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Targeted PFAS analyses and Extractable Organofluorine – Enhancing our Understanding of the presence of unknown PFAS in Norwegian wildlife

Dorte Herzke[1], Vladimir Nikiforov[1], Leo W.Y. Yeung[2], Børge Moe[3], Heli Routti[4], Torgeir Nygård[3], Geir. W. Gabrielsen[4], Linda Hanssen[1]

[1] Norwegian Institute for Air Research (NILU), Fram Centre, Tromsø, Norway

[2] Man-Technology-Environment (MTM) Research Centre, School of Science and Technology, Örebro University, Sweden, SE-701 82

[3] Norwegian Institute for Nature Research (NINA), Trondheim, Norway

[4] Norwegian Polar Institute, Fram Centre, Tromsø, Norway

***Corresponding author**

Dorte Herzke

Norwegian Institute for Air Research (NILU), Fram Centre, 9296 Tromsø, Norway

*dorte.herzke@nilu.no

Highlights

- A broad range of PFAS are detected in Norwegian wildlife, mostly in marine species
- Otters belong to the highest exposed species
- PFECHS detected in polar bear plasma
- Triflouro acetic acid (TFA) is a major contributor to PFAS burden
- EOF is a useful tool to assess the presence of unknown organic fluorinated compounds

ABSTRACT

With the current possible presence of thousands of PFAS compounds in industrial emissions, there is an increasing need to assess the impacts of PFAS regulation of conventional PFAS on one hand and the exposure to emerging and yet unknown PFAS on the other. Today's analytical methodologies using targeted approaches are not sufficient to determine the complete suite of PFAS present. To evaluate the presence of unknown PFAS, we investigated in this study the occurrence of an extended range of target PFAS in various species from the marine and terrestrial Norwegian environment, in relation to the extractable organic fluorine (EOF), which yields the total amount of organic fluorine. The results showed a varying presence of extractable fluorinated organics, with glaucous gull eggs, otter liver and polar bear plasma showing the highest EOF and a high abundance of PFAS as well. The targeted PFAS measurements explained 1% of the organic fluorine for moose liver as the lowest and 94% for otter liver as the highest. PFCAs like trifluoro acetic acid (TFA, reported semi-quantitatively), played a major role in explaining the organic fluorine present. Emerging PFAS as the perfluoroethylcyclohexane sulfonate (PFECHS), was found in polar bear plasma in quantifiable amounts for the first time, confirming earlier detection in arctic species far removed from emission sources. To enable a complete organic fluorine mass balance in wildlife, new approaches are needed, to uncover the presence of new emerging PFAS as cyclic- or ether PFAS together with chlorinated PFAS as well as fluorinated organic pesticides and pharmaceuticals.

KEYWORDS: Top predators, Arctic, Norway, PFAS, trifluoro acetic acid, extractable organic fluorine

GRAPHICAL ABSTRACT FOR TABLE OF CONTENTS

Figure by Gabrielsen, Herzke, Heimstad

INTRODUCTION

The group of poly- and perfluoroalkyl substances (PFAS), contains both emerging and legacy compounds which are broadly present in various consumer products, technical applications and production aids, thanks to their surfactants and water repellent properties (1, 2). Numerous applications have been described (e.g., aqueous film–forming foams (AFFFs), floor polish, ski waxes, and water-proof coatings of textile fibres and paper cardboard as well as applications in cosmetics and many others (3, 4)). Even though PFAS have been used since the 1950s, their occurrence in wildlife has not been studied in depth before the early 2000s, with some of them found to be ubiquitous, persistent and to biomagnify along food chains (5-11). Some PFAS were also found to have potential adverse effects on human and animal health in several *in vitro* and *in vivo* studies (12-18). Of the legacy PFAS, perfluorooctane sulfonic acid (PFOS) and related products are regulated in the European Union (EU) since 2006 and were added in 2009 to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs). This restricts their use but does not completely ban it. Currently, PFOS and related chemicals can only be used for the following purposes: insect baits with sulfur amid, hard-metal plating only in closed-looped systems, fire-fighting foam for liquid fuel vapor suppression and liquid fuel fires (Class B fires) in installed systems (SC-9/4). Perfluorooctanoic acid (PFOA) and higher homologues, have been phased-out as well by the main producers in the United States since the end of the 2000s, but PFOS, PFOA and numerous emerging PFAS are still produced in some countries (19-27).

In Norway, firefighting facilities at airports have been one of the most important local emission sources due to the use of AFFFs containing PFAS leading to significant environmental contamination and exposure of local wildlife (28-32).

In addition to local sources, perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) may reach the Norwegian coastal mainland and arctic archipelagos via oceanic- and atmospheric currents, as well as riverine outputs and sea spray (33-38). Alternatively, their volatile precursors, for examples fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamide (FOSA) and their derivatives, may undergo long-range atmospheric transport and degrade to PFSAs and PFCAs in atmosphere and snow (26, 27, 38-49). In Norway, recent studies on terrestrial and marine fauna showed decreasing time trends of PFOS over the past decade, while PFCAs have been unchanging over the same period, with concentration still high in Arctic top predators (35, 50-55). To counter regulations and develop new applications, alternative PFAS have been introduced by industry in the past 20 years with similar potential risk of environmental emissions and biological uptake (21-23, 27, 28). Consequently, there is an urgent need to assess the impacts of PFAS regulation of traditional PFAS on one hand and the exposure of emerging and yet unknown PFAS to the Norwegian continental and High-Arctic environment on the other hand. With a large variety of PFAS circulating in society, but little information on their chemical structure and lack of authentic standards, today's analytical methodologies are not able to determine the complete suite of possible PFAS present. Recently, new methodological approaches combined with new analytical methods have become available to tackle a broad range of PFAS as a group rather than individual compounds (56-61). As one example, analysing the extractable organofluorine (EOF) yields the amount of fluorine present in an organic extract of a certain matrix (62, 63).

Here we investigated for the first time the presence of a large variety of target PFAS (n=73), including ultrashort perfluorinated carbon chain lengths (C_2-C_3) and emerging cyclic and chlorinated PFAS in combination with the EOF in samples from wildlife from the Norwegian mainland and the Arctic; a detailed list of target PFAS is provided in Table SI 1. Since some of the samples were collected in both 2017 and 2018 (i.e., plasma samples of polar bear and egg samples of glaucous gull; the samples were from different individuals), cross-sectional interannual variations of PFAS and EOF can be investigated."

The studied species from the mainland included terrestrial herbivores (moose (*Alces alces*), roe deer (*Capreolus capreolus*)) and a predator (wolf (*Canis lupus*)), two semi-aquatic predators ((American mink (*Neovison vison)* and otter (*Lutra lutra*)), two seabirds (common gull (*Larus canus*) and European shag or common shag (*Phalacrocorax aristotelis*)) and a generalist avian predator (white-tailed eagle (*Haliaeetus albicilla*)). Species collected from Svalbard included three seabird species (Common eider (*Somateria mollissima*) (a benthic feeder), kittiwakes (*Rissa tridactyla tridactyla;* a pelagic feeder) and glaucous gull (*Larus hyperboreus*; a predator and a scavenger)), and polar bear (*Ursus maritimus;* a top predator of the marine ecosystem), and Artic fox (*Vulpes lagopus*; a generalist predator/scavenger of both terrestrial and marine ecosystems) (64-66).

Specifically, we studied the contribution of conventional PFAS and unknown organofluorine compounds into EOF at species level. We provide valuable insights into the applicability of the EOF as a screening method for the presence of unknown and known PFAS as a group variable.

MATERIALS AND METHODS

Sampling

We sampled 5 individual samples per species, except for polar bear, where 10 samples were collected in 2018. Sample collection from the Norwegian mainland was led by the Norwegian Institute for Nature Research (NINA), whilst the Norwegian Polar Institute (NPI) was responsible for the sample collection in the Arctic (Figure 1).

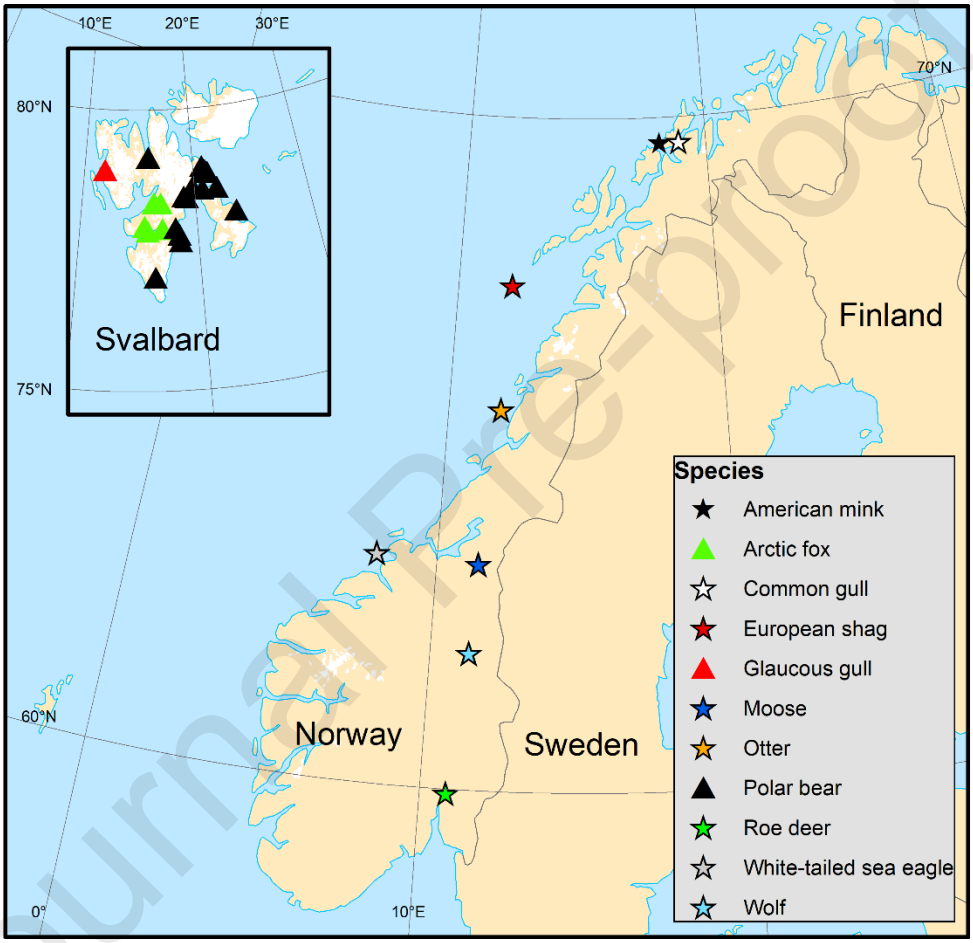


Figure 1: Sampling stations on A: Svalbard (triangles) and B: Mainland Norway (stars).

Sampling was carried out during 2017 and 2018. The sampling was performed with authorisation from the Norwegian Environment Agency, the Norwegian Food Safety Authority. and the Governor of Svalbard.

Liver samples

White-tailed eagles were sampled on the island Smøla. The birds had died after collision with wind turbine blades. For this project, liver samples from a total of five individuals, one male and four females, were collected. Wolfs and moose were shot in the fall 2018 by local hunters. Liver samples of two male and three female wolfs and one male and four female moose were collected. Roe deer liver was sampled as road kill in 2021 in Bærums Verk, Nesoddtangen, Oslo as part of the Urban terrestrial monitoring project (67). All three roe deer samples were from female individuals. Arctic foxes were caught during the annual harvest by local trappers in Svalbard (n=5, all male). Liver samples were collected during dissection after the animals were skinned. The otter (n=5; two females and three males) were shot at the Vega archipelago in spring of 2018, with the permission from the Nordland County. Liver of American mink was sampled at the islands Sommarøy and Hillesøy, in Troms County, Northern Norway (n=5, collected randomly in 2013 and 2014). All samples were excised and placed in aluminium foil before storage in a ziplock bags at -20 °C until analysis.

Eggs

Eggs from Glaucous gull, common eider and black-legged kittiwake were sampled in Kongsfjorden, Svalbard. Eggs from European common gull were sampled at the island of Grindøya, Norwegian mainland. Eggs from European shag or common shag were sampled at the island of Røst, Norwegian mainland. For Glaucous gull a total of five eggs (n=5) were collected in both in 2017 and 2018. For common eider, kittiwakes, European shag and common gulls a total of 5 eggs were collected in 2017 for each species.

The eggs were either wrapped in aluminium foil and stored frozen until laboratory analysis (68) or kept individually in polyethylene bags in a refrigerator (+4°C), before being shipped to NINA's laboratory in Trondheim for measurements and emptying. When emptying, the whole

content of the eggs was removed from the shell and transferred to clean glass vials for storage at − 21 °C.

Plasma samples

Polar bears from Svalbard were immobilized by a remote injection from a helicopter in April of 2017 and 2018 (2017: n = 5 females and n= 5 males; 2018: n= 5 females). Blood samples were collected into heparinized vacutainers, kept cool and out of light and centrifuged within 10 hours, and the plasma transferred to cryogenic vials, frozen in the field and stored at -20 °C.

Targeted PFAS determination

The chemical analysis of PFAS in plasma, egg and liver samples was carried out at NILU in Tromsø, Norway. All the reported concentrations hereafter are on weight basis. For plasma samples, we used the method previously described by Jouanneau *et al.* (32), while for eggs and liver the method described by Warner *et al.*, was applied (37). In short, tissue and plasma samples were homogenised and subsampled for extraction with methanol. After ultrasonication and centrifugation the organic phase was transferred into a new vial and treated with suspensive ENVI-Carb prior to analyses. Analyses were conducted by ultrahigh pressure liquid chromatography triple-quadrupole mass spectrometry (UHPLC-MS/MS), as previously described by Hanssen *et al.* (69). The chromatograms were quantified with LCQuan software (version 2.6, Thermo Fisher Scientific Inc., Waltham, MA, USA). Quantification was done using the isotopic dilution method with ^{13}C mass labelled compounds applying an eight-point calibration curve with a concentration range from 0.02 pg/µL to 50 pg/µL. A broad mix of conventional and emerging PFAS were measured, see SI for the full list of 73 targeted PFAS including ultrashort chain PFCAs, fluorotelomer sulfonic acids, a mixture of 6:2 and 8:2 chlorinated polyfluorinated ether sulfonate (F-53B), dodecafluoro-3H-4,8-dioxanonanoate (ADONA) and hexafluoropropylene oxide dimer acid (Gen-X).

Ultrashort chain PFAS included the analysis of C_{2-3} PFSAs and PFCAs. They were separated by a supercritical fluid chromatography system (SFC, also known as UPC2-ultra performance convergence chromatograph), connected to a Waters XEVO TQ-S MS/MS detector. The SFC mobile phases were CO_2 and MeOH (with 0.1 % NH_4OH as an additive), the analytical column was an SFC Torus DIOL column (3.0 mm i.d., 150 mm length, 1.7 um). Trifluoroacetic acid (TFA) was obtained from Sigma-Aldrich, Munich, Germany. PFPrA was from Sigma-Aldrich, Oakville, ON, Canada. The potassium salt of perfluoroethane sulfonate was obtained from Kanto Chemical Co., Inc., Portland, OR, USA. PFPrS was obtained from Wellington Labs. Details of the methods are provided elsewhere (70). All chromatographs, analytical columns and mass spectrometers were from Waters Corporation, Milford, MA, U.S. Quantifications of C_{2-3} PFCAs and PFSAs in the samples were based on the relative responses to ^{13}C-PFBA and ^{13}C-PFBS, respectively. Due to the lack of suitable internal standards and only one single mass transition available the ultrashort chain PFCAs, these results have to be considered as semi-quantitative. Some discussions of TFA analysis are provided in the SI. The isotopic dilution method was used for quantification, applying either carbon and/ or deuterium labelled compounds (SI for more information).

EOF

All samples collected in 2017 and 2018 were also analysed for EOF to evaluate the presence of additional organic fluorinated compounds. Extraction of EOF followed the method described above for targeted PFAS analyses with the exception that no mass-labelled internal standards were spiked into the samples before extraction. The EOF content of the sample extract was analyzed by combustion ion chromatography (CIC). Contribution of each of the known PFAS into the EOF was calculated on the basis of fluorine content of the molecule and its respective concentration in the sample (see SI).

Quality control and assurance

To assure the quality and control for repeatability and precision of the targeted PFAS method, one blank and a standard reference material (human serum INSPQ within the Arctic Monitoring and Assessment Program ring test) were analysed every 15 samples to verify quality of the prepared samples, test reproducibility and precision of the method (see SI for more information, including EOF). For EOF determination, the background fluoride levels varied from day to day; the background fluoride indicated as instrumental (boat) blank was found to be 8 ng F (geomean of 9 replicates). The analysis of organofluorine in samples started when the relative standard deviation of three sequential combustion blanks (empty sample boat analysis) was below 5 %. An additional combustion blank was run after every 5 samples to monitor for carry-over. The combustion blank response (average of combustion blanks before and after the sample) was subtracted from the sample responses, before further data processing. A PFOA standard of 240 ng F/mL was injected in between every 10 samples to evaluate the stability of the system; the measured mean value of the standard injection was 251 ng F/mL (R.S.D.: 13%, n=10); intra-day variability: at most 14% and inter-day variability: 15%).

Data analyses

Linear regression on log-transformed data was used to assess relationships between the amount of F in measured PFAS and EOF, the linear relationship between the targeted PFAS in different species groups.

RESULTS AND DISCUSSION

The targeted PFAS analyses covered 73 individual PFAS compounds (Table SI1). Among the 73 PFAS, PFOS, PFNA, PFDA and PFUnDA were detected in all samples. A SumPFAS9 (PFHxS, PFOS, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA) value of the

arithmetic mean was calculated of the most prevalent PFAS present in all samples (detection rate > 60%). Non detects were substituted with ½ of the LOD.

A detection rate for EOF of < 100% in some low trophic species was caused by the detection limit of the applied method not being able to result in a quantifiable amount of EOF despite the presence of trace concentrations of PFAS (Table SI3).

PFAS levels in birds

Common gull and kittiwake eggs showed the highest $SumPFAS_9$ concentrations in seabird eggs, with PFOS as the dominating PFAS. The white-tailed eagle liver showed similarly high $SumPFAS_9$ concentrations with PFOS averaging with 18.3 ng/g (sum of branched and linear isomers). Of the PFCAs, PFUnDA and PFTrDA were generally the dominating PFCAs in the bird samples present between 1.7 – 2.6 times lower concentrations than PFOS except for egg sample of KW (Table 1)." In white-tailed eagle liver we also detected the emerging PFAS 6:2 FTSA and 8:2 FTSA in quantifiable concentrations. The 6:2 FTSA concentrations ranged from 5.2 - 25.1 ng/g and 8:2 FTSA concentrations ranges were <0.2 - 77.5 ng/g, exceeding PFOS concentrations in some cases. The ultrashort chain PFCA trifluoroacetic acid (TFA), was detected in the white-tailed eagle liver and glaucous gull eggs only. In white-tailed eagle, TFA was detected in all samples with an average concentration of 35 ng/g, dominating over most PFAS detected in the white-tailed eagle samples. In glaucous gull eggs, TFA concentrations dominated over all other PFAS as well (average of 20 ng/g). Of the additionally analysed ultrashort chain PFAS, only glaucous gull eggs showed detectable concentrations of PFPrS (0.05 – 0.2 ng/g).

Table 1: Concentrations of selected PFAS in marine birds from Norway mainland and Svalbard (ng/g ww, eggs for all species except white-tailed eagle (liver); n = 5 for every species). Range in parentheses.

Sample type	PFHxS	PFOS'	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	$SumPFAS_9$
	(Min – max) **Median / Mean***									
WTE (Liver)	(0.51-1.00) **0.62** **0.67**	(6.71-30.2) **18.2** **18.3**	(0.17-0.44) **0.30** **0.30**	(0.68-2.06) **1.72** **1.56**	(0.89-2.10) **2.00** **1.66**	(1.37-6.51) **4.89** **4.27**	(0.44-2.08) **1.75** **1.38**	(1.01-8.85) **6.35** **5.13**	(0.22-1.09) **0.69** **0.63**	33.9
CE (Egg)	(0.05-0.31) **0.10** **0.13**	(2.4-4.4) **3.00** **3.10**	(0.12-0.46) **0.18** **0.25**	(0.32-1.1) **1.01** **0.81**	(0.13-0.32) **0.21** **0.22**	(0.26-0.68) **0.43** **0.45**	(0.6-1.1) **0.19** **0.17**	(1.7-4.0) **0.57** **0.72**	(0.2-0.5) **0.21** **0.16**	6.01
KW (Egg)	(<0.05-0.07) **nd** **0.03**	(6.0-26) **6.89** **12.0**	(0.08-0.18) **0.10** **0.11**	(0.38-1.7) **0.64** **0.64**	(0.72-2.0) **1.34** **1.40**	(4.8-8.4) **6.74** **6.50**	(1.3-2.1) **1.64** **1.64**	(6.4-9.8) **8.87** **8.69**	(0.7-1.6) **1.46** **1.21**	32.2
GG. (Egg) 2017	(<0.05-0.17) **0.11** **0.10**	(4.1-6.9) **5.76** **5.60**	(0.13-0.83) **0.48** **0.44**	(0.30-1.1) **0.74** **0.72**	(0.21-0.49) **0.30** **0.35**	(0.76-1.6) **1.24** **1.20**	(0.1-0.8) **0.36** **0.39**	(1.1-2.1) **1.64** **1.65**	(0.1-0.4) **0.21** **0.24**	10.7
GG. (Egg) 2018	(0.14-0.34) **0.23** **0.25**	(4.82-6.61) **4.90** **5.33**	(0.37-1.02) **0.57** **0.60**	(1.08-2.07) **1.30** **1.41**	(0.41-0.88) **0.47** **0.56**	(1.06-3.42) **1.12** **1.57**	(0.21-1.16) **0.23** **0.42**	(0.65-3.86) **0.98** **1.49**	(0.14-0.68) **0.25** **0.30**	11.9
CG (Egg)	(0.48-1.2) **0.79** **0.82**	(35-97) **55.9** **31.1**	(0.55-2.2) **0.94** **1.10**	(0.48-1.6) **0.76** **0.92**	(0.65-3.5) **1.26** **1.70**	(2.2-8.1) **3.41** **4.10**	(2.6-10.3) **4.65** **5.25**	(4.4-14.4) **7.03** **8.22**	(2.1-11.6) **4.23** **5.29**	45.0
ES (Egg)	(0.23-0.57) **0.49** **0.45**	(12-16) **12.2** **13.1**	(0.28-0.52) **0.37** **0.39**	(0.52-0.80) **0.71** **0.69**	(0.63-0.95) **0.79** **0.78**	(1.9-3.1) **2.44** **2.40**	(0.6-1.1) **0.71** **0.75**	(1.7-4.0) **3.20** **2.85**	(0.2-0.5) **0.29** **0.32**	21.7

*: For the non-detects, LOD/2 was used for calculating mean.
': sum of branched and linear isomers
WTE: white tailed eagle, CE: Common eider, KW: kittiwake, GG: Glaucous gull, CG: Common gull, ES: European Shag.

When comparing our data from white-tailed eagle with the reviewed data in (71), PFCAs were of the same order of magnitude while PFOS was almost a tenth in the current study (mean of 18.3 ng/g - current study and 146 ng/g (71)). In a recent study by Badry et al., a 30-fold higher mean PFOS concentrations of 615 ng/g ww in white-tailed eagle liver from Germany was

reported, while the PFCAs were present at similar concentrations as reported in our study (72). Not much information can be found on toxicity thresholds for PFAS in liver and eggs of species from Northern European wildlife. As an alternative, toxicity reference values (TRVs) for PFOS in liver (600 ng/g ww) of birds were deduced in 2005, based on the no observed adverse effect level (NOAEL) of PFOS in birds (73). None of the liver data in our study came even close to this TRV, but possible toxicity caused by chronic exposure as well as mixture of PFAS cannot be ignored.

PFAS levels in mammals

Besides containing high concentrations of conventional PFAS, both 6:2- and 8:2 FTSAs were detected in liver samples in otter (range 11.2 – 27.8 ng/g and 38.3 – 76.8 ng/g, respectively). Of the other alternative PFAS measured, as for example ADONA and GenX (HFPO DA), no species showed concentrations above the LOD. The cyclic perfluoro-4-ethylcyclohexanesulfonate (PFECHS) on the other hand was for the first time detected in all polar bear plasma samples in quantifiable concentrations varying between 1.26 – 3.09 ng/mL (average at 1.98 ng/mL in 2017) and 0.26 – 0.85 ng/mL (average at 0.54 ng/mL in 2018). This compound has been recently reported in surface water of the North and Baltic Seas, herring gull eggs from the Great lakes and the Arctic ice cap (74-77). PFECHS likely shares similar biological mechanisms for uptake and distribution as branched and linear PFOS (74, 76). Spaahn et al. and Liu et al., were able to identify PFECHS in liver of polar bears (n=3) and harbour and ring seals from Sweden (n=2, pooled), but did not state any quantitative data (78, 79).

With respect to the $SumPFAS_9$, otter and mink were the species with highest concentrations in liver tissues in this study, with PFOS the dominating compound followed by PFNA (Table 2). Otter was recently also identified as majorly exposed to a broad range of PFAS in liver samples

from Sweden, UK, Netherlands and Germany (average of 6321 ng/g sumPFAS$_9$) (80). The sumPFAS$_9$ concentrations found in our study for otter (average of 267 ng/g) were considerably lower but comparable with those reported for Norwegian otter sampled in 2010 with an average of 381 ng/g by Roos *et al.* (81). Similarly, the sumPFAS$_9$ in mink liver from our study was ten times lower than concentrations reported for mink in Sweden (sumPFAS$_9$ of 2110 ng/g ww) (81, 82).

When comparing with the terrestrial mammals, concentrations of SumPFAS$_9$ were 1-2 orders of magnitude lower in wolf, deer and moose, but comparable to reported concentrations in wolf elsewhere (83). Despite their different status as predator and prey, sumPFAS$_9$ of wolf and deer liver were in fact comparable, mostly caused by considerably higher PFOS and PFDA concentrations in deer than in moose, comparable to earlier findings (84). The close vicinity of an urban centre, the city of Oslo, could be a reason. Otters, minks, polar bears and arctic foxes feed partly on the marine/aquatic food webs, which are more complex and more heavily contaminated with PFAS than the shorter terrestrial food chains.

Table 2: *Concentrations of selected PFAS concentrations in marine and terrestrial mammals (ng/g ww), n=5 for every species except for polar bear (2017: n = 5 females & n = 5 males; 2018: n= 5 females) and Roe deer (n=3). Range in parentheses.*

	PFHxS	PFOS'	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	SumPFAS$_9$
	(Min – max) **Median/ Mean***									
Mink (Liver)	(3.4-6.0) **8.32** **4.50**	(86-201) **264** **135**	(0.26-5.4) **1.79** **2.30**	(13-31) **27.36** **21.0**	(4.7-11) **15.94** **8.20**	(4.3-11) **18.50** **8.00**	(0.7-3.7) **2.45** **2.30**	(0.8-5.3) **2.84** **3.20**	(0.1-0.9) **0.37** **0.50**	185
Otter (Liver)	(1.80-4.35) **3.13** **3.09**	(72.2-218) **116** **130**	(6.30-17.5) **9.89** **10.4**	(53.7-151) **70.5** **84.0**	(14.7-38.1) **20.5** **23.2**	(12.0-16.2) **13.5** **14.1**	(1.29-1.74) **1.65** **1.57**	(2.25-3.89) **3.20** **3.14**	(0.26-0.37) **0.29** **0.30**	270
Wolf (Liver)	(<0.05-0.65) **0.03** **0.20**	(0.68-2.20) **1.81** **1.61**	(<0.05-0.09) **nd** **0.04**	(0.55-1.91) **1.18** **1.18**	(0.25-1.49) **0.70** **0.75**	(0.22-1.33) **0.70** **0.69**	(<0.05-0.25) **0.14** **0.13**	(<0.10-0.32) **0.10** **0.13**	(<0.10) **nd** **nd**	4.73

Moose (Liver)	(<0.05) **nd** **nd**	(0.18-0.39) **0.27** **0.27**	(<0.05-0.08) **nd** **0.04**	(0.09-0.25) **0.18** **0.19**	(0.06-0.18) **0.09** **0.11**	(0.10-0.19) **0.11** **0.13**	(<0.05) **nd** **nd**	(<0.10) **nd** **nd**	(<0.10) **nd** **nd**	0.74
Roe Deer (Liver)	(<0.05) **nd** **nd**	(1.08-4.15) **2.85** **3.30**	(0.06-0.11) **0.09** **0.10**	(0.22-0.53) **0.34** **0.27**	(0.07-1.20) **0.56** **0.41**	(<0.05-0.44) **0.21** **0.17**	(<0.05-0.53) **0.21** **0.09**	(<0.10) **nd** **nd**	(0.10) **nd** **nd**	4.26
Arctic Fox (Liver)	(1.18-9.28) **8.50** **5.90**	(12.6-171) **69.4** **86.0**	(0.48-1.88) **0.83** **0.97**	(4.85-19.9) **5.40** **20.0**	(1.73-10.7) **4.32** **6.90**	(1.56-13.3) **4.24** **14.0**	(0.20-1.75) **0.59** **0.75**	(0.51-6.35) **1.80** **2.38**	(0.15-0.90) **0.30** **0.38**	137
Polar bear (Plasma) 2017	(11-35) **23.4** **25.0**	(56-201) **111** **113**	(0.86-5.1) **3.79** **3.30**	(8.8-38) **18.4** **20.0**	(3.6-13) **6.29** **6.90**	(7.0-24) **13.1** **14.0**	(0.9-2.7) **1.55** **1.66**	3.58 **2.97** **3.58**	(<0.1-0.7) **0.13** **0.21**	188
Polar bear (Plasma) 2018	(26.0-44.1) **33.5** **34.3**	(47.1-188) **125** **120**	(4.34-6.72) **5.27** **5.35**	(30.2-41.5) **38.2** **36.7**	(6.10-13.1) **9.49** **10.0**	(10.2-24.6) **18.3** **19.1**	(0.90-3.04) **2.61** **2.36**	(1.55-6.02) **4.45** **4.32**	(<0.05-0.77) **0.75** **0.61**	233

*: For the non-detects, LOD/2 was used for calculating mean.
‘: sum of branched and linear isomers

Of the short-chain PFAS, PFBS was detected only sporadically in most species, except for polar bear plasma and mink liver. In polar bear, it was detected in 60% of all 2017- and 100% in all 2018 samples, ranging between 0.02 and 0.14 ng/mL. In mink liver, PFBS concentrations varied between 0.16 and 0.6 ng/g when detected. PFSA with a shorter carbon chain length than PFBS were not detected in mammalian samples. In contrast, TFA was detected in all mammalian liver samples (except for mink, which was not analysed for TFA). Average concentrations of 9.93, 40, 46 and 66 ng/g were found for roe deer, moose, wolf, and otter respectively, suggesting TFA being the major PFAS in the terrestrial species deer, moose and wolf. The highest TFA concentrations were found in arctic fox, with an average of 141 ng/g. TFA in arctic foxes dominated also over the other detected PFAS. Due to the contamination observed in the batch of analysis of polar bear samples, TFA was not reported in this species. No PFCA with a chain length with two and three perfluorinated carbons were found (PFPrA and PFBA).

Because of its low pKa, TFA rapidly forms salts and dissolved in water when released to the terrestrial environment and surface waters (74). It is very water soluble and not bioaccumulative, which suggest low accumulation in mammalian and avian predators. Several anthropogenic sources of TFA have been identified. First, in the U.S., TFA has been widely used in industry; in 2002 it was estimated that between 450 and 4,500 tonnes of TFA was produced (PubChem 2015). Second, other studies have also shown the formation of TFA from biodegradation of FTOHs or by photochemical oxidation atmospheric degradation of HFC-gases (85-88). The yield of TFA from for example HFC-134a was reported to be 21%, whereas that from other HFCs and HFO-1234yf was shown to be 100% (89, 90). Any substitution of phased out HFCs by other products on a molecule-for-molecule basis might result in an increase in the overall formation of TFA (73). The authors estimated a total yield from HFC and HFOs up to the year 2050 of 20,625 kt. When TFA is formed in the atmosphere, it is presumed that TFA will partition into fog and cloud water, potentially leading to elevated concentrations in rainwater as well as the aquatic environment in general (91). Third, degradation of pesticides and pharmaceuticals that contain a $–CF_3$ group would most likely result in the formation of TFA; however, the lack of environmental degradation studies of these chemicals of large production volumes prevents any assessment to their contribution to the global TFA pool (74). The presence of natural sources is currently debated, possibly rendering all TFA sources as anthropogenic (92).

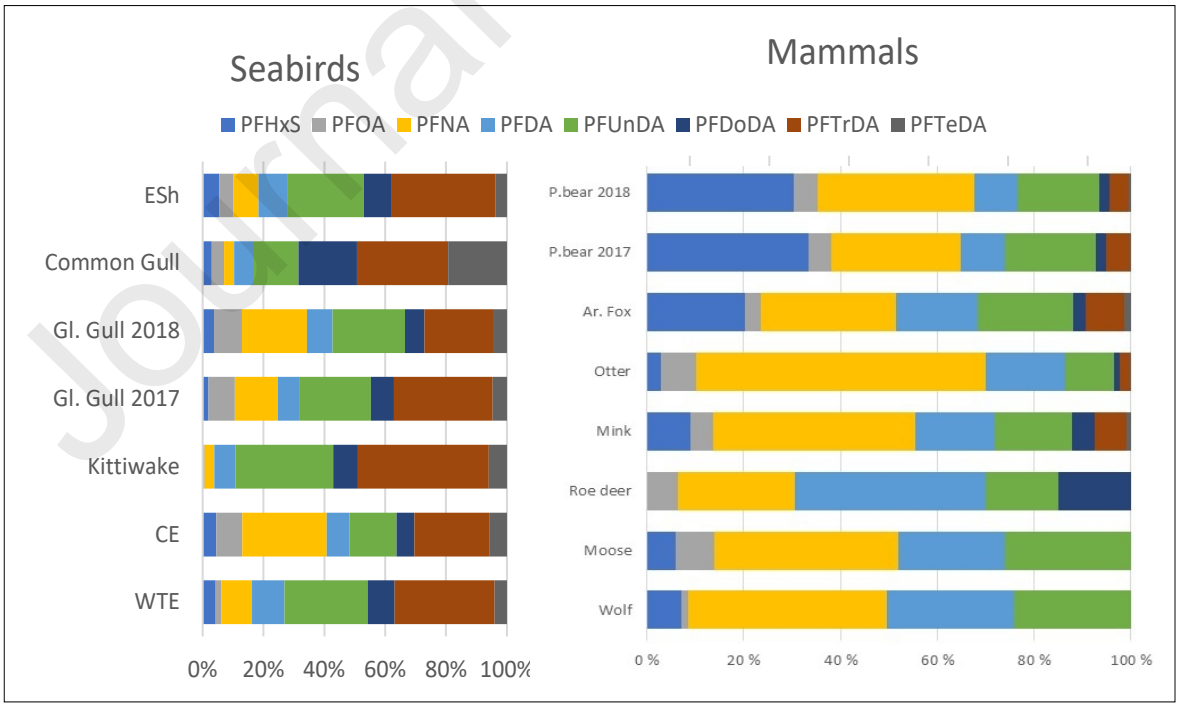
PFAS pattern comparison

PFOS was the dominating contributor with more than 50% in all studied species, in some cases only exceeded by TFA in mammalian liver. Conventional PFAS exhibited different patterns in seabirds compared to marine and terrestrial mammals. When comparing the contribution of other major detectable PFAS, when PFOS is excluded, the difference becomes more prominent (Figure 2). The long chain PFCAs, PFUnDA and PFTrDA, accounted for more than 50% of the

remaining PFAS load in seabirds; while PFNA, PFDA and PFUnDA accounted for more than 70% in most mammalian samples. Further, with the limited abundance of PFHxS and PFDoDa, PFTrDA anobservable difference was noted in PFAS pattern between terrestrial and marine mammals. Comparisons between the species are, however, limited by the different tissue types analysed and the respective differences in tissue distribution (93).

Figure 2: Relative contribution of conventional PFAS, excluding PFOS, in seabirds and mammals from the Norwegian mainland and the Arctic (WTE: white tailed eagle (liver), CE: Common eider (egg), Gl. Gull: Glaucous gull (egg), Esh: European Shag (egg), Ar. Fox: Arctic Fox (liver), P.bear: Polar bear (plasma)).

PFTrDA was among the dominating PFCA in the seabirds and white-tailed eagle, whereas this compound had only a minor contribution to the PFCA exposure in the mammalian samples.



PFNA shows an opposite pattern. The source of odd-numbered long-chain PFCA into the environment is still disputed. Historic technical mixtures of the PFOA- and PFNA production

exhibited a symmetric distribution of PFCA homologues centring around PFNA (electrochemical fluorination production process) while the prevalence of even-numbered homologues was a result of the telomerisation production process (94) . Chen *et al.* reviewed the presence of PFAS in apex predators, representing both the marine and the terrestrial ecosystem (71), also pointing out PFUnDA as the most abundant PFCA in the reviewed apex predators. If PFUnDA is a by-product of the industrial production of PFNA and/or the degradation of 10:2 fluorotelomer alcohol (10:2 FTOHs) is still unclear (40, 95). Atmospheric oxidation of FTOHs to corresponding even- and odd-chain length PFCAs, followed by preferential bioaccumulation of the odd (i.e., longer) chain length homologues has been discussed before (96, 97). The similarily observed high abundancy of PFTrDA in our study would be for example requiring a 12:2 fluorotelomer precursor or an equivalent perfluorinated side-chain fluoropolymer as a potential source. PFTrDA contributed to a larger degree to the total PFCA exposure in samples from seabirds than in samples from mammals. The interspecies differences are potentially also related to the differences in tissue-type, metabolic capabilities, habitat and prey choices. Liver is a storage reservoir of PFAS, while the low-density lipoprotein in the yolk is formed in the liver of the mother with PFOS bonded and then transferred to the yolk for maternal transfer (71). Different exposure scenarios dependent on location, feeding strategy and habitat are additional possible reasons, as also recently observed in marine mammals (79).

EOF

All samples collected in 2017 and 2018 were also analysed for EOF to evaluate the presence of additional organic fluorinated compounds (Figure 3).

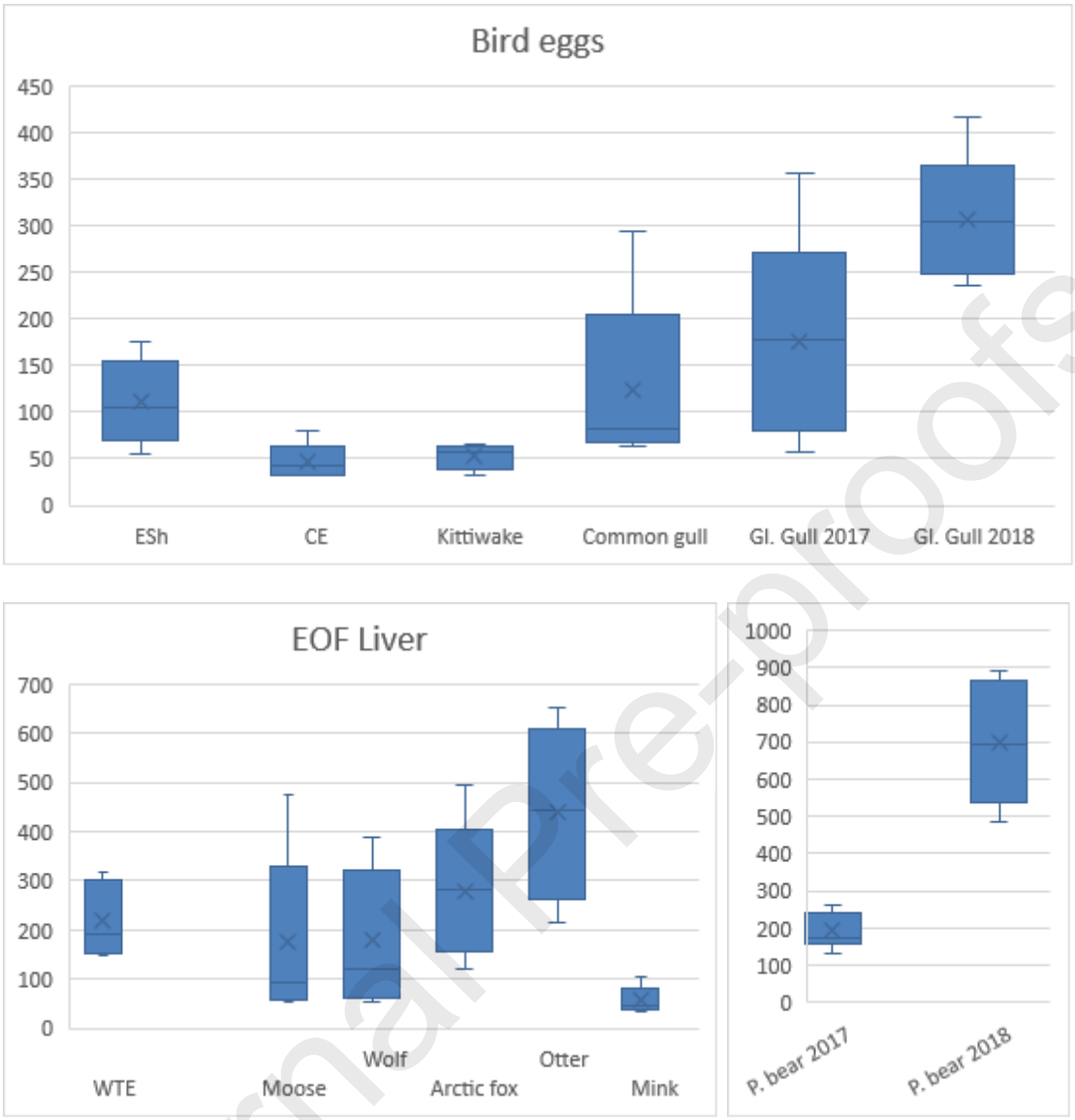


Figure 3: EOF concentrations in Norwegian wildlife samples in ng F/g or ng F /mL. Upper panel: in eggs, lower panel: in liver and plasma (polar bear); Whiskers: Min/max, x: mean, horizontal line: median, lower and upper borders of box: value of 1st and 3rd quartile

In Figure 3 we sorted the EOF data with respect to sampling matrix eggs, liver and plasma. The egg samples showed an average of 136 with the common eider and kittiwake eggs exhibiting the lowest mean EOF concentrations with 46.5 and 52 ng F/g respectively. Highest EOF was found in eggs from glaucous gulls sampled in 2018 (average of 306 ng F/g). Samples from 2017

from the same species, however, showed lower EOF, averaging 176 ng F/g, suggesting interannual variations in EOF exposure. Liver samples analysed for EOF averaged at 218 ng F/g with mink exhibiting the lowest EOF with 58 ng F/g. All the other species showed comparable average EOF concentrations with white tailed eagle 221 ng F/g, moose 174 ng F/g, wolf 179 ng F/g, arctic fox 280 ng /g F and otter 361 ng F/g. Otter showed the highest EOF in accordance with the highest sum$PFAS_9$ observed in the same species (Figure 2). Considerable variations were observed within each species, except for mink liver (Figure 3).

The polar bear samples show a similar interannual variation as observed in glaucous gull eggs, with lower EOF concentrations observed in 2017 compared to 2018 (average of 242 and 875 ng F/g respectively). When comparing with the very limited other available data, the here reported EOF in plasma was 10-30% of the EOF observed in polar bear liver from east Greenland (78, 79).

Contribution of targeted PFAS to EOF

When comparing the contribution of the known PFAS with the measured EOF in eggs, the EOF content in common gull eggs was explained by approximately 60% with the analysed PFAS (Figure 4). In contrast, only 6% of the analysed PFAS can explain the measured EOF in glaucous gull eggs. TFA was measured in the glaucous gull egg samples from 2018, resulting in an increase of explainable EOF to an average of 8%, indicating a minor importance of TFA for this species.

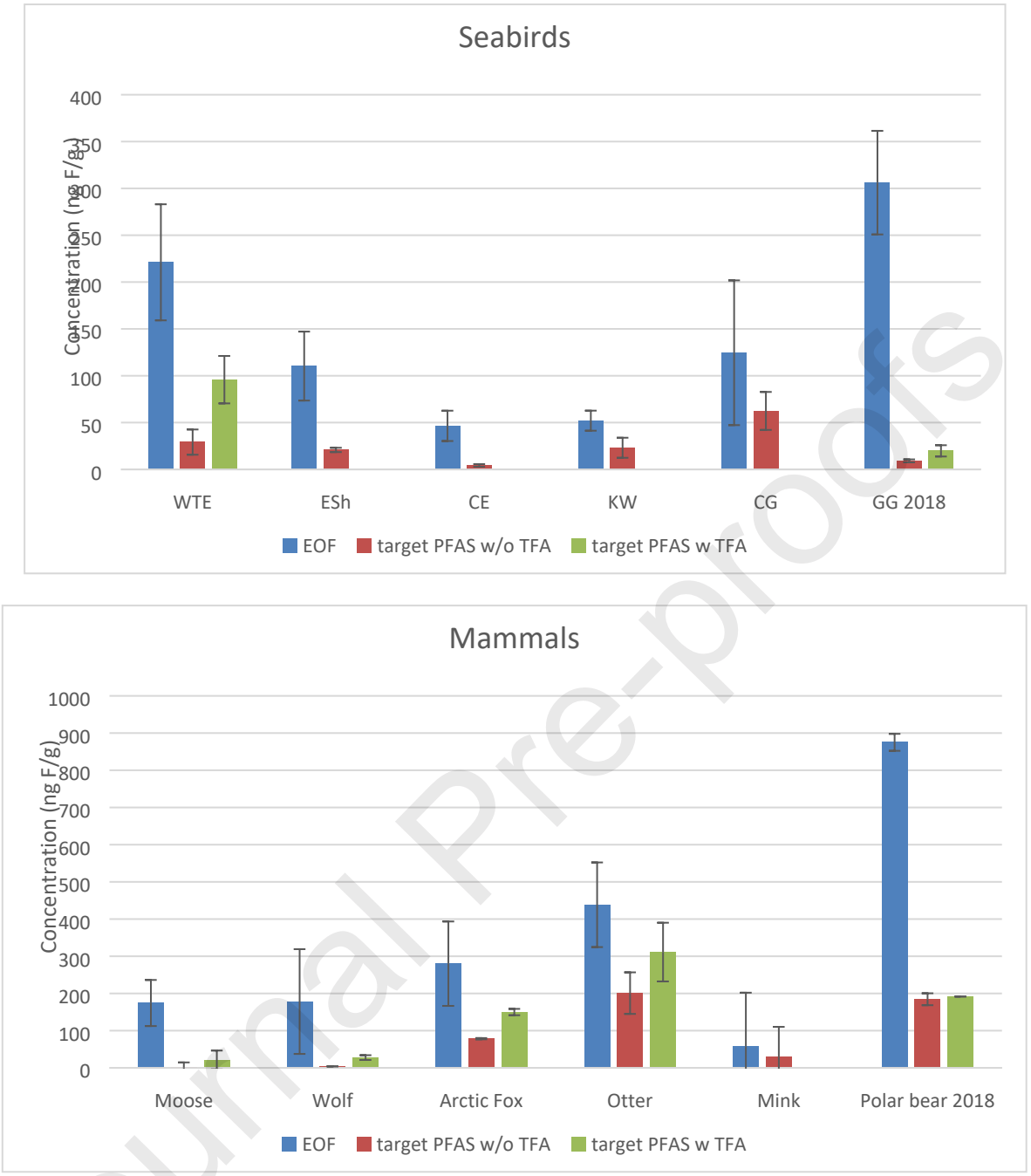


Figure 4: Concentration of targeted PFAS and measured EOF in seabirds and mammals in ng F/g; blue bars indicate EOF concentrations, whereas red and green bars indicate targeted PFAS without and with TFA; (WTE: White tailed eagle, ESh: European shag*, CE: Common eider*, KW: kittiwakes*, CG: Common gull*, GG: Glaucous gull). *: no TFA measured

In liver samples, the contribution of targeted PFAS to EOF varied widely between species (average of 17% for white tailed eagle, 1.5% for moose, 5% for wolf, 36% for Arctic fox, 59%

for otter and 64% of the measured EOF for mink), with terrestrial mammals being exposed to the highest unexplained EOF percentages. When including TFA, the ratio increased to on average 58% for white-tailed eagle, 28% for moose, 36% for wolf, 73% for Arctic fox, 94% for otter. This is illustrating the importance of the inclusion of stable short-chain PFAS into the analytical procedure and also highlights possible differences in tissue distribution (relatively higher contribution of TFA to liver samples but lower importance for eggs and plasma). The polar bear plasma showed organic F contribution by targeted PFAS of 81% in 2017 and 28% in 2018. When including TFA for the samples from 2018, the contribution by targeted PFAS increased only slightly by additional 3.5% to 29 ng F/g. In general, for all species, the observed gap between measured EOF and calculated F contribution by targeted PFAS indicated the presence of either unknown PFAS, PFAS precursors or other fluorinated organic compounds as monofluorinated pesticides and pharmaceuticals.

The amount of F in targeted PFAS (excluding TFA) vs. EOF showed no relationship in seabirds, polar bears and terrestrial mammals, while the liver data from mammals mostly feeding within the marine food chain (otter and mink included, arctic fox excluded due to mixed feeding) showed a strong linearity (R^2= 0.976; Figure 5). The lack of correlation between targeted PFAS and measured EOF indicated that unknown organofluorine compounds might have different sources, uptake characteristics and metabolic properties than targeted PFAS (e.g., pesticides or pharmaceuticals).

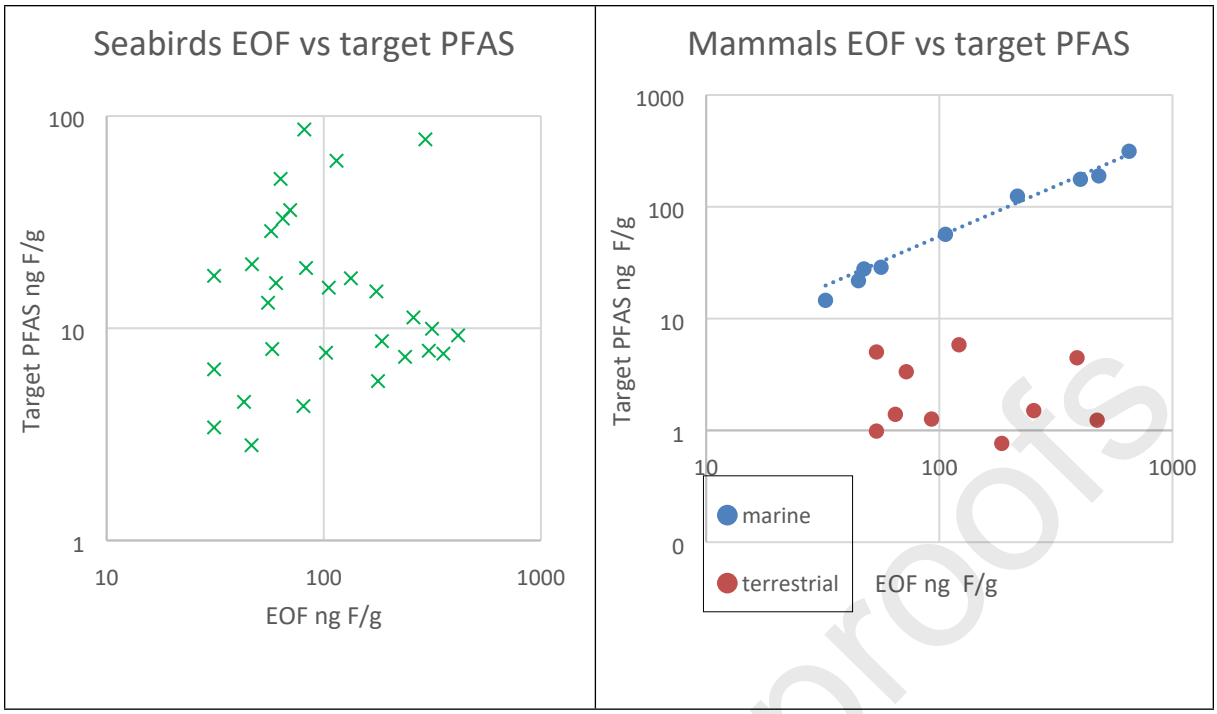


Figure 5: Relationship between ng F/g by targeted PFAS (excluding TFA) and by EOF measurements in seabirds (eggs) and mammals (liver). Linear regression coefficient R^2 is shown.

Implications

This investigation shows that sub-arctic and arctic animals from Norway mainland and Svalbard are contaminated with a larger spectrum of PFAS than targeted by most studies. Concerningly, the conventional measured PFAS accounted only for 8% to 67% of EOF in the samples. The levels reported for ultrashort chain PFAS were not quantitative due to the fact that different surrogate internal standards were used. However, our results indicated that the contribution of TFA to the overall PFAS burden and EOF can be important in liver (e.g. white-tailed sea eagle, arctic fox, otter) but may be of minor importance in eggs. This highlights that fluorinated compounds show varying abilities to accumulate to different tissues and express different metabolic capabilities, which is likely related to their differing physical-chemical properties. The presence of ultrashort chain PFAS in biota samples emphasizes the need to develop suitable internal standards for the quantitation of these compounds.

To answer the question of the unexplained organofluorine contribution, completing the organic fluorine inventory, the total oxidisable oxidation assay (TOPA) might improve our understanding towards PFAS contamination by providing further information about the presence of unknown PFAS precursors in Norwegian wildlife. To answer the question of the unexplained organofluorine contribution by completing the organofluorine inventory, the total oxidizable oxidation assay (TOPA) might improve our understanding towards PFAS contamination by providing further information about the presence of unknown PFAS precursors in Norwegian wildlife (98). Additionally, remaining unknown fluorinated fractions could be due to the contribution of other novel PFAS or other PFAS that were not included in this study. Spaan *et al.* (2020) discovered novel PFASs, such as PFECAs, double-bond/cyclic PFSAs, ether PFSAs and enol-ether, cyclic-ether or carbonyl PFSAs, in the liver of marine mammals (including polar bears, Pinnipeds and cetaceans); however, the TOPA could not yield measurable PFAAs on these novel PFAS (79). Alternative approaches as precursor hydrolysation as described by Nikiforov *et al.* (2021) or an extended comprehensive targeted approach are a prerequisite to complete the PFAS picture, also including chlorinated PFAS (99). To assess the organofluorine mass balance in wildlife, a battery of fine-tuned and interlinked analytical methodologies is required, still progressing to harmonisation. With ever growing human activities in remote regions of Northern Europe, the habitats of many of the studied species are already under pressure resulting in fragile ecosystems.

Authors contribution

D.H.: Conceptualization, Methodology, Resources, Writing-Original Draft, Writing-Review & Editing, Supervision, Project Administration, Funding Acquisition, **L.H.:** Conceptualization, Methodology, Resources, Writing-Review & Editing, Supervision, Project Administration, Funding Acquisition, **V.N**.: Methodology, Writing-Review & Editing, **L.Y.:** Methodology,

Resources, Writing-Review & Editing, **H.R.:** Resources, Writing-Review & Editing, **B.M.:** Resources, Writing-Review & Editing, **G.W.G.:** Resources, Writing-Review & Editing.

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Jon Aars and Magnus Andersen (Norwegian Polar Institute) collected the polar bear samples. Local trappers and the Governor of Svalbard/Norwegian Polar Institute collected the arctic fox carcasses and Eva Fuglei (Norwegian Polar Institute) conducted the arctic fox dissections and sample collection. Svein Are Hansen assisted with sampling of samples from the Norwegian mainland. Merete Miøen, Lovise Skogeng Pedersen and Unni Mette Nordang contributed to the analyses of the samples in the NILU lab. We are thankful to Martin Schlabach who contributed with securing financial support and project administration.

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CRediT author statement

D.H.: Conceptualization, Methodology, Resources, Writing-Original Draft, Writing-Review & Editing, Supervision, Project Administration, Funding Acquisition, **L.H.:** Conceptualization, Methodology, Resources, Writing-Review & Editing, Supervision, Project Administration, Funding Acquisition, **V.N**.: Methodology, Writing-Review & Editing, **L.Y.:** Methodology, Resources, Writing-Review & Editing, **H.R.:** Resources, Writing-Review & Editing, **B.M.:** Resources, Writing-Review & Editing, **G.W.G.:** Resources, Writing-Review & Editing.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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