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Persistent organic pollutants in Baltic herring (*Clupea harengus*)—an aspect of gender

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Abstract Persistent organic pollutants (POPs) are monitored regularly in water, sediment, and biota in the Baltic Sea. Lipophilic substances are measured in remarkable concentrations especially in the fatty parts of fish, such as herring (*Clupea harengus*). However, less lipophilic POPs, e.g. perfluorinated compounds (PFCs), can also be detected. For the first time to our knowledge, this study provides a broad range of contaminant concentrations simultaneously measured in filet, liver, and gonads of both sexes of Baltic herring. We analysed organochlorines, polybrominated diphenyl ethers (PBDEs), and PFCs in mature autumn-spawning individuals and found distinct organ pollutant pattern for all POPs in both sexes. POP concentrations found in the gonads of both sexes indicate that not only females but also males tend to reduce contaminants via reproduction. However, sex-dependent differences could be identified for hexachlorobenzene, PBDEs, and were most remarkable for PFCs. This transfer of contaminants to the gonads in both male and female herring is being underestimated, as it may directly affect the general reproduction success as well as the healthy development of the next generation. Hence, the accumulation of contaminants in the gonads should be considered one possible threat to a healthy wildlife as its achievement is stated by the Baltic Sea Action Plan. Inclusion of a periodic monitoring of POP concentrations in gonads of fish may be an important bioeffect measure to assess the environmental status of biota in the Baltic Sea.

Keywords Baltic Sea · Perfluorinated compounds · Organochlorines · Polybrominated diphenyl ethers · Tissue distribution

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Introduction

The Baltic Sea environment has long been ranked among the most polluted marine areas worldwide (Koistinen et al. 2008; HELCOM 2010). The concentrations of persistent organic pollutants (POPs) are annually observed in an extensive Baltic Sea monitoring program (Pikkarainen and Parmanne 2006; Karl and Ruoff 2007; Szlinder-Richert et al. 2008; Karl et al. 2010; Roots et al. 2010; Reindl et al. 2013; Airaksinen et al. 2014). For the environmental assessment, POP concentrations are compared to existing threshold values in water, sediment, and biota. One of the applied threshold values, the 'Environmental Assessment Criteria' (EAC), is defined as the 'contaminant concentration in the environment below which no chronic effects are expected to occur in marine species'

(OSPAR 2009). A reproduction impairment, leading to a reduced spawning success, or a general fitness reduction of the following generation, could be among the possible consequences of a POP accumulation (Rolland 2000; He et al. 2011; Papoulias et al. 2014). Such a significant decline in body condition was reported for autumn-spawning Baltic herring (*Clupea harengus*) during the last decade (HELCOM 2007a), even though the decline depends on several factors, such as food availability, hydrothermal conditions, and selective fishing (Casini et al. 2011). High POP concentrations may also negatively influence the survival of a population especially if the population is already under threat.

The Baltic herring has become one of the keystone species in Baltic Sea monitoring because of its broad geographical distribution, its high abundance, and its high body fat content (Bignert et al. 1998; Kiviranta et al. 2003; Parmanne et al. 2006; Szlinder-Richert et al. 2008; Koistinen et al. 2008; Szlinder-Richert et al. 2009; Bignert et al. 2010; HELCOM 2010; Airaksinen et al. 2014). Generally, the body burden of bioaccumulating POPs in herring varies between the regions of the Baltic Sea. The POP concentration in open sea areas can be lower compared to coastal zones (Galassi et al. 2008) because most sources for contaminants are located nearshore. Nonetheless, the degree of pollution is still remarkable in offshore regions, such as the Arkona Basin. Monitoring of this sea basin was established in the 1990s. Since then, chlorinated POPs such as polychlorinated biphenyls (PCB) are annually recorded in the filets of herring to assess the pollution status of the Arkona Basin (HELCOM 2010). However, information on the concentrations of brominated and fluorinated compounds in herring from this region are lacking in the literature so far but are demanded for assessing the current status of this region (HELCOM 2010).

In many studies, only one tissue type is investigated for its pollutant content (Strandberg et al. 1998b; Pikkarainen and Parmanne 2006; Parmanne et al. 2006; Karl and Ruoff 2007; Szlinder-Richert et al. 2008; Szlinder-Richert et al. 2009; Karl et al. 2010). Herring accumulates high lipophilic POP concentrations in liver and filet due to the relatively high body fat content. The filet of herring has been found most appropriate for monitoring lipophilic POPs, such as PCBs and polybrominated diphenyl ethers (PBDE), and was therefore recommended as target tissue by HELCOM (HELCOM 2015). However, POPs distribute throughout the whole body and accumulate in various tissues according to organ-specific characteristics (e.g. fat content) and to the physicochemical characteristics of the POPs (e.g. octanol-water partition coefficient) themselves (Fent 2013). Knowledge on the inter-organ distribution of POPs in herring is scarce (Hansen et al. 1985; Reindl et al. 2013) and needs further attention to investigate possible effects of high POP concentrations on reproduction for evaluating POP-mediated effects on the next generation since contaminants can be transferred from adults to the offspring (e.g. Rolland 2000; Dabrowska et al. 2009; Peng et al. 2010; Sühring et al. 2015).

One of the ecological objectives of the Baltic Sea Action Plan (BSAP) considers the conservation of 'healthy wildlife' to 'restore the good environmental status of the Baltic marine environment by 2021' (HELCOM 2007b). Reproductive success is not considered as bioeffect in the BSAP so far, even though it is one important trait of healthy wildlife. POPs have the potential to impair reproduction leading to reduced numbers and/or health of the next generation (He et al. 2011; Papoulias et al. 2014). Therefore, their contents in fish gonads could be used as putative bioeffect measure for the reproductive success of a species to assess the healthiness of marine wildlife. Furthermore, sex-dependent accumulations were reported from Baltic cod and North Sea dab (Kammann et al. 1993; Dabrowska et al. 2009) which indicates investigating gonads of both sexes may be necessary.

In the present study, we provide new data for the current assessment in the Arkona Basin by measuring a broad range of POPs in Baltic herring and compare our results to existing threshold values. We bridge a gap of knowledge by presenting measurements of PBDEs and perfluorinated chemicals (PFCs) in herring from Arkona Basin for the first time. Additionally, we elucidate organ pollutant patterns and sex-specific differences to investigate the potential impairment of the reproductive processes by POPs. We discuss our results in the light of the ecological objective "healthy wildlife" as it is demanded in the BSAP.

Material and methods

Sampling

Autumn spawners (gonadal maturity stage IV–V) of Baltic herring (n = 30) were collected from Arkona Basin (54°34.00'N - 55°00.00'N, 13°55.00'E -

14°20.00’E) in an offshore region of the Baltic Sea in August 2012. Individuals were examined for sex and sexual maturity directly on board (Bucholtz et al. 2008). In total, 20 females and 10 males were measured for weight and length prior to the dissection of the liver, gonads, and filets for contaminant analysis and otoliths collection for age determination (Peltonen 2002). In the present study, filet refers to a piece of muscle tissue without skin and subcutaneous fat. Condition factor (cf; [(100 × total weight)/(total length^3)]), gonadosomatic index (GSI; [(100 × gonad wet weight)/(body weight)]), and hepatosomatic index (HSI; [(100 × liver wet weight)/(body weight)]) of each individual were calculated.

Chemical analysis

Prior to preparation and analysis, 30 fishes have been divided into two groups comprising 10 females and 5 males, respectively. One group was used for analysing organochlorines and PBDEs and the second group for perfluorinated compounds.

Storage and preparation of 15 samples were performed according to procedures as described in the technical annexes of the OSPAR JAMP guideline for contaminants in biota (OSPAR 2012; HELCOM 2015) and in ICES publications (Webster et al. 2009; Ahrens et al. 2010; Webster et al. 2013). All solvents used were pesticide grade or better. The following procedures were applied: for analysis of organochlorine compounds and brominated diphenyl ethers (PBDEs): drying in a microwave, manual homogenisation, extraction with toluene by accelerated solvent extraction (DIONEX AS 200), lipid removal by gel permeation chromatography (cyclohexane/ethyl acetate 1:1; Biobeds SX3); clean-up by fractionation on silica gel with hexane and hexane/toluene. Determination of organochlorine compounds was performed by GC-ECD (HP 6890 with micro-ECD) on J&W DB5 and J&W DB1701 (60 m, 0.25 mm i.d., 0.25-μm film thickness); PBDEs were measured by GC-MS (J&W DB-5 ms [30 m, 0.25 mm i.d., 0.25-μm film thickness] on Agilent 6890N GC with 5973 MSD detector) in NCI single ion mode.

For PFCs, sample preparation and lipid reduction were performed by extracting the chopped tissue with acetonitrile and separation of fat after deep freezing, as described by Theobald et al. (Theobald et al. 2007).

PFCs were separated and detected by HPLC-MS-MS tandem mass spectrometry (Dionex/Thermo Scientific Ultimate 3000 and AB Sciex 5500QTrap) with Phenomenex Synergi Polar-RP column (50 mm × 2 mm, particle size 4 μm) and Phenomenex Kinetex C18 column (100 × 2.1 mm, particle size 2.6 μm) with water and methanol as mobile phases.

Quality assurance

The analytical laboratories are working according to DIN/EN ISO/IEC 17025 and are participating regularly in an international laboratory performance testing scheme (QUASIMEME) for all methods applied in the present study. Appropriate certified reference materials have been investigated for organochlorines and PBDEs. The detection limit of GC-MS was between 0.0018 and 0.125 ng/g wet weight (ww), for GC-ECD ranged from 0.02 to 0.12 ng/g ww. For HPLC-MS-MS, recovery rates and internal standards were used for quality assurance. Its detection limit ranged between 0.02 and 0.09 ng/g ww.

Expression of results

All results are expressed on a ww basis to maintain the comparability of the broad range of POPs we measured in different tissues. Organochlorines and PBDEs should be based on both, ww and lipid weight basis (lw); PFCs should be expressed on ww as PFCs bind to proteins. Individual congeners were combined in different sums for PCBs as listed in Table 1.

Pollutant transfer rates

Concentration ratios between gonads and filet (GFR) and between gonads and liver (GLR) can be used as indicator for a putative redistribution of POPs within an organism during maturation and as an indicator of a putative POP reduction in adults when eggs and/or sperm are released (Serrano et al. 2008; Peng et al. 2010; Sühring et al. 2015). However, none of the ratios do provide absolute evidence for the reduction rate or redistribution rate of POPs from or within an organism. The transfer rates were calculated using the following equations:

$$GFR = c_{\text{gonad}}/c_{\text{filet}}$$

$$GLR = c_{\text{gonad}}/c_{\text{liver}}$$

where c is the concentration (μg/kg ww) in the gonads, liver, or filet, respectively.

Statistics

The importance of gender (male/female) or tissue (filet/liver/gonads) was considered by determining linear mixed effect models (linear mixed effect (lme)-function within the linear and nonlinear mixed effect model (nlme)-package) for each contaminant with the statistic software R (R Core Team 2014). The most complex model form included interactions between tissue and sex with the maximization of log-likelihood as chosen method (in R terminology):

$$\textit{pollutant content} \sim \mathrm{sex} \bullet \mathrm{tissue} \quad \textit{random} = \sim 1 \,\Big|\, \textit{individual}$$

All different models were compared by ANOVA (anova-function) to investigate the impact of the two factors tissue and sex. A student t test was conducted to identify gender-specific differences of GLR and GFR. For comparing sex-specific differences between HSI and GSI a Wilcox rank test was conducted.

Table 1 Congeners combined as sums: polychlorinated biphenyls (e.g. ΣPCBs), dichlorodiphenyltrichloroethanes (ΣDDTs), hexachlorocyclohexanes (ΣHCHs), polybrominated diphenyl ethers (ΣPBDEs/ ΣBDEs), and perfluorinated compounds (ΣPFCs)

Sums	Congeners/substances
ΣPCBs	CB28, 31, 52, 101, 105, 118, 129, 138, 149, 153, 156, 170, 180, and 187
$\Sigma PCBs_6$	CB28, 52, 101, 138, 153, and 180
$\Sigma PCBs_6$ + CB118	CB28, 52, 101, 118, 138, 153, and 180
ΣDDT	*o*′,*p*′-DDT, *p*′,*p*′-DDT, *p*′,*p*′-DDD, and *p*′,*p*′-DDE
ΣHCHs	α, β, γ, and δ–HCH
ΣPBDEs	BDE28, 47, 66, 99, 100, 85, 154, 153, and 183
$\Sigma BDEs_6$	BDE28, 47, 99, 100, 153, and 154
ΣPFCs	Perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDOA), perfluorohexane sulfonate (PFHxS), perfluorononanoic acid (PFNA), perfluorooctanoic acid (PFOA), linear and branched perfluoro-1-decanesulfonate (PFOS), perfluorooctane sulfonamide (PFOSA), perfluorotetradecanoic acid (PFTeDA), perfluorotridecanoic acid (PFTrDA), and perfluoroundecanoic acid (PFUDA)

Results

Constitutional fish parameters

Investigated fishes were in similar biological conditions considering age, length, weight, and condition factor (cf) (Table 2). However, the gonad weight was higher in males than in females resulting in a higher gonadosomatic index (GSI) in males. The livers of male fish were smaller resulting in lower hepatosomatic index (HSI) in males compared to females. The differences of GSI and HSI between males and females were found statistically significant (Table 2).

Contaminants in herring tissues

The highest mean concentration was found for ΣDDTs, closely followed the ΣPCBs in filets of both sexes. Three different sums of PCBs were given (Table 3) representing the sum of all 14 measured PCBs (ΣPCBs), the six indicator PCBs ($\Sigma PCBs_6$), and the sum of $\Sigma PCBs_6$ and CB118. $\Sigma PCBs_6$ is generally monitored in the Baltic Sea because it is reliably found in fish. CB118 is the most dominant dioxin-like PCB and therefore often combined with $\Sigma PCBs_6$.

The mean concentration of hexachlorobenzene (HCB) in herring filet was lower by one order of magnitude than ΣPCBs. The lowest mean concentrations in

Table 2 Measured and calculated constitutional parameters of Baltic herring (*Clupea harengus*) from the Arkona Basin

Parameters	All fish (n = 30)	Males (n = 10)	Females (n = 20)
Age (year)	3.93 ± 0.98	3.89 ± 0.93	3.93 ± 1.03
Length (mm)	235.86 ± 10.36	231 ± 12.87	238.42 ± 8
Weight (g)	102.1 ± 12.53	97.69 ± 13.37	104.42 ± 11.77
cf (g/cm^3)	0.78 ± 0.05	0.79 ± 0.04	0.77 ± 0.05
GSI	20.45 ± 4.13	23.76 ± 1.36[a]	18.71 ± 4.04[a]
HSI	1.52 ± 0.81	0.68) ± 0.62[b]	1.96 ± 0.48[b]

All values are given as means with standard deviation (sd)

Cf condition factor, *GSI* gonadosomatic index, *HSI* hepatosomatic index

[a] Statistically significant difference between males and females (Wilcox rank test: $w = 77$, $p < 0.01$)

[b] Statistically significant difference between males and females (Wilcox rank test: $w = 215$, $p < 0.01$)

filets have been found for ΣPBDEs, ΣPFCs, and ΣHCHs, respectively (Table 3).

Organ-related distribution of contaminants

The concentrations of chlorinated contaminants were highest in the filets, mediate in liver, and lowest in gonads (Table 3; Fig. 1). In contrast, ΣPBDE concentration was highest in the liver, mediate in filets, and lowest in gonads. ΣPFC concentration was highest in the liver, mediate in gonads, and lowest in filets of Baltic Herring.

Sex-dependent POP distribution in Baltic herring

The mean lipid contents of both sexes were almost similar in the filets of Baltic herring but differed in the liver and gonads. Male liver and gonads exhibited twice as much fat as female liver and gonads (Table 3). The distribution of ΣPCBs, ΣDDTs, and ΣHCHs in the filets was similar in both sexes, but concentrations of HCB, ΣPBDE, and ΣPFC differed in the liver and gonads (Fig. 1; Table 3). Using ANOVA, we found statistically significant influences of the tissue type for all tested contaminants ($p < 0.0001$). An additional statistically significant effect of sex was determined for HCB ($p < 0.001$) and ΣPFCs ($p < 0.001$). Furthermore, mutual interaction effects between sex and tissue were found statistically significant for ΣPFCs ($p < 0.001$), HCB ($p < 0.001$), and ΣPBDEs ($p < 0.001$).

Discussion

Contaminants in herring filets of the Arkona Basin

POP concentrations in filets of herring from the Arkona Basin were generally in accordance with contents in herring from many different locations in the Baltic Sea (Strandberg et al. 1998a; Kiviranta et al. 2003; Isosaari et al. 2006; Parmanne et al. 2006; Karl and Ruoff 2007; Szlinder-Richert et al. 2008; Roots et al. 2009; Szlinder-Richert et al. 2009; Karl et al. 2010; Airaksinen et al. 2014). However, this POP concentration was higher than concentrations measured in filets of herring from Arkona Basin before: HELCOM reported concentrations of 1 μg CB153/kg ww and 5 μg DDE/kg ww (HELCOM 2010). In comparison, we found approximately four times higher median concentrations for CB153 (4.2 μg/kg ww) and three times higher median concentration for DDE (15.2 μg/kg ww). Fishes of the present study were larger and presumably older than fish used by HELCOM (2010). In general, the age of a specimen is positively correlated to the content of organochlorins (Larsson et al. 1993; Kiviranta et al. 2003). Sampling time in year was in accordance with the samples reported by HELCOM (2010).

Concentrations of PBDEs and PFCs from herring filets of the Arkona Basin were lacking in literature thus far. However, ΣPBDE content in herring filets (Table 3) is comparable with concentrations reported from specimens of different locations of the Baltic Sea (Isosaari et al. 2006; Roots et al. 2009; Airaksinen et al. 2014). The median concentration of ΣPFCs reported in the filets and subcutaneous fat of Baltic herring from the Finnish coast line was 1.7 μg/kg ww (Koponen et al. 2014). In contrast, lower median concentrations (0.72 μg/kg ww) were recorded in the filets in the present study which is presumably a consequence of the general lower POP concentration level in offshore regions (Galassi et al. 2008).

However, higher PFC concentrations were determined in the livers of herring from various regions of the Baltic Sea (Berger et al. 2009; Ullah et al. 2014). PFCs are less lipophilic than organochlorines or PBDEs and have a higher tendency to bind to blood or liver proteins rather than to accumulate in fatty filets. Furthermore, an enterohepatic cycle favor the presence of PFCs in liver tissue (Fent 2013). From various regions of the Baltic Sea, perfluorooctane sulfonate (PFOS) concentrations in the liver were reported to range around 10 μg/kg ww (HELCOM 2010). This concentration is generally in accordance with our findings for PFOS for pooled data of both sexes (data not shown).

Comparisons with threshold values

Currently used threshold values in the Baltic Sea were either derived from existing EACs for roundfish determined by OSPAR (OSPAR 1997; 2009; HELCOM 2010) or adopted from the 'Environmental Quality Standards' (EQS) for whole fish from the 'Water framework directive' (WFD) (EU 2013). While the derivation concepts differ between EAC and EQS, their purpose is similar. Both values are considered as transition points; concentrations below these points are not of significant risk to the environment while concentrations above are

Table 3 Contaminant concentrations (μg/kg ww) and lipid contents (%) of Baltic herring (*Clupea harengus*) from the Arkona Basin.

Parameters	EAC/EQS	Filets			Liver			Gonads		
	μg/kg ww	Total	Males	Females	Total	Males	Females	Total	Males	Females
Lipid content [%]	–	7.24 ± 3.51	7.03 ± 3.74	7.34 ± 3.59	3.15 ± 2.05	5 ± 2.74	2.26 ± 0.72	2.3 ± 1.10	3.6 ± 0.28	1.7 ± 0.79
ΣPCBs[a]	–	21.29 ± 8.42	25.21 ± 10.21	19.33 ± 7.15	12.52 ± 3.34	11.07 ± 2.97	13.25 ± 3.42	3.07 ± 1.08	2.84 ± 0.60	3.3 ± 1.31
ΣPCBs$_6$[b]	–	13.75 ± 5.64	16.32 ± 6.77	12.46 ± 4.66	7.63 ± 2.14	6.56 ± 1.79	8.17 ± 2.18	2.00 ± 0.83	1.81 ± 0.39	2.10 ± 0.99
ΣPCBs$_6$[b]+ CB118	1–10[h]	15.81 ± 6.28	18.73 ± 7.61	14.35 ± 5.33	8.61 ± 2.45	7.39 ± 2.07	9.21 ± 2.49	2.29 ± 0.94	2.07 ± 0.45	2.39 ± 1.11
CB118	0.65[i]	2.06 ± 0.75	2.40 ± 0.85	1.89 ± 0.68	0.97 ± 0.32	0.82 ± 0.28	1.04 ± 0.32	0.28 ± 0.10	0.26 ± 0.05	0,29 ± 0.12
ΣDDTs[c]	–	24.12 ± 8.91	26.62 ± 10	22.87 ± 8.59	10.75 ± 3.63	8.9 ± 3.25	11.67 ± 3.60	2.92 ± 1.08	2.58 ± 0.45	3.09 ± 1.27
p′,p′-DDE	5–50[h]	16.65 ± 5.98	18.61 ± 6.52	15.57 ± 5.80	7,29 ± 2.58	6.03 ± 2.05	7.92 ± 2.67	2.17 ± 0.86	1.88 ± 0.36	2.31 ± 1.01
HCB	16.7[i]	2.37 ± 1.16	2.54 ± 1.39	2.29 ± 1.11	1.6 ± 0.57	1.14 ± 0.43	1.83 ± 0.50	0.79 ± 0.51	0.36 ± 0.03	0.99 ± 0.51
ΣHCHs[d]	33[b]	0.79 ± 0.37	0.85 ± 0.45	0.76 ± 0.34	0.44 ± 0.16	0.34 ± 0.11	0.5 ± 0.16	0.1 ± 0.07	0.1 ± 0.01	0.1 ± 0.08
γHCH	1.1[j]	0.08 ± 0.04	0.09 ± 0.05	0.08 ± 0.03	0.10 ± 0.03	0.07 ± 0.02	0.12 ± 0.03	0.03 ± 0.04	0.02 ± 0.00	0.01 ± 0.05
ΣPBDEs[e]	–	0.81 ± 0.33	0.95 ± 0.31	0.79 ± 0.34	1.56 ± 1.17	2.84 ± 1.22	1.13 ± 0.83	0.14 ± 0.05	0.15 ± 0.03	0.14 ± 0.05
ΣBDE$_6$[f]	0.0085[k]	0.78 ± 0.32	0.92 ± 0.3	0.76 ± 0.33	1.54 ± 1.15	2.79 ± 1.19	1.11 ± 0.82	0.13 ± 0.04	0.14 ± 0.03	0.13 ± 0.05
ΣPFCs[g]	–	0.84 ± 0.43	1.15 ± 0.47	0.67 ± 0.33	21.96 ± 16.33	42.14 ± 8.02	10.75 ± 2.35	4.99 ± 1.96	1.96 ± 1.75	3.85 ± 1.37
PFOS	9.1[k]	0.52 ± 0.27	0.74 ± 0.29	0.39 ± 0.17	13.70 ± 10.75	26.96 ± 5.43	6.34 ± 1.45	3.01 ± 1.17	4.13 ± 1.21	2.39 ± 0.55

Contents were measured in the filets, livers, and gonads of 10 females and five males, respectively. Mean values are given with standard deviation (sd). Environmental assessment criteria (EAC) from OSPAR and environmental quality status (EQS) (μg/kg ww) adapted from the Water framework directive (WFD) are presented

[a] ΣPCBs: CB28, 31, 52, 101, 105, 118, 129, 138, 149, 153, 156, 170, 180, 187

[b] ΣPCBs$_6$: CB28, 52, 101, 138, 153, 180

[c] ΣDDTs: *o′,p′*-DDT, *p′,p′*-DDT, *p′,p′*-DDD, and *p′,p′*-DDE

[d] ΣHCHs: α, β, γ, and δ –HCH

[e] ΣPBDEs: BDE28, 47, 66, 99, 100, 85, 154, 153, and 183

[f] ΣBDEs$_6$: BDE28, 47, 99, 100, 153, and 154

[g] ΣPFCs: PFDA, PFDOA, PFHxS, PFNA, PFOA, linear and branched PFOS, PFOSA, PFTeDA, PFTrDA, and PFUDA

[h] EAC from OSPAR, based on whole fish (OSPAR 1997)

[i] EAC from OSPAR, based on whole fish, (OSPAR Commission 2010)

[j] EAC from OSPAR, based on whole round fish (OSPAR 2005)

[k] EQS from WFD, based on whole fish (EU 2013)

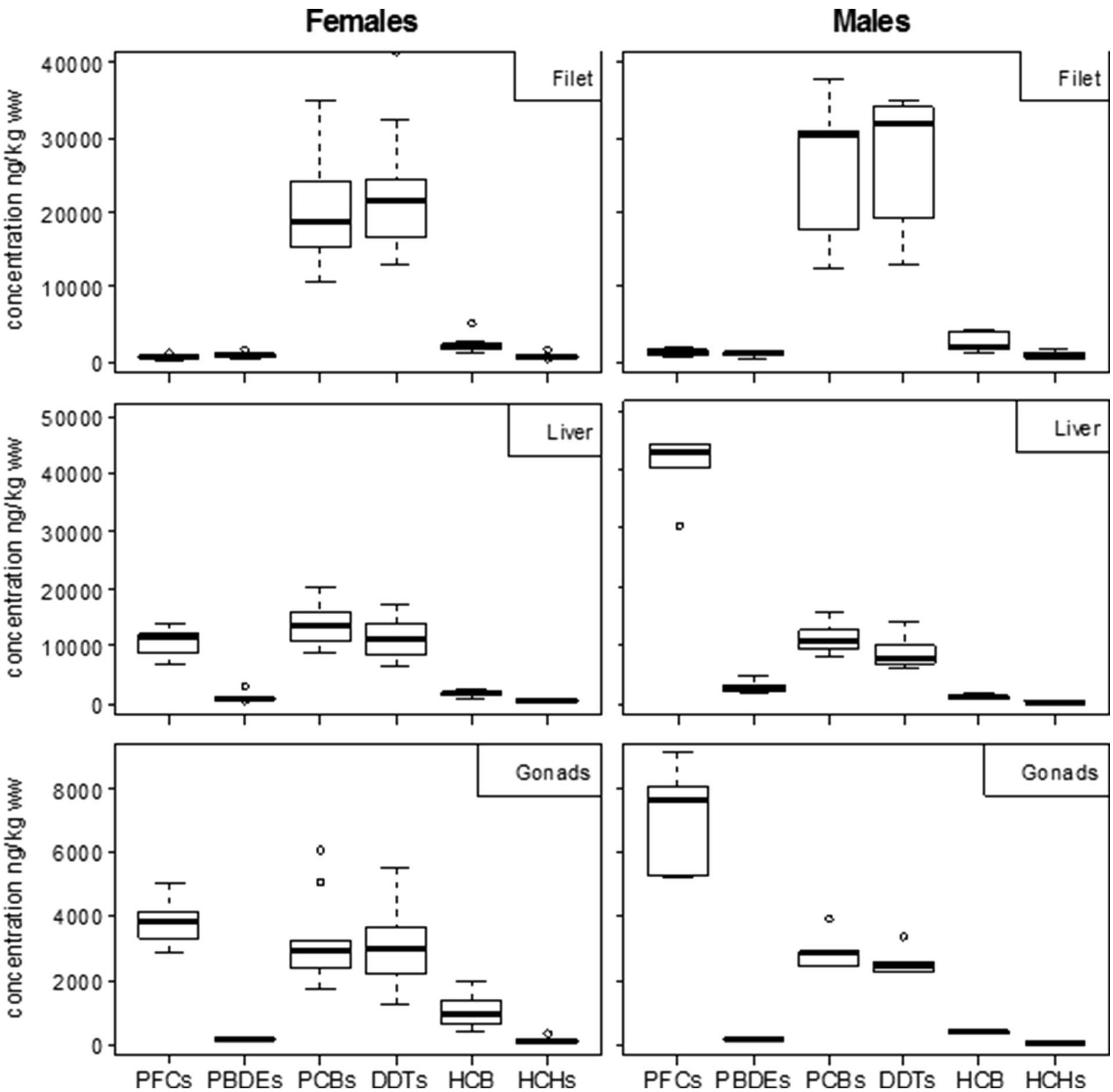

Fig. 1 Boxplots of contaminant concentrations (ng/kg ww) in Baltic herring (*Clupea harengus*) from the Arkona Basin. The contents of all 14 polychlorinated biphenyls (PCBs: CB28, 31, 52, 101, 105, 118, 129, 138, 149, 153, 156, 170, 180, 187), dichlorodiphenyltrichloroethanes (DDTs: *o′*,*p′*-DDT, *p′*,*p′*-DDT, *p′*,*p′*-DDD, and *p′*,*p′*-DDE.), hexachlorocyclohexanes (HCHs), polybrominated diphenyl ethers (PBDEs: BDE28, 47, 66, 99, 100, 85, 154, 153, and 183), and perfluorinated compounds (PFCs: PFDA, PFDOA, PFHxS, PFNA, PFOA, linear and branched PFOS, PFOSA, PFTeDA, PFTrDA, and PFUDA) were measured in the filet, liver, and gonads of 5 males and 10 females, respectively

of concern and require direct measures for reduction (Roose et al. 2011).

EACs exist for the most relevant PCBs in fish filet, among them are the six indicator PCBs (CB28, CB52, CB101, CB138, CB153, CB180) and three dioxin-like PCBs, i.e. CB105, CB118, and CB156. Further threshold values are available for *p′*,*p′*-DDE, HCB, and γHCH (OSPAR 1997; 2009; HELCOM 2010). EQS exist for PFOS and all its derivates as well as for the sum of six PBDEs, which are BDE28, BDE47, BDE99, BDE100, BDE153, and BDE154 ($\Sigma BDEs_6$) (EU 2013).

In the present study, the concentrations of most chlorinated compounds found in herring filets varied around the thresholds and only occasionally exceeded existing

EACs (Table 3). The situation was different for CB118 which exceeded the threshold value of 24 μg/kg lw (OSPAR 2009) in 12 out of 15 samples (80 %) in the filet. Furthermore, the concentrations of *p′,p′*-DDE in herring filets from the Arkona Basin, 16.65 ± 5.98 μg/kg ww, noticeably exceeded the lower threshold value for roundfish filets at 5 μg/kg ww (OSPAR 1997). Concentrations below threshold values were found for HCB and ΣHCHs (Table 3).

EQS for PFOS and its derivates (9.1 μg/kg ww) was exceeded in the liver tissues of the Baltic herring but not in the gonads or filet (Table 3). In contrast, EQS for ΣBDE_6 (0.0085 μg/kg ww) derived by the WFD was exceeded in all tested tissues.

Even though a decreasing trend for most POPs was reported from the Baltic Sea during the last decades (HELCOM 2010), we found that some organochlorines exceeded the existing threshold values. Hence, the tissue contamination of herring is remarkable in the Arkona Basin and should further be investigated and observed.

Organ-related distribution of contaminants

Herring as rather fatty fish comprises a high lipid content in filets (Table 3). Filet was therefore recommended as target tissue for the environmental monitoring of organochlorines and PBDEs in this species (HELCOM 2015). Our results mainly contribute to this assumption. The concentrations of organochlorines were higher in the filets compared to the liver or gonad tissue of Baltic herring (Table 3; Fig. 1). As most POPs, like organochlorines and PBDEs are lipophilic, they tend to accumulate in fat-rich tissues. However, the major force for accumulating these POPs in a specific tissue is rather its fat composition than the total amount of lipids within a tissue (Ewald and Larsson 1994; Burreau et al. 2000; Elskus et al. 2005). Basically two groups of lipids do exist in organisms. These are polar and non-polar lipids. Polar representatives, like phospholipids and sphingolipids, comprise an amphiphatic character and are therefore incorporated as membrane lipids into cells. Non-polar lipids, like triacylglycerols (TAGs), are found in fat vacuoles of adipose tissues serving as storage lipids and thermal insulators, and they are used for buoyancy control. Taken together, the tissue distribution of POPs and lipid composition of single tissues, such as the liver, filet, or gonads, former results suggest that concentrations of lipophilic and non-polar organochlorines are directly correlated with the percentage of TAGs instead of the whole lipid content of a tissue (Elskus et al. 2005). As data on lipid composition are lacking here, this discussion about higher percentage of TAGs in filet compared to liver tissue is only speculative and need to be addressed in further investigations. Additionally, concentration of PBDEs was highest in liver residues of male herring. The livers of males showed concomitantly a higher mean fat content than liver tissues of females. A relation between PBDEs and total fat content was demonstrated in the liver and filets, but not in gonads of Baltic flounder (*Platichthys flesus*) indicating that the mechanisms behind the accumulation of POPs may differ from substance group to substance group. Questioning this assumption, PBDE content in the livers of herring males exceeded the concentration in the filet (Table 3). Metabolic action in the liver may be responsible for the higher PBDE content as it was suggested for pike (Burreau et al. 2000). In general, the relationship of lipid composition and the tendency of POPs to accumulate within tissues is still poorly understood and needs continuous research in the future. Highest PFC concentrations have been found in the livers which are presumably caused by the special characteristics described in the former section. Similarly, the highest PFC concentrations have been measured in the livers of several freshwater fish, like eel, pike, and perch (Gerst et al. 2008). Interestingly, PFC concentrations in the gonads exceeded the contents of all other POPs measured in the same tissue which may be a consequence of the higher protein content in the gonads (Klinkhardt 1996; Elskus et al. 2005) and the tendency of PFCs to bind to proteins rather than lipids (Fent 2013).

In conclusion, we found an organ-specific distribution of all measured POPs in herring of the Arkona Basin. The dynamics of bioaccumulation among tissues in herring needs further investigation especially with view on the fat content in combination with the organ-specific fat composition as major force for the accumulation potential of lipophilic POPs.

Sex-dependent POP distribution in Baltic herring

In general, herring invest rather high proportions of energy for gaining maturity in spite of gender; the mean gonadosomatic index (GSI) of males reaches about 23 and 27 % in female herring (Klinkhardt 1996). In comparison in male pike, GSI reaches approximately 2 %, whereas in females, this number is 10–15 % (Larsson et al. 1993). In this study, caught herring showed high GSIs in both sexes while GSI of males (23.76 %) was significantly higher than the GSI of females (18.71 %) (Table 2). This difference in GSIs between both sexes of herring is presumably caused by an earlier entrance into maturity of males while females generally achieve maturation slightly later (Klinkhardt 1996). In contrast, the hepatosomatic index (HSI) was smaller in males (0.68 %) compared to females (1.96 %), and the statistical difference was significant between sexes (Table 2). This difference in HSI may lead to the assumption that the liver is possibly similarly involved in the processes during maturation in males as it is in females of this species. However, vitellogenesis, a process during which fatty acids are mobilized from adipose tissues and transported to the liver for biosynthesis of egg lipoproteins, has only been found evident in females so far (Lubzens et al. 2010). Pollutants stored in the energy reserves of the females are concomitantly transferred to the ovaries (Ungerer and Thomas 1996). POPs can have direct effects on reproduction since they influence estrogen levels, affect oocyte number or quality, or are transported from the females of the parental generation to the offspring via maternal pollutant transfer (Kime 1995; Nyholm et al. 2008). In contrast, the processes during maturation in male fish are poorly understood, are known to be less distinct, and offer scope for future investigations with special emphasis on POP redistribution and reproductive loss. This may be of special interest in this sense that spermatozoon have been found to be more susceptible to the effects of POPs than the ovaries (Kime 1995). Interestingly, in the present study, mean fat content of the livers and gonads of males were higher compared to females, whereas in filets it was the other way around (Table 3). These results also assist in the assumption that male herring enter maturity earlier than females.

Besides the inter-organ distributions of all POPs, we found additional sex-dependent differences. In filets, males showed slightly higher concentrations than females even though their fat content was smaller in this compartment (Fig. 1; Table 3). These findings again contribute to the assumption that not only the fat content (Dabrowska et al. 2009) but also the fat composition (Elskus et al. 2005; Waszak et al. 2012; Lana et al. 2014) is putatively one major determinant for the accumulation of lipophilic substances. Differences in pollutant accumulation between males and females could also be identified in the liver and gonads. Organochlorine concentrations were higher in the livers of females compared to males. In contrast, higher concentrations in liver tissues of males were found for ΣPBDEs and ΣPFCs statistically significant ($p < 0.001$). Also, the amount of PFCs in the testes exceeded the concentration in the ovaries. Concomitantly, the contents of organochlorines and PBDEs have been equal or higher in the ovaries compared to the testes. Similar to these findings, an early study also found lower PCB and DDT contents in testes of female Dutsch whiting compared to the ovaries of females (Von Westernhagen et al. 1987) (Table 3; Fig. 1).

Physiological differences between males and females appear to cause varying accumulation potentials of POPs in different tissue types of both sexes such that males and females differ in their lipid composition. Cholesterol was found as the main component in the testis of Atlantic herring. Phosphatidylcholine constituted the main proportion in oocytes from the same species. Furthermore, the ovaries of females showed higher proportions of triacylglycerols than the testes of males (Henderson and Almatar 1989). The percentage of triacylglycerols was positively correlated with POP concentration in Atlantic bluefin tuna (*Thunnus thynnus*, *L.*) (Sprague et al. 2012) but was also indicated as being species specific (Ewald and Larsson 1994). Hence, the higher proportion of triacylglycerols in female gonads of herring may simultaneously be responsible for the higher accumulation of lipophilic POPs compared to male gonads, as indicated by our results (Fig. 1).

As mentioned earlier, the liver plays an important role in vitellogenesis of female fish. Hence, the POP ratio measured in the gonads and liver (GLR) can be seen as one possible measure of the pollutant transfer during vitellogenesis (Serrano et al. 2008). The putative redistribution of POPs from the liver to gonads or from filets to gonads has only been investigated as maternal pollutant transport in many fish species such as cod (Dabrowska et al. 2009), sturgeon (Peng et al. 2010), and eel (Sühring et al. 2015) so far. We calculated the ratio for both sexes on a wet weight basis (Table 4) as all investigated POPs were also present in male gonads. Our results indicate that POP partition into the liver and gonads on a ratio of 0.56 implies that generally less than half of the pollutant load is transferred from the liver to gonads. In conclusion, we found all GLRs except DDTs to be equally or higher in females compared to males (Table 4). These results suggest that the redistribution of POPs is higher in females than in males which is likely a consequence of the processes during vitellogenesis. In males, processes during maturation are known to be less distinct (Kime 1995). Whether the liver in male fish is similarly involved in the processes during maturation as in females is still not clarified, which opens a field for further studies addressing POP accumulation and redistribution during maturation in males.

In addition, we calculated the gonad to filet ratio (GFR) to identify differences in POP partition between genders (Table 4). Again, ratios calculated for females were higher than ratios calculated for males with one exception. The ratio of PFCs was far higher than all other calculated ratios in both sexes and was higher in males compared to females. This difference between males and females was found statistically significant (student *t* test: $t = -3.6044$, $df = 11.04$, $p < 0.01$). Physiological differences arising during the processes of maturation between sexes may play a major role in causing this variation. Moreover, GFRs of ΣPFCs in herring were higher than values reported for the egg to filet ratio (EMR 0.79–5.5) in Chinese sturgeon (*Acipenser sinensis*) (Peng et al. 2010), which may be due to species dependent differences as a result of varying life-histories, or simply a consequence of investigating two different ratios.

Table 4 Gonad to filet ratio (GFR) and gonad to liver ratio (GLR) of persistent organic pollutants in Baltic herring (*Clupea harengus*) from the Arkona Basin.

Contaminants	Ratios	All fish (n = 15)	Males (n = 5)	Females (n = 10)
ΣPCBs[a]	GFR	0.17 ± 0.10	0.13 ± 0.06	0.19 ± 0.11
	GLR	0.27 ± 0.13	0.28 ± 0.13	0.26 ± 0.13
ΣDDTs[b]	GFR	0.14 ± 0.09	0.11 ± 0.06	0.14 ± 0.09
	GLR	0.30 ± 0.16	0.33 ± 0.15	0.29 ± 0.16
ΣHCHs[c]	GFR	0.16 ± 0.16	0.11 ± 0.06	0.16 ± 0.16
	GLR	0.24 ± 0.12	0.24 ± 0.07	0.23 ± 0.14
HCB	GFR	0.42 ± 0.36	0.20 ± 0.12	0.54 ± 0.39
	GLR	0.50 ± 0.27	0.37 ± 0.12	0.56 ± 0.31
ΣPBDEs[d]	GFR	0.20 ± 0.10	0.18 ± 0.08	0.21 ± 0.11
	GLR	0.14 ± 0.08	0.06 ± 0.02	0.18 ± 0.08
ΣPFCs[e]	GFR	6.30 ± 3.22	6.59 ± 1.62	6.15 ± 3.86
	GLR	0.28 ± 0.14	0.17 ± 0.04	0.34 ± 0.14

Values are means with standard deviation (sd), given for 10 females and 5 males, respectively, and pooled for both sexes

[a] ΣPCBs: CB28, 31, 52, 101, 105, 118, 129, 138, 149, 153, 156, 170, 180, 187

[b] ΣDDTs: *o′,p′*-DDT, *p′,p′*-DDT, *p′,p′*-DDD, and *p′,p′*-DDE

[c] ΣHCHs: α, β, γ, and δ –HCH

[d] ΣPBDEs: BDE28, 47, 66, 99, 100, 85, 154, 153, and 183

[e] ΣPFCs: PFDA, PFDOA, PFHxS, PFNA, PFOA, linear and branched PFOS, PFOSA, PFTeDA, PFTrDA, and PFUDA

Similarly for HCB, the GFR differed significantly among sexes (student t test: $t = -2.3111$, $df = 9.512$, $p < 0.05$). The elevated GFR and GLR levels for HCB in females suggest that this POP presumably tend to be eliminated at least partly via maternal transfer processes as it was reported for HCB in dab before (Knickmeyer and Steinhart 1989; Kammann et al. 1993). However, all ratios should only be considered preliminary evidence for the putative redistribution of POPs in fish and as a method of measuring differences between species and target substances. The variation of parental transfer processes on a molecular basis still offers scope for further investigation.

Considering GFR or GLR as measures of putative ways to discard pollutants, females eliminate higher proportions of organochlorine and ΣPBDEs than males which is presumably due to differences in lipid contents in the gonads, including the proportion of triacylglycerols. In contrast, the elimination routes for PFCs may differ from other POPs. Perfluorinated substances are less lipophilic and proportions of ΣPFCs eliminated in males are higher than in females (Table 4).

In general, the transfer of POPs into the gonads is described as one of six possible elimination routes of contaminants out off an organism (Mackay and Fraser 2000). Such a route of elimination throughout the gonads is mostly investigated in females only (Serrano et al. 2008; Dabrowska et al. 2009; Peng et al. 2010; Sühring et al. 2015). However, our results indicate that elimination of POPs occurs in both sexes. The extent and effect might have been underestimated so far and should be considered especially for less lipophilic POPs.

Synopsis and consequences for marine monitoring

The results of the present study indicate that the POP concentration in herring from an offshore region such as the Arkona Basin is remarkably high. The exceedance of threshold values by CB118, DDE, ΣBDE_6, and PFOS is a reason for concern and may impair the "good environmental status" of the Baltic Sea as it is targeted by the European Marine Strategy Framework Directive (MSFD). Therefore, monitoring of chlorinated POPs in herring should continue and monitoring of brominated and flourinated compounds should also be initiated in the Baltic Sea. However, the validity of threshold values used for the assessment of the environmental status of the Baltic Sea needs to be reviewed again. Notably, it is questionable whether the EQS which have been adopted from the WFD are applicable in the marine environment as marine fish may have different sensitivities than fresh water species. Applying assessment factors without adequate evidence to support their use can undoubtedly lead to inappropriate threshold values for the marine environment.

The recommended tissue for monitoring of most POPs in herring is the filet (HELCOM 2015). Due to the high PBDE and PFC concentrations, the liver may be an appropriate target tissue as well and could be incorporated into the current monitoring procedure. Additionally, we suggest monitoring the POP concentrations of the gonads on a regular basis and use it as a bioeffect measure in the assessment of healthy wildlife as demanded by the BSAP. Addition of gonad monitoring would enable assessment of the potential risk for the next generation and therefore the whole population to the current Baltic Sea monitoring program which is presently mainly focussed on the assessment of the current status as well as time trends of the environmental pollution.

Conclusion

In conclusion, the results of our study clearly show that (1) body burden of POPs in Baltic herring from the Arkona Basin is remarkably high and in some cases exceeds the 'threshold levels for acceptable values'. (2) Accumulation of POPs in Baltic herring differed depending on the target tissue as well as (3) the sex. (4) Transfer of contaminants to the gonads and potential contaminant loss through reproduction processes appear to occur in both sexes although the degree differed depending on the sex and the substance. Females appear to eliminate higher contents of lipophilic substances, like HCB through reproduction than males, whereas males appear to eliminate higher contents than females of less lipophilic substances, such as PFCs. Since both processes directly affect reproductive success and therefore the healthy development of offspring, gonad contamination monitored on a regular basis in both sexes could be used as a putative and additional bioeffect measure to assess the healthy wildlife as demanded by the BSAP.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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