chinese mitten crab specimens analyzed were only males. The percentage of females in the Chinese mitten crab population is usually slightly lower than that of males (Kobayashi and Matsuura 1994, 1995, Normant *et al.* 2000). In all the analyzed samples it was confirmed that CB 153 and CB 138 were the most prominent of the many PCBs present in the biota (Lee *et al.* 1996a, b, Andersson *et al.*, 1998, Falandysz *et al.* 1998a, b, c, d, Sapota 2002). The invasive species analyzed are not of any commercial importance in the Baltic Sea region, but this may change in the nearest future. Scientific research is being conducted into the possible commercial exploitation of this species. The Chinese mitten crab is the largest crustacean species inhabiting Baltic coastal waters, and their interesting appearance contributes to their frequent decorative use in food preparation (Normant *et al*. 2002).

The lipid contents in the tissues of the analyzed species were high in comparison with those of other species from the Baltic Sea. Seasonal changes were noted in the levels of the POPs determined in the round goby; they were also very low in comparison with other fish species from the Baltic Sea. The level of POPs determined in the bodies of the American crayfish was lower than in other species of Baltic crustaceans.

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