Oceanological and Hydrobiological Studies

International Journal of Oceanography and Hydrobiology

Volume 42, Issue 3

ISSN 1730-413X
eISSN 1897-3191

(251–259)
2013

VERSITA

DOI: 10.2478/s13545-013-0081-z
Original research paper

Received: December 06, 2012
Accepted: May 09, 2013

# Residue of chlorinated pesticides in fish caught in the Southern Baltic

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**Key words:** DDT, heksachlorobenzen, edible fish, Gulf of Gdańsk, Vistula Lagoon

**Abstract**

The aim of this study was to estimate the residue of chlorinated pesticides in the edible fish caught in the Gulf of Gdańsk and in the Vistula Lagoon. The highest mean concentrations of total DDT were found in the muscles of salmon (331.45 ng $g^{-1}$ lw.) and sabre carp (306.29 ng $g^{-1}$ lw.) caught in the Vistula Lagoon, and in the muscles of cod (309.88 ng $g^{-1}$ lw.) and herring (304.86 ng $g^{-1}$ lw.) from the Gulf of Gdańsk. Moreover, it was discovered that the following were present in the muscles of fish: DDT metabolites (pp'-DDE and pp'-DDD isomers) as well as hexachlorobenzene and its metabolites and endrin, dieldrin, α-endosulfan isomers and methoxychlor. Pesticides concentrations were higher in the livers of fish than in the muscles, which proves that the removal of toxins from the fish systems dominates over their accumulation. Because no concentration limits for pesticides have been defined, consumer safety assessment of fish caught in the Southern Baltic and in the Vistula Lagoon is not possible. The authors, having observed an increase in heksachlorobenzen in fish tissues suggested the existence of contemporary sources of pesticides which introduce them into the coastal zone.

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## INTRODUCTION

Organochlorine pesticides were introduced into the agricultural practice in the 1950s. They were used in agrotechnical and zootechnical treatments the same way as insecticides, i.e. against ants and termites, and some of them were used in the 1980s to protect sowing seeds against ectoparasites. However, there are justifiable suspicions that they have been used also after that time. The presence of some of them detected in the air over Gdańsk in the 1990s indicated their continued use. Furthermore, some waste brought into Poland at the end of the 1980s also contained these pesticides (Falandysz et al. 1999a, b; Zitko 2003). The pesticides are still present in the environment despite the fact that they have been withdrawn from the use about 30 years ago. Gradual elimination of chloroorganic pesticide disposal sites is not without significance, as it may have resulted in mobilization of pesticides and, in consequence, their transportation by the wind. The transport of fungicides and other pesticides to a hazardous waste incineration plant, located in the close vicinity of the Gulf of Gdańsk, and their temporary storage may also contribute to their increasing concentrations in the fish from the research area.

All the studied fish species are commercially caught in the Gulf of Gdańsk and in the Vistula Lagoon, as they constitute valuable food for humans, but they are also the food of marine mammals and birds, hunted for (by porpoises, seals, gulls and cormorants) or collected from the fishing boats. Huge flocks of seagulls feed on the dredges hauled aboard the fishing boats, as well as on the entrails of fish gutted on the returning boats. While the food of marine mammals and birds tends to be whole fish, for humans it is mostly the muscle tissue.

The aim of the undertaken study was to estimate the residue of chlorinated pesticides in the fish caught in the Gulf of Gdańsk and in the Vistula Lagoon. The study focused on the freshwater and sea fish on different trophic levels, which made it possible to determine the influence of diet and habitat of fish in its concentrations in their systems. The aspect of removing the toxins from the system through their transfer to ovaries and testes of the Baltic herring (*Clupea harengus*) was also studied.

**Biological description of the study material**

The study included species of fish from the Gulf of Gdańsk and the Vistula Lagoon, which are most valuable in terms of consumption. The collected biological material included: fish caught in Gulf of Gdańsk, like the pelagic herring (*Clupea harengus*), the demersal cod and flounder (*Gadus morhua, Platichthys flesus*) and species inhabiting the Vistula Lagoon: freshwater bream (*Abramis brama*), sabre carp (*Pelecus cultratus*) and roach (*Rutilus rutilus*) as well as the anadromous salmon (*Salmo salar*).

The Baltic herring (*Clupea harengus membras*) is a subspecies of the Atlantic herring (*Clupea harengus).* Two reproductive populations can be distinguished among the Baltic herring: the herring from the spring spawn reaching about 20 cm in length, and the fish from the autumn spawn, which grow up to 30 cm. The spring spawn herring have dominated in the Baltic since the 1960s. Depending on the region of the Baltic, the breeding lasts from February till July. The herring is a pelagic shoaling fish found in the surface water, but also at a depth of 100 m. The amount and the type of their food depends on the region of the sea in which they live, the variant of the species, the gonad stadium, the water temperature, the age and the size of the fish. In the initial stages of the development, herring feed on copepods (*Copepoda*), mostly *Temora longicornis* and *Pseudocalanus elongatus*. Adult specimens feed on the mysidacea, mainly *Mysis mixta.* The largest specimens, however, prefer juvenile stages of the *Gobiidae* fish (Arrhenius, Hansson 1992; Jackowski 2002; Casini et al. 2004).

The Baltic cod (*Gadus morrhua callarias*), one of the three subspecies of the Atlantic cod, is a predator. The young live in shallow coastal waters, where they feed on small crustaceans, such as *Mysidacea*, *Gammaridaeus* and *Pantoporeia.* Adult cod live in the open sea and usually feed on the sea bed, hunting other fish such as *Clupea harengus membras, Sprattus sprattus*, *Gobiidae* and *Hyperoplus lanceolatus*, and larger invertebrate such as *Saduria entomon, Crangon crangon* and Polychaeta. Cannibalism is also widespread and adult specimens will not pass up the opportunity to feed on a representative of their own species (Kosior 2001).

The flounder (*Platichthys flesus*) is found in the Baltic up to the middle part of the Gulf of Bothnia and the Gulf of Finland, but does not occur in the Gulf of Riga. Within the Polish economic zone of the Baltic, two groups can be distinguished: the Bornholm Basin and the Gulf of Gdańsk. Flounders inhabit sandy beds in the coastal zones of brackish waters down to a depth of 50 m. Owing to their high tolerance to changes in salination, they can also be found in the lower reaches of the rivers. In the summer, they prefer shallower waters, where they stay buried in the sand during the day, while in the winter they inhabit deeper regions of the sea, feeding in shallow waters during the night. The lifespan of the Baltic flounder is 8-9 years (Jackowski 2002).

The bream (*Abramis brama*) is a fresh- or brackish water species which inhabits estuary zones, where the current is slow and the bottom is silty. The young inhabit the littoral waters, while older fish live deeper but still search for food in silty shallows close to the shore. Bream feed mainly on small aquatic invertebrates buried in silt, and the length of their body is usually between 30 and 50 cm, but they can reach up to 75 cm (Gąsowska 1962, Brylińska 2001).

The sabre carp (*Pelecus cultratus*) is a freshwater, pelagic, planktivorous fish. Adult specimens are opportunistic predators, feeding on small fish such as smelt, perch or roach. In the waters of the Vistula Lagoon, these fish reach a length of 25-35 cm, although they can grow up to 60 cm (Terlecki 2000). In Poland, the sabre carp is a protected species, except for the Vistula Lagoon region (Journal of Laws (Dz. U.) No. 130 items 1455 & 1456 of the 26$^{th}$ September 2001).

The roach (*Rutilus rutilus*) is a freshwater fish, which can also be found in brackish offshore waters. Young specimens live in shallows and feed on phyto- and zooplankton. Older specimens prefer to search for food close to the bottom of the sea, mainly crustaceans and smaller insect larvae, but also feed on algae and benthic plants. Roach which are about 20 cm long or larger also feed on mollusks. The roach grows slowly, reaching 10 cm by the age of 10 years, and lives for 15-18 years (Gąsowska 1962, Brylińska 2001).

The Baltic salmon (*Salmo salar*) is a variant of the Atlantic salmon. It is a large fish which in the spawning season travels from the sea to its native rivers, and can reach a length of 150 cm and a weight of over 20 kg. Young specimens after about 2 years spent in rivers, where they feed on insect larvae, crustaceans and small fish, swim out to sea where fish become their sole food: herring, European sprat and greater sand eels. The next 2-5 years are spent in the brackish Baltic waters, during which the sexual maturity is reached, and after which the salmon returns to its native river to spawn, i.e. usually in early autumn. At that time, salmon cease feeding. The species is extinct in the Polish rivers probably since the 1980s (Bartel 2001), but the reintroduction projects have been continued and so far succeeded in returning the species to the tributaries of the Middle Oder and the Upper Vistula, as well as smaller rivers: Reda, Parsęta, Wieprza, Słupia and Łeba (Bartel 2001, Wiśniewolski et al. 2004).

## Environmental description of the Gulf of Gdańsk and the Vistula Lagoon

The Gulf of Gdańsk is a relatively shallow shelf area of the Southern Baltic with an average depth of 70 meters (the maximum depth of 118 meters) located on the northern edge of the basin. River tributaries supply fresh water, whereby the salinity in the coastal area of the gulf is 1-3 PSU, i.e. much lower compared to surface waters of the open part of the basin (7 PSU). The salinity levels increase with the depth, reaching 10-13 PSU below the halocline, which is caused by vertical layering of the gulf. The density stratification restricts the mixing of water in the gulf, which results in oxygen deficiency near the bottom of the deepest area. The Vistula is the main tributary, a river which causes the eutrophication of the gulf by supplying large amounts of nitrate and phosphate salts (Buszewski et al. 2005). Rivers also bring residues of chlorinated pesticides into the Gulf of Gdańsk. The organochlorine halides, which are brought into the gulf, are present in suspensions and marine sediment, as well as in organisms living in the Baltic (Falandysz, Strandberg 2004; Kot-Wasik et al. 2004; Sapota 2006; HELCOM 2010).

The Vistula Lagoon is the second largest lagoon in the region of the Baltic Sea. It is a shallow offshore basin (average depth of 3.1 m), separated from the Gulf of Gdańsk by the Vistula Spit, and 45% of the Lagoon area (388 km$^2$) belongs to Poland, the rest to Russia. The waters of the Vistula Lagoon are under strong influence from the land, and the main tributaries on the Polish side are Nogat, Szkarpawa, Bauda, Pasłęka and Elbląg, and on the Russian side − Pregolya. Water exchange is limited, especially in the Polish part of the lagoon, and takes place only via the Strait of Baltiysk. Therefore, the salinity of the Vistula Lagoon is low and amounts to 4 PSU on average. In the south-western part, which belongs to Poland, the salinity periodically decreases to 1-2 PSU. This salinity concentration is not harmful to freshwater species, which reach the lagoon from the rivers. Location of the basin in the vicinity of a large agricultural area results in the fact that artificial fertilizers and plant protection agents are washed out and transported with the rivers and atmosphere to the basin, contributing to its pollution. An additional source of pollutants introduced into the lagoon is waste from mechanical-chemical water purification plants in small towns (up to 100,000 inhabitants) located along the Vistula Spit. The presence of organochlorine pesticides, such as DDT and its metabolites (as well as lindane and hexachlorobenzene), has been discovered in the sediment of the Vistula Lagoon. Observations carried out on the concentrations of these xenobiotics in sediment have proved a gradual decrease in their concentration (Sapota 1997, 2006). In order to protect the nature in the Vistula Lagoon region, the area was included in the Natura 2000 programme and placed on the list of Protected Baltic Areas.

# MATERIALS AND METHODS

## Collection and preparation of samples

The fish were caught by fishermen in September (Vistula Lagoon) and October (Gulf of Gdańsk) 2011. Following the taxonomic identification in the laboratory, samples of muscles and livers, as well as ovaries from females and testes (including protective membranes) from males were taken during dissection. Homogenization of samples was followed by freeze drying and then repeated homogenization.

Chlorinated pesticides were extracted from the lyophilized biological material weighing min. 1 g using cellulose thimbles. Extracts were prepared with the Soxhlet method, using a mixture of n-hexane and acetone at a ratio of 1:1. The extraction solvent was enriched with n-tetradecane as a "keeper" whose role was to keep the more volatile pesticides in the extract. The obtained extract was then concentrated to 1 cm$^3$ and cleaned up with concentrated $H_2SO_4$

(1 cm³) in order to remove fats. Further extracts were purified using the SPE method with C18 cartridges. For elution, the solvent used for extraction was applied. Eluate was concentrated to 1 cm³ and analyzed (Falkowska et al. 2013).

**Reagents and standards**

Standard organochlorine compound material was used to determine the pesticides (for all analyzed pesticides). The material supplied by AccuStandard was over 99% pure (GC area ≥99.8%). The extraction solvents: n-hexane, acetone and n-tetradecane, also with the minimum purity of 99% (GC area ≥99%) for the chromatographic analysis were supplied by MERCK. The following were used in the procedure: sulfuric acid (min. 95%), SPE columns with Thermo Scientific HyperSep type C18 cartridges, rounded cellulose extraction thimbles from Whatman. Also, technical gases from Linde were used: 99.995% pure helium, and 99.994% pure nitrogen.

**Quality control**

During the analysis of persistent organic pollutants, vessels and containers which came in contact with samples were thoroughly washed and heated in 150°C for 12 hours (El-Mekkawi et al. 2009). The pesticides were recovered by adding standards of the analyzed substances to a given sample before their extraction. The applied analytical method made it possible to recover between 87.4% and 96.3% of the substance. The results were validated in an external laboratory which has ISO 17025 certificate. This comparison showed no statistical differences in the determination of the analyzed pesticides. In the analytical procedure, triple quantification of the blank sample was used. The limit of detection (1 pg $cm^{-3}$ and 4 pg $cm^{-3}$) and quantification (7 pg $cm^{-3}$ to 12 pg $cm^{-3}$) was calculated for all analyzed pesticides separately and recalculated to extract the volume which represents the content of 1 g of a lyophilized sample.

**Quantification**

Organochlorine compound concentrations were quantified using a gas chromatograph equipped with an electron capture detector $^{63}$Ni (GC-ECD, Varian 450-GC). Separation was carried out on a Varian capillary column of fused silica (50 m long, film thickness 0.25 μm, external diameter 0.53 mm, internal diameter 0.70 mm), with helium used as a carrier gas (constant flow speed 5 $cm^3$ $min^{-1}$). The detector's temperature was set to 300°C, using a temperature program presented by Vorkamp et al (2004), but with a modified injection temperature of 250°C as described by Falkowska et al. (2013). The injection mode – splitless. The lipid content in the tissue was determined by weight after solvent extraction as previously described by Reindl et al. (2013).

## RESULTS AND DISCUSSION

Organochlorine pesticides continue to be chemical components of the Baltic ecosystem even though 30 years have passed since their use was banned in agriculture. Their constant presence, however, is accompanied by a gradual decrease in their concentrations in suspensions, precipitates and marine organisms (HELCOM 2010). Several publications report about the ability of permanent organic pollutants to accumulate and expand in the marine trophic chain (Bignert et al. 1995; Roots, Talvari 1997; Strandberg et al. 1998b; Sapota 2006; Koistinen et al. 2008; Nfon et al. 2008; HELCOM 2010). While the literature abounds with data on hexachlorobenzene, lindane and DDT and its metabolites, there is little data on the content of other cyclodiene insecticides, particularly in the region of the Southern Baltic (Strandberg et al. 1998a, Falandysz et al. 1999b, Falkowska et al. – unpublished data). The amount of data is even more inadequate since the presence of some of the insecticides has been detected both in the air and in the atmospheric precipitation in the Tricity metropolitan area (Falandysz et al. 1999a, Grynkiewicz et al. 2001, Kosikowska et al. 2011).

The research presented herein proves the constant presence of organochlorine carbohydrates in the muscle of fish from the Gulf of Gdańsk and the Polish part of the Vistula Lagoon. Residues of fungicides, cyclodiene insecticides, DDT and its metabolites were found in the fish caught in the Vistula Lagoon in 2011 (Table 1). Among the fungicides, hexachlorobenzene (HCBz) was detected in the highest concentrations in the muscles of anadromous salmon and benthos-eating bream living in the brackish waters of the lagoon. The highest concentrations of cyclodienes were determined for the same fish. While some fungicides and insecticides occurred below the detection level

**Table 1**

Organochlorine pesticides in muscles and livers of fish caught in the Vistula Lagoon in autumn 2011

| Parameter | Bream muscles | Bream liver | Salmon muscles | Roach muscles | Sabre carp muscles |
|---|---|---|---|---|---|
| | n=1 (11) | n=1 (11) | n=1 (3) | n=1 (9) | n=1 (6) |
| Lipids (%) | 4.7 | 3.8 | 6.4 | 2.8 | 3.3 |
| Trichlorobenzene | - | - | 2.87 | - | - |
| Pentachlorobenzene | 4.01 | - | 3.19 | - | 5.91 |
| Hexachlorobenzene | 22.07 | 36.54 | 29.07 | 16.13 | 12.43 |
| γ-HCH (lindane) | 25.32 | - | 32.32 | - | 9.47 |
| α-endosulfan | - | 6.50 | - | - | 1.72 |
| dieldrin | 2.97 | 3.49 | 2.04 | - | - |
| endrin | 1.49 | 4.75 | - | - | - |
| methoxychlor | 14.41 | - | - | 4.35 | 8.49 |
| pp'-DDT | 24.82 | 57.81 | 33.67 | 26.03 | 25.32 |
| pp'-DDD | 5.71 | 11.01 | - | - | 9.59 |
| pp'-DDE | 235.31 | 393.07 | 297.78 | 207.54 | 271.38 |
| DDTs. | 265.84 | 461.89 | 331.45 | 233.57 | 306.29 |

'-' – below the limit of detection
n – the number of samples, in brackets, the number of fish in each sample

(pentachlorophenol, isodrin, aldrin, β-endosulfan and endosulfan sulfide), DDT and its metabolites were found in each of the examined fish from the Vistula Lagoon. The highest concentrations were obtained for isomer pp'-DDE, which determined the total value of this insecticide in fish. Residues of pesticides were also found in other fish species caught for consumption in the Gulf of Gdańsk (Table 2) and the highest HCBz concentrations were found in the muscles of the pelagic herring. Among the examined fish, flounder and cod are predators on the highest level of the benthic and benthic-pelagic trophic chains. Also high concentrations of HCBz, lindane and dieldrin were found in these fish. Herring, flounder and cod from the Gulf of Gdańsk had similar concentrations of DDT and its metabolites to fish from the Vistula Lagoon. Pentachlorophenol, isodrin, aldrin, β-endosulfan or endosulfan sulfide were not detected in the fish caught in any of the areas.

The previous research conducted by Strandberg et al. (1998a) on lindane in the whole herring, caught in 1991-1992 in the Gulf of Gdańsk, showed concentrations of 35 ng $g^{-1}$ lw. and in the case of HCBz − 41 ng $g^{-1}$ lw. Studies repeated by Reindl et al. (2013) after about 20 years have proved that lindane content in the whole herring caught in the Gulf of Gdańsk has dropped by about 35% (25.31 ng $g^{-1}$ lw.), but the concentration of HCBz has increased to an average level of 48.54 ng $g^{-1}$ lw. The constant presence of lindane, hexachlorobenzene, DDT and its metabolites in the muscles of edible fish caught in the Southern Baltic was confirmed by Schindler-Richert et al. (2008). However, lindane and HCBz concentrations in the muscles of Baltic herring caught in 2006 and flounder caught in 2003 in the Gulf of Gdańsk were lower than in the fish caught in 2011. The relatively high concentrations of γ-HCH isomer and HCBz indicate the existence of a source supplying the ecosystem with these pesticides. The lack of standards related to pesticide residues in fish makes it impossible to assess their safety for consumption.

In the muscles of bream, salmon and sabre carp (Table 1), as well as herring, flounder and cod (Table 2), the presence of pentachlorophenol was determined. Trichlorobenzene was found only in the muscles of salmon (Table 1) and herring (Table 2). The presence of HCBz depolymerization products in the muscle tissue indicates a gradual disintegration of this fungicide and proves the ability of HCBz metabolites to accumulate in the systems of fish.

The differences in the concentrations of DDT and its depolymerization products in herring indicates a regional diversity, typical of the Baltic, both at the end of the 20th century and in the first decade of the 21st century. In the muscles of herring from the Gulf of Riga, the total concentration of DDT amounted to 190.7 ng $g^{-1}$ lw., while in the Gulf of Finland, it varied within the range of 387.6 ng $g^{-1}$ lw. – 731.6 ng $g^{-1}$ lw. (Roots, Talvari 1997). The studies by Strandberg et al. (1998a) proved that the

**Table 2**

Organochlorine pesticides (± standard deviation) in muscles and livers of fish caught in the Gulf of Gdańsk in autumn 2011 (ng $g^{-1}$ lw.)

| Parameter | Herring muscles | Herring liver | Flounder muscles | Flounder liver | Cod muscles |
|---|---|---|---|---|---|
| | n=6 (3) | n=6 (3) | n=1 (9) | n=1 (9) | n=1 (6) |
| Lipids (%) | 7.16 (5.81-8.62)* | 3.94 (2.97-5.01)* | 5.1 | 4.3 | 2.3 |
| Trichlorobenzene | 4.89 (± 2.61)* | - | - | - | - |
| Pentachlorobenzene | 15.78 (± 7.66)* | - | 1.43 | - | 2.21 |
| Hexachlorobenzene | 36.45 (± 6.89)* | - | 8.15 | - | 11.72 |
| γ-HCH (lindane) | 19.27 (± 6.43)* | 16.50 (± 9.40)* | 9.17 | 17.54 | 23.18 |
| α-endosulfan | 22.19 (± 7.00) | 14.65 (± 7.20) | - | 16.08 | - |
| dieldrin | 5.32 (± 3.51) | 17.32 (± 4.76) | 7.98 | 15.09 | 11.23 |
| endrin | 2.38 (± 0.85) | 4.60 (± 2.49) | - | - | - |
| methoxychlor | 52.14 (± 14.77) | 58.82 (± 26.36) | - | 25.09 | - |
| pp'-DDT | 106.99 (± 55.91) | 109.55 (± 58.00) | 45.09 | 58.16 | 71.93 |
| pp'-DDD | 26.14 (± 11.78) | 56.92 (± 20.39) | - | 10.05 | 9.97 |
| pp'-DDE | 171.73 (± 78.01) | 273.41 (± 140.43) | 184.09 | 218.69 | 227.98 |
| DDTs. | 304.86 (± 140.60) | 439.88 (± 201.22) | 229.18 | 286.90 | 309.88 |

n – the number of samples, in brackets, the number of fish in each sample
'-' – below the limit of detection
* – Reindl et. al. 2013

concentrations of total DDT in the whole herring caught in 1991-1992 were at the levels of 159 ng $g^{-1}$ lw. in the Gulf of Bothnia, 1017 ng $g^{-1}$ lw. in the Bothnian Sea and 1257 ng $g^{-1}$ lw. in the Gulf of Gdańsk. The results of the study for herring caught in 2008, over 15 years later, in the littoral waters of the Southern Baltic showed a 2.5-fold decrease in the concentrations of total DDT to the level of 487 ng $g^{-1}$ lw. In the muscles of flounder caught in 2003 in the Polish part of the Baltic, the total DDT concentration was found to be 442 ng $g^{-1}$ lw. (Szlindler-Richter et al. 2008). The above results provide evidence for the spatial and temporal fluctuations in DDT concentrations with a decreasing trend in the concentration of this xenobiotic (Moilanen et al. 1982, Bignert et al. 1995, Olsson et al. 2003, Koistinen et al. 2008, Bignert et al. 2010, HELCOM 2010). The results described in the present paper (Tables 1 and 2) confirm the continual decrease in DDT content in the fish caught commercially.

DDT depolymerization in the environment takes place in two directions, and DDD and DDE isomers are the disintegration products of the original substance. The proportion of DDT isomers to DDE isomers is an indicator of the time in which a given organism was exposed to this insecticide. A proportion smaller than one testifies to the predominance of the DDE isomer in organisms and a relatively earlier exposure to DDT. The studies of muscles in the Baltic herring from the Gulf of Riga proved the DDT/DDE proportion to be at the level of 0.56, while in the herring from the Gulf of Finland, the proportion of these isomers was 1.1. This proves the predominance of DDT, which is an active ingredient of agrotechnical agents introduced to the waters of the Gulf of Finland, while the organisms in the Gulf of Riga are exposed to the product of this insecticide's environmental depolymerization – DDE (Roots, Talvari 1997). The results of research on the whole herring carried out by Strandberd et al. (1998a) indicated the proportion of DDT/DDE concentrations to be at the level of 0.32 in the Gulf of Bothnia, 0.26 in the Bothnian Sea and 0.62 in the Gulf of Gdańsk. The proportion of DDT/DDE concentrations determined by Szlindler-Richert et al. (2008) in the muscle of herring caught in the Southern Baltic in 2006 amounted to 0.31, while in flounder caught in 2003, the proportion was 0.18. The results presented herein are close to the results obtained by Stranberg et al. (1998a) for the Gulf of Gdańsk but higher than the results of Szlindler-Richert (2008), and prove the DDT/DDE proportion in the muscles of herring to be at 0.62, and in the muscles of flounder – at 0.24 (Table 2). It follows from the above that the seabed-feeding flounder is more exposed to the influence of DDT depolymerization products (i.e. of the DDE isomer), while the pelagic-feeding herring is exposed to an increased influence of the original product – DDT.

Additionally, the studies showed that the proportion volume of DDT/DDE concentrations determined for fish from the Gulf of Gdańsk (Table 2) is higher than the proportion found in fish caught in the Vistula Lagoon (Table 1). The differences discovered on the basis of these studies prove that the DDT isomer has the predominant influence on the fish in the Gulf of Gdańsk, whereas in the Vistula Lagoon − the depolymerization product. These differences may indicate different courses both for the kinetics of the depolymerization process (different temperatures and salinity levels in the two basins) and the mechanic and physical-chemical disintegration of organic polymers in the two basins of the Southern Baltic. Another significant difference may result from the resuspension process from the surface of precipitates during the seasonal mixing of waters in the shallow Vistula Lagoon. Owing to strong winds in spring and autumn, the lagoon is stirred up from the bottom. The surface of precipitates is agitated and the suspensions with pollutants are mobilized to water column. This makes the xenobiotics more available to fish.

Xenobiotic concentrations determined in the livers of fish (Tables 1 and 2) were higher than in the muscles. The organochlorine pesticide contents in the livers of fish from the Gulf of Gdańsk and the Vistula Lagoon testify to their accumulation, but also to their removal by means of liver metabolism. With the exception of lindane and α-endosulfan in herring, assessments of other compounds in each of the fish species showed a proportion higher than 1:1 of the xenobiotic content in the liver compared to its content in the muscles (Tables 1 and 2). This indicates dominance of detoxification over accumulation processes. Several studies have shown that the liver has the ability to accumulate large amounts of pollutants from the external environment and plays an important role in their storage, redistribution, detoxification and transformation (Evans et al. 1993; Wiener et al. 2003; Kwaśniak, Falkowska 2012). No fungicides were found in the liver. Parallel research into fungicides in the marine trophic chain also excluded their presence in the liver of Baltic herring (Reindl et al. 2013).

The presence of organochlorine pesticides in the muscles of fish proves the accumulative ability, while their presence in the ovaries and testes of Baltic herring (*Clupea harengus*) proves their subsequent removal from the system. The spawn of Baltic herring contained 5.8% of lipids and the presence of the following was determined: hexachlorobenzene (42.87 ng $g^{-1}$ lw.), lindane (32.13 ng $g^{-1}$ lw.), methoxychlor (19.91 ng $g^{-1}$ lw.) and the isomers pp'-DDT (7.11 ng $g^{-1}$ lw.) and pp'-DDE (87.08 ng $g^{-1}$ lw.). The formation process of reproductive cells is a creative mechanism aiming at the preservation of the species. It has been proved, however, that it is accompanied by a transfer of toxins. Consequently, the new generation is burdened with transferred pollutants from the first stage of development.

## SUMMARY

The research carried out on the xenobiotic content in edible sea fish caught in the Gulf of Gdańsk and in the Vistula Lagoon proves the constant presence of residues of organochlorine pesticides. Although a continuous downward trend should be observed in the xenobiotics which have been withdrawn from use (Bignert et al. 2010), the increasing content of other compounds, still in use, is observed in the Baltic fish (HELCOM 2010). Therefore, it is important to explore the way in which these compounds behave in the trophic chain and their reactions with new organic compounds, i.e. the derivatives of phenols or bromine introduced into the Baltic.

Our studies prove the occurrence of fungicides and lindane in the concentrations higher than so far reported for the fish of the Southern Baltic, and indicate a shorter exposure compared to open waters of the Baltic (Schindler-Richert et al. 2008). These results may suggest the existence of another source or sources supplying the coastal zone of the Gulf of Gdańsk with these pollutants. Transportation via the atmosphere may be one of them. Moreover, the presence of HCBz and DDT disintegration products in fish proves both their durability due to the presence of the original compounds and confirms the accumulative ability of the disintegration products.

Owing to the content of protein and numerous nutrients, such as unsaturated fatty acids, vitamins and micro- and macroelements, fish are commonly recognized as a valuable food source. Due to the lack of norms for the concentrations of organochlorine pesticide residues, it is not possible to assess the safety of fish consumption. Nonetheless, with alimentary exposure, the bioaccessibility of xenobiotics from food could be the key parameter for the assessment of fish toxicity to consumers.

## FINANCIAL SUPPORT

The present paper was prepared with the financial support of the Polish Ministry of Science and Higher Education within the framework of the research project No. N N304 161637.

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