Perfluoroalkyl acids (PFAAs) and selected precursors in the Baltic Sea environment: do precursors play a role in food web accumulation of PFAAs?

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SUPPORTING INFORMATION

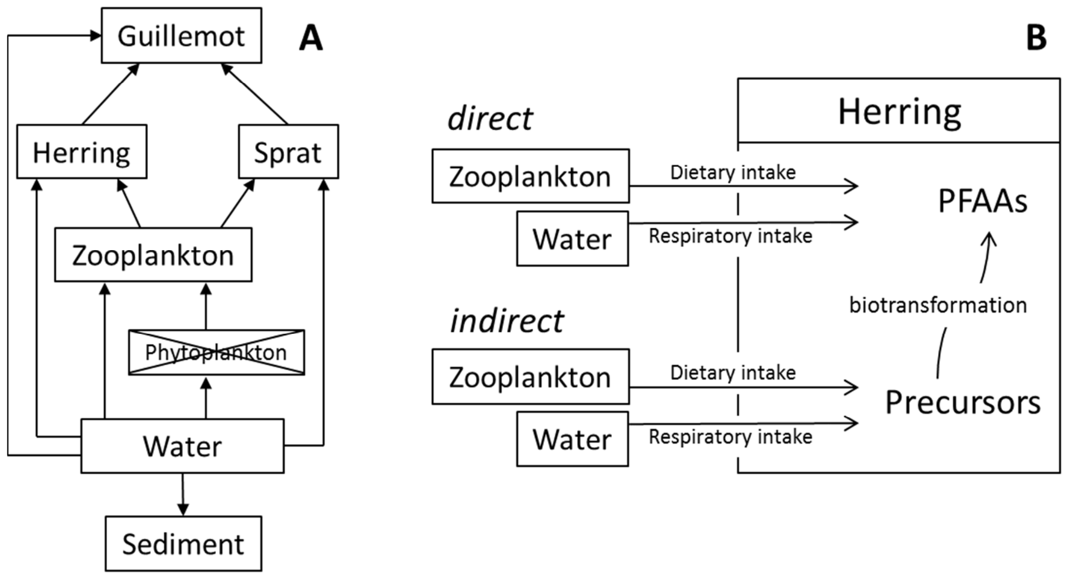

Figure S1. Simplified schematic of the Baltic Sea guillemot food web and possible intake exposure pathways for PFAAs and precursors for species in this food web (phytoplankton was not included in the present study) (A), and schematic of direct and indirect (precursor) exposure to total PFAAs, exemplified for herring (B).

Table S1. Target compounds and selected instrumental parameters for quantification of each compound by UPLC/ESI¯MS/MS.

Compound[1]	Supplier	Precursor > product ion (m/z)[2]	Cone voltage (V)	Collision energy (eV)	Internal standard used[3]
PFBS	Wellington	299 > 80	45	30	$^{13}C_2$-PFHxA
PFHxS	Wellington	399 > 80	55	36	$^{18}O_2$-PFHxS
Br-PFOS	Wellington	499 > 99 (80)	65	40	$^{13}C_4$-PFOS
L-PFOS	Wellington	499 > 99 (80)	65	40	$^{13}C_4$-PFOS
PFDS	Wellington	599 > 80	80	46	$^{13}C_2$-PFUnDA
FOSA	Wellington	498 > 78 (478)	8	28	$^{13}C_8$-FOSA
MeFOSA	3M	512 > 169 (219)	44	28	d_3-MeFOSA
EtFOSA	3M	526 > 169 (219)	32	28	d_5-EtFOSA
FOSAA	Wellington	556 > 498 (419)	8	26	d_3-MeFOSAA
MeFOSAA	Wellington	570 > 419 (483)	8	20	d_3-MeFOSAA
EtFOSAA	Wellington	584 > 419 (526)	8	22	d_5-EtFOSAA
PFHxA	Wellington	313 > 269	20	10	$^{13}C_2$-PFHxA
PFHpA	Wellington	363 > 319	21	11	$^{13}C_4$-PFHpA
PFOA	Wellington	413 > 369	22	11	$^{13}C_4$-PFOA
PFNA	Wellington	463 > 419	24	11	$^{13}C_5$-PFNA
PFDA	Wellington	513 > 469	26	11	$^{13}C_2$-PFDA
PFUnDA	Wellington	563 > 519	28	11	$^{13}C_2$-PFUnDA
PFDoDA	Wellington	613 > 569	30	12	$^{13}C_2$-PFDoDA
PFTrDA	Wellington	663 > 619	32	12	$^{13}C_2$-PFDoDA
PFTeDA	Wellington	713 > 669	35	12	$^{13}C_2$-PFDoDA
PFPeDA[4]		763 > 719	35	12	$^{13}C_2$-PFDoDA
4:2/4:2 diPAP	Xenia Trier[5]	589 > 343 (97)	20	16	$^{13}C_4$-6:2/6:2 diPAP
4:2/6:2 diPAP	Zonyl-RP[6]	689 > 443 (343)	20	28	$^{13}C_4$-6:2/6:2 diPAP
6:2/6:2 diPAP	Wellington	789 > 443 (97)	20	20	$^{13}C_4$-6:2/6:2 diPAP
6:2/8:2 diPAP	Wellington	889 > 443 (543)	14	32	$^{13}C_4$-6:2/6:2 diPAP
8:2/8:2 diPAP	Wellington	989 > 543 (97)	16	24	$^{13}C_4$-8:2/8:2 diPAP
6:2/10:2 diPAP	Zonyl-RP[7]	989 > 443 (643)	16	22	$^{13}C_4$-8:2/8:2 diPAP
8:2/10:2 diPAP	Zonyl-RP[7]	1089 > 543 (643)	20	28	$^{13}C_4$-8:2/8:2 diPAP
6:2/12:2 diPAP	Zonyl-RP[7]	1089 > 443 (743)	20	26	$^{13}C_4$-8:2/8:2 diPAP
10:2/10:2 diPAP	Chiron	1189 > 643 (97)	50	28	$^{13}C_4$-8:2/8:2 diPAP
8:2/12:2 diPAP	Zonyl-RP[8]	1189 > 543 (743)	50	28	$^{13}C_4$-8:2/8:2 diPAP
6:2/14:2 diPAP	Zonyl-RP[8]	1189 > 443 (843)	50	28	$^{13}C_4$-8:2/8:2 diPAP
$^{13}C_8$-PFOA[9]	Wellington	421 > 376	22	11	
$^{13}C_8$-PFOS[9]	Wellington	507 > 80	65	42	

[1] Acronyms are according to Buck et al., 2011.
[2] Product ions in brackets were used as confirmation ions for PFOS precursors and diPAPs.
[3] All internal standards were purchased from Wellington Laboratories.
[4] PFPeDA is commercially not available, and was quantified using the PFTeDA calibration curve.
[5] 4:2/4:2 diPAP was donated by Dr Xenia Trier (National Food Institute, Denmark).
[6] 4:2/6:2 diPAP was identified using Zonyl-RP technical mixture; quantification was done using the 6:2/6:2 diPAP calibration curve.
[7] DiPAPs were identified using Zonyl-RP technical mixture; quantification was done using the 8:2/8:2 diPAP calibration curve.
[8] DiPAPs were identified using Zonyl-RP technical mixture; quantification was done using the 10:2/10:2 diPAP calibration curve.
[9] $^{13}C_8$-PFOA and $^{13}C_8$-PFOS were used as recovery internal standards.

Figure S2. Sampling location of sediment, water, zooplankton, herring, sprat, and guillemot eggs from the Baltic Sea (See Table S2 for sample information).

Table S2. Sampling location and sample information for sediment, water, zooplankton, herring, sprat, and guillemot eggs collected from the Baltic Sea.

Sampling site[1]	Location	Species	Sample type	n	Collection date
1	Landsort Island		Sediment	4	Summer 2013
2	Landsort Island		Water	4	Summer 2013
3	Landsort Island		Zooplankton	4	Summer 2014
4	Utlängen	Herring *Clupea harengus membras*	Whole body homogenate	10	Spring 2013
5	Utlängen	Sprat *Sprattus sprattus*	Whole body homogenate	10	Autumn 2013
6	Stora Karlsö	Guillemot *Uria aalge*	Egg homogenate	10	Spring 2013

[1] See Figure S1 for sampling location in the Baltic Sea.

Table S3. Body length (cm ± SE) and weight (g ± SE) information on herring and sprat collected from the Baltic Sea.

	Herring	Sprat
Number of individuals	10	10
Males	5	1
Females	5	9
Body length (cm) – all	16.3 ± 0.2	12.0 ± 0.1
Males	16.2 ± 0.3	11.6
Females	16.4 ± 0.3	12.0 ± 0.1
Body weight (g) – all	48.0 ± 2.7	17.6 ± 0.2
Males	48.2 ± 3.4	16.9
Females	47.8 ± 4.6	17.7 ± 0.2

Table S4. Mobile phase gradient program for FASAs (fraction 1) and PFSAs, PFCAs, and FASAAs (fraction 2).

Time	Mobile phase A (%)[1]	Mobile phase B (%)[2]
0.0	90	10
0.5	90	10
5.0	20	80
5.1	0	100
8.0	0	100
10.0	90	10

Note: Flow rate was 0.4 mL/min, column temperature was 40 °C, and injection volume was 5 µL.
[1] Mobile phase A: 95 % water and 5 % methanol containing 2 mM ammonium acetate and 5 mM 1-methyl piperidine (1-MP).
[2] Mobile phase B: 75 % methanol, 20 % acetonitrile, and 5 % water containing 2 mM ammonium acetate and 5 mM 1-methyl piperidine (1-MP).

Table S5. Mobile phase gradient program for mono- and diPAPs (fraction 2).

Time	Mobile phase A (%)[1]	Mobile phase B (%)[2]
0.0	80	20
4.0	0	100
6.0	0	100
7.5	80	20
9.0	80	20

Note: Flow rate was 0.3 mL/min, column temperature was 40 °C, and injection volume was 5 µL.
[1] Mobile phase A: 95 % water and 5 % methanol containing 2 mM ammonium acetate and 5 mM 1-methyl piperidine (1-MP).
[2] Mobile phase B: 75 % methanol, 20 % acetonitrile, and 5 % water containing 2 mM ammonium acetate and 5 mM 1-methyl piperidine (1-MP).

Table S6. Method quantification limit (MQLs) for individual PFASs in sediment (ng/g dw), water (ng/L), and biota (ng/g ww).

PFAS	Sediment	Water	Zooplankton	Herring	Sprat	Guillemot egg
PFBS	0.0001	0.04	0.002	0.01	0.06	0.00004
PFHxS	0.001	0.01	0.0005	0.02	0.01	0.002
br-PFOS	0.0002	0.1	0.02	0.3	0.2	0.2
l-PFOS	0.0001	0.03	0.02	0.6	0.3	0.003
PFDS	0.04	0.002	0.0003	0.0005	0.002	0.009
br-FOSA	0.001	0.001	0.007	0.01	0.01	0.003
l-FOSA	0.004	0.02	0.04	0.01	0.01	0.001
FOSAA	0.0001	0.1	0.0008	0.0001	0.0001	0.0001
MeFOSAA	0.0001	0.001	0.0001	0.0001	0.0002	0.0001
EtFOSAA	0.0001	0.001	0.0004	0.002	0.0004	0.0001
PFHxA	0.02	0.1	0.04	0.2	0.5	0.0004
PFHpA	0.006	0.1	0.1	0.01	0.01	0.001
PFOA	0.005	0.05	0.01	0.03	0.07	0.08
PFNA	0.005	0.02	0.05	0.01	0.02	0.004
PFDA	0.002	0.005	0.001	0.005	0.003	0.006
PFUnDA	0.004	0.001	0.008	0.005	0.002	0.003
PFDoDA	0.002	0.04	0.001	0.002	0.004	0.006
PFTrDA	0.001	0.02	0.004	0.001	0.0001	0.008
PFTeDA	0.001	0.03	0.1	0.0003	0.0001	0.002
PFPeDA	0.001	0.03	0.05	0.0005	0.0001	0.002
6:2/6:2 diPAP	0.0002	0.0001	0.0001	0.002	0.001	0.005
6:2/8:2 diPAP	0.003	0.02	0.0001	0.001	0.01	0.001
8:2/8:2 diPAP	0.0003	0.002	0.0001	0.001	0.01	0.05
6:2/10:2 diPAP	0.0001	0.003	0.0001	0.001	0.01	0.05
8:2/10:2 diPAP	0.0003	0.001	0.0001	0.003	0.003	0.006
6:2/12:2 diPAP	0.0001	0.001	0.0001	0.003	0.003	0.006
10:2/10:2 diPAP	0.001	0.01	0.0003	0.001	0.001	0.001
8:2/12:2 diPAP	0.001	0.001	0.0002	0.001	0.001	0.001
6:2/14:2 diPAP	0.001	0.001	0.0003	0.001	0.001	0.001

Table S7. Recoveries (mean ± SE) of labeled internal standards.

	Sediment	Water	Zooplankton	Herring	Sprat	Guillemot egg
$^{18}O_2$-PFHxS	78 ± 2	78 ± 2	83 ± 1	75 ± 2	69 ± 2	72 ± 1
$^{13}C_4$-PFOS	72 ± 2	54 ± 8	77 ± 1	75 ± 1	72 ± 1	72 ± 2
$^{13}C_8$-FOSA	62 ± 2	66 ± 6	83 ± 3	58 ± 2	52 ± 4	45 ± 6
d3-MeFOSA	51 ± 2	32 ± 3	70 ± 2	41 ± 2	45 ± 3	27 ± 3
d5-EtFOSA	60 ± 3	32 ± 2	62 ± 2	35 ± 1	38 ± 3	30 ± 1
d3-MeFOSAA	58 ± 2	35 ± 4	66 ± 2	72 ± 2	62 ± 2	77 ± 2
d5-EtFOSAA	59 ± 1	33 ± 3	69 ± 2	88 ± 2	62 ± 2	77 ± 1
$^{13}C_2$-PFHxA	74 ± 3	62 ± 2	73 ± 1	70 ± 1	96 ± 12	81 ± 1
$^{13}C_4$-PFHpA	83 ± 2	66 ± 1	83 ± 1	66 ± 3	61 ± 1	81 ± 1
$^{13}C_4$-PFOA	75 ±1	71 ± 3	78 ±1	76 ± 1	73 ± 2	79 ± 1
$^{13}C_5$-PFNA	76 ± 2	64 ± 8	78 ± 1	46 ± 3	45 ± 5	56 ± 1
$^{13}C_2$-PFDA	67 ± 2	46 ± 7	75 ± 1	63 ± 1	107 ± 11	69 ± 1
$^{13}C_2$-PFUnDA	62 ± 1	32 ± 3	71 ± 1	59 ± 1	87 ± 9	61 ± 1
$^{13}C_2$-PFDoDA	51 ± 2	27 ± 1	57 ± 1	85 ± 8	56 ± 6	55 ± 1
$^{13}C_4$-6:2/6:2 diPAP	68 ± 2	17 ± 1	157 ± 7	255 ± 18	108 ± 9	105 ± 4
$^{13}C_4$-8:2/8:2 diPAP	51 ± 2	26 ± 1	41 ± 1	97 ± 12	43 ± 4	30 ± 2

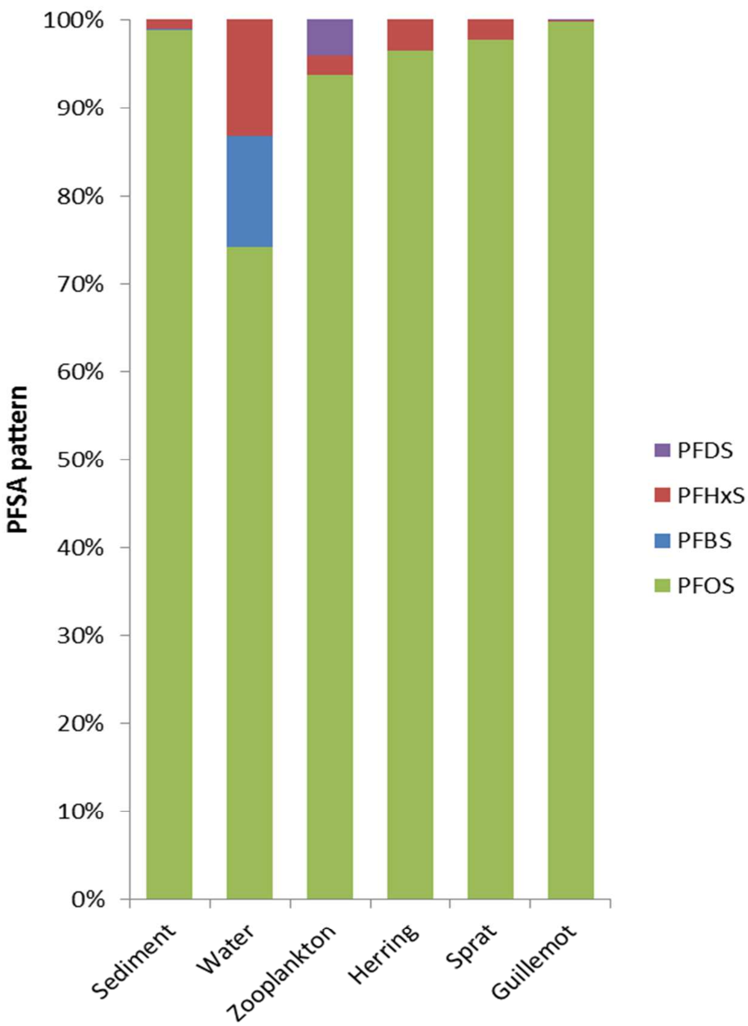

Figure S3. Relative abundance of detected perfluoroalkane sulfonic acids in sediment, water, and biota collected from the Baltic Sea.

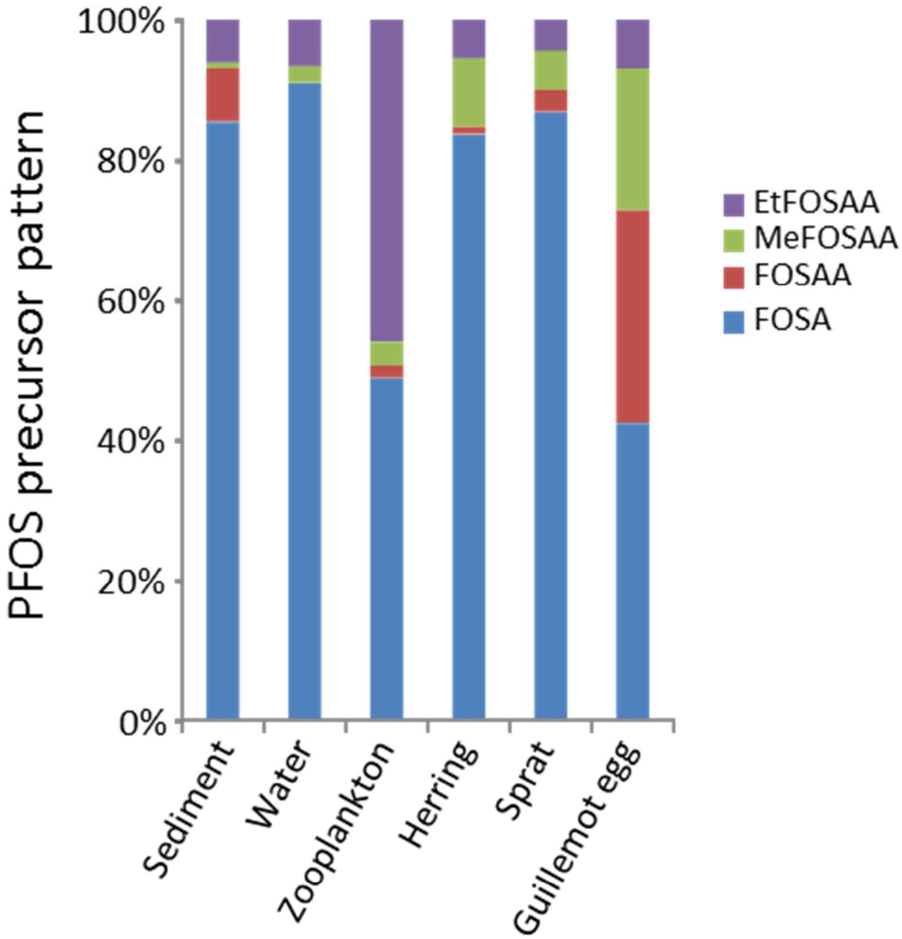

Figure S4. Relative abundance of detected PFOS precursors in sediment, water, and biota collected from the Baltic Sea.

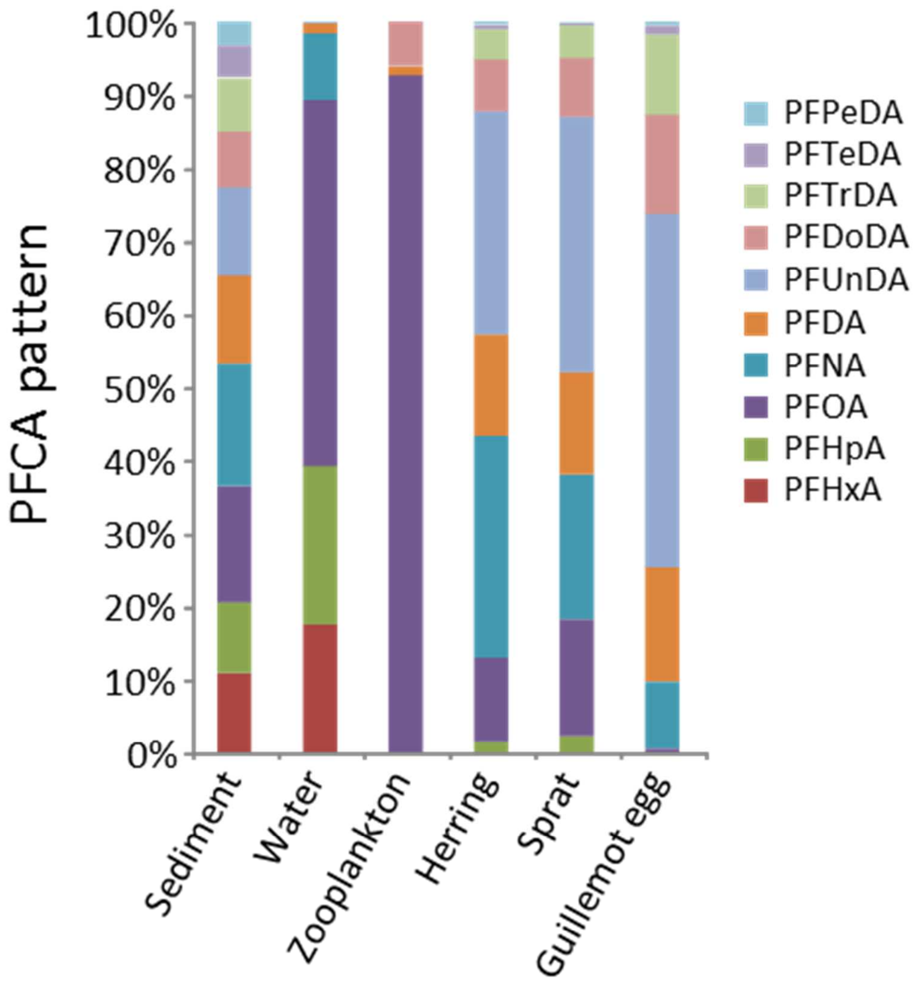

Figure S5. Relative abundance of detected perfluoroalkyl carboxylic acids in sediment, water, and biota collected from the Baltic Sea.

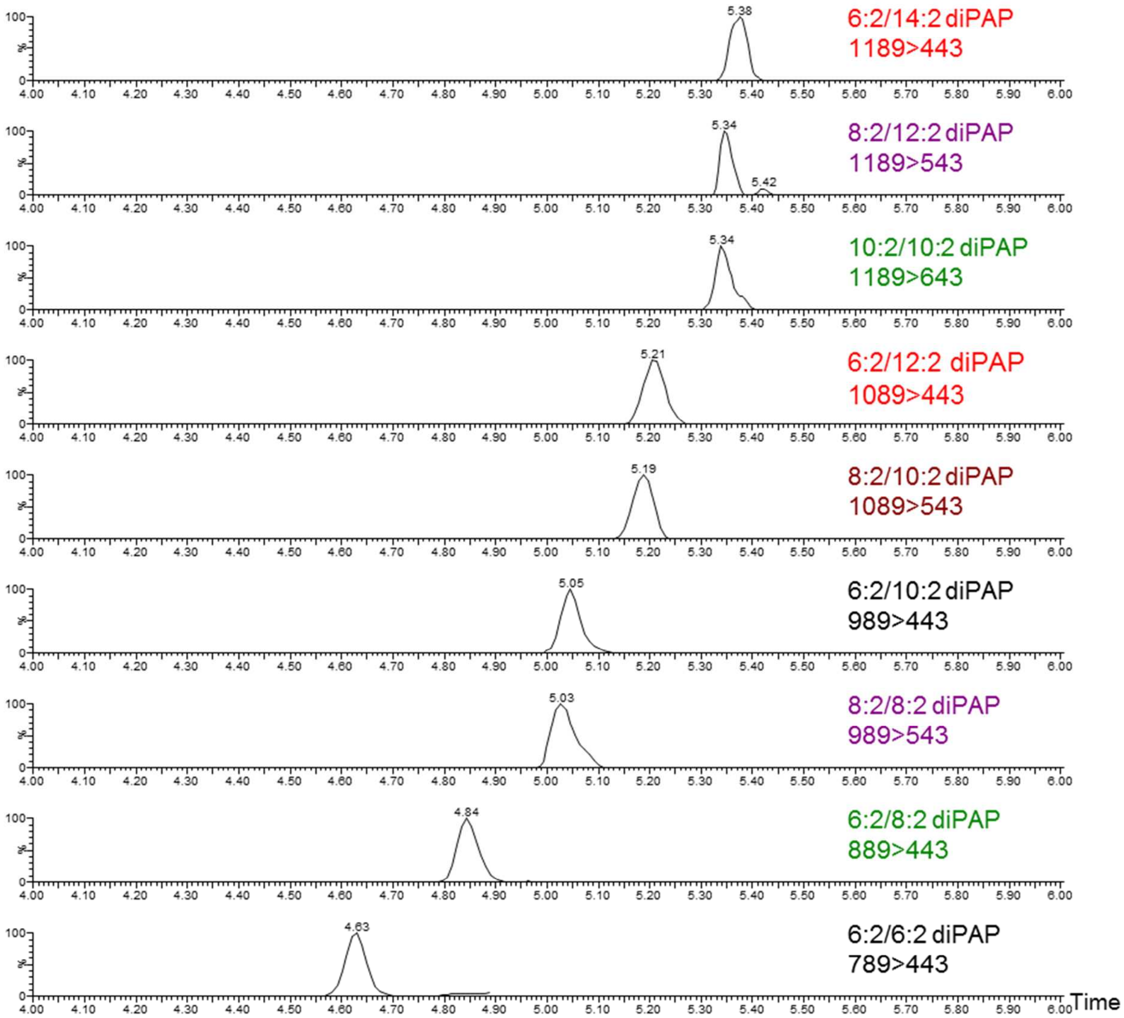

Figure S6. Chromatograms of detected diPAPs in zooplankton collected from the Baltic Sea.

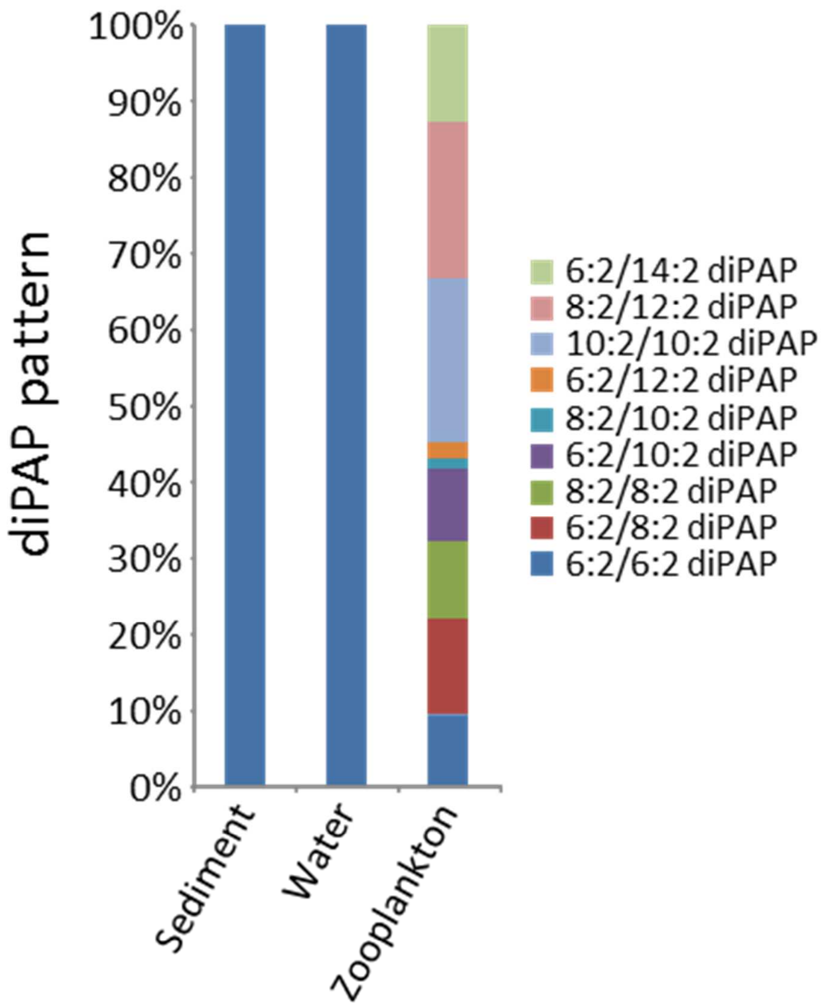

Figure S7. Relative abundance of detected diPAPs in sediment, water, and zooplankton collected from the Baltic Sea.

Table S8. Percent sum-branched and linear PFOS and FOSA isomers (average ± SE) in Baltic Sea sediment, water, zooplankton, herring, sprat, and guillemot eggs.

Sample type	% Br-PFOS	% L-PFOS	% Br-FOSA	% L-FOSA
Sediment	3.2 ± 0.4	96.8 ± 0.4	31.3 ± 6.8	68.7 ± 6.8
Water	49.7 ± 3.0	50.3 ± 3.0	36.5 ± 6.4	63.5 ± 6.4
Zooplankton	25.8 ± 5.5	74.2 ± 5.5	44.6 ± 7.9	55.4 ± 7.9
Herring	18.0 ± 0.8	82.0 ± 0.8	55.7 ± 3.6	44.3 ± 3.6
Sprat	12.3 ± 1.1	87.7 ± 1.1	49.4 ± 3.9	50.6 ± 3.9
Guillemot egg	18.3 ± 0.8	81.7 ± 0.8	66.9 ± 3.5	33.1 ± 3.5

Table S9. Field-based sediment/water distribution coefficient (log K_D ± SE) and biota/water bioaccumulation factors (log BAF ± SE) of individual PFASs detected in the Baltic Sea environment.

PFAS	Log K_D	Log BAF		
	Sediment/ water	Zooplankton/ water	Herring/ water	Sprat/ water
PFBS	0.26 (0.09)	<1.31	<2.01	<2.79
PFHxS	1.34 (0.05)	1.30 (0.13)	3.29 (0.08)	3.14 (0.02)
Br-PFOS	1.45 (0.07)	1.91 (0.18)	3.66 (0.04)	3.49 (0.04)
L-PFOS	2.94 (0.03)	2.47 (0.08)	4.32 (0.04)	4.35 (0.03)
tot-PFOS	2.65 (0.03)	2.26 (0.10)	4.11 (0.04)	4.11 (0.03)
Br-FOSA	2.33 (0.01)	3.38 (0.03)	3.86 (0.05)	3.74 (0.02)
L-FOSA	2.39 (0.08)	3.18 (0.14)	3.46 (0.06)	3.45 (0.07)
tot-FOSA	2.38 (0.06)	3.29 (0.07)	3.65 (0.05)	3.58 (0.05)
FOSAA	>1.12	>1.62	>1.41	>1.91
MeFOSAA	1.93 (0.02)	3.69 (0.01)	4.21 (0.09)	3.99 (0.03)
EtFOSAA	2.39 (0.03)	4.40 (0.06)	3.54 (0.08)	3.45 (0.03)
PFHxA	2.78 (0.01)	<2.32	<3.02	<3.41
PFHpA	2.63 (0.01)	<2.62	1.98 (0.09)	2.01 (0.06)
PFOA	2.49 (0.01)	2.30 (0.04)	2.34 (0.15)	2.52 (0.03)
PFNA	3.25 (0.01)	<2.70	3.58 (0.12)	3.35 (0.03)
PFDA	3.95 (0.01)	1.84 (0.24)	4.17 (0.08)	4.03 (0.04)
PFUnDA	4.72 (0.01)	<3.51	5.34 (0.04)	5.20 (0.04)
PFDoDA	>3.31	>2.46	>3.51	>3.35
PFTrDA	>3.59	n.d.	>3.56	>3.35
PFTeDA	>3.19	n.d.	>2.45	>1.89
PFPeDA	>3.05	n.d.	>2.35	>1.77
6:2/6:2 diPAP	1.37 (0.05)	2.29 (0.04)	<0.89	<0.59
6:2/8:2 diPAP	n.d.	>3.54	n.d.	n.d.
8:2/8:2 diPAP	n.d.	>4.45	n.d.	n.d.
6:2/10:2 diPAP	n.d.	>4.24	n.d.	n.d.
8:2/10:2 diPAP	n.d.	>3.87	n.d.	n.d.
6:2/12:2 diPAP	n.d.	>3.99	n.d.	n.d.
10:2/10:2 diPAP	n.d.	>4.04	n.d.	n.d.
8:2/12:2 diPAP	n.d.	>4.99	n.d.	n.d.
6:2/14:2 diPAP	n.d.	>4.79	n.d.	n.d.

n.d. - Log K_D or log BAF could not be estimated as concentrations in the two matrices were below method detection limit.
> - Concentration in water, zooplankton, herring, or sprat was below MQL, therefore the MQL was used for calculation of the K_D and BAF. These values represent a lower bound estimate of the true K_D and BAF.
< - Concentration in zooplankton, herring, or sprat was below MQL, therefore the MQL was used for calculation of the BAF. These values represent an upper bound estimate of the true BAF.