



Spatial distribution and load of per- and polyfluoroalkyl substances (PFAS) in background soils in Sweden

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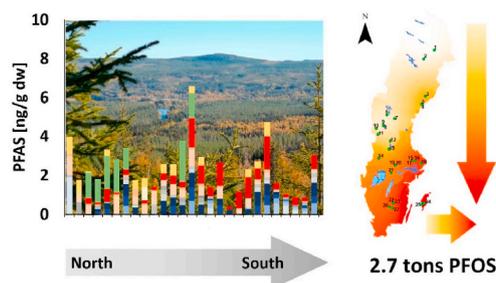
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HIGHLIGHTS

- PFAS were sampled in background forest soils across Sweden.
- PFAS occurred in every sample, with up to 16 of 28 target compounds detected.
- Detection frequency was highest for PFOS, PFBS, and PFUnDA (89%, 70%, and 70%).
- PFOS had a southward and eastward spatial gradient, explained by population density.
- Estimated total PFAS sink in soil was 2.7 tons PFOS and 16 tons of combined PFAS.

GRAPHICAL ABSTRACT



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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are known to be persistent, bioaccumulative, and have adverse health effects, but very little is known about PFAS in the terrestrial environment and factors influencing their distribution. This paper presents one of the first comprehensive studies investigating PFAS ($n = 28$) in background forest soils ($n = 27$) on national scale across Sweden. The results showed that 16 of 28 target PFAS were present and all sites contained at least three PFAS compounds, with total concentrations ranging between 0.40 ng/g dry weight (dw) and 6.6 ng/g dw. Perfluorooctanesulfonic acid (PFOS) showed the highest detection frequency of 89% and a median concentration of 0.39 ng/g dw. The PFOS loads (ng/m^3) showed a distinct spatial distribution, with a significant exponential increase from north to south ($R^2 = 0.55$; $p < 0.001$) and west to east ($R^2 = 0.35$; $p < 0.01$). In some parts of Sweden, the compound 6:2 fluorotelomer sulfonate (6:2 FTSA) had a higher median concentration (1.4 ng/g dw), but was in comparison to PFOS more impacted by local sources. Partial least squares discriminant analysis (PLS-DA) showed regional clustering of PFAS compositional profiles, indicating that PFAS soil background concentrations are functions of spatial variations at local, regional, and countrywide scale. Such spatial trends have not been observed previously and it could not be deduced whether they are indicative of trends on a global scale, or country-specific and better explained by proximity to densely populated urban areas. An interpolation and extrapolation raster map created from the results was used to calculate the average total PFAS load on Swedish soils. Estimated total load in the top 10-cm soil layer was 2.7 ± 2.4 tons for PFOS and 16 ± 14 tons for \sum PFAS, indicating that soil carries a considerable legacy of past PFAS release.

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) make up a diverse chemical group of highly fluorinated synthetic organic compounds (Ahrens, 2011) comprising >4700 species (OECD, 2018) with unique chemical characteristics (Buck *et al.*, 2011; Martin *et al.*, 2019). PFAS show high resistance to natural degradation (Ellis *et al.*, 2004; Lemal, 2004; Merino *et al.*, 2016; Yamada *et al.*, 2005) and are now commonly known as 'forever chemicals' (Turns, 2021). Because of their useful properties, including chemical stability and surfactant-like properties (hydrophobic characteristics with hydrophilic functional groups), PFAS have been produced in large quantities to support the growing demand 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; Herzke *et al.*, 2012; Schultes *et al.*, 2018). However, because of their environmental persistence and bioaccumulation in biota (Pan *et al.*, 2014; Rich *et al.*, 2015) and in humans (Gyllenhammar *et al.*, 2015), coupled with adverse health effects (DeWitt, 2015; Schrenk *et al.*, 2020), serious concerns have been raised regarding their use. Regulation of these substances is therefore underway (Ahrens and Bundschuh, 2014), including restrictions on the use of perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and their related salts under the Stockholm Convention on persistent organic pollutants (Stockholm Convention on Persistent Organic Pollutants, 2022).

The production and use of PFAS have led to their distribution in urban, rural and remote environment worldwide (Sima and Jaffé, 2021). Release of PFAS occurs during all stages of the product life cycle, from production through use until final disposal (Ahrens and Bundschuh, 2014). Emission sources can be both direct, i.e., discharge hotspots such as factories and firefight training sites using aqueous film-forming foam (AFFF), or diffuse, in the form of atmospheric deposition and urban surface run-off (Ahrens and Bundschuh, 2014; Davis *et al.*, 2007; Wang *et al.*, 2018). Even in remote areas, such as the Arctic and Antarctica, long range atmospheric air transport and subsequent wet and dry deposition is a likely source of PFAS contamination (Ellis *et al.*, 2004; Casal *et al.*, 2017).

The major exposure pathway for humans is through food and drinking water (European, 2012), for which soil contamination is a relevant source. Exposure through agricultural products has been highlighted in studies showing the global occurrence of PFAS contaminants on agricultural land and in drinking water when PFAS reach groundwater and surface waters from direct and diffuse sources (Dalahmeh *et al.*, 2018; Li *et al.*, 2019; Röhler *et al.*, 2021). Diffuse sources are difficult to manage. For example, estimated atmospheric deposition of PFOS and PFOA on coastal soils of the Bohai and Yellow Sea (China) accounts for 93% (>4400 kg) and 70% (>4300 kg), respectively, of the total amount of PFAS found in this urbanized area (Meng *et al.*, 2018).

While several previous studies have explored background concentrations in oceans, surface waters, and air, to our knowledge studies of background concentrations in soil are scarce and only a limited set of studies have considered soil background concentrations (Strynar *et al.*, 2012; Wang *et al.*, 2018; Rankin *et al.*, 2016). Most soil studies focus on contamination hotspots, urban areas, and agricultural land. PFAS concentrations in Nordic remote surface waters are suggested to be caused by infiltrating PFAS from surrounding soils (Filipovic *et al.*, 2015; Nguyen *et al.*, 2017; Junntila *et al.*, 2019).

The aims of this study were to investigate: (i) background PFAS concentrations in forest top soil ($n = 28$) in Sweden, (ii) PFAS spatial distribution; and (iii) to estimate total terrestrial deposited load, where the terrestrial soil acts as a PFAS sink.

2. Methodology

2.1. Standards

In total, 28 PFAS were targeted in the analysis: 11 perfluoroalkyl carboxylic acids (PFCAs) (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, and PFOcDA), four perfluoroalkyl sulfonic acids (PFSAs) (PFBS, PFHxS, PFOS, and PFDS), three perfluorooctanic sulfonamides (FOSAs) (FOSA, MeFOSA, and EtFOSA), two perfluorooctanic sulfonamidoethanols (FOSEs) (MeFOSE and EtFOSE), three perfluorooctanic sulfonamide acetates (FOSAA) (FOSAA, MeFOSAA, and EtFOSAA), and three fluorotelomer sulfonates (6:2 FTSA, 8:2 FTSA, and 10:2 FTSA) (Table S1 in Supporting Information (SI)). In addition, a mixture of 16 isotopically labeled internal standards (IS) was used, containing: $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_5$ -PFNA, $^{13}\text{C}_2$ -PFDA, $^{13}\text{C}_2$ -PFUnDA, $^{13}\text{C}_2$ -PFDoDA, $^{18}\text{O}_2$ -PFHxS, $^{13}\text{C}_4$ -PFOS, $^{13}\text{C}_8$ -FOSA, d_3 -MeFOSA, d_5 -Et-FOSA, d_3 -MeFOSAA, d_5 -EtFOSAA, d_7 -MeFOSE, and d_9 -EtFOSE (Table S2 in SI).

2.2. Sampling

In total, 27 sites were investigated and 31 samples were randomly collected (triplicates for two sites) from the Swedish Forest Soil Inventory 2017 (Nilsson *et al.*, 2017) (Table S3 in SI). The sampling locations were exclusively mature forest soils without any known local contaminant impacts. Sampling was performed in sub-sampling cross-hairs of five composite samplings (Figure S1 in SI), where the top 10 cm of the organic horizon (O-horizon) in the soil profile was sampled at each site, either collected by hand or cut out by knife. If the depth of the O-horizon was less than 10 cm, the whole horizon was sampled. All samples were stored in pre-rinsed 50 mL PP-tubes (rinsed 3 times with methanol) and on their return to the laboratory they were stored under dark conditions at -20°C until analysis.

2.3. PFAS analysis

PFAS analysis was performed in accordance with a previously validated method (Ahrens *et al.*, 2009) with some modifications and an extended cleanup step (for details, see text S1 in SI). In short, a two-step soil extraction was performed using ammonium hydroxide, methanol (MeOH), and spiking 100 μL of 0.05 $\mu\text{g}/\text{L}$ IS mixture in MeOH comprising individual PFAS. Samples were concentrated using nitrogen gas evaporation, followed by Millipore water dilution, cleanup using solid phase extraction (SPE) with WAX cartridges (Waters, 150 mg, 6 mL, 30 μm), elution with methanol and methanol plus 0.1% ammonium hydroxide, and again concentration with nitrogen gas, addition of Millipore water and finally filtration into injection vials. The instrument used for analysis was a DIONEX UltiMate 3000 ultra-performance liquid chromatography (UPLC) system (Thermo Scientific, Waltham, MA, USA) coupled to a triple quadrupole mass spectrometer (MS/MS) (TSQ QUANTIVA; Thermo Scientific, Waltham, MA, USA).

2.4. Quality assurance and quality control (QA/QC)

The method detection limit (MDL) for each PFAS was set to instrument detection level (IDL), which corresponded to the lowest point in the calibration curve where the average response factor did not deviate by more than 30%. If target compounds were detected in the laboratory blanks, MDL was set to the average blank concentration plus three times its standard deviation. PFAS blank concentrations were observed for PFBA, PFPeA, and PFHxA, with concentrations up to 3.8, 310, and 9.2 ng/mL, respectively, explaining the higher MDLs for these PFAS. Relative method recoveries were calculated from losses of IS instrumentation response (area of peaks) compared with the calibration curve. Recovery ranged between 5.2% (MeFOSE) and 66% (PFOS) (Figure S2 in SI). Although low recoveries were observed for some PFAS precursors, the

use of perfect matching IS and careful inspection of peaks allowed these substances to be included in the data evaluation. The relative average standard deviation for the two triplicate (site 12 and 15) samples was <30% for individual PFAS above MDL, with standard deviation ranging from 4.5% (FOSAA) to 30% (PFOS), Table S4, showing good reproducibility of the analytical method.

2.5. Calculations

Linear regressions and *t*-test of the slope of the regression lines between the independent coordinate variables and PFAS concentrations were performed. For multilinear and Gaussian regression, the Curve Fitting Tool in Matlab (R2017b) was used. SIMCA (SIMCA 14) was used for partial least squares discriminant analysis (PLS-DA), including biplots and dendrograms. ArcGIS and its kriging function was used for spatial analysis and estimation of total PFAS load in Swedish soils. Equation (1) was used for conversion of measured PFAS soil concentration [ng/g dw] to areal concentration [ng/m²], using bulk density (BD) [kg/m³] for calculation of dry matter in the 10 cm top soil layer (in accordance with sampling depth) per m² [kg/m²]:

$$C_{\text{PFAS soil;spatial}} \left[\frac{\mu\text{g}}{\text{m}^2} \right] = \text{BD} \left[\frac{\text{kg}}{\text{m}^3} \right] \times 0.1 \left[\frac{\text{m}^3}{\text{m}^2} \right] \times C_{\text{PFAS soil;measured}} \left[\frac{\mu\text{g}}{\text{kg}} \right] \left(\left[\frac{\text{ng}}{\text{g}} \right]^2 \right) \quad (1)$$

where BD was calculated from a numerical model based on organic carbon content (OC) [%] in Swedish forest soils (Eq. 16 in Nilsson and Lundin, 2006):

$$\text{BD} \left[\frac{\text{kg}}{\text{m}^3} \right] = \left(-0.0182 + \frac{5.2558}{\text{OC}} \right) \times 1000 \quad (2)$$

and where OC was measured from loss of ignition. For the total country load, BD was multiplied by Sweden's total land area of 450,295 km² (excluding lakes).

3. Results and discussion

3.1. PFAS concentrations in soil

Of the 28 PFAS analyzed, 16 were detected above MDL in at least one

sample (Fig. 1, Table S5 and Figure S3 in SI). Five analytes (PFOS, PFBS, PFUnDA, PFHxS, and PFTriDA) were quantified at detection frequencies >50% and were included in further statistical analyses (Section 3.2). The median sum of PFAS ($\Sigma_{16}\text{PFAS}$) was 2.3 ± 1.3 ng/g dw per site and ranged from 0.40 to 6.6 ng/g dw (at sites 18 and 14, respectively). All sites contained at least three species of PFAS, suggesting that PFAS are ubiquitously distributed in Sweden, which is in accordance with previous world-wide findings on similar PFAS at background levels in other environmental compartments such as oceans (Muir and Miaz, 2021) and air (Yamazaki et al., 2021). A previous study investigating water and soil from a pristine boreal forest in Sweden (close to sites 3–5 in this study) detected similar PFAS species as found in this study (9 out of 10), but in different composition profiles (e.g., PFOA >> PFOS compared with this study) (Filipovic et al., 2015).

From a meta-study on global scale (38 studies), PFOS and PFOA were found to have the highest detection frequencies in soil, and a median maximum concentration in background soil of 4.9 ng/g dw for both PFOS and PFOA was reported (Brusseau et al., 2020). Other studies have reported median PFOS and PFOA concentrations of 0.47 and 0.12 ng/g dw (Rankin et al., 2016), which are comparable levels to those found in this study (0.39 and 0.38 ng/g dw). Also the detection frequencies for PFOS and PFOA (48% and 22%, respectively) were similar to ours (89% and 19%, respectively), albeit somewhat lower for PFOS. On the other hand, ΣPFAS median concentrations (predominantly PFOS and PFOA) in background soils in China have been found to range between 2.8 and 14 ng/g dw (max. 64 ng/g dw) (Meng et al., 2018), which is higher than in this study. This can be explained by the higher population density and greater industrial areas in China than in Sweden.

Neither the median nor the maximum PFOS concentration exceeded the preliminary Swedish guideline value of 3.0 and 20 ng/g dw for sensitive and non-sensitive land use, respectively (Pettersson and Berggren Kleja, 2015). Use of PFOS and PFOA has been phased out in most countries worldwide (Land et al., 2018), indicating that further pure PFOS accumulation is less likely to occur. However, the risk of accumulation of PFOS precursors is still not well studied. Also, it is well known that other PFAS, both short-chain PFAS homologs and longer-chain precursors, have replaced PFOS and PFOA (Lu et al., 2019). This is reflected in findings in this study, where e.g., PFBS and FOSAA showed high detection frequency (70% and 44%, respectively), suggesting that PFAS deposition and accumulation in background soils

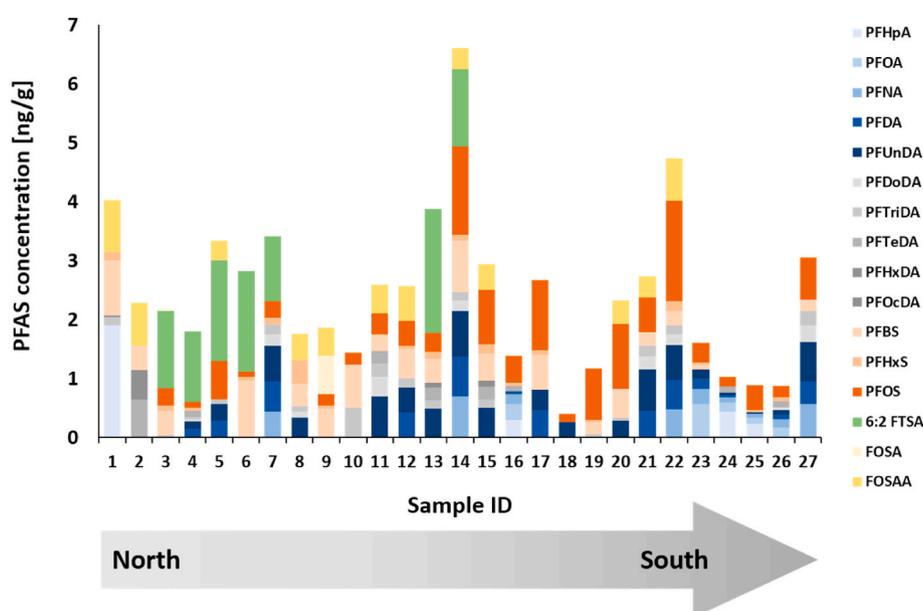


Fig. 1. Concentrations [ng/g dw] of PFAS detected in background soils (n = 27), Sweden. Sample ID numbers represent sites 1–27, arranged in order from north to south.

should be kept under surveillance in the future.

For the PFCAs, seven homologs were quantified at levels above the MDLs, with a noteworthy high prevalence of PFUnDA (detection frequency 70%). This high prevalence of PFUnDA differs from those found in previous studies of background soils, water, and air (Brusseau et al., 2020; Muir and Miaz, 2021; Yamazaki et al., 2021). The detection frequencies of the PFCAs correlated well with perfluorocarbon chain length by a Gaussian distribution, with the maximum at a perfluorocarbon chain length of 10 (PFUnDA) and 12 (PFTriDA), respectively ($R^2 = 0.78$) (Fig. 3). There was also a significant linear correlation ($n = 5$; $p < 0.1$) between detection frequency for perfluorocarbons with chain length C_6 to C_{10} and increasing detection frequency, by 12% per CF_2 moiety (Figure S4 in SI). On the other hand, PFASs did not show any such trend as observed for the PFCAs. The median concentrations of PFBS and PFHxS were low (0.33 and 0.052 ng/g dw, respectively), although the detection frequencies of PFBS and PFHxS (70% and 67%, respectively) were relatively high. This can be compared to a previous study in the USA with detection frequencies of 20% and 70% for PFBS and PFHxS, respectively (Rankin et al., 2016), and a global study which only detected PFHxS (20%) but no PFBS (Strynar et al., 2012).

Being a persistent precursor (Lu et al., 2017), the polyfluorinated 6:2 FTSA was only detected in certain parts of Sweden, at sites 3–7 and 13–14, but at relatively high concentrations (1.1–2.1 ng/g dw) in comparison with the other PFAS. The 6:2 FTSA concentration in drinking water in Sweden is regulated by the Swedish food agency (2009), but this compound has also been reported in soil and plants (Gobelius et al., 2017), wastewater (Yeung et al., 2016), and air (Ahrens et al., 2011). However, 6:2 FTSA has not been detected in major river estuaries in Sweden (Nguyen et al., 2017) but it has been detected at low levels in most Finnish river waters indicating long-range transport (Junttila et al., 2019).

3.2. Spatial distribution

For the spatial distribution analysis, PFAS soil concentrations [ng/g dw] were converted into total amount per square meter [ng/m²] representing the top 10-cm soil layer, taking into account the bulk density [kg/m³] and organic carbon content (Eq. (1)) and normalizing to absolute PFAS amount per area unit [ng/m²] (Eq. (2)). The median Σ PFAS load was 28,000 ng/m² per site, while the median load of PFOS and PFUnDA was 6600 and 3600 ng/m², respectively (Table S6 in SI). Spatial distribution analysis was performed on PFAS with detection frequency of >50%, comprising PFOS, PFBS, PFUnDA, PFHxS, PFTriDA and Σ PFAS, in relation to latitude and longitude coordinates (SWEREF99 coordinate system), for which both are two independent values suitable for correlation analysis. In the correlation analysis, only PFOS, PFBS, PFUnDA, PFHxS, and PFTriDA were included and values < MDL were replaced with half MDL.

The PLS-DA biplot analysis, based on logarithmic values, clearly indicated a north to south gradient for the target PFAS, with PFOS and PFUnDA as the models' most important variable, while the response on a west to east gradient was negligible (Figure S5 in SI). On excluding the two northernmost data points (sites 1 and 2), the north to south gradient remained intact, but in addition a west to east gradient emerged (Figure S2 in SI). This suggests that the PFAS load per square meter increases towards the south of Sweden, while the trend of increasing PFAS concentrations from west to east is limited to southern Sweden. However, more studies are needed to determine the spatial distribution of PFAS in background soils, in particular in coastal areas of both southern and northern Sweden, for which this study provided limited data. Following the trend from north to south, the PLS-DA clustered sites: [1–2], [3–5], [6–11], [12–14], [19–21], [15–18], [22–23, 26–27], and [24–25], and confirmed the trend from west to east (Figure S6 in SI).

Determining the PFAS composition profile is referred to "PFAS fingerprinting" (Möller et al., 2010). The biplot cluster patterns showed that PFAS occurrence and environmental fate had a three-dimensional

spatial pattern, influenced by local, regional, and national sources and transport (Fig. 2). Correlation analysis based on the biplot showed that the logarithmic total amount per square meter was linearly correlated with logarithmic latitude and longitude (Fig. 3). Also, PFOS and PFUnDA showed a significant linear correlation ($R^2 = 0.55$; $p < 0.001$ and $R^2 = 0.36$; $p < 0.001$, respectively) with increasing load from north to south (latitude), both varying exponentially by over three orders of magnitude, Fig. 3. As seen in the biplot, PFOS also showed a significant linear trend on the log scale of total amount per square meter from west to east (longitude) ($R^2 = 0.35$; $p < 0.01$), and a north to south gradient ($R^2 = 0.69$; $p < 0.001$) (Figure S7 in SI). No significant linear correlations on the log scale were found for the other high detection frequency PFAS (i.e., PFBS, PFHxS, PFUnDA, etc.). A trend of increasing concentrations from north to south in Sweden has already been reported for the estuaries of major Swedish rivers, where it has been explained by population density and also possibly by differences in soil background contamination from atmospheric deposition (Nguyen et al., 2017), as confirmed in this study. Elevated levels of other airborne pollutants in Sweden, e.g., sulfate, ammonium, and nitrate, show a similar north to south spatial distribution, which has also been explained by closer proximity to urban areas, in Sweden (SCB, 2021) and adjacent countries (Ferm et al., 2019). PFOS followed the same spatial trend as these other airborne pollutants, which indicates that the background concentrations of PFOS also originate from atmospheric deposition. Consequently, wind direction has been shown to influence deposition of other organic pollutants in the Nordic region, i.e., dioxins, furans, and polychlorinated biphenyls (Backe et al., 2002; Korhonen et al., 2016). However, those airborne pollutants show an opposing trend to that seen here for PFOS, with decreasing concentrations from west to east (longitude). In addition, sea water along the Swedish southwestern coast shows considerably higher concentrations of Σ PFAS compared with the northeastern coast of the Baltic Sea (Nguyen et al., 2017). Thus, the spatial distribution of PFOS from west to east (longitude) needs to be more thoroughly investigated in future studies.

In general, identifying main deposition pathways of PFAS from the atmosphere is challenging. A previous study from the US has showed that PFAS atmospheric deposition mainly was attributed to wet deposition, while dry deposition was relatively minor (one order of magnitude lower) (Shimizu et al., 2021). Precipitation volumes over Sweden have relatively low spatial variability (Figure S8, SMHI, 2022); hence, variability in spatial distribution cannot be attributed to variation in rain- and snowfall amounts. Instead, source areas and transport

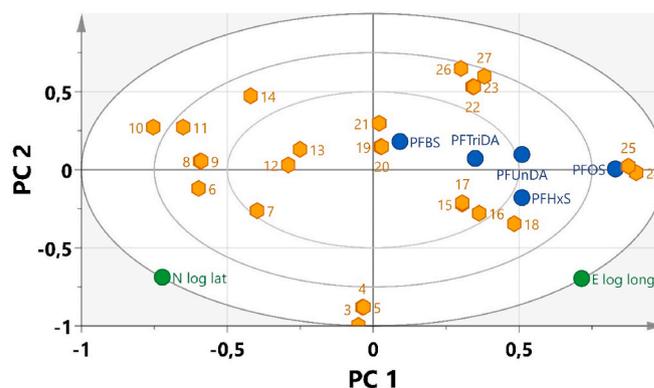


Fig. 2. Biplot of results of partial least squares discriminant analysis (PLS-DA) using logarithmic latitudinal northward (N log lat) and longitudinal eastward (E log long) coordinates as x-variable (green) and PFAS concentrations [μ g/m²] as y-variables (detection rates >50% encompassing PFUnDA, PFTriDA, PFBS, PFHxS, and PFOS) based on analyzed sites 3–27 (northernmost sites 1–2 were excluded as outliers, see Fig. 5 in SI) (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

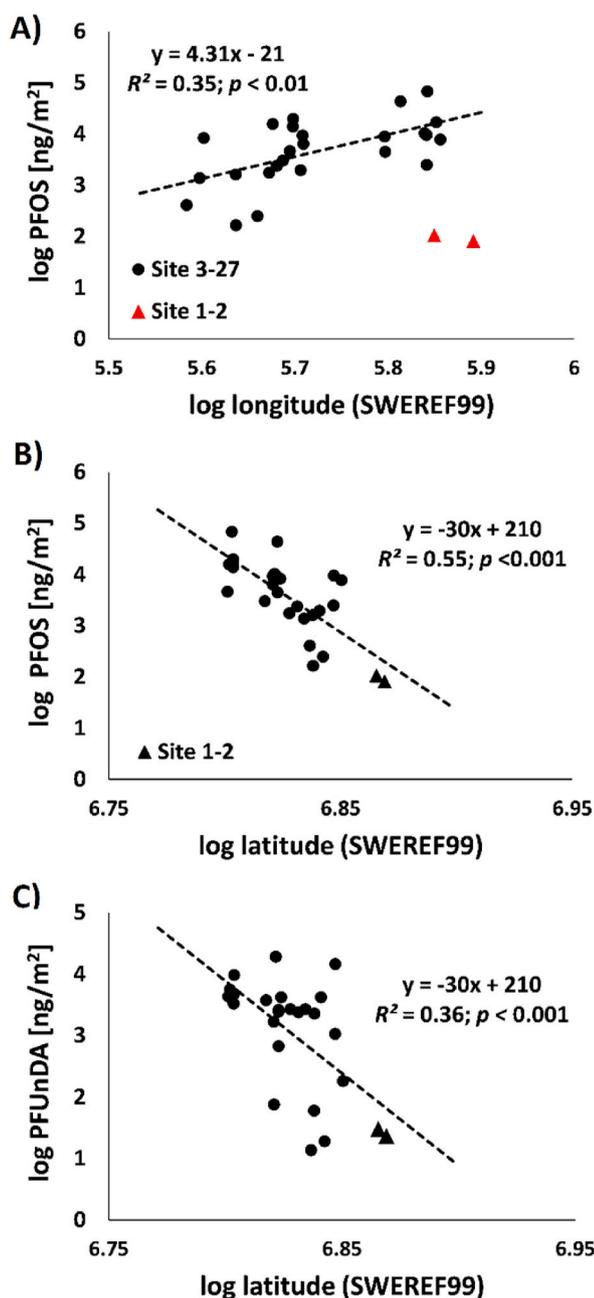


Fig. 3. Logarithmic (log) PFOS and PFUnDA concentrations [ng/m^2] as a function of the independent variables log longitude and latitude, respectively. For longitudinal regression of PFOS (A), the northernmost sites 1 and 2 were excluded (red triangles as outliers). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

pathways may have an important impact of spatial variability of air concentrations and subsequent atmospheric deposition of PFAS. Previous studies on PCDD/Fs have shown that air mass origins largely determines air concentrations and profiles of these substances in Baltic Sea air (Sellström et al., 2009; Assefa et al., 2018) and an in depth deposition source tracing study on particulate matter >2.5 nm and aerosols identified eastern continental Europe as the main (but not only) source of the pollutants (Jönsson et al., 2013). On the other hand, PFAS with its unique physiochemical properties and sources may not follow the same transport mechanisms as either PCDD/Fs or particulate matter >2.5 nm. Shimizu et al. (2021) concluded that PFAS transition into water droplets is fast for PFAS, which resulted in high washout affects by precipitation

and no correlation with air mass origin was found. Yet another recent study showed that the influence of PFAS in sea spray aerosols from the Norwegian Sea had a significant impact on PFAS air concentrations on the Norwegian coast affecting air concentrations 300 km inland, respectively (Sha et al., 2022). Some of our sampling sites are within this distance from the sea, and may have been affected by PFAS in sea spray. Ultimately, previous studies show that atmospheric source tracing of PFAS is challenging and not well understood. Based on limitation in the type of data in this study, specific sources or air mass origins and how they play a role in the spatial variability observed in this study cannot be investigated in detail.

A large number of PFAS have not yet been identified or are not analyzed using routine target methods for PFAS using LC-MS/MS, but are known to be present from total oxidizable precursor assay analysis (TOP) (Houtz et al., 2013). By using this TOP method, the PFAS precursor proportion was up to 53% in precipitation in China (Chen et al., 2019). The precursor fraction will eventually degrade into the persistent PFCAs and PFSAs, and 6:2 FTSA and FOSAA were two such precursor compounds identified in this study. Furthermore, ultra-short chained PFCAs (C_2 – C_3) was overlooked in this study, but has been shown to account for 22–91% (including TOP assay) and 58–92% (excluding TOP assay) in China and in Sweden (Chen et al., 2019; Jansson, 2019). Still, more studies are needed to fully understand the distribution and transport of PFAS in different environmental compartment.

3.3. National load

To assess the total load in Sweden from background soil levels based on spatial variations (Fig. 4), a geographical map was created using kriging interpolation and extrapolation to form a raster where the PFAS concentration [$\mu\text{g}/\text{m}^2$] was calculated for each grid cell. Concentrations below MDL were not included in order to avoid overestimating the total load. The load of PFOS and Σ PFAS in Sweden was estimated to be $2.7 \pm$

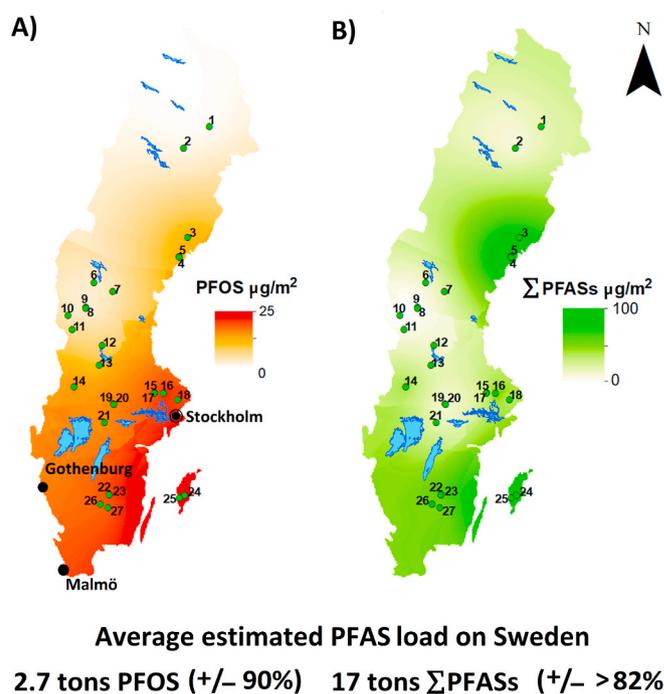


Fig. 4. Interpolated and extrapolated raster maps of background concentrations above the detection limit [$\mu\text{g}/\text{m}^2$] in Swedish soils at sites 1–27 of: A) PFOS (red) and B) Σ PFASs ($n = 16$) (green). Average estimated load was calculated from average grid cell value over the area of Sweden (450,000 km^2). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2.4 tons for PFOS (standard deviation (SD) based on the arithmetic mean from spatial kriging SD and measurement SD from triplicates) and $16 \pm >14$ tons for Σ PFAS. This shows that the terrestrial land mass is a considerable sink of PFAS and can be expected to remain so for a long period, impacting ecosystems (Rich et al., 2015). In addition, terrestrial environments can act as a source of PFAS and release them into the aquatic environment, impacting aquatic ecosystems (Ahrens et al., 2015; Koch et al., 2021). It should be noted that the standard deviations were high, indicating that the national load estimates were rough because the assessments were based on only 27 samples. In particular, the two northern sites (1–2) represented a very large area with high uncertainty, e.g., PFHpA showed a high concentration at site 1 (1.9 ng/g dw) compared with site 2 (<MDL ng/g dw) although their close proximity to each other. For comparison, PFOS and PFOA loads of 4.3 and 4.4 tons, respectively, have been estimated by calculations in background soils in China (Meng et al., 2018), representing an area of 213,000 km² (47% of Sweden's area), giving a 3.3-fold higher PFOS load than in this study. Moreover the PFOS concentration in background soils in China is 10- to 20-fold higher than in this study, which indicates that the method used for total spatial load estimation has a large impact on the results (although the methodology used in Meng et al., 2018 is not specified). More studies with higher sampling density are needed for validation.

PFAS concentrations in background soil were affected by deposition on local, regional and national scales indicating that PFAS pollution come from both short and long range atmospheric transport. However, because of limitations in this study, deposition mechanisms could not be elucidated, and future studies is required addressing knowledge gaps in source tracing. Although, this study included a wide range of PFAS ($n = 28$), there exist a large number of other PFAS and transformation products which were not included in this study (Barzen-Hanson et al., 2017). In addition, the calculation of the total PFAS load was a rough estimate (e.g. limited number of sites) and the mathematical calculations used both interpolated values over large distances (i.e. between sites 2–3 and 2–6) and large areas extrapolated values in both south-western and northwestern Sweden. A higher resolution and complete coverage sampling is therefore needed for a more accurate assessment. Because of unique conditions in Nordic countries, it is not certain that our results directly can be transferred to other regions.

4. Conclusions

For the first time a wide spectrum of PFAS ($n = 28$), including both short-to long-chained PFAS as well as some PFAS precursors, were analyzed on a national level in background soils. The most widely occurring PFAS based on average concentrations was PFOS, followed by PFUnDA. Considering the sum of the 16 detected PFAS, the Σ PFAS concentration was four-fold higher than for the commonly detected PFOS, which shows the importance of including a wide spectrum of PFAS of concern in future studies. The spatial distribution of PFOS and PFUnDA showed increasing concentrations from north to south, but concentrations increased from west to east only for PFOS in southern Sweden. Moreover, Σ PFAS and other target PFAS did not show this spatial trend. Very few studies have examined PFAS in background soil on national scale, and thus more studies are needed to confirm the spatial trends observed in this study. The estimated total load of PFAS in Swedish soils was 2.7 tons PFOS and 16 tons Σ PFAS, indicating that background terrestrial soil is a sink of PFAS and a potential source of release to the terrestrial and aquatic environment.

Author contributions statement

Söregård Mattias: Was the main author and managed data analysis and formation of hypothesis and response to them; Johannes Kikuchi: Laboratory analyses, method developments and data analysis; Karin Wiberg: Project management and study design, Ahrens Lutz: Project

management and study design.

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.2022.133944>.

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