

## PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs) IN SWEDISH RIVERS AND RECIPIENT SEAS

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### Introduction

Per- and polyfluoroalkyl substances (PFASs) are synthetic chemical substances that have been produced and used intensively all over the world since the 1950s<sup>1,2</sup>. PFASs have both hydrophobic and hydrophilic properties and are used as surfactants in, for example, textiles, carpets, leather, paper products, and fire-fighting foams<sup>3,4</sup>. They are chemicals of concern due to their extreme persistence, bioaccumulative potential, and toxicity<sup>5,6</sup>. The sign of carcinogenic and endocrine disrupting toxicity of PFASs has been reported for wildlife and humans, and their toxicity has been shown to increase with chain length<sup>7,8</sup>. Perfluoroalkyl sulfonates (PFASs) are found to be more toxic in comparison to perfluoroalkyl carboxylates (PFCAs)<sup>7,8</sup>. PFASs can undergo long-range transport from point and diffuse sources to remote areas through the atmosphere and water currents<sup>3,9</sup>. As a consequence, PFASs are ubiquitously distributed in the abiotic environment, wildlife and humans<sup>1,10,11</sup>.

Several studies have focused on PFASs in river water, finding concentrations up to 1400 ng L<sup>-1</sup> for  $\Sigma$ PFASs<sup>12-15</sup>. Organic pollutants are eventually transported into sea bodies<sup>16</sup>, where the Baltic Sea has been shown to be one of the most contaminated seas globally<sup>17</sup>. A mass balance study indicated that atmospheric deposition is the dominant contamination source<sup>18</sup>, however, this is in contradiction with other studies indicating that effluents from sewage treatment plants (STPs) are dominant sources<sup>19</sup>. The Baltic Sea, located in Northern Europe, is an ideal study area for source apportionment studies due to its large influence by rivers (catchment area of 1 720 270 km<sup>2</sup>), draining an area populated by 85 million people, and its semi-closed character with a limited water exchange with surrounding seas (Kattegat, Skagerrak, and North Sea)<sup>20</sup>.

The objectives of this study were to *i*) investigate spatial variation and composition profiles of PFASs in 41 Swedish rivers and the receiving Kattegat Sea (Swedish west coast) and Baltic Seas (Swedish east coast), *ii*) estimate fluxes of PFASs into the recipients and compare with modelled data, and *iii*) investigate possible correlating factors (dissolved/total organic carbon (DOC/TOC), catchment size, flow, latitude, population density, run off, salinity, sewage density, total population, total sewage treatment, water temperature) with PFASs concentrations to trace their sources.

### Materials and methods

Native PFASs standards including C<sub>4</sub>-C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub> PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrIDA, PFTeDA, PFHxDA, PFOcDA), C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub> PFASs (PFBS, PFHxS, PFOS, PFDS), 6:2 fluorotelomer sulfonate (6:2 FTSA), perfluorooctanesulfonamide (FOSA), *N*-alkyl(C1,C2)-FOSA (MeFOSA, EtFOSA), 2-(perfluorooctanesulfonamido)acetic acid (FOSAA), 2-(*N*-alkyl-FOSAA (MeFOSAA, EtFOSAA), *N*-alkyl perfluorooctane sulfonamido ethanol (MeFOSE, EtFOSE) were used for making calibration curve. The internal standard solution (IS) included 16 mass-labeled [<sup>13</sup>C] compounds: [<sup>13</sup>C<sub>4</sub>]-PFBA, [<sup>13</sup>C<sub>6</sub>]-PFHxA, [<sup>13</sup>C<sub>4</sub>]-PFOA, [<sup>13</sup>C<sub>9</sub>]-PFNA, [<sup>13</sup>C<sub>10</sub>]-PFDA, [<sup>13</sup>C<sub>11</sub>]-PFUnDA, [<sup>13</sup>C<sub>12</sub>]-PFDoDA, [<sup>13</sup>C<sub>8</sub>]-FOSA, [d<sub>3</sub>]-MeFOSAA, [d<sub>5</sub>]-EtFOSAA, [d<sub>3</sub>]-MeFOSA, [d<sub>5</sub>]-EtFOSA [d<sub>7</sub>]-MeFOSE, [d<sub>9</sub>] N-EtFOSE, [<sup>18</sup>O<sub>2</sub>]-PFHxS, [<sup>13</sup>C<sub>4</sub>] PFOS, and the injection standard (InjS) included [<sup>13</sup>C<sub>8</sub>]-PFOA. All mass labelled and reference compounds were purchased from Wellington laboratories, Ontario, Canada.

Water samples were collected in October 2013 from 44 sampling sites representing 41 rivers from Haparanda (Torne älv) in the north to Kristianstad (Helge Å) in the south of Sweden along the east coast and some additional samples from the Swedish west coast. Additionally, 3 upstream sites were included (Vindelälven – a tributary to Ume River, Ume River at Gubböle and Göta River near Trollhättan). Seawater samples were collected in the Baltic Sea during a cargo ship tour (TransPaper cargo ship) in August-September 2013 at 14 off-shore sites, starting at the west coast (Kattegat Sea, *n*=4) and then going east and north in the Baltic Sea covering

the Baltic Proper ( $n=7$ , south), the Bothnian Sea ( $n=4$ , central), and Bothnian Bay ( $n=5$ , north). Samples were collected in pre-cleaned (MeOH) 1 L polypropylene (PP) bottles. In the field, the bottles were rinsed three times with sea water prior to sampling. Temperature, pH, and conductivity were measured at each sampling site. Suspended particulate matter (SPM) was measured in the laboratory. Directly after sampling, the bottles were kept dark and cool (on the ship), and at arrival to the laboratory, they were stored at +4°C until analysis (within 4 weeks).

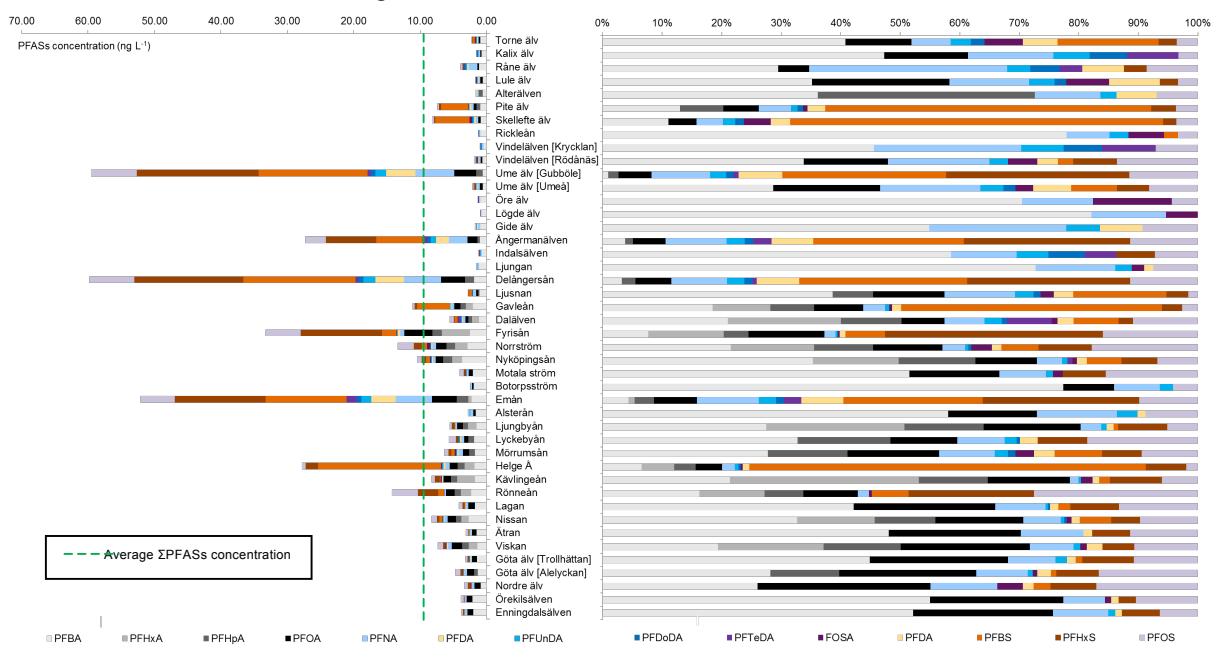
The samples were filtrated using pre-weighed glass microfiber filters (Whatman GF/F; diameter 47 mm, 0.7  $\mu\text{m}$  pore size) and glass filtration equipment under vacuum. Prior to filtration, the glass material and the GFFs were heated at 400°C overnight. Glass material was then cleaned with MeOH. After filtration, the filters were placed in a vacuum desiccator overnight to remove water and thereafter weighed to determine the amount of SPM. Filters were then stored in freezer until extraction. Prior to extraction, each filter and filtered water sample were spiked with 100  $\mu\text{L}$  of the internal standard mix (IS, 20  $\mu\text{g L}^{-1}$ ).

For the dissolved phase, solid phase extraction (SPE) was performed for all samples using Oasis weak anion exchange (WAX) cartridges (6cc, 500 mg, 60  $\mu\text{m}$ ) as described previously by Ahrens et al. (2009)<sup>21</sup>. For the particle phase, all GFFs were extracted with MeOH 3 times in pre-cleaned (MeOH) 15 mL PP tubes. The first extraction was performed by shaking with 6 mL of MeOH for 30 minutes. The second and third extractions were carried out by shaking with 4 mL of MeOH for 15 minutes each time. The combined extracts were concentrated to approx. 1 mL by a gentle stream of nitrogen ( $\text{N}_2$ ) followed by rinsing 1 time with MeOH before centrifugation at 3000 rpm for 5 minutes. The extracts were then transferred to 1 mL glass vials before further solvent reduction to 1 mL.

Before instrumental analysis, each of the extracts was spiked with 10  $\mu\text{L}$  of InjS (200  $\mu\text{g L}^{-1}$ ). In total, 25 PFASs were analyzed using high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS; Agilent Technologies LC 1200 series coupled to 6460 Triple Quad system) as described by Ahrens et al. (2009)<sup>3</sup>. A calibration curve with 6 calibration solutions at concentrations 0.05, 0.25, 1.0, 4.0, 8.0 and 40  $\text{ng mL}^{-1}$  was used. The isotope dilution method was applied for the quantification of PFASs using Agilent QQQ Mass Hunter software. Statistical calculations were performed using SIMCA<sup>®</sup> software (Umetrics AB).

## Results and discussion

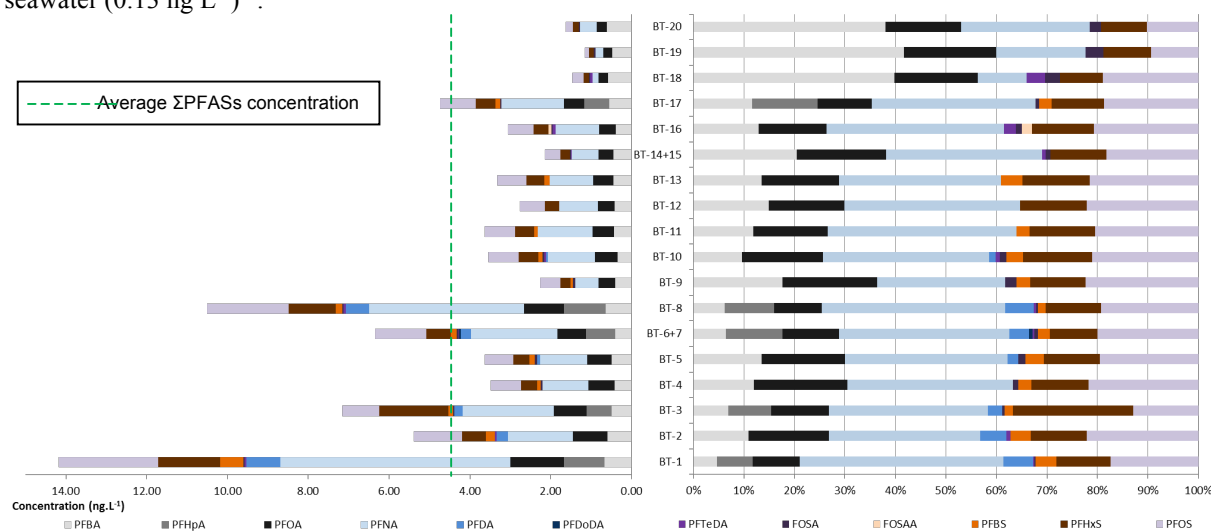
Out of 25 analyzed PFASs, including current use and banned substances, 15 were detected at all sites including rivers, the Baltic Sea and the Kattegat Sea.



**Figure 1.** Levels ( $\text{ng L}^{-1}$ ) and composition of PFASs in 44 Swedish river samples (representing 41 rivers) from north (upper) to south (lower) along the Swedish east coast until Helge å, then the Swedish west coast from south to north

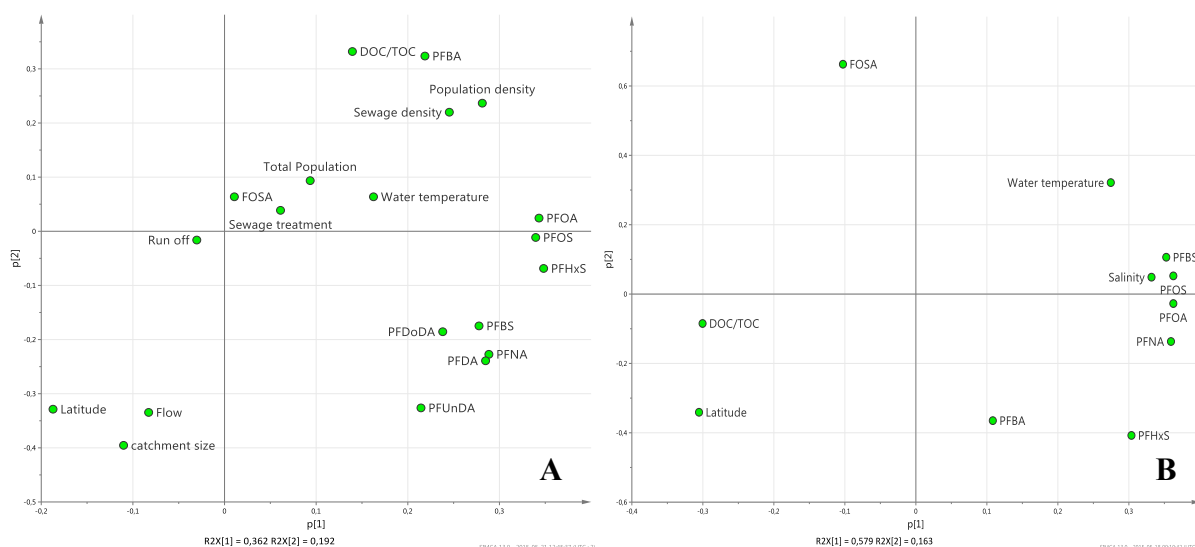
Rivers in the north generally showed lower levels of PFASs than in the south (Figure 1). These northern rivers showed generally higher fractions of long chained PFCAs (i.e. 9, 10, 11, 12, and 14 carbons) than the southern, which instead showed higher fraction of PFCAs with a chain length of 6-8. The average  $\Sigma$ PFAS concentration in the rivers was  $9.9 \pm 14 \text{ ng L}^{-1}$  with PFBS, PFHxS, and PFBA as the compounds with highest average levels. At 12 river sites, the PFOS levels exceeded the European annual average environmental quality standard (AA-EQS) for river water ( $0.65 \text{ ng L}^{-1}$ )<sup>22</sup>. The total riverine input of  $\Sigma$ PFASs from the investigated Swedish rivers ( $n=41$ ) into recipient seas was  $3.2 \text{ kg day}^{-1}$  ( $1190 \text{ kg yr}^{-1}$ ).

A similar concentration trend was observed in the sea water areas, where the levels of PFASs were generally lower in the northern subbasins of the Baltic Sea than in Baltic Proper and the Kattegat Sea (Figure 2). The average  $\Sigma$ PFAS level in the sea water ( $4.5 \pm 3.3 \text{ ng L}^{-1}$ ) was approximately half compared to the rivers. Out of 18 sites in the Baltic Sea and Kattegat Sea, almost all ( $n=17$ ) exceeded the AA-EQS standard for PFOS in seawater ( $0.13 \text{ ng L}^{-1}$ )<sup>22</sup>.



**Figure 2. Levels and compositions of PFASs in the Kattegat Sea (BT-1(north) to BT-4(south)) and Baltic Sea (BT-5(south) to BT-20(north))**

A principle component analysis (PCA) was performed to investigate the relation between potential correlating factors (DOC/TOC, catchment size, flow, latitude, population density, run off, salinity, sewage density, total population, total sewage treatment, water temperature) and PFAS concentrations (PFAS substances with a detection frequency <50% were excluded).



**Figure 3. Principle component analysis (PCA) of potential correlating factors and PFAS concentrations (log-transformed) in (A) river and (B) seawater samples**

It was observed from the river study (Figure 3A) and the Baltic and Kattegat Sea study (Figure 3B) that most of the PFASs (except for FOSA) are negatively correlated to latitude, which shows that at lower latitude (southern, more populated areas) have higher PFAS water levels than the northern areas. In the river study, it can be seen that the highly used PFOS (Stockholm Convention (SC), Annex B) and PFOA (on the EC watch list) are positively correlated with e.g. 'population density' and 'sewage density', demonstrating that although restricted, these two PFASs can still be predicted from human activities. PFBA is the substance with strongest correlation to population density indicating contemporary usage of PFBA containing products. PFBA also shows a strong correlation to DOC/TOC in the rivers, which indicates a different mechanism of transport compared to the other investigated PFASs.

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