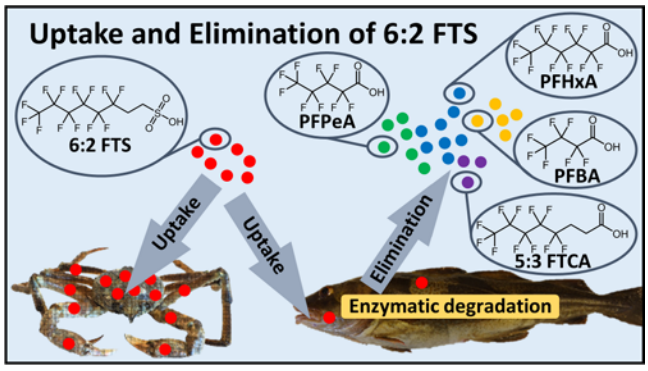
Bioaccumulation of fluorotelomer sulfonates and perfluoroalkyl acids in marine organisms living in aqueous film forming foam (AFFF) impacted waters

Håkon A. Langberg [a, b, *], Gijs D. Breedveld [a, c], Hege M. Grønning [a], Marianne Kvennås [a], Bjørn M. Jenssen [b], Sarah E. Hale [a]

[a] Environmental Department, Norwegian Geotechnical Institute (NGI), Oslo, Norway
[b] Department of Biology, Norwegian University of Science and Technology (NTNU), Trondheim, Norway
[c] Department of Geosciences, University of Oslo (UiO), Norway

ABSTRACT

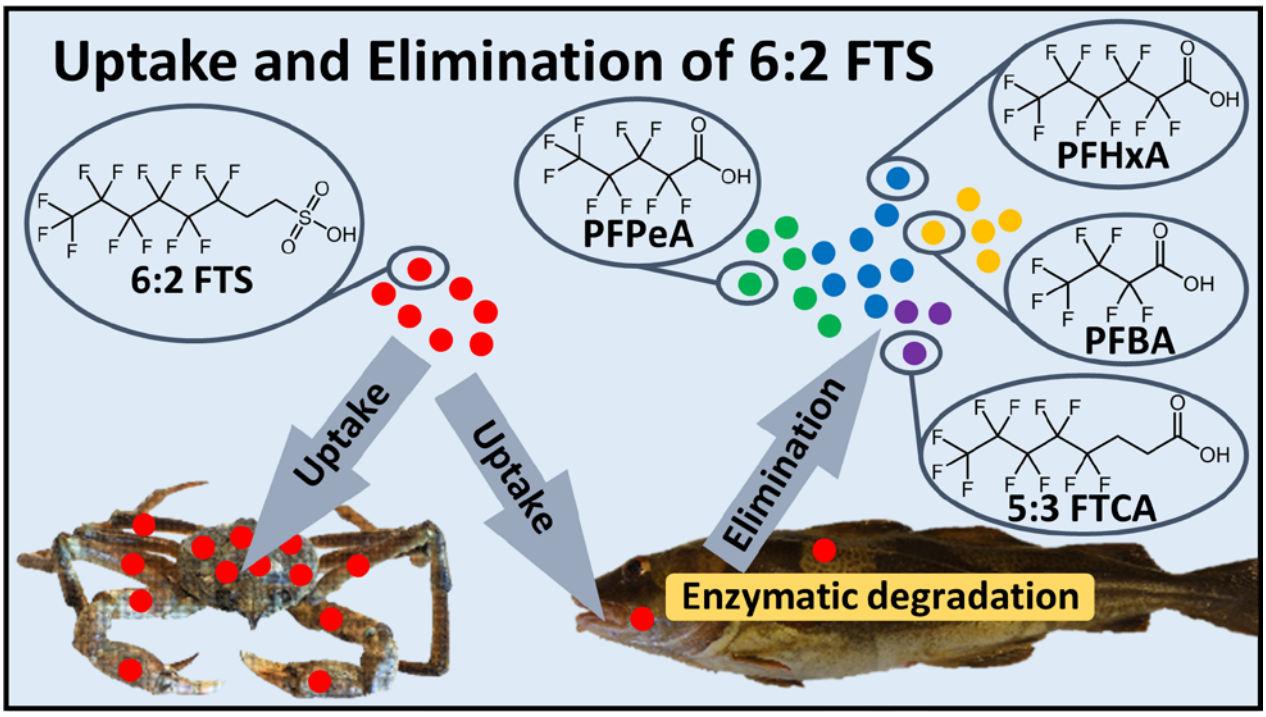
The use of aqueous film forming foams (AFFF) has resulted in hot spots polluted with poly- and perfluorinated alkyl substances (PFAS). The phase out of long chained perfluoroalkyl acids (PFAA) from AFFF resulted in the necessity for alternatives, and short chained PFAA and fluorotelomer based surfactants have been used. Here, the distribution of PFAS contamination in the marine environment surrounding a military site in Norway was investigated. Up to 30 PFAS were analysed in storm, leachate and fjord water, marine sediments, marine invertebrates (snails, green shore crab, great spider crab, and edible crab) and teleost fish (Atlantic cod, European place, and Lemon sole). Perfluorooctane sulfonic acid (PFOS) was the most abundantly detected PFAS. Differences in PFAS accumulation levels were observed between species, likely reflecting different exposure routes between trophic levels and different capabilities for depuration and/or enzymatic degradation. In agreement with previous literature, almost no 6:2 fluorotelomer sulfonate (6:2 FTS) was detected in teleost fish. However, this study is one of the first to report considerable concentrations of 6:2 FTS in marine invertebrates, suggesting bioaccumulation. Biota monitoring and risk assessments of sites contaminated with fluorotelomer sulfonates (FTS) and related compounds, should not be limited to fish, but also include invertebrates.



Keywords:

PFAS, PFOS, 6:2 FTS, Biota, Biotic monitoring, Accumulation, Invertebrates, Crab, Fish, Point source, Passive sampling, Airport, Military base, Norway,

* Corresponding author. Phone: +47 47242944; e-mail: hakon.austad.langberg@ngi.no, ORCID: Håkon Austad Langberg: 0000-0002-6186-6962



Graphic abstract. Large version

INTRODUCTION

The use of AFFF at firefighting training areas, airports, military sites and fire stations has resulted in hot spots of PFAS polluted soil, sediment and water.[1–3] PFAS have been shown to exert toxic effects on ecosystems and human health,[4,5] and since the early 2000s, perfluorooctane sulfonic acid (PFOS) and related long chained perfluoroalkyl acids (PFAA) (defined here as perfluoroalkyl carboxylic acids [PFCA] with number of carbon atoms [C] ≥8, and perfluoroalkyl sulfonic acids [PFSA] with C ≥6), have been phased out in AFFF. This has resulted in the need for alternatives, and short chained PFAA and fluorotelomer based surfactants (6:2 fluorotelomer sulfonate [6:2 FTS], and fluorinated telomer products with 6:2 configuration) have been used as replacements in AFFF.[6–10]

The physiochemical properties of PFAS suggests that water, and water-living organisms, are important environmental compartments for PFAS partitioning.[11] Different toxicokinetics have been reported for different organisms and PFAS groups, and elimination rates for PFAA show large species and gender dependent variations.[12] As an example, the serum half-life of PFOS was 1 to 2 months in rodents, but several years in humans.[12] Long chained PFAA have been reported to accumulate in a wide range of fish species, however half-lives are generally shorter (days)[13] than those for rodents and humans. PFSA have been shown to have longer half-lives than PFCA of the same chain length.[11,13,14] Half-lives of 4.5 days for perfluorooctanoic acid (PFOA) and 12 days for PFOS have been reported in blood of rainbow trout (*Oncorhyncus mykiss*).[13] 6:2 FTS has been shown to be effectively eliminated in teleost fish,[15] and has, based on fish bioaccumulation data, been considered as unlikely to bioaccumulate in aquatic systems.[9]

The environmental quality standard for PFOS in the European Water Framework Directive (9.1 μg kg^{-1}) refers to fish,[16] and biota monitoring at PFAS hot spots has thus focused on fish.[17–20] Less is known about PFAS in invertebrates. PFAA have been detected in insect larvae, bivalves, zooplankton, and larger crustaceans such as prawns and crabs.[21–28] Depuration of long chained PFAA are reported for

some crustaceans. The half-lives of PFOS and perfluorohexane sulfonic acid (PFHxS) in school prawn (*Metapenaeus macleayi*) were 159 hours and 6 hours, respectively,[29] demonstrating the effect of chain length. Half-lives in mud crab (*Scylla serrata*) in the same study were considerably longer at 998 hours for PFOS and 190 hours for PFHxS,[29] illustrating species dependent depuration rates. Therefore, with the exception of a few species, PFAS behaviour in invertebrates is largely unexplored. A wider understanding related to PFAS accumulation, elimination, and toxicity in aquatic invertebrates is needed to identify possible implications for risk assessments of PFAS contamination in aquatic ecosystems.

In the present study, the accumulation of PFAS (arising from the use of AFFF) in the marine food chain was investigated. The objective was to evaluate potential species-specific differences in PFAS accumulation. The military site at Bodø Airport, Bodø Air Station, was chosen as the case study site. PFAS profiles and concentrations in invertebrates (marine snails and crabs), representing less mobile organisms living close to point sources of AFFF polluted storm water, were compared to mobile teleost fish. PFAS profiles and concentrations in storm water, leachate water, fjord water (sea water), and marine sediments were used to evaluate PFAS distribution in the abiotic environment. To the best of our knowledge this is the first study to evaluate the accumulation of long chained PFAA and replacement products in invertebrates living close to an AFFF pollution hot spot.

MATERIALS AND METHODS

Case study site

Bodø Air Station (67.26° N, 14.36° E) is a military airbase located on a peninsula in the Norwegian Arctic. It experiences strong winds and tidal currents resulting in strong water circulation and thus, dilution of contaminants. In the period 2013-2017 (the time frame of this study and the two preceding years), the average wind speed was 6.5 m s^{-1},[30] and the average tidal range was 1.9 m.[31] The Air Station shares facilities with the civil airport in Bodø (Bodø Airport). Little is known about the first use of AFFF

at the site, but it has probably been used since the mid-1960s. The use of PFOS based AFFF was phased out in Norway in 2007 (as an early adoption of EU regulations).[32] As a result, firefighting foam containing fluorotelomer based surfactants (6:2 FTS and/or related products) was used at the Air Station from 2007. According to the Norwegian Defence Estates Agency (personal communication, C.E. Amundsen, June 2016), the process of phasing out PFAS based foam started in 2012 and was completed at airport firefighting training areas in 2015.

Eight sampling stations around the Air Station were selected to capture the main outlets of PFAS in storm water and soil leachate (Figure 1). A reference station was located on the other side of the fjord, about 5 kilometres (km) from the Air Station. Stations A, C, D, G, and H are located near discharge points for storm water not associated with any particular PFAS source. These areas were assumed to represent nominal levels of PFAS discharge from the Air Station. Station B is close to the outlet of PFAS contaminated storm water from a fire station. Sampling stations E and F are situated in an area extensively used for firefighting training. Station E is at an outlet of storm water assumed to have high concentrations of AFFF related PFAS compounds. Station F is an area where AFFF contaminated water leaches from the soil at the firefighting training area. There are no known sources of PFAS contamination in proximity to the reference station.

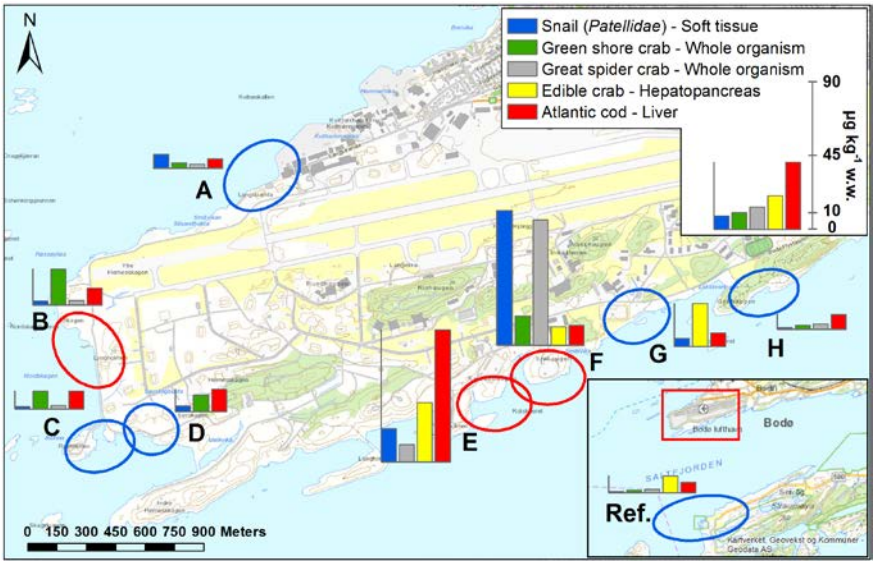


Figure 1. Geographical location of the sampling stations around the Air Station (stations A-H) and the reference station (Ref.) on the other side of the fjord. Stations A, C, D, G, and H are located near discharge points for storm water not associated with any particular PFAS source (blue circles). Stations B, E, and F are point sources for PFAS contaminated leachate and storm water (red circles). Bar charts show the average concentrations of Σ_{22} PFAS in biotic tissue at each sampling station. The numerical values are given in Table S7. Not all species were caught at all sampling stations.

Leachate and storm water

Storm water was sampled in several campaigns during 2015-2016. At station F, which has been used for firefighting training, soil leachate water entering the fjord was sampled at the same time as storm water. No soil leachate water was observed at other stations. Sampling was performed for storm water (3 to 5 times), and soil leachate water (twice) to capture concentration spikes (see details in Table S1 in the supplementary information (SI)). Unfiltered samples were collected by submerging a 0.5 L high density polyethylene bottle in the water source. Samples were kept cool and dark and sent for chemical analysis within 48 hours of sampling. Water flow rates (L s^{-1}) were estimated at the time of sampling (March and May) by measuring the cross section and velocity of the water. The water amount from each station per year (L $year^{-1}$) was calculated as described in equation I. The average PFAS concentrations (ng L^{-1}) were multiplied by the amount of water from each station per year (L $year^{-1}$) to estimate the amount of PFAS released to the sea (g $year^{-1}$), equation II.

Amount of water per year:

I. $Q_a = v \times t$

Where Q_a is the annual discharge volume (L year^{-1}), v is the flow rate (L s^{-1}) and t is the time (s year^{-1}).

Amount of PFAS released per year:

II. $m_{PFAS} = Q_a \times C_{PFAS}$

Where m_{PFAS} is the amount of PFAS released to the sea per year (g year^{-1}), Q_a is the annual discharge volume (L year^{-1}), and C_{PFAS} is the PFAS concentration (ng L^{-1}).

Marine abiotic environment

Sediments were sampled in May 2017 at all stations, except for station G where the sea floor consisted of rocks. Water depths varied between 1-5 m depending on station (details provided in the SI). A mixed sample of fine grained sediments was collected from a radius of 20 m from the emission point. Sediments were collected by pushing a plexiglas tube (7.5 cm diameter) into the sea floor to a depth of approximately 10 cm.

Passive samplers (deployed at the same time as sediment sampling) were used to measure concentrations in the fjord water (sea water) at all stations. The passive sampler, the SorbiCell (described elsewhere[33]), is a flow through sampler, based on sorption and sampler volume, with an entrance filter, two zones with adsorbent material, and a tracer salt for the calculation of the water volume that has passed the sorbent (details are provided in the SI). Passive samplers were deployed in the fjord, as close as possible to the emission point, 0.5 meters below the water surface. Passive samplers were collected 3 weeks after deployment, the cartridges were kept cool and dark until analysis.

Marine biota

Biota were sampled at the same time as sediments and the deployment of passive samplers. Marine invertebrates: snails (*Patellidae*); two species of small crabs: green shore crab (*Carcinus maenas*) and

great spider crab (*Hyas araneus*); and the larger edible crab (*Cancer pagurus*), and teleost fish: Atlantic cod (*Gadus morhua*); and two species of flatfish: European place (*Pleuronectes platessa*) and Lemon sole (*Microstomus kitt*) were sampled. Species available for sampling varied between stations (Table S2).

Snails were collected by hand from rocks in the intertidal zone as close to the emission source as possible. At the reference station, snails were collected over a length of approximately 100 m along the shore in the intertidal zone. Small crabs were collected by hand from a radius of 20 m from the emission point at water depths between 1 and 5 m depending on station (details in the SI), using waders in the intertidal zone and in shallow water, and by divers in deeper water. Edible crab and fish were sampled using commercial fish traps placed on the sea floor, approximately 200 m from shore at water depths between 5 and 30 m depending on the station (as it was not possible to catch fish within 20 m from the emission points, details in the SI). Raw shrimps and mackerel were used as bait (in a closed bait-bag). Fish were killed with a blow to the head and crabs were killed by spiking the crab from the underside. The weight (g) and length (cm) of the fish (fork-length) and edible crabs (carapace width), and sex of all three crab species were recorded (Table S3). For safety reasons and in order to avoid cross contamination, clean nitrile coated gloves were used during sampling of large crabs and fish. Clean nitrile gloves were used during sampling of other matrixes and during handling of all samples. Equipment was washed and dried, and nitrile gloves were changed between samples. Crabs and fish were wrapped in clean aluminium foil (whole organisms to avoid risk of contamination). All biotic samples were frozen at -20 °C before they were sent for dissection and chemical analysis.

Sample preparation and analysis

Analyses were performed by Eurofins Environment Testing Norway AS according to DIN EN ISO/IEC 17025:2005. A total of 30 PFAS compounds were analysed, however the number of analysed compounds varied between the different sampled media (see Table S4).

PFAS concentrations in sediments were quantified using method DIN 38414-S14. Total organic carbon (TOC) in sediments was calculated using a loss on ignition method. Water was analysed for PFAS following method DIN 38407-F42. The SorbiCell sorbent material was extracted using methanol. Extraction of biotic tissue was performed by freeze drying the sample, adding internal standards before extraction with methanol in an ultrasonic bath and solvent clean-up. Extracts were analysed using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS). Clean sand was used as a blank sample for biota and sediments. Distilled water was used as a blank sample for water samples. Sediment, biota, and water blank concentrations were acceptable according to the accredited lab procedures. For passive samplers, sorbent material from the same batch as used in the samplers was used as blank. Extractions were carried out for both adsorbent zones to check whether the sorption capacity had been exceeded. To validate the actual volume the Sorbicell samples, the depletion of the tracer salt in the sampler and the field volume (water which has passed through the sampler during deployment) was monitored. PFAS was not detected in passive sampler blanks. However, PFBA was detected in both adsorbent zones for all samplers, which may indicate that the sorption capacity was exceeded for this compound. Thus, although peaks were seen for PFBA they were not quantified. Samples from the reference site were used as a control as they had close to background PFAS concentrations. See SI for details about extraction, analysis, and limits of quantification (LOQ).

Snails (soft tissue) were analysed as one pooled and thoroughly mixed sample ($n>30$) from each sampling station. One pooled and mixed sample of whole organisms ($1 \leq n \leq 11$) was made for each of the two species of small crabs per station. Hepatopancreas in edible crab was analysed individually. Fish liver were weighed and analysed individually (Table S3). Stomach contents of the fish were removed before the remaining tissue was homogenized and analysed individually.

Data handling and statistical analysis

Statistical analyses were carried out using R version 3.4.2[34] (packages: vegan[35], agricolae[36], factoextra[37], and FactoMineR[38]). Concentrations in biota are given on wet weight basis (w.w.). Errors (±) in the present work are reported as standard error of the mean (SEM). Concentrations below the LOQ were assigned values of half the LOQ. Details about the statistical analysis are given in SI.

Concentrations in whole fish (μg kg^{-1}) were calculated using whole fish weight (kg), liver weight (kg), and concentrations in liver and remaining tissue (μg kg^{-1}). In Atlantic cod, the ratio between PFOS concentrations in liver and in remaining tissue was estimated, and possible relationships between Fulton's condition factor (weight to length ratio, K) or liver somatic index (LSI), and PFAS burdens in liver (sum $[\Sigma]_{22}$ PFAS) were investigated (equations are given in the SI).

RESULTS AND DISCUSSION

Leachate and storm water

Overall, the most dominant compounds in storm water were 6:2 FTS, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), PFHxS, and PFOS detected at maximum concentrations of 921, 738, 194, 142, and 1010 ng L^{-1}, respectively. The calculated amount of Σ_{19} PFAS released to the fjord at each station (g $year^{-1}$) and the site specific levels of dominating compounds, given as percentages (%) of the Σ_{19} PFAS, are listed in Table 1 (See Figure S1 for PFAS amounts in storm water and concentrations in biota at the different stations). As stations E and F are in close proximity to each other (approx. 150 m), and as it was not possible to distinguish between PFAS loads, they were treated as one station. PFAS profiles in storm water were similar at all stations, however PFAS concentrations and loads varied. The highest loads were estimated at the stations associated with PFAS sources: stations B and E/F (182 g and 1552 g Σ_{19} PFAS $year^{-1}$, respectively). PFOS was generally detected in the highest proportions of total PFAS (10-100%), followed by PFPeA (13-45%). PFHxS and PFHxA were detected at approximately comparable concentrations (0-25% and 0-20%, respectively). The level of 6:2 FTS (0-

38%) showed large variability between the stations. 6:2 FTS constituted a relatively large proportion of the total PFAS at stations B (0-36%), E/F (7-27%), G (0-38%), and H (9-16%), while it was not detected at stations A, C, and D.

Table 1. Calculated amount of PFAS (g year^{-1}) following storm water, in each sampling station (at the Air Station).

Station	A	B	C	D	E/F [1]	G	H
PFAS loads released to the sea per year (g year^{-1})	66	182	0	94	1552 [2]	16	161
Relative frequency of dominant PFAS compounds (%) [3]	**PFPeA** 28-35 **PFHxA** 0-14 **PFHxS** 0-24 **PFOS** 48-55	**6:2 FTS** 0-36 **PFPeA** 22-45 **PFHxA** 10-12 **PFHxS** 5-25 **PFOS** 15- 100	**PFPeA** 29- 40 **PFHxA** 13-14 **PFHxS** 0-16 **PFOS** 24-60	**PFPeA** 13-26 **PFHxA** 6-13 **PFHxS** 9-15 **PFOS** 33-57	**6:2 FTS** 7-27 **PFPeA** 17-25 **PFHxA** 5-11 **PFHxS** 3-10 **PFOS** 35-48	**6:2 FTS** 0-38 **PFPeA** 36-45 **PFHxA** 0-20 **PFOS** 26-35	**6:2 FTS** 9-16 **PFPeA** 27-41 **PFHxA** 10-16 **PFHxS** 5-16 **PFOS** 10-23

[1] Stations E/F are in close proximity to each other and were treated as one station
[2] In addition to runoff with storm water, leachate from PFAS contaminated soil is expected to result in an additional 340 g of 6:2 FTS and 128 g of PFOS being released to the fjord from station E/F.
[3] Sampling was performed in several rounds, thus the PFAS profiles are given as ranges

Soil leachate water was only sampled at station F. The leachate water was dominated by 6:2 FTS and PFOS (average of 89 µg L^{-1} 6:2 FTS and 33 µg L^{-1} PFOS), and the yearly contributions to the fjord were estimated to be 340 g and 128 g, respectively. Station F has been extensively used for firefighting training, thus PFAS loads from soil leachate at all other sites are expected to be smaller. However, the nominal level of PFAS contamination observed all over the Air Station suggests some runoff from PFAS contaminated soil at all locations.

The reported levels herein are similar to levels reported in the groundwater at another Norwegian airport.[39] Previous studies have reported highly variable concentrations of PFAS in water from areas where AFFF has been used. At a closed down military airfield in Sweden (used from 1946 to 1994) PFHxS and PFOS dominated surface water samples (lakes and ponds) (highest concentrations were 25 ng L^{-1} and 45 ng L^{-1}), while PFHxA and PFOA were detected in significantly lower concentrations (max 4 and 9 ng L^{-1}).[17] Analysis of PFPeA and fluorotelomers were not included in that study. Surface water

from a military airport in France was dominated by 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) (max 426 ng L^{-1}) with lower levels of PFHxA (max 19 ng L^{-1}) and other PFCA, while PFSA concentrations were below the LOQ.[40] At two fire training areas at U.S. military bases in operation from 1942 to 1990 and 1950 to 1993 respectively, both fluorotelomers, PFCA, and PFSA were detected in high concentrations in groundwater. 6:2 FTS was detected at maximum concentrations of 220,000 and 37,000 ng L^{-1}, and maximum concentrations of PFPeA were 120,000 and 35,000 ng L^{-1}. Concentrations of PFHxA (max 350,000 and 99,000 ng L^{-1}) and PFHxS (max 360,000 and 170,000 ng L^{-1}) were comparable to, or higher than, PFOS concentrations (max 78,000 and 65,000 ng L^{-1}).[41] Concentrations in the latter study are much higher than concentrations found in our study, however several of the most dominant compounds are also the ones that dominate in our study. The large differences in PFAS composition between locations could be due to differences in the historical use of AFFF. For example, PFCA were not detected in AFFF formulations used by the US military from 1988 to 2001.[7] However, PFCA were used worldwide in AFFF formulations from approximately 1965 to 1975.[42] In addition, the use of fluorotelomer based AFFF has been linked to significant *in situ* production of PFCA[2] and 6:2 FTS is known to degrade to PFCA (≤ 7 C),[43–45] with PFHxA being one of the major degradation products.[43] Thus, the relatively high levels of PFHxA reported in our study (up to 20% of the total PFAS, and a max concentration of 194 ng L^{-1}) may indicate that older AFFF formulations (based on PFCA) have been used at Bodø Air Station. However, PFHxA levels at the Air Station may also be due to degradation of newer, fluorotelomer based AFFF (fluorinated telomer products with 6:2 configuration such as 6:2 FTS and/or 6:2 FTAB).

Marine abiotic environment

PFBA was detected in all passive samplers, but not quantified as discussed above. No other PFAS were detected in the samplers. Thus, total fjord water PFAS concentrations were considered below the limit of detection (0.5-3 ng L^{-1}) at all sites. A previous study at Oslo Airport (OSL) demonstrated the SorbiCell to be suitable for monitoring PFAS in ground and surface water (reported concentrations of Σ_{16} PFAS

between 113 ng L^{-1} and 6744 ng L^{-1}) (manuscript in preparation). All PFAS concentrations in sediments were close to, or below the LOQ. Only sediments from sites B and D contained concentrations of PFAS above the LOQ (0.10 - 0.20 µg kg^{-1}). PFPeA (0.26 µg kg^{-1}) and PFOS (0.32 µg kg^{-1}) were detected at sampling station B, and PFOS (0.29 µg kg^{-1}) was detected at station D. The TOC content in sediments was low and in the range of 0.4 to 1.6%. PFAS concentrations in soil and sediments have previously been shown to be correlated with organic carbon content, however in cases where significantly higher carbon contents have been reported than in the present study.[46,47] The low PFAS concentrations in sea water indicate that dissolved PFAS released to the fjord system are relatively efficiently diluted and removed from water surrounding the airport. Based on Endo et al.,[48] we do not consider salting out to have an important influence on neutral PFAS partitioning, however for anionic PFAS (i.e. the compounds analysed here) sorption to cationic salts and suspended solids can play a role in overall sorption processes.[49] In addition, sorption of PFAA onto clay has previously been shown to increase with salinity.[50] Therefore, due to the higher salt-content in sea water compared to leachate and storm water, distribution coefficients (Kd) for the analysed PFAS are expected to be higher in the marine environment compared to leachate and storm water. The amount of, and PFAS sorption to, suspended solids was not investigated in the present study. However, a fraction of the suspended solids are deposited on the sea floor with time, thus sediment concentrations are expected to be affected by sorption to suspended solids. The low PFAS concentrations in sediments observed here indicate that salting out and sorption to suspended solids are not the main mechanisms for PFAS removal from the water surrounding the airport. It is possible that PFAS accumulation at the marine boundary layer for sea spray aerosol formation contributes to losses from the sea water to the atmosphere.[51] Thus, the low concentrations of PFAS in the marine abiotic environment at the Air Station are likely due to the local geographical characteristics which, due to strong winds and currents, favour sea spray formation, water circulation and dilution of contaminants.

Marine biota

Normalization for dry weight, lipid or protein content was not carried out, thus potential differences in PFAS concentrations caused by differences in affinity between tissues could not be evaluated. Nevertheless, the dominant PFAS in all samples, both at the Air Station and the reference station, was PFOS. This is in agreement with the reported concentrations in leachate and storm water herein, with previous studies that have shown PFOS to dominate soil samples from Norwegian airports,[52,53] and studies that have shown PFOS and other long chained PFAA to have high bioaccumulation potential in aquatic organisms.[13–15,21,29,54,55]. PFAS concentrations were higher at the airport compared to the reference station, and concentrations were generally highest at the source areas (station B, E and F), shown in figure 1. PFAS concentrations in biotic samples are given in Table S7.

Fish PFAS burdens and biological parameters

A (weak) negative relationship was found between the liver somatic index (LSI) and Σ_{22} PFAS in Atlantic cod liver ($p<0.01$, figure S2). This is in agreement with previously reported negative correlations for Atlantic cod in Norwegian fjords and harbours,[56] and for the freshwater and diadromous species fathead minnow (*Pimephales promelas*) and rainbow trout exposed to PFOS.[57] Nevertheless, liver enlargement is reported in the freshwater species blacknose dace (*Rhinichthys atratulus*) and common shiner (*Luxilus cornutus*) living in an AFFF contaminated area.[20] The relationship between PFAS exposure and LSI in fish should be investigated in future studies, including potential differences between fresh water and marine species. No relationships were found between length, weight, or Fulton's condition factor K, and PFAS levels ($p>0.05$). This is in accordance with previous studies reporting no relationships between PFAS levels and length, weight or age in Lake Ontario Lake Trout,[58] or in perch from Swedish lakes.[59] Nevertheless, a positive relationship was reported for PFOS concentrations and fork-length (but not body weight) of polar cod in the Barents Sea.[60]

Invertebrate PFAS burdens and biological parameters

A relationship between size and PFAS levels in hepatopancreas in edible crabs was not found ($p>0.05$). There is a general lack of studies investigating the relationship between invertebrate size or sex, and PFAS levels. However, the lack of relationships reported herein is in accordance with a study investigating mud crabs,[29] where no relationships between size and PFAS levels were observed (nor any differences between sex). Potential relationships should be investigated further in future studies.

Biota PFOS concentrations

At the Air Station, no significant differences in fish liver PFOS concentrations were observed between sampling stations (A to H) ($p>0.05$). A previous study investigating the spatial PFOS distribution in fish and invertebrate species from source areas (approx. 5 km between sampling stations) found a clear relationship with distance for one site, while the opposite was shown for another,[23] possibly reflecting fish migration.

Tracking and re-capturing experiments with coastal Atlantic cod have shown that average core areas for populations are about 8 km^2 [61] (movement between a few hundred meters to a few km were reported for study periods up to 20 months[62,63]). The distance between stations A and H is 6 km, and the average distance between stations is 750 m. Thus, in the present study, some migration between sampling stations was expected. PFOS concentrations in Atlantic cod caught at the Air Station (stations A-H), both liver and whole fish (including liver), were significantly higher than in individuals from the reference station on the other side of the fjord, about 5 km from the Air Station ($p_{liver}=0.01$, $p_{whole}=0.03$), as shown in Figure 2. PFOS concentrations in Atlantic cod liver were 6.48 ± 2.6 μg kg^{-1} at the Air Station and 1.63 ± 0.26 μg kg^{-1} at the reference station. PFOS concentrations in whole fish were 1.98 ± 0.74 μg kg^{-1} at the Air Station and 0.60 ± 0.09 μg kg^{-1} at the reference station. In comparison, an average PFOS liver concentration of 3.1 μg kg^{-1} were reported for Atlantic cod in the northern parts of Norway.[56] Thus, even though some migration can be expected, cod caught near the Air Station showed

higher concentrations compared to cod from the reference station, as well as cod from other parts of northern Norway.

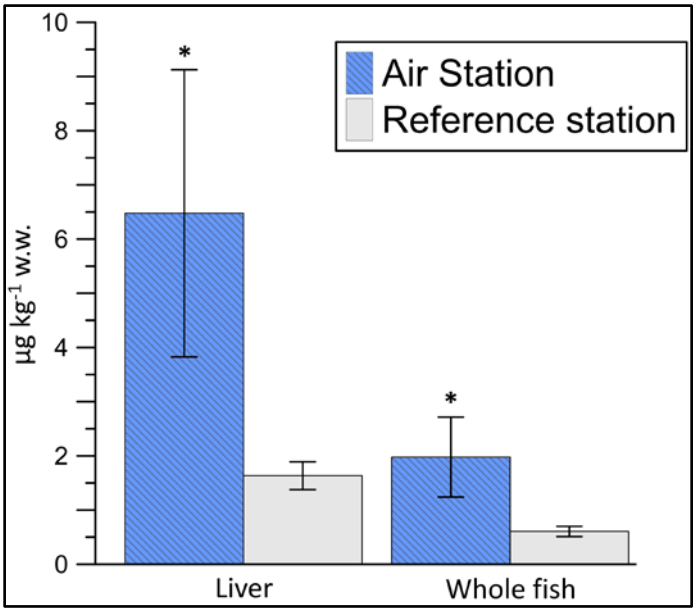


Figure 2. PFOS concentrations in Atlantic cod (µg kg^{-1} in liver, and in whole fish including the liver) caught near the Air Station (stations A-H, n_{liver} = 26, $n_{whole\ fish}$ = 24) and at the reference station (n=6), respectively. Concentrations are given as average ± standard error of mean (SEM). Asterisk (*) denotes concentrations significantly different from reference station (Unpaired Wilcoxon Test, p<0.05).

The average ratio between PFOS concentrations in liver and in whole fish (including liver) for Atlantic cod was 3.5 ± 0.4 and did not differ significantly between the Air station and the reference station (Figure S3, p>0.05) (ratios for all PFAS compounds detected in both liver and in remaining fish are shown in Table S5). PFOS ratios were relatively consistent and no trends with size or contamination level in Atlantic cod were observed. However, some individuals caught in stations not associated with any particular PFAS source (A, C, and D) had much higher ratios (>5). Based on tissue specific elimination rates, ratios between liver and other tissues (e.g. muscle, carcass, or remaining whole fish homogenates) might be an expression of the exposure history of individual fish. The validity of this observation should be explored in future studies. Falk et al.[55] reported that the ratio between concentrations in different tissues of rainbow trout was relatively constant when the fish were exposed to contaminated water. Following exposure, the ratio of liver versus other tissues (especially muscle and carcass) increased owing to the longer half-life of PFAS in liver. PFOS was estimated to have a half-

385 life of 8.4 days in muscle while the half-life in liver was estimated to be 20.4 days. Therefore, in cases
386 where high ratios were observed, it may indicate that the particular individuals were previously
387 exposed in one more contaminated location, before moving to the less contaminated location.
388
389 PFOS concentrations in snails from the Air Station were 3.86 ± 0.36 μg kg^{-1} and the highest detected
390 concentration was 14.30 μg kg^{-1} (station E). For the small crab species, green shore crab and great
391 spider crab, PFOS concentrations were 5.50 ± 0.80 μg kg^{-1} and 3.92 ± 0.79 μg kg^{-1} respectively. The
392 highest detected concentrations were 13.60 μg kg^{-1} (station B) and 16.20 μg kg^{-1} (station F),
393 respectively. Concentrations in hepatopancreas of edible crab were 6.15 ± 0.90 μg kg^{-1} and the highest
394 detected concentration was 17.00 μg kg^{-1} (station G). PFOS concentrations in snails, green shore crab,
395 and great spider crab at the reference station were 0.08 μg kg^{-1}, 0.40 μg kg^{-1} and 0.34 μg kg^{-1},
396 respectively. Hepatopancreas in the two individuals of edible crab from the reference station
397 contained PFOS concentrations of 4.38 μg kg^{-1} and 5.91 μg kg^{-1}. Stations that had the largest PFAS loads
398 from storm and leachate water (B, E and F) also had the highest concentrations in invertebrates. In
399 school prawn (meat) and mud crab (claw meat) living in PFAS contaminated source areas, PFOS
400 concentrations of 5.60-15.00 μg kg^{-1} and 3.70-39.00 μg kg^{-1} respectively, have been observed
401 depending on location.[29] PFOS concentrations of 38-82 μg kg^{-1} dry weight were observed in swimming
402 crab from an industrial area in China.[26] Although these organisms and tissues are different to those in
403 our study, they represent invertebrate species in source areas showing comparable levels to those at
404 the Air Station (sampling station A-H). PFOS levels in invertebrate organisms (bivalve, lugworm, crab),
405 including hepatopancreas in a small crab species, from the coast of Japan (no known local PFAS
406 sources) were not reported above the LOQ (0.3 μg kg^{-1}).[64] This is consistent with the low levels reported
407 in small crabs from the reference station in our study.
408

Biota PFAS distribution

Principal component analysis (PCA) was carried out using relative PFAS concentrations (expressed as % of the Σ_{22} PFAS in biota from the Air Station) in order to determine how PFAS profiles varied (Figure 3). Average PFAS profiles in biota are shown in a stacked bar chart in Figure 4, and listed in Table S6. The score plot (Figure 3A) shows individual biotic samples plotted according to their PFAS profile. Biotic samples did not group according to sampling stations (and as such this is not shown in the manuscript), indicating that PFAS profiles in biota were similar between the different stations. The loading plot (Figure 3B) shows PFAS compounds plotted according to their distribution in biota. Principal component 1 (PC1, X-axis) explained 50% of the variance in the dataset and is dominated by 6:2 FTS and PFOS on the right. PC2 (Y-axis) explained 14% of the variance. The most important compounds in PC2 are long chained PFCA in the upper part of the plot and fluorotelomer sulfonates (FTS) in the lower part of the plot. Profiles in fish consisted of a higher proportion of long chained PFCA and almost no FTS, and grouped in the upper part of the plot. The Σ of long chained PFCA (PFOA, perfluorononanoic acid [PFNA], perfluorodecanoic acid [PFDeA], perfluoroundecanoic acid [PFUnA], perfluorododecanoic acid [PFDoA], perfluorotridecanoic acid [PFTrA], and perfluorotetradecanoic acid [PFTA]) were on average 24.6 and 29.1% of Σ_{22} PFAS in fish liver and remaining tissue. Snails and small crabs (green shore crab and great spider crab) grouped in the lower part of the plot, dominated by FTS. On average the Σ of long chained PFCA made up 8.4% of the total detected PFAS in whole body snails and small crabs. Hepatopancreas in edible crab is seen in both parts of the plot, reflecting that the tissue contains significant portions of both FTS and long chained PFCA (also shown in Figure 4). The latter made up 25.8% of Σ_{22} PFAS. The multivariate PERMANOVA analysis followed by Bonferroni correction showed significant differences in PFAS profiles ($p<0.05$) among Atlantic cod, both liver and remaining tissue, and the invertebrate organisms (snail, green shore crab, great spider crab, and hepatopancreas in edible crab). No other significant differences were found. The observed higher proportion of long chained PFCA in fish is likely due to their higher potential for biomagnification as reported in studies showing concentrations of PFCA with 8-14 C increasing with trophic level.[28,65,66] The same reasoning

likely applies to the higher proportion of long chained PFCA in hepatopancreas in the large crab species (edible crab), compared to smaller crabs (green shore crab and great spider crab) and snails.

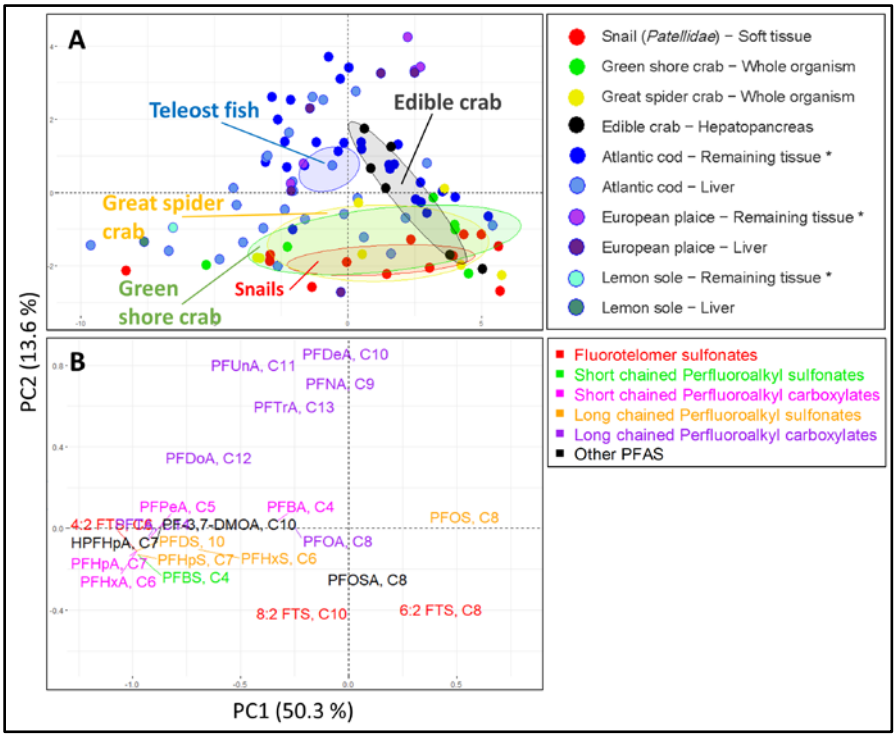
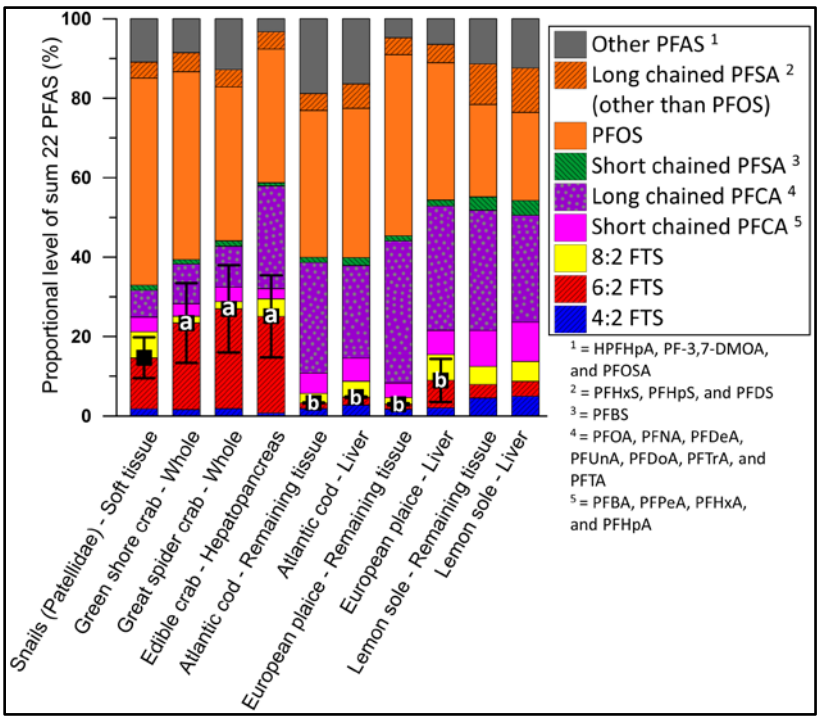


*Figure 3. Principal Components Analysis (PCA) based on proportional levels (% Σ_{22} PFAS) in samples of biotic tissue. PC1 and PC2 explain 63.9% of the variance. Figure 3A (score plot): Biotic samples are plotted according to their PFAS profile.*Analysis on fish remaining tissue is performed on homogenized whole fish after removal of liver and gut content. Figure 3B (loading plot): PFAS compounds are plotted according to their distribution in biotic samples. Ellipses show 99% confidence intervals for the respective groups. Concentrations below the detection limit (LOQ) are treated as half the LOQ*

6:2 FTS accumulation

The most noticeable difference between PFAS profiles in fish and invertebrate species was the proportion of 6:2 FTS. Figure 4 shows the proportion 6:2 FTS (as a percentage) of Σ_{22} PFAS. Statistically significant lower percentage 6:2 FTS were observed in Atlantic cod and European plaice (both liver and remaining tissue), compared to all three crab species ($p<0.05$). The highest concentrations of 6:2 FTS in invertebrates were: 56.3 µg kg^{-1} in snails, 12.3 µg kg^{-1} in green shore crab, and 56.8 µg kg^{-1} in great spider crab caught at sampling station F, and 26.4 µg kg^{-1} in hepatopancreas of edible crab caught at sampling station E (the two stations in the area used for used for firefighting). In contrast 6:2 FTS was only detected in 3 of 39 fish and the highest level was 3.25 µg kg^{-1} in the liver of a European plaice

455 caught at station A. These results indicate significant differences in PFAS accumulation in marine
456 invertebrates compared to teleost fish and this is one of the first studies to show this.
457



458
459 *Figure 4. PFAS profiles in different biota tissues (station A-H). Profiles are given as relative concentrations (of Σ_{22}*
460 *PFAS). Error bars show ± standard error of mean (SEM) for 6:2 FTS (not shown for Lemon sole where n=1).*
461 *Different letters denote significant differences in 6:2 FTS proportion (Kruskal-Wallis and Bonferroni correction,*
462 *p<0.05). Concentrations below the LOQ are treated as half the LOQ*
463

464 Biotransformation of fluorotelomer-based compounds has been reviewed by Butt et al.,[67] and shows
465 that few biotransformation studies have included fish. Studies on rainbow trout have found that tissue
466 concentrations of 6:2 FTS increases at the beginning of an exposure period (first days or few weeks).
467 However, it appears that elimination rates increase in response to exposure, and tissue concentrations
468 rapidly decrease to a low level.[9,15] 6:2 FTS has been shown to be biotransformed to shorter more water
469 soluble PFAS (5:3 fluorotelomer carboxylic acid [5:3 FTCA], perfluorobutanoic acid [PFBA], PFPeA, and
470 PFHxA).[45] This has been suggested as the main mechanism behind the rapid elimination,[15] because
471 these compounds show little accumulation in fish.[9,13,14] It is possible that fish exposed to a 6:2 FTS point
472 source acquire the enzymatic ability to eliminate 6:2 FTS at a fast rate. An increased enzyme activity
473 could possibly be used as a biomarker of exposure to 6:2 FTS.

6:2 FTS has previously been found in invertebrates.[21,60] However, this study is one of the first to report 6:2 FTS bioaccumulation to such an extent. High levels have previously been found in earthworms (max 14,834 μg kg^{-1}) and in marine snails (>100 μg kg^{-1}) in the vicinity of firefighting training areas in Norway.[68] Invertebrates have different detoxification pathways and enzymes than fish and mammals, e.g. different expression of cytochrome P450 (CYP) enzymes.[69,70] Different accumulation potentials for polycyclic aromatic hydrocarbons (PAH) between invertebrates and vertebrates have previously been suggested to be partly due to these differential biotransformation capacities.[71] Although PAH and PFAS are two distinct chemical classes of contaminants with different toxicokinetics and dynamics, this explanation cannot be ruled out.

Environmental implications

The results of this study suggest that 6:2 FTS has the potential to bioaccumulate in marine invertebrates. Marine invertebrates are food sources to higher trophic organisms like fish, birds and mammalian species. Marine invertebrates are also used as food sources for humans. Possible effects of 6:2 FTS accumulation in invertebrates and subsequent effects of a repeated dietary exposure should be investigated further.

The observed different accumulation pattern between teleost fish and invertebrates suggests that future biota monitoring and risk assessment of AFFF contaminated areas, and other sites possibly contaminated with FTS and related compounds, should include invertebrates. Data on accumulation in aquatic invertebrates and possible effects of species differences and parameters such as sex, size, and moulting stage, will provide vital contributions to future PFAS monitoring.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available online.

Raw data, statistical and analytical methods, and other materials in figures and tables.

AUTHOR INFORMATION

Corresponding Author

* Phone: +47 47242944; e-mail: hakon.austad.langberg@ngi.no

ORCID

Håkon Austad Langberg: 0000-0002-6186-6962

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

We thank the Norwegian Defence Estates Agency for funding analysis and field work. The research was funded by the Norwegian Research Council under the MILJØFORSK program for the project 268258/E50.

REFERENCES

(1) Moody, C. A.; Field, J. A. Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity. *Environ. Sci. Technol.* **1999**, *33* (16), 2800–2806.

(2) Anderson, R. H.; Long, G. C.; Porter, R. C.; Anderson, J. K. Occurrence of Select Perfluoroalkyl Substances at U.S. Air Force Aqueous Film-Forming Foam Release Sites Other than Fire-Training Areas: Field-Validation of Critical Fate and Transport Properties. *Chemosphere* **2016**, *150*, 678–685.

(3) Rahman, M. F.; Peldszus, S.; Anderson, W. B. Behaviour and Fate of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) in Drinking Water Treatment: A Review. *Water Res.* **2014**, *50*, 318–340.

(4) Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. Perfluoroalkyl Acids: A Review of Monitoring and Toxicological Findings. *Toxicol. Sci.* **2007**, *99* (2), 366–394.

(5) Stahl, T.; Mattern, D.; Brunn, H. Toxicology of Perfluorinated Compounds. *Environ. Sci. Eur.* **2011**, *23* (1), 38.

(6) Moe, M. K.; Huber, S.; Svenson, J.; Hagenaars, A.; Pabon, M.; Trümper, M.; Berger, U.; Knapen, D.; Herzke, D. The Structure of the Fire Fighting Foam Surfactant Forafac®1157 and Its Biological and Photolytic Transformation Products. *Chemosphere* **2012**, *89* (7), 869–875.

(7) Place, B. J.; Field, J. A. Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams Used by the US Military. *Environ. Sci. Technol.* **2012**, *46* (13), 7120–7127.

(8) Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbuehler, K. Hazard Assessment of Fluorinated Alternatives to Long-Chain Perfluoroalkyl Acids (PFAAs) and Their Precursors: Status Quo, Ongoing Challenges and Possible Solutions. *Environ. Int.* **2015**, *75*, 172–179.

(9) Hoke, R. A.; Ferrell, B. D.; Ryan, T.; Sloman, T. L.; Green, J. W.; Nabb, D. L.; Mingoia, R.; Buck, R. C.; Korzeniowski, S. H. Aquatic Hazard, Bioaccumulation and Screening Risk Assessment for 6:2 Fluorotelomer Sulfonate. *Chemosphere* **2015**, *128*, 258–265.

(10) The Swedish Chemicals Agency (KEMI). *Chemical Analysis of Selected Fire-Fighting Foams on the Swedish Market 2014*; 2015.

(11) Conder, J. M.; Hoke, R. A.; Wolf, W. de; Russell, M. H.; Buck, R. C. Are PFCAs Bioaccumulative? A Critical Review and Comparison with Regulatory Criteria and Persistent Lipophilic Compounds. *Environ. Sci. Technol.* **2008**, *42* (4), 995–1003.

(12) Krafft, M. P.; Riess, J. G. Per- and Polyfluorinated Substances (PFASs): Environmental Challenges. *Curr. Opin. Colloid Interface Sci.* **2015**, *20* (3), 192–212.

(13) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. Bioconcentration and Tissue Distribution of Perfluorinated Acids in Rainbow Trout (*Oncorhynchus Mykiss*). *Environ. Toxicol. Chem.* **2003**, *22* (1), 196–204.

(14) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. Dietary Accumulation of Perfluorinated Acids in Juvenile Rainbow Trout (*Oncorhynchus Mykiss*). *Environ. Toxicol. Chem.* **2003**, *22* (1), 189–195.

(15) Yeung, L. W. Y.; Mabury, S. A. Bioconcentration of Aqueous Film-Forming Foam (AFFF) in Juvenile Rainbow Trout (*Oncorhyncus Mykiss*). *Environ. Sci. Technol.* **2013**, *47* (21), 12505–12513.

(16) Directive 2013/39/EU. *Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 Amending Directives 2000/60/EC and 2008/105*; 2013.

(17) Filipovic, M.; Woldegiorgis, A.; Norström, K.; Bibi, M.; Lindberg, M.; Österås, A. H. Historical Usage of Aqueous Film Forming Foam: A Case Study of the Widespread Distribution of Perfluoroalkyl Acids from a Military Airport to Groundwater, Lakes, Soils and Fish. *Chemosphere* **2015**, *129*, 39–45.

(18) Munoz, G.; Desrosiers, M.; Duy, S. V.; Labadie, P.; Budzinski, H.; Liu, J.; Sauvé, S. Environmental Occurrence of Perfluoroalkyl Acids and Novel Fluorotelomer Surfactants in the Freshwater Fish *Catostomus Commersonii* and Sediments Following Firefighting Foam Deployment at the Lac-Mégantic Railway Accident. *Environ. Sci. Technol.* **2017**, *51* (3), 1231–1240.

(19) Cerveny, D.; Grabic, R.; Fedorova, G.; Grabicova, K.; Turek, J.; Zlabek, V.; Randak, T. Fate of Perfluoroalkyl Substances within a Small Stream Food Web Affected by Sewage Effluent. *Water Res.* **2018**, *134*, 226–233.

(20) Oakes, K. D.; Benskin, J. P.; Martin, J. W.; Ings, J. S.; Heinrichs, J. Y.; Dixon, D. G.; Servos, M. R. Biomonitoring of Perfluorochemicals and Toxicity to the Downstream Fish Community of Etobicoke Creek Following Deployment of Aqueous Film-Forming Foam. *Aquat. Toxicol.* **2010**, *98* (2), 120–129.

(21) Bertin, D.; Ferrari, B. J. D.; Labadie, P.; Sapin, A.; Garric, J.; Budzinski, H.; Houde, M.; Babut, M. Bioaccumulation of Perfluoroalkyl Compounds in Midge (*Chironomus Riparius*) Larvae Exposed to Sediment. *Environ. Pollut.* **2014**, *189*, 27–34.

(22) Taylor, M. D.; Johnson, D. D. Preliminary Investigation of Perfluoroalkyl Substances in Exploited Fishes of Two Contaminated Estuaries. *Mar. Pollut. Bull.* **2016**, *111* (1–2), 509–513.

(23) Taylor, M. D.; Beyer-Robson, J.; Johnson, D. D.; Knott, N. A.; Bowles, K. C. Bioaccumulation of Perfluoroalkyl Substances in Exploited Fish and Crustaceans: Spatial Trends across Two Estuarine Systems. *Mar. Pollut. Bull.* **2018**, *131* (December 2017), 303–313.

(24) Yoo, H.; Yamashita, N.; Taniyasu, S.; Lee, K. T.; Jones, P. D.; Newsted, J. L.; Khim, J. S.; Giesy, J. P. Perfluoroalkyl Acids in Marine Organisms from Lake Shihwa, Korea. *Arch. Environ. Contam. Toxicol.* **2009**, *57* (3), 552–560.

(25) Habibullah-Al-Mamun, M.; Ahmed, M. K.; Raknuzzaman, M.; Islam, M. S.; Ali, M. M.; Tokumura, M.; Masunaga, S. Occurrence and Assessment of Perfluoroalkyl Acids (PFAAs) in Commonly Consumed Seafood from the Coastal Area of Bangladesh. *Mar. Pollut. Bull.* **2017**, *124* (2), 775–785.

(26) Wang, T.; Lu, Y.; Chen, C.; Naile, J. E.; Khim, J. S.; Giesy, J. P. Perfluorinated Compounds in a Coastal Industrial Area of Tianjin, China. *Environ. Geochem. Health* **2012**, *34* (3), 301–311.

(27) Casal, P.; González-Gaya, B.; Zhang, Y.; Reardon, A. J. F.; Martin, J. W.; Jiménez, B.; Dachs, J. Accumulation of Perfluoroalkylated Substances in Oceanic Plankton. *Environ. Sci. Technol.* **2017**, *51* (5), 2766–2775.

(28) Fang, S.; Chen, X.; Zhao, S.; Zhang, Y.; Jiang, W.; Yang, L.; Zhu, L. Trophic Magnification and Isomer Fractionation of Perfluoroalkyl Substances in the Food Web of Taihu Lake, China. *Environ. Sci. Technol.* **2014**, *48* (4), 2173–2182.

(29) Taylor, M. D.; Bowles, K. C.; Johnson, D. D.; Moltschaniwskyj, N. A. Depuration of Perfluoroalkyl Substances from the Edible Tissues of Wild-Caught Invertebrate Species. *Sci. Total Environ.* **2017**, *581–582*, 258–267.

(30) The Norwegian Meteorological Institute www.eklima.no (accessed Nov 29, 2018).

(31) The Norwegian Mapping Authority www.kartverket.no (accessed Nov 29, 2018).

(32) Norwegian Government. Begrensningsdirektivet - PFOS (Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006 relating to restrictions om the marketing and use of perfluorooctane sulfonates (amending of Council Directive 76/769/EEC) https://www.regjeringen.no/no/sub/eos-notatbasen/notatene/2006/jan/begrensningsdirektivet---pfos/id2431732/ (accessed Sep 7, 2018).

(33) De Jonge, H.; Rothenberg, G. New Device and Method for Flux-Proportional Sampling of Mobile Solutes in Soil and Groundwater. *Environ. Sci. Technol.* **2005**, *39* (1), 274–282.

(34) R Core Team. R: A Language and Environment for Statistical Computing. Vienna, Austria 2017.

(35) Oksanen, J.; Blanchet, F. G.; Friendly, M.; Kindt, R.; Legendre, P.; McGlinn, D.; Minchin, P. R.; O'Hara, R. B.; Simpson, G. L.; Solymos, P.; et al. Vegan: Community Ecology Package. 2018.

(36) de Mendiburu, F. Agricolae: Statistical Procedures for Agricultural Research. 2019.

(37) Kassambara, A.; Mundt, F. Factoextra: Extract and Visualize the Results of Multivariate Data Analyses. 2017.

(38) Lê, S.; Josse, J.; Husson, F. {FactoMineR}: A Package for Multivariate Analysis. *J. Stat. Softw.* **2008**, *25* (1), 1–18.

(39) Høisæter, Å.; Pfaff, A.; Breedveld, G. D. Leaching and Transport of PFAS from Aqueous Film-Forming Foam (AFFF) in the Unsaturated Soil at a Firefighting Training Facility under Cold Climatic Conditions. *J. Contam. Hydrol.* **2019**, *222*, 112–122.

(40) Dauchy, X.; Boiteux, V.; Bach, C.; Rosin, C.; Munoz, J. F. Per- and Polyfluoroalkyl Substances in Firefighting Foam Concentrates and Water Samples Collected near Sites Impacted by the Use of These Foams. *Chemosphere* **2017**, *183*, 53–61.

(41) Backe, W. J.; Day, T. C.; Field, J. A. Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS. *Environ. Sci. Technol.* **2013**, *47* (10), 5226–5234.

(42) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, Fate and Transport of Perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40* (1), 32–44.

(43) Yang, X.; Huang, J.; Zhang, K.; Yu, G.; Deng, S.; Wang, B. Stability of 6:2 Fluorotelomer Sulfonate in Advanced Oxidation Processes: Degradation Kinetics and Pathway. *Environ. Sci. Pollut. Res.* **2014**, *21* (6), 4634–4642.

(44) Weiner, B.; Yeung, L. W. Y.; Marchington, E. B.; D'Agostino, L. A.; Mabury, S. A. Organic Fluorine Content in Aqueous Film Forming Foams (AFFFs) and Biodegradation of the Foam Component 6 : 2 Fluorotelomermercaptoalkylamido Sulfonate (6 : 2 FTSAS). *Environ. Chem.* **2013**, *10* (6), 486–493.

(45) Wang, N.; Liu, J.; Buck, R. C.; Korzeniowski, S. H.; Wolstenholme, B. W.; Folsom, P. W.; Sulecki, L. M. 6:2 Fluorotelomer Sulfonate Aerobic Biotransformation in Activated Sludge of Waste Water Treatment Plants. *Chemosphere* **2011**, *82* (6), 853–858.

(46) Milinovic, J.; Lacorte, S.; Vidal, M.; Rigol, A. Sorption Behaviour of Perfluoroalkyl Substances in Soils. *Sci. Total Environ.* **2015**, *511*, 63–71.

(47) Higgins, C. P.; Luthy, R. G. Sorption of Perfluorinated Surfactants on Sediments. *Environ. Sci. Technol.* **2006**, *40* (23), 7251–7256.

(48) Endo, S.; Pfennigsdorff, A.; Goss, K. U. Salting-Out Effect in Aqueous NaCl Solutions Increases with Size and Decreases with Polarities of Solute Molecule. *Environ. Sci. Technol.* **2012**, *46* (1), 1496–1503.

(49) Hong, S.; Khim, J. S.; Park, J.; Kim, M.; Kim, W. K.; Jung, J.; Hyun, S.; Kim, J. G.; Lee, H.; Choi, H. J.; et al. In Situ Fate and Partitioning of Waterborne Perfluoroalkyl Acids (PFAAs) in the Youngsan and Nakdong River Estuaries of South Korea. *Sci. Total Environ.* **2013**, *445–446*, 136–145.

(50) Jeon, J.; Kannan, K.; Lim, B. J.; An, K. G.; Kim, S. D. Effects of Salinity and Organic Matter on the Partitioning of Perfluoroalkyl Acid (PFAs) to Clay Particles. *J. Environ. Monit.* **2011**, *13* (6), 1803–1810.

(51) Johansson, J. H.; Salter, M. E.; Acosta Navarro, J. C.; Leck, C.; Nilsson, E. D.; Cousins, I. T. Global Transport of Perfluoroalkyl Acids *via* Sea Spray Aerosol. *Environ. Sci. Process. Impacts* **2019**, *21* (4).

(52) Kupryianchyk, D.; Hale, S. E.; Breedveld, G. D.; Cornelissen, G. Treatment of Sites Contaminated with Perfluorinated Compounds Using Biochar Amendment. *Chemosphere* **2016**, *142*, 35–40.

(53) Hale, S. E.; Arp, H. P. H.; Slinde, G. A.; Wade, E. J.; Bjørseth, K.; Breedveld, G. D.; Straith, B. F.; Moe, K. G.; Jartun, M.; Høisæter, Å. Sorbent Amendment as a Remediation Strategy to Reduce PFAS Mobility and Leaching in a Contaminated Sandy Soil from a Norwegian Firefighting Training Facility. *Chemosphere* **2017**, *171*, 9–18.

(54) Higgins, C. P.; McLeod, P. B.; MacManus-Spencer, L. A.; Luthy, R. G. Bioaccumulation of Perfluorochemicals in Sediments by the Aquatic Oligochaete Lumbriculus Variegatus. *Environ. Sci. Technol.* **2007**, *41* (13), 4600–4606.

(55) Falk, S.; Failing, K.; Georgii, S.; Brunn, H.; Stahl, T. Tissue Specific Uptake and Elimination of Perfluoroalkyl Acids (PFAAs) in Adult Rainbow Trout (*Oncorhynchus Mykiss*) after Dietary Exposure. *Chemosphere* **2015**, *129*, 150–156.

(56) Valdersnes, S.; Nilsen, B. M.; Breivik, J. F.; Borge, A.; Maage, A. Geographical Trends of PFAS in Cod Livers along the Norwegian Coast. *PLoS One* **2017**, *12* (5), 1–15.

(57) Oakes, K. D.; Sibley, P. K.; Martin, J. W.; Maclean, D. D.; Solomon, K. R.; Mabury, S. A.; Kraak, G. J. Van Der. Short-term Exposures of Fish to Perfluorooctane Sulfonate: Acute Effects on Fatty Acyl-CoA Oxidase Activity, Oxidative Stress, and Circulating Sex Steroids. *Environ. Toxicol. Chem.* **2005**, *24* (5), 1172–1181.

(58) Gewurtz, S. B.; De Silva, A. O.; Backus, S. M.; McGoldrick, D. J.; Keir, M. J.; Small, J.; Melymuk, L.; Muir, D. C. G. Perfluoroalkyl Contaminants in Lake Ontario Lake Trout: Detailed Examination of Current Status and Long-Term Trends. *Environ. Sci. Technol.* **2012**, *46* (11), 5842–5850.

(59) Åkerblom, S.; Negm, N.; Wu, P.; Bishop, K.; Ahrens, L. Variation and Accumulation Patterns of Poly- and Perfluoroalkyl Substances (PFAS) in European Perch (*Perca Fluviatilis*) across a Gradient of Pristine Swedish Lakes. *Sci. Total Environ.* **2017**, *599–600*, 1685–1692.

(60) Haukås, M.; Berger, U.; Hop, H.; Gulliksen, B.; Gabrielsen, G. W. Bioaccumulation of Per- and Polyfluorinated Alkyl Substances (PFAS) in Selected Species from the Barents Sea Food Web. *Environ. Pollut.* **2007**, *148* (1), 360–371.

(61) Espeland, S. H.; Olsen, E. M.; Knutsen, H.; Gjøsæter, J.; Danielssen, D.; Stenseth, N. C. New Perspectives on Fish Movement: *Mar. Ecol. Prog. Ser.* **2008**, *372*, 231–241.

(62) Neat, F. C.; Wright, P. J.; Zuur, A. F.; Gibb, I. M.; Gibb, F. M.; Tulett, D.; Righton, D. A.; Turner, R. J. Residency and Depth Movements of a Coastal Group of Atlantic Cod (*Gadus Morhua* L.). *Mar. Biol.* **2006**, *148* (3), 643–654.

(63) Bergstad, O. A.; Jørgensen, T.; Knutsen, J. A.; Berge, J. A. Site Fidelity of Atlantic Cod *Gadus Morhua* L. as Deduced from Telemetry and Stable Isotope Studies. *J. Fish Biol.* **2008**, *72* (1), 131–142.

(64) Nakata, H.; Kannan, K.; Nasu, T.; Cho, H. S.; Sinclair, E.; Takemura, A. Perfluorinated Contaminants in Sediments and Aquatic Organisms Collected from Shallow Water and Tidal Flat Areas of the Ariake Sea, Japan: Environmental Fate of Perfluorooctane Sulfonate in Aquatic Ecosystems. *Environ. Sci. Technol.* **2006**, *40* (16), 4916–4921.

(65) Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Surridge, B.; Hoover, D.; Grace, R.; Gobas, F. A. P. C. Perfluoroalkyl Contaminants in an Arctic Marine Food Web: Trophic Magnification and Wildlife Exposure. *Environ. Sci. Technol.* **2009**, *43* (11), 4037–4043.

(66) Loi, E. I. H.; Yeung, L. W. Y.; Taniyasu, S.; Lam, P. K. S.; Kannan, K.; Yamashita, N. Trophic Magnification of Poly- and Perfluorinated Compounds in a Subtropical Food Web. *Environ. Sci. Technol.* **2011**, *45* (13), 5506–5513.

(67) Butt, C. M.; Muir, D. C. G.; Mabury, S. A. Biotransformation Pathways of Fluorotelomer-Based Polyfluoroalkyl Substances: A Review. *Environ. Toxicol. Chem.* **2014**, *33* (2), 243–267.

(68) Amundsen, C. E.; Forfang, I.; Aasen, R.; Eggen, T.; Sørheim, R.; Hartnik, T.; Næs, K. *Screening of Polyfluorinated Organic Compounds At Four Fire Training Facilities in Norway. Nowegian Pollution Control Authority, Document Number TA-2444/2008*; 2008.

(69) Han, J.; Won, E. J.; Kim, H. S.; Nelson, D. R.; Lee, S. J.; Park, H. G.; Lee, J. S. Identification of the Full 46 Cytochrome P450 (*CYP*) Complement and Modulation of *CYP* Expression in Response to Water-Accommodated Fractions of Crude Oil in the Cyclopoid Copepod *Paracyclopina Nana*. *Environ. Sci. Technol.* **2015**, *49* (11), 6982–6992.

(70) Chaty, S.; Rodius, F.; Vasseur, P. A Comparative Study of the Expression of CYP1A and CYP4 Genes in Aquatic Invertebrate (Freshwater Mussel, *Unio Tumidus*) and Vertebrate (Rainbow Trout, *Oncorhynchus Mykiss*). *Aquat. Toxicol.* **2004**, *69* (1), 81–94.

(71) Baumard, P.; Budzinski, H.; Garrigues, P.; Sorbe, J. C.; Burgeot, T.; Bellocq, J. Concentrations of PHAs (Polycyclic Aromatic Hydrocarbons) in Various Marine Organisms in Relation to Those in Sediments and to Trophic Level. *Mar. Pollut. Bull.* **1998**, *36* (12), 951–960.