Nordic Council of Ministers

NordicScreening.org
Joint Nordic Screening of Chemicals

Screening of Poly- and perfluoroalkyl substances (PFASs) and extractable organic fluorine (EOF) in the Nordic Environment

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Objectives of the study

Screening of an extensive list of conventional and emerging PFASs, in a wide variety of environmental matrices from the Nordic countries

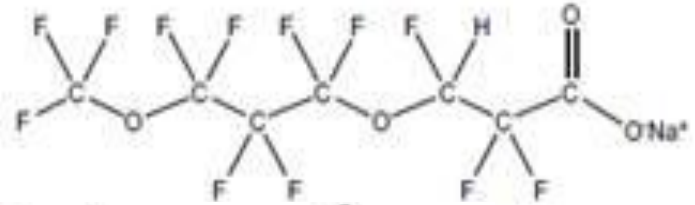
Measure extractable organic fluorine (EOF) in order to account for any unknown organofluorine compounds.

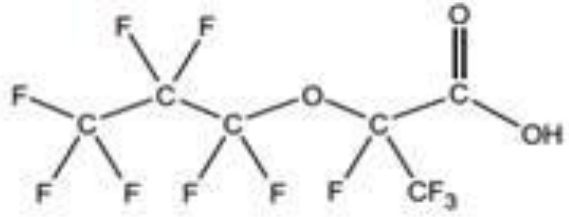
PFAS classes

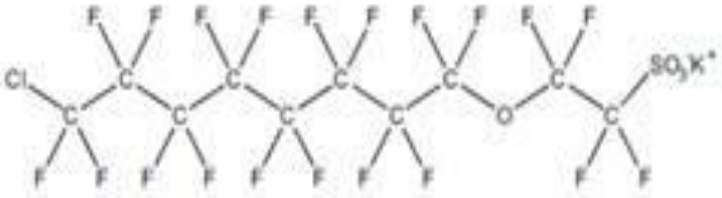
1) volatile PFASs (vPFASs),
2) ultra-short chain PFASs,
3) perfluoroalkyl carboxylic acids and sulfonic acids (PFCAs and PFSAs),
4) precursor compounds
5) perfluoroalkyl phosphonic and phosphinic acids (PFPA/PFPiAs),
6) novel PFASs

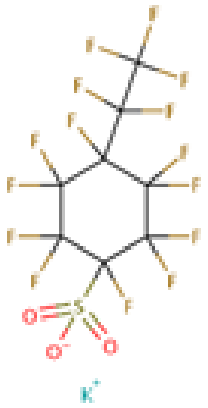
Novel PFAS

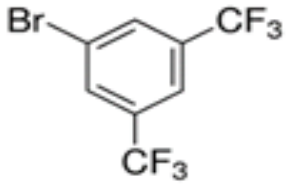
Name	Abbreviations	CAS
3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid]	ADONA	958445-44-8
Hexafluoropropylene oxide dimer acid	HFPO-DA GenX	62037-80-3
6:2 chlorinated polyfluorinated ether sulfonate	6:2 Cl-PFESA F-53B	73606-19-6
Perfluoro-4-ethylcyclohexanesulfonate	PFECHS	335-24-0 (potassium salt)
1,3-bis-(trifluoromethyl)-5-bromobenzene	BTFBB	328-70-1











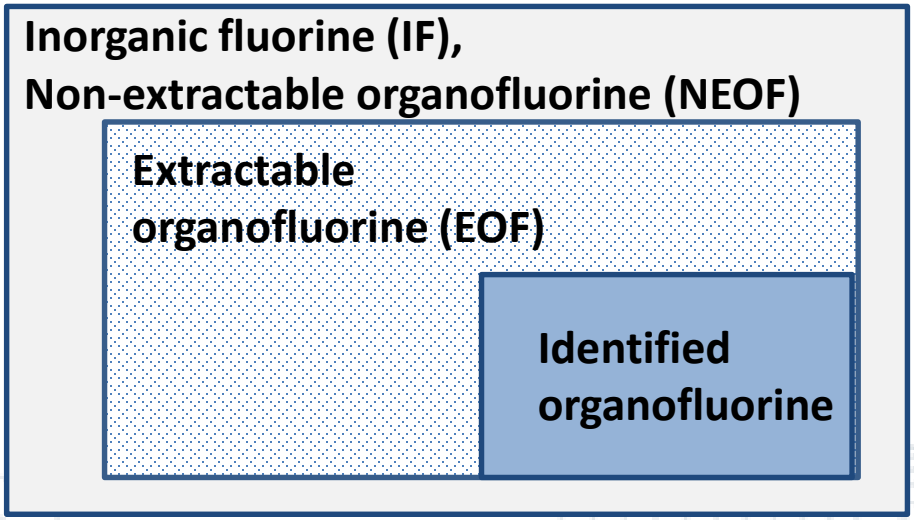
Extractable organofluorine

Total fluorine (TF) can be analyzed by combustion-ion chromatogrpahy

The TF content in a sample can be divided into:

Mass balance: EOF versus identified organofluorine

$$C_F = n_F \times \frac{MW_F}{MW_{PFAS}} \times C_{PFAS}$$



Samples

	Denmark	Faroe Island	Finland	Greenland	Iceland	Norway	Sweden
Bird eggs , whole egg(n=10)							
Black guillemot (*Cepphus grylle*)		1					
Northern fulmar (*Fulmarus glacialis*)		5					
Common guillemot (*Uria aalge*)					2		2
Marine fish liver (n=6)	2						
Greenland cod (*Gadus ogac*)				1			
Atlantic pollock (*Pollachius pollachius*)						1	
Herring (*Clupea)*							2
Fresh water fish liver (n=13)							
European perch (*Perca fluviatilis*)	2		3			1	2
Brown trout (*Salmo trutta*)		1			2		
Arctic char (*Salvelinus alpinus*)		1		1			
Marine mammal liver (n=12)							
Harbour porpoise (*Phocoena phocoena*)	1						
Gray seal (*Halichoerus grypus*)	1						
Pilot whale (*Globicephala melas*)		5					
Humpback whale (*Megaptera novaeangliae)*				1			
Ringed seal (*Pusa hispida*)				1			
White-beaked dolphin *(Lagenorhynchus albirostris)*				1			
Polar bear (*Ursus maritimus*)				2			
Terrestrial mammal liver (n=9)							
Brown bear (*Ursus arctos*)			1				
Reindeer (*Rangifer tarandus*)			2	2	2		2
Lake water (n=14)	2	2	2	2	2	2	2
WWTP effluent (n=14)	2	2	2	2	2	2	2
WWTP sludge (n=10)	2	2	2			2	2
Air (n=14)				3	6	3	2

Target Analytes in biota, water, sludge

ÖREBRO UNIVERSITY

PFAS∑74

Ultra-short chain (n=4)

PFEtS (C2), PFPrS (C3), TFA (C2), PFPrA (C3),

Perfluoroalkylsulfonic acids (PFSAs) (*n=10*)

PFBS (C4), PFPeS (C5), PFHxS (C6), PFHpS (C7), PFOS (C8), PFNS (C9), PFDS (C10), PFDoDS (C12)

Precursors of PFSAs (*n=5*)

FOSA, FOSAA, MeFOSAA, EtFOSAA, diSAmPAP

Perfluorinated phosphonic acids (PFPAs) (*n=3*)

PFHxPA (C6), PFOPA (C8), PFDPA (C10)

Perfluorinated phosphinic acids (PFPiAs) (*n=3*)

6:6, 6:8, 8:8 PFPiA

Perfluoroalkyl carboxylates (PFCAs) (*n=15*)

PFBA (C4), PFPeA (C5), PFHxA (C6), PFHpA (C7), PFOA (C8), PFNA (C9), PFDA (C10), PFUnDA (C11), PFDoDA (C12), PFTrDA (C13), PFTDA(C14), PFHxDA (C16), PFOcDA (C18)

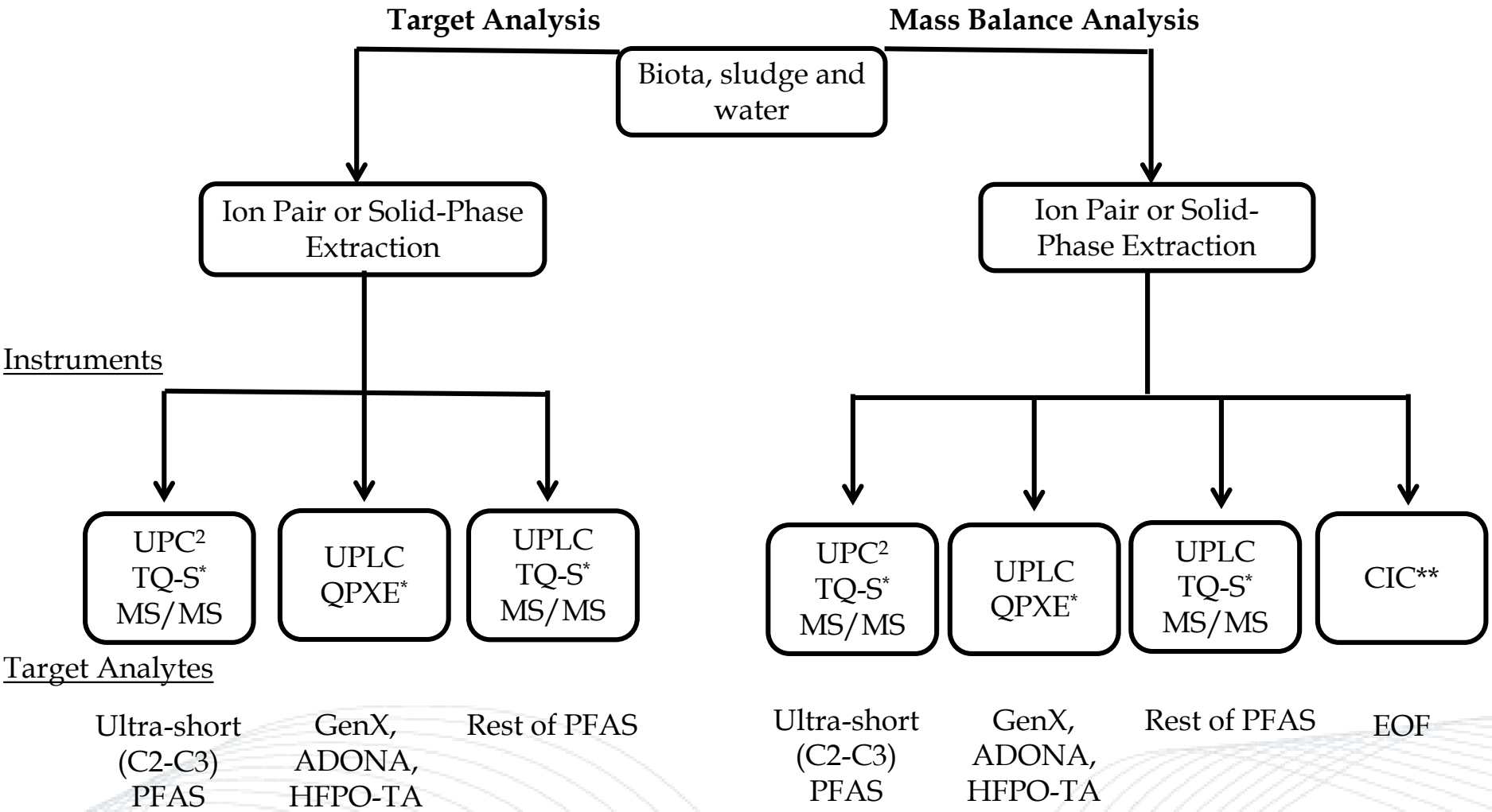
Precursors of PFCAs (*n=32*)

FTSAs (*n=3*), FTCAs (*n= 2*), FTUCAs (*n=3*), PAPs (*n=24*)

Novel PFASs (*n=6*)

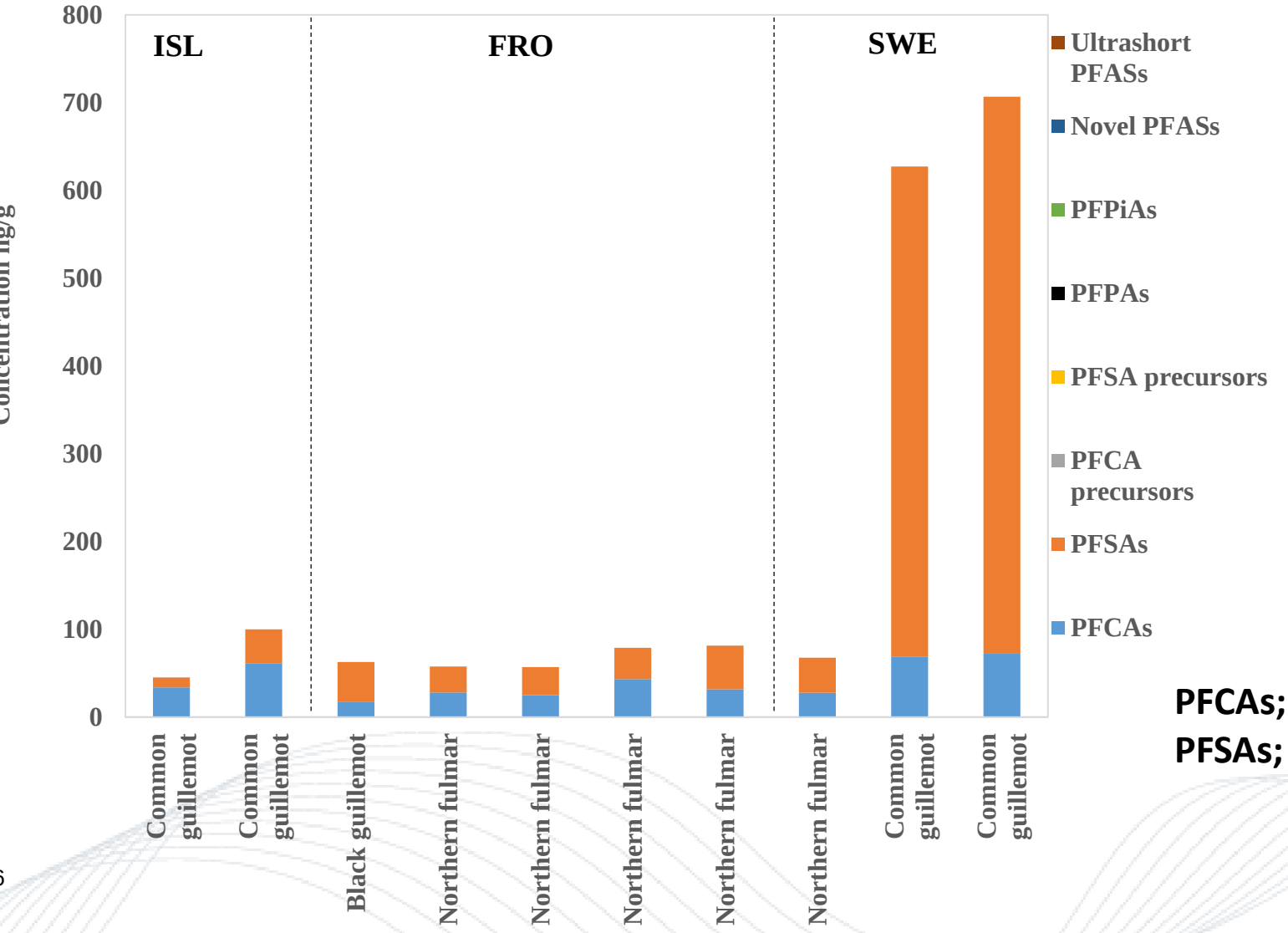
ADONA, HFPO-DA, HFPO-TA, F-53B, PFECHS

Analysis of biota, sludge and water



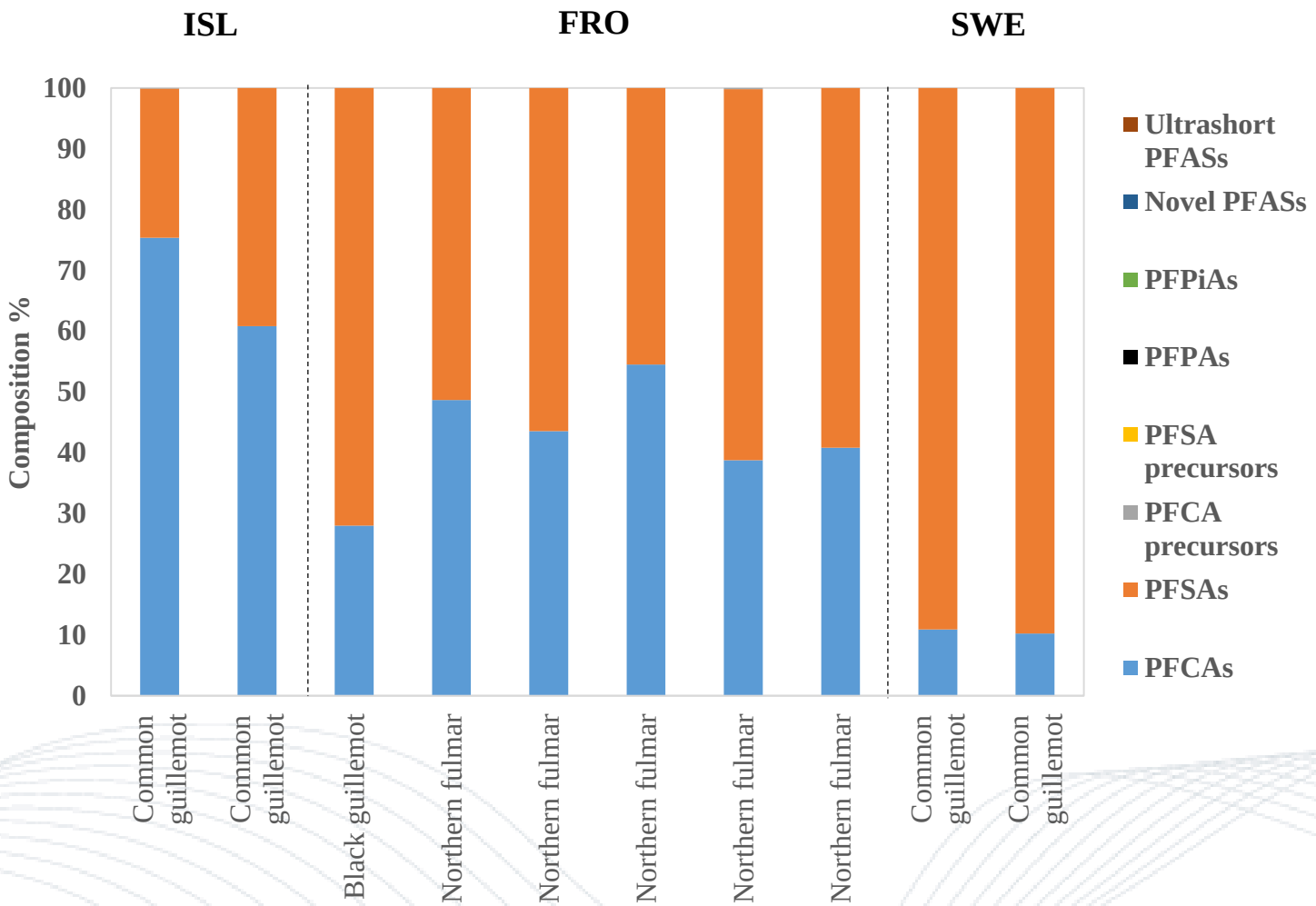
* Waters Corporation Milford, USA ** Metrohm

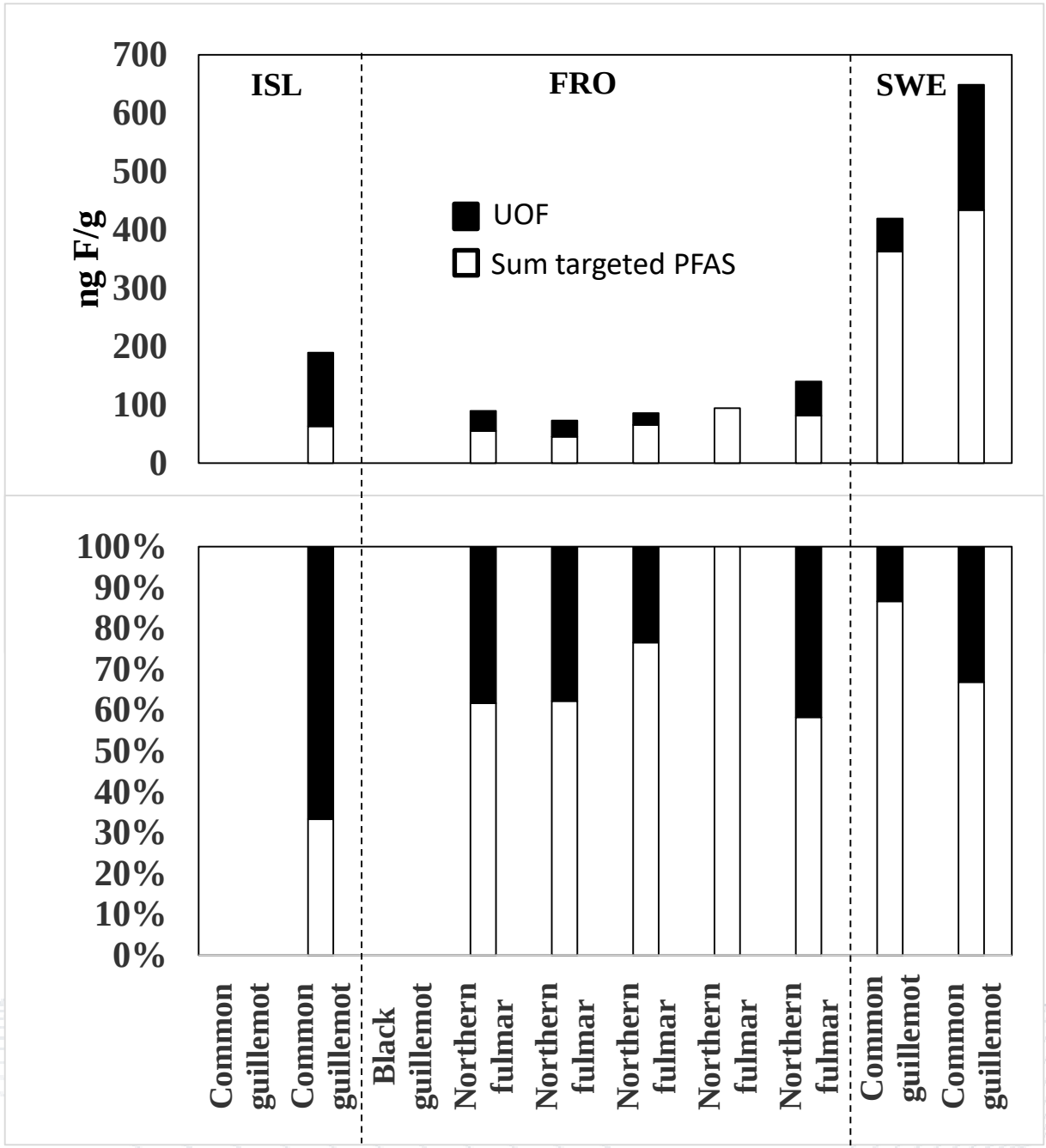
Bird eggs



PFCAs; PFUnDA, PFTrDA
PFSAs; PFOS

Bird eggs

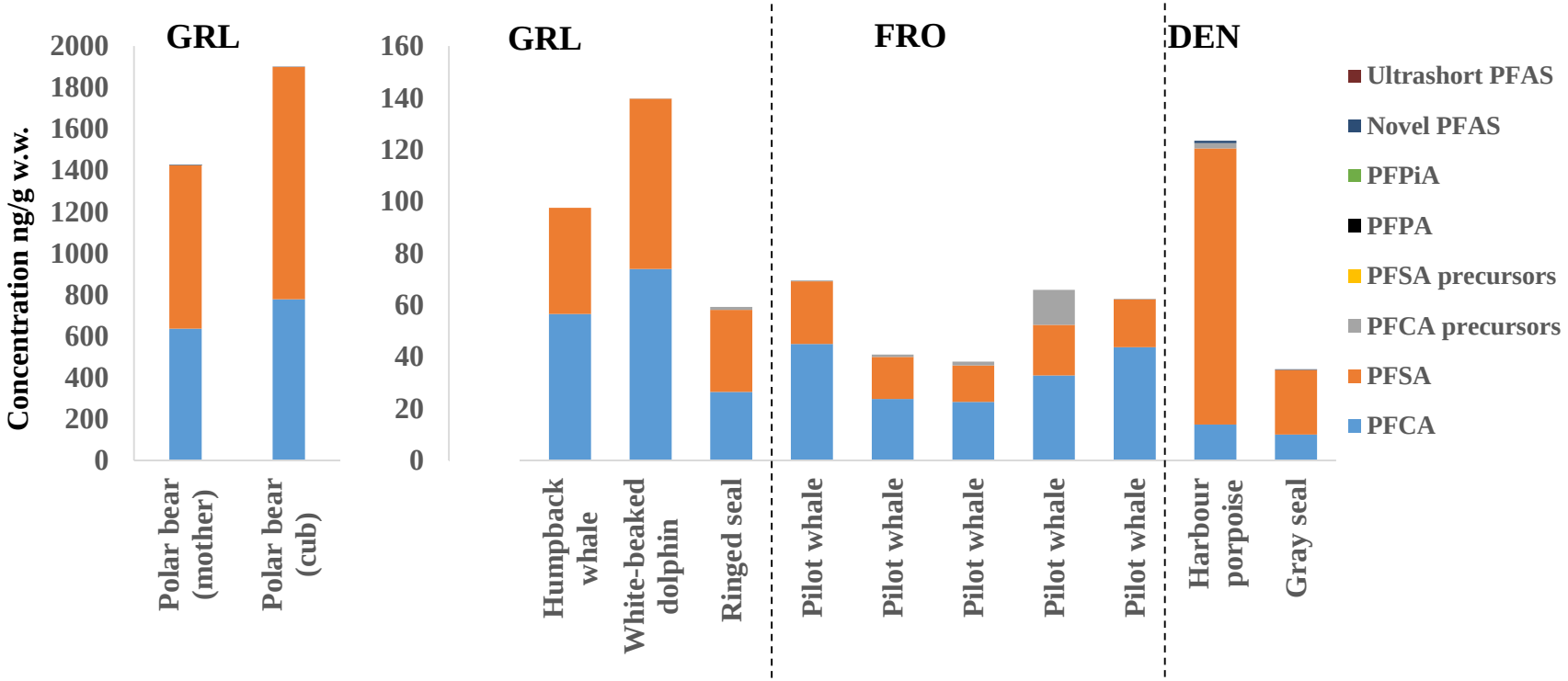

ISL
FRO
SWE
Composition %
100
90
80
70
60
50
40
30
20
10
0
Common guillemot
Common guillemot
Black guillemot
Northern fulmar
Northern fulmar
Northern fulmar
Northern fulmar
Northern fulmar
Common guillemot
Common guillemot
Ultrashort PFASs
Novel PFASs
PFPiAs
PFPAs
PFSA precursors
PFCA precursors
PFSAs
PFCAs



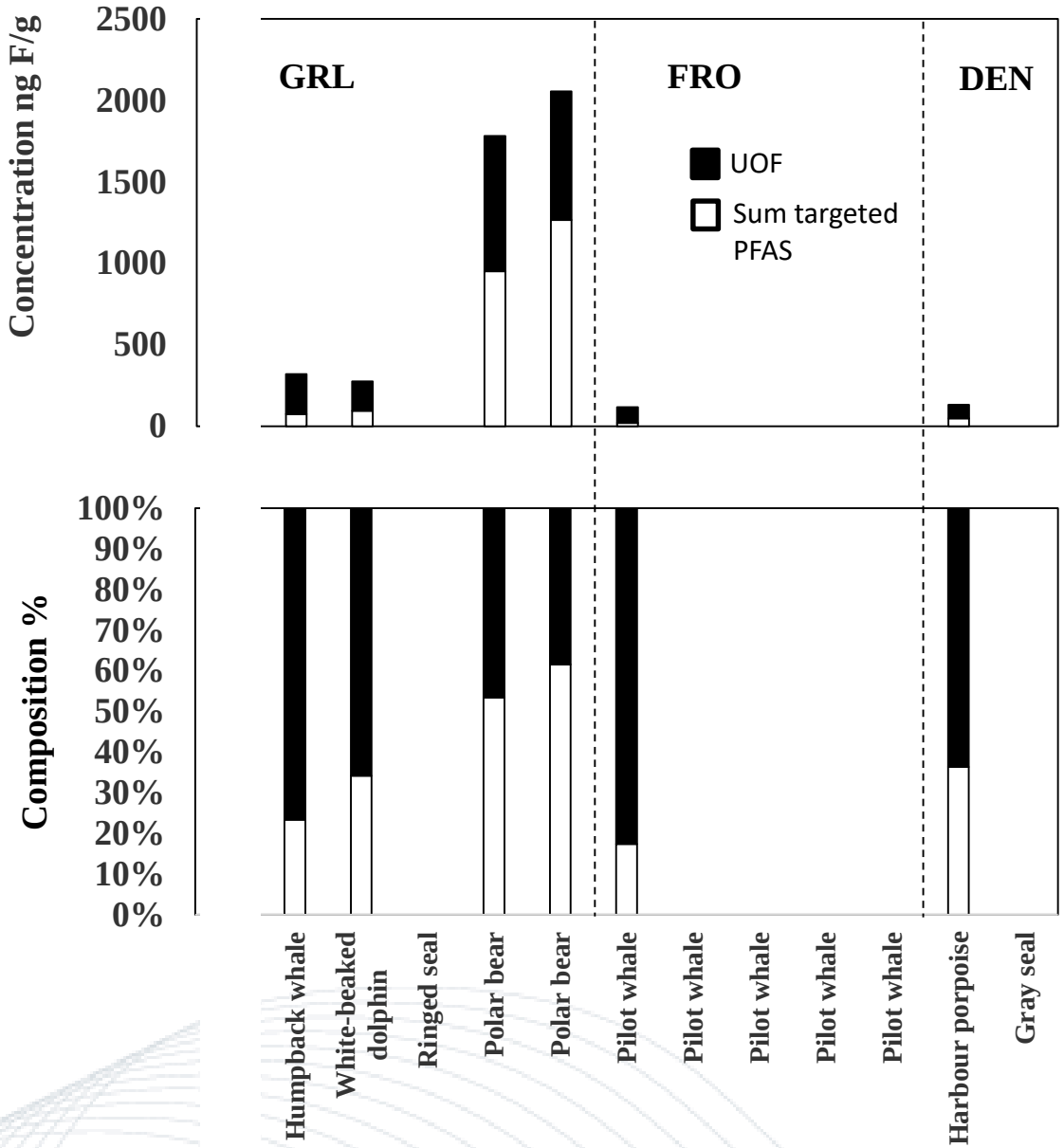
<40 – 649 ng F/g

67-87% SWE
58-102% FRO
33% ISL

Marine mammals



PFCAs; PFUnDA>PFNA>PFDA> PFTrDA (Polar bears; PFNA>PFDA
PFSAs; PFOS
Novel; PFECHS (DE)
PFCA precursors; 7:3 FTCA, 6:2 FTUCA, 6:2 diPAP

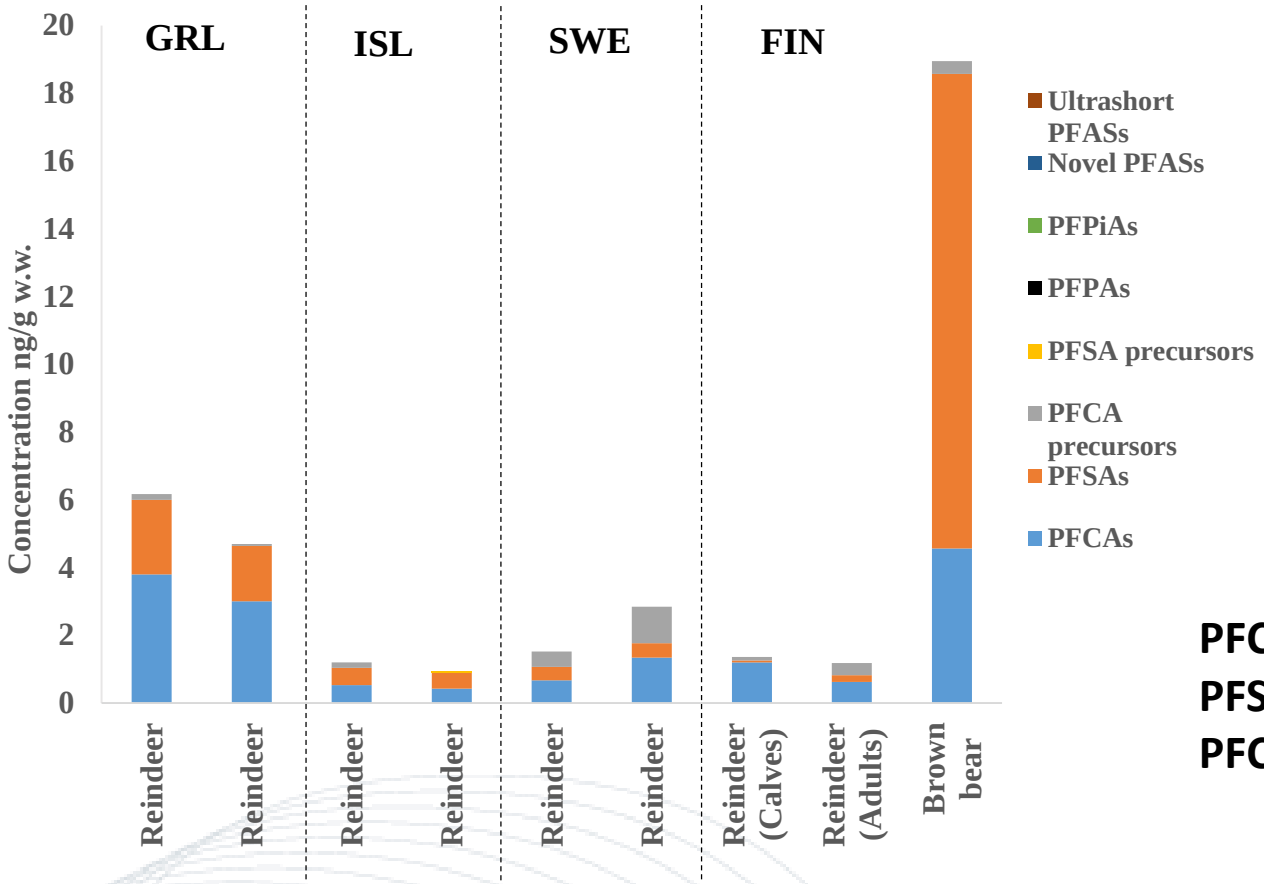


<40 – 2056 ng/g

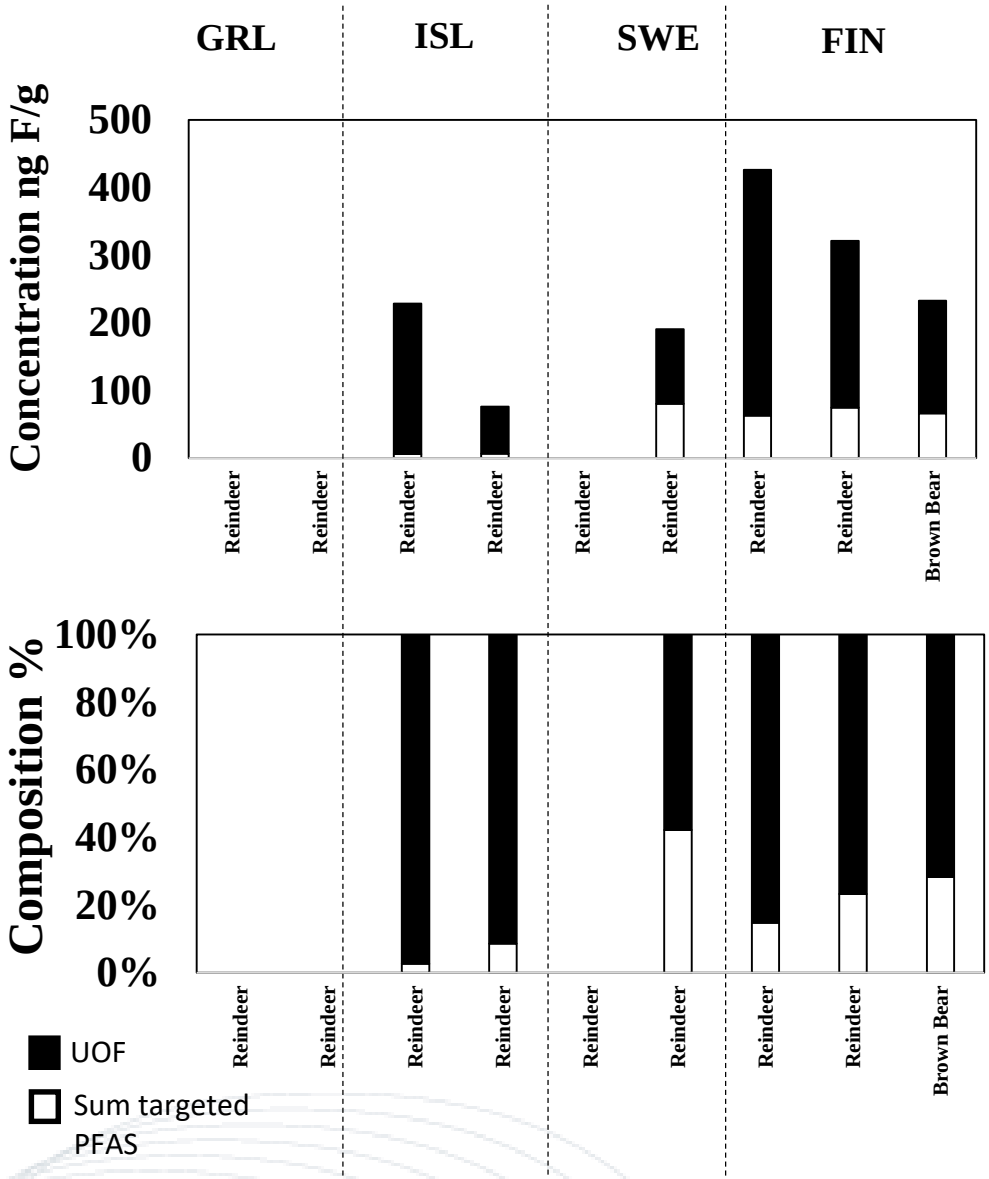
Mass balance 10-62%

Polar bears 53-62%

Terrestrial mammals



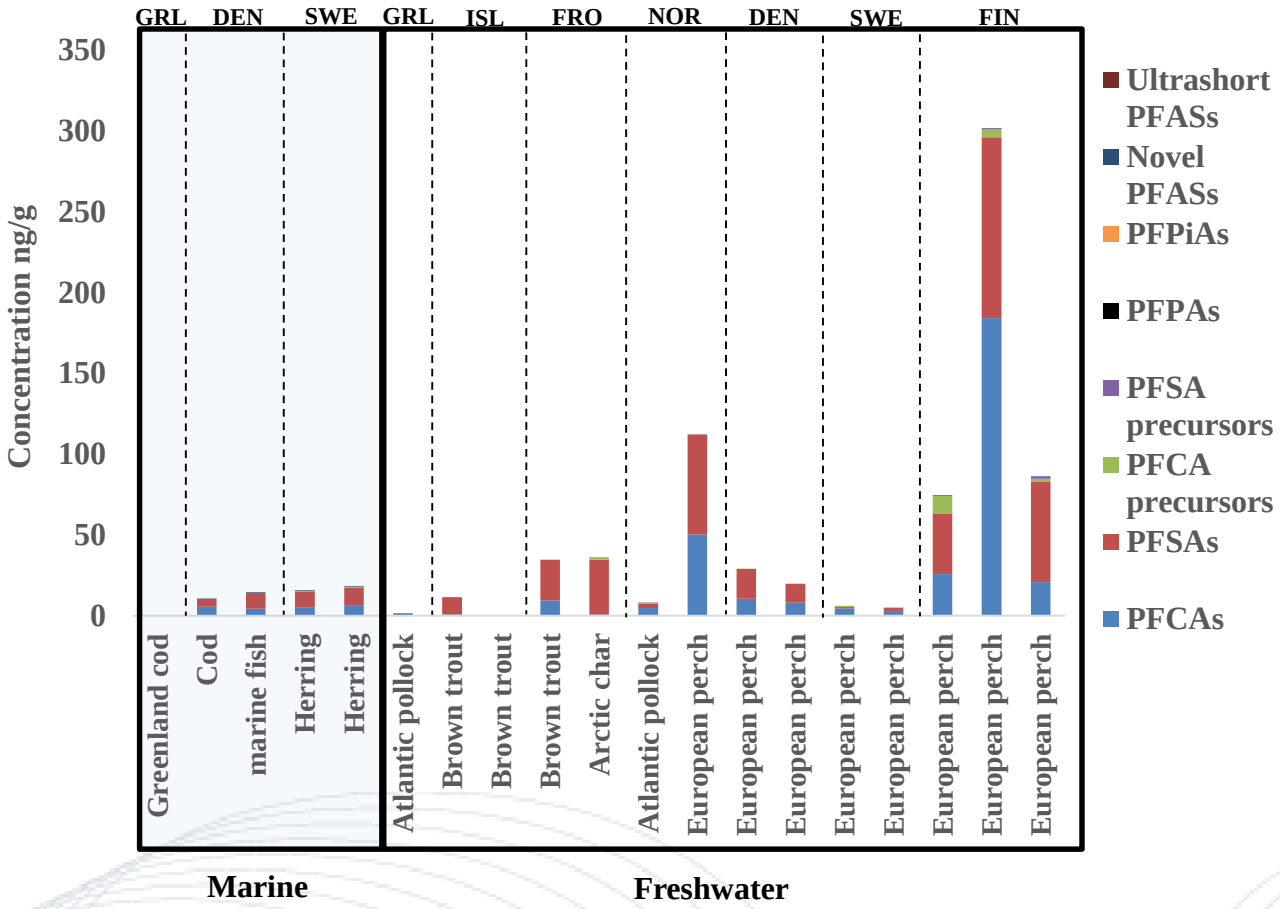
PFCAs; long chain homologues
PFSAs; PFOS
PFCA precursors; diPAP

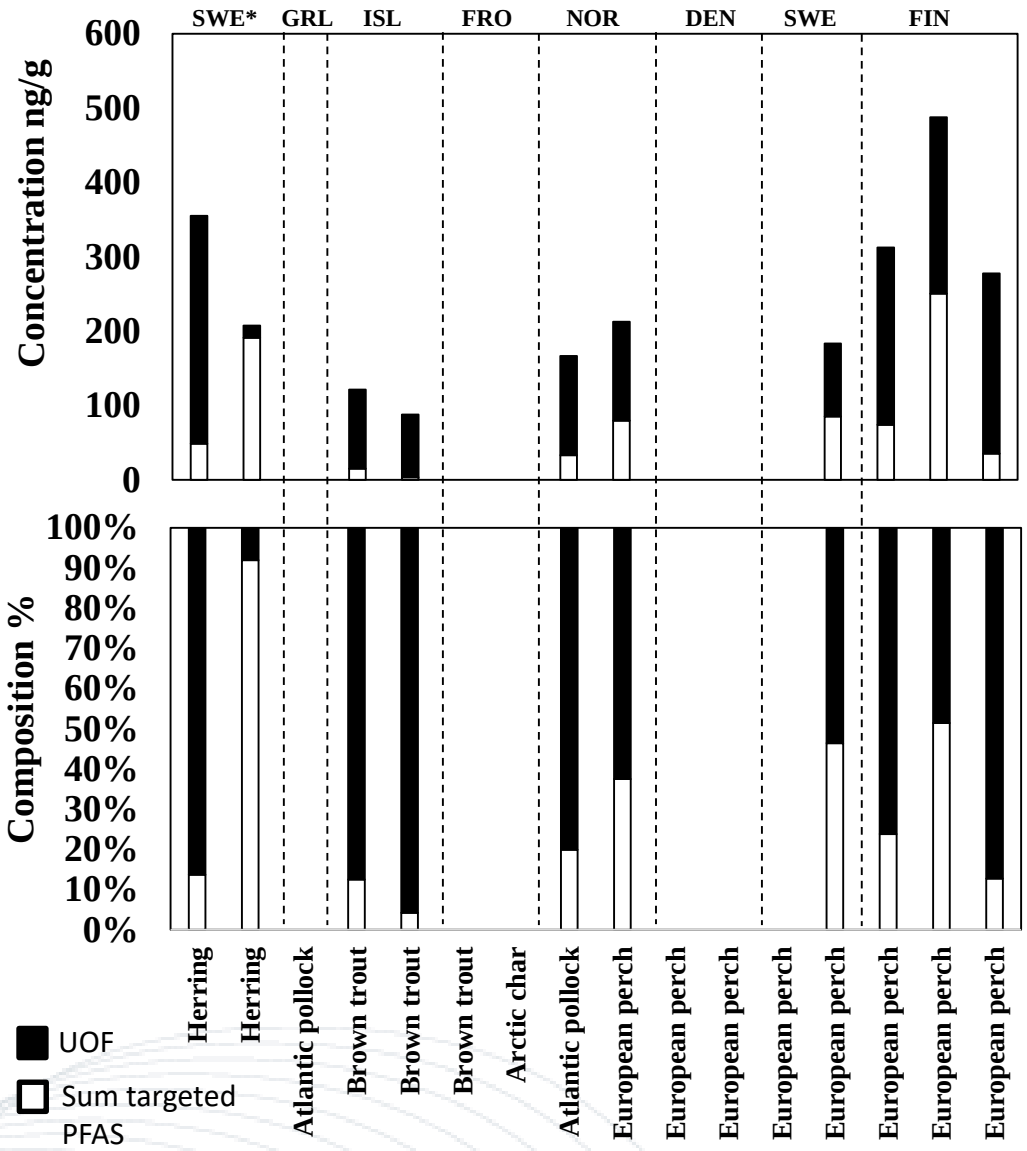


<115 – 427 ng/g

Mass balance 3-42%

Fish


GRL
DEN
SWE
GRL
ISL
FRO
NOR
DEN
SWE
FIN
Concentration ng/g
350
300
250
200
150
100
50
0
Greenland cod
Cod
marine fish
Herring
Herring
Atlantic pollock
Brown trout
Brown trout
Brown trout
Arctic char
Atlantic pollock
European perch
European perch
European perch
European perch
European perch
European perch
European perch
European perch
Ultrashort PFASs
Novel PFASs
PFPiAs
PFPAs
PFSA precursors
PFCA precursors
PFSAs
PFCAs
Marine
Freshwater

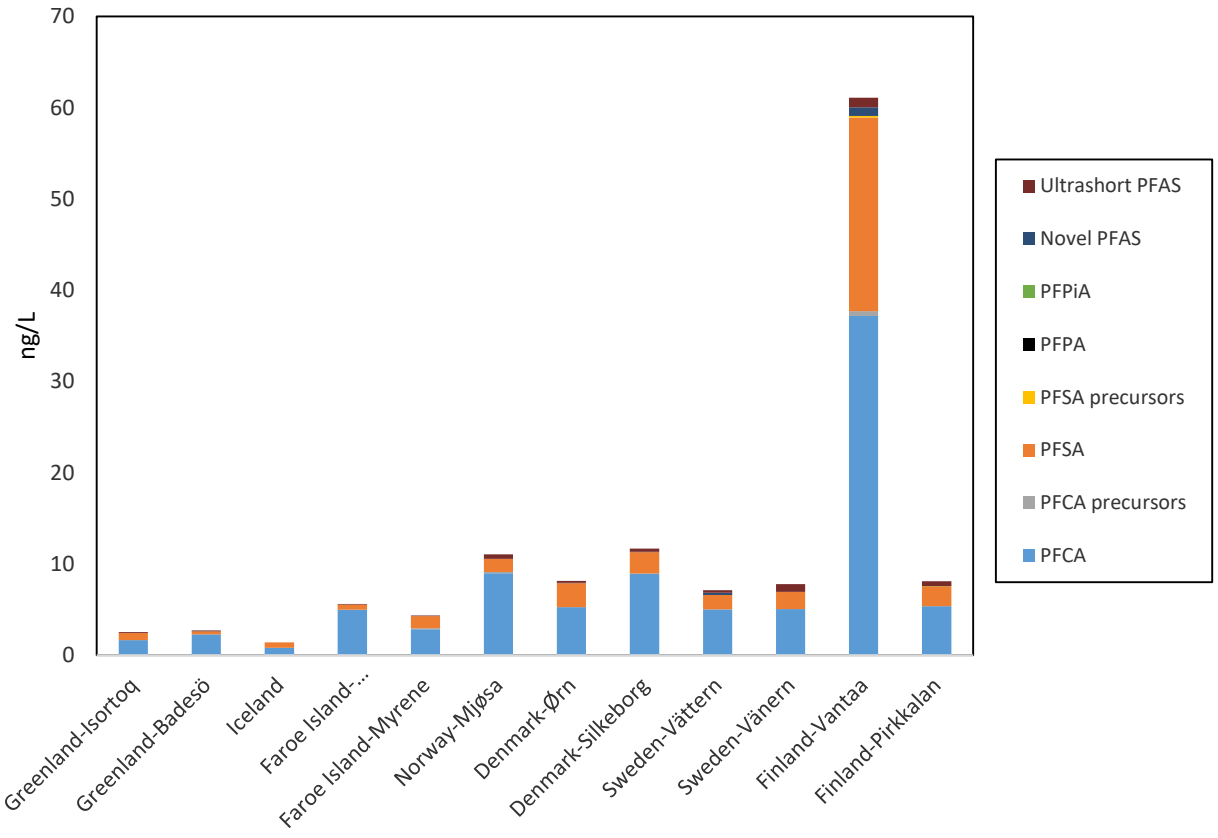


<120 – 488 ng/g

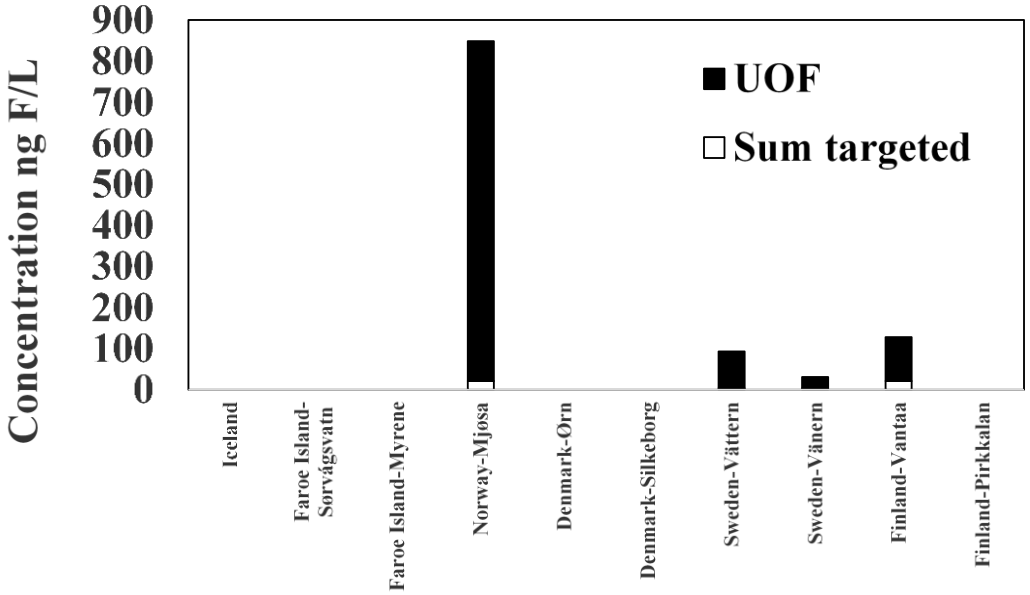
Mass balance 8-96%

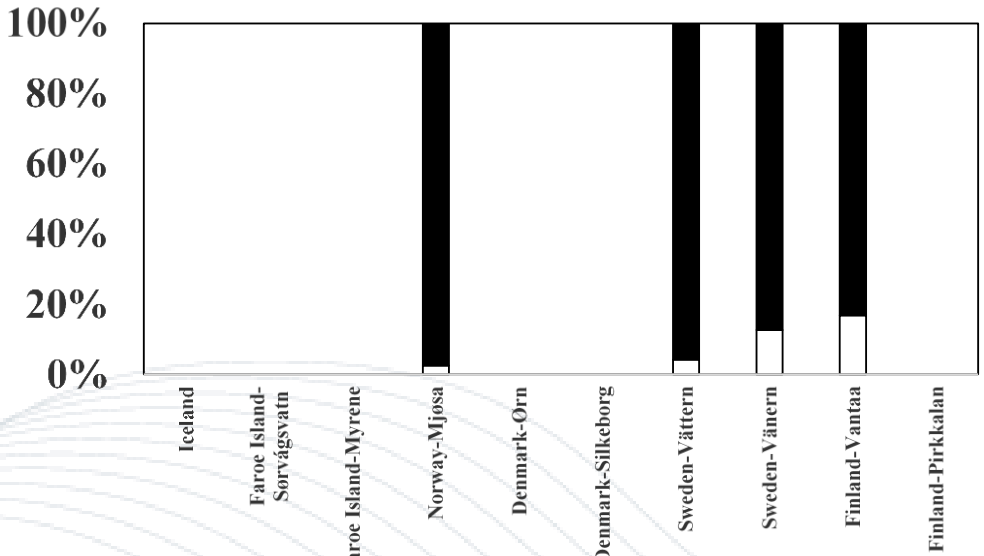
(herring SWE 8% and 96%, two pools)

Surface water



PFCAs; PFHxA>PFBA>PFOA>PFHpA>PFPeA>PFPrA
Finland-Vantaa had a different profile
Novel; PFECHS (FIN, SWE)

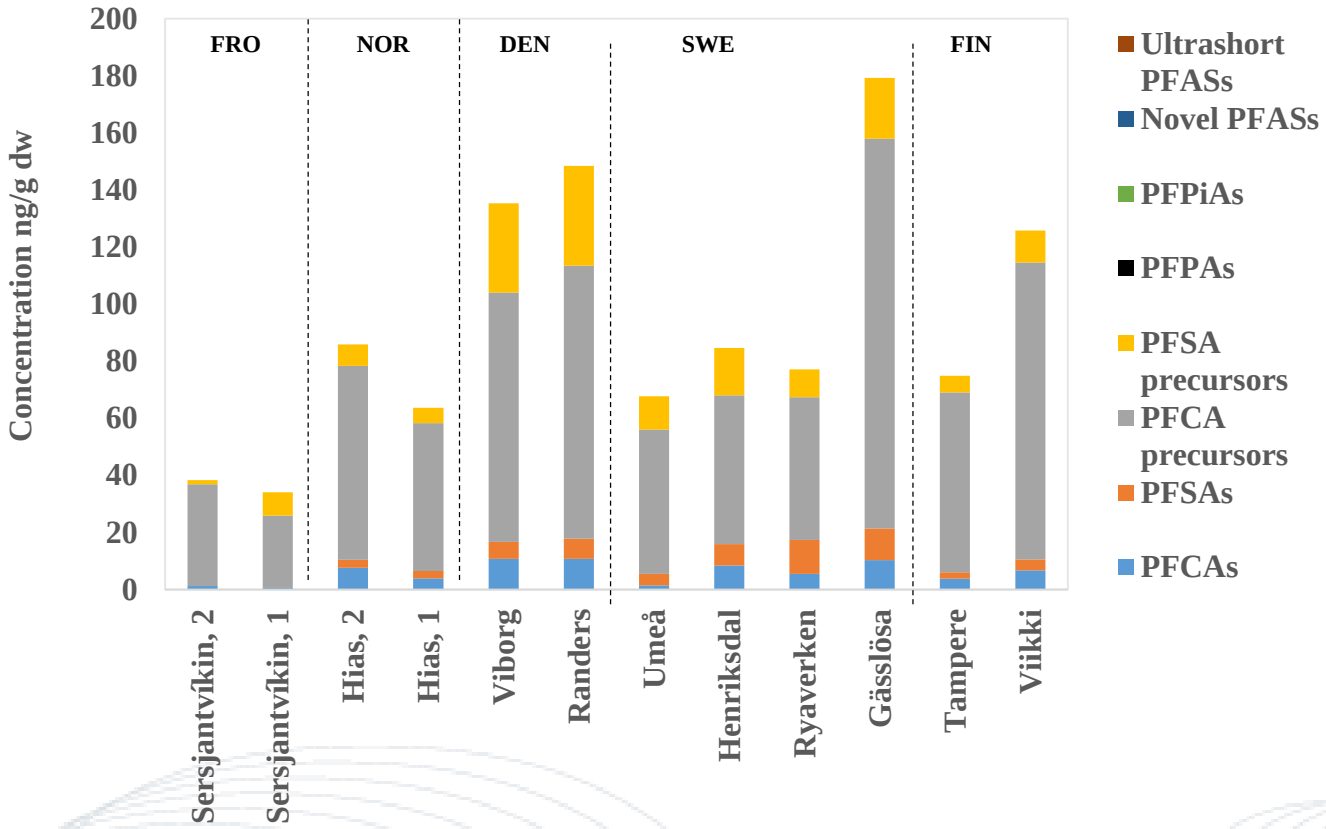




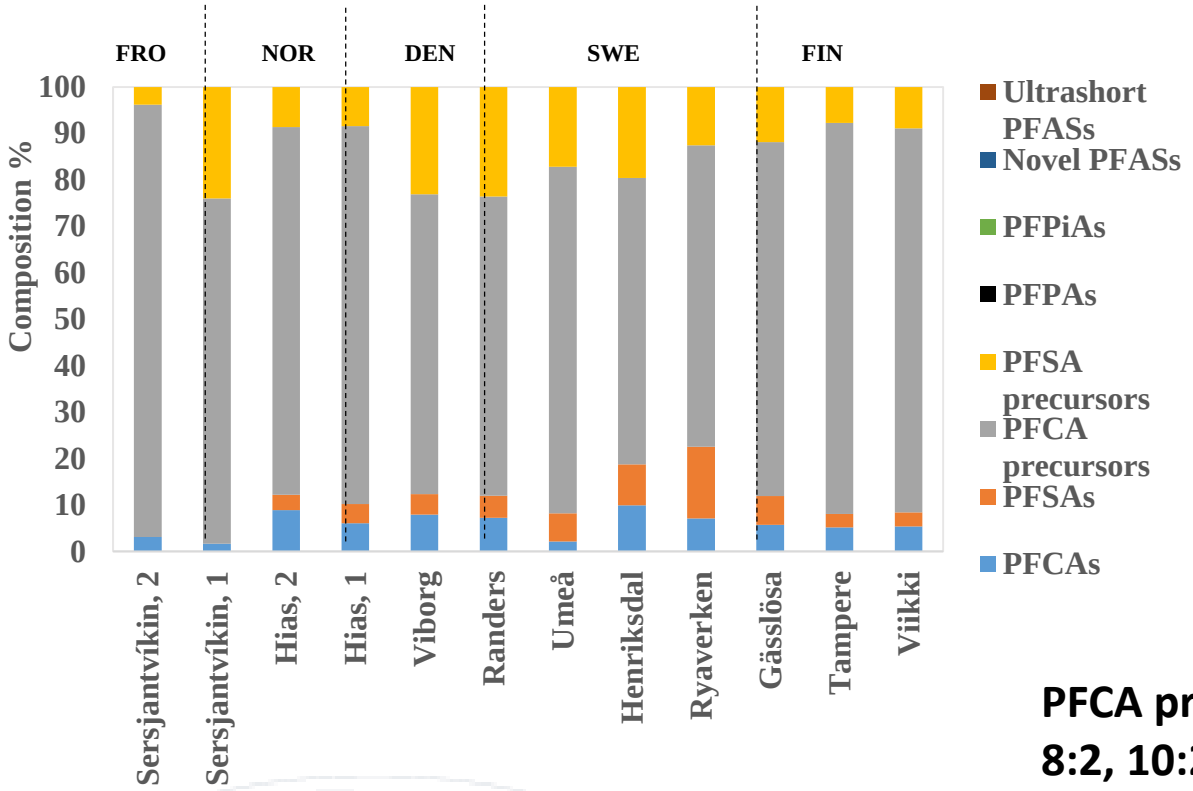
<41 – 849 ng/g

Mass balance 2-17%

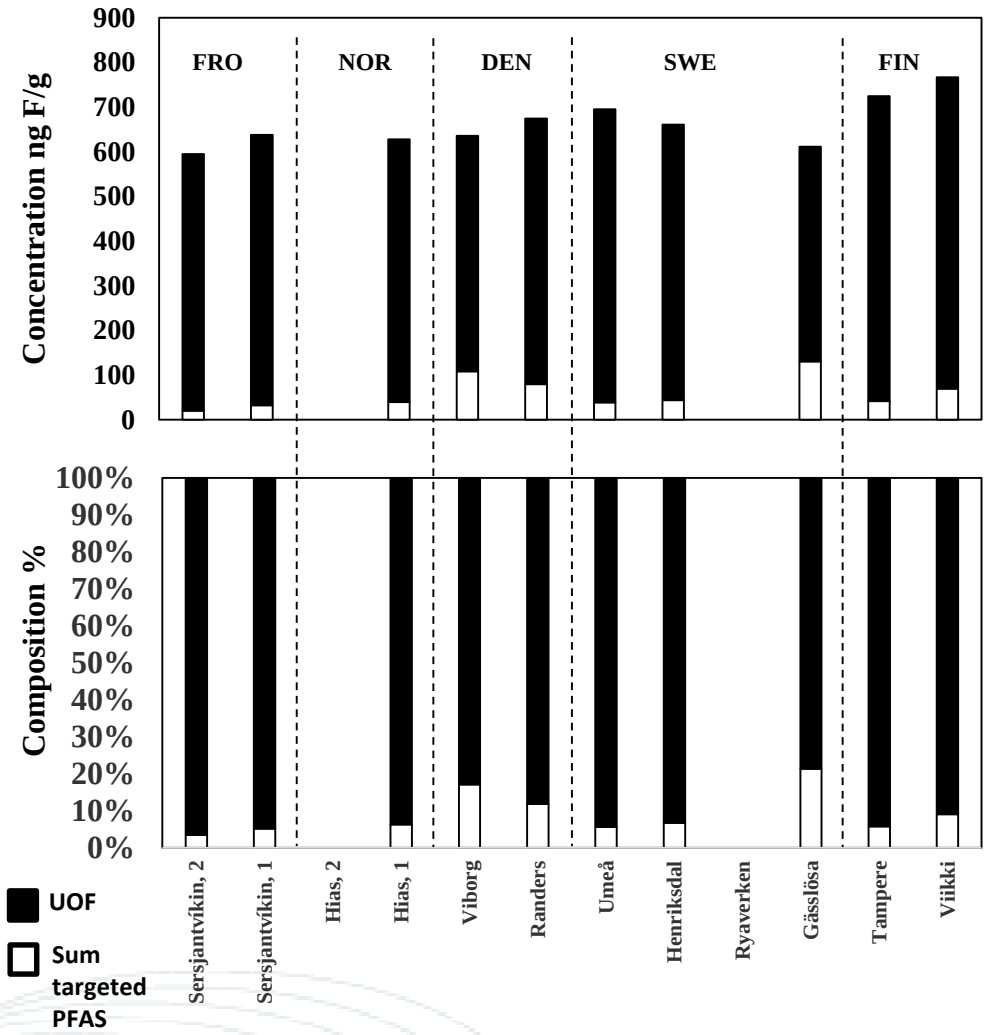
Sludge


Concentration ng/g dw
200
180
160
140
120
100
80
60
40
20
0
FRO
NOR
DEN
SWE
FIN
Sersjantvikin, 2
Sersjantvikin, 1
Hias, 2
Hias, 1
Viborg
Randers
Umeå
Henriksdal
Ryaverken
Gässlösa
Tampere
Viikki
Ultrashort PFASs
Novel PFASs
PFPiAs
PFPAs
PFSA precursors
PFCA precursors
PFSAs
PFCAs

Sludge

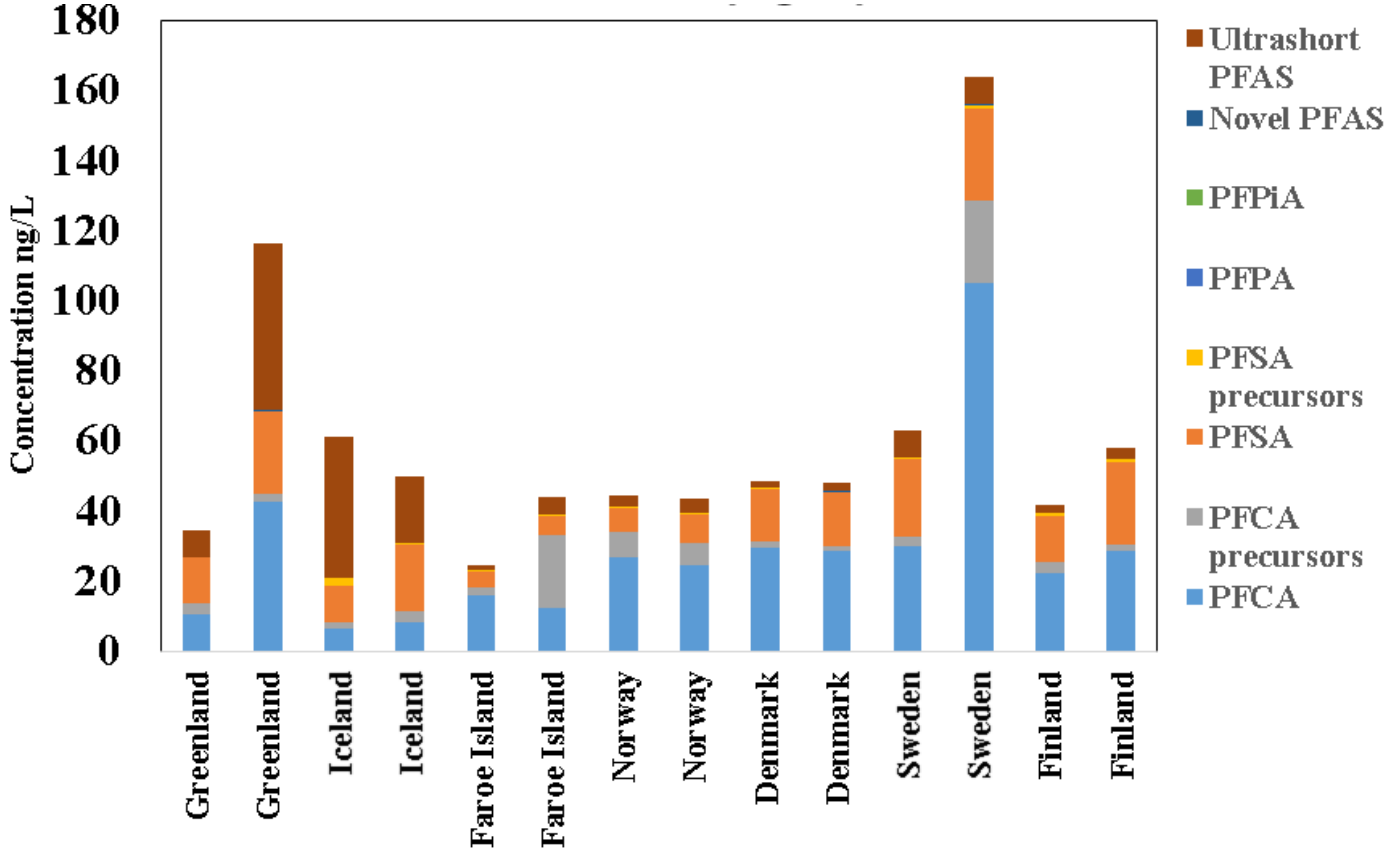


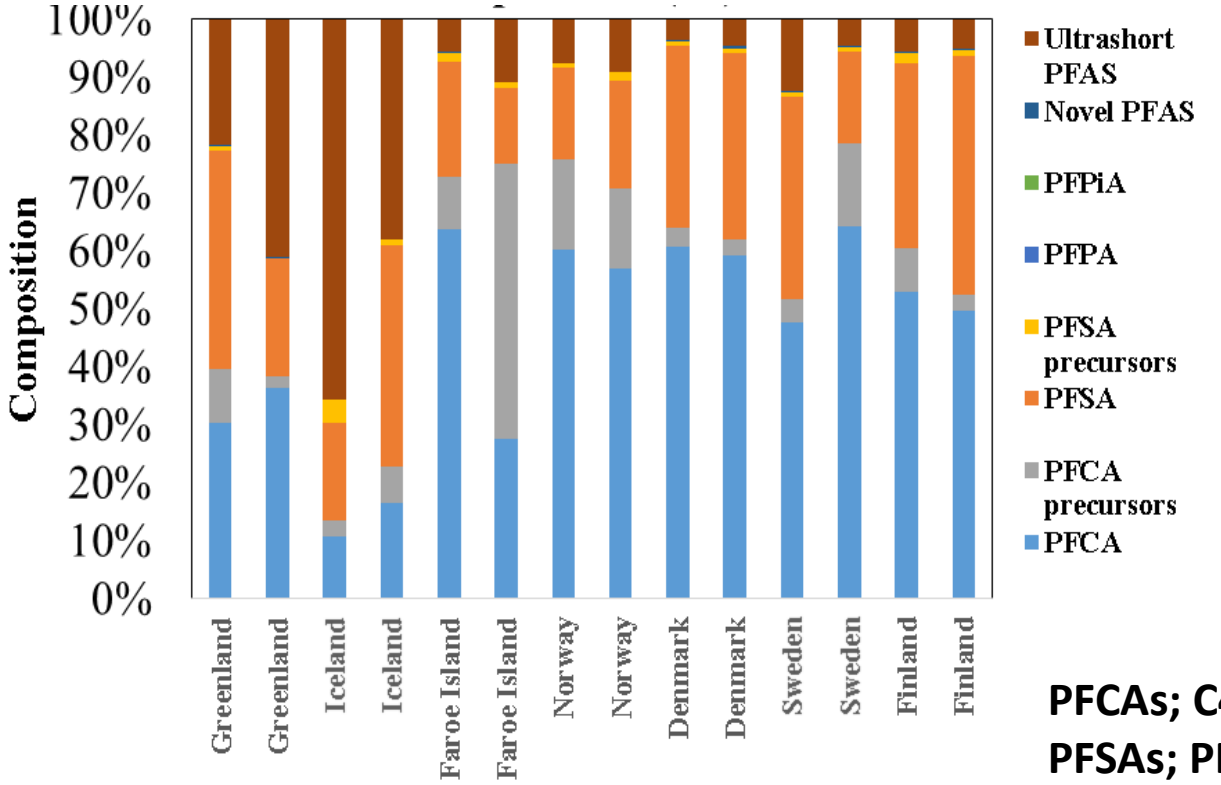
PFCA precursors; diPAPs (6:2, 8:2, 10:2)
PFSA precursors; MeFOSAA, EtFOSAA



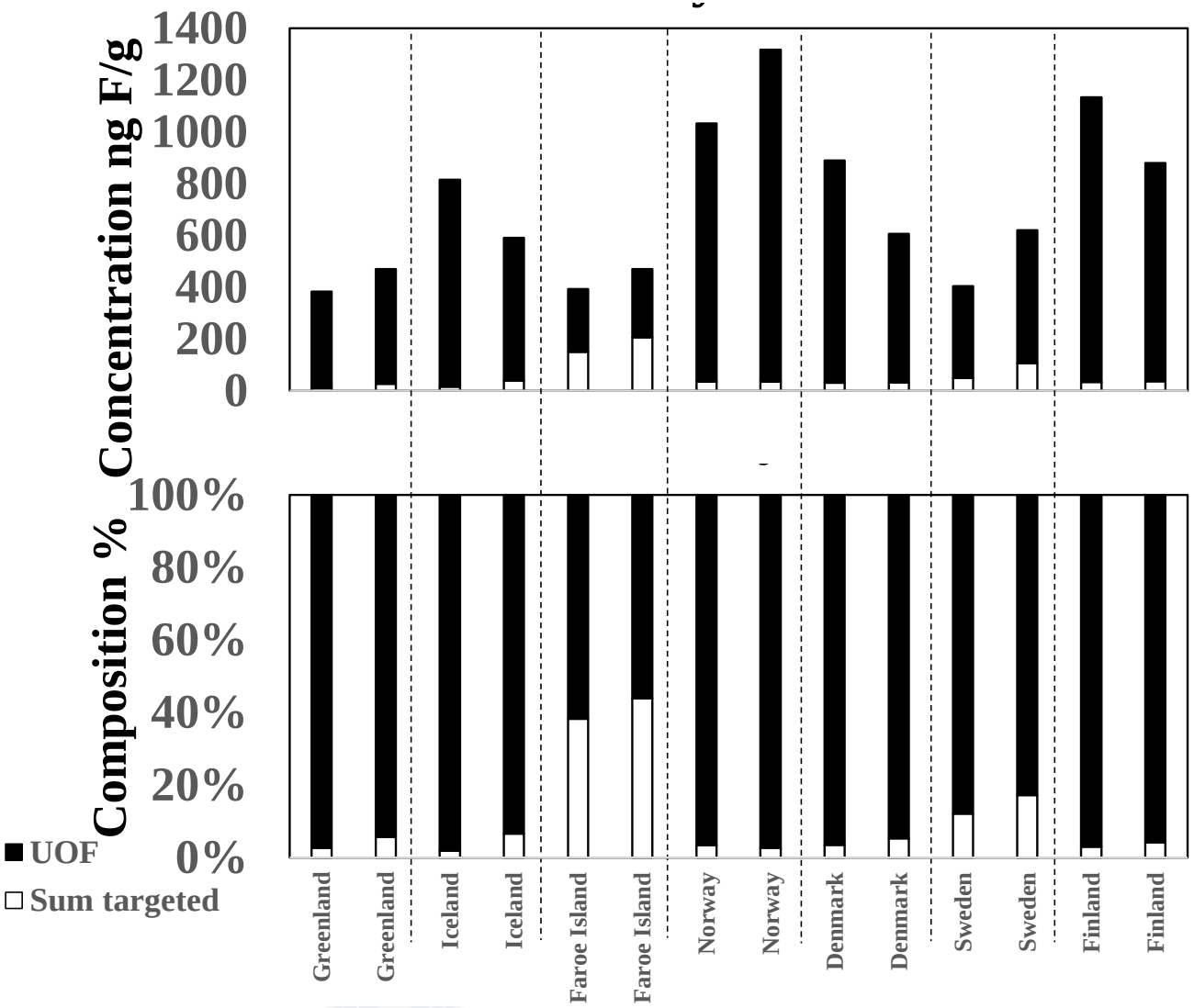
High blank level

Effluent (dissolved phase





PFCAs; C4-C7
PFSAs; PFBS>PFOS
Ultra-short-chain; PFPrA
PFCA precursors; 6:2 FTSA, 8:2 FTSA, 5:3 FTCA

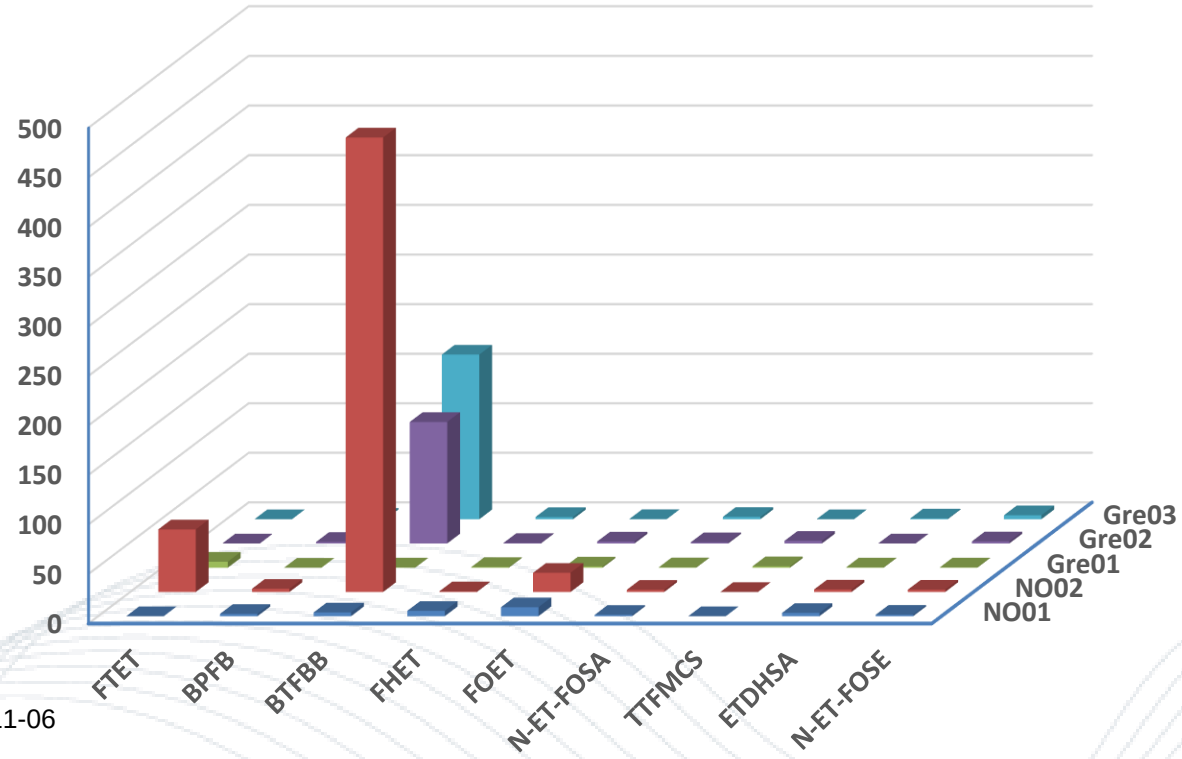


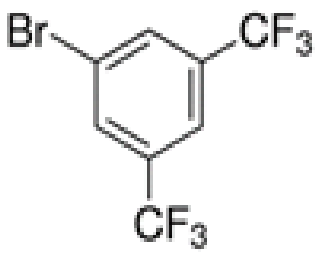
383 – 1317 ng/g

Mass balance 2-44%

Volatile PFAS

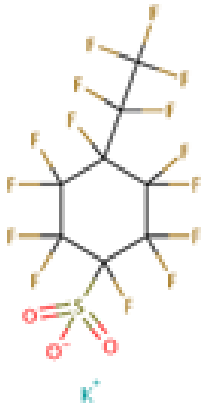
Sampling was done with different sorbents (GFF, PUF, XAD-2)





BTFBB

Novel PFAS



	PFECHS	
Surface water	<MDL-0.94 ng/L	Vantaanjoki, Vättern
WWTP effluent	0.01-0.35 ng/L	Randers, Henriksdal, Gässlösa, Viikki, Tampere
Fish liver	<MDL -0.44 ng/g	Marine fish Sweden, Finland
Marine mammals	<MDL -0.87 ng/g	Polar bear, gray seal (DE), harbour porpoise (DE)

- anticorrosive additive in aircraft hydraulic fluids (De Silva et al., 2011)
- raw product for cosmetics (as adsorbent, anticaking, skin conditioning, binding, emulsion stabilising), (Fisher, 2018)
- semiconductors and actives (Fisher, 2018)

Mass balance

	Average F (ng/g) (range)	Average mass balance, target PFAS/EOF (range)
Marine mammals	707 (<40 – 2056)	37% (9.6-62%)
Reindeer	249 (<76 – 427)	18% (2.7-42%)
Bird eggs	221 (<40-649)	68% (33-102%)
Marine fish	(<132-355)	(14-92%)
Fresh water fish	241 (<140-488)	26% (4.2-51%)
Sludge	663 (<556-767)	9.2% (3.4-21%)
Effluent	437 (<123-893)	11% (1.9-44%)

Biota

- Highest explaination for bird eggs, lowest for reindeers
- Explanation not improved with PFAS∑74 compared to PFAS∑20, more biotransformation products should be included

Water and WWTPs

- Relatively high blank levels for sludge, but results are in line with previous studies (Eriksson et al. 2017)
- Large number of low-fluorinated substances are used and should be included in the mass balance analysis

Concluding remarks

- Shorter chain PFASs with carbon chain lengths of 2-4 were frequently detected in surface water and WWTP effluent.
- Precursor compounds contributed to the total PFASs in the present study and were frequently detected in many matrices
- Several novel PFASs were detected in biota, water and air in the present study
- The identity of the additional organofluorine substances contributing to the EOF needs to be elucidated

Acknowledgment

- Sample collection was organized through:
  - DCE-Danish Centre for Environment and Energy, DCE, Aarhus University, Denmark
  - Finnish Environment Institute (SYKE)
  - Environment Agency, the Faroe Islands
  - Ministry of Housing, Nature and Environment, Greenland
  - The Environment Agency of Iceland
  - Norwegian Environment Agency,
  - Swedish Environmental Protection Agency

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