

Spatial distribution and source tracing of per- and polyfluoroalkyl substances (PFASs) in surface water in Northern Europe[☆]

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ABSTRACT

The impact of point and diffuse sources for 26 per- and polyfluoroalkyl substances (PFASs) in northern Europe were investigated by studying Swedish rivers ($n = 40$) and recipient seawater (Baltic Sea and Kattegat; $n = 18$). Different composition profiles were observed in the rivers, with ten rivers having a remarkably high fraction of perfluoroalkane sulfonic acids (PFASs; 65% of the Σ PFASs) as compared to other rivers (19%) suggesting major impact of one or several source types dominated by PFASs. Population density and low latitude (south) were strongly correlated to the widely used perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA) as well as to perfluorohexanesulfonic acid (PFHxS). Significant relationships between several PFCAs and PFASs (i.e. perfluorobutanoic acid (PFBA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorobutanesulfonic acid (PFBS), and PFHxS) and dissolved organic carbon (DOC) were detected ($p < 0.05$), indicating chemical binding and co-transport with DOC in fresh water and seawater. Partial least squares regression analysis showed that perfluoroalkyl carboxylic acids (PFCAs) were related to latitude according to their perfluorocarbon chain length (C_3 , C_7 , C_8 , C_9 , C_{10} and C_{11}), with longer chains associated with higher latitudes. This suggests the presence of mechanisms promoting higher prevalence of longer chained PFCAs in the north, e.g. precursor degradation, and/or aerosol associated stabilization of PFCAs and their precursors.

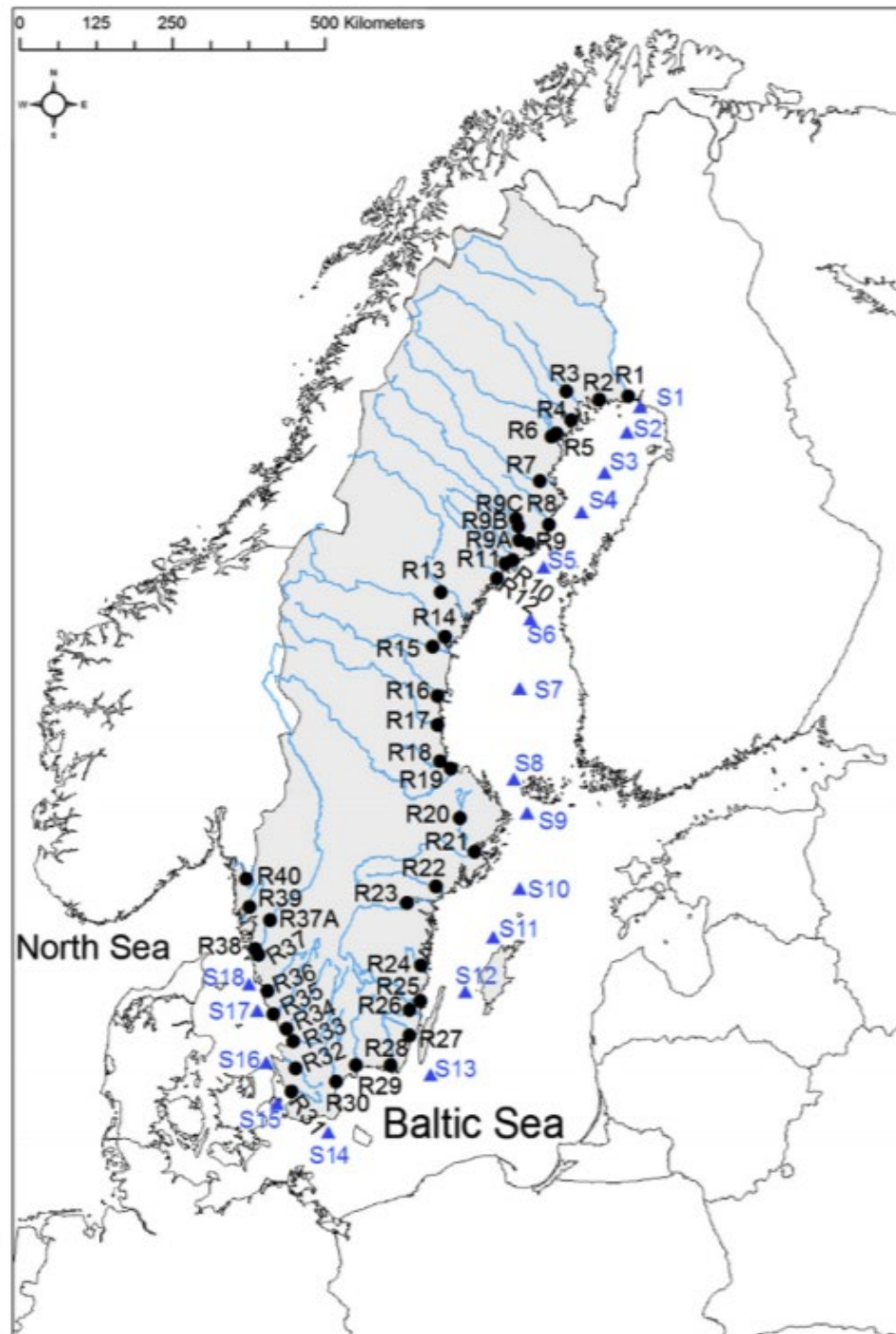


Fig. 1. The river (R1-R40), Baltic Sea (S1-S14), and Kattegat (S15-S18) sampling sites. Black dots (●) represent river sampling sites and blue triangles (▲) sea sampling sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

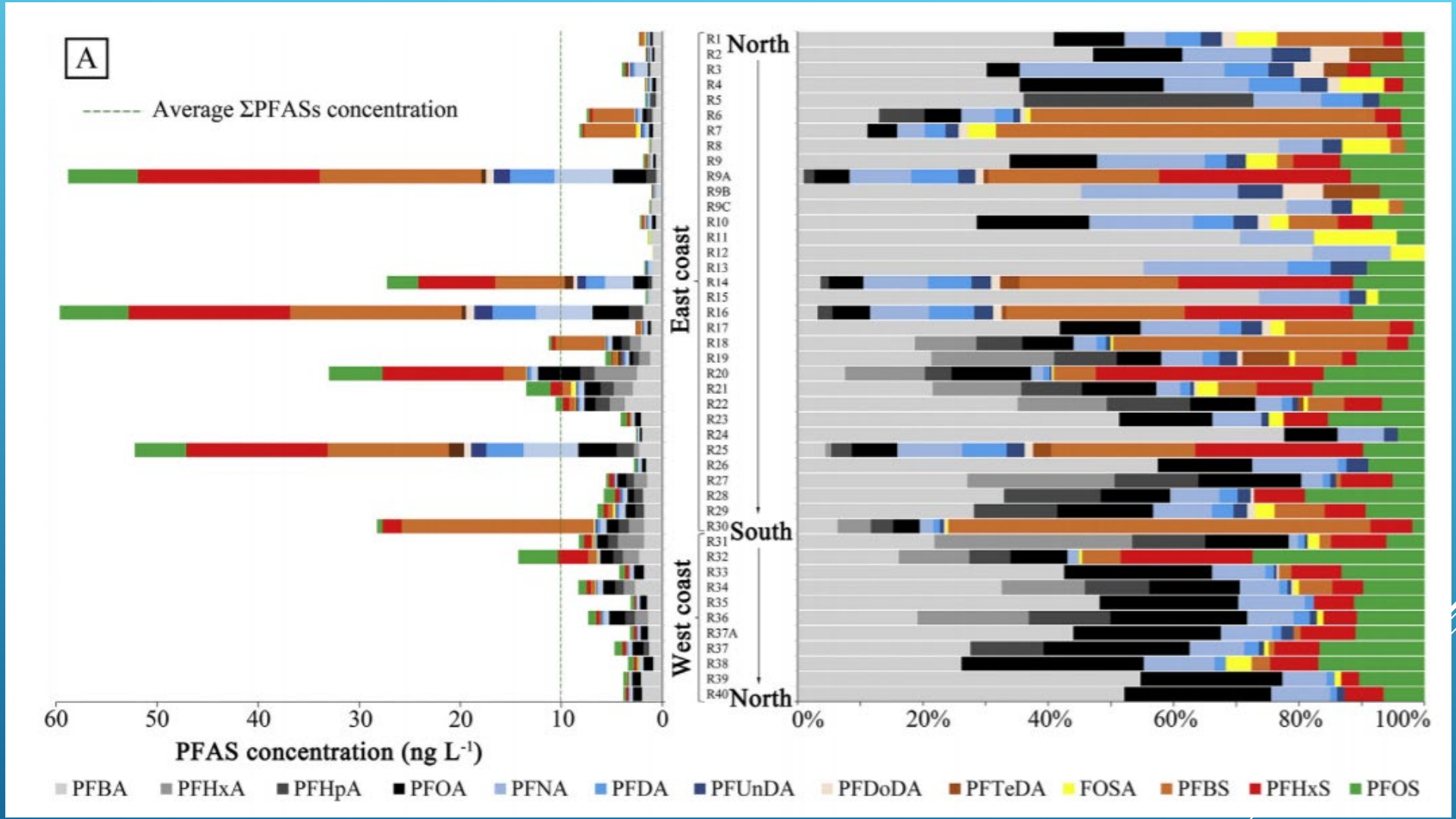
2.1. Sampling

The riverine sampling sites were located along the Swedish coast, close to the mouths of rivers that contribute most of the water discharge to the Baltic Sea and Kattegat (Brandt et al., 2008). The sites correspond to sites in the National Environmental Monitoring and Assessment Program for freshwater in Sweden (Fölster et al., 2014). The samples were collected at a depth of approximately 0.4 m in October 2013 (Fig. 1; R1 to R40). In addition to the 40 river mouth samples, 4 upstream river sites were also included (Vindel River – a tributary to Ume River (R9B and R9C), Ume River at Gubböle (R9A) and Göta River near Trollhättan (R37A)). Duplicate samples were taken at sites R4, R7, R15, R17, and R23.

Seawater samples were collected in the Baltic Sea during a cargo ship tour (TransPaper Cargo Ship) in August–September 2013 at 18 off-shore sites (Fig. 1, S1 to S18) in the Bothnian Bay ($n = 5$, north), the Bothnian Sea ($n = 3$, central), the Baltic Proper ($n = 6$, south), and the west coast of Sweden (the Kattegat, $n = 4$). Duplicate samples were taken at sites S6 and S13. The seawater samples were collected at approximately 2 m depth.

2.2. Chemicals

Target analytes included perfluoroalkyl carboxylic acids (PFCAs) with perfluoroalkyl carbon chain length of C_3 – C_{13} , C_{15} , and C_{17} (i.e. PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, and PFOcDA), C_4 , C_6 , C_8 , and C_{10} perfluoroalkane sulfonic acids (PFSAs) (i.e. PFBS, PFHxS, PFOS, and PFDS), 6:2 fluorotelomer sulfonate (6:2 FTSA), perfluorooctanesulfonamide (FOSA), *N*-methyl and *N*-ethyl FOSAs (MeFOSA and EtFOSA), 2-(perfluorooctanesulfonamido) acetic acid (FOSAA), methyl and ethyl FOSAs (MeFOSAA and EtFOSAA), and *N*-methyl and *N*-ethyl perfluorooctane sulfonamido ethanol (MeFOSE and EtFOSE) (compilation of all target analytes and their log K_{ow} values can be found in Table S3, Supporting Information). The mass-labelled internal standard (IS) mix included [$^{13}C_4$]-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]-*N*-MeFOSA, [d_5]-*N*-EtFOSA, [d_3]-*N*-MeFOSAA, [d_5]-*N*-EtFOSAA, [d_7]-*N*-MeFOSE, and [d_9]-*N*-EtFOSE, and the injection standard (InjS) was [$^{13}C_8$]-PFOA. All reference and mass-labelled compounds were purchased from Wellington Laboratories, Ontario, Canada.



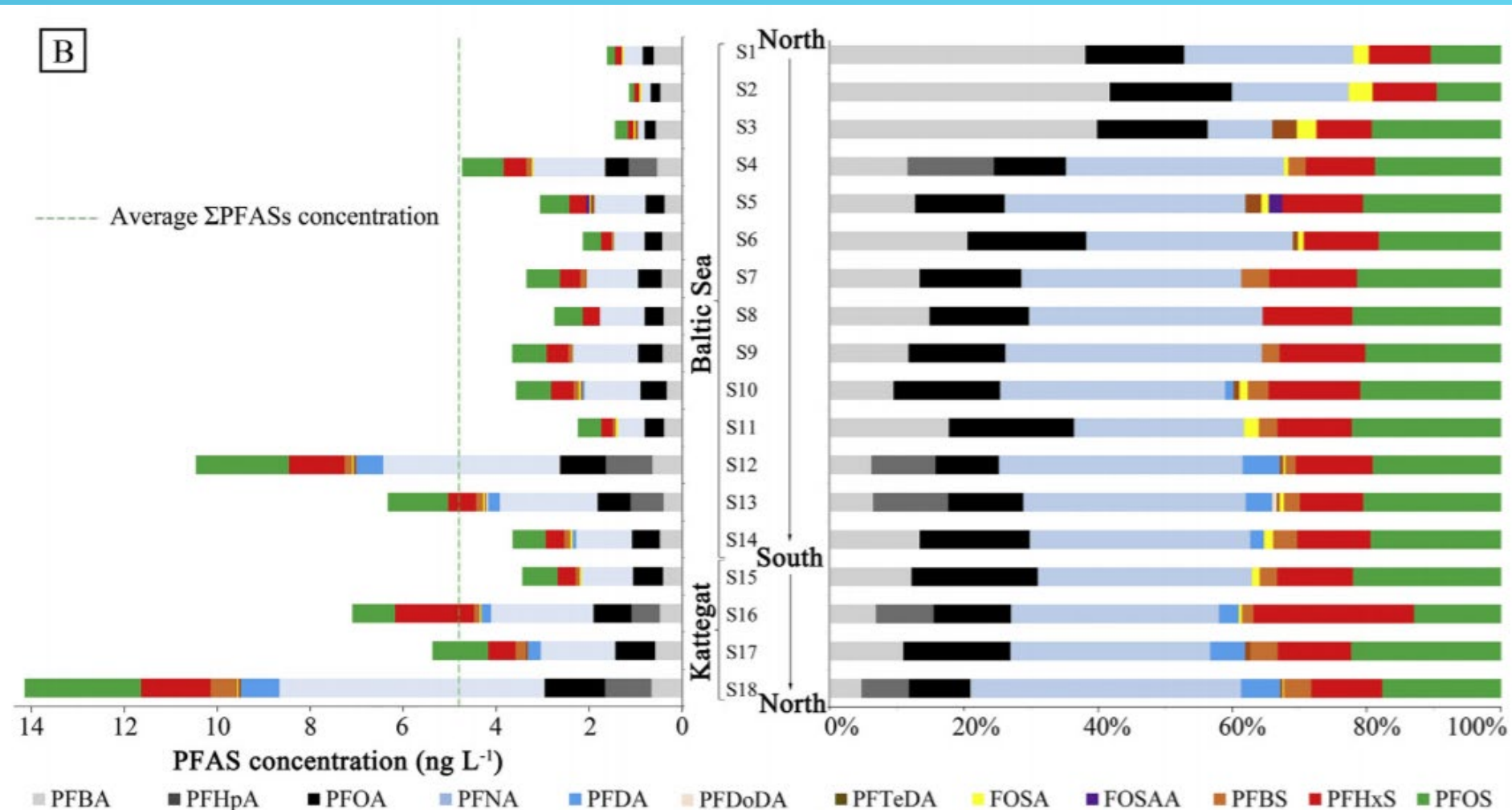


Fig. 2. Levels (ng L^{-1}) and composition profiles of individual PFASs in (A) 44 Swedish river samples (representing 40 rivers) from north to south along the Swedish east coast (R1–R30), and then from south to north along the Swedish west coast (R31–R40) and (B) the Bothnian Bay (S1 (north) to S5 (south)), the Bothnian Sea (S6 (north) to S8 (south)), the Baltic Proper (S9 (north) to S14 (south)) and the Kattegat (S15 (south) to S18 (north)).

Table 1

Detection frequency (%), concentration range (ng L⁻¹) and average concentrations (in brackets) of detected PFASs in river (*n* = 40) and seawater samples (*n* = 18).

PFAS	Rivers		Recipient sea	
	Detection frequency (%)	Concentration range (ng L ⁻¹) (Average)	Detection frequency (%)	Concentration range (ng L ⁻¹) (Average)
PFBA	100	0.47–3.7 (2.1)	100	0.34–0.67 (0.51)
PFHxA	27	0.51–4.2 (2.4)	0	NA ^a
PFHpA	48	0.36–1.7 (1.0)	30	0.61–1.0 (0.81)
PFOA	82	0.21–4.2 (2.2)	100	0.21–1.3 (0.76)
PFNA	100	0.090–5.8 (2.9)	100	0.14–5.7 (2.9)
PFDA	80	0.024–4.4 (2.2)	40	0.045–0.83 (0.44)
PFUnDA	86	0.018–1.8 (0.91)	0	NA ^a
PFDoDA	50	0.016–0.82 (0.42)	5	0.045
PFTeDA	23	0.093–1.5 (0.80)	40	0.016–0.072 (0.044)
PFBS	59	0.030–19 (9.5)	65	0.062–0.57 (0.32)
PFHxS	77	0.051–18 (9.0)	100	0.11–1.7 (0.91)
PFOS	98	0.040–6.9 (3.5)	100	0.11–2.5 (1.3)
FOSAA	0	NA ^a	5	0.061
FOSA	59	0.032–0.46 (0.25)	75	0.019–0.051 (0.035)

^a NA = not available

4. Conclusions

Distinct composition profiles with high fraction of PFASs were observed in rivers with high \sum PFAS concentrations as compared to other rivers suggesting source specific patterns of PFASs. This finding may be used for source tracing (e.g. fire-fighting training sites, effluents from sewage treatment plants and atmospheric deposition) of PFASs in the rivers; however, sampling along the course of the rivers is needed due to a multitude of potential source sites. Significant relationship between PFBA, PFHpA, PFOA, PFBS, PFHxS and DOC was detected ($p < 0.05$) for rivers and recipient seas. This may indicate chemical binding and co-transport of those PFASs with DOC in fresh water and sea water. Levels of PFCAs in rivers were related to the latitude of the sampling sites according to their perfluorocarbon chain length, with longer chains associated with higher latitudes. A number of possible mechanisms promoting a higher prevalence of longer chained PFCAs in the north were suggested. Further investigations on mechanisms driving the long-range atmospheric transport of long chain PFCAs and the spatial distribution of PFCAs observed are needed.