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Fluorine mass balance analysis of selected environmental samples from Norway

Rudolf Aro [a], Pernilla Carlsson [b], Christian Vogelsang [c], Anna Kärrman [a], Leo WY. Yeung [a,*]

[a] Man-Technology-Environment (MTM) Research Centre, School of Science and Technology, Örebro University, SE-701 82, Sweden
[b] Norwegian Institute for Water Research (NIVA), Fram Centre, Hjalmar Johansens vei 14, NO-9007, Tromsø, Norway
[c] Norwegian Institute for Water Research (NIVA), Gaustadalléen 24, 0234, Oslo, Norway

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ABSTRACT

The presence of unidentified organofluorine compounds (UOF) has been investigated in recent publication, but their environmental occurrence is still poorly understood. Fluorine mass balance analysis was performed on environmental samples from lake Mjøsa and river Alna (surface water ($n = 9$), sediment ($n = 5$) and fish liver ($n = 4$)) and sewage samples from Oslo ($n = 5$), to reveal to the fraction of UOF. In samples that had extractable organofluorine (EOF) concentrations above the limit of detection (LoD), more than 70% of their EOF could not be accounted for by the 37 PFAS monitored in this study. The surface water samples from lake Mjøsa had EOF concentrations several times higher than what has been reported elsewhere in Nordic nations. The flux of EOF in river Alna and selected sewage pipes revealed that it was 1-2 orders of magnitude higher than the flux of the measured PFAS. The elevated concentrations of EOF in all samples pose a potential health and environmental hazard, as their composition remains mostly unknown.

1. Introduction

Fluorine mass balance analysis has risen as a prospective technique for tackling the challenge of per- and polyfluoroalkyl substance (PFAS) analysis by combining target PFAS and extractable organofluorine (EOF) data. The reason for this is due to the large number of PFAS being used for various applications (Buck et al., 2011), with OECD identifying more than >5000 CAS numbers corresponding to PFAS (Toward A New Comprehensive Global Database Of Per- And Polyfluoroalkyl Substances (PFASs), 2018), while routine target analyses in national environmental monitoring programs often include only the most commonly used and identified, usually the C4–C15 perfluorinated carboxylic acids (PFCAs) and C4–C10 perfluorinated sulfonic acids (PFSAs) (US EPA, 2015; Apler and Josefsson, 2016). To better understand the total amount of PFAS in environmental samples, analyses of EOF content may serve as an important metric alongside target analysis, total oxidizable precursor assay and non-target analysis. This method was first applied to human blood and water samples by Miyake et al. (Miyake et al., 2007a; Miyake et al., 2007b), and has been adopted for a range of environmental samples such as invertebrates (Koch et al., 2019), sediment (Yeung et al., 2013; Codling et al., 2014), surface water (Koch et al., 2019; D'Agostino and Mabury, 2017) and marine mammals (Spaan et al., 2020). These results have demonstrated that traditional target PFAS analysis is overlooking a significant portion of the organofluorines, both in human and environmental samples (Yeung and Mabury, 2016; Kärrman et al., 2019; Miaz et al., 2020).

Combustion ion chromatography (CIC) is an analytical apparatus employed in EOF analysis, but this instrument measures the total fluorine content in a sample, indiscriminate of its type. Therefore, it is up to the analyst to design an extraction method to remove or avoid co-extraction of inorganic fluoride (IF) since its levels can be an order of magnitude higher than that of PFAS in environmental samples (Yeung et al., 2008). As an example, IF in sea water off the coast of Japan were shown to be 79.6 mg/L, while target PFAS was in the range of 1 ng/L (Miyake et al., 2007a), in other matrices the difference between IF and EOF can be several orders of magnitude (Spaan et al., 2020). Bear in mind that the analysis of EOF using CIC does not provide any structural information on the species of organofluorines in the sample, unless achieved by sample preparation (e.g. separating the compounds into groups such as anionic and neutral fractions). On the other side, it is impossible to include all registered PFAS in an analytical workflow, as of 2018 almost 5000 PFAS related compounds had a CAS number (Toward A New Comprehensive Global Database Of Per- And Polyfluoroalkyl Substances (PFASs), 2018). The analytical picture is further complicated

* Corresponding author.
E-mail address: leo.yeung@oru.se (L.WY. Yeung).

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by degradation products, studies have shown that only a fraction of a precursor compound degrades to readily measurable perfluoroalkyl acids (PFAAs) (Wang et al., 2011; Liu et al., 2010), meaning that the majority of the precursor is transformed into various degradation intermediates. By subtracting the amount of fluorine accounted for by the measured PFAS from the EOF concentration, it is possible to elucidate the fraction of unidentified organofluorines (UOF). In addition to EOF, methods such as total oxidizable precursor (TOP) assay (Houtz and Sedlak, 2012) and non-target screening (NTA) (Rotander et al., 2015) are used to gain additional information about the PFAS contamination and they have been combined with EOF and target analyses to obtain a more comprehensive picture of the contamination profile. However, these methods come with their own limitations, TOP assay assumes that the unidentified compounds can oxidize to measurable PFAAs (Houtz and Sedlak, 2012) and NTA provides only semi-quantitative results, which can lead to underestimation of the organofluorine content (Dubocq et al., 2020).

The UOF fraction can be assumed to be of anthropogenic origin, since the number and amount of naturally occurring compounds with a C–F bond is miniscule (O'Hagan and Harper, 1999) in comparison to the number of PFAS. As the commonly monitored PFAS account for only a few percent of the potential analytes, it is important to assess the levels of UOF since PFAS have been already linked to adverse health effects (e.g. immunotoxicity (Liu et al., 2010; Houtz and Sedlak, 2012)) the potential health risk from the unidentified compounds cannot be ignored until their safety is proven.

Fluorine mass balance analysis can be used to identify pollution hotspots, as it does not require prior knowledge of the pollutants to measure them. A recent study from Germany found perfluorooctanoic acid (PFOA) replacement product levels, both 3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid] (ADONA) and hexafluoropropylene oxide dimer acid (HFPO-DA, also known as GenX), 10–100 times higher than that of PFOA in River Alz (Joerss et al., 2020). Similar situation has been reported earlier in River Cape Fear in the United States as well (Sun et al., 2016). This finding prompts the question about other possible PFOA replacement products. Including fluorine mass balance analysis in such a study would also show if this "novel" pollutant is the only culprit or whether there are additional fluorinated contaminants.

The aim of this study was to follow up on previous research on PFAS and EOF in the Norwegian environment (Kärrman et al., 2019) and to gain an insight into the types of data that can be generated using the fluorine mass balance approach. Two locations (River Alna and Lake Mjøsa) were chosen based on the contamination record from a previous study, historical or current industrial activity, and differences in population density. River Alna flows through an urban industrial area and Lake Mjøsa has a history of brominated flame retardant, mercury and siloxane pollution (Fjeld et al., 2015). Different matrices (surface water, sediment and fish) were sampled to obtain a better picture of where the contamination occurred. Sample from River Alna were taken during both rainfall and dry conditions to see whether additional PFAS were washed into the environment from the urban area. These results are intended to inform and guide more detailed future studies on the prevalence of PFAS and EOF contamination in Norway and elsewhere. A total of 37 PFAS were measured, including PFAAs, some of their precursors, perfluorooctane sulfonic acid (PFOS) replacement products 6:2 and 8:2 chlorinated polyfluorinated ether sulfonic acid (PFESA) and perfluoroethylcyclohexane sulfonic acid (PFECHS).

2. Materials and methods

2.1. Chemicals

Most isotope labelled internal standards (IS) and native (^{12}C) standards were purchased from Wellington Laboratories (Guelph, Canada). The exceptions were: trifluoroacetic acid (TFA; from Merck KGaA; Darmstadt, Germany) and perfluoropropanoic acid (PFPrA; from Sigma-Aldrich). Further details on suppliers of solvents and chemicals are given in SI 1.

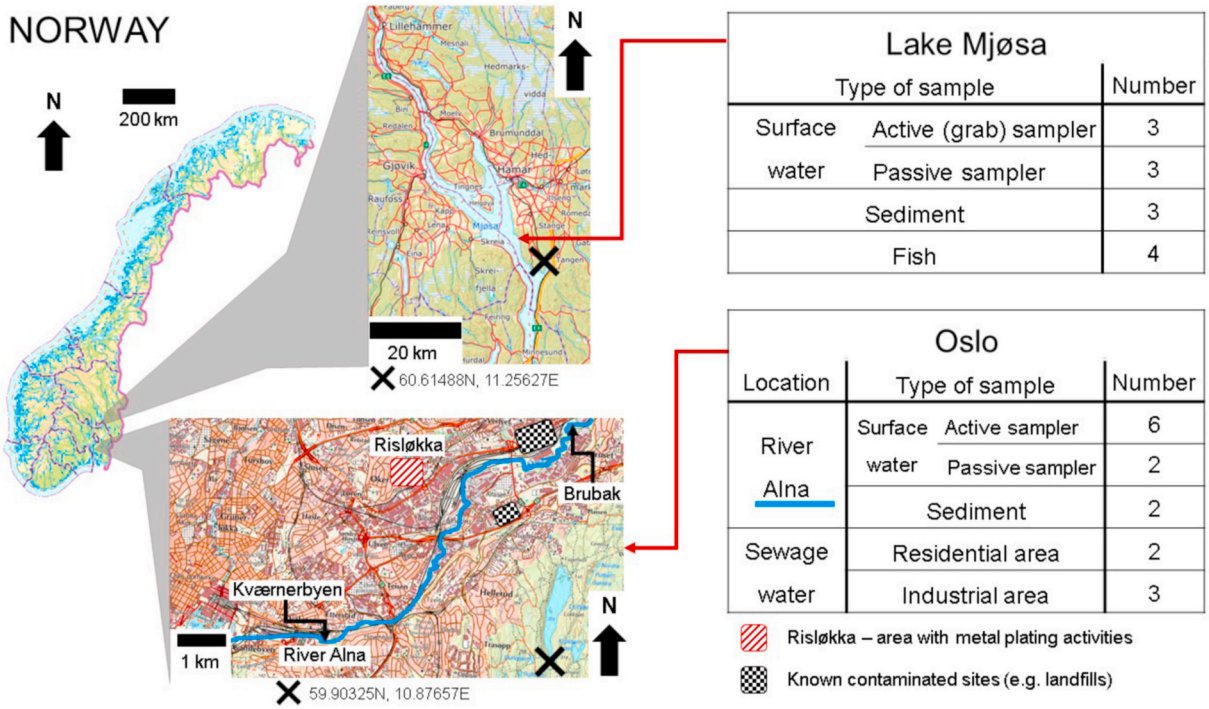
2.2. Sample collection

Two sites were chosen: River Alna in Oslo and Lake Mjøsa 60 km north of Oslo (Fig. 1 and section 2 in the SI). These sites were chosen due to known contamination issues. Additional considerations were access to the sampling sites and their proximity to potential sources. River Alna flows through an industrial area in Oslo (see Fig. S2 in the SI), where there are several companies related to vehicle reparation and sales, industries (recycling, logistics terminals) and also highly populated areas before reaching Oslo Fjord. Samples from River Alna were collected during rainfall and dry conditions to see whether additional PFAS were washed into the environment during rainfall. Lake Mjøsa also has a record of industrial activity and related pollution such as the flame retardant group polybrominated diphenyl ethers (PBDEs) as well as sewage, which may be a source of siloxanes (Fjeld et al., 2015). Earlier Norwegian monitoring programmes have revealed higher concentrations of PFOA in Mjøsa compared to other south-Norwegian lakes (Herzke, 2013). Samples were collected following the guidelines from the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) (CEMP, 1999). As the surface water samples were stored at +4 °C, some precursors might have degraded before analysis (Woudneh et al., 2019), which is a limitation of the study.

The surface water samples from River Alna (Fig. 1) were collected as time-integrated composite samples using Avalanche ® (Teledyne ISCO; NE, United States) automatic samplers (additional details in SI section 2.2 and Fig. S2). After sampling using the Avalanche ® samplers, subsamples were immediately taken into 1 L PE bottles and sent to Örebro for analysis. These time-integrated composite samples were taken at two sites between June and August 2018: Brubak (SW-A-1 and -2) and Kværnerbyen (samples SW-A-3 to 6). The river flow at Brubak was roughly estimated from the measured level in the river using an ISCO 2150 flow meter. River flow data at Kværnerbyen was supplied by the Water and Sanitation agency (VAV). Samples were collected during heavy rain, denoted by a "-W" suffix, and during dry weather conditions, denoted by a "-D" suffix. Precipitation and river flow data is presented in the SI, Table S1. Composite river sediment samples were collected at Brubak and Kværnerbyen using a small sediment core sampler (additional details in SI 2.2). The top 2 cm of the sediment layer were sampled, these composite samples were collected into glass jars, covered with baked aluminum foil and in turn sealed with a lid.

All raw sewage samples were collected (from sewage pipelines between the sources and the local treatment plant) as time-integrated composite samples using ISCO 6700 automatic samplers and ISCO 2150 flow meters were used to measure the flow during sampling (additional details in SI 2.2, Fig. S2 and Table S1). The raw sewage samples were collected from two locations (a residential site and an industrial site) at the same time as the surface water samples: between June and August 2018. No fish were present at the sampling sites along River Alna, thus no biota samples were available for this site.

Surface water samples from Lake Mjøsa (Fig. 1) were collected in polyethylene (PE) 1 L bottles at a depth of 0–20 cm from the surface, which were rinsed twice with local water before taking the samples. The sampling described in more detail in SI 2.1. Sediment samples were collected at the same sites as the water samples. Approximately 100 g of top layer of sediments (0–10 cm) were collected using a small van Veen grab sampler in the littoral zone (0–50 cm depth). The sediment samples were collected in glass jars with baked aluminum foil underneath the lid. Perch (*Perca fluviatilis*) were caught using bottom nets at a depth of 25 m in Lake Mjøsa. Fig. S1 in the SI presents in more detail where the samples were collected from Lake Mjøsa. The fish were untangled from the net using disposable gloves, immediately wrapped in baked aluminum foil



Lake Mjøsa

Type of sample		Number
Surface water	Active (grab) sampler	3
	Passive sampler	3
Sediment		3
Fish		4

Oslo

Location	Type of sample		Number
River Alna	Surface water	Active sampler	6
		Passive sampler	2
	Sediment		2
Sewage water	Residential area		2
	Industrial area		3

Fig. 1. Location of the sampling sites in Norway and the number of samples collected for this study. Modified from Norgeskart (https://www.norgeskart.no/).

and kept frozen upon shipment to the laboratory. The sample from Lake Mjøsa were collected in August 2018.

2.3. Sample preparation

All samples were extracted in duplicates, where replicate 1 was spiked with isotopically labelled IS (1 ng–5 ng); it was used for target PFAS analysis. Replicate 2 was extracted without adding any IS and used for EOF analysis because IS also contributed to EOF in the sample. To calculate the amount of fluorine originating from the target analytes for the fluorine mass balance, a subsample from the replicate 2 extract was analyzed for its PFAS content. The PFAS content was then converted to fluorine equivalents (e.g. from ng/L PFAS to ng/L F) using formula presented in SI. The repeatability of the extraction was verified by comparing the measured PFAS content between the two replicates (without recovery correction from the replicate 1 values), the average difference between the L-PFOS and PFOA content in the two replicates was below 20%. A schematic representation of the workflow is given in SI 3, Fig. S3.

The surface and sewage water samples were extracted with a solid phase extraction (SPE) method adapted with changes from (Eriksson et al., 2017) and (ISO, 2009). In brief, subsamples of 200 mL were extracted with Oasis (Waters Corporation, Milford, MA, U.S.) WAX cartridges (6 mL, 150 mg sorbent, 30 μm particle size). Firstly, the SPE cartridges were conditioned: 4 mL of methanol (MeOH) with 0.1% NH_4OH, 4 mL MeOH and 4 mL MilliQ water. After the samples were completely loaded onto the cartridge, a washing step was employed to remote IF. This is an important step to ensure IF will not conflate the EOF measurement. The replicate 2 subsamples (used for EOF analysis) were washed with 20 mL of 0.01% NH_4OH in water. The next step was to wash all cartridges with 4 mL or 10 mL of MilliQ water (replicates 1 and 2 respectively), 4 mL of 25 mmol/L ammonium acetate buffer at pH 4 in water and 4 mL 20% MeOH solution. Thereafter, the cartridges were dried under vacuum for 30 min and eluted with 4 mL MeOH (fraction of neutral, zwitterionic, basic and cationic compounds, later abbreviated as neutral fraction (D'Agostino and Mabury, 2017)) and 4 mL 0.1% NH_4OH in MeOH (anionic compounds, later as anionic fraction). These extracts were evaporated to a final volume of 0.5 mL. The target PFAS were analyzed only in the anionic fraction, EOF was measured in neutral and anionic fractions separately. Suitability of the method for EOF extraction has been demonstrated by Kaiser et al. (Kaiser et al., 2020).

Subsamples of fish liver (approximately 0.16 g) and sediment (approximately 1 g) were extracted with a method adapted from Yoo et al. (Yoo et al., 2009). The fish were dissected with washed and baked utensils, the liver samples were cut into small pieces prior to homogenization using an ULTRA TURRAX ® tube drive system. The sediment samples were first freeze-dried and then subjected to alkaline digestion, soaked in 0.4 mL of 0.2 mol/L NaOH in MeOH for 30 min and the excess alkali were neutralized by adding 80 μL of 1 M HCl at the end. These sediment samples were then extracted with 2 mL of MeOH by ultrasonication for 15 min and this step was repeated once again after removing the supernatant from the first cycle and both MeOH extracts were combined for respective samples. The MeOH extracts from sediment samples and fish liver (wet) samples were then extracted with ion pair extraction (IPE), 5 mL of methyl *tert*-butyl ether (MTBE) and 2 mL of 0.5 mol/L tetrabutyl-ammonium sulfate (TBA) in water were added to each sample and shaken for 15 min (600 rpm, YellowLine OS 2 basic, IKA; Staufen, Germany), followed by centrifugation (8000 g for 10 min, Sigma 3–16L, Sigma Laborzentrifugen; Osterode am Harz, Germany). The extraction was repeated two more times using 3 mL of MTBE, after removing the organic solvent layer. The MTBE extracts from all three cycles were combined for respective samples, evaporated to 0.2 mL and reconstituted to 1.0 mL with MeOH. These MeOH extracts were evaporated to 0.5 mL. Suitability of the method for EOF extraction has been demonstrated by Miyake et al. (Miyake et al., 2007b).

The passive sampler method was based on the method published Baz-Lomba et al. (2017) and the results in this work for the passive samplers are reported as ng per mL of sample extract. In brief, the passive samplers were exposed for 10 days, after which the sorbent material was transferred into an empty SPE cartridge. These were washed twice with 6 mL of MilliQ water, followed by: 4 mL of MeOH with 1% NH_4OH, 4 mL of MeOH and 4 mL of MeOH with 1% of formic acid. The combined extract of 12 mL was evaporated under nitrogen flow to 0.1 mL and reconstituted to 1 mL with MeOH.

2.4. Instrumental analysis

2.4.1. EOF analysis

EOF content was analyzed by CIC. This system had a combustion module and an autosampler (both from Analytik Jena, Germany), an absorber module (920 Absorber Module) and an ion chromatograph (IC; 930 Compact IC Flex), both from Metrohm, Switzerland. A schematic representation of the CIC apparatus is presented in SI 4 (Fig. S4). The anions were separated with an ion exchange column (Metrosep A Supp 5–150/4), carbonate buffer (64 mmol/L sodium carbonate and 20 mmol/L sodium bicarbonate) as eluent and isocratic elution. The autosampler injected 100 μL of the extract from replicate 2 on a quartz boat. The boat was inserted into the oven (1000–1050 °C), the hydrogen fluoride (HF) formed during combustion was absorbed in MilliQ water (in the absorber module). Once the combustion was complete, a 2 mL subsample of the absorber solution was injected onto the ion chromatograph by a trap column. The F^- concentration was measured via conductivity.

2.4.2. Target PFAS analysis

A total of 37 PFAS were included in PFAS analysis: C2–C3 perfluoroalkyl acids (ultra-short chain PFCAs), C 4-C7 PFCAs (short chain PFCAs), C8–C14, C16, C18 PFCAs (long chain PFCAs), C2–C3 perfluoroalkyl sulfonic acids (ultra-short chain PFSAs), C4–C5 PFSAs (short chain PFSAs), C6–C10, C12 PFSAs (long chain PFSAs), PFCA precursors and intermediates (fluorotelomer phosphate diesters (diPAPs), fluorotelomer sulfonic acids (FTSAs)), PFSA precursors and intermediates (perfluoroalkyl sulfonamidoacetic acids (FOSAAs)), Cl-PFESAs and PFECHS. Because the ultra-short chain PFCA analysis was qualitative due to the lack of suitable internal standards; their levels were only included in the fluorine mass balance and sum PFAS profiles in section 3.2 are presented as a sum of 35 PFAS (∑35PFAS). A full list of target analytes and their abbreviations are provided in SI 5, Table S2).

Ultra performance liquid chromatography electrospray ionization tandem mass spectrometry (UPLC-ESI-MS/MS) in negative mode was used to analyze most compounds. The chromatograph was an Acquity UPLC with a C18 BEH column (2.1 mm × 100 mm, 1.7 μm) with XEVO TQ-S MS/MS as the detector. The mobile phases were MeOH and 30:70 MeOH:water mixture, both with 2 mmol/L ammonium acetate and 5 mmol/L 1-methylpiperidine as additives; the column was kept at 50 °C. Further details on the UPLC method are also given in SI 6, Fig. S5. Ultra-short chain compounds (C2–C3) were separated by a supercritical fluid chromatography system (SFC, also known as UPC 2-ultra performance convergence chromatograph), the detector was 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 (3.0 mm × 150 mm, 1.7 μm DIOL) was kept at 35 °C. More details on the SFC method are given in SI 6, Fig. S6. All chromatographs, analytical columns and mass spectrometers were from Waters Corporation, Milford, MA, U.S.

Native and isotope labelled IS were used to quantify the analytes, Table S3 in SI 7 presents which IS was used for each target analyte. The analyte concentrations were recovery-corrected using isotope dilution. If a corresponding IS was missing, the IS of the same compound group with the closest retention time was used. Multiple reaction monitoring (MRM) was used and at least two transitions were monitored for the majority of analytes, the transitions are presented in SI7, Table S3. With the exception of PFOS only linear isomers were quantified.

2.5. Quality assurance/quality control

2.5.1. EOF measurement and mass balance

The CIC system used an external five-point calibration curve to calculate the amount of fluoride. The calibration samples were made from a PFOS potassium salt and analyzed along with the environmental samples and the calibration curve had a correlation coefficient $R^2 > 0.99$. The calibration range was 50–1000 ng/mL F in the sample extract injected onto the CIC.

The analysis of samples was started when the relative standard deviation (RSD) of three sequential combustion blanks (empty sample boat analysis) was below 5%. An additional combustion blank was run after every sample 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 PFOS standard (100 ng/mL F), was analyzed after every 10 injections. The average measurement result was 87.0 ng/mL F, with a standard deviation of 13.3 ng/mL F. Each extraction batch included a dedicated procedural blank for EOF analysis which was used to estimate the limit of detection (LoD).

The LoD for EOF analysis was calculated separately for all sample types and it was determined as the average procedural blank concentration plus three times the standard deviation of the procedural blanks. The LoD covers both the sample extraction step and the instrumental analysis (thus equal to method detection limit, MDL). The LoD for the different sample types were as follows: surface water neutral fraction – 36 ng/L F, surface water anionic fraction – 40 ng/L F, passive sample extracts – 119 ng/mL F, sediment – 22 ng/g F w.w., fish liver – 88–145 ng/g F w.w. (depending on sample size).

2.5.2. Target PFAS analysis

A mixture of target analytes was analyzed after every 10 injections to monitor instrumental performance. This standard sample was prepared with every batch of samples and had to be within ±20% of the calibration curve. Calibration curves had eight points and ranged from 0.02 to 60 ng/mL. Further details on the calibration range of individual compounds are given in SI 8, Table S4. All results below the limit of quantification (LoQ) were replaced with zero during further calculations.

The LoD was calculated as the average concentration in the procedural blanks plus three times the standard deviation of the procedural blanks. Both LoD and the limit of quantification (LoQ) were calculated for the whole analytical procedure (from sample preparation to instrumental analysis. The LoQ was calculated as the average concentration in the procedural blanks plus 10 times their standard deviation. If an analyte was not detected in the procedural blanks, the lowest calibration curve point was used as the LoQ. When at least two product ions were available, the results were only reported if both were detected and their ratio was within 50% of the expected value (from standard samples). The recovery for a given IS in each sample, calculated by mass labelled recovery standards (RS) added prior injection, had to be between 20% and 150%. The recoveries of the IS have been provided in the SI, Table S5 and S6.

A procedural blank of MilliQ water was included in each extraction batch to monitor for contamination. No detectable contaminations were observed for target PFAS. As a quality control (QC) sample for SPE extractions, a MilliQ water sample spiked with native PFAS was used. The RSD of these QC samples ($n = 7$) was below 15% for all of the 11 PFAS included by the Swedish Food Agency for monitoring in drinking water (SI 9, Table S8). A single field blank from River Alna was also analyzed and no detectable levels of target analytes were found. However, a blank sample was not available for the Avalanche ® sampling system. The IPE method performance was monitored with dry domestic sludge, SRM 2781 (NIST, USA), the results ($n = 2$) were in good agreement with the values stated in the certificate of analysis, with the exception of perfluoroheptanoic acid (PFHpA, SI 9, Table S7).

3. Results

3.1. Extractable organic fluorine

Detectable levels of EOF were measured in samples from Lake Mjøsa, River Alna and sewage water samples from Oslo. Of these samples, EOF was above the LoD in 58% of samples from Lake Mjøsa and in all River Alna and sewage samples from Oslo. To estimate the levels of UOF

compounds, fluorine mass balance analysis was performed on the samples that had EOF levels above LoD. The concentrations of individual PFAS (from replicate 1) and EOF (replicate 2) can be found in SI 10, Tables S7-S10.

3.1.1. Surface water grab sample fluorine mass balance analysis

The EOF levels were measured in both the neutral and anionic fractions of the surface water grab samples (active sampling) separately. EOF was divided into neutral UOF, anionic UOF and identified EOF. Target analytes were measured only in the anionic fraction, the amount of fluorine accounted for by the target PFAS was subtracted from the anionic EOF. One of the surface water grab samples from Lake Mjøsa had EOF levels below LoD and this sample was excluded from further data analysis. The EOF profiles and the ∑EOF levels (anion + neutral) are shown in Fig. 2. The concentrations of EOF in individual samples are also given in SI 10, Table S9.

In brief, the target analytes accounted for 0.2% of the ∑EOF, in Lake Mjøsa samples. The anionic UOF was the largest fraction, on average accounting for 76.8% of the ∑EOF. The remaining 23.0% of ∑EOF was attributable to neutral UOF. The identified EOF fraction was larger in River Alna samples, ranging from 0.8 to 2.9% of ∑EOF (average of 1.6%). The neutral UOF accounted for 58% of ∑EOF in (12–89%) and anionic UOF for 41% (10–87%).

3.1.2. Sewage, sediment and FISH liver fluorine mass balance analysis

All five sewage water samples from Oslo had EOF concentrations exceeding the LoD, details shown in Fig. 3. The EOF concentrations in found in these samples are also presented in SI 10, Table S11. In both samples from the residential area, the breakdown of EOF was similar, with anionic UOF being the largest fraction with 53% of EOF, followed by neutral UOF at 46% and the target analytes accounted for 1% of the EOF. In comparison, the fraction of anionic UOF was larger in the sewage samples from the industrial area (64% of EOF). The remainder of EOF was broken down to neutral UOF (33%) and EOF from target PFAS (3%).

Of the three sediment samples from Lake Mjøsa, only one had EOF levels above LoD, details are provided in Fig. 4. In that sample, nearly all of the EOF (99.9%) was unidentified, and the small fraction of identified EOF was attributable to short- and long chain PFCAs. Both sediment samples collected from River Alna had detectable levels of EOF, of which 96.6% was unidentified. Nearly half of the remaining EOF was attributable to short- and long chain PFCAs, 1.8% and 0.4% of EOF, respectively. Two of the perch liver samples had quantifiable levels of EOF and 83.8% of it was unidentified. The PFAS classes with the largest contribution to the fluorine mass balance were long chain PFSAs (8.1%).

3.2. Target PFAS

Across all samples, the most prevalent PFAS were PFCAs – both short and long chain PFCAs, followed by long chain PFSAs (as shown in Figs. 5 and 6). The highest detection frequencies were observed for perfluorodecanoic acid (PFDA, 89%), PFOA (86%) and L-PFOS (82%). The most commonly found PFCA precursors were 6:2 FTSA and 8:2 FTSA, both were detected in 68% of the samples; diPAPs were detected in fewer than 35% of the samples. Precursors. Two perfluorooctane sulfonamidoacetates, FOSAA and methyl perfluorooctane sulfonamidoacetic acid (MeFOSAA), were detected in 4% and 7% of samples respectively. The PFAS profiles are shown in Figs. 5 and 6, additional details are given in SI 10 Tables S7-S10.

PFECHS was found in all surface water passive sampler extracts from both Lake Mjøsa and River Alna and in all of the surface water grab samples from River Alna and all industrial sewage samples. The ultra-short chain PFCAs, i.e. TFA and PFPrA, were detected in 18% and 11% of samples respectively. Of the ultra-short chain PFSAs, only perfluoroethane sulfonic acid (PFEtS) was found in one of the passive sampler extracts from Lake Mjøsa.

The ultra-short chain PFCAs were excluded from the target analysis due to lack of suitable mass labelled standards. These compounds were only reported as detected or not detected in the target analysis.

3.2.1. Surface water grab and passive samples

The average $\sum_{35}$PFAS concentration in surface water grab samples from Lake Mjøsa ranged from 1.68 to 7.68 ng/L and from 24.50 to 50.60 ng/L in River Alna samples, details are shown in Fig. 5 and in SI 10 Tables S9-S10. The dominant PFAS groups in surface water grab samples from Lake Mjøsa were short – and long chain PFCAs, 49% and 46% of the $\sum_{35}$PFAS on average. The most prominent PFAS class in the surface water grab samples from River Alna were short chain PFCAs, 46% of $\sum_{35}$PFAS.

The $\sum_{35}$PFAS concentrations in surface water passive sampler extracts from Lake Mjøsa were 46.20 and 73.30 ng/mL and ranged between 31.30 and 68.00 ng/mL in River Alna samples, details in Fig. 5 and in SI 10 Tables S7-S8. In the surface water passive samplers extracts from Lake Mjøsa, the $\sum_{35}$PFAS profiles were dominated by short- and long chain PFCAs, 42% and 34% of $\sum_{35}$PFAS respectively. Most of the $\sum_{35}$PFAS profile in passive sampler extracts from River Alna samples

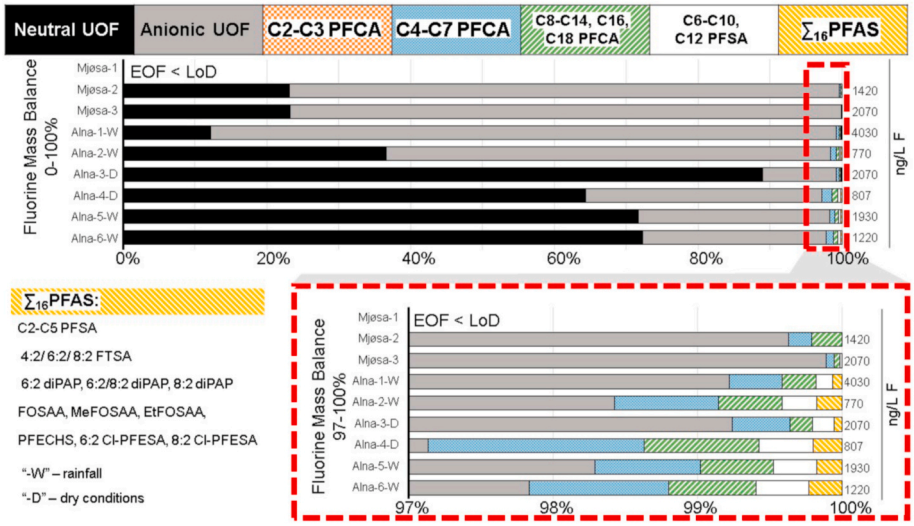


Fig. 2. Fluorine mass balance analysis of surface water grab samples (active sampling) from Lake Mjøsa and River Alna. Samples from River Alna were collected during rainfall (denoted by "-W") and dry conditions ("-D"). Lower part of the figure is an enlarged view of the 97–100% range of the overall fluorine mass balance.

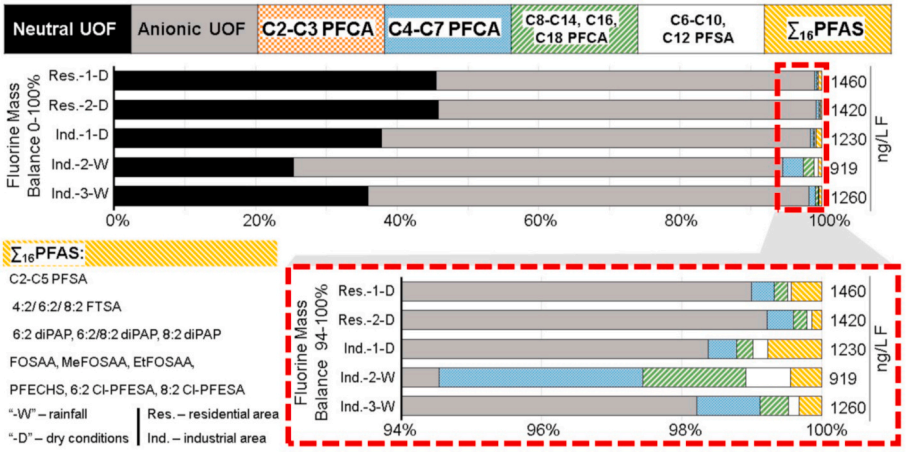


Fig. 3. Fluorine mass balance analysis of sewage water samples from Oslo. Samples from River Alna were collected during rainfall (denoted by "-W") and dry conditions ("-D"). Lower part of the figure is an enlarged view of the 94–100% range of the overall fluorine mass balance.

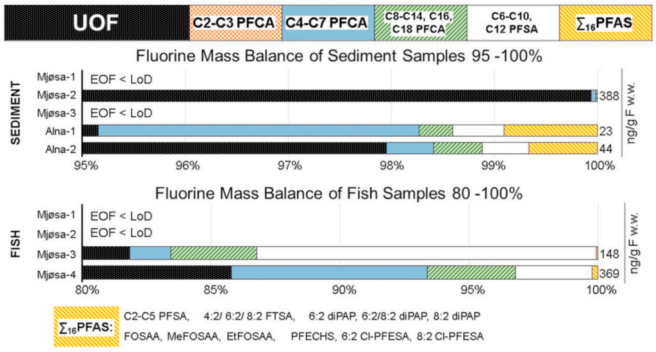


Fig. 4. Fluorine mass balance analysis of sediment and fish liver samples. Above figure is in the range 95–100% of the fluorine mass balance and the lower figure is in the 80–100% range.

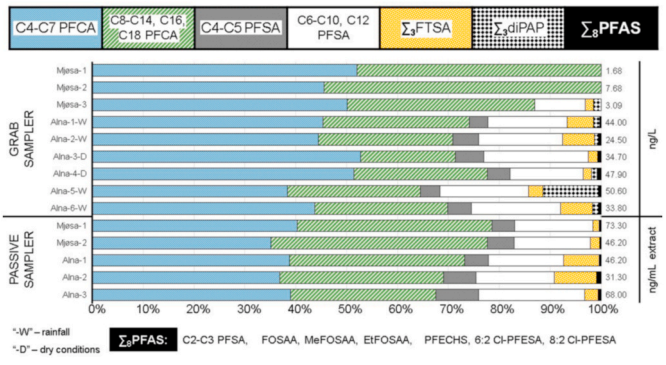


Fig. 5. PFAS profiles of the grab and passive samples from Lake Mjøsa and River Alna along with $\sum_{35}$PFAS levels. The $\sum_{35}$PFAS concentrations in the passive samplers are given on sample extract basis.

was attributable to short- and long chain PFCAs, 38% and 32% of $\sum_{35}$PFAS respectively. Long chain PFSAs accounted for an additional 17%.

The $\sum_{35}$PFAS profiles were similar between the surface water grab and passive samples, both were dominated by short and long chain PFCAs. However, diPAPs and FOSAAs were not detected in any passive sampler extracts, while they were observed in the grab samples. This could be due to the grab samples containing particulate matter, to which these compounds had adsorbed. During SPE extraction the particulate

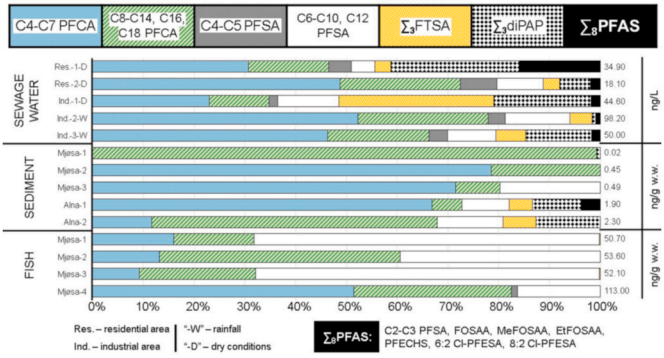


Fig. 6. PFAS profiles of the raw sewage water, sediment and fish liver samples from Lake Mjøsa and River Alna along with $\sum_{35}$PFAS levels (w.w. – wet weight).

matter would be loaded onto the SPE cartridge and the compounds would be desorbed during elution with MeOH. The passive samplers were not intended to capture particulate matter.

3.2.2. *Sewage, sediment and FISH samples*

The $\sum_{35}$PFAS concentrations in residential area sewage samples were 18.10 and 34.90 ng/L. In sewage samples from the industrial area they were between 44.60 and 98.20 ng/L, details in Fig. 6 and SI 10 Tables S11-S12. The PFAS profiles from the residential area samples were dominated by short chain PFCAs (40% of $\sum_{35}$PFAS). The second largest group of PFAS were long chain PFCAs (20%). The most prominent PFAS group in the sewage samples from the industrial area were short chain PFCAs (41% of $\sum_{35}$PFAS), followed by long chain PFCAs (19%).

The $\sum_{35}$PFAS concentration in sediment samples from Lake Mjøsa ranged from 0.02 to 0.49 ng/g w.w. (wet weight) and from 1.90 to 2.30 ng/g w.w. in samples from River Alna, details in Fig. 6 and SI 10 Tables S9-S10. In the samples from Lake Mjøsa, PFCAs dominated the $\sum_{35}$PFAS profiles, on average accounting for 93% of $\sum_{35}$PFAS and the remainder coming from long chain PFSAs. The $\sum_{35}$PFAS profiles of the sediment samples from River Alna was dominated by short- and long chain PFCAs (39% and 31% of $\sum_{35}$PFAS, respectively). Long chain PFSAs accounted for 11% of $\sum_{35}$PFAS. Both PFCA and PFSA precursors were present, diPAPs accounted for 11% $\sum_{35}$PFAS, FTSAs and FOSAAs a further 6% and 2% respectively.

The $\sum_{35}$PFAS concentration in fish liver samples from Lake Mjøsa was between 50.70 and 113.00 ng/g w.w., details in Fig. 6 and SI 10

Tables S9-S10. The $\sum_{35}$PFAS were dominated by long chain PFSAs (48% of $\sum_{35}$PFAS). A further 29% and 22% were accounted for by long- and short chain PFCAs, respectively.

4. Discussion

4.1. Fluorine mass balance and levels of EOF

The fluorine mass balance analysis in this study showed a higher fraction of UOF (99% on average, details in Fig. 2 and SI 10 Tables S7-S8) in surface water grab samples than previously reported for Scandinavian samples (83–98%) (Koch et al., 2019; Kärrman et al., 2019). One class of PFAS, the ultra-short chain PFAS, could be a contributing factor to the high proportion of UOF in surface water samples. The current analytical method might have underestimated the concentrations of ultra-short chain PFAS due to the use of other surrogate standards (e.g. mass labelled PFBA for TFA) in this investigation. Previous studies have found high levels of ultra-short chain PFAS near suspected point sources (Björnsdotter et al., 2019) and in river and rain water samples (Yeung et al., 2017). Although the method used in this study was qualitative for ultra-short chain PFCAs, their presence was detected in more than 10% of the water samples (detection frequencies of 20% and 12% for TFA and PFPrA respectively). The ultra-short chain PFCAs could be released unintentionally, for example TFA has been shown to be formed during ozonation of wastewater (Scheurer et al., 2017) and may thereafter be released into local lakes/rivers. In addition, TFA is known to be a degradation product of hydrofluorocarbons (HFCs) in the atmosphere (Wallington et al., 1994), which is another source of TFA to the ground and eventually river and other water bodies through rain (Yeung et al., 2017). Ultra-short chain PFSA appeared to be less ubiquitous as perfluoroethane sulfonic acid (PFEtS) was found at trace levels only in one sample, but this study did not include trifluoromethane sulfonic acid (TFMS), which was recently reported by Björnsdotter et al. (2019) in surface water collected from firefighting training sites with historical use of aqueous film forming foams, which could account for a part of the EOF.

The UOF fraction could also contain compounds that are not PFAS, containing only a single fluorine atom or a CF_3 group, for example pesticides. A total of 315 pesticide products were approved for usage by the Norwegian Food Safety Authority as of September 2020 (Godkjente, 2020). Of those products 24% contain an active ingredient with at least one fluorine atom (e.g. florasulam $C_{12}H_8F_3N_5O_3S$). This reflects a larger trend in the agrochemical industry, where fluorine has become a common part of pesticides. A recent review paper reported that 25% of herbicides sold globally contain one or more fluorine atoms (Fujiwara and O'Hagan, 2014), elsewhere it has been reported that 30–40% of agrochemicals are fluorinated (THAYER, 2006). While these organofluorine compounds often contain fewer fluorine atoms than PFAS, their concentrations can be higher than those of PFAS. A recent study found flutolanil ($C_{17}H_{16}F_3NO_2$) in 20% of surface water samples from an agricultural area in Georgia (U.S.), with a maximum concentration of 350 ng L (Glinski et al., 2018). For context, nearly 330 tonnes of pesticides of all types were used in Norway in 2014 (Pesticide). The impact of this on the various samples included in this study would be difficult to quantify without including these compounds in the analytical method and is recommended for future studies investigating the fluorine mass balance in environmental samples from areas with agricultural activity. A study published in 2015 compiled data on samples collected from agricultural streams between 1995 and 2012 on the levels of 61 different pesticides (Stenrød, 2015). Five of those compounds contained fluorine and the highest detection frequency was observed for fluazinam ($C_{13}H_4Cl_2F_6N_4O_4$) at 15% with a mean concentration of 0.32 μg/L. Further effort to close the mass balance analysis will be also measuring these fluorinated pesticides.

An additional source of UOF could be fluorinated pharmaceuticals, as approximately 25% of them are reported to contain at least a single fluorine atom (Wang et al., 2014). In 2017, two of the 30 drugs in Norway with the highest number of users were fluorinated (Berg et al., 2013). These were atorvastatin ($C_{33}H_{35}FN_2O_5$), used to prevent cardiovascular disease, and pantoprazole ($C_{16}H_{15}F_2N_3O_4S$), used in the treatment of stomach ulcers. They were used by 5.6 and 5.0% of the Norwegian population in 2017, respectively. These two compounds have pKa values of 4.3 for atorvastatin and 3.96 for pantoprazole. This would lead them to be deprotonated in the surface water samples and would be eluted during sample extraction within the anionic fraction, thus contributing to the anionic UOF fraction of the fluorine mass balance. At the same time, the fungicide mentioned in the previous paragraph (fluazinam, pKa of 7.22) would elute in the neutral fraction and contribute to the neutral UOF. Thus, it cannot be stated that fluorinated pharmaceuticals and agrochemicals are bound to contribute to either neutral or anionic UOF. Due to the wide range of potential compounds, these compound classes are likely to increase the fraction of UOF of both anionic and neutral OF. Further investigation is needed to clarify this point.

Whether it was due to these ultra-short chain PFAS or some other organofluorine compounds, the overall EOF concentration surface water grab samples, was higher in this study than previously reported in Lake Mjøsa (1750 vs 830 ng/L F, this and the previous study respectively; Fig. 2 and SI 10 Table S9) (Kärrman et al., 2019). In this investigation, the EOF concentrations were more than 5 times higher than those reported in Nordic surface water (Lake Vättern in Sweden – 64 ng/L F, River Vantaanjoki in Finland – 163 ng/L F, Lake Badesø in Greenland – 61 ng/L F) (Kärrman et al., 2019). The concentration of EOF in River Alna (between 807 and 4030 ng/L F) was 1-2 orders of magnitude higher than recently reported from Germany (Moselle; 40–60 ng/L F, Rhine 50–300 ng/L F) (Metzger et al., 2019). However, the study on German rivers used a different extraction method (using hydrophilic-lipophilic balance sorbent in SPE) and a different analysis technique (continuum source molecular absorption spectrometry) for EOF determination. A recent study compared EOF extraction methods for bovine serum in brief and the EOF results could differ by approximately 50%. It is very likely that a similar extraction method dependency is present with environmental samples as well and hence, care should be taken when comparing studies with different methodologies (Kaiser et al., 2020).

The result of fluorine mass balance analysis of sediment samples was similar (the difference in their mean values was not statistically significant, two-tailed *t*-test, $p>0.05$) to that of surface water sample, between 95.2 and 99.9% of the EOF content in sediment samples was of unidentified origin (Fig. 4 and SI 10 Table S11). However, the detection frequency of EOF was lower, with only 3 out of 5 samples having EOF concentrations above LoD. The EOF levels and the UOF fraction in the sediment in this study were in a similar range to those found in sediment samples from Lake Ontario, Canada (Yeung et al., 2013). However, higher EOF concentrations have been reported in samples from Lake Michigan ranging 600000–4800000 ng/g F d.w. (Codling et al., 2014). Since these studies used different extraction methods, the results are not directly comparable (Codling et al., 2014; Response).

The high fraction of UOF in both surface water grab samples and sediment samples could be due to degradation intermediates, as previous studies have shown that only a small percentage of the original precursor compound degrades into readily measurable PFAAs (Wang et al., 2011; Liu et al., 2010; Zhang et al., 2013). The degradation process also depends on the compound and conditions (Zhang et al., 2013; Liu et al., 2010). The presence of PFAA precursors in stormwater samples has been reported by Houtz and Sedlak (2012). As PFAS are not readily removed by wastewater treatment methods (Baz-Lomba et al., 2017), they could reach water, possibly contributing to the UOF fraction.

The UOF fraction of EOF in perch livers from the present study (84%; Fig. 4 and SI 10 Table S11) was in line with a study by Kärrman et al. who reported UOF fractions between 49 and 87% in perch liver samples from Norway, Finland and Sweden (comparison of these results is

presented in SI 11, Table S13) (Kärrman et al., 2019). That study also contained a pooled sample from Lake Mjøsa (pool of 10 perch liver samples), where 63% of the EOF was unidentified, which is slightly less than in perches from the present study. This might be due to the different ages of the fish caught, data on which is unfortunately unavailable. The levels of EOF in perch liver samples, <LoD – 370 ng/g F, are in the same range as what has been found from Lake Mjøsa (210 ng/g F), Finland and Sweden (Kärrman et al., 2019).

4.2. Potential sources of PFAS

An earlier study showed an effective source-attribution technique by using PFAS profiles and a distance impact factor from nearby sources for better understanding PFAS sources in urban areas (Zhang et al., 2016). The PFAS contamination profiles from the surface water grab samples from Lake Mjøsa (Fig. 5) suggest their sources to be from industrial applications; most of the PFCAs found in these samples have been linked to mixed industrial use (C6–C10 PFCAs) (Zhang et al., 2016). The surface water passive sampler extracts showed similar PFAS profiles to those of grab samples, in both cases, the dominant PFAS classes were short and long chain PFCAs (Fig. 5).

While PFCAs were prevalent in the surface water grab samples from River Alna, indicating mixed industrial sources as with Lake Mjøsa, the samples from River Alna also had detectable levels of PFOS, FTSAs and diPAPs. As River Alna flows through an industrial area in Oslo, several urban sources such as industries and landfills could be relevant. Perfluoropentanoic acid (PFPeA), PFOS and 6:2 FTSA have been linked to metal plating industry (Zhang et al., 2016). The surface water passive sampler extracts had similar PFAS profiles to surface water samples, short- and long-chain PFCAs were the dominant PFAS classes, with sizeable (approximately 20% of sum PFAS) contribution from PFSAs (short- and long-chain PFSAs combined).

PFECHS has been detected in different environmental samples from Scandinavia (surface water, wastewater treatment plant effluent, fish and marine mammals) (Kärrman et al., 2019), North America (surface water and fish) (De Silva et al., 2011; M et al., 2013; Houde et al., 2016) and China (Wang et al., 2016). In this study, PFECHS was detected in all surface water grab samples from River Alna in Oslo (0.11–0.35 ng/L). The PFECHS concentrations in River Alna were in line with those of the previous study (up to 0.94 ng/L) (Kärrman et al., 2019), but lower than what has been found in North America (up to 5.65 ng/L) (De Silva et al., 2011). The sources of PFECHS in River Alna are likely linked to the industrial activities in the surrounding area, since PFECHS was detected in all 3 industrial sewage samples taken in Oslo (PFECHS, 0.82–0.89 ng/L). In addition to metal plating (Wang et al., 2013), PFECHS has been linked to hydraulic fluids (De Silva et al., 2011), cosmetics and semiconductors (Fischer, 2018). PFECHS was detected both in the passive and grab samples from River Alna, but was only found in the passive sampler extracts from Lake Mjøsa. One explanation could be that it was detected through enrichment on the passive samplers, but was below the detection limit in the grab samples.

5. Conclusion

Unidentified organofluorine compounds (UOF) were the largest contributors to EOF in all sample matrices, which shows the importance of including EOF when the environmental loadings of total PFAS and other fluorine related compounds are of interest. This study was limited by the low number of samples taken at both locations, preventing statistical analysis, and the exclusion of the most common fluorinated agrochemicals and pharmaceuticals from the list of target analytes. Future screening methods should include common fluorinated agrochemicals and/or pharmaceuticals, as their annual use far exceeds that of PFAS (offsetting their low degree of fluorination). Currently, there is no universally accepted methodology for EOF analysis and to our knowledge, no standard reference materials or ring tests are available. This makes comparison between studies challenging at the moment. The levels of EOF were elevated in surface water samples from Norway compared to other Scandinavian sampling campaigns.

Credit author statement

Rudolf Aro: Investigation, Writing - Original Draft. **Pernilla Carlsson:** Conceptualization, Funding acquisition, Writing - Review & Editing. **Christian Vogelsang:** Writing - Review & Editing. **Anna Kärrman:** Resources, Funding acquisition,Writing - Review & Editing. **Leo WY Yeung:** Resources, Funding acquisition, Conceptualization, Methodology, Writing - Review & Editing.

Declaration of competing interest

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.131200.

References

Apler, A., Josefsson, S., 2016. Swedish Status and Trend Monitoring Programme Chemical Contamination in Offshore Sediments 2003– 2014.

Baz-Lomba, J.A., Harman, C., Reid, M., Thomas, K.V., Sep. 2017. Passive sampling of wastewater as a tool for the long-term monitoring of community exposure: illicit and prescription drug trends as a proof of concept. Water Res. 121, 221–230. https://doi.org/10.1016/j.watres.2017.05.041.

C. Berg et al., "Reseptregisteret 2013–2017 [The Norwegian Prescription Database 2013–2017]," Norwegian Institute of Public Health. Accessed: Mar. 27, 2021. [Online]. Available: https://www.fhi.no/globalassets/dokumenterfiler/rapporter/2018/reseptregisteret-2013_2017-temadel-om-legemidler-og-eldre.pdf.

Björnsdotter, M.K., Yeung, L.W.Y., Kärrman, A., Jogsten, I.E., Oct. 2019. Ultra-short-chain perfluoroalkyl acids including trifluoromethane sulfonic acid in water connected to known and suspected point sources in Sweden. Environ. Sci. Technol. 53 (19), 11093–11101. https://doi.org/10.1021/acs.est.9b02211.

Buck, R.C., et al., Oct. 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integrated Environ. Assess. Manag. 7 (4), 513–541. https://doi.org/10.1002/ieam.258.

CEMP Guidelines for Monitoring Contaminants in Biota, 1999. OSPAR Commission. Accessed: Mar. 26, 2021. [Online]. Available: https://www.ospar.org/convention/agreements?q=biota&t=&a=&s=.

Codling, G., et al., Nov. 2014. Historical trends of inorganic and organic fluorine in sediments of Lake Michigan. Chemosphere 114, 203–209. https://doi.org/10.1016/j.chemosphere.2014.03.080.

De Silva, A.O., Spencer, C., Scott, B.F., Backus, S., Muir, D.C.G., Oct. 2011. Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate, in the great lakes of north America. Environ. Sci. Technol. 45 (19), 8060–8066. https://doi.org/10.1021/es200135c.

Dubocq, F., Wang, T., Yeung, L.W.Y., Sjöberg, V., Kärrman, A., Jan. 2020. Characterization of the chemical contents of fluorinated and fluorine-free firefighting foams using a novel workflow combining nontarget screening and total fluorine analysis. Environ. Sci. Technol. 54 (1), 245–254. https://doi.org/10.1021/acs.est.9b05440.

D'Agostino, L.A., Mabury, S.A., Dec. 2017. Certain perfluoroalkyl and polyfluoroalkyl substances associated with aqueous film forming foam are widespread in Canadian surface waters. Environ. Sci. Technol. 51 (23), 13603–13613. https://doi.org/10.1021/acs.est.7b03994.

Eriksson, U., Haglund, P., Kärrman, A., Nov. 2017. Contribution of precursor compounds to the release of per- and polyfluoroalkyl substances (PFASs) from waste water treatment plants (WWTPs). J. Environ. Sci. 61, 80–90. https://doi.org/10.1016/j.jes.2017.05.004.

Fischer, S., 2018. Personal Communication. " Swedish Chemical Agency, Mar.

Fjeld, E., Bæk, K., Rognerud, S., Rundberget, J.T., Schlabach, M., Warner, N.A., 2015. Environmental Pollutants in Large Norwegian Lakes. " Norwegian Environment Agency. M–548, 2016. Accessed: Nov. 25, 2020. [Online]. Available: https://www.miljodirektoratet.no/globalassets/publikasjoner/M548/M548.pdf.

Fujiwara, T., O'Hagan, D., Nov. 2014. Successful fluorine-containing herbicide agrochemicals. J. Fluor. Chem. 167, 16–29. https://doi.org/10.1016/j.jfluchem.2014.06.014.

Glinski, D.A., Purucker, S.T., Van Meter, R.J., Black, M.C., Henderson, W.M., Oct. 2018. Analysis of pesticides in surface water, stemflow, and throughfall in an agricultural area in South Georgia, USA. Chemosphere 209, 496–507. https://doi.org/10.1016/j.chemosphere.2018.06.116.

"Godkjente kjemiske og mikrobiologiske preparater - Norwegian Food Safety Authority. accessed Sep. 15, 2020. https://www.mattilsynet.no/plantevernmidler/godk.asp.

Herzke, D., 2013. Perfluorinated Alkylated Substances, Brominated Flame Retardants and Chlorinated Paraffins in the Norwegian Environment - Screening. Norwegian Environmental Agency. M–40, 2013. Accessed: Nov. 25, 2020. [Online]. Available: https://www.informea.org/en/perfluorinated-alkylated-substances-brominated-flame-retardants-and-chlorinated-paraffins-norwegian.

Houde, M., et al., Nov. 2016. Endocrine-disruption potential of perfluoroethylcyclohexane sulfonate (PFECHS) in chronically exposed Daphnia magna. Environ. Pollut. 218, 950–956. https://doi.org/10.1016/j.envpol.2016.08.043.

Houtz, E.F., Sedlak, D.L., Sep. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. Environ. Sci. Technol. 46 (17), 9342–9349. https://doi.org/10.1021/es302274g.

14:00-17:00, "ISO 25101, 2009. ISO accessed Jul. 02, 2019. http://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/04/27/42742.html.

Joerss, H., Schramm, T.-R., Sun, L., Guo, C., Tang, J., Ebinghaus, R., Dec. 2020. "Per- and polyfluoroalkyl substances in Chinese and German river water – point source- and country-specific fingerprints including unknown precursors. Environ. Pollut. 267, 115567. https://doi.org/10.1016/j.envpol.2020.115567.

Kaiser, A.-M., et al., 2020. "Comparison of extraction methods for per- and polyfluoroalkyl substances (PFAS) in human serum and placenta samples—insights into extractable organic fluorine (EOF). Anal Bioanal Chem. https://doi.org/10.1007/s00216-020-03041-5.

Kärrman, A., et al., 2019. PFASs in the nordic environment : screening of poly- and perfluoroalkyl substances (PFASs) and extractable organic fluorine (EOF) in the nordic environment. Nordisk Ministerråd. https://doi.org/10.6027/TN2019-515.

Koch, A., Kärrman, A., Yeung, L.W.Y., Jonsson, M., Ahrens, L., Wang, T., 2019. Point source characterization of per- and polyfluoroalkyl substances (PFASs) and extractable organofluorine (EOF) in freshwater and aquatic invertebrates. Environ. Sci.: Processes & Impacts. https://doi.org/10.1039/c9em00281b.

Liu, J., et al., Jan. 2010. 6-2 Fluorotelomer alcohol aerobic biodegradation in soil and mixed bacterial culture. Chemosphere 78 (4), 437–444. https://doi.org/10.1016/j.chemosphere.2009.10.044.

M, H., M, D., Sp, D., Ao, D.S., C, S., Feb. 2013. Induction of gene responses in St. Lawrence River northern pike (Esox lucius) environmentally exposed to perfluorinated compounds. Chemosphere 92 (9), 1195–1200. https://doi.org/10.1016/j.chemosphere.2013.01.099.

Metzger, M., Ley, P., Sturm, M., Meermann, B., Jul. 2019. "Screening method for extractable organically bound fluorine (EOF) in river water samples by means of high-resolution–continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS). Anal. Bioanal. Chem. 411 (19), 4647–4660. https://doi.org/10.1007/s00216-019-01698-1.

Miaz, L.T., et al., 2020. Temporal trends of suspect- and target-per/polyfluoroalkyl substances (PFAS), extractable organic fluorine (EOF) and total fluorine (TF) in pooled serum from first-time mothers in Uppsala, Sweden, 1996–2017. Environ. Sci.: Processes Impacts 22 (4), 1071–1083. https://doi.org/10.1039/C9EM00502A.

Miyake, Y., et al., 2007a. Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: a mass balance approach to determine individual perfluorinated chemicals in water. J. Chromatogr. A 1143 (1), 98–104. https://doi.org/10.1016/j.chroma.2006.12.071.

Miyake, Y., et al., 2007b. Trace analysis of total fluorine in human blood using combustion ion chromatography for fluorine: a mass balance approach for the determination of known and unknown organofluorine compounds. J. Chromatogr. A 1154 (1), 214–221. https://doi.org/10.1016/j.chroma.2007.03.084.

O'Hagan, D., Harper, D.B., Dec. 1999. Fluorine-containing natural products. J. Fluor. Chem. 100 (1), 127–133. https://doi.org/10.1016/S0022-1139(99)00201-8.

Pesticide use in Norway - Statistics Norway," ssb.no. https://www.ssb.no/en/jord-skog-jakt-og-fiskeri/statistikker/jordmil/friland/2015-10-22 (accessed Sep. 16, 2020).

"PFAS Response - PFAS Sites." https://www.michigan.gov/pfasresponse/0,9038,7-365-86511_95645—,00.html (accessed Nov. 29, 2020).

Rotander, A., Kärrman, A., Toms, L.-M.L., Kay, M., Mueller, J.F., Gómez Ramos, M.J., 2015. Novel fluorinated surfactants tentatively identified in firefighters using liquid chromatography quadrupole time-of-flight tandem mass spectrometry and a case-control approach. Environ. Sci. Technol. 49 (4), 2434–2442. https://doi.org/10.1021/es503653n.

Scheurer, M., et al., Dec. 2017. "Small, mobile, persistent: trifluoroacetate in the water cycle – overlooked sources, pathways, and consequences for drinking water supply. Water Res. 126, 460–471. https://doi.org/10.1016/j.watres.2017.09.045.

Spaan, K.M., et al., Apr. 2020. Fluorine mass balance and suspect screening in marine mammals from the northern hemisphere. Environ. Sci. Technol. 54 (7), 4046–4058. https://doi.org/10.1021/acs.est.9b06773.

Stenrød, M., Apr. 2015. Long-term trends of pesticides in Norwegian agricultural streams and potential future challenges in northern climate. Acta Agric. Scand. Sect. B Soil Plant Sci 65 (Suppl. 2), 199–216. https://doi.org/10.1080/09064710.2014.977339.

Sun, M., et al., Dec. 2016. Legacy and emerging perfluoroalkyl substances are important drinking water contaminants in the Cape fear river watershed of North Carolina. Environ. Sci. Technol. Lett. 3 (12), 415–419. https://doi.org/10.1021/acs.estlett.6b00398.

Thayer, A.M., Jun. 2006. Fabulous fluorine. Chem. Eng. News Archive 84 (23), 15–24. https://doi.org/10.1021/cen-v084n023.p015.

Toward A New Comprehensive Global Database Of Per- And Polyfluoroalkyl Substances (PFASs), 2018. SUMMARY REPORT on UPDATING the OECD 2007 LIST of PER- and POLYFLUOROALKYL SUBSTANCES (PFASs)." Inter-organisation Programme for the Sound Management of Chemicals (IOMC). ORGANISATION FOR ECONOMIC COOPERATION AND DEVELOPMENT.

US EPA, O., Sep. 01, 2015. Third Unregulated Contaminant Monitoring Rule. *US EPA* accessed Nov. 12, 2020). https://www.epa.gov/dwucmr/third-unregulated-contaminant-monitoring-rule.

Wallington, T.J., et al., Jul. 1994. The environmental impact of CFC replacements - HFCs and HCFCs. Environ. Sci. Technol. 28 (7), 320A–326A. https://doi.org/10.1021/es00056a002.

Wang, N., et al., Feb. 2011. 6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants. Chemosphere 82 (6), 853–858. https://doi.org/10.1016/j.chemosphere.2010.11.003.

Wang, S., et al., Sep. 2013. First report of a Chinese PFOS alternative overlooked for 30 Years: its toxicity, persistence, and presence in the environment. Environ. Sci. Technol. 47 (18), 10163–10170. https://doi.org/10.1021/es401525n.

Wang, J., et al., Feb. 2014. "Fluorine in pharmaceutical industry: fluorine-containing drugs introduced to the market in the last decade (2001–2011). Chem. Rev. 114 (4), 2432–2506. https://doi.org/10.1021/cr4002879.

Wang, Y., et al., Oct. 2016. Identification, tissue distribution, and bioaccumulation potential of cyclic perfluorinated sulfonic acids isomers in an airport impacted ecosystem. Environ. Sci. Technol. 50 (20), 10923–10932. https://doi.org/10.1021/acs.est.6b01980.

Woudneh, M.B., Chandramouli, B., Hamilton, C., Grace, R., Nov. 2019. Effect of sample storage on the quantitative determination of 29 PFAS: observation of analyte interconversions during storage. Environ. Sci. Technol. 53 (21), 12576–12585. https://doi.org/10.1021/acs.est.9b03859.

Yeung, L.W.Y., Mabury, S.A., 2016. Are humans exposed to increasing amounts of unidentified organofluorine? Environ. Chem. 13 (1), 102. https://doi.org/10.1071/EN15041.

Yeung, L.W.Y., Stadey, C., Mabury, S.A., 2017. Simultaneous analysis of perfluoroalkyl and polyfluoroalkyl substances including ultrashort-chain C2 and C3 compounds in rain and river water samples by ultra performance convergence chromatography. J. Chromatogr. A 1522, 78–85. https://doi.org/10.1016/j.chroma.2017.09.049.

Yeung, L.W.Y., et al., 2008. Perfluorinated compounds and total and extractable organic fluorine in human blood samples from China. Environ. Sci. Technol. 42 (21), 8140–8145. https://doi.org/10.1021/es800631n.

Yeung, L.W.Y., et al., Sep. 2013. Perfluoroalkyl substances and extractable organic fluorine in surface sediments and cores from Lake Ontario. Environ. Int. 59, 389–397. https://doi.org/10.1016/j.envint.2013.06.026.

Yoo, H., Washington, J.W., Jenkins, T.M., Laurence Libelo, E., Nov. 2009. Analysis of perfluorinated chemicals in sludge: method development and initial results. J. Chromatogr. A 1216 (45), 7831–7839. https://doi.org/10.1016/j.chroma.2009.09.051.

Zhang, S., et al., May 2013. 6:2 and 8:2 fluorotelomer alcohol anaerobic biotransformation in digester sludge from a WWTP under methanogenic conditions. Environ. Sci. Technol. 47 (9), 4227–4235. https://doi.org/10.1021/es4000824.

Zhang, X., et al., Sep. 2016. Source attribution of poly- and perfluoroalkyl substances (PFASs) in surface waters from Rhode Island and the New York metropolitan area. Environ. Sci. Technol. Lett. 3 (9), 316–321. https://doi.org/10.1021/acs.estlett.6b00255.