Science of the Total Environment 408 (2010) 2474–2481

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Concentrations of organotin compounds in various fish species in the Finnish lake waters and Finnish coast of the Baltic Sea

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A R T I C L E   I N F O

Article history:
Received 27 October 2009
Received in revised form 15 February 2010
Accepted 16 February 2010
Available online 19 March 2010

Keywords:
Organotin compounds
Finland
Baltic Sea
Concentrations in fish
Perch
Tributyltin
Triphenyltin

A B S T R A C T

Organotin compounds (OTCs) leaching from the antifouling paints used in boats and ships have contaminated many water areas worldwide. The purpose of this study was to obtain a general view of the organotin contamination in fish in Finnish lake areas and Finnish coast of the Baltic Sea using perch as the main indicator species. Perch sampling covered areas presumed as less contaminated and areas suspected as more contaminated. Besides perch, 12 other species were sampled from sites presumed as less contaminated. OTCs measured were mono-, di- and tributyltin, mono-, di-, and triphenyltin and dioctyltin. The sum concentration of OTCs (ΣOTCs) in perch in the least contaminated areas of the Baltic Sea were around 20 ng/g fresh weight (fw) and less than 10 ng/g fw in lake areas. In heavily contaminated areas of the Baltic Sea 150–500 ng/g fw in perch were detected. In lake areas the maximum ΣOTCs in perch was only 30 ng/g fw. With regard to the other species in the Baltic Sea, salmon, sprat, flounder, whitefish, vendace and lamprey contained low concentrations (ΣOTCs mainly less than 20 ng/g fw), whereas in pike, pike-perch, burbot and bream concentrations were higher. ΣOTCs in lake fish were generally lower than in the Baltic Sea. In a distance gradient study, ΣOTCs in perch decreased quickly from nearly 200 ng/g fw at a contaminated harbor area to 35 ng/g fw during a distance of 5 km. Further decrease was slower and reached 15 ng/g fw at 100 km. In a size dependence study triphenyltin showed better correlation with the fish length than tributyltin for all species studied, i.e. for perch (0.16 vs 0.26), pike-perch (0.13 vs 0.24) and roach (0.46 vs 0.80). High correlation for roach may be partly explained by smaller number of samples collected and small length range.

1. Introduction

Organotin compounds (OTCs) are a large class of compounds with widely varying properties, and they have been used for many different purposes. Trisubstituted OTCs, tributyltin (TBT), and triphenyltin (TPhT) have a wide range of uses, mostly associated with their strong biocidal activity toward aquatic organisms such as bacteria, fungi, algae, molluscs, and crustaceans. From an environmental point of view, most attention has been given to the widespread TBT and TPhT pollution of waters, sediments, and aquatic biota resulting from their use in antifouling paints in boats and ships. TBT and TPhT are highly toxic to many aquatic species, and the most sensitive endocrine effect, imposex, occurs in some molluscs at TBT concentrations in water as low as 1 ng/l (Fromme et al., 2005; Hoch, 2001). In addition, very recent research has highlighted the importance of high accumulation potential and toxicity of TPhT at environmentally relevant concentrations to some fish species. First, the exposure of medaka (*Oryzias latipes*) to different levels of TPhT for 5 weeks markedly suppressed the spawning success and induced various forms of teratogenesis in the F1 generation. As a whole, this resulted in a significant decrease in the capacity to produce viable offspring (Zhang et al., 2008). Second, under controlled laboratory conditions the incidences of both ocular and skeletal/morphological deformations were directly proportional to the TPhT concentration in the eggs of both the Chinese sturgeon (*Acipenser sinensis*) and the Siberian sturgeon (*Acipenser baerii*). The rates of deformities in the controlled studies were consistent with the rates that were found at the similar concentrations in eggs collected from wild Chinese sturgeon from the Yangtze River. Thus, TPhT was deduced to be the causal agent to induce the malformation of larvae of Chinese sturgeon. Also, none of the organotins except TPhT were sufficiently potent to cause deformities at the concentrations that were detected in the eggs of wild Chinese sturgeon (Hu et al., 2009).

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doi:10.1016/j.scitotenv.2010.02.029

In both studies TPT levels were similar to those reported in wild fish around the world, indicating that TPT contamination in the real world may have a significant adverse effect on the health of fish population.

Due to their toxic effects, antifouling use of organic tin compounds in all vessels in EU has been banned in 2003. Later, the Antifouling System Convention under the International Maritime Organisation has also entered into force in 2008. In the same year, the European ports banned the entrance of all ships having organotin containing antifouling paints (European Union, 2003). In addition to antifouling use, TPhT has also been used as pesticide. The pesticide use of TPhT has been banned in Europe since 2002 due to safety of pesticide operators potentially exposed to it and its possible impacts on non-target organisms (European Union, 2002a; European Union, 2002b). A scientific panel of the European Food Safety Authority (EFSA) has assessed the health risks to consumers associated with exposure to OTCs in foodstuffs. The most critical toxicological endpoint for risk assessment was considered to be immunotoxicity. Due to immunotoxic similarities, a Tolerable Daily Intake (TDI) of 250 ng/kg body weight was established for the sum of TBT, dibutyltin (DBT), TPhT, and dioctyltin (DOT) (European Food Safety Authority, 2004). For humans, fish is the main source of trisubstituted OTCs (Rantakokko et al., 2006).

There are some reports regarding the OTC concentrations in various fish species in the Baltic Sea. In the liver of flounder (*Platichthys flesus*) caught from the Gulf of Gdansk (Polish coast) that contains many potential OTC sources, sum concentrations of monobutyltin (MBT), DBT, TBT, and TPhT up to 760 ng/g fresh weight (fw) as OT cation were measured. However, only 18 ng/g fw was observed in samples in the reference site outside the Gulf of Gdansk (Albalat et al., 2002). In the Danish sea areas the sum of MBT, DBT and TBT in the liver of various fish species collected in 1998 and 1999 ranged from 18 (cod, *Gadus morhua*) to 260 (flounder) ng/g fw. Concentrations of monophenyltin (MPhT), diphenyltin (DPhT) and TPhT were low in most of these samples (Strand and Jacobsen, 2005). The sum of TBT and TPhT in the muscle of eelpout (*Zoarces viviparus*) caught from a less contaminated areas of the German coast during the years 1994–1998 were around 20 ng/g fw (Rüdel et al., 2003). OTC concentrations in fish from a few European freshwater areas have also been reported. Sum of butyl- and phenyltins in muscle of bream (*Abramis brama*) from various German rivers and lakes collected between 1993 and 2003 were less than 100 ng/g fw for the majority of samples, but in river Elbe a maximum level of 750 ng/g fw was measured in 1993 (Rüdel et al., 2007). In perch (*Perca fluviatilis*) caught from a shallow lake with multiple potential OT-sources in the Netherlands in 1993 the sum of butyl- and phenyltins was from 200 to 330 ng cat/g fw (Stäb et al., 1996). Detailed information on the concentrations of OTCs in Finnish fish is quite limited. In a study carried out in the vicinity of twelve cities in Finland, the sum of OTCs (mostly TBT and TPhT) in pooled pike (*Esox lucius*) muscle samples was 1–33 ng/g fw in lake pike and 8–141 ng/g fw in coastal pike (Mannio et al., 2005).

The objective of this study was to obtain a general view of the current level of OTC contamination in fish caught from Finnish lake areas and the Finnish coast of the Baltic Sea.

2. Materials and methods

2.1. Fish species, representative sampling sites, collection and preparation of fish samples

Perch was chosen as an indicator of regional OTC contamination, since it is a common, relatively stationary fish species found throughout the Finnish waters. Furthermore, perch is the most common catch species in the Finnish recreational fishery and it is an important species for the coastal commercial fishery, too. Perch sampling sites covered both areas presumed as less contaminated and areas suspected as more contaminated. Also other fish species were sampled, but only from sites presumed as less contaminated. Additional fish species from the Baltic Sea areas were salmon (*Salmo salar*), herring (*Clupea harengus membras*), sprat (*Sprattus sprattus*), pike, pike-perch (*Sander lucioperca*), burbot (*Lota lota*), flounder, bream, whitefish (*Coregonus lavaretus*), roach (*Rutilus rutilus*), vendace (*Coregonus albula*) and lamprey (*Lampetra fluviatilis*). In addition to perch, lake areas were sampled for pike, pike-perch, burbot, bream, whitefish and vendace. Sampling took place between May 2005 and April 2007. All lake and Baltic Sea sampling sites for all fish species are shown in Fig. 1. Fish species and total number of composite fish samples from lake and Baltic Sea areas collected and subjected for chemical analysis are shown in Table 1. Sampling sites were classified into three different categories. First sampling sites were those presumed as less contaminated. These were important open sea fishing areas and two large lake water bodies with no known nearby sources of contamination. Perch was sampled from all of these sites. Other species were sampled from both lake sites and from selected Baltic Sea sites. These sampling sites (Fig. 1, circles C1–C8 and triangles T1, and T7) aimed at providing a general view of OTC concentrations in different fish species in different areas presumed as less contaminated. The second type of sampling sites, from where only perch was sampled, were those suspected as more contaminated. These were harbors, dock yards, shipping routes, and areas close to pulp and paper or other industry. These sampling sites (Fig. 1, squares S1–S10, triangles T2–T6, and T8–T14) aimed at providing a broad view of OTC concentrations in the most relevant Finnish sites where OTC contamination could be suspected using just one indicator species to eliminate the interspecies difference in the OTC uptake. Third category of sampling sites was those for a distance gradient and a size dependence study. In the distance gradient study (Fig. 1, square S6 and pentagons P1–P5) change in OTC concentrations in perch was studied when departing from contaminated Turku–Naantali harbor and dock yard area towards the open sea covering a distance of about 100 km through Turku Archipelago. In the size dependence study (Fig. 1, pentagon P6) impact of fish size on OTC concentration was explored in perch, pike-perch and roach from a popular recreational fishing area, Vanhakaupunki Bay, in Helsinki. Table 2 summarises types of sampling sites, symbols used and names of sampling sites shown in Fig. 1 with the exception of point P6 fully described in the text above. For each type of sampling site and study the number of individual fish mixed to composite samples, number of composite samples from each site, length range of fish from each site and measured OTC concentrations are shown in online appendixes Tables S1–S4.

For all fish species 2–4 length groups were collected, except for whitefish, vendace and lamprey, for which only one size group was collected. Fish samples were not allowed to come in contact with metals, plastics and painted surfaces to avoid contamination. Weight, length and sex were recorded from intact fish. Due to poor catch, the planned number of fish was not caught from all sites. Detailed treatment of the dependence of length, weight and age on the OTC concentrations in single fish and in composite samples is the topic of another publication.

To analyse OTC concentrations in single fish and composite fish samples, edible parts of the muscle tissue was taken from each fish, fresh weight was recorded and the muscle was homogenized. Individual fish were grouped into different composite samples according to their length. From each individual fish, the weight of the muscle tissue mixed into the composite sample was equal to the weight of the muscle homogenate of the smallest fish in the composite.

2.2. Chemical analysis of fish samples and quality control

The chemical analysis was carried out in the Chemical Exposure Unit of the National Institute for Health and Welfare, which is an accredited testing laboratory (Centre for Metrology and Accreditation code T077, EN ISO/IEC 17025). The compounds analysed were MBT, DBT, TBT, MPhT, DPhT, TPhT, and DOT. Individual, pure model OT compounds were bought either from DrEhrenstorfer or from Acros. Perdeuterated