Sveriges lantbruksuniversitet
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Analysis of per- and polyfluoroalkyl substances (PFASs) in soil from Swedish background sites

Analys av PFAS i mark från bakgrundsområden

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Sammanfattning

Syftet med denna studie var att undersöka miljökoncentrationer, sammansättning och potentiella geografiska trender av 28 PFAS-ämnen i mark från svenska bakgrundsområden. Totalt analyserades 31 jordprover tagna på olika skogsmarksområden i Sverige. Vi detekterade 15 PFAS-ämnen och den totala koncentrationen var i genomsnitt 2,4 ng $\sum_{28}$PFAS per gram torrsubstans (TS). De dominerande PFAS-ämnena var perfluoroktansulfonsyra (PFOS, 20 %), fluoroktansulfonamidättiksyra (FOSAA, 15 %), 6:2 fluortelomersulfonsyra (6:2 FTSA, 14 %) och perfluorbutansulfonsyra (PFBS, 13 %). PFOS hade också den högsta detektionsfrekvensen (77 %) och en mediankoncentration på 0,30 ng g^{-1} TS ($n = 31$). Dess halt översteg dock inte riktvärdet för känslig markanvändning (3 ng g^{-1} TS; Statens geotekniska institut) i något av fallen. Om man antar samma toxicitet för samtliga PFAS-ämnen, så översteg $\sum_{28}$PFAS riktvärdet för PFOS i 9 fall av 31 (29 %). PFOS och perfluorundekankarboxylsyra (PFUnDA) uppvisade ökande koncentrationer från norr till söder (signifikant negativ korrelation med latitud; $p < 0,05$), medan FOSAA uppvisade det motsatta ($p <0,05$). Andelen PFOS (%) uppvisade på samma sätt en ökande trend från norr till söder (signifikant negativ korrelation med latitud; $p < 0,05$) och motsatt trend för FOSAA ($p < 0,05$). Koncentrationen av PFBS uppvisade ökande koncentrationer från väst till öst (signifikant negativ korrelation med longitud; $p < 0,05$). Några PFAS-ämnen uppvisade signifikant positiv korrelation med markens halt av totalt organiskt kol (TOC, mg g^{-1} TS), t.ex. FOSAA, PFBS och perfluortridekankarboxylsyra (PFTriDA) som var signifikant positivt korrelerade med TOC ($p < 0,05$). En signifikant positiv korrelation påvisades också mellan halten FOSAA och PFTriDA samt PFBS ($p < 0,05$). Vår studie har visat att PFAS-ämnen kan detekteras i skogsmark i hela landet och att det finns signifikanta geografiska trender, både i riktningarna nord-syd och väst-öst. Ytterligare studier behövs för att kunna förklara dessa samband, klargöra mekanismerna för spridningen och för att finna eventuella områden med högre halter (s.k. hot-spots).

Summary

Per- and polyfluoroalkyl substances (PFASs) are persistent organic pollutants with bio-accumulative and toxic potential. This study investigated the levels, composition profiles and geographical distribution of 28 PFASs in 31 soil samples from Swedish background areas. In total, 15 of the 28 analysed PFASs were detected, with an average concentration of 2.4 ng g^{-1} dw (median of 1.9 ng g^{-1} dw, $n = 31$). The dominant PFASs in the soil samples were perfluorooctane sulfonic acid (PFOS) (20 % of the $\sum_{28}$PFASs), perfluorooctane sulfonamidoacetic acid (FOSAA, 15 %), 6:2 fluorotelomer sulfonic acid (6:2 FTSA, 14 %) and perfluorobutane sulfonic acid (PFBS, 13 %). Perfluorooctane sulfonic acid (PFOS) had also the highest detection frequency of the studied PFASs (77 %) in the soil samples with a median concentration of 0.30 ng g^{-1} dw. However, the guideline value for PFOS in soil for sensitive land use from the Swedish Geotechnical Institute (SGI) (3 ng g^{-1} dw) was not exceeded in any sample. However, assuming the same toxicity for all PFASs, the $\sum_{28}$PFAS concentrations exceeded the guideline value (3 ng g^{-1} dw) in 9 out of 31 samples (29 %). PFOS and perfluoroundecanoic acid (PFUnDA) concentrations showed higher concentrations towards the south (significant negative correlation with latitude; $p < 0.05$), while FOSAA showed an opposite trend ($p < 0.05$). Furthermore, PFBS showed higher concentrations towards the west (significant negative correlation with longitude; $p < 0.05$). The proportion of PFOS (%) decreased significantly with latitude (i.e. towards the south), while the proportion of FOSAA (%) increased with latitude ($p < 0.05$). Furthermore, the concentrations of FOSAA, PFBS and perfluorotridecanoic acid (PFTriDA) showed a significant positive correlation with total organic carbon (TOC) ($p < 0.05$). The concentrations of FOSAA correlated significantly positive with both PFTriDA and PFBS ($p < 0.05$). Overall, PFASs were ubiquitously detected in Swedish background soil samples and showed distinguish geographical distribution. However, more data are needed regarding the pathways and sources of PFASs in soil and identifying potential hot spots.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are highly fluorinated, organic compounds (Ahrens, 2011). The surfactant-like properties of these substances (hydrophobic tail and hydrophilic functional groups) make them usable in a wide array of consumer and industrial products such as textile, paints, lubricants, waxes and aqueous fire-fighting foams (AFFFs) (Buck *et al.*, 2011). However, PFASs are extremely persistent and have the potential to bioaccumulate and have toxic effects (Ahrens and Bundschuh, 2014). The universal use of PFASs has led to a broad environmental distribution of these compounds globally even in remote ecosystems (Giesy and Kannan, 2001).

PFASs are chemically and thermally extremely stable due to the presence of perfluoroalkyl moieties (CF_2-moieties). Having the highest electronegativity of all elements, fluorine atoms (F) have a high propensity to attract electron density. As such, the C-F bond is highly polarized, with negative charge shifted towards the fluorine. The strength and persistency of the C-F bond is attributed to the electrostatic attraction arising between the $F^{\delta-}$ and $C^{\delta+}$ (O'Hagan, 2008). The general chemical formula of *per*fluoroalkyl substances is $C_nF_{2n+1}R$, indicating that, except for potential carbons in the functional head group R, all carbons are fully fluorinated. Examples of common functional groups are carboxylic acids ($-CO_2H$, perfluoroalkyl carboxylic acids; PFCAs) and sulfonic acids ($-SO_3H$, perfluoroalkyl sulfonic acids; PFSAs). There are also compounds where not all C atoms are fully fluorinated, these are called *poly*fluoroalkyl substances (Buck *et al.*, 2011).

Release of PFASs occurs during all stages of the product life cycle, from production, throughout its use until its final disposal (Ahrens and Bundschuh, 2014). Emissions can be both direct (during the product life cycle) and indirect through transformation of precursor substances to PFASs (Ellis *et al.*, 2004; Wang *et al.*, 2005). Common point sources of PFASs can be manufacturing sites, wastewater treatment plants, use of AFFFs at fire training facilities and landfills. Diffuse sources consist of, amongst others, atmospheric deposition and surface run-off (Davis *et al.*, 2007; Wang *et al.*, 2013; Ahrens and Bundschuh, 2014). In remote areas, where direct anthropogenic impacts are negligible, the most likely source of PFASs is through atmospheric deposition (Ellis *et al.*, 2004). Meng *et al.* (2018) estimated that the atmospheric deposition of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) to coastal soils of the Bohai and Yellow Sea (China) accounted for 93 % (4431 kg) and 70 % (4335 kg) respectively of the total amount found of respective substances.

In Sweden, there are no generic guideline values for PFASs (except for PFOS) regarding the assessment of environmental and health risks of contaminated soils and groundwater. The Swedish Geotechnical Institute (SGI) developed preliminary guideline values for PFOS in soil and groundwater. For soil there are two guideline values, 3 ng g^{-1} dry weight (dw) (sensitive land use) and 20 ng g^{-1} dw (less sensitive land use), reflecting the subsequent risks posed to people and environment accompanying the intended use of the land (e.g. housing, schools and industry etc.) (SGI, Publikation 21). For groundwater the generic guideline value of PFOS is set to 45 ng L^{-1}. SGI also concluded that data to develop guideline values for other PFASs were insufficient or lacking (SGI, Publikation 21).

The aim of this study was to determine concentrations of PFASs in soil from background areas across Sweden to serve as basis line and to improve future efforts to establish generic guideline values for PFASs in soil.

2. Materials and Methods

2.1 Chemicals

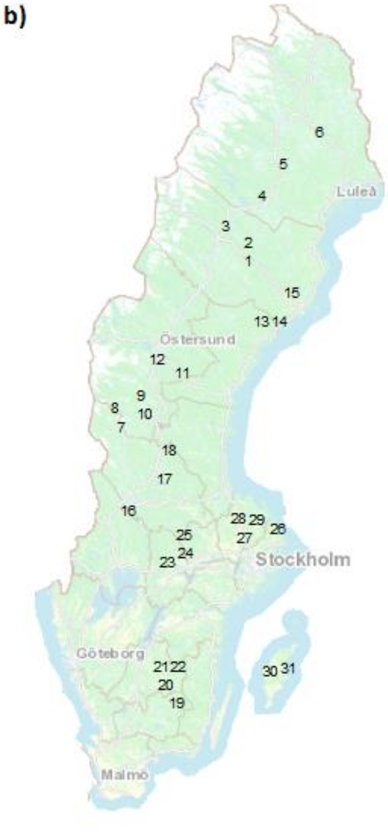
In total 28 PFASs were targeted for analysis: four PFSAs (PFBS, PFHxS, PFOS and PFDS), 13 PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA and PFOcDA), three perfluoroctane sulfonamides (FOSAs) (FOSA, MeFOSE and EtFOSE), two perfluorooctane sulfonamidoethanols (FOSAAs) (FOSAA, MeFOSAA and EtFOSAA) and three fluorotelomer sulfonates (6:2 FTSA, 8:2 FTSA and 10:2 FTSA) (Table 1). In addition, 16 isotopically labelled internal standard (IS) were used: $^{13}C_8$-FOSA, d_3-MeFOSAA, d_5-EtFOSAA, d_3-MeFOSA, d_5-EtFOSA, d_7-MeFOSE, d_9-EtFOSE, $^{13}C_4$-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 and $^{13}C_4$-PFOS.

Table 1. PFAS target compounds

Substance	Acronym	Molecular formula	CAS-number
PFCAs			
Perfluorobutanoic acid	PFBA	$C_3F_7CO_2H$	375-22-4
Perfluoropentanoic acid	PFPeA	$C_4F_9CO_2H$	2706-90-3
Perfluorohexanoic acid	PFHxA	$C_5F_{11}CO_2H$	307-24-4
Perfluoroheptanoic acid	PFHpA	$C_6F_{13}CO_2H$	375-85-9
Perfluorooctanoic acid	PFOA	$C_7F_{15}CO_2H$	335-67-1
Perfluorononanoic acid	PFNA	$C_8F_{17}CO_2H$	375-95-1
Perfluorodecanoic acid	PFDA	$C_9F_{19}CO_2H$	335-76-2
Perfluoroundecanoic acid	PFUnDA	$C_{10}F_{21}CO_2H$	2058-94-8
Perfluorododecanoic acid	PFDoDA	$C_{11}F_{23}CO_2H$	307-55-1
Perfluorotridecanoic acid	PFTriDA	$C_{12}F_{25}CO_2H$	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	$C_{13}F_{27}CO_2H$	376-06-7
Perfluorohexadecanoic acid	PFHxDA	$C_{15}F_{31}CO_2H$	67905-19-5
Perfluorooctadecanoic acid	PFOcDA	$C_{17}F_{35}CO_2H$	16517-11-6
PFSAs			
Perfluorobutane sulfonic acid	PFBS	$C_4F_9SO_3H$	375-73-5 or 59933-66-3
Perfluorohexane sulfonic acid	PFHxS	$C_6F_{13}SO_3H$	355-46-4
Perfluorooctane sulfonic acid	PFOS	$C_8F_{17}SO_3H$	1763-23-1
Perfluorodecane sulfonic acid	PFDS	$C_{10}F_{21}SO_3H$	335-77-3
FASAAs			
Perfluorooctane Sulfonamidoacetic acid	FOSAA	$C_8F_{17}SO_2N(CH_2CO_2H)H$	2806-24-8
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	$C_8F_{17}SO_2N(CH_3)CH_2CO_2H$	2355-31-9
N- ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	$C_8F_{17}SO_2N(C_2H_5)CH_2CO_2H$	2991-50-6
FOSAs			
Perfluorooctane sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	754-91-6
N-methylperfluoro-1-octanesulfonamide	MeFOSA	$C_8F_{17}SO_2N(CH_3)H$	31506-32-8
N-ethylperfluoro-1-octanesulfonamide	EtFOSA	$C_8F_{17}SO_2N(C_2H_5)H$	4151-50-2
FOSEs			
2-(*N*-methylperfluoro-1-octanesulfonamido)-ethanol	MeFOSE	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	24448-09-7
2-(*N*-ethylperfluoro-1-octanesulfonamido)-ethanol	EtFOSE	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	1691-99-2
FTSAs			
6:2 fluorotelomer sulfonate	6:2 FTSA	$C_8H_4F_{13}SO_3H$	425670-75-3
8:2 Fluorotelomer sulfonate	8:2 FTSA	$C_{10}H_4F_{17}SO_3H$	481071-78-7 or 39108-34-4
10:2 Fluorotelomer sulfonate	10:2 FTSA	$C_{12}H_4F_{21}SO_3H$	120226-60-0

2.2 Sampling and sampling sites

In total 35 samples (including 2 triplicates) were collected by the Swedish Forest Soil Inventory (Appendix, Table A1). Sampling sites were randomly selected within the Swedish Forest Soil Inventory’s sampling plots considering potential latitudinal gradients (north to south) in contaminant levels and secondarily to reflect longitudinal differences (east to west) (Figure 1b). Furthermore, sampling was focused on soils in mature forests without known local contaminant impacts. Soils from mature forests were selected because i) forest is the dominant landscape type in Sweden, ii) provides data for research on forest soils and forest ecosystems (e.g. forest filter effect), and iii) provides data for international reporting from Sweden, for example, requested by the Convention of Long Range Transboundary Air Pollution (LRTAP). Composite soil samples, consisting of 5 sub-samples of equal proportions, which were taken from the top 10 cm of the organic horizon (O-horizon) of the soil profile in each sampling plot. If the depth of the O-horizon was below 10 cm, the whole layer was sampled. The 5 sub-samples were sampled in a crosshair-fashion across the sampling plot, one sub-sample from the center of the plot and four from its periphery, as illustrated in Figure 1a. Rubber/silicon gloves were worn by the field staff when taking the samples. Each composite-sample was collected either by hand or dug out by knife and put in rinsed 50 mL PP-tubes (rinsed 3 times with methanol). Upon arrival at the Department of Soil and Environment, SLU (Uppsala) the samples were stored in the freezer (-20°C) until analysis.



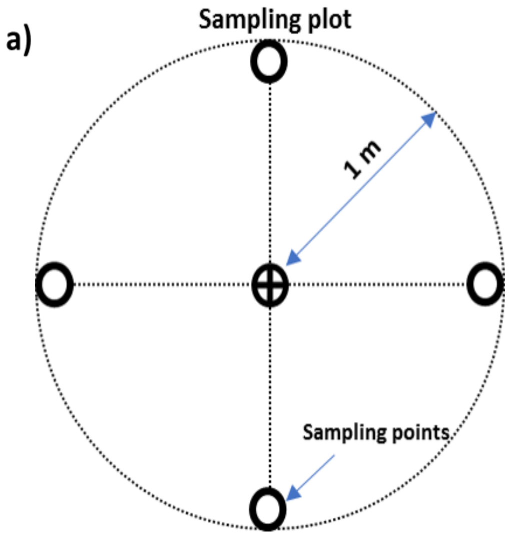


Figure 1. a) Sampling plot with the five composite sampling points, and b) map with sampling locations and sample ID numbers.

2.3 Determination of water content and organic carbon content

All samples were thawed and mixed gently with spatulas in beakers. A small, representative sample aliquot of ~1 g (wet weight) was taken from each sample for determination of water content (12 h at 105 °C) and organic matter content (loss-on-ignition (LOI), 4 h at 550 °C). A conversion factor of 0.58 was used to convert the LOI to total organic carbon (TOC) reported either as percent (%) or mg g^{-1} dw (Essington, 2015). For PFAS analysis, the remaining soil sample was frozen overnight and then freeze-dried for 7 days.

2.4 PFAS analysis

Samples were analysed by the POPs lab at SLU, Uppsala (Dept. of Aquatic Sciences and Assessment). Analysis was performed according to a method previously described with modifications (Ahrens *et al.*, 2009).

Prior to extraction, the dried soil samples were homogenized three times at 4500 rpm for 10 s using the Precellys® Evolution Tissue Homogenizer (Precellys® Lysing Kit Hard tissue homogenizing CK28, 15 mL) due to the heterogenous nature of the samples (soil mixed with pine needles and roots). On average, 2 g of homogenized soil was weighed into 50 mL PP-tubes and a two-step solid-liquid extraction was performed. Firstly, samples were soaked for 30 min in 2 mL of 100 mM sodium hydroxide (NaOH) in methanol. Then 15 mL of methanol and 100 µL of IS mixture was added and subsequently the samples were shaken horizontally at 200 rpm for 1 h. After shaking, samples were centrifuged (3000 rpm for 15 min) and the supernatant was decanted into new 50 mL PP-tubes. A second extraction was then performed with the addition of only 1 mL 100 mM NaOH in methanol, 5 mL of methanol and 30 min of shaking. The supernatants were then combined and the sample volume evaporated (nitrogen evaporation, N-EVAP™ 112) down to ~5 mL.

Due to the high organic matter content of the samples, a solid phase extraction (SPE) clean-up step was necessary An aliquot of 5 mL sample extract was diluted with Millipore-water at a ratio of 1:20 (v/v) in 250 mL HDPE bottles and SPE was performed using Oasis® weak anion exchange (WAX) cartridges (6 cm^3, 150 mg, 30 µm, Waters, Wexford, Ireland). Before extraction, cartridges were preconditioned with 4 mL 0.1 % ammonium hydroxide in methanol, 4 mL methanol and 4 mL Millipore-water. Samples were loaded into the cartridges and the flow was regulated to one drop per second. Upon loading, cartridges were washed with 4 mL of 25 mM ammonium acetate buffer (pH 4) and dried by centrifugation. Analytes were then eluted from the cartridges into 15 mL PP-tubes by the addition of 4 mL methanol and 8 mL 0.1 %

ammonium hydroxide in methanol. Samples were then placed under nitrogen evaporation and concentrated to ~0.5 mL. The sample aliquots were then quantitatively transferred to LC-MS sampling 1.7 ml PP-vials and evaporated once again to 0.5 mL. Right before analysis, 0.5 mL of Millipore-water was added to the samples. The adding of Millipore-water caused precipitation in the sample extract and thus the sample was filtrated using syringe filters (0.45 µm, 1.7 cm^2 regenerate cellulose) to remove the precipitate. Finally, analysis was performed using liquid chromatography-mass spectrometry (Ahrens *et al.*, 2016).

2.5 Blanks and method detection limits (MDLs)

The average blank levels ranged between not detected to 0.22 ng absolute (except for PFPeA). The method detection limits (MDLs) ranged between 0.0049 to 8.78 ng g^{-1} dw (except for PFPeA). The relative average standard deviation for the 2 triplicate samples was 10% for individual PFASs.

2.6 Statistical analysis

The data was evaluated to investigate potential relationships between PFAS concentrations and latitude, longitude and content of TOC. For this analysis, only PFASs with a detection frequency above 45 % were included (i.e. PFUnDA, PFTriDA, PFBS, PFHxS, PFOS and FOSAA) and the PFAS concentrations below the method detection limit (MDL) were replaced by MDL/2. The significance level was set to $\alpha = 0.05$.

Pearson correlation was used to determine relationships between individual PFASs and latitude, longitude and TOC. The correlation coefficients were then squared and correlations with $R^2 > 0.1$ where chosen for regression analysis and calculations of statistical significance. The concentrations of PFASs and TOC was log 10 transformed to reduce skewness of the data before analysis.

3. Results and discussion

3.1 Detection frequency and concentrations of PFASs in soil

In total, 15 out of 28 PFASs were detected in the 31 samples (Table 2 and Appendix Table A2). The average concentration of $\sum_{28}$PFASs in all samples was 2.4 ng g^{-1} dw, with a median of 1.9 ng g^{-1} dw ($n = 31$). The PFASs with the highest detection frequency in all samples were PFOS (77 %), FOSAA (68 %), PFBS (61 %), and PFUnDA (58 %). Highest average $\sum_{28}$PFAS concentrations were found in PFOS and 6:2 FTSA both with 0.43 ng g^{-1} dw, followed by PFTriDA with0.35 ng g^{-1} dw.

Table 2. Number of detection (*n*), detection frequency (%), concentration range (ng g^{-1} dw), average and median concentrations of detected PFASs in soil samples (*n* = 31)[a]

PFASs	Number of detection	Detection frequency (%)	Concentrations (ng g^{-1} dw)			
			min	**max**	**average**	**median**
PFBA	0	0	<3.9	NA	NA	NA
PFPeA	0	0	NC[b]	NA	NA	NA
PFHxA	0	0	<8.8	NA	NA	NA
PFHpA	4	13	<0.024	0.44	0.035	NA
PFOA	5	16	<0.024	0.57	0.041	NA
PFNA	9	29	<0.016	0.70	0.094	NA
PFDA	12	39	<0.0083	0.68	0.12	NA
PFUnDA	18	58	<0.014	0.76	0.22	0.07
PFDoDA	9	29	<0.024	0.33	0.050	NA
PFTriDA	17	55	<0.024	8.3	0.35	0.042
PFTeDA	1	3.2	<0.24	0.64	0.021	NA
PFHxDA	0	0	<0.024	NA	NA	NA
PFOcDA	1	3.2	<0.049	0.08	0.0026	NA
PFBS	19	61	<0.038	0.96	0.29	0.23
PFHxS	14	45	<0.045	0.40	0.050	NA
PFOS	24	77	<0.024	1.7	0.43	0.30
PFDS	0	0	<0.0048	NA	NA	NA
FOSA	2	6	<0.018	0.65	0.022	NA
MeFOSA	0	0	<0.24	NA	NA	NA
EtFOSA	0	0	<0.24	NA	NA	NA
MeFOSE	0	0	<0.24	NA	NA	NA
EtFOSE	0	0	<0.024	NA	NA	NA
FOSAA	21	68	<0.090	0.88	0.27	0.28
MeFOSAA	0	0	<0.0048	NA	NA	NA
EtFOSAA	0	0	<0.24	NA	NA	NA
6:2 FTSA	8	26	<0.75	2.96	0.43	NA
8:2 FTSA	0	0	<0.24	NA	NA	NA
10:2 FTSA	0	0	<0.024	NA	NA	NA

[a] NA = not available. [b] NC = not calculable due to high background contamination.

The guideline value for PFOS for sensitive land use (3 ng g^{-1} dw) was not exceeded in any sample (SGI., Publikation 21). Assuming the same toxicity for all PFASs, the $\sum_{28}$PFASs exceeded the guideline value 3 ng g^{-1} dw in 9 out of 31 samples (29 %) (Figure 2).

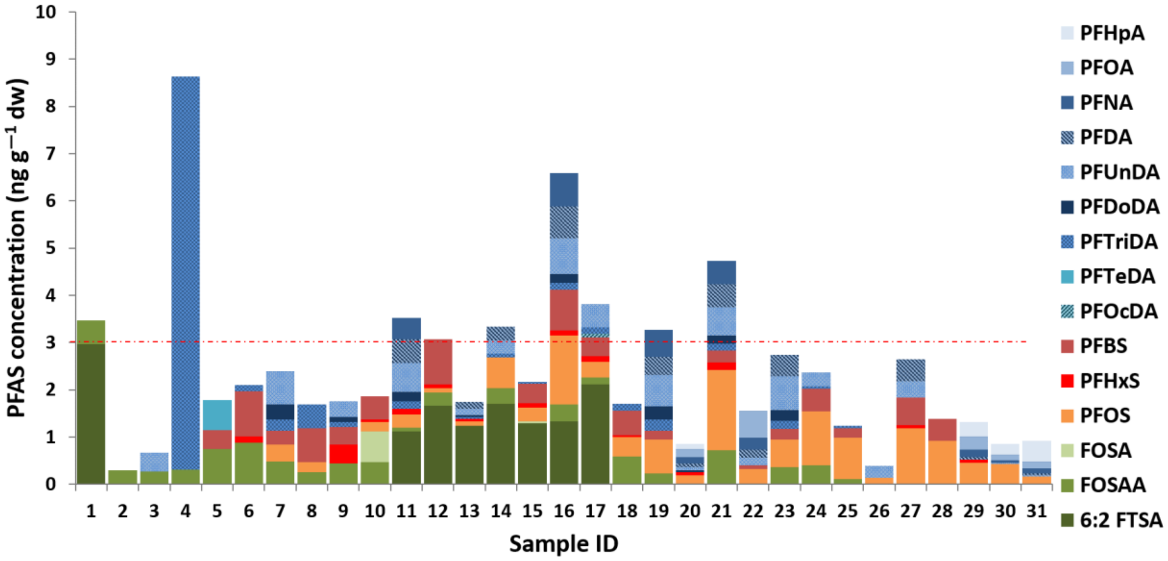


Figure 2. Concentration of PFASs in soil samples (*n* = 31) from Swedish background areas. The red line represents the sensitive land use guideline value of 3 ng g^{-1} dw for PFOS from the Swedish Geotechnical Institute (SGI). Detected PFASs below MDL are not included in the figure.

3.2 Composition profiles of PFASs

The PFASs analyzed in this study can be divided into groups based on their functional groups and degree of fluorination. These groups are: ∑PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA and PFOcDA), ∑PFSAs (PFBS, PFHxS, PFOS and PFDS) and ∑PFAS precursors (FOSA, MeFOSA, EtFOSA, EtFOSE, FOSAA, MeFOSAA, EtFOSAA and 6:2 FTSA).

The composition profiles differed between samples and with latitude (Figure 3 and Figure 4). There was an increasing composition of ∑PFSAs with decreasing latitude (i.e. towards the south), whereas the ∑PFAS precursors exhibited the opposite relationship. The highest composition of the $\sum_{28}$PFASs had PFOS (20 %), FOSAA (15 %), 6:2 FTSA (14 %), PFBS (13 %), PFUnDA (11 %) and PFTriDA (6 %). The composition of the other PFASs was generally <4 %.

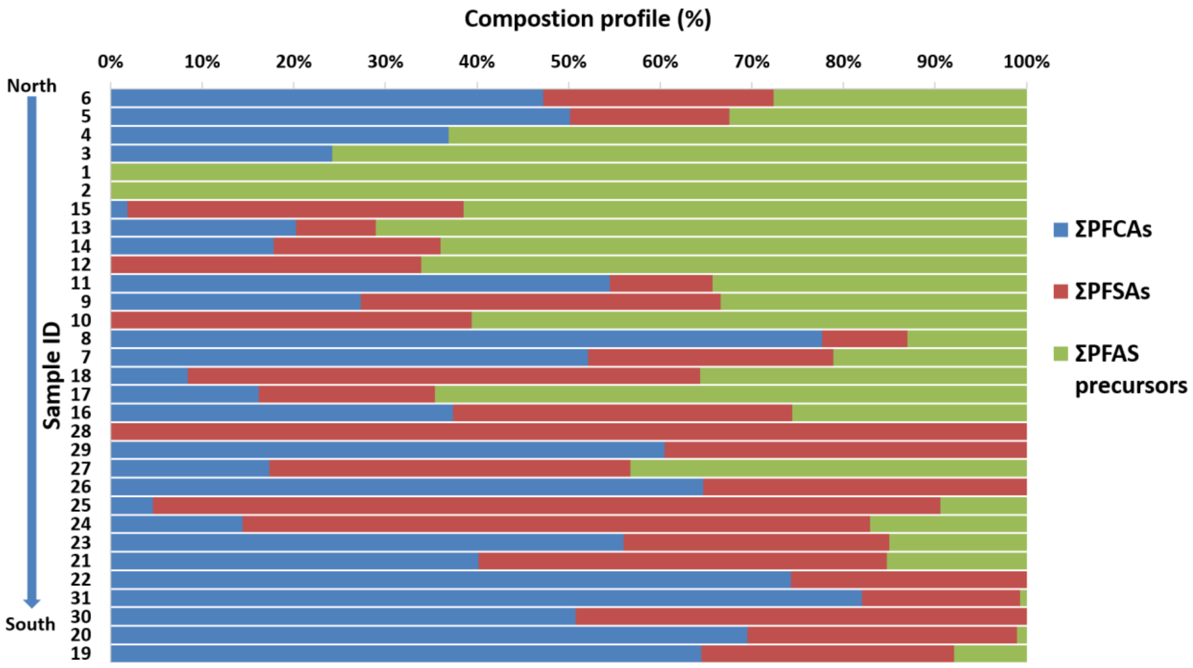


Figure 3. Composition profiles (%) for ∑PFCAs, ∑PFSAs and ∑PFAS precursors for soil samples ordered latitudinally from north to south.

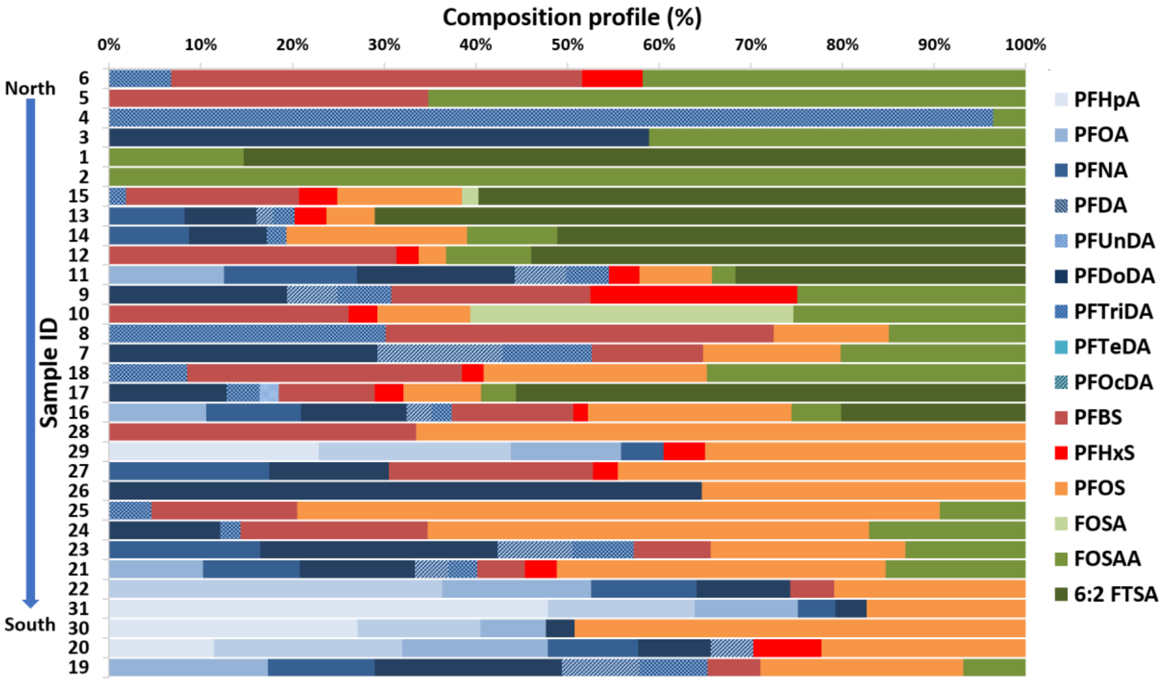


Figure 4. Composition profiles (%) for individual PFASs for soil samples ordered latitudinally from north to south.

3.3 Latitudinal and longitudinal distribution of PFASs

Linear regression showed significant negative correlation ($p < 0.05$) between concentrations (ng g^{-1} dw) of PFOS and PFUnDA with latitude (i.e. higher concentrations towards the south), whereas FOSAA was significantly positive correlation ($p < 0.05$) with latitude (i.e. higher concentrations towards the north) (Figure 5a, b and c). Only PFBS showed significant negative correlation ($p < 0.05$) with longitude (i.e. higher concentrations towards the west) (Figure 5d). It should be noted that for the correlation of PFBS with longitude and, to some extent, for PFOS with latitude, that the non-detected concentrations (i.e. concentrations that were replaced by MDL/2) might bias the correlation analysis. In addition, the TOC correlated significantly positive both with longitude and latitude ($p < 0.05$) and might impact the spatial distribution of PFASs (Table 3). Significant correlations between PFASs and the parameters latitude, longitude and TOC are compiled in Table 3.

Analysis of compositional profiles based on the selected PFASs (i.e. PFUnDA, PFTriDA, PFBS, PFHxS, PFOS and FOSAA) showed that the relative amount of PFOS decreased significantly with increasing latitude while FOSAA showed the opposite trend ($p < 0.05$) (Figure 6a and b, Table 4).

Table 3. Significant correlations (*p*) between PFAS concentrations and latitude (Sweref99_Nord), longitude (Swered99_Ost), and total organic carbon (TOC). TOC content (mg g^{-1} dw) and PFAS concentrations (ng g^{-1} dw) were log 10 transformed before analysis, $\alpha = 0.05$

	Latitude	**Longitude**	**PFUnDa**	**PFTriDA**	**PFBS**	**PFHxS**	**PFOS**	**FOSAA**
TOC	<0.05	<0.05	-	<0.01	<0.01	-	-	<0.001
PFUnDa	<0.05	-	-	-	-	-	-	-
PFTriDA	-	-	-	-	-	-	-	-
PFBS	-	<0.05	-	-	-	-	-	-
PFHxS	-	-	-	-	-	-	-	-
PFOS	<0.001	-	-	-	-	-	-	-
FOSAA	<0.05	-	-	<0.05	<0.05	-	-	-

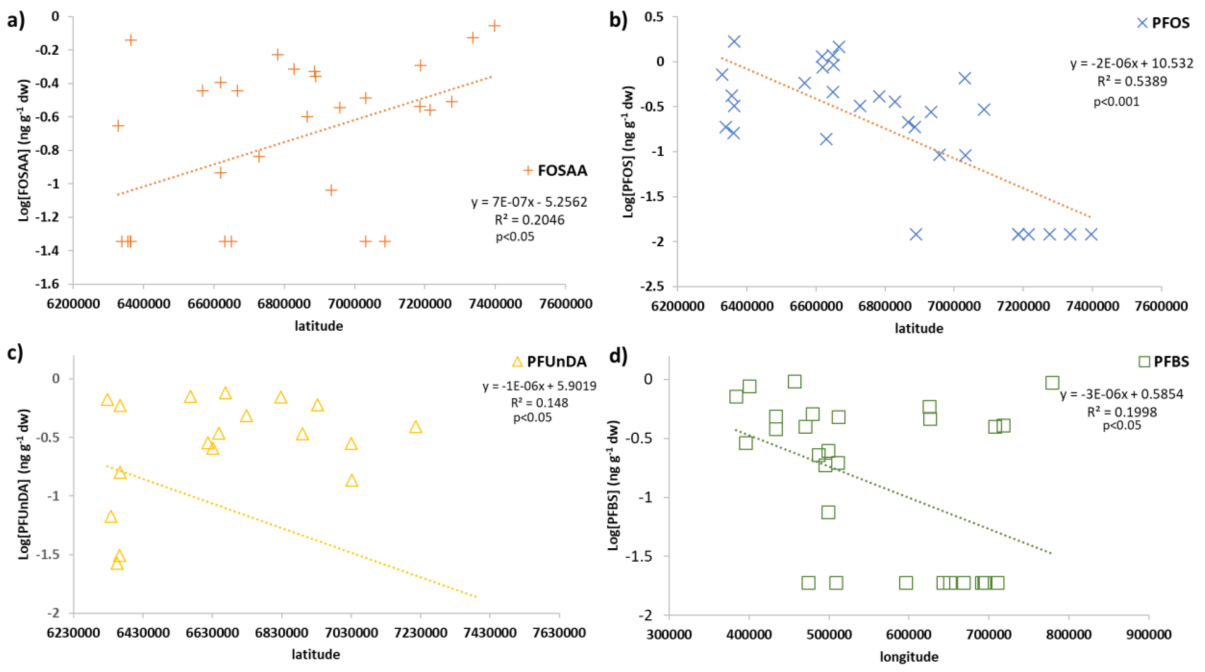


Figure 5. Latitude (Sweref99_north) plotted against a) FOSAA, b) PFOS, c) PFUnDA, and d) longitude (Sweref99_east) plotted against PFBS concentrations. Note: Logarithmic scale for PFAS concentrations.

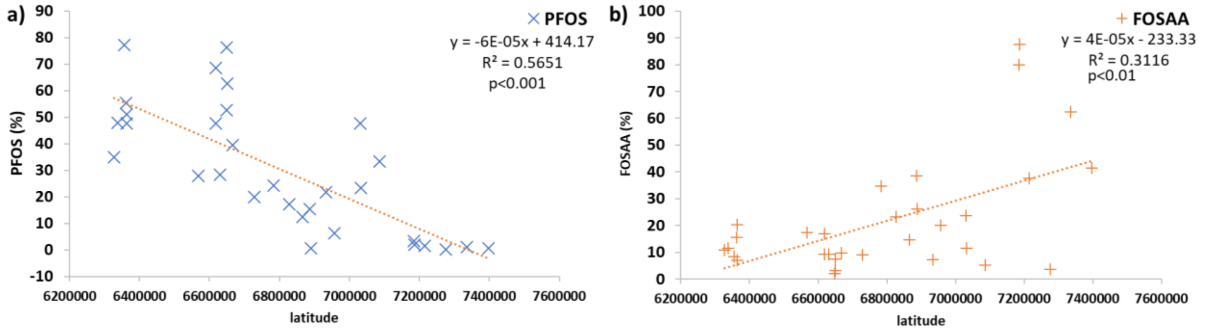


Figure 6. Latitude (Sweref99_north) plotted against the relative composition (%) of a) PFOS and b) FOSAA.

Table 4. Significant correlations (p) between PFAS composition profile and latitude (Sweref99, Nord), longitude (Swered99, Ost), and total organic carbon (TOC), α = 0.05

	Latitude	Longitude	PFUnDa	PFTriDA	PFBS	PFHxS	PFOS	FOSAA
TOC	-	-	-	-	<0.05	<0.05	<0.01	-
PFUnDa	-	-	-	-	-	-	-	-
PFTriDA	-	-	-	-	-	-	-	-
PFBS	-	-	<0.01	-	-	-	-	-
PFHxS	-	-	-	-	-	-	-	-
PFOS	<0.001	-	-	-	-	-	-	-
FOSAA	<0.01	-	-	-	-	-	<0.01	-

3.4 Correlation of PFASs to total organic carbon (TOC)

The content of TOC is an important factor for the partitioning and retainment of PFASs on particulate matter and in soils (Ahrens et al., 2010; Milinovic et al., 2015). A significant positive correlation was found between TOC and FOSAA, PFBS and PFTriDA ($p < 0.05$) (Figure 7a, b and c). As previously mentioned, the non-detected concentrations (MDL/2) might bias the correlation analysis. Furthermore, analysis of the relative composition (%) of the selected PFASs showed that PFHxS and PFOS decreased with increasing TOC content (%) (Figure 8a and c), while the relative amounts of PFBS showed the inverse relationship ($p < 0.05$) (Figure 8b).

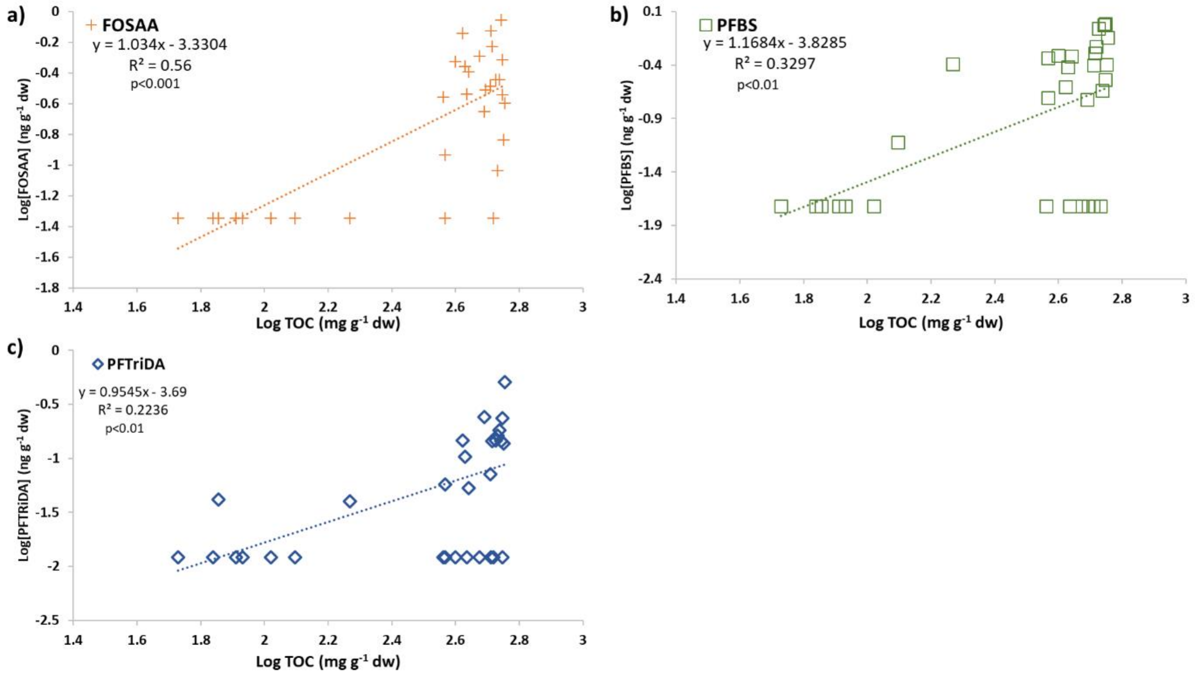


Figure 7. TOC (mg g^{-1} dw) plotted against a) FOSAA, b) PFBS and c) PFTriDA. Note: Logarithmic scale for PFAS concentrations.

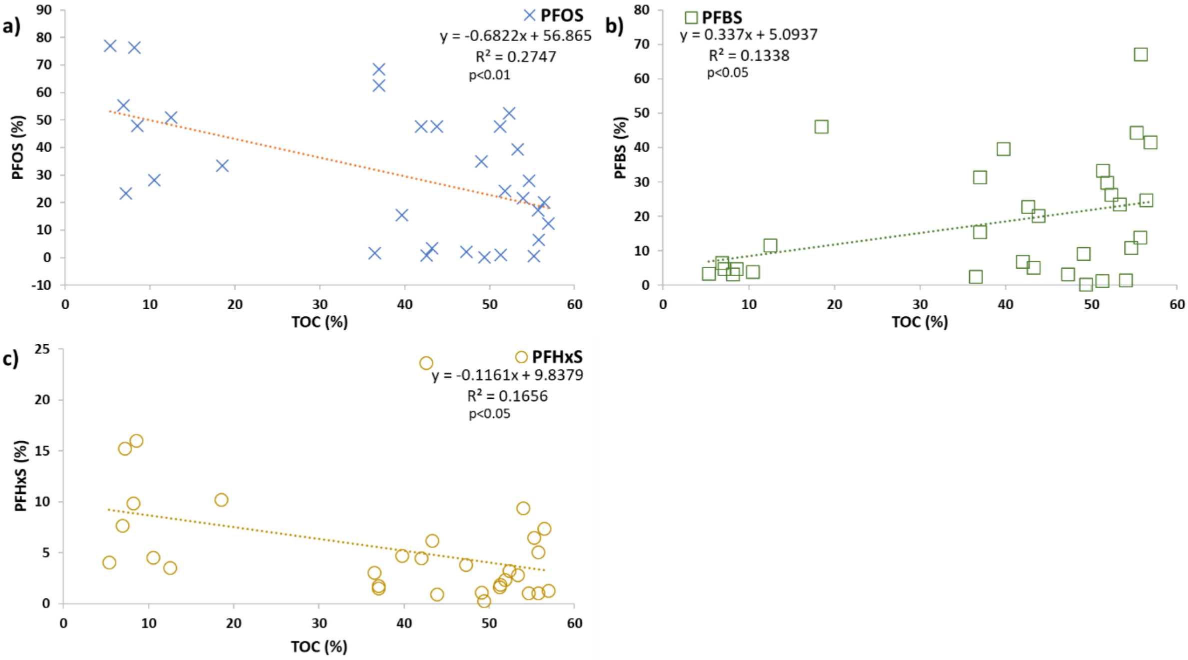


Figure 8. TOC content (%) plotted against the relative composition profile (%) for a) PFOS, b) PFBS and c) PFHxS.

3.5 Correlations between PFASs

Correlations between PFASs are shown in Figure 9 and Figure 10. Interestingly, for PFAS precursors, FOSAA correlated significantly positive with both PFTriDA and PFBS (Figure 9a and b) (p < 0.05). Comparing the relative composition profile, significant negative correlations were found between FOSAA and PFOS as well as PFBS and PFUnDA (p < 0.05) (Figure 10a and b).

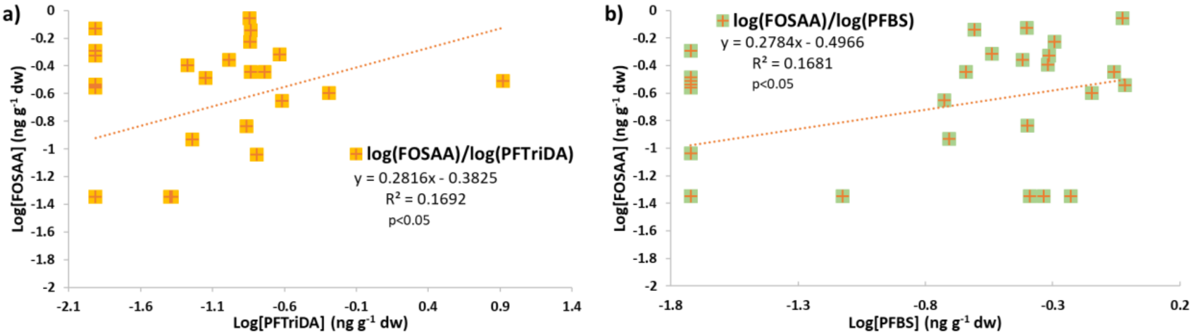


Figure 9. FOSAA plotted against a) PFTriDA and b) PFBS. Note: Logarithmic scale.

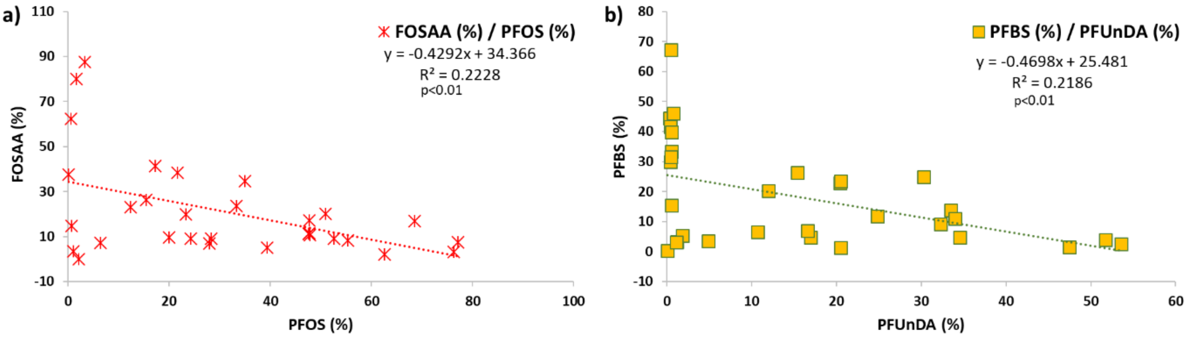


Figure 10. Relative amount (%) of a) FOSAA plotted against PFOS and b) PFBS plotted against PFUnDA.

The ∑PFAS precursors increased with increasing latitude, whereas ∑PFSAs showed the opposite trend (Figure 3). This trend was mainly driven by the decreasing concentration of PFOS and increasing concentration of FOSAA and 6:2 FTSA with increasing latitude (towards north) (Figures 4–6). However, it is important to note that the non-detected concentrations (MDL/2) influenced the trends to some extent. The decrease in PFOS concentrations with latitude, agrees with the study from Nguyen *et al.* (2017) investigating the spatial distribution of PFASs in surface waters in northern Europe. However, they showed that PFBS was negatively correlated with latitude, which could not be found in this study. Additionally, it was shown that longer chain PFASs (PFNA, PFDA, PFUnDA, PFDoDA) correlated positively with latitude, which was also not confirmed in this study, and in contrast showing a negative correlation of PFUnDA with latitude (Figure 5c). It is possible that the non-detected concentrations (MDL/2) is responsible for this discrepancy and that our study is focusing on soil. PFBS was the only PFAS which showed a decreasing trend with increasing longitude (towards west) (Figure 7). This trend might be affected by the TOC content which slightly increased (but statistically significant) with longitude (towards the east) (Table 3).

Acknowledgement

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Appendix

Table A1. Sample details including organic matter content (OM) and total organic carbon (TOC) in percent

Sample ID	LIMS ID	Longitude[b]	Latitude[b]	Water content (%)	OM (%)	TOC (%)[c]
1	242716	642461	7186521	89	81	47
2	242715	642563	7184938	59	75	43
3	242713	596168	7215415	69	63	36
4	242717	668093	7275705	70	85	49
5	248625	707411	7336236	74	88	51
6	245249	779168	7397035	78	95	55
7	242974	396112	6827893	75	96	56
8	245357	383567	6866202	87	98	57
9	245360	433083	6889112	68	73	43
10	245359	433014	6886718	62	68	40
11	249285	508309	6933568	55	93	54
12	245358	456806	6957705	82	96	56
13	242071	694057	7032205	27	12	7
14	242070	694615	7030867	77	88	51
15	241747	718152	7086111	51	32	19
16	242558	400132	6667055	65	92	53
17	242301	470278	6728102	63	97	56
18 (1)[a]	242300 (1)	479395	6782403	72	89	52
18 (2)[a]	242300 (2)	479395	6782403	67	81	47
18 (3)[a]	242300 (3)	479395	6782403	67	78	45
19	242065	495080	6327983	64	85	49
20	242066	474401	6337949	30	15	9
21	242890	498808	6363717	61	72	42
22	242891	499140	6363678	24	22	12
23	241683	486492	6567432	66	94	55
24	241684	511684	6618255	71	76	44
25	241685	510742	6618909	56	64	37
26	241755	690524	6630603	23	18	10
27	241756	625668	6649044	54	90	52
28 (1)[a]	241752 (1)	626377	6650444	69	88	51
28 (2)[a]	241752 (2)	626377	6650444	71	91	53
28 (3)[a]	241752 (3)	626377	6650444	71	89	52
29	241753	650702	6649171	23	14	8
30	243142	695291	6356018	14	9	5
31	243141	710732	6361707	27	12	7

[a] Triplicates, [b] SWEREF99 [c] TOC (%) ≈ OM (%) * 0.58.

Table A2. Levels of detected PFASs in Swedish soils (ng g^{-1} dw)[a]

Sample ID	LIMS ID	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFOcDA	PFBS	PFHxS	PFOS	FOSA	FOSAA	6:2 FTSA
1	242716	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	<0.024	<0.24	<0.049	<0.038	<0.045	<0.024	<0.018	0.51	2.96
2	242715	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	<0.024	<0.24	<0.049	<0.038	<0.045	<0.024	<0.018	0.29	<0.75
3	242713	<0.024	<0.024	<0.016	<0.0083	0.39	<0.024	<0.024	<0.24	<0.049	<0.038	<0.045	<0.024	<0.018	0.28	<0.75
4	242717	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	8.32	<0.24	<0.049	<0.038	<0.045	<0.024	<0.018	0.31	<0.75
5	248625	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	<0.024	0.64	<0.049	0.40	<0.045	<0.024	<0.018	0.74	<0.75
6	245249	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	0.14	<0.24	<0.049	0.94	0.14	<0.024	<0.018	0.88	<0.75
7	242974	<0.024	<0.024	<0.016	<0.0083	0.70	0.33	0.23	<0.24	<0.049	0.29	<0.045	0.36	<0.018	0.48	<0.75
8	245357	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	0.51	<0.24	<0.049	0.72	<0.045	0.21	<0.018	0.25	<0.75
9	245360	<0.024	<0.024	<0.016	<0.0083	0.34	0.10	0.10	<0.24	<0.049	0.38	0.40	<0.024	<0.018	0.44	<0.75
10	245359	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	<0.024	<0.24	<0.049	0.49	0.06	0.19	0.65	0.47	<0.75
11	249285	<0.024	<0.024	0.44	0.51	0.60	0.20	0.16	<0.24	<0.049	<0.038	0.12	0.28	<0.018	0.09	1.11
12	245358	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	<0.024	<0.24	<0.049	0.96	0.07	0.09	<0.018	0.29	1.66
13	242071	<0.024	<0.024	<0.016	0.14	0.14	0.03	0.04	<0.24	<0.049	<0.038	0.06	0.09	<0.018	<0.090	1.24
14	242070	<0.024	<0.024	<0.016	0.29	0.28	<0.024	0.07	<0.24	<0.049	<0.038	<0.045	0.66	<0.018	0.33	1.70
15	241747	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	0.04	<0.24	<0.049	0.41	0.09	0.30	0.04	<0.090	1.30
16	242558	<0.024	<0.024	0.70	0.68	0.76	0.18	0.15	<0.24	<0.049	0.87	0.10	1.46	<0.018	0.36	1.33
17	242301	<0.024	<0.024	<0.016	<0.0083	0.49	<0.024	0.14	<0.24	0.08	0.40	0.12	0.32	<0.018	0.15	2.12
18[b]	242300	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	0.15	<0.24	<0.049	0.51	0.04	0.41	<0.018	0.59	<0.75
19	242065	<0.024	<0.024	0.57	0.38	0.67	0.28	0.24	<0.24	<0.049	0.19	<0.045	0.72	<0.018	0.22	<0.75
20	242066	0.10	0.17	0.14	0.08	0.07	0.04	<0.024	<0.24	<0.049	<0.038	0.06	0.19	<0.018	<0.090	<0.75
21	242890	<0.024	<0.024	0.48	0.50	0.59	0.18	0.15	<0.24	<0.049	0.25	0.16	1.70	<0.018	0.72	<0.75
22	242891	<0.024	0.57	0.25	0.18	0.16	<0.024	<0.024	<0.24	<0.049	0.07	<0.045	0.33	<0.018	<0.090	<0.75
23	241683	<0.024	<0.024	<0.016	0.45	0.71	0.22	0.18	<0.24	<0.049	0.23	<0.045	0.58	<0.018	0.36	<0.75
24	241684	<0.024	<0.024	<0.016	<0.0083	0.29	<0.024	0.05	<0.24	<0.049	0.48	<0.045	1.14	<0.018	0.40	<0.75
25	241685	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	0.06	<0.24	<0.049	0.20	<0.045	0.87	<0.018	0.12	<0.75
26	241755	<0.024	<0.024	<0.016	<0.0083	0.26	<0.024	<0.024	<0.24	<0.049	<0.038	<0.045	0.14	<0.018	<0.090	<0.75
27	241756	<0.024	<0.024	<0.016	0.46	0.35	<0.024	<0.024	<0.24	<0.049	0.59	0.07	1.18	<0.018	<0.090	<0.75
28[b]	241752	<0.024	<0.024	<0.016	<0.0083	<0.014	<0.024	<0.024	<0.24	<0.049	0.46	<0.045	0.92	<0.018	<0.090	<0.75

29	241753	0.30	0.27	0.16	0.06	<0.014	<0.024	<0.024	<0.24	<0.049	<0.038	0.06	0.46	<0.018	<0.090	<0.75
30	243142	0.23	0.11	0.06	<0.0083	0.03	<0.024	<0.024	<0.24	<0.049	<0.038	<0.045	0.42	<0.018	<0.090	<0.75
31	243141	0.44	0.15	0.10	0.04	0.03	<0.024	<0.024	<0.24	<0.049	<0.038	<0.045	0.16	<0.018	<0.090	<0.75

[a] PFBA, PFPeA, PFHxA, PFHpDA, PFDS, MeFOSA, EtFOSA, MeFOSE, EtFOSE, MeFOSAA, EtFOSAA, 8:2 FTSA, 10:2 FTSA. <x than the respective method detection limit (MDL). [b]Average of triplicates.