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Source tracking and impact of per- and polyfluoroalkyl substances at Svalbard – FluorosImpact –

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SVALBARDS
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Abstract

Per- and polyfluoroalkyl substances (PFASs) are characterized by their global and ubiquitous distribution in the environment, even found in remote regions like the Arctic. In this study, the distribution of PFASs was investigated in water, snow, sediment, soil and biota on the Svalbard archipelago (Norwegian Arctic). Furthermore, the impact from potential local primary sources (i.e. waste water, fire fighting training sites at airports and landfills) in contrast to PFAS contributions from long range transport (i.e., atmosphere, ocean currents) was assessed using and identifying characteristic PFAS composition profiles (finger prints). Perfluoroalkyl sulfonates (PFASs) and 6:2 fluorotelomer sulfonate (FTSA) were identified as predominant in local water and soil, while perfluoroalkyl carboxylates (PFCAs) were highly abundant in water and sediment from a background area on Svalbard. PFAS composition profiles in the remote region indicate that atmospheric transport and oxidation of volatile precursors is an important source for PFCAs on Svalbard. In remote and coastal areas, meltwater had the highest average total PFAS concentration ($6.5 \pm 1.3 \text{ ng L}^{-1}$), followed by surface snow ($2.5 \pm 1.7 \text{ ng L}^{-1}$), surface lake water ($2.3 \pm 1.1 \text{ ng L}^{-1}$), seawater ($1.05 \pm 0.64 \text{ ng L}^{-1}$), lake sediments ($0.084 \pm 0.038 \text{ ng g}^{-1}$ dry weight (dw)) and sea sediments ($0.077 \pm 0.15 \text{ ng g}^{-1}$ dw, median 0.015 ng g^{-1} dw). PFAS levels were determined in archived biota. In these samples, total PFAS concentrations in muscle tissue were highest in polar bear ($26 \pm 24 \text{ ng g}^{-1}$ wet weight (ww), median 15 ng g^{-1} ww), followed by Arctic char ($0.53 \pm 0.073 \text{ ng g}^{-1}$ ww) and Svalbard reindeer ($1.69 \pm 4.62 \text{ ng g}^{-1}$ ww, median 0.11 ng g^{-1} ww). This study provides the first confirmation for the presence of perfluorobutanoate (PFBA) in terrestrial Arctic wildlife as PFBA was the predominant PFAS in reindeer. PFBA was also predominant in fresh water, complying with the replacement of C_8 -chained PFASs. Furthermore, the relatively high PFAS levels in meltwater (especially PFBA) suggests that melting of snow and ice during the Arctic spring is an important diffuse local PFAS source, which will likely become even more important with the offset of global warming.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are ubiquitously present in remote environments as already demonstrated for remote regions such as the Arctic (Butt et al., 2010; Kwok et al., 2013; Lescord et al., 2015; Stock et al., 2007; Young et al., 2007). Concerns about their environmental stability, bioaccumulation potential and possible toxic effects on humans and wildlife has led to national and international regulations restricting the use of certain long-chain perfluoroalkyl sulfonic acids (PFASs, $C_nF_{2n+1}SO_3H$, $n \geq 6$), perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, $n \geq 7$) and related compounds (Buck et al., 2011). In 2009, perfluorooctane sulfonic acid (PFOS) was added to the priority persistent organic pollutants list of the Stockholm Convention (under annex B, restricted usage). However, PFOS and its derivatives are still being produced in China (Buck et al., 2011). Moreover, alternative compounds (precursors) which can degrade to persistent PFCAs and PFASs (Ellis et al., 2004; Martin et al., 2006), are continued to be produced, used and ultimately emitted to the environment and distributed both via atmosphere and waterborne pathways (Wang et al., 2014).

PFASs are used in a variety of industrial and consumer applications, such as in textile stain and water repellents, aqueous film-forming foams (AFFFs) and as processing aids during fluoropolymer production (Buck et al., 2011). During all stages of their lifecycle, PFASs can be emitted to the environment (Prevedouros et al., 2006) and subsequently transported to the Arctic (Armitage et al., 2006; Stock et al., 2007; Wallington et al., 2006; Zhao et al., 2012). There are two known major transport pathways to the Arctic identified. A first long range atmospheric transport (LRAT) of volatile precursors followed by atmospheric oxidation to PFCAs and PFASs and subsequent wet and dry deposition is considered as an important atmospheric entrance route into the Polar environments (Stock et al., 2007; Young et al., 2007; Zhao et al., 2012). This atmospheric pathway includes also the direct atmospheric transport of volatile PFCAs and PFASs in the gas-phase or particle bound PFASs *via* aerosol-mediated transport (Ahrens et al., 2012; McMurdo et al., 2008). A second pathway is associated with long range oceanic transport of PFASs such as PFCAs and PFASs mainly associated with particle-bound transport (Ahrens et al., 2010; Armitage et al., 2009; Prevedouros et al., 2006). Possible PFASs exchange between the water – atmosphere interface adds to the complexity of the here postulated combined distribution profile in remote environments.

Volatile PFAS precursors, such as fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamido ethanols (FOSEs), have been detected in the Arctic atmosphere (Ahrens et al., 2011a; Shoeib et al., 2006; Stock et al., 2007) and can undergo atmospheric degradation to persistent PFCAs and PFASs (Ellis et al., 2004; Young and Mabury, 2010). The relative importance of indirect atmospheric vs direct oceanic transport is not yet fully understood and subject for international priority research (Butt et al., 2010). Most of today's research results on PFASs distribution supports the LRAT precursor hypothesis (Ellis et al., 2004; Stock et al., 2007; Young et al., 2007), while modeling studies have shown that also direct emissions and oceanic transport is significantly contributing to the high PFAS loads transported to the Arctic (Armitage et al., 2009). In addition to long range transport, local sources of PFASs such as discharge from waste water treatment plants (Becker et al., 2008; Sinclair and Kannan, 2006), fire fighting training sites (Ahrens et al., 2015; Kärrman et al., 2011) and local landfills (Ahrens et al., 2011b; Busch et al., 2010) are also considered important direct sources for PFASs contamination in Arctic regions (Lescord et al., 2015; Stock et al., 2007). To date, Arctic studies have been performed in the Canadian Arctic

(Lescord et al., 2015; Stock et al., 2007; Young et al., 2007), Greenland (Bossi et al., 2015; Greaves et al., 2012), or on Svalbard (Kwok et al., 2013).

The here presented study was conducted in Nordenskiöld land on the West coast of Spitsbergen, the main island of the Svalbard archipelago (Norwegian Arctic) in early summer 2015 (June – July). PFASs were analysed in a representative multimedia environment on Svalbard (water, sediment, soil and biota). This approach was chosen in order to investigate the influence of local sources and LRAT on the occurrence of PFASs in the Svalbard environment. Our objectives were

- i)* to evaluate the PFASs distribution in representative samples of the abiotic environment,
- ii)* to assess levels and bioaccumulation of PFASs in muscle tissue of vertebrate biota inclusive Svalbard reindeer (*Rangifer tarandus platyrhynchus*), polar bear (*Ursus maritimus*) and Arctic char (*Salvelinus alpinus*)
- iii)* to estimate the contribution of local sources (i.e. waste water, fire fighting training sites at airports and landfills) to the PFAS contribution compared to diffusive secondary sources such as long-range transport (atmospheric and oceanic LRT). For this, PFAS composition profiles (fingerprints) were identified and applied.

2. Materials and method

2.1. Sampling

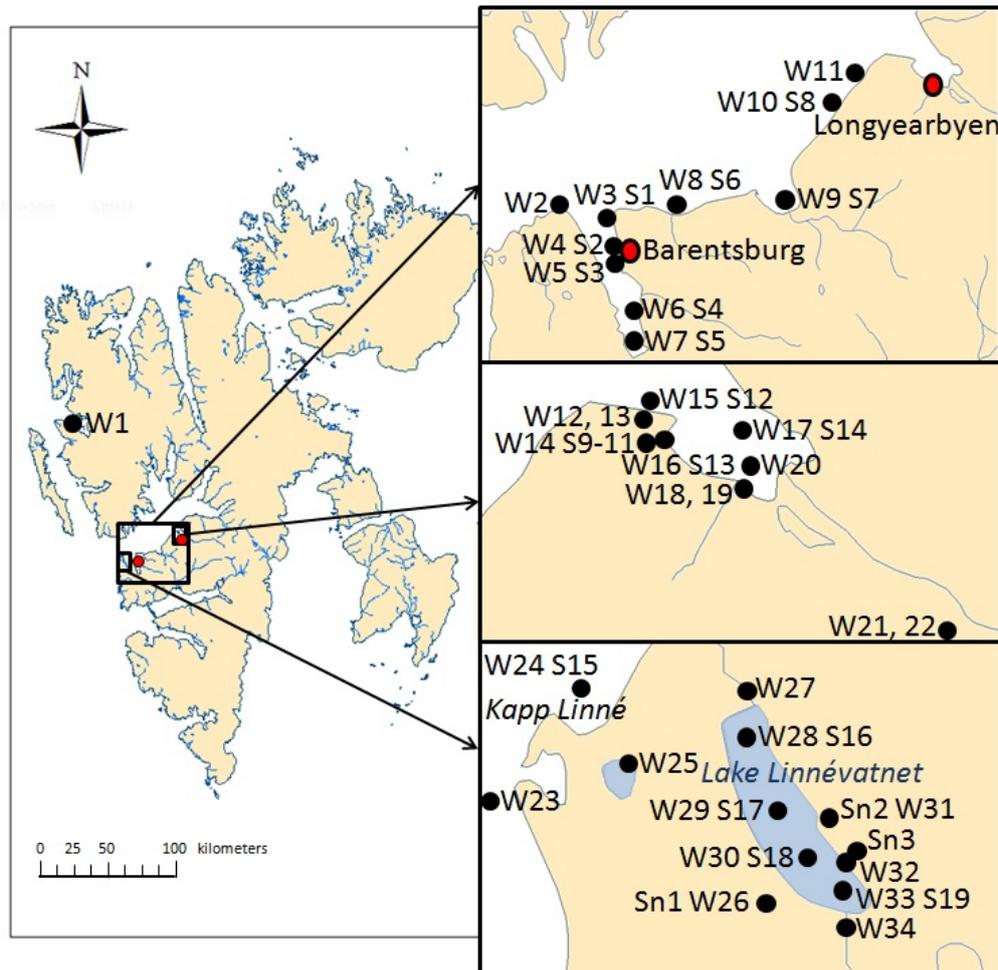


Figure 1. Sample locations for water (W), snow (Sn), sediment and soil (S) on Svalbard. Note: sampling location W22 was 700 m uphill from W21.

Seawater (W1-11, W15, W17, W20, W23-24) and sediment samples (S1-8, S12, S14-15) were collected along the coast from Longyearbyen (~2200 inhabitants) to Kapp Linné including the Grønnfjorden fjord near Barentsburg (~400 inhabitants) (**Figure 1**, **Figure 2**). Furthermore, a seawater sample was collected from Kongsfjord as reference sample (bay close to small airport, W1). In addition, fresh water (W21), waste water (W12-13 and W18), landfill leachate from old and current landfills (W19 and W22, respectively) were collected in the Longyearbyen area in Longyeardalen valley as well as the adjacent Adventdalen valley. In order to evaluate PFAS distribution patterns around the active fire fighting training site at Svalbard airport, soil and water samples were obtained from representative locations (S9-11, W14) and further downhill (S13, W16). Furthermore, lake water (W25, W27-30, W33-34), meltwater (W26, W31-32), surface snow (Sn1-3) and surface sediment (S16-19) samples were collected in and around Lake Linnévatnet. Finally, biota samples were obtained from the archives of The University Centre in Svalbard (UNIS), including Svalbard reindeer, polar bear and Arctic char.

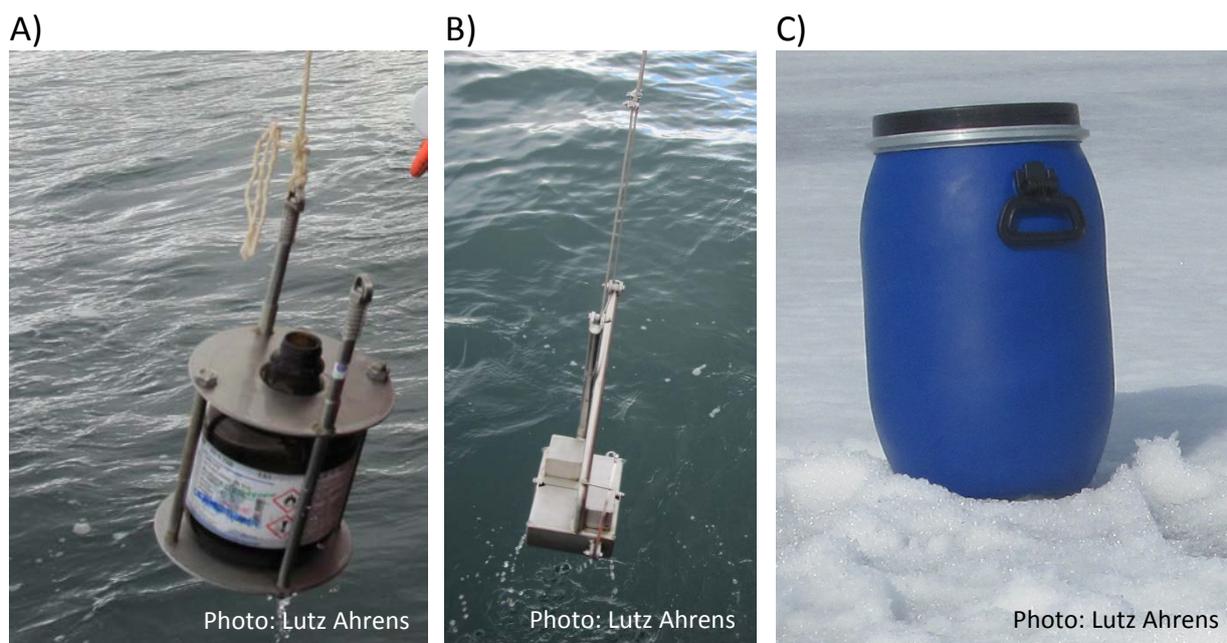


Figure 2. A) Surface seawater sampling, B) sediment sampling (van Veen grab sampler), and C) surface snow sampling.

2.2. Chemicals

In this study, 26 PFASs were analysed, including C_4 – C_{14} , C_{16} , C_{18} PFCAs (i.e. PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), C_4 , C_6 , C_8 , C_{10} PFSAAs (i.e. PFBS, PFHxS, PFOS, PFDS,) FOSAs (i.e. FOSA, MeFOSA, EtFOSA), FOSEs (i.e. MeFOSE, EtFOSE) and perfluorooctane sulfonamidoacetic acids (FOSAAAs) (i.e. FOSAA, MeFOSAA, EtFOSAA) and 6:2 fluorotelomer sulfonates (FTSA). 16 internal standards (IS) were used for quality assurance (i.e. $^{13}C_4$ -PFBA, $^{13}C_2$ -PFHxA, $^{13}C_4$ -PFOA, $^{13}C_5$ -PFNA, $^{13}C_2$ -PFDA, $^{13}C_2$ -PFUnDA, $^{13}C_2$ -PFDoDA, $^{18}O_2$ -PFHxS, $^{13}C_4$ -PFOS, $^{13}C_8$ FOSA, d_3 -MeFOSA, d_5 -EtFOSA, d_7 -MeFOSE, d_9 -EtFOSE, d_3 -MeFOSAA and d_5 -EtFOSAA, $c = 0.1 \text{ ng } \mu\text{L}^{-1}$).

2.3. Sample preparation and analysis

Before extraction, all samples were spiked with 100 μL IS mixture ($c = 0.1 \text{ ng } \mu\text{L}^{-1}$). For the water samples, solid-phase extraction (SPE) (Waters Oasis WAX, 6 cm^3 , 500 mg) was used according to a method previously described by Yamashita et al. (2004), with a few modifications (Ahrens et al., 2009a). The sediment and soil samples were oven-dried (25 $^\circ\text{C}$), sieved (2 mm), and an aliquot of 5 g dry weight (dw) was extracted using methanol and cleaned with 25 mg ENVI-Carb (Supelco) as described previously (Powley et al., 2005), with a few modifications (Ahrens et al., 2009c). The biota samples were homogenized and an aliquot of 1 g muscle tissue was extracted using methanol and cleaned with 25 mg ENVI-Carb as described previously (Powley et al., 2005), with a few modifications (Ahrens et al., 2009b). All sample extracts were concentrated to 1 mL and analysed using high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) according to a method described in Ahrens et al. (2009a).

2.4. Quality assurance

Method detection limits (MDLs) were calculated as average blank concentration plus 3 times of their absolute standard deviation (σ) for each environmental matrix (i.e. water, sediment/soil and biota). If a compound was not detected in the blanks, MDL was set to the lowest calibration standard level (i.e. 0.05 ng L⁻¹ for water, 0.01 ng g⁻¹ dw for sediment and 0.05 ng g⁻¹ ww for biota). The MDLs ranged between 0.0020–0.11 ng L⁻¹ in water, 0.0026–0.12 ng g⁻¹ dw (1.2 ng g⁻¹ dw for 6:2 FTSA) in sediment/soil and 0.013–0.13 ng g⁻¹ ww (1.06 ng g⁻¹ ww for 6:2 FTSA) in biota. The average standard deviations of triplicates were 15% for water, 15% for sediment/soil and 10% for biota. The mean recoveries of quantified PFASs ranged from 59–103% (except for 31% for MeFOSE) for water, 42–101% for sediment/soil and 40–119% for biota.

2.5. Statistical analysis

Mann-Whitney U-test (i.e. Wilcoxon rank sum test) ($\alpha = 0.05$) was used to assess significant differences between the mean total PFAS concentrations (Σ PFAS) in different environmental matrices and between different biota samples. Before performing Mann-Whitney U-test, all PFAS concentrations <MDL were set as half of MDL.

3. Results and discussion

3.1 Multimedia distribution of PFASs in the abiotic environment

Out of 26 target compounds, 13 were detected (>MDL) in surface water (lake water, meltwater and seawater) and surface snow, including C₄–C₁₂ PFCA, PFBS, PFOS, 6:2 FTSA and FOSA. Meltwater had the highest average Σ PFAS concentration ($6.5 \pm 1.3 \text{ ng L}^{-1}$, W26, W31–32), followed by surface snow ($2.5 \pm 1.6 \text{ ng L}^{-1}$, Sn1–3), lake water ($2.3 \pm 1.1 \text{ ng L}^{-1}$, W27–30, W33–34), seawater samples W3–9 (SW2) ($1.5 \pm 0.60 \text{ ng L}^{-1}$) and seawater samples W2, W10–11, W15, W17, W20 and W23–24 (SW1) ($0.62 \pm 0.24 \text{ ng L}^{-1}$) (**Figure 3**). The observed difference in Σ PFAS concentrations in seawater indicates that coastal waters in Svalbard are affected by local sources in addition in combination with long-range oceanic transport. Moreover, Σ PFAS in meltwater was found to be significantly higher concentrated compared to surface lake water in a remote Arctic lake ($p = 0.028$). In addition, indications for higher concentrations in meltwater compared to snow was observed, however not significant ($p = 0.08$). This statistical finding indicates, thus, that meltwater from snow, ice and glaciers are obviously subject to repeated evaporation processes resulting in up-concentration and higher PFAS concentrations compared to surface snow and the lake water recipient. Meltwater might thus be an important input source for the nearby aqueous environment. Similarly, Kwok et al. (2013) detected higher PFAS concentrations in glacier water from Longyearbyen glacier compared to glacial surface snow in the vicinity of Longyearbyen, Svalbard (Kwok et al. 2013).

Σ PFAS concentrations in Lake Linnévatnet was in the same range as observed in four remote lakes in the Canadian Arctic and ranged from 1.9 ± 0.42 to $2.4 \pm 0.40 \text{ ng L}^{-1}$ (Lescord et al., 2015). Furthermore, Σ PFAS in surface snow (in average, $2.5 \pm 1.6 \text{ ng L}^{-1}$) in the present study is found in agreement with Σ PFAS reported in surface snow from 2006, downstream from Longyearbreen glacier in the vicinity of Longyearbyen (1.5 ng L^{-1}), while the levels in glacial snow from the same study were by a factor of 3 lower (0.46 ng L^{-1}) (Kwok et al., 2013). It is important to note that concentrations in snow are expected to vary considerably, since the deposition profile is mainly dependent on the recent weather events which adds to the integrated pollutant levels in the weathered surface snow. Nevertheless, higher levels in snow compared to other abiotic samples (except for meltwater) supports clearly the theory that PFASs levels in Arctic remote region are strongly impacted by atmospheric deposition sources and pathways.

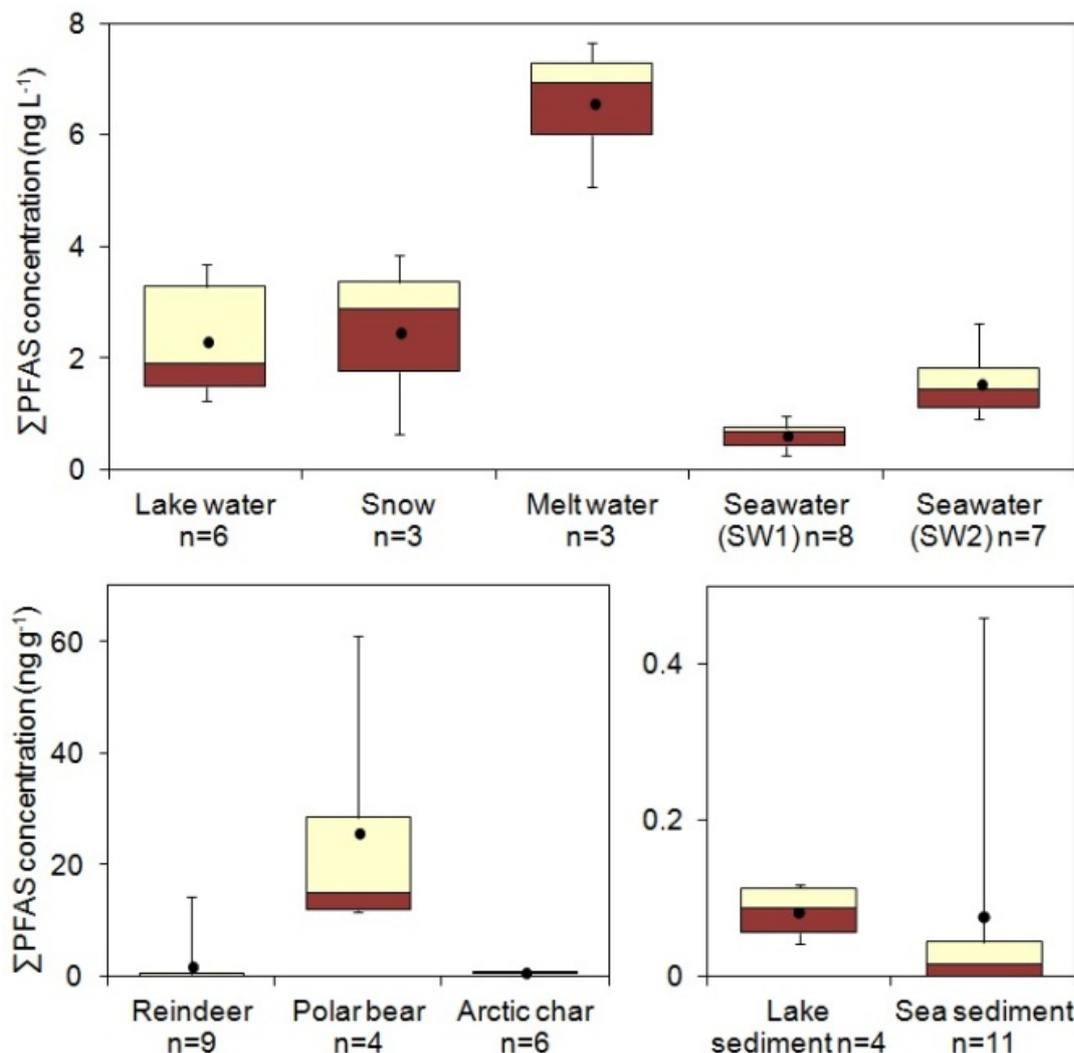


Figure 3. Distribution of Σ PFAS concentrations in surface water (ng L^{-1}), snow (ng L^{-1}), biota (ng g^{-1} ww) and surface sediment (ng g^{-1} dw). Box-and-whisker plots show minimum and maximum concentrations, boxes show 25th, median and 75th percentiles, and dots show the arithmetic means.

In the case of surface sediments from Lake Linnévatnet, only three out of 26 target compounds were detected, including PFOA, PFNA and PFUnDA. The absence of short-chain PFCAs (<8 carbons) is expected since longer-chain compounds have stronger sorption to particles and can, thus, displace shorter-chain compounds (Gellrich et al., 2012). Average Σ PFAS concentrations in lake sediments ($0.083 \pm 0.038 \text{ ng g}^{-1} \text{ dw}$) (Figure 3) were lower than previously observed in four remote lakes in the Canadian Arctic (where levels in the range 0.19 ± 0.03 to $2.7 \pm 0.18 \text{ ng g}^{-1} \text{ dw}$ are reported (Lescord et al., 2015). In marine sediments, Σ PFAS ranged between <MDLs– $0.46 \text{ ng g}^{-1} \text{ dw}$ and only two PFASs were detected (i.e. FOSA and PFUnDA) (Figure 3). FOSA and PFUnDA have a higher particle-water partitioning coefficient (K_d)-value compared to shorter-chain PFCAs and PFSA (Ahrens et al., 2015; Higgins and Luthy, 2006), which can explain their presence in the low contaminated sediments. The differences in PFAS composition of lake and sea sediments indicate that the major PFAS source in the remote region around Lake Linnévatnet is of atmospheric origin.

3.2 Bioaccumulation of PFASs in Arctic reindeer, polar bear and Arctic char

The Σ PFAS concentrations in polar bear muscle tissue (12–61 ng g⁻¹ wet weight (ww), median 15 ng g⁻¹ ww) were significantly higher than in Arctic char (0.53 ± 0.073 ng g⁻¹ ww) ($p = 0.014$) (**Figure 3**). Meanwhile, Σ PFAS concentrations in Svalbard reindeer were found in the concentration range <MDLs–14 ng g⁻¹ ww (median 0.11 ng g⁻¹ ww). In polar bears, PFOS was the predominant compound (66% of Σ PFASs, 7.4–44 ng g⁻¹ ww), followed by PFUnDA (10%, 1.1–4.7 ng g⁻¹ ww) and PFHxS (6.9%, 0.71–2.8 ng g⁻¹ ww). Σ PFAS levels in polar bears were in the same range as previously reported for muscle tissue from East Greenland polar bears (35 ± 2.7 ng g⁻¹ ww) and the PFAS composition was similar, with PFOS as the predominant compound, followed by PFUnDA and PFTriDA (Greaves et al., 2012).

In Svalbard reindeer, PFBA was detected in 5 out of 9 samples at levels ranging between 0.079–14 ng g⁻¹ ww (median 0.42 ng g⁻¹ ww). FOSAA was detected in one sample (0.18 ng g⁻¹ ww), whereas no other PFASs were observed. The presence of PFBA in reindeer is indicating a direct source, since short-chain PFCAs are not considered bioaccumulative in biota (Conder et al., 2008). However, it has been reported that plant uptake of PFASs increase with decreasing perfluoroalkyl chain length and that bioaccumulation factors in edible parts of plants were highest for PFBA and PFPeA (Blaine et al., 2014). In view of this, our results suggest that PFBA might be ingested *via* plants and/or *via* water intake and accumulate in muscle tissue. The observed variation in PFBA concentrations is likely caused by differences in feeding pattern in combination with local PFBA contamination. The absence of other PFASs in muscle tissue of Svalbard reindeer reflects the generally low levels in Arctic herbivores (Bossi et al., 2015; Butt et al., 2010), coupled with the generally lower PFAS concentrations reported for muscle tissue compared to liver tissue (Ahrens et al., 2009b; Greaves et al., 2012). However, few studies have investigated PFASs in terrestrial Arctic biota (Bossi et al., 2015; Butt et al., 2010). A different PFAS composition profile was found in liver samples from South Greenland reindeer, in which PFOS (1.42 ng g⁻¹ ww) was predominant, while C₉-C₁₁ PFCAs were detected at low levels (0.28–0.84 ng g⁻¹) (Bossi et al., 2015).

The major PFASs in Arctic char from Lake Linnévatnet were PFOS (49% of Σ PFASs, 0.26 ± 0.046 ng g⁻¹ ww), PFUnDA (28%, 0.15 ± 0.019 ng g⁻¹ ww) and PFDA (13%, 0.072 ± 0.024 ng g⁻¹ ww). All PFASs detected in Arctic char were also present in lake water or sediments (except PFHxS), however, the chars from Lake Linnévatnet expressing an anadromous life style and, thus, might have migrated and therefore have been exposed to contaminants from another area. Average Σ PFAS concentrations in Arctic char muscle tissue (0.53 ± 0.073 ng g⁻¹ ww) were in the same range as observed in most of the remote lakes in the Canadian Arctic (ranging from 0.28 ± 0.09 to 3.7 ± 2.4 ng g⁻¹ ww) (Lescord et al., 2015). The PFAS levels observed in Arctic char muscles in the present study are only an indication of the potential PFAS burden to fish in the European Arctic, since the tissue distribution of PFASs has been shown to vary (Ahrens et al., 2015).

3.3 Local point sources (waste water, landfill leachate and a fire fighting training site) vs atmospheric deposition from long range transport of PFASs

The highest Σ PFAS concentrations were detected in soil from the fire fighting training site (1600 ng g⁻¹, S9) and in a nearby pond (~2750 ng L⁻¹, W14, some PFASs in the pond were semi-quantitative due

to peak interferences). In a ditch 600 m downhill of the fire fighting training site, Σ PFAS was 3.9 ng g^{-1} dw in soil (S13) and $120 \pm 0.56 \text{ ng L}^{-1}$ in meltwater (W16), which shows that PFASs were being transported from local sources to the nearby aquatic environment. The predominant PFASs in soil around the fire fighting training site (S9–11, S13) were PFOS (51% of Σ PFASs), 6:2 FTSA (17%) and PFHxS (7.9%), similar to the pond (W14). This corresponds to previous studies, since PFOS and 6:2 FTSA generally predominate in AFFF affected areas (Ahrens et al., 2015; Kärrman et al., 2011). The PFAS composition in soil and water changed with increasing distance from the site. For example, 6:2 FTSA was the major compound at the site S9 (56% of Σ PFASs), but it was not detected in soils a few hundred meter away (S11, S13), suggesting that 6:2 FTSA was degraded and/or retained in the soil. PFHxA (18% of Σ PFASs) and PFPeA (7.2%) were amongst the predominant compounds in meltwater downhill of the fire fighting training site (W16), while 6:2 FTSA was less predominant (4.2 %), indicating that 6:2 FTSA degraded to PFPeA and PFHxA (Wang et al., 2011). High Σ PFAS concentrations were also observed in untreated landfill leachate (Σ PFAS = 410 ng L^{-1} , W22), with PFOS (30% of Σ PFASs) and PFOA (22%) as the predominant compounds. In addition, elevated Σ PFAS concentrations were detected in waste water from the airport workshop (570 ng L^{-1} , W12), Longyearbyen airport (170 ng L^{-1} , W13) and Longyearbyen (65 ng L^{-1} , W18). The major PFASs in waste water were PFHxS (74% of Σ PFASs) for airport workshop (W12), PFOS (57%) and 6:2 FTSA (28%) for Svalbard airport (W13) and PFNA (56%) and PFOA (17%) for Longyearbyen waste water (W18).

In locally contaminated water samples mainly PFASs and/or 6:2 FTSA dominated, such as in fire fighting training site leachate (28% and 53%, respectively, W14), waste water (72% and 28%, respectively, W13), workshop waste water (100% PFASs, W12) and landfill leachate (42% PFASs, W22). In contrast, PFCAs predominated around Lake Linnévatnet in lake water (93%, W27–30, W33–34), surface snow (80%, Sn1–3) and meltwater (86%, W26, W31–32). This indicates that atmospheric transport from long-range transport or local sources (i.e. Barentsburg, coal mine fire) and oxidation of volatile precursors (e.g. FTOHs), which can degrade to PFCAs, is an important PFCA source in remote regions on Svalbard (Ellis et al., 2004; Stock et al., 2007; Wallington et al., 2006; Young et al., 2007). The PFAS composition in meltwater was similar to the composition in the recipient lake water, with PFBA (57% and 53%, respectively), PFOA (10% and 15 %, respectively), PFHpA (7.8% in both) and PFNA (6.0% and 7.3%, respectively) as major compounds. In surface snow PFNA (41% of Σ PFASs) predominated, followed by PFOA (17%), PFDA (12%) and PFUnDA (5.9%). In a previous study, the predominant PFAS in surface snow on Svalbard was PFOA, followed by PFBA and PFNA (Kwok et al., 2013), similar to our study. However, PFBA was not a major compound in snow in the here reported study ($<0.096 \text{ ng L}^{-1}$ in Sn1, Sn3 and 0.14 ng L^{-1} in Sn2). However, PFBA dominated in meltwater from snow and ice (57% of Σ PFASs, $3.7 \pm 0.92 \text{ ng L}^{-1}$, W26, W31–32). Similarly, higher PFBA concentrations were observed in melted glacier water ($0.29 \pm 0.057 \text{ ng L}^{-1}$) compared to surface snow and ice cores in the previous study. Interestingly, the mean ratio of PFOA to PFNA in meltwater ($n = 3$), lake water ($n = 6$) and surface snow ($n = 3$) around Lake Linnévatnet (1.7 ± 0.8) is comparable to ratios previously observed in atmospherically supplied Canadian Arctic ice cores (1.5 ± 0.8) (Young et al., 2007) and glacial ice cores on Svalbard (1.9 ± 0.7 and 1.3 ± 0.4) (Kwok et al., 2013), indicating a common atmospheric source.

Differences in Σ PFAS concentrations and composition profiles in seawater were observed and these differences were mainly attributed to the absence of PFBA in several seawater samples (W2, W11, W15, W17, W20) (**Figure 1, Figure 4**). PFBA was the major compound in meltwater and the recipient

lake water, and Σ PFAS concentrations in meltwater were higher than in lake and seawater (**Figure 3**), indicating that meltwater might be an important local diffuse PFAS source for nearby aqueous environments. Interestingly, the seawater samples with the highest Σ PFAS concentrations had a high proportion of PFBA (49% of Σ PFASs) and were located nearby outlets of rivers fed by meltwater from glaciers and snow (W4–9) (**Figure 1, Figure 4**).

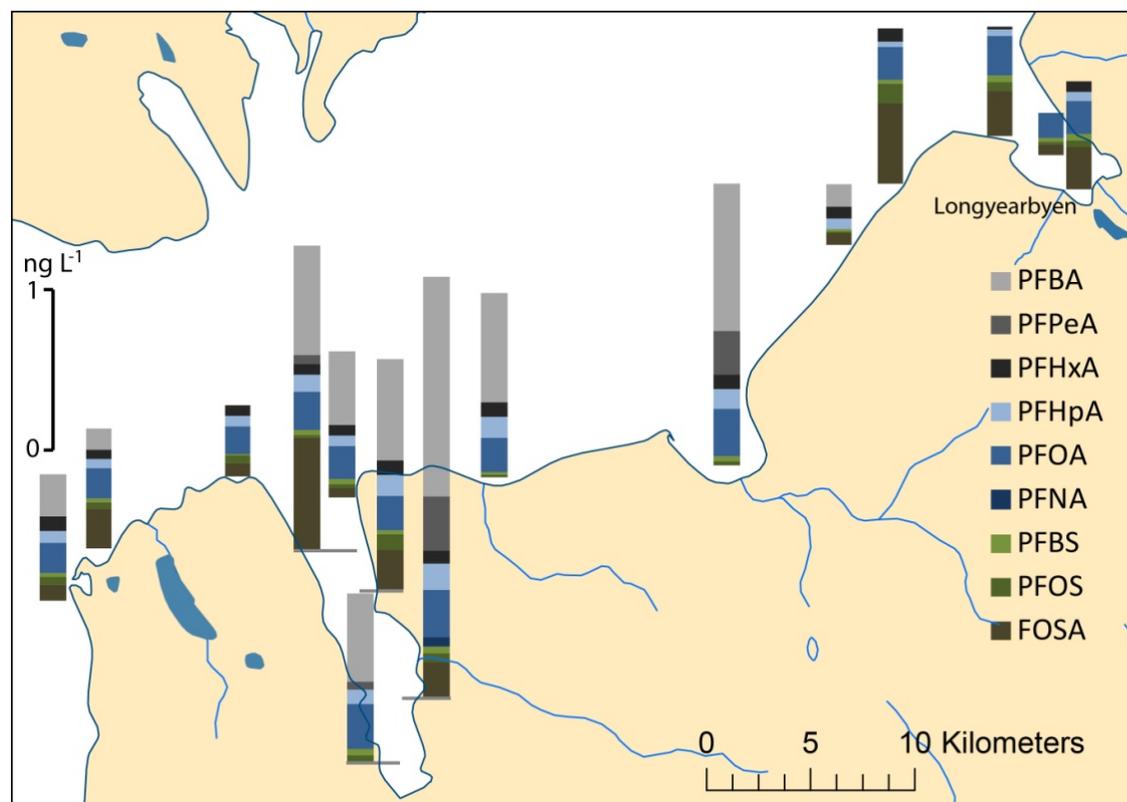


Figure 4. PFAS concentrations and composition in seawater along the coast from Longyearbyen to Kapp Linné (left).

3.4 Conclusions and future implication

In this study, PFASs were ubiquitously detected on Svalbard due to a combination of local sources and atmospheric deposition. Landfill leachate, AFFF contaminated water and waste water were identified as local point sources with 200x higher Σ PFAS concentrations (in average, $\sim 680 \text{ ng L}^{-1}$) compared to background levels (in average, $\sim 3.5 \text{ ng L}^{-1}$) in water and snow from the remote region around Lake Linnévatnet. The waste water is currently released untreated into the sea (except for oil separation of workshop waste). In order to reduce the PFAS loads from waste water, implementation of efficient treatment techniques are urgently needed (Arvaniti and Stasinakis, 2015). In soils around the fire fighting training site (S9–10), Σ PFAS concentrations were from 25x to 20000x higher compared to remote lake sediments (0.083 ng g^{-1}). The predominance of 6:2 FTSA at the fire fighting training site (S9) is an additional prove of the use and release of PFAS containing AFFFs. Furthermore, Σ PFAS concentrations in meltwater 600 m downhill of the site were 20x higher than in meltwater from the remote region ($6.5 \pm 1.3 \text{ ng L}^{-1}$) and the proportion of PFASs was larger (51% of Σ PFASs compared to 2%). This shows that PFASs are being transported from the AFFF contaminated site *via*

meltwater out to the sea. In order to decrease the environmental impact of PFASs in this region, a switch to the use of fluor-free AFFFs is advisable. Furthermore, in order to reduce the environmental impact from AFFF contaminated sites, new remediation techniques for soil are needed in the future (McGuire et al., 2014). The local contamination of PFASs indicate a potential risk for, in particular, top predators in this region (e.g. polar bears) and humans due to contamination of drinking water and local food (e.g. fish, reindeer).

PFCAs predominated in the abiotic environment, except for at locally contaminated sites in which mainly PFASs and 6:2 FTSA were dominant. This suggest that LRAT and oxidation of volatile precursors is a major transport route for PFCAs to the Arctic (Ellis et al., 2004; Stock et al., 2007; Wallington et al., 2006; Young et al., 2007). Furthermore, the predominance of PFBA in fresh water, complies with the replacement of C₈-chained PFASs (i.e. PFOS and PFOA) to short-chain PFASs (Möller et al., 2010). PFBA was also detected in Svalbard reindeer and likely originated from ingestion *via* plants and/or *via* water intake. Finally, higher PFAS levels were observed in meltwater compared to other surface water and surface snow. Meltwater from ice and snow contains the accumulated atmospheric deposition of PFASs and is an important local diffuse PFAS source in Arctic regions, which likely caused the observed differences in PFAS levels in seawater. Furthermore, global warming might potentially accelerate the input of PFASs to the aquatic environment due to melting of glaciers and ice sheets in the Arctic.

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