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Persistent organic pollutants in selected fishes of the Gulf of Finland

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ABSTRACT

Fish samples of Baltic herring, sprat, flounder, perch, salmon, and river lamprey were collected from the Gulf of Finland in 2013 and 2014 with the aim to get an overview of the occurrence of pollutants in fish caught in Estonian waters. The content of non-dioxin-like polychlorinated biphenyls (ndl PCBs), polybrominated diphenyl ethers (PBDEs), organic tin (OT) and perfluorocompounds (PFAS) are examined and discussed in the study. The results revealed that potentially higher content of organo-tin compounds, perfluorocompounds and polybrominated diphenyl ethers in Baltic herring, salmon and river lamprey may cause concern regarding human exposure.

It is important to link pollutant content to lipid content of fish taking into account their seasonal variation in different age classes.

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1. Introduction

The Baltic Sea is a complex ecosystem with a multitude of physical, chemical and biological interactions functioning on various temporal and spatial scales. The environmental state of the Baltic Sea is influenced by both natural and anthropogenic factors. The key environmental stressors are (1) eutrophication, (2) over-fishing, (3) risk of chemical and/or oil spills, (4) marine litter, (5) invasive species and (6) hazardous substances. These environmental problems together with climate changes downscale the Baltic Sea's ability to provide ecosystem goods and services. The changes in the ecosystem state can have impacts also to human welfare.

Hazardous substances, both natural and artificial compounds, cause adverse effects on the ecosystem. Examples are persistent organic pollutants (POPs) – PCB, DDT, dioxins, etc., which can be toxic even in very low concentrations, and also trace metals – mercury, lead, cadmium, etc., which are toxic in much higher concentrations generally. Pollution with the hazardous substances constitutes a serious threat to the Baltic Sea environment and has already led to detrimental effects

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on biodiversity harming flora's and fauna's immune- and hormone systems impairing their general health and reproduction status. While some of hazardous substances bio-accumulating properties they magnify through the food chain to higher species at higher trophic levels posing a threat also for humans who consume fish caught in the Baltic Sea. The long residence time of hazardous substances, in combination with the introduction of new compounds, poses a grave threat for the state of the future Baltic Sea and health of future generations. (Bignert et al., 1998; HELCOM, 2010a, 2010b, 2010c).

However, regardless to the actuality of the issue, the research of hazardous substances in the Baltic Sea (incl. the Gulf of Finland) environment has a fairly short history. Presently one of the four segments of the ecosystem health targeted by the HELCOM BSAP (Baltic Sea Action Plan) is monitoring of hazardous substances, with an ambitious zeroemission target for all manmade hazardous substances in the whole Baltic Sea catchment by 2021 (HELCOM, 2010c).

The objectives of current study were:

1. to get a short overview of the content of selected persistent organic pollutants: non-dioxin-like polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organotin (OT) and perfluorinated compounds (PFC), in five most consumable fish species: Baltic herring, sprat, flounder, perch and highly profitable species salmon and river lamprey, of the Gulf of Finland, Baltic Sea.

2. to link the pollutant content to lipid content of fish and follow their seasonal variation in different age classes.

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3. to collect information as the basis for potential negotiation with EU about some specific clauses for the maximum allowable concentration values.

2. Material and methods

2.1. Study area

The Gulf of Finland (Fig. 1) is located in the north-eastern part of the Baltic Sea and is the easternmost arm of the Baltic Sea. About 5% of the water mass in the Baltic Sea is located in the Gulf of Finland. The gulf is a continuation of the Baltic Proper without having any separating sill and can be characterised as a transition zone between brackish coastal sea and open sea conditions. The hydrological conditions are variable depending on the distance from the Baltic Proper. The small bays of the southern coast have good connection to the open Gulf of Finland and are strongly influenced by the main Baltic Sea current, upwelling and river inflow (Soomere et al., 2009). The eastern part is shallower and more brackish than western part of the gulf.

Besides to the natural changes in the environmental conditions the Gulf of Finland suffers of major human pressures: high input of nutrients, organic matter and hazardous substances, as well as heavy maritime transport. The human impact is more evident in the coastal regions and in the smaller semi-enclosed bays where clearly pronounced changes in water quality and biodiversity can be observed. Therefore, the Gulf of Finland has been reported as one of the most polluted areas of the Baltic Sea (HELCOM, 2015).

2.2. Fish sampling and laboratory analyses

The fish samples were collected in six sampling sites of the Gulf of Finland in 2013–14 (Fig. 1). The biological material used as a basis of present study was taken randomly. Baltic herring and sprat were sampled from Estonian commercial pelagic trawl fishery in western- and eastern part in the Gulf of Finland in October (herring) and April–May (sprat) 2013 and 2014. Perch, founder and salmon samples were taken from Estonian commercial coastal fishery in the western part of the Gulf of Finland in May 2013 and 2014. The biological material of

river lamprey was collected from commercial catch in the Kunda River in February 2014. The sampling sites for studied fish species are presented in Fig. 1.

The total length and weight of sampled fish was measured. Additionally age, sex and maturity stage using six-grade scale (ICES, 2010) was assessed. Counting of the growth zones on otoliths was used to age herring and sprat. The opercular bones and scales were used for perch and salmon, respectively. Since the river lamprey lack any kind of age registering structures we used the mean age of spawners (Saat et al., 2003).

Sampling process, biological analyses and compiling of biological material for chemical analyses followed requirements of Manual KJ I/ 16 (Biological tissue sampling from fish and molluscs for chemical analysis). The method (reg. No L179) is accredited by Estonian Accreditation Centre against the requirements of standards EVS-EN ISO/ITC 17025: 2006.

2.3. Chemical analyses

2.3.1. Polychlorinated biphenyls (PCB) and polybrominated diphenyl ethers (PBDE)

After pooling and homogenization the samples were freeze-dried and fat was extracted with ethanol-toluene (15%/85% v/v) in Accelerated Solvent Extractor (Dionex ASE 300). After that solvent was exchanged to hexane and the fat content was determined gravimetrically. Further the samples were defatted on an acidic multilayer silica column and purified and fractionated on alumina and carbon columns. PCBs and PBDEs were analysed with GC/HRMS (Autospec Ultima) using selected ion monitoring mode with a 10,000 resolution. PCBs and PBDEs were separated on a DB5 MS column (60 m \times 0.25 $mm \times 0.25 \mu m$; for BDE209 the column length was 5 m). Status of the used instruments was assessed on a daily basis and the instruments were calibrated and serviced regularly. ¹³C-labelled PCB congeners (PCB 28, 52, 101, 138, 153, 180), were used as internal standards for PCBs. ¹³C-labelled PBDE standards (BDE 28, 47, 77, 99, 100, 153, 154, 183 ja 209) were used for quantification of PBDEs. The recoveries of the individual internal standards of PCB and PBDE congeners were determined by adding the recovery standards just before mass spectral



Fig. 1. Study area and sampling sites.

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