Perfluoroalkylated substances (PFASs) and legacy persistent organic pollutants (POPs) in halibut and shrimp from coastal areas in the far north of Norway: important dietary foodstuffs for coastal communities

Pernilla Carlsson[a,b,c], John Crosse[d], Crispin Halsall[d], Anita Evenset[e], Eldbjørg Heimstad[f], Mikael Harju[f]

[a] Arctic Monitoring and Assessment Programme (AMAP), NO–0134 Oslo, Norway, [b]Akvaplan-Niva, NO–9171 Longyearbyen, Svalbard, Norway, [c] Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, CZ-625 00 Brno, Czech Republic, [d] Lancaster Environment Centre, Lancaster University, LA14YQ Lancaster, United Kingdom, [e]Akvaplan-Niva, NO-9296 Tromsø, Norway, [f]NILU-Norwegian Institute for Air ResearchNO-9296 Tromsø, Norway.

Abstract

Halibut (*Hippoglossus hippoglossus*) and shrimps (*Pandalus borealis*) are regular dietary foodstuffs for communities in northern Norway and are important species for the coastal fishing industry. The concentrations of an array of POPs are reported for halibut fillets (muscle tissue) as well as whole and peeled shrimp locally caught from two coastal areas close to the coastal town of Tromsø in the Arctic Circle. In general, contaminant concentrations were found to be low, e.g. the median ΣPCBs were 4.9 and 2.5 ng/g ww for halibut and unpeeled shrimps, respectively. Median concentrations of PFOS – the most abundant PFAS - were 0.9 and 2.7 ng/g ww in halibut and shrimp, respectively.

The halibut filets were dominated by PCBs, which contributed to 50% of the total POPs load, followed by DDTs (26%) and PFAS (18%). Unpeeled shrimps were dominated by PFAS (74%). All legacy POPs on a lipid weight basis showed higher concentrations in halibut compared to shrimps, but PFAS were present at highest concentrations in the shrimps on a wet weight basis. This emphasizes that emerging POPs requires new methodology and insight in order to predict the potential exposure risks for humans. The present study assesses a wide range of pollutants to facilitate an overview and exposure risk modelling in the future.

Keywords: halibut, shrimps, PFOS, diet, PFCAs, PBDE, PCB, Arctic,

Introduction

Halibut (*Hippoglossus hippoglossus*) and shrimp (*Pandalus borealis*) are popular marine foods in Norway and are important commercial species present in coastal waters of northern Norway. Halibut are long-lived, benthic fish species that are pisciverous whereas shrimp are epibenthic and feed on detritus, as well as on pelagic lower trophic level organisms such as phytoplankton and zooplankton (IMR 2014). Both organisms are important human dietary foodstuffs particularly for coastal communities in northern Norway. The Norwegian fishing industry catches 5000 tonnes of coastal shrimps every year, with 1400 tonnes of halibut in 2009 (IMR 2014). The median fish intake among the Norwegian population is 65 g fish/day, with high-consumers eating 118-174 g fish/day (Bergsten 2014; VKM 2006; VKM 2014b). However, it is not known how much of this comprises of shrimps and halibut. Marine foodstuffs are regularly scanned and analysed for nutrients, legacy and new pollutants by the National Institute of Nutrition and Seafood Research (NIFES) with data published in an open archive (NIFES 2014). To date, however there have been relatively few surveys that have examined the levels of persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs) and polybrominated diphenyl ethers (PBDEs), in halibut and shrimps despite the fact that these chemicals are still cause for concern regarding their bioaccumulation and negative effects on both humans and wildlife (AMAP 2011a; Stockholm Convention 2013). Furthermore, there are fewer data for newer contaminants such as the perfluoroalkylated substances (PFAS) and new brominated flame retardants (BFRs), which, in some cases, may bioaccumulate and biomagnify in marine foodwebs and hence provide a dietary exposure pathway to humans (Carlsson et al. 2011; Haukås et al. 2007; Sørmo et al. 2009). Recent investigations of PFASs, PBDEs, PCBs and OC pesticides in marine food stuffs has been undertaken in the Faroe Islands (only PFAS though), Greenland and Iceland (Carlsson et al. 2014a; Carlsson et al. 2014b; Eriksson et al. 2013; Jörundsdóttir et al. 2012; Sturludottir et al. 2014). Some of these data are comparable to the coastal species examined here, allowing us to compare them with each other.

POPs reach the Arctic via long-range environmental transport (AMAP 2003), although activities in coastal areas such as fisheries and shipping activities, the presence of harbours and associated coastal runoff from Arctic settlements, may all serve to increase the levels of these contaminants. Secondary sources such as melting sea ice and glaciers, increased run off from land and rivers of legacy POPs as well as new and unregulated POPs are cause for concern in the Arctic and coastal communities may provide additional, local sources to the marine environment (Carlsson 2013; Christensen et al. 2002; Kallenborn et al. 2012; Stock et al. 2007), Most of these secondary sources are affected and related to the ongoing climate change (AMAP 2011b; ArcRisk 2014).

Fewer marine datasets exist for emerging contaminant groups like PFAS. The amount of PFOS for example allowed in products, e.g. textiles and firefighting foam in Norway and European Union is strictly regulated (European Union 2010). However, there are several PFASs that are not regulated, but are cause for concern. In general, PFAS are associated with proteins, while the legacy POPs accumulate in fatty tissues (Lau et al. 2007). Hence, new exposure routes, sources and pathways need to be considered for these chemicals and compared with the legacy POPs. For the two species considered in this study, the lipid-normalised concentrations of legacy POPs might be expected to be higher in halibut than in shrimp, due to biomagnification processes and the higher trophic status of the halibut.

The aim of this study was to investigate the contaminant concentrations in halibut and shrimps collected from coastal fishing regions in northern Norway ; species for which contaminant data are lacking and to compare levels to similar species from more remote parts of the Arctic. This provides insight into whether coastal fisheries have higher contaminant levels due to proximity of additional sources of pollution. A further aim was to examine PFAS concentrations in relation to POPs to provide insight into their biological uptake and distribution within these two species Given the health concern of emerging compounds as well as legacy POPs in marine foodstuff, this study provides insight into the relevance of these organisms as contributors to human dietary exposure to these chemicals. There are on-going long-term studies about human health in Tromsø (Jacobsen et al. 2012), and the results from this study provides important new data for the improvement of human exposure models.

Fig. 1 Map showing northern Norway with the sampling locations of Malangen (shrimps and halibut), Tromsø (halibut) and Kvænangen (shrimps) marked. Map from www.google.com

Methods

Fresh filets of halibut (*Hippoglossus hippoglossus*) were purchased from local fishermen and fishmarkets (n=1; 4 fishes pooled together) and were caught from coastal waters close to Tromsø (n=5) over the period 2008-12. Shrimps (*Pandalus borealis*) caught from the Malangen and Kvænangen regions, to the southwest and east of Tromsø, respectively, were provided by a supplier. Length and weight of each halibut is reported in table S1. The shrimps were caught from the Malangen and Kvænangen regions, to the west and east of Tromsø, respectively, during 2012 (Fig. 1). Halibut filets and shrimp samples were separately wrapped in Al-foil and stored at -20^{o}C in zip-lock polythene bags prior to chemical analysis. The shrimps from each region were divided into three pooled samples of 20 unpeeled shrimps in each sample. Shrimps from Malangen had a length of approx. 10 cm with 163, 181 and 186 g per pooled sample, while shrimps from Kvænangen were approximately 10-11 cm, with 179, 196 and 205 g per pooled sample. Halibut filets (i.e. the part of the fish consumed by humans) were homogenized and about 2 g (PFAS analysis) and 20g (PCBs, PBDEs, OCs) of each homogenized composite sample was used for further sample preparation and extraction. PFASs in whole unpeeled shrimps (with carapace) and halibut filets were analysed by Norwegian Institute for Air Research (NILU), Tromsø, Norway. PCBs, PBDEs, DDTs, chlordanes and HCB in the same samples were analysed at Lancaster University, UK. At Lancaster University peeled shrimp samples were analysed in addition to whole shrimps with carapace. The shrimp samples from both locations were treated as one uniform group to improve the statistical power.

Extraction and clean-up

Perfluoroalkylated substances

All solvents were of Licrosolv quality and were purchased from Merck, Darmstadt, Germany. Shrimp and halibut samples were spiked with a ^{13}C-labeled internal standard (IS) (2 ng of ^{13}C-labelled PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDcA, PFUnA, PFDoA, PFHxS, PFOS and PFOSA (Wellington Laboratories Inc., Guelph, Ontario, Canada)) and extracted in an ultrasonic bath (3 x 10 min) using 8 mL of methanol (shrimps) or acetonitril (halibut, high fat content). The samples were centrifuged and the supernatant transferred to new tubes and evaporated down to 1 mL. Thereafter, the supernatant was eluted through 25 mg of ENVI-carb (Sigma-Aldrich, Taufkirchen, Germany) and then 50 µL glacial acetic acid (Merck, Darmstadt, Germany) was added and the extract was vortex mixed and further centrifuged. 100 µL of the supernatant was transferred to a vial and a recovery standard (RSTD) consisting of 3,7-dimethyl-branched perfluorodecanoic acid (bPFDA; 97% purity, ABCR Karlsruhe, Germany) and a buffer solution (100 µL of a 2 mM aqueous ammonium acetate (NH_4OAc, Sigma-Aldrich, St. Louis, MO, USA)) was added. Further details can be found in Herzke et al. (2009).

Brominated and chlorinated compounds

Homogenised samples (either halibut or shrimp) were mixed with sodium sulphate (Alfa Aesar, Heysham, Lancashire, UK), spiked with IS (^{13}C-PCB; -28, -52, -138, -153, -180, ^{13}C-PBDE; -28, -47, -99, -100, -153, -154) from Cambridge Isotope Laboratories, Andover, Massachusetts, US and soxhlet extracted for 16 h with 300 mL dichloromethane (DCM; Rathburn Chemicals, Walkerburn, Scotland). After extraction an aliquot of 15 mL was taken for gravimetric lipid determination (extracted organic material; EOM) while the remainder of the extract was reduced and transferred into *n*-hexane (Sigma Aldrich Company, Gillingham, Dorset, UK) and cleaned by eluting through an acidified silica column (25 mm id, 15 g 1:2 w/w H_2SO_4:silica). The eluent was then evaporated to <1 mL and further cleaned by gel permeation chromatography (GPC; 6 g biobeads column eluted with 1:1 v/v hexane/DCM; the first 16 mL was discarded and the next 35 mL retained). This eluent was then evaporated under nitrogen and transferred into *n*-dodecane keeper solvent (25 mL) containing the following RSTDs: PCB-30 and ^{13}C-labelled PCBs -141 and -208 (Wellington Laboratories Inc., Guelph, Ontario, Canada) and ^{13}C-labelled BDE -77 and -138 (Cambridge Isotope Laboratories, Andover, Massachusetts, US). Further details can be found in Crosse et al (2012).

Chromatographic separation and quantification

Perfluoroalkylated substances

PFAS (listed in table S2) were analysed by ultrahigh pressure liquid chromatography tandem mass-spectrometry (UHPLC-MS/MS) consisting of. a Thermo Scientific quaternary Accela 1250 pump with a PAL Sample Manager coupled to a Thermo Scientific Vantage MS/MS (Vantage TSQ). The injection volume was 10 µL and the column was a Waters Acquity UPLC HSS 3T column (2.1 × 100 mm, 1,8 µm) equipped with a Waters Van guard HSS T3 guard column (2.1 × 5mm, 1.8 µm). Separation was achieved using 2 mM ammonium acetate (NH_4OAc) in 90:10 methanol/water (A) and 2 mM methanolic NH_4OAc (B) as the mobile phases. A Waters XBridge C_{18} column (2.1 x 50mm, 5 µm) was installed as a guard column after the pump and before the injector. Monitored transitions are presented in table S2 and other details about the analytical LC and MS conditions, the parent ions, collision energies and S-lens settings can be found in the literature (Carlsson et al. 2014b; Hanssen et al. 2013). LCQuan (version 2.5.6, Thermo Fisher Scientific Inc., Stockholm, Sweden) was used for quantification of the PFAS compounds.

Brominated and chlorinated compounds

Extracts were analysed on a Thermo Trace GC-MS (MS operating in electron ionisation mode) with analytes resolved on a 50 m CP-SIL8 pesticide column, following a 1 µL injection (split/splitless injector port). Further details are presented in Crosse et al. (2012). Analyte quantification was based on a set of external calibrants with concentrations ranging over: PCBs/OCs, 2.5-250 pg/µL; PBDEs, 1-100 pg/µL). The PCB and PBDE congeners quantified are listed in table S3a.

Quality control

For confirmation quantifier and qualifier mass transitions were acquired for each analyte including the PFASs, except for PFBA and PFPA, where only a quantifier mass was acquired (table S2). For PFAS analysis a laboratory blank and a standard reference material (SRM) were analysed for every 10th sample PFAS ‘ILS 2011’ ‘fish tissue’ (developed during the PERFOOD project, KBBE; grant agreement no. 227525) was used as a reference material. The measured levels in these SRMs varied within an acceptable range (±20 %) compared to the reference levels for the various batches of shrimp and halibut samples. For PCB, PBDE and OC analysis a QC standard was run for every 10th sample with an acceptable precision of ±10%.

Limits of detection (LODs) were derived from signal-to-noise ratios equal to 3 in the calibration sequences and method detection limits (MDLs) were defined for each analyte as the average level in the blank media + 3*standard deviation. The limit of quantification (LOQ) was calculated as 10 times the laboratory blank for target PFAS analytes. Table S3a and S3b present blank and MDL data for the contaminant groups in this study. For analytes not present in the blank media (e.g. soxhlet thimbles, chromatography sorbents etc) the corresponding instrumental LOD was utilised. The systematic occurrence of certain PCB and PBDE congeners in the blanks (particularly lower chlorinated/brominated congeners) resulted in blank subtraction from the sample extracts. All analyte data were recovery corrected. The average recoveries for PFAS were 54-97%. The median recoveries for PCBs were 74-100 % and 80-101 % for the PBDE congeners (table S4).

Statistical analyses

Basic statistics were performed with the Paleontological statistics software package for education and data analysis (PAST), e.g. Mann-Whitney's test or Kruskal-Wallis test (Hammer et al. 2001). A *p*-value of 0.05 was considered statistically significant if nothing else is stated. Samples <LOD are not included in the median or mean calculations (table 1).

Results and discussion

Overview to concentrations in biota

Due to the relatively low number of shrimp samples from each location, shrimps from Kvænangen and Malangen were treated as a uniform group unless stated otherwise, with the effect of increasing the statistical power when comparing contaminant data with the halibut samples or other published data. The halibuts were also treated as one group. Concentrations of 'legacy' POPs such as PCBs, OCs and PBDEs being lipophilic, were expressed on a lipid weight basis. However, for comparison of PFAS concentrations and in agreement with European Commission guidelines the wet weight concentrations are provided in Table 1. In general, blank levels were low and corresponding limits of detection (LODs) were acceptable. For example, for the PFAS compounds, LODs were typically <10 pg/g ww (see Table S2) although for the C_4 PFBA the LOD was ~50 pg/g ww and this compound does not feature in the discussion.

Concentrations of the analysed compounds in shrimps were found to the order ΣPFAS>ΣPCBs>ΣDDTs/HCB/ΣPBDEs and this is illustrated in Fig 2. For the halibut fillets the contaminant profile differed markedly and was dominated by ΣPCBs>ΣDDTs> ΣPFAS> ΣPBDEs For the lipophilic POPs, PCB-138, -118 and -153 were the dominant congeners in all samples. Nevertheless, the distribution differed between the samples. E.g. *p,p'*-DDE and PCB-138 were found at the same concentration in halibut (1.1 ng/g ww), while *o,p'*-DDD was the dominating DDT-compound in the unpeeled shrimps. Hexa-PCBs dominated all samples, followed by penta-PCBs. Tri-PCBs contributed to almost 50% of ΣPCB in the peeled shrimps, but only to 3-6% in the unpeeled shrimps and the halibut.

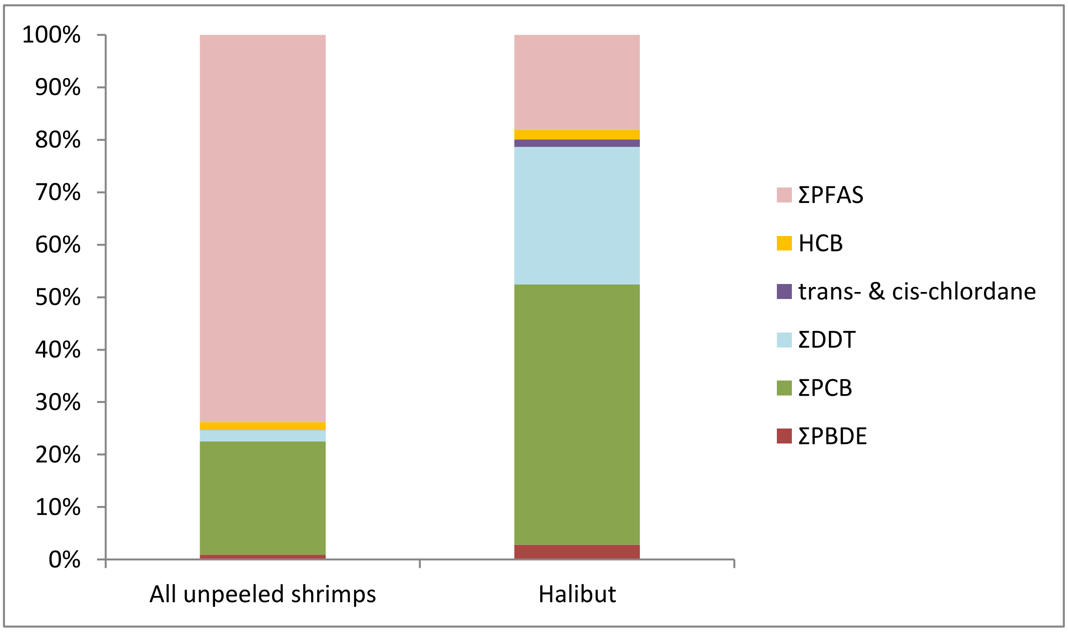

Fig. 2 Relative distribution (ww comparison) of ΣPCBs, ΣDDTs, ΣPBDEs, HCB, ΣPFAS, *trans*- and *cis*-chlordane in unpeeled shrimps and halibut fillets

Table 1 Median and mean (pg/g ww) of PCBs, PBDEs, PFASs and pesticides analysed in peeled and unpeeled shrimps and halibut filet. Number of samples with respective compound >LOD, standard deviation, minimum and maximum values are also presented

	PCB18	PCB22	PCB28/31	PCB41/64	PCB44	PCB49	PCB52	PCB60/56	PCB70	PCB74	PCB87	PCB95	PCB99
N (unpeeled shrimps)	5	6	6	9	9	8	9	8	9	9	8	8	9
Median	13	81	57	5	8	9	30	12	36	50	22	17	147
Mean	13	78	56	5	8	10	33	11	36	52	23	16	156
Stand. Dev	3	32	12	2	5	5	20	4	19	24	8	6	77
Min	<LOD	<LOD	<LOD	2	2	<LOD	6	<LOD	10	19	<LOD	<LOD	48
Max	17	115	68	9	20	16	79	19	75	105	37	25	335
N (peeled shrimps)	2	3	2	2	2	2	2	4	3	4	ND	3	5
Median	11	29	34	3	5	5	8	4	9	8		9	9
Mean	11	36	34	3	5	5	8	4	9	8		8	16
Stand. dev	1	13	2	1	2	1	4	1	6	5		5	12
Min	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	7
Max	12	51	35	3	6	5	11	4	14	15		12	35
N (halibut)	3	4	3	6	6	6	6	5	6	6	6	6	6
Median	11	45	86	16	36	45	97,5	19	50,5	92,5	85,5	55,5	258
Mean	10	42	182	35	78	95	204	39	104	210	196	123	529
Stand. dev	3	31	199	46	103	123	266	50	114	283	297	181	677
Min	<LOD	<LOD	<LOD	8	20	24	44	<LOD	29	48	39	28	146
Max	12	70	410	127	287	343	738	127	324	778	798	489	1894

	PCB101/90	PCB104	PCB105	PCB110	PCB114	PCB118	PCB123	PCB138	PCB141	PCB149	PCB151	PCB153	PCB155
N (unpeeled shrimps)	9	2	9	8	9	9	9	9	9	9	3	9	5
Median	92	3	74	26	6	263	12	491	23	102	17	434	1
Mean	96	3	75	30	7	276	11	510	23	108	16	475	1
Stand. dev	46	1	23	16	3	107	5	221	8	53	12	194	1
Min	27	<LOD	28	<LOD	2	101	2	172	5	19	<LOD	186	<LOD
Max	203	3	111	54	12	507	21	1011	36	224	27	899	2
N (peeled shrimps)	5	ND	5	2	2	5	2	5	2	2	ND	5	ND
Median	8		7	11	3	20	4	34	7	37		41	
Mean	11		10	11	3	32	4	55	7	37		51	
Stand. dev	9		6	5	2	22	3	42	4	16		30	
Min	3		6	<LOD	<LOD	14	<LOD	25	<LOD	<LOD		24	
Max	26		21	14	4	66	6	126	10	48		98	
N (halibut)	6	ND	6	6	6	6	6	6	6	6	4	6	5
Median	131		142	128	12	450	14,5	1073	62	141	110	770	3
Mean	310		219	308	23	949	37	2833	173	452	341	1925	5
Stand. dev	472		238	471	31	1282	48	4186	271	771	498	2650	7
Min	67		75	73	5	279	7	731	32	85	<LOD	547	<LOD
Max	1268		697	1265	87	3546	130	11321	723	2021	1086	7274	18

	PCB157	PCB156	PCB158	PCB167	PCB170	PCB174	PCB180	PCB183	PCB187	PCB188	PCB189	PCB194	PCB199
N (unpeeled shrimps)	9	9	7	9	9	7	9	9	9		7	9	1
Median	15	26	21	29	53	18	148	55	54		2	9	3
Mean	16	30	22	36	45	18	162	58	65		4	11	3
Stand. dev	10	12	6	18	20	7	75	28	37		2	4	
Min	9	15	<LOD	14	15	<LOD	67	21	10		<LOD	6	<LOD
Max	41	53	29	72	75	29	342	121	116		7	18	3
N (peeled shrimps)	3	4	ND	2	3	1*	3	2	3	ND	1*	5	2
Median	19	4		5	13	10	18	15	11		2	2	6
Mean	14	7		5	13	10	18	15	17		2	2	6
Stand. dev	9	7		4	2	0	10	6	16		0	1	1
Min	<LOD	<LOD		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD		<LOD	2	<LOD
Max	20	18		7	15	10	28	19	36		2	3	7
N (halibut)	6	6	6	6	6	6	6	6	6	2	6	6	
Median	22	69	50	65	158	27	409	103	182	5	7	32	
Mean	60	225	154	187	147	66	1037	267	459	5	17	88	
Stand. dev	83	388	250	281	64	85	1449	344	542	2	25	134	
Min	17	39	40	46	33	13	244	68	144	<LOD	6	20	
Max	228	1014	664	756	219	233	3945	942	1506	6	68	361	

	PCB203	ΣPCB	HCB	Trans-chlordane	Cis-chlordane	o,p-DDE	p,p-DDE	o,p-DDD	p,p-DDD	o,p-DDT	p,p-DDT	ΣDDT
N (unpeeled shrimps)	8	9	9	1*	8	8	9	5	6	1		9
Median	11	2466	170	2	8	28	127	352	17	44		244
Mean	12	2523	144	2	10	28	148	364	27	44		401
Stand.	6	1015	60		9	12	91	357	26			362

dev												
Min	<LOD	815	29	<LOD	<LOD	<LOD	26	<LOD	<LOD			37
Max	22	4766	202	2	33	46	324	874	78			1048
N (peeled shrimps)	2	5	4	ND	1	3	3	1	ND	ND	ND	5
Median	2	155	21		4	11	16	47				20
Mean	2	325	25		4	10	28	47				33
Stand. dev	1	284	15			4	23					36
Min	<LOD	117	<LOD		<LOD	<LOD	<LOD	<LOD				<LOD
Max	2	768	44		4	14	55	47				74
N (halibut)	6	6	6	5	6	6	6	4	6	4	2	6
Median	43	4932	112	14	108	27	943	104	202	135	544	2029
Mean	88	11985	349	31	239	106	1811	171	644	146	544	2954
Stand. dev	122	16856	187	46	352	200	2102	163	855	62	412	2796
Min	23	3154	85	<LOD	40	9	394	<LOD	60	<LOD	<LOD	817
Max	334	46068	167	112	952	514	5943	411	2211	225	835	8185
	BDE28	**BDE32**	**BDE35**	**BDE37**	**BDE47**	**BDE49**	**BDE71**	**BDE99**	**BDE100**	**BDE153**	**BDE154**	**ΣPBDE**
N (unpeeled shrimps)	2	ND	9	ND	9	8	5	2	9	1	6	9
Median	5		12		66	5	6	7	13	4	6	111
Mean	5		13		74	6	6	7	15	4	6	118
Stand. Dev	3		6		48	3	2	1	9		2	68
Min	<LOD		5		21	<LOD	<LOD	<LOD	5	<LOD	<LOD	36
Max	7		28		191	12	9	8	37	4	8	284
N (peeled shrimps)	ND	ND	ND	ND	5	ND	ND	ND	ND	ND	1	5
Median					9						4	9
Mean					9						4	10
Stand. Dev					3							2
Min					4						<LOD	8
Max					13						4	13
N (halibut)	5	2	4	1	6	3	4	6	6	3	6	6
Median	17	14	25	7	170	12	38	15	52	6	15	294
Mean	23	14	50	7	491	22	100	36	142	8	36	845
Stand. Dev	20	11	61		751	24	142	55	206	6	47	1276
Min	<LOD	<LOD	<LOD	<LOD	89	<LOD	<LOD	10	25	<LOD	9	159
Max	56	21	141		2007	49	311	148	553	14	130	3416
	braPFOS	**linPFOS**	**PFHxA**	**PFOA**	**PFNA**	**PFDcA**	**PFUnA**	**PFDoA**	**PFTrA**	**PFTeA**	**FOSA**	**ΣPFAS**
N unpeeled shrimps	6	6	6	6	6	6	6	6	6	3	3	6
Median	159	2723	49	204	384	541	1594	402	1475	313	632	8437
Mean	136	2773	58	197	394	543	1637	417	1461	338	632	8473
Stand. dev	59	464	18	21	154	177	679	184	826	45	13	2544
Min	54	2097	45	164	242	358	920	211	475	<LOD	<LOD	5486
Max	199	3334	81	221	610	751	2540	667	2439	390	645	11127
N halibut	8	9	ND	ND	9	9	9	9	9	1	ND	9
Median	56	887			63	66	367	48	276	549		1882
Mean	84	951			83	66	379	83	491	549		2189

Stand. dev	74	508			71	42	335	108	702			1678
Min	<LOD	247			26	16	102	13	118			611
Max	206	1722			252	155	1186	357	2341			6162

PS= peeled shrimps, US=unpeeled shrimps, H=halibut filet. TC= *trans*-chlordane, CC=*cis*-chlordane, braPFOS= branched PFOS, linPFOS= linear PFOS. Please note that N=9 for unpeeled shrimps, N=5 for peeled shrimps and N=6 for the halibuts, except for PFAS where N=9. PFAS were not analysed in peeled shrimps. * Mean and median are calculated based on samples >LOD.

Perfluoroalkylated substances

In general shrimps from Kvænangen had the highest concentrations of all PFAS compounds analysed. The shrimp samples from Kvænangen and Malangen contained 4-fold higher concentrations of ΣPFAS compared to the halibut samples (on a wet weight basis). While fillet samples were taken from the halibuts, the shrimps analysed whole for PFAS were not peeled (i.e. the carapace or shell was not removed prior to extraction). Hence, the protein rich head (and carapace) was included and can therefore contribute to the higher concentrations compared to the halibut. The average protein concentration in Norwegian halibut (filets) and peeled shrimps are 19.4 and 22.9 g/100g ww, respectively (NIFES 2014), so it is likely that the unpeeled shrimp analysed here would have an even higher protein content. Low concentrations of PFAS, accompanied by frequent non-detects have recently been reported in smoked halibut fillet from Greenland (Carlsson et al. 2014b), fish collected from the Faroe Islands (Eriksson et al. 2013) and cod (*Gadus morhua*), haddock (*Melanogrammus aeglefinus)*, lumpfish (*Cyclopterus lumpus)* and mackerel (*Scomber scombrus*) fillets from Iceland (Jörundsdóttir et al. 2012). The Icelandic study did report PFOS as the only PFAS >LOD in Greenland halibut (0.26 ng/g ww), which is lower than the levels measured in the present study (median 0.9 ng/g ww; table 1). The low PFAS concentrations in halibut in the present study compared to levels of legacy POPs are most likely due to the tissue distribution of PFAS, with higher concentrations expected in the protein and blood rich liver, rather than the fillet (muscle tissue).

Fig 3 illustrates the mean PFAS concentrations for shrimp and halibut. All shrimp samples were dominated by the linear PFOS isomer (range: 2.1-3.3 ng/g ww), followed by PFUnA (range: 0.9-2.6 ng/g ww) and PFTrA (range 0.5 -2.4 ng/g ww). Median ΣPFAS concentrations (8.4 ng/g ww) in the shrimps were higher than recently reported concentrations (1.8 ng/g ww) in cod (*Gadus morhua*) liver from northern Norway (Norwegian Environment Agency 2013). Cod liver from harbours and certain fjords in Norway has earlier been of high interest due to its relatively high dioxin- and PCB-levels in relation to human exposure (Nilsen et al. 2011). However, a few investigations of PFAS in Norwegian cod liver that are available do not indicate that dietary exposure via this route presents a risk with regards to PFAS exposure and human health (EFSA 2012; NIFES 2014; Norwegian Environment Agency 2013). The mean PFOS concentrations in the shrimps were higher (2.8 ng/g ww) compared to cod liver (0.6 ng/g ww) from Lofoten, Norway in 2012 (Norwegian Environment Agency 2013), but within the concentration range of PFOS (<1-3.6 ng/g ww) in cod liver from Norway, 2007 (NIFES 2014). These studies did not analyse shrimps, and as far as we know, there are only few data available about PFAS in Norwegian shrimps. E.g. PFOS in peeled Norwegian shrimps were in the range of <1-10 ng/g ww in 2010 (NIFES 2014).

The halibut filets contained lower levels of PFAS compared to the shrimps but followed a similar PFAS profile, although relatively higher levels of the PFTeA (C_{14}) were observed in the filets. Based on mean concentrations, linear PFOS dominated (range: 0.2-1.7 ng/g ww), followed by PFTrA (range: 0.1-2.3 ng/g ww) and PFUnA (range: 0.1—1.2 ng/g ww) in the halibut fillets. Concentrations of PFOS were observed to be inversely related to halibut mass (Fig. S1), with the heaviest specimens showing the lowest concentrations (Mann-Whitney test, p=0,05, r^2 = 0.38). Even though there are few samples (N=9), this relationship between weight and PFOS as well as length and PFOS was statistically significant. However, there are other explanations than size (which, to a certain extent, represent the age) that are of importance for the PFAS concentrations, such as feeding preferences and habitat. PFAS can undergo bioconcentration via gills in fish although the main uptake is through their diet (Butt et al. 2010; Martin et al. 2003). A direct uptake of PFAS from the water into the shrimps cannot be excluded as a possible pathway. PFAS are more polar relative to the hydrophobic POPs and hence additional or alternative pathways other than the diet of the shrimp (e.g. plankton) need to be considered for controlling the PFAS burden in shrimp and similar organisms.

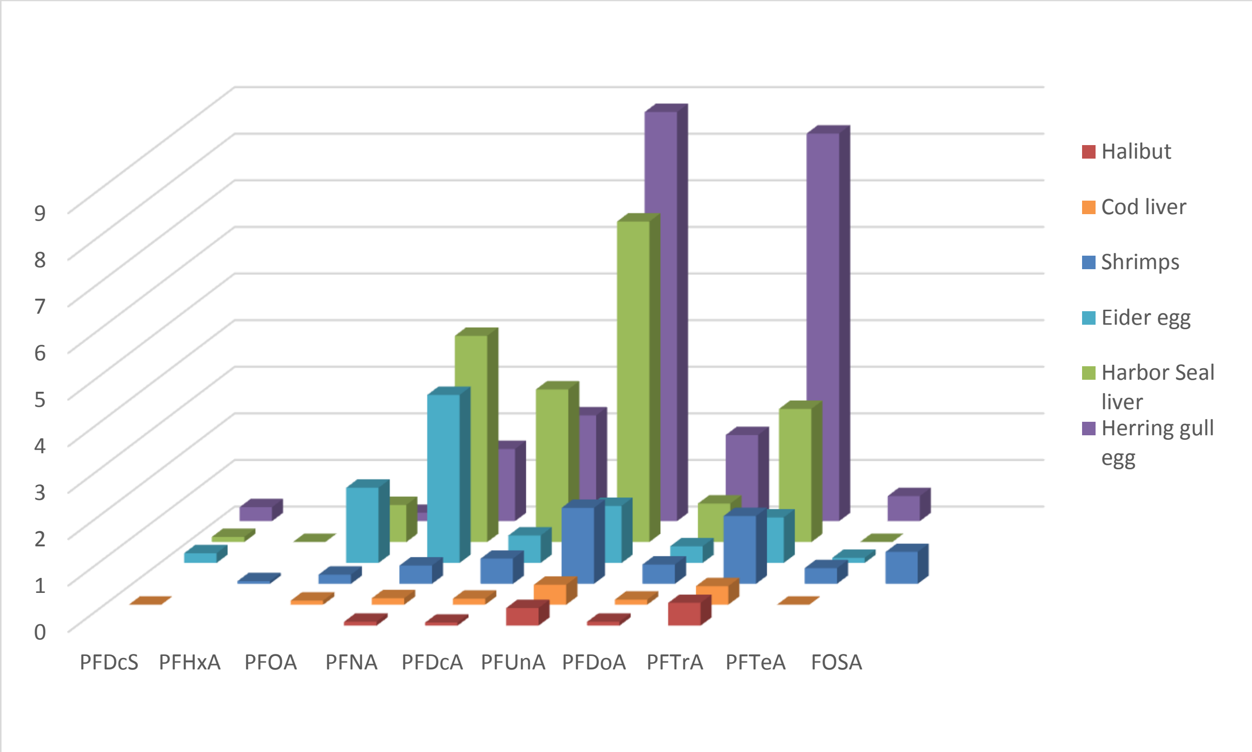

Fig. 3 Mean concentrations of unregulated PFAS (ng/g ww) in halibuts and shrimps in the present study, compared to recent data of eider *(Somateria mollissima)* and herring gull (Larus argentatus)eggs (collected in Troms and Finnmark, North Norway), harbour seal and cod liver from Lofoten, North Norway (Norwegian Environment Agency 2013). To show the concentration differences between the unregulated PFAS, PFOS is not included in since the levels were 2-48 times higher than the other PFAS. The mean PFOS levels (ng/g ww) were as follows; halibuts (1.0) and shrimps (2.8) from the present study, eider eggs (10.1), herring gull eggs (48.2), harbour seal liver (66.3) and cod liver (0.6) (Norwegian Environment Agency 2013).

Polybrominated diphenyl eters

BDE-47 (median 2.8 ng/g lw) was the dominant PBDE congener in the unpeeled shrimp samples, followed by BDE-100 and BDE-35 (0.5 ng/g lw, respectively). These levels were much lower than in unpeeled shrimps from the North Sea (BDE-47; 37 ng/g lw, ΣPBDE 56 ng/g lw) (Boon et al. 2002). The levels of BDE-47 were lower than the PCB-138 and -153 concentrations, although they were comparable to PCB-118 (median 2.3 ng/g lw), which was a common PCB-congener in the shrimps. The peeled shrimps showed a similar pattern, with median BDE-47 and PCB-118 at 0.9 and 1.0 ng/g lw, respectively. Concentrations of BDE-47 and ΣPBDE were significantly higher (Kruskal-Wallis, p=0.01) in the unpeeled shrimps compared to the peeled (n=9) shrimps, although there were few unpeeled samples (n=5). Shrimps have relatively low lipid content and the POPs are prone to be associated with the more lipid-rich intestines (located in/close to the head and removed by peeling). The median lipid content of the peeled shrimp was 0.99% as opposed to 2.38% in the unpeeled shrimp and both PBDEs and PCBs have been found to occur at higher concentrations in foodstuffs containing a higher lipid content. The ∑PBDE in peeled shrimps were in accordance with analyses by NIFES (BDE-28, -47, -99, -100, -153, -154 and 183); 0.01 ng/g ww in the present study, compared to shrimps from the Norwegian coast collected between 2007-2010; 0.01-0.03 ng/g ww (NIFES 2014). The unpeeled shrimps in the present study showed slightly lower than recent analysed shrimps from Norway (average 0.05-0.12 ng/g ww during 2008-11). Only BDE-47 was detected in the unpeeled shrimps in the present study.

All analysed PBDE congeners were detected in the halibut samples, although BDE-32 and -35 were only above LOD in two and one sample, respectively. BDE-47 dominated the halibut samples (median 11.3 ng/g lw), followed by BDE-100 and BDE-154 (median 3.5 and 1.1 ng/g lw, respectively). The BDE-47 concentrations were comparable to the most abundant PCB congener (PCB-138; 10.8 ng/g lw). Halibut is a benthic fish, and POPs deposited to the sediment and bottom fauna will result in higher levels of POP in benthic fishes compared to pelagic fishes (Bustnes et al. 2012). The median ΣPBDE (20 ng/g lw) in halibut fillets were higher than levels salmon fillet from Nuuk, Greenland (9.1 ng/g lw), comparable to cod fillet from large cod sampled in Iceland waters (16 ng/g lw), and whale beef from Nuuk, Greenland (20.7 ng/g lw) and lower than in medium-sized cod

(37 ng/g lw) from Iceland (Carlsson et al. 2014b; Jörundsdóttir et al. 2012). The halibuts in the present study contained lower levels of ∑PBDE (average 0.015 ng/g ww of the congeners analysed by NIFES) compared to Norwegian halibuts in 2006 (2.3 ng/g ww) and Greenlandic halibut (*Reinhardtius hippoglossoides*; 1.4 ng/g ww) caught in Norway 2011 (NIFES 2014). This difference can be due to the time lag and phase-out of penta-BDE, which was added to the Stockholm Convention in may 2009, but also feeding behaviour and habitat.

The concentrations in the halibut samples were higher compared to the shrimp samples, except for comparable levels of BDE-35 and -49 in the unpeeled shrimps. This is interesting since shrimps are epibenthic and feed at lower trophic levels compared to the halibuts. Hence, the explanation for these similar concentrations must be due to other factors than trophic levels, e.g. metabolism. PBDEs are prone to metabolism within fish (Browne et al. 2009; Luo et al. 2013; Munschy et al. 2011; Stapleton et al. 2004; Zeng et al. 2012). Higher levels of BDE-47 compared to BDE-99, as well as the presence of BDE-49 can, to some extent be due to metabolism in the halibut, although the degradation capability for PBDEs is species-specific (Luo et al. 2013; Munschy et al. 2011; Roberts et al. 2011; Stapleton et al. 2004). A high BDE-47:BDE-99 ratio could indicate higher degradation of BDE-99 than for BDE-47. The median ratio BDE-47:BDE-99 was 12 in the halibuts, and 6 and 9 in the two shrimp samples where BDE-99 was detected. Whether BDE-99 was <LOD in the other shrimp samples due to metabolism or other factors needs further investigation. To our knowledge, little is known about metabolism of PBDEs in Crustaceans. Boon et al. (2002) reported broadly comparable PBDE concentrations and congener profiles to our study in marine animals including shrimp from the North Sea and Skagerrak Strait (southern Norway). Fig. 4 shows the relative distribution of PBDE-congeners in halibuts and shrimps, as well as in the technical penta-BDE mixtures “DE-71” and “Bromkal 70-5DE”. The relative proportion of BDE-99 decreases while BDE-47 increases in biota compared to the technical mixtures (La Guardia et al. 2006).

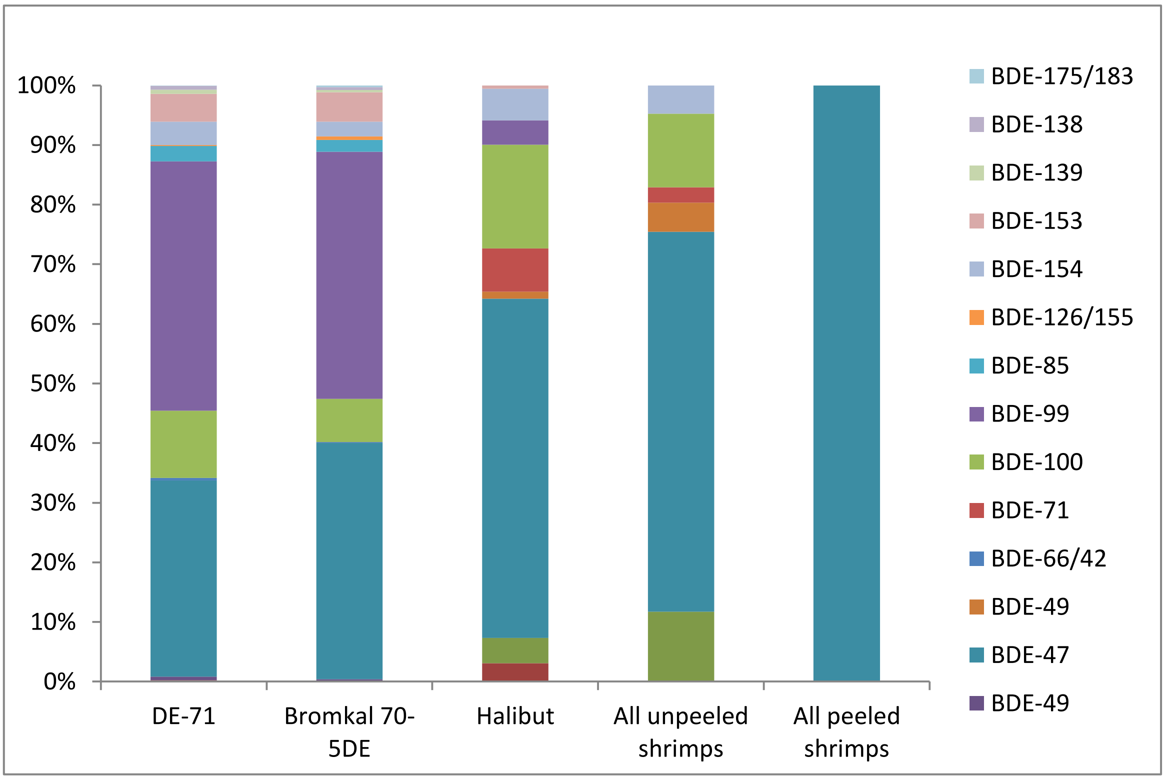

Fig. 4 Relative distribution of congeners (>0.2% w/w) in the technical penta-BDE mixtures “DE-71” and “Bromkal 70-5DE” and in the halibut and shrimp samples from the present study

Pesticides

Similar to PBDEs, concentrations of all the organochlorine pesticides analysed were generally found to be higher in the unpeeled shrimp than in the peeled (Table 1). Again, this is likely due to the lipophilicity of these compounds – the unpeeled shrimp containing approximately 2.5 times higher lipid content than the peeled shrimp. *p,p'*-DDE dominated among the DDT compounds (range <LOD-1.2 ng/g lw) in the peeled shrimps,

followed by *o,p'*-DDE (see Table 1). The unpeeled shrimps were dominated by *o,p'*-DDD (range <LOD-7.1 ng/g lw), followed by *p,p'*-DDE. *o,p'*-DDT were detected in one of the unpeeled shrimps samples. *p,p'*-DDD was present in all unpeeled shrimps from Kvænangen, and in two of the Malangen unpeeled shrimps, being 2-8 times higher in the Malangen shrimps when *p,p'*-DDD was present >LOD. However, given the small sample size, it may be the case that this is the result of natural variation. It is also possible that any spatial interaction is distorting comparison of ΣDDT concentrations despite isomer-specific variation. Levels of ∑DDT in peeled Norwegian shrimps from 1995 and 2000 were 0.1 ng/g ww (NIFES 2014), which was higher than in the present study (0.02 ng/g ww, table 1).

p,p'-DDE was the most prominent of the DDTs in halibuts, followed by *p,p'*-DDD. *p,p'*- and *o,p'*-DDT were detected in two and four of the samples, respectively. Due to metabolic processes, the ratio between those two compounds cannot distinguish between the possible effect of dicofol usage compared to degradation of DDT to its sister compounds; DDE and DDD. The ΣDDT levels (13.7 ng/g lw) were significantly higher in the halibuts compared to the shrimps (Mann-Whitney test, $p=0.05$) where the median levels were 2.2 and 1.3 ng/g lw in the unpeeled and peeled shrimps, respectively. Fillet from Greenlandic halibut caught near Iceland had 7 times higher levels of ΣDDT (92 ng/g lw), while haddock (*Melanogrammus aeglefinus*) fillets from Iceland were comparable (8-12 ng/g lw) to the halibut from this study (Jörundsdóttir et al. 2012).

While other POPs analysed (except PFAS) showed significantly higher concentrations in halibut compared to shrimps, this was not true for HCB. The unpeeled shrimps and the halibut fillets contained similar levels (1.2 and 1.1 ng/g lw, respectively), while the levels in unpeeled shrimps were lower; 0.7 ng/g lw. One possible explanation is higher degradation/metabolism of HCBs in the halibut compared to the shrimp. The peeled shrimps contained lower levels (0.02 ng/g ww) compared to earlier Norwegian studies from 1995 and 2000, where the HCB concentrations were 0.1 ng/g ww. The halibuts in the present study (0.2 ng/g ww, table 1) were also lower compared to earlier analysed halibuts; 1.7 ng/g ww in 2006 (NIFES 2014). A comparison on lw-basis shows higher levels in smoked halibut (23 ng/g lw) from Nuuk, Greenland than in the halibut fillets from the present study (Carlsson et al. 2014a). This can be due to the smoke process; concentration of lipids (by removal of water).

Cis-chlordane was present in the unpeeled shrimps (median 0.06 ng/g lw) at significantly lower concentrations (Mann-Whitney test, $p=0.05$) than in the halibuts (median 1.3 ng/g lw). Only one of the peeled shrimp samples contained *cis*-chlordane above the detection limit. *Trans*-chlordane was >LOD in only one of all the shrimp samples and present at low concentrations in the halibuts (0.1 ng/g lw). Smoked halibut from Nuuk contained higher levels; 8.6 ng/g lw of *cis*-chlordane and 3.6 ng/g lw of *trans*-chlordane (Carlsson et al. 2014a) than the halibut fillet. The smoking process will remove water and hence concentrate lipids and lipid-associated POPs, which can explain some of the difference between Norway and West Greenland here, but also size and age matters. *Cis*-chlordane have shown higher bioaccumulation factors than *trans*-chlordane (Hoekstra et al. 2003). This feature is reflected in the present study as well, with trans-chlordane <LOD in almost all shrimps and lower levels of *trans*- compared to *cis*-chlordane in the halibuts. Earlier investigations of halibuts (2006) and peeled shrimps (2007) from Norway showed levels of *trans*-chlordane <LOD, while *cis*-chlordane was <LOD-1.9 ng/g ww in the halibuts (NIFES 2014). The low *trans*-chlordane:*cis*-chlordane ratio in halibuts (median: 0.1), together with the high ratio of BDE-47:BDE-99 (median: 12) indicates ongoing metabolic processes in the halibuts.

Polychlorinated biphenyls

ΣPCBs accounted for 71-75% of the contaminant burden of legacy POPs in both unpeeled and peeled shrimp, suggesting that despite the cessation of their usage some 50 years ago, the contaminants are still environmentally relevant and warranted in ongoing investigations. Out of 44 PCB congeners analysed, 43 were detected in unpeeled shrimps, while 39 were detected in the peeled shrimps, and in fewer samples compared to the unpeeled shrimps. Removal of the head and organs can explain this difference between the unpeeled and peeled shrimps. PCB-138, -153 and -118 were the dominant congeners in all shrimp samples with respective contributions each of 8-19% to the ΣPCB burden. The mean and median concentrations are presented in Table 1. PCB-118 is a mono-ortho substituted dioxin-like PCB; seven other mono-ortho substituted dioxin-like PCB congeners ($PCB_{(8\ dioxin\text{-}like)}$; PCB-105, -114, -118, -123, -156, -157, -167 and -189) were detected in one or more peeled or unpeeled shrimp samples, with PCB-105 and -118 being detected in all samples. $\Sigma PCB_{(8\ dioxin\text{-}like)}$ congeners accounted for 18-25% of the ΣPCB burden across all samples with the majority of this attributable to PCB-118 (Table S2). Levels of PCB_7 ((PCB-28, -52, -101, -118, -138, 153 and -180; table S2) in the peeled shrimps (mean 0.2 ng/g ww) were comparable to earlier Norwegian studies (2000-2010) that reported 0.2-0.9 ng/g ww of PCB_7 in peeled shrimps (NIFES 2014). The unpeeled shrimps (mean 1.6 ng/g ww) were in the lower range compared to recent Norwegian investigations from 2008-11 where the mean concentrations in unpeeled shrimps were 1.6-3.8 ng/g ww (NIFES 2014). Median PCB_7 in the halibut fillets (3.0 ng/g ww) in the present study were similar to smoked halibut from Nuuk, Greenland (3.7 ng/g ww), but lower than in halibut from Iceland (6.7 ng/g ww). Mackerel and lumpfish from Iceland had slightly higher PCB_7 levels (3.5-5.7 ng/g ww) than the halibut in the present study (Carlsson et al. 2014b; Jörundsdóttir et al. 2012). Unfortunately, the Icelandic report does not contain information about whether the data were presented on a mean or median basis.

Similarly to the shrimps, PCB-138 dominated in the halibut filets, followed by PCB-153, -118 and -180. The highest individual levels of PCB-153 and -180 were found in the largest of the halibuts analysed in contrast to PFOS. These PCBs are among the most stable congeners, and hence, long lived (i.e. large size) halibuts are expected to have higher levels of these congeners compared to smaller specimens. The significantly higher levels of PCBs, pesticides and PBDEs in halibut, followed by the unpeeled shrimps and lowest levels in the peeled shrimps are most likely due to bioaccumulation and biomagnification of these hydrophobic POPs.

Human exposure A low fish-intake group of Norwegians (27 g fish/day) only eating shrimps would have a PFAS exposure (228 ng PFAS/fish meal) similar to a group with high fish-intake, where halibut would be the fish consumed (119 g fish/day; 224 ng PFAS/fish meal) (Norwegian Food Safety Authority, 2014. As the shrimps in this study were analysed unpeeled the actual dietary exposure will most likely be lower. However, if people choose to eat the roe, these numbers are more representative for the actual exposure than peeled shrimps. This shows the importance of adapting a new way of thinking when health issues related to emerging contaminants are addressed. While the largest exposure risks to the older, legacy POPs (e.g. PCBs) are associated with organisms at high trophic levels, such as large old halibuts, this may not be the case for emerging contaminants like PFAS.For these chemicals, protein content of the food, metabolites of the parent compounds and hence levels in “metabolic organs” such as liver and kidneys may be more important with regards to human dietary exposure than age and trophic level status of the marine organism.

Food basket studies from Scandinavia have shown that fish consumption is the major human exposure route for legacy POPs, although PCBs and PBDEs have been found to be well within TDIs (Darnerud et al. 2006; Kiviranta et al. 2004; Törnkvist et al. 2011). PFASs were not analysed in these studies. A recent European foodbasket study concluded with a dietary exposure below or close to 1 ng kg^{-1} bw $day^{-1}$for perfluorinated alkylated acids; PFAAs (Klenow et al. 2013). This is well below the EFSA guidelines for PFOA (1500 ng kg^{-1} bw day^{-1}) and PFOS (150 ng kg^{-1} bw day^{-1}) intake (EFSA 2012). Even the total PFAS exposure for persons with a high intake of shrimps would be well below the EFSA guidelines for PFOS exposure. E.g. 1004 ng ∑PFAS intake from 119 g shrimps would equal 17 ng kg^{-1} bw day^{-1} for a 60 kg person. While consumption of shrimp is likely to comprise only one of the daily meals, it is unlikely that other non-seafood items would substansially increase PFAS exposure resulting in exceedance of the EFSA guidelines. With regards to PFAS, indoor air and consumer products need to be taken into account for a thorough exposure assessment to be complete (Herzke et al. 2012). We recommend that food basket studies with emphasis on emerging compounds should be combined and linked to indoor exposure (e.g. air, dust inhalation) as well as dermal exposure to account for the various exposure pathways. Since PFAS are associated with proteins to some extent, we would also recommend that the protein content of food items to be reported in food basket studies.

To date TDI levels have not been set for PBDEs by the EU due to the limited data available, only benchmark doses (computed and estimated “safe levels” of the PBDEs) exist. These benchmark doses are currently 309 µg/kg bw for BDE-47, 12 µg/kg bw for BDE-99, 83 µg/kg bw for BDE-153 and 1700 µg/kg bw for BDE-209 (EFSA 2011). All benchmark doses are expressed as per day. The European Food Safety Authority panel (EFSA) in EU concluded that only BDE-99 would be of potential health concern for the European population (EFSA 2011). The concentrations measured in halibut and shrimps in this study (Table 1) are too low to exceed these benchmark doses for given consumption pattern. A concentration of 0.015 ng/g ww of BDE-99 in halibut filet would give a weekly intake of 12 ng BDE-99 for the high fish-consumers (119 g fish/day), (assuming they consume only halibut). The European Food Safety Authority concluded that only BDE-99 would be of potential health concern for the European population (EFSA 2011) but this congener was present at low levels in this study.

Available data for intake and food regulations are most often expressed as ΣPCB or PCB_6 or PCB_7. Recently, maximum permissible levels for PCBs and mono-ortho substituted dioxin-like PCBs (PCB-77, 81, 126, 169, 105, 114, 118, 123, 156, 157,167 and 189) in foodstuffs have been set by the European Commission to 6.5 TEQ-pg/kg ww (TEQ; toxic eqvivalents) in ‘muscle meat of farmed fish and fishery products’, which includes shrimps (EUR-Lex 2011). The maximum concentration of PCB_6 in fish and Crustacean muscle meat and sold for consumption in EU is 75 ng/g ww (EUR-Lex 2011). PCB_6 include all PCB congeners in PCB_7, except PCB-118, since it is included in the dioxin-like PCBs. The median levels of mono-ortho substituted dioxin-like PCBs in peeled and unpeeled shrimp and halibut of 0.011, 0.024 and 0.027 TEQ-pg/g ww respectively measured in this study fall well below the maxima of 6.5 TEQ-pg/g ww (EUR-Lex 2011; Van den Berg et al. 2006). Depending on the amount of PCB-77, -81, -126 and -169 in these samples, the levels are acceptable in halibut and low in the shrimps compared to the EU legislation.Sum PCB_6 in halibut, peeled and unpeeled shrimps was 2.7, 0.1 and 1.3 ng/g ww, respectively). These concentrations are well below the EU guidelines of non-dioxin like PCBs in food. Peeling the shrimps reduces PCB exposure to humans compared to exposure for marine predators that eat whole shrimps. The most recent food advices for Norwegian fish consumption states that PCBs and dioxins are not cause for concern at today's concentrations in Norwegian fish (VKM 2014a). Fatty fish was mainly represented by farmed salmon, where the levels of PCBs and dioxins have decreased since the feed were changed from almost only fish to consist mostly of vegetable oils. Nevertheless, concentrations of dioxins and dioxin-like PCBs have been reported to be of concern in Greenlandic halibut caught outside Lofoten, North-West Norway, which is close to the sample area in the present study (van der Meeren et al. 2014). Hence, it is still important to assess the concentrations of these chemicals in benthic fish species and their POP load, with regards to human exposure.

Conclusion

The concentrations of legacy POPs and PFAS measured in both shrimp and halibut are comparable to other studies conducted elsewhere in the Arctic. This would indicate that a major town like Tromsø, with associated port facilities and shipping, is not contributing significantly to the POPs burden observed in these species. This is perhaps less clear for PFAS, as levels of PFOS and PFAAs were higher in the shrimp compared to halibut filets. However, this may reflect the higher protein content in these tissues or a direct uptake of PFAS from the water into the shrimps. This is also a reflection of the different contamination pathways for PFAS compounds compared to older legacy POPs, like PCBs. We recommend that protein content of food items be analysed and included when PFAS concentrations are discussed, akin to lipids or extracted organic matter for legacy POPs.

The significantly higher levels of PBDEs, PCBs, OCs in the halibut compared to the shrimp are indicative of the biomagnification of these compounds, reflecting the longevity and higher trophic level status of this organism compared to the shrimp. PFOS was significantly higher in shrimps than in halibut, which may reflect the higher protein content in shrimps The overall concentrations of POPs, including the dioxin-like PCBs, as well as PFAS were well below the European guidelines for human consumption in shrimps and halibut and human dietary exposure through moderate consumption of these organisms falls within TDIs or benchmark doses. Filets from larger and older halibuts may contain higher POP concentrations, although these concentrations are not a cause for concern with regards to human consumption. The extensive data on POPs presented in this paper provide input to models of human exposure to POPs in northern Norway.

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References

AMAP (2003) AMAP Assessment 2002: The Influence of Global Change on Contaminant Pathways to, within and from the Arctic. Oslo, Norway

AMAP (2011a) Combined Effects of Selected Pollutants and Climate Change in the Arctic Environment. Oslo, Norway

AMAP (2011b) Snow, Water, Ice and Permafrost in the Arctic (SWIPA): Climate Change and the Cryosphere. Oslo, Norway
ArcRisk (2014) Arctic Health Risks: Impacts on health in the Arctic and Europe owing to climate-induced changes in contaminant cycling. 2014-10-12
Bergsten C (2014) Norwegian fish- and game study, part B. Norwegian Food Safety Authority. Accessed 2014-11-17
Boon JP et al. (2002) Levels of Polybrominated Diphenyl Ether (PBDE) Flame Retardants in Animals Representing Different Trophic Levels of the North Sea Food Web Environ Sci Technol 36:4025-4032
Browne EP, Stapleton HM, Kelly SM, Tilton SC, Gallagher EP (2009) In vitro hepatic metabolism of 2,2 ',4,4 ',5-pentabromodiphenyl ether (BDE 99) in Chinook Salmon (Onchorhynchus tshawytscha) Aquatic Toxicology 92:281-287 doi:10.1016/j.aquatox.2009.02.017
BSEF (2013) Bromine Science and Environmental Forum. Bromine Science and Environmental Forum, www.bsef.com. Accessed 2013-05-25 2013
Bustnes JO, Borgå K, Dempster T, Lie E, Nygård T, Uglem I (2012) Latitudinal Distribution of Persistent Organic Pollutants in Pelagic and Demersal Marine Fish on the Norwegian Coast Environ Sci Technol 46:7836-7843 doi:10.1021/es301191t
Butt CM, Berger U, Bossi R, Tomy GT (2010) Levels and trends of poly- and perfluorinated compounds in the arctic environment Sci Total Environ 408:2936-2965 doi:10.1016/j.scitotenv.2010.03.015
Carlsson P (2013) Selective processes for bioaccumulative up-take of persistent organic pollutants (POPs) in Arctic food webs. UiT The Arctic University of Norway and University Centre in Svalbard (UNIS)
Carlsson P, Herzke D, Kallenborn R (2014a) Enantiomer-Selective and Quantitative Trace Analysis of Selected Persistent Organic Pollutants (POP) in Traditional Food from Western Greenland Journal of Toxicology and Environmental Health, Part A 77:616-627 doi:10.1080/15287394.2014.887425
Carlsson P, Herzke D, Kallenborn R (2014b) Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and perfluorinated alkylated substances (PFASs) in traditional sea-food items from western Greenland Environ Sci Pollut Res 21:4741-4750 doi:10.1007/s11356-013-2435-x
Carlsson P, Herzke D, Wedborg M, Gabrielsen GW (2011) Environmental pollutants in the Swedish marine ecosystem, with special emphasis on polybrominated diphenyl ethers (PBDE) Chemosphere 82:1286-1292 doi:10.1016/j.chemosphere.2010.12.029
Crosse JD, Shore RF, Wadsworth R, Jones KC, Pereira MG (2012) Long term trends in PBDEs in sparrowhawk (Accipiter nisus) eggs indicate sustained contamination of UK terrestrial ecosystems Environ Sci Technol 46:13504-13511 doi:10.1021/es303550f
Darnerud PO, Atuma S, Aune M, Bjerselius R, Glynn A, Grawé KP, Becker W (2006) Dietary intake estimations of organohalogen contaminants (dioxins, PCB, PBDE and chlorinated pesticides, e.g. DDT) based on Swedish market basket data Food and Chemical Toxicology 44:1597-1606
EFSA (2011) Scientific Opinion on Polybrominated Diphenyl Ethers (PBDEs) in Food vol 2012, 9(5) edn. European Food Safety Authority. doi:10.2903/j.efsa.2011.2156
EFSA (2012) Perfluoroalkylated substances in food: occurrence and dietary exposure vol 2012, 10(6) edn. European Food Safety Authority. doi:10.2903/j.efsa.2012.2743
Eriksson U, Kärrman A, Rotander A, Mikkelsen B, Dam M (2013) Perfluoroalkyl substances (PFASs) in food and water from Faroe Islands Environ Sci Pollut Res:1-9 doi:10.1007/s11356-013-1700-3
EUR-Lex (2011) http://eur-lex.europa.eu/. European Union, accessed September 2013,
European Union (2010) Commission Regulation (EU) No 757/2010.
European Union (2011) Commission Regulation (EU) No. 1259/2011.
Hammer Ø, Harper DAT, Ryan PD (2001) PAST: Paleontological statistics software package for education and data analysis Palaeontologia Electronica 4:9pp doi:http://palaeo-electronica.org/2001_1/past/issue1_01.htm
Hanssen L, Dudarev AA, Huber S, Odland JØ, Nieboer E, Sandanger TM (2013) Partition of perfluoroalkyl substances (PFASs) in whole blood and plasma, assessed in maternal and umbilical cord samples from inhabitants of arctic Russia and Uzbekistan Sci Total Environ 447:430-437 doi:http://dx.doi.org/10.1016/j.scitotenv.2013.01.029
Haukås M, Berger U, Hop H, Gulliksen B, Gabrielsen GW (2007) Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web Environmental Pollution 148:360-371
Herzke D, Nygard T, Berger U, Huber S, Rov N (2009) Perfluorinated and other persistent halogenated organic compounds in European shag (*Phalacrocorax aristotelis*) and common eider (*Somateria mollissima*) from Norway: A suburban to remote pollutant gradient Sci Total Environ 408:340-348 doi:10.1016/j.scitotenv.2009.08.048
Herzke D, Olsson E, Posner S (2012) Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study Chemosphere 88:980-987 doi:10.1016/j.chemosphere.2012.03.035

Hoekstra PF, Hara TMO, Karlsson H, Solomon KR, Muir DCG (2003) Enantiomer-specific biomagnification of α-Hexachlorocyclohexane and selected chiral chlordane-related compounds within an arctic marine food web Environ Toxicol Chem 22:2482-2491 doi:10.1897/02-459
Christensen JH, Glasius M, Pecseli M, Platz J, Pritzl G (2002) Polybrominated diphenyl ethers (PBDEs) in marine fish and blue mussels from southern Greenland Chemosphere 47:631-638 doi:10.1016/s0045-6535(02)00009-7
IMR (2014). 2014-06-03
Jacobsen BK, Eggen AE, Mathiesen EB, Wilsgaard T, Njølstad I (2012) Cohort profile: The Tromsø Study International Journal of Epidemiology 41:961-967 doi:10.1093/ije/dyr049
Jörundsdóttir HÓ, Baldursdóttir V, Desnica N, Ragnarsdóttir Þ, Gunnlaugsdóttir H (2012) Undesirable substances in seafood products – results from the Icelandic marine monitoring activities in the year 2011. Matis - Food Research, Innovation & Safety, Reykjavik, Iceland. doi:ISSN: 1670-7192
Kallenborn R, Halsall C, Dellong M, Carlsson P (2012) The influence of climate change on the global distribution and fate processes of anthropogenic persistent organic pollutants Journal of Environmental Monitoring 14:2854-2869 doi:10.1039/c2em30519d
Kiviranta H, Ovaskainen ML, Vartiainen T (2004) Market basket study on dietary intake of PCDD/Fs, PCBs, and PBDEs in Finland Environ Int 30:923-932 doi:10.1016/j.envint.2004.03.002
Klenow S, Heinemeyer G, Brambilla G, Dellatte E, Herzke D, de Voogt P (2013) Dietary exposure to selected perfluoroalkyl acids (PFAAs) in four European regions Food Additives & Contaminants: Part A 30:2141-2151 doi:10.1080/19440049.2013.849006
La Guardia MJ, Hale RC, Harvey E (2006) Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures Environ Sci Technol 40:6247-6254 doi:10.1021/es060630m
Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A (2007) Perfluoroalkyl Acids: A Review of Monitoring and Toxicological Findings Toxicol Sci 99:366-394
Luo X-J, Zeng Y-H, Chen H-S, Wu J-P, Chen S-J, Mai B-X (2013) Application of compound-specific stable carbon isotope analysis for the biotransformation and trophic dynamics of PBDEs in a feeding study with fish Environmental Pollution 176:36-41 doi:http://dx.doi.org/10.1016/j.envpol.2013.01.025
Martin JW, Mabury SA, Solomon KR, Muir DCG (2003) Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss) Environ Toxicol Chem 22:196-204
Munschy C, Héas-Moisan K, Tixier C, Olivier N, Gastineau O, Le Bayon N, Buchet V (2011) Dietary exposure of juvenile common sole (Solea solea L.) to polybrominated diphenyl ethers (PBDEs): Part 1. Bioaccumulation and elimination kinetics of individual congeners and their debrominated metabolites Environmental Pollution 159:229-237 doi:http://dx.doi.org/10.1016/j.envpol.2010.09.001
NIFES (2014) Seafod data. The National Institute of Nutrition and Seafood Research (NIFES). 2014-12-01
Nilsen BM, Frantzen S, Julshamn K (2011) Fremmedstoffer i Villfisk med vekt på Kystnære Farvann -En undersøkelse av innholdet av dioksiner og dioksinlignende PCB i torskelever fra 15 fjorder og havner langs norskekysten.
Norwegian Environment Agency (2013) Perfluorinated alkylated substances, brominated flame retardants and chlorinated paraffins in the Norwegian Environment - Screening 2013 vol M40/2013. Norwegian Environment Agency,,
Roberts SC, Noyes PD, Gallagher EP, Stapleton HM (2011) Species-Specific Differences and Structure−Activity Relationships in the Debromination of PBDE Congeners in Three Fish Species Environ Sci Technol 45:1999-2005 doi:10.1021/es103934x
Sørmo EG, Jenssen BM, Lie E, Skaare JU (2009) Brominated flame retardants in aquatic organisms from the North Sea in comparison with biota from the high Arctic marine environment Environ Toxicol Chem 28:2082-2090
Stapleton HM, Letcher RJ, Baker JE (2004) Debromination of Polybrominated Diphenyl Ether Congeners BDE 99 and BDE 183 in the Intestinal Tract of the Common Carp (Cyprinus carpio) Environ Sci Technol 38:1054-1061 doi:10.1021/es0348804
Stock NL, Furdui VI, Muir DCG, Mabury SA (2007) Perfluoroalkyl Contaminants in the Canadian Arctic: Evidence of Atmospheric Transport and Local Contamination Environ Sci Technol 41:3529-3536 doi:10.1021/es062709x
Stockholm Convention (2013) http://chm.pops.int/default.aspx. Secretariat of the Stockholm Convention. Accessed 2014-11-02 2014
Sturludottir E, Gunnlaugsdottir H, Jorundsdottir HO, Magnusdottir EV, Olafsdottir K, Stefansson G (2014) Temporal trends of contaminants in cod from Icelandic waters Sci Total Environ 476–477:181-188 doi:http://dx.doi.org/10.1016/j.scitotenv.2014.01.005

Törnkvist A, Glynn A, Aune M, Darnerud PO, Ankarberg EH (2011) PCDD/F, PCB, PBDE, HBCD and chlorinated pesticides in a Swedish market basket from 2005-Levels and dietary intake estimations Chemosphere 83:193-199 doi:10.1016/j.chemosphere.2010.12.042
Van den Berg M et al. (2006) The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds Toxicol Sci 93:223-241 doi:10.1093/toxsci/kfl055
van der Meeren GI et al. (2014) Forvaltningsplan Barentshavet – rapport fra overvåkingsgruppen 2014. Fisken og havet, special ed. 1b-2014. 115p.
VKM (2006) A comprehensive assessment of fish and other seafood in the Norwegian diet. Norwegian Scientific Committee for Food Safety, www.vkm.no
VKM (2014a) Benefit-risk assessment of fish and fish products in the Norwegian diet –an update. Scientific Opinion of the Scientific Steering Committee vol 15. Norwegian Scientific Committee for Food Safety (VKM), Oslo, Norway. doi:ISBN 978-82-8259-159-1
VKM (2014b) Norwegian Scientific Committee for Food Safety. Accessed 2014-03-19
Xie S, Wang T, Liu S, Jones KC, Sweetman AJ, Lu Y (2013) Industrial source identification and emission estimation of perfluorooctane sulfonate in China Environ Int 52:1-8 doi:10.1016/j.envint.2012.11.004
Zeng Y-H, Luo X-J, Chen H-S, Yu L-H, Chen S-J, Mai B-X (2012) Gastrointestinal absorption, metabolic debromination, and hydroxylation of three commercial polybrominated diphenyl ether mixtures by common carp Environ Toxicol Chem 31:731-738 doi:10.1002/etc.1716