

Fingerprinting PFAS pollution in European surface waters

Robin Schröder^{a,*}, Jens Prothmann^b, Tobias Licha^b, Hans H. Dürr^a, Martina Flörke^a

^a*Engineering Hydrology and Water Resources Management, Faculty of Civil and Environmental Engineering, Ruhr University Bochum, Universitätsstraße 150, 44801 Bochum, Germany*

^b*Hydrogeochemistry & Hydrogeology, Institute of Geosciences, Ruhr University Bochum, Universitätsstraße 150, 44801 Bochum, Germany*

Abstract

Per- and polyfluoroalkyl substances (PFAS) comprise a large group of synthetic chemical substances used across industries and find application in a diverse range of consumer products. Owing to their ubiquitous use and ongoing emissions, such substances are distributed throughout the environment. PFAS and their metabolites pose considerable risk to environmental and human health due to their high persistence, toxicity, and bioaccumulation. However, PFAS in European surface waters have not been systematically investigated across multiple substances. We compiled and harmonised daily concentration data from multiple open data sources for the years 2019 to 2026, comprising 1,907,309 samples from 9,072 sites and 34 substances. We used factor-rotated principal component analysis and hierarchical clustering to characterise co-occurrence patterns, identified hotspots as nearby clusters of samples above substance-specific 85th-percentile concentrations, and screened potential ecological risk. Recurring co-occurrence patterns involved short-chain perfluoroalkyl carboxylic acids (PFCAs), PFOS and PFHxS, PFBA and PFBS, and the long-chain PFCA pair PFNA and PFDA. TFA and HFPO-DA showed relatively distinct loading patterns, indicating that their co-occurrence profiles differed from those of other compounds in the analysis. Potential hotspots involving multiple compounds were identified in Belgium, Germany and Italy. These findings illustrate the complexity of PFAS co-occurrence patterns in European surface waters and support the need for coordinated monitoring that includes both legacy and emerging substances. The patterns identified here can inform future research, while source attribution should be treated as tentative because co-occurrence patterns alone do not establish sources or pathways.

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*Corresponding author

Email address: robin.schroeder@hydrology.ruhr-uni-bochum.de (Robin Schröder)

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) represent a diverse class of synthetic organic substances that have been manufactured and widely used since the 1940s due to their unique properties, such as high thermal and chemical stability (Buck et al., 2011; Evich et al., 2022). This stability is attributed to the strong carbon-fluorine bond of its fluorinated perfluorocarbon chain (Cousins et al., 2020). Due to their high hydrophobicity, oleophobicity and heat tolerance, PFAS are used in various industries and consumer products (Glüge et al., 2020). Common applications include manufacturing of Aqueous Film-Forming Foams (AFFFs), semiconductors, surface coatings, surfactants, paper production, and wood processing as well as their incorporation in household appliances and food packaging (Glüge et al., 2020; Sunderland et al., 2019). Most impactful industries concerning PFAS pollution are metal, advanced electronics, textile, and polymer industries (Kim et al., 2021).

The environmental fate and transport of PFAS are influenced by their chemical structure, particularly perfluorocarbon chain length and isomer configuration (Ateia et al., 2019; Nguyen et al., 2020; Ohoro et al., 2024; Conder et al., 2008). For instance, perfluorosulfonic acids (PFSAs) tend to sorb more strongly to organic carbon than to perfluorocarboxylic acids (PFCAs) of equal chain length (Higgins and Luthy, 2006), and linear isomers were found to be more sorptive than their branched counterparts (Kärman et al., 2011). Additionally, PFAS with a sulfonic acid functional group (PFSAs) tend to be more readily bioaccumulated than substances with a carboxylic acid group (PFCAs) of the same perfluorocarbon chain length (Conder et al., 2008). Perfluoroalkyl acids (PFAAs), i.e. PFCAs and PFSAs, are generally categorised according to their perfluorocarbon chain length. Long-chain substances refer to PFCAs with 7 or more perfluorocarbons and PFSAs with 6 or more perfluorocarbons. Short-chain PFAS refer to molecules with fewer perfluorocarbons, respectively (OECD). PFAS with three or less carbon atoms are commonly referred to as ultrashort-chain (Neuwald et al., 2022).

Major emission sources of PFAS into the environment include wastewater treatment plants (WWTPs), landfills, textile and leather industries, chemical industries producing PFAS as well as AFFF-related sites such as firefighting activities and military or civilian airports (e.g. Li et al., 2023; Röhrig et al., 2026; Beggs et al., 2023; Ankley et al., 2020; Ackerman Grunfeld et al., 2024; Kurwadkar et al., 2022; Stoiber et al., 2020; Moneta et al., 2023). Volatile PFAS precursors can undergo atmospheric oxidation to form PFAAs, including trifluoroacetic acid (TFA), which can subsequently be deposited from the atmosphere, explaining a large fraction of TFA inputs to surface waters (Freeling and Björnsdotter, 2023; Björnsdotter et al., 2022). In marine environments, sea-spray aerosols can transfer PFAAs from seawater into the atmosphere, where

they may be transported inland over long distances before deposition (Sha et al., 2022). PFAS have the potential to contaminate groundwater, surface water and subsequently drinking and irrigation water sources (Ackerman Grunfeld et al., 2024; Ankley et al., 2020). Industrial and municipal wastewaters are commonly treated in WWTPs. However, conventional treatment processes do not eliminate PFAS, while advanced techniques’ elimination rates are also low, especially for ultrashort- and short-chain substances. Instead, some substances are transformed into other PFAS, making WWTPs secondary sources, whereas others sorb to sewage sludge (Kurwadkar et al., 2022; Brunn et al., 2023; Stoiber et al., 2020; Moneta et al., 2023). Sewage sludge is usually incinerated, where some PFAS are thermally destroyed (Stoiber et al., 2020) or applied as fertiliser to agricultural fields, where PFAS can leach into groundwater or be carried into nearby rivers via surface runoff (Ankley et al., 2020; Behnami et al., 2024). Rain events may lead to resorption, resuspension and mobilisation of certain PFAS altering the chemical composition of surface runoff (Codling et al., 2020; Kali et al., 2025).

Due to their widespread occurrence, humans are exposed to PFAS through multiple concurrent pathways, including inhalation, dermal contact, and ingestion of contaminated food and water as well as maternal transfer during pregnancy and breastfeeding (Arnesdotter et al., 2025; Ghisi et al., 2019). Exposure to such substances has been linked to multiple adverse health outcomes for both aquatic and terrestrial organisms (Byns et al., 2022). Beyond the immediate risks to human health, the widespread emission and transport pathways are also posing a threat to aquatic organisms and ecosystems. Long-chain PFAS such as perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are generally considered particularly relevant for bioaccumulation and ecological risk, whereas short-chain PFAS are often more mobile and may be less strongly retained by organisms and sediments as well as artificial barriers such as WWTPs (Brunn et al., 2023; Rüdél et al.). Nevertheless, their higher mobility and frequent occurrence, together with the limited toxicological information available for many emerging PFAS and precursors, complicate an assessment based only on legacy substances, i.e. PFOA and PFOS, (Li et al., 2023; Röhrig et al., 2026). The large number of substances and their potential co-occurrence further challenge substance-specific risk assessment, highlighting the need for multi-substance monitoring and spatially resolved evaluations of PFAS contamination in aquatic ecosystems.

Numerous studies have reported the environmental presence of PFAS in European freshwater systems, along with their associated emissions and pathways. Since the regulation of PFOS and PFOA in the 2000s, PFAS contamination in European surface waters has been characterised by a transition to alternative substances, such as short-chain PFAAs, fluorotelomersulfonic acids (FTSs), perfluoroalkane sulfonyl fluorides (PASFs), and perfluoroalkylether carboxylic acids (PFECAs) (Li et al., 2023; Beggs et al., 2023; Giglioli et al., 2023; Zarebska et al., 2024; Gebbink et al., 2017). Among these, short-chain alternatives, such as perfluorobutanoic acid (PFBA) and perfluorobutane sulfonic acid (PFBS), often dominate (Röhrig et al., 2026; Giglioli et al., 2023; Gebbink et al., 2017; Zareb-

ska et al., 2024). However, the dominance of PFBA and PFBS may be an artifact of analytical limitation as recent studies have shown that ultrashort-chain TFA often exhibit concentrations multiple orders of magnitude higher than other regularly monitored PFAS (Röhrig et al., 2026; Björnsdotter et al., 2019), indicating potentially substantial contributions to total PFAS loads. While legacy PFAS show declining concentrations, they remain frequently detected in surface waters (Beggs et al., 2023; Zarębska et al., 2024; Röhrig et al., 2026) indicating ongoing emissions or precursor transformation. Against this background, reported ecological risks vary considerably among PFAS and monitoring locations. Although risk is reported to be low for many substances, PFOS remains of particular concern because concentrations frequently exceed the annual average environmental quality standard (AA-EQS) (Li et al., 2023; Navarro et al., 2020; Röhrig et al., 2026; Zarębska et al., 2024; Beggs et al., 2023).

Multivariate methods, such as principal component analysis (PCA) and clustering techniques, are often applied in studies of environmental fate and transport of PFAS to identify and differentiate pollution sources as well as substance grouping patterns (Röhrig et al., 2026; Giglioli et al., 2023; Zarębska et al., 2024; Björnsdotter et al., 2019; Beggs et al., 2023). Such machine learning (ML) techniques benefit from large datasets; however, the total number of sampling sites, samples, and substances monitored are usually comparatively low. To address this, a large amount of European PFAS concentration datasets from research and authoritative sources have been unified (Cordner et al., 2024). The resulting dataset, provided by the Forever Pollution Project, <https://foreverpollution.eu/>, is still maintained; however, it has been under-utilised to this date.

While a recent study used ML to map PFAS concentrations and predict risk (Zhao et al., 2025), a systematic, multi-substance PCA-based investigation into co-occurrence patterns and source-specific signatures across the entire European dataset is still lacking. In this study, we unified existing surface water PFAS concentration datasets and applied multivariate statistical analyses to assess large-scale PFAS pollution patterns in European surface waters. Additionally, we evaluate the ecological risk of PFAS, including PFAAs, PASF-based substances (perfluorooctanesulfonamide (FOSA), N-Ethylperfluorooctanesulfonamide (N-Et-FOSA), N-methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA), and N-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA)), fluortelomer-based substances, and PFECAs (hexafluoropropylene oxide dimer acid (HFPO-DA), and 4,8-dioxa-3H-perfluorononanoic acid (DONA)) and identify PFAS hotspots. This study lays the foundation for future research, such as environmental modelling approaches and impact studies, and further elucidates the need for a unified European PFAS monitoring programme.

2. Methods

2.1. Data collection and preparation

We retrieved daily PFAS concentrations in European surface waters from the Forever Pollution Project, <https://foreverpollution.eu/>, (Cordner et al.,

2024). Due to its uneven spatial distribution focusing on France (Zhao et al., 2025), we assembled additional openly accessible data from local authorities (Bundesanstalt für Gewässerkunde; Kanton Basel-Stadt; Rijkswaterstaat Waterinfo; ELWAS Web) and peer-reviewed publications (Kali et al. (2025); Teymorian et al. (2025)). The detailed data processing and included datasets can be retrieved from the code and data repository (see "Code and data availability" section). We harmonised spatial reference systems, units, environmental matrices, and substance identifiers using CAS (Chemical Abstracts Service) Registration Numbers for translation and unification. Quality checks were conducted for implausible values, unit inconsistencies, and duplicate records. In general, quality control was assumed to have been carried out by the data providers, however, implausible values, i.e. concentrations larger than 10 gL^{-1} , were excluded after visual inspection. Additionally, few samples with concentrations of 0 ngL^{-1} were discarded. In this study, only measurements in surface waters (rivers, streams, lakes, ponds) containing a date of measurement were retained in the dataset. To reflect recent monitoring practices and legislation while retaining sufficient sample size, we restricted our analyses to data from 2019 to the most recently available data from 2026. The resulting compilation contained over 100 different PFAS. Since analysing such a vast range of substances was not feasible within the scope of this study, a substance subset was extracted. We prioritised substances with broad monitoring coverage, requiring either 4,000 total measurements or more than 200 detections over the period 2019-2026, as this was deemed the lower appropriate limit for further ML analysis. Finally, analysed substances in this study are summarised in Table A.1. Each measurement is either reported as a concentration above the limit of quantification (LOQ) or flagged as below the LOQ. As such, we calculated detection frequencies as the ratio of substance measurements above the LOQ to the total number of measurements. To assess common sum parameters, "Sum of 20 PFAS" and "Sum of 4 PFAS" were computed. For "Sum of 20 PFAS", all measured PFAAs included in the "Sum of PFAS" definition by Directive (EU) 2020/2184, were summed at a given sampling site and date. Since not all PFAAs were monitored at each sampling site, we decided to compute multiple "Sum of 20 PFAS", each including a minimum of a fixed number of substances. Results from this computation are reported in Table B.6. For "Sum of 4 PFAS", the concentrations of PFOA, PFOS, perfluorohexane sulfonic acid (PFHxS), and perfluorononanoic acid (PFNA) were summed, albeit only sampling site-day combination were included, which contained all four substances.

2.2. Statistical analysis and hotspot detection

General statistical analysis was performed using Python 3.14 (Python Software Foundation, <https://www.python.org>) and Pandas 3.0.5 (The pandas development team, 2026), while geospatial operations were computed using GeoPandas 1.1.4 (den Bossche et al., 2026). Basin statistics were computed using shapefiles from HydroBASINS v1.0 (level 04) (Lehner and Grill, 2013), whereas basin shapes were named as appropriate by main rivers and regions (Figure 1). PFAS hotspot detection was carried out in QGIS by examining the

spatial distribution of samples exceeding the 85%-percentile concentration for each substance, respectively. In the context of this study, hotspots are defined heuristically as clusters of such samples in close vicinity. We used this approach because sampling locations were highly heterogeneous across Europe.

Concentration ratios between equal-perfluorocarbon-numbered PFCAs and PFSAAs as well as between even- and odd-perfluorocarbon-numbered long-chain PFCAs (PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), and perfluorotetradecanoic acid (PFTeDA)) were calculated to infer possible effects of the functional acid group and to investigate differences in long-chain PFCAs. Concentrations of the respective substance pairs with corresponding timestamps and sampling locations were extracted. To further investigate the concentration differences, we used a one-sided, paired Wilcoxon signed-rank test (Wilcoxon, 1945) to determine whether the concentrations of the first compound were significantly greater than that of the second. Statistical significance was assessed at $p < 0.05$. The results were additionally summarised by basins (HydroBASINS v1.0, level 04 (Lehner and Grill, 2013)).

2.3. Factor analysis

We used PCA (Hotelling, 1933) with factor rotation (PCA/FA; FA: Factor Analysis) and hierarchical clustering to characterise patterns of PFAS co-occurrence. In this study, we define a PFAS fingerprint as the pattern of associations among substances within an analysed group, which is represented by their loadings on the rotated component (RC) and their cluster assignment. Analyses were conducted using python libraries scikit-learn 1.9.0 (Pedregosa et al., 2011), SciPy 1.18.1 (Virtanen et al., 2020), and factor_analyzer 0.5.1 (Biggs and Madnani, 2022).

Records below LOQ were excluded from the factor analysis because their exact concentrations were unknown. Because the monitored PFAS differed by location and substance occurrence varied, we defined multiple groups of substances according to their co-occurrence above the LOQ, while aiming to retain comparability between groups (Table B.7). We minimised the total number of groups, while ensuring at least ten samples (i.e. PFAS profiles for one date and sampling location) per substances in each group, in order to retain stable covariance estimates during PCA (Hair et al., 2019). Substances with insufficient co-occurrence were therefore excluded. PCA and subsequent analyses were conducted separately for each group. Across the groups, the analysis included 6:2 fluorotelomer sulfonic acid (6:2 FTS), EtFOSAA, FOSA, HFPO-DA, N-MeFOSAA, DONA, PFBA, PFBS, PFDA, perfluoroheptanoic acid (PFHpA), perfluoroheptane sulfonic acid (PFHpS), perfluorohexanoic acid (PFHxA), PFHxS, PFNA, PFOA, PFOS, perfluoropentanoic acid (PFPeA), perfluoropentane sulfonic acid (PFPeS), and TFA.

Daily substance concentration profiles were computed for each location. When multiple measurements were available for a substance at the same location on the same day, we aggregated them using the median. We applied

the Yeo-Johnson power transformation to concentrations across locations to reduce skewness (Yeo and Johnson, 2000) followed by z-score standardisation to prepare the data for PCA (Hotelling, 1933).

We assessed the suitability of the data for PFCA using the Kaiser-Meyer-Olkin (KMO) criterion (Kaiser, 1970) and Bartlett’s test of sphericity (Bartlett, 1937). KMO values exceeded 0.8 across groups, and Bartlett’s test was significant for each group ($p < 0.05$). Across substance groups, the cumulative variance explained by the first three components ranged between 86.1 % and 96.5 %. The third component contributed no more than 7.8 %. We fixed dimensionality to three to maintain comparability across groups. To improve the interpretability of the extracted PCA loading matrix, orthogonal (varimax) rotation was applied (Kaiser, 1958). As a robustness check, we fitted an oblique (quartimin) rotation (Fabrigar et al., 1999). Factor correlations in the oblique solution were small (maximum $|\phi| < 0.20$ across groups, Table B.7), indicating almost orthogonality. Therefore, varimax-rotated results are presented. Because rotation was applied to PCA, we refer to the rotated axes as RCs and interpret the rotated substance loadings. Loadings were oriented so that the largest absolute loading is positive, which was done to improve the readability of bi-plots and does not change the interpretation. Absolute loadings greater than 0.5 were interpreted as strong, 0.3-0.5 as moderate, and < 0.3 as negligible association (Hair et al., 2019). Negative loadings were noted as inverse associations. To guide interpretation, we hierarchically clustered substances on their vectors of rotated loadings using Ward minimum-variance linkage (i.e. Euclidean distance). Clusters were defined by cutting the dendrogram at height 0.6. This empirically chosen threshold captured coherent clusters across substance groups. Cluster assignment was subsequently used to support the interpretation of substance co-occurrence across all groupings. Results from clustering were summarised within a consensus matrix (Figure A.4)

2.4. Ecological risk evaluation

Screening of PFAS pollution risk was carried out using a risk quotient (RQ) approach (Zarębska et al., 2024; Röhrig et al., 2026). RQ was calculated as the ratio of a measured environmental concentration and the substances’ predicted no-effect concentrations (PNECs). A PNEC is a concentration below which adverse effects concerning an ecosystem in a specified environmental compartment, e.g. freshwater, are considered unlikely. Following the RQ approach, quotients above 1 indicate high ecological risk, while quotients below 0.01, between 0.01-0.1, and 0.1-1 indicate negligible risk, low risk, and medium ecological risk, respectively (Sánchez-Bayo et al., 2002). Lowest PNECs for freshwater were acquired from the NORMAN Database System (NORMAN Database System, 2026) (Table B.4). An exception was made for PFBA, which, according to the NORMAN Database System (2026), has a PNEC multiple orders of magnitude lower than the other included substances (0.0044 ngL^{-1}), especially PFBS. In general, PFASs are less toxic compared to PFCAs, and short-chain substances show less toxicity than their longer-chain homologues (Wang et al., 2024). To

reflect this, we chose PNEC of PFBA to be equal to that of PFBS ($4,400 \text{ ngL}^{-1}$), which was also adapted by Röhrig et al. (2026).

We evaluated RQ by employing two different approaches: First, risk categories were calculated based on each sample’s concentration. Secondly, we calculated risk categories of individual basins to account for potential bias towards higher risk caused by increased sampling rates at known polluted sites. Spatial discretisation was based on the HydroBASINS level 12 dataset (Lehner and Grill, 2013), which allows for an analysis with high spatial resolution. The study area for Europe encompasses an area of $17,858,911 \text{ km}^2$. Basins containing sampling locations were extracted from this study area to compute substance-specific risks. To characterise the overall risk for each basin, the highest observed risk category among the substances was selected.

3. Results

3.1. PFAS monitoring effort

The compiled dataset contained 1,907,309 samples from 9,072 sites across Europe in the analysed period (2019-2026) for a total of 34 substances (Figure 1). Among these, 252,362 samples had quantifiable concentrations above the LOQ (13 %), which were observed at 7,019 sites, while the remaining sampling sites contained no samples above the LOQ. General statistics of the analysed dataset can be found in Table B.3. The distribution of detected substances across monitoring locations was right-skewed, with most sites exhibiting only a small number of detections (Figure 2). In most cases, single substances were detected above the LOQ at a given sampling site (1,381 sites). The most frequently reported numbers of monitored substances were 32, 1, and 20, recorded at 1,221, 663, and 570 sampling sites, respectively. Despite the wide analytical scope, locations with high numbers of substances above the LOQ were rare. At most, 30 substances were detected at a given sampling site ($n = 1$), which was in Antwerp, Belgium.

3.2. Detection frequencies

Detection frequencies spanned multiple orders of magnitude across substances and reflected both environmental occurrence and heterogeneity in analytical targeting and reporting (Figure 3a, and Table B.3 for reported minimum and maximum limit of quantification see Table B.5). Out of the 34 analysed substances, four showed detection frequencies higher than 30 %, including PFOS, TFA, PFHxA, and PFPeA. Notably, TFA, the second most frequently detected substance, showed a comparatively low total count of samples ($n = 7,117$), whereas the other three substances were sampled more than 64,000 times, each.

Nineteen substances were detected in less than 2 % of samples, which included long-chain PFCAs and PFSAAs as well as precursors and emerging substances. Monitoring effort for these substances was heterogenous with five substances (DONA, perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), 6:2 fluorotelomer carboxylic acid (6:2 FTCA), and N-Et-FOSA)

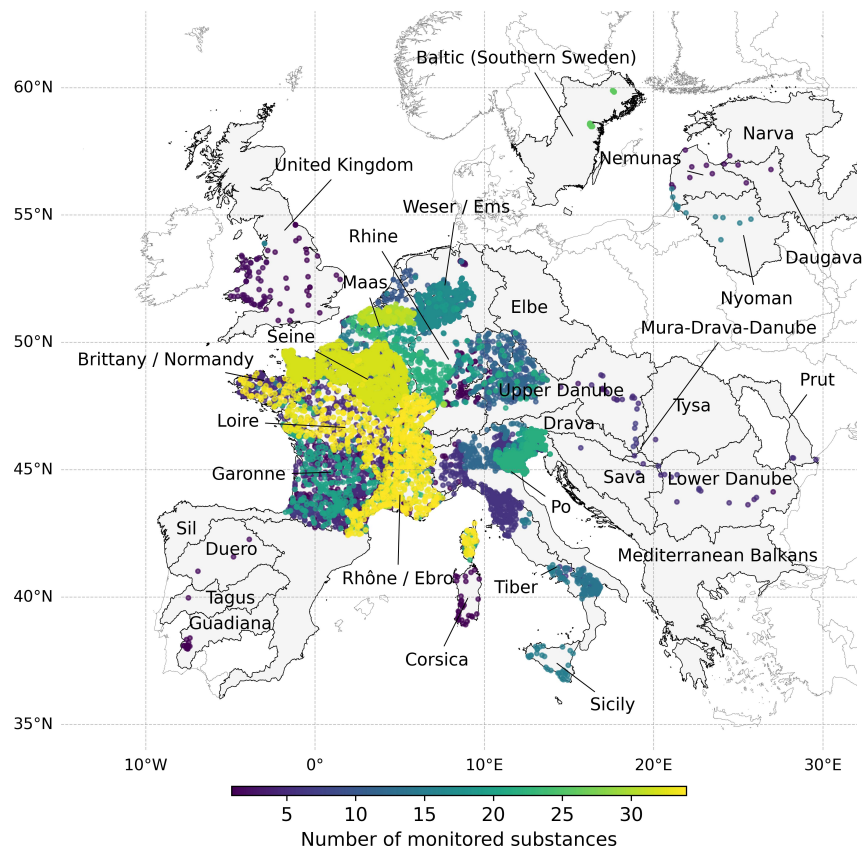


Figure 1: Basin naming scheme used in this study and PFAS sampling sites for the timespan 2019-2026. Colours denote the number of monitored substances at a single sampling site out of the PFAS subset defined in Table A.1. Sampling sites with greater number of monitored substances are rendered on top of sites with fewer. Basins are derived from HydroBASINS level 04 shapefiles (Lehner and Grill, 2013), with names assigned by the authors of this study based on the major rivers within each basin.

having less than 20,000 data points, each. Meanwhile, long-chain PFAAs showed comparatively high representation in the dataset such as PFDA ($n = 117,190$), perfluorodecane sulfonic acid (PFDS) ($n = 87,916$), PFUnDA ($n = 75,649$), and PFDoDA ($n = 72,459$), despite their low detection frequencies (Table B.3).

For PFCAs and PFSAs, detection frequency increased with decreasing number of carbon atoms with a few exceptions. PFOS and PFOA, as well as PFHxA and PFHxS, showed higher detection frequencies than their respective short-chain homologues. Additionally, C4-C6 PFCAs exhibited decreasing detection rates with decreasing chain lengths. Regarding the functional group, PFCAs showed higher detection rates compared to their PFSAs counterparts of equal perfluorocarbon chain length, except for PFOS compared to PFNA. Out of the

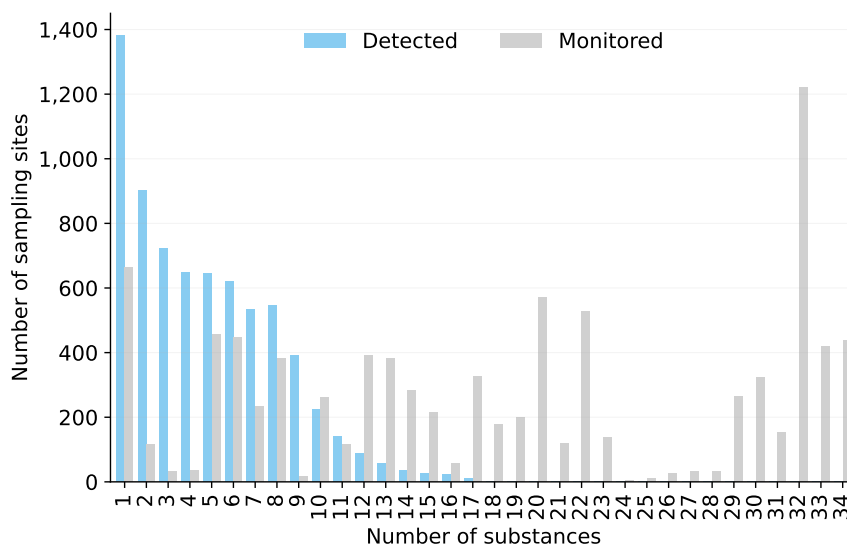


Figure 2: Distribution of the number of European sampling locations, depending on the respective number of substances detected (above LOQ) and monitored; for the period 2019-2026. Colours denote the number of monitored substances at a single sampling site out of the PFAS subset listed in Table A.1.

four fluorotelomer-based substances, 6:2 FTS showed the highest detection rate (10 %, $n = 33,415$). The two PFECAs, HFPO-DA and DONA, were reported above LOQ in 3 % and 2 % of samples, respectively. Out of the four PASF-based substances, EtFOSAA showed the highest detection rate of 7 %.

3.3. Surface water concentrations and PFAS hotspots

Across the 34 PFAS and two sum parameters, i.e. "Sum of 4 PFAS", and "Sum of 20 PFAS", surface water concentrations spanned multiple orders of magnitude (Figure 3b). The median concentration of the "Sum of 4 PFAS" (34.5 ngL^{-1} , $n = 1,339$) was only exceeded by that of TFA, whereas the "Sum of 20 PFAS" concentration was dependent on the minimum number of included substances, reaching median concentrations of up to $65,498 \text{ ngL}^{-1}$ (Table B.6). Exceedance of the EU's drinking water regulation (Directive (EU) 2020/2184, 2020) for the "Sum of PFAS" (100 ngL^{-1}) by "Sum of 20 PFAS" increased from 6.4 % of samples based on a single substance to 100 % upon inclusion of 16 or more substances (Table B.6). All "Sum of 4 PFAS" data points exceeded the threshold of 2 ngL^{-1} set by Danish authorities (Miljøministeriet, 2025).

The highest median concentration was observed for the ultrashort-chain TFA ($1,100 \text{ ngL}^{-1}$). Although other substances occasionally exhibited higher maximum concentrations than TFA, all other PFAS had median concentrations that were multiple orders of magnitude below those of TFA. For example, the second highest median concentration was observed for PFODA (22 ngL^{-1}), even though

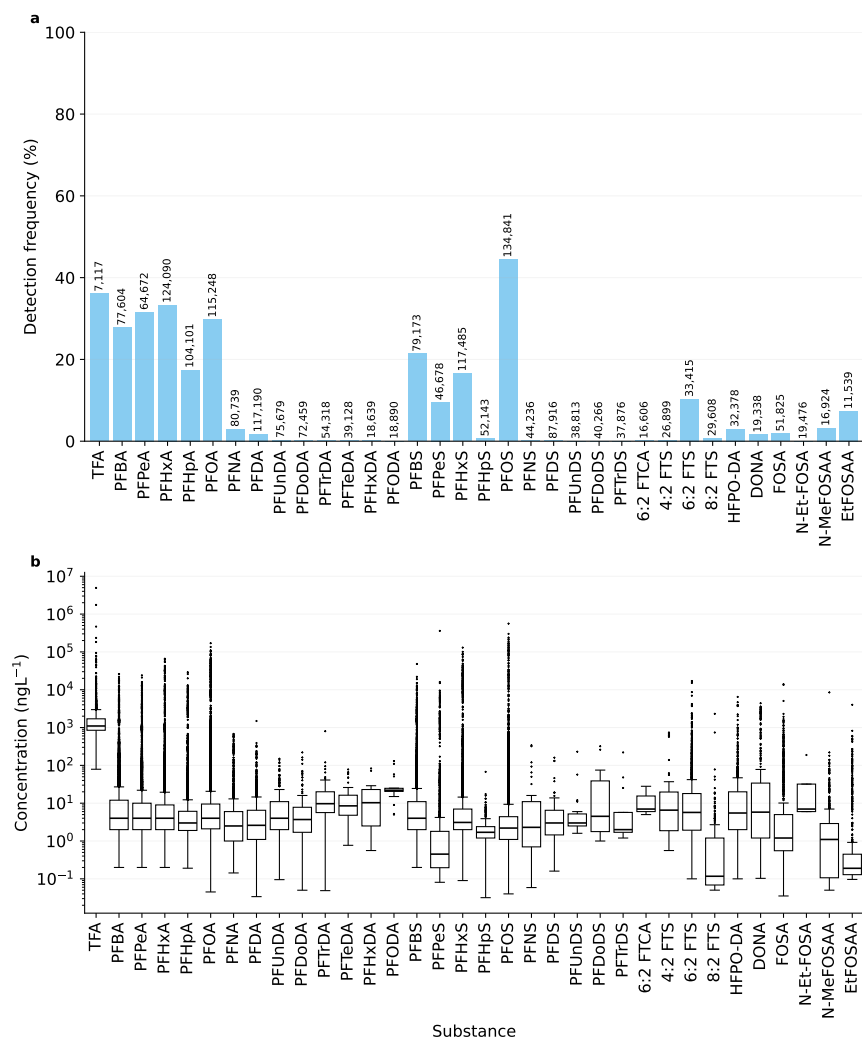


Figure 3: Statistics of the analysed daily PFAS concentrations in the period 2019-2026. Substances are shown in the same order as presented in Table A.1. (a) Detection frequencies as the ratio of measurements above the limit of quantification to total reported measurements for the analyte. Numbers denote the total count of measurements. (b) Boxplots of European surface water concentration. The y-axis is shown on a logarithmic scale.

the dataset contained only 18 observations above the LOQ for this substance (Table B.3).

In general, comparatively high median concentrations were observed for substances with eight or fewer carbon atoms. For C9-C18 PFCAs, there appeared to be an increase in concentration with increasing chain length. The highest median concentrations among the long-chain PFCAs were observed for PFODA and PFHxDA (10.3 ngL^{-1}). For C8-C13 PFCAs, the uneven-carbon-numbered PFUnDA and PFTrDA showed higher median concentrations compared to their adjacent shorter-chain substances, whereas the median concentration of PFOA was higher than that of PFNA. The comparison of daily concentration ratios of these substances showed, that the higher concentrations of PFUnDA and PFTrDA were insignificant ($p > 0.05$), and the respective medians of daily ratios were close to equality (Table B.2, Figure A.2). Contrary, daily PFOA concentrations were significantly ($p < 0.05$) higher than comparable PFNA concentrations (Table B.2). On a basin-wide scale, PFOA concentrations were higher across all studied basins, most dominantly in the Po basin ($n = 180$, Figure A.1).

Concentration ratios of equal-perfluorocarbon-numbered PFCAs in comparison to PFSAAs between four and eight perfluorocarbons revealed significantly higher concentrations of odd-perfluorocarbon-numbered PFCAs and even-perfluorocarbon-numbered PFSAAs (Table B.2, Figure A.2). For these substances, most observations were computed for the Rhône/Ebro, Po, Seine, Rhine and Maas basins (Figure A.1, Table B.1). Here, PFPeA was most dominant in the Rhône/Ebro ($n = 870$) basin and PFBS in the Po basin ($n = 3,248$). PFHxA dominated in all basins, especially in the Po basin ($n = 354$). Concentration ratios most inclined towards PFHxS were found in the Seine ($n = 3,044$). PFOS dominated across most basins, with highest ratios in the Po basin ($n = 179$). Only few concentration ratios could be computed for PFOA and PFHpS ($n = 333$).

Furthermore, the spatial analysis of PFAS contamination across Europe revealed distinct geographical patterns, with specific countries and river basins emerging as hotspots, i.e. containing multiple sampling sites with concentrations above the 85th' percentile within proximity, for different substances (Section A.5 "Hotspots" in Supplementary Information A). Belgium showed elevated concentrations across the broadest range of PFAS. In the West Flanders region and Antwerp, the highest concentrations for the replacement substances 6:2 FTS and HFPO-DA as well as the short-chain sulfonic acid PFPeS were observed (Figure A.18, Figure A.33). Additionally, high concentrations of a wide array of additional substances, including PFBA, PFBS, PFHpA, PFHxA, PFHxS, PFOA, and PFOS as well as EtFOSAA and FOSA, were seen in Belgium (Figure A.21, Figure A.23, Figure A.24, Figure A.27, Figure A.28, Figure A.29, Figure A.30, Figure A.31). Germany was found to be a hotspot for short-chain PFCAs like PFBA, PFHpA, PFHxA, and PFPeA, and the legacy substances PFOA and PFOS (Figure A.23, Figure A.27, Figure A.28, Figure A.32, Figure A.30, Figure A.31). We identified hotspots for a range of short-chain PFCAs (PFBA, PFHxA, PFPeA) and the sulfonic acids PFBS and PFOS in Italy (Figure A.23, Figure A.24, Figure A.28, Figure A.31, Figure A.32). The legacy substance PFOA stands out as its concentrations are amongst the highest in

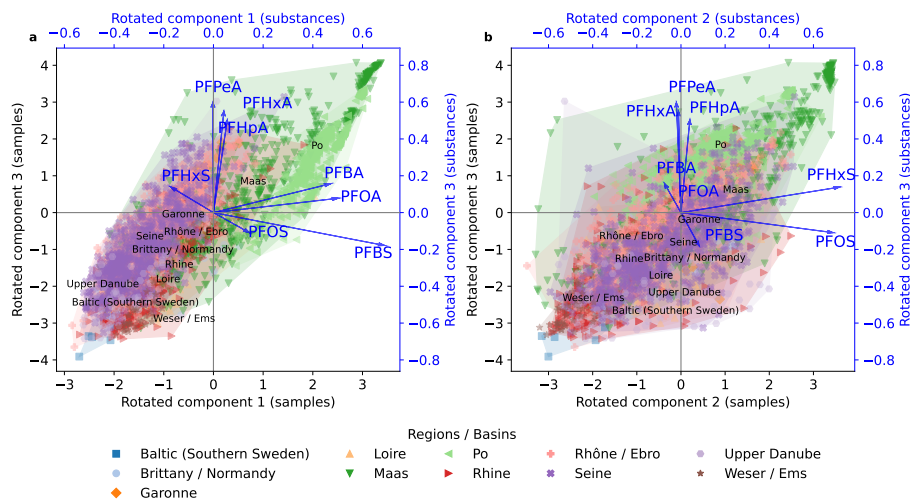


Figure 4: Bi-plot of varimax-rotated principal components, i.e. RCs, of the Group A substances (groups are defined in Table B.7 in Supplementary Information A). Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3, where PFOA, PFBA, and PFBS showed strong positive loadings for RC 1 and PFPeA, PFHxA, and PFHpA showed strong positive loadings for RC 3. (b) RCs 2 and 3, where PFHxS, and PFOS showed strong positive loadings for RC 2.

Europe. Elevated concentration of PFOS were also found in Switzerland (Figure A.31). France exhibited widespread, low-to-moderate level contamination across many PFAS, but with fewer hotspots compared to Belgium, Germany, or Italy. Notably, sulfonic acids PFOS and PFHxS and short-chain PFHxA and PFPeA were observed regularly in France (Figure A.28, Figure A.29, Figure A.31, Figure A.32). This specific pollution hotspot was spatially limited to France’s southern coastal regions, especially in the south of Lyon, and the Paris metropolitan area. The Netherlands showed moderate contamination, particularly with legacy PFAS and several short-chain compounds. These mainly included PFOS, PFBA, PFHxA, and PFOA (Figure A.23, Figure A.28, Figure A.30, Figure A.31).

3.4. PFAS co-occurrence fingerprints

Varimax-rotated PCA revealed recurring patterns of PFAS co-occurrence across sampling sites and European river basins. We refer to these patterns as PFAS fingerprints, which represent descriptive profiles resulting from substances’ rotated component loadings and are supported by cluster assignments (Figure 4 and Section A.4 "PCA/FA Consensus Matrix and Bi-plots" in Supplementary Information A). Three fingerprints were identified in Group A (Figure 4), which comprised the largest sample size, and commonly occurred across

the majority of groups despite differences in substance composition and monitored basins (Table B.7). A fourth recurring fingerprint was observed in other groups. Cluster assignments across all groups and an overview of the fingerprints are shown in Figure A.4. Total explained variance and robustness checks of PCA before rotation are reported in Table B.7 together the definition of groups and respective sample sizes.

The first recurring fingerprint was characterised primarily by a mixture of short-chain PFCAs, primarily PFPeA, PFHxA, and PFHpA (Figure 4 RC 1), which formed clusters in more than 80 % of groups (Figure A.4). Short-chain PFCAs are widely associated with fluorochemical industries and household waste (Glüge et al., 2020). They are used as processing aids in the manufacturing of fluoropolymers and incorporated into a broad range of consumer products, including food packaging, textiles, paper, cosmetics, lubricants, and paints (Souza and Domingo, 2025; Glüge et al., 2020). In some instances, this fingerprint also showed contributions from PFOA and PFBA (Figure A.5, Figure A.9, Figure A.14). In addition, 6:2 FTS formed a dominant component with moderate co-loadings with PFHpA, PFHxA, and PFPeA, and negligible association to PFOS and PFHxS (Figure A.6). The presence of PFOA alongside these substances is consistent with its historical use and subsequent phase-out in the early 2000s, after which it was largely replaced by short-chain PFCAs (Kurwadkar et al., 2022; Krlovic et al., 2024b; Zhang et al., 2025).

The second fingerprint was dominated by PFSAs, primarily PFOS and PFHxS, with occasional contributions from PFHpS, PFPeS, and in some cases PFOA (Figure 4). PFOS and PFHxS clustered together in more than 60 % of groups, while PFHpS and PFPeS co-clustered within the same groups (Figure A.4, Figure A.7, Figure A.12, Figure A.17). PFOS and PFHxS are both associated with electrochemical fluorination (ECF)-derived emissions (Paul et al., 2009) as well as AFFF-usage at firefighting training areas, airports, and military installations (Paul et al., 2009; Moody and Field, 2000; Ackerman Grunfeld et al., 2024). These substances are also applied in metal plating, surface treatments for textiles and leather, and specialty applications such as printer inks (Kotthoff et al., 2015; Glüge et al., 2020; Paul et al., 2009).

A third fingerprint was associated with the short-chain substances PFBA and PFBS, occasionally including PFOA. The two short-chain substances formed clusters in 70 % of groups, while PFOA clustered together with PFBA and PFBS, in 50 % and 40 % of groups, respectively (Figure A.4). These short-chain substances are common substitutes of their long-chain homologues, with PFBS used as a replacement for PFOS in applications in the electroplating industry and AFFF-manufacturing (Kurwadkar et al., 2022; Glüge et al., 2020) and PFBA used as a replacement for PFOA (Buck et al., 2021). In general, both short-chain substances serve similar functions to their homologues and share similar sources. PFBA and PFBS are less effectively removed by WWTPs and are thus frequently detected in WWTP effluents and in landfill leachates, which act as major sources to the aquatic environment (Kurwadkar et al., 2022; Brunn et al., 2023).

A fourth recurring fingerprint was characterised by the long-chain substances

PFNA and PFDA (Figure A.5, Figure A.17). Both substances clustered together in all groups. In some of the groups this factor included the long-chain PFAS PFOS and PFHxS (Figure A.8, Figure A.9).

In groups including precursor substances, such as FOSA, N-MeFOSAA, Et-FOSAA, and DONA more complex patterns emerged, with these substances variably co-loading with long-chain PFAS, and short-chain PFCAs, or formed independent components, or exhibited inverse relationships with other PFAS classes (Figure A.11, Figure A.13, Figure A.14, Figure A.15).

While the four fingerprints were largely consistent, several substance-specific deviations were found. In some groups PFOA, and PFBS exhibited strong and isolated loadings on single components, with minimal co-loading from other PFAS (Figure A.9, Figure A.12, Figure A.16). Distinct signals were observed for some emerging and less commonly detected substances. HFPO-DA formed a dominant and isolated component, with negligible association with most other PFAS (Figure A.10). Similarly, TFA exhibited a strong, isolated loading, separating it from all other analysed substances (Figure A.16). Amongst the isolated substances, inverse relationships between components were observed in several groups. Precursors FOSA exhibited inverse loadings relative to both short- and long-chain PFCAs (Figure A.11), whereas DONA inversely loaded to PFOS in one component (Figure A.15), indicating opposing associations. Additionally, 6:2 FTS showed inverse loadings to short-chain substances PFBS and PFBA (Figure A.6).

Samples from the Po region were strongly associated with short-chain PFCAs and PFOA as well as PFHxS and PFOS, whereas associations with other longer-chain PFCAs were comparatively weak. Within the Po basin subset, two clusters formed with strong positive loadings, both of which were in the Vicenza province. The Maas region exhibited a broad compositional range, with two clusters showing high loadings for short-chain PFCAs, PFOA and PFHxS. These two clusters were in close vicinity of Antwerp. Samples from the Seine region were partly associated with PFPeA, PFHxA, PFHpA, and PFOA. Unlike other regions, most samples were also associated with 6:2 FTS similar to samples from the Loire basin. Similarly, profiles from Toulouse (Garonne basin) exhibited mixtures of PFHpA, PFPeA, and PFHxA as well as long-chain PFASs. Conversely, the Baltic (Southern Sweden), Upper Danube, Brittany/Normandy, Rhône/Ebro, Oder, Rhine, and Weser/Ems basins scored predominantly negative for most of the substances. Notably, the Baltic (Southern Sweden), Brittany/Normandy, Rhône/Ebro basins clustered similarly; however the coastal profiles of Brittany/Normandy were more strongly associated with PFHxS, PFOS, and PFBS, whereas profiles from the Rhône/Ebro basins exhibited fingerprints characterised by PFHxA, PFOA, PFBS, PFHxS, and PFHpS. Generally, profiles in the Upper Danube basin were depleted along most components but showed some association to PFBS and PFOS. Samples in the Rhine basin loaded mostly negatively, with some samples associated more with short-chain PFCAs and PFOA.

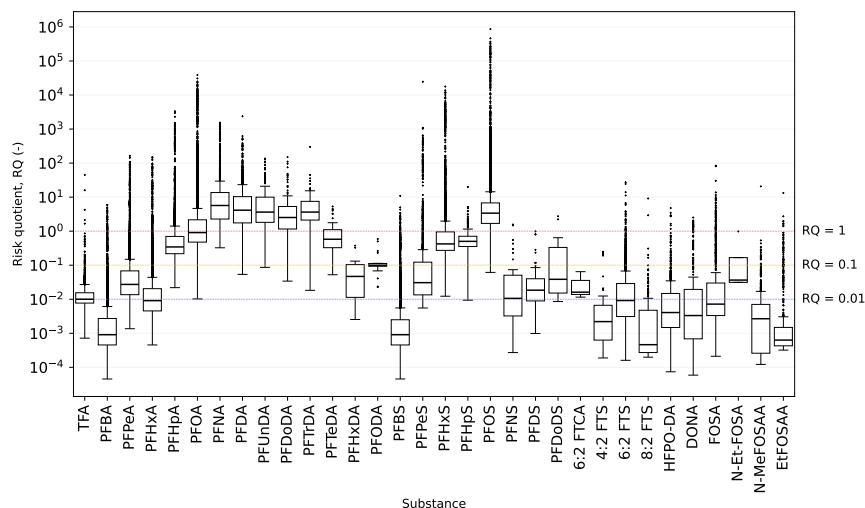


Figure 5: Distribution of RQs for PFAS across all surface water samples in Europe (period 2019-2026). PNEC data for freshwater were obtained from the NORMAN Database System (NORMAN Database System, 2026). Dotted horizontal lines indicate $RQ = 1$, $RQ = 0.1$, and $RQ = 0.01$ from top to bottom.

3.5. Ecological risk evaluation

The majority of PFAS exerted high ecological risk except for 4:2 fluorotelomer sulfonic acid (4:2 FTS), 6:2 FTCA, N-Et-FOSA, PFDS, PFHxDA, and PFODA (Figure 5). The median RQ of the six long-chain PFAS PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFOS exceeded the high ecological risk threshold of 1. The PFAAs PFHpA, PFOA, PFTeDA, PFODA, PFHxS, and PFHpS showed a moderate median risk.

When comparing the RQ on basin area basis, PFOS, PFOA, PFNA, and PFHxS showed the largest total area in the high ecological risk class, covering 335,898 km², 170,889 km², 67,211 km² and 66,715 km², respectively (Figure A.3). These substances also constitute the "Sum of 4 PFAS" parameter. The largest monitored areas captured by the analysed dataset belong to PFOS (549,706 km²), PFOA (508,664 km²), and PFHxA (507,987 km²), while many emerging PFAS and precursors are monitored on a comparatively small scale. Notably, basins that included PFOS covered about 3 % of the total European basin area.

4. Discussion

4.1. State of PFAS monitoring in Europe

The distribution of monitored and detected PFAS shows a broad range of surface water monitoring efforts in Europe. This observed pattern aligns with the heterogeneous analytical scope reported in European monitoring studies,

where the targeted lists of analytes have ranged from four to more than 30 substances, reflecting specific objectives such as regulatory compliance, source investigation, or broad screening (Schmidt et al., 2019; Grung et al., 2024; Gobelius et al., 2018). In contrast to the broad range of monitored substances, the distribution of detected substances is right-skewed. Similar discrepancies between the analytical scope and the observed substances have been reported in European studies (Zarebska et al., 2024; Göckener et al., 2021).

This divergence suggests that the number of detections is driven by factors beyond mere target list size. Such factors typically include site-specific contamination profiles, concentrations falling below detection limits, sampling design, and matrix interferences, as well as the extent to which the target list truly represents the PFAS present at a given site (Ng et al., 2022). Consequently, the detection of only one or a few PFAS should not automatically be interpreted as evidence that other PFAS are absent. Furthermore, target analysis inherently captures only a fraction of the total PFAS burden, as mobile substances often remain undetected (Göckener et al., 2021).

The high frequency of single-substance measurements may also reflect monitoring programmes designed around individual regulatory substances or site-specific investigative objectives. More broadly, European PFAS monitoring remains predominantly target-based, whereas suspect and non-target screening studies have identified many additional PFAS outside conventional target lists (Ng et al., 2022).

Sum parameter concentrations provide a broad overview of PFAS pollution in Europe. The frequent exceedance of the Danish 2 ngL^{-1} threshold for "Sum of 4 PFAS" (Miljøministeriet, 2025) is concerning, as extensive drinking-water treatment is usually required, which is often difficult and expensive (Grung et al., 2024; Calore et al., 2023; Neuwald et al., 2022). The exceedance of "Sum of 20 PFAS" limit relative to the drinking-water threshold for the "Sum of PFAS" (100 ngL^{-1}) (Directive (EU) 2020/2184, 2020) raises concern for European surface waters for these specific targeted compounds. Notably, the advised inclusion of TFA to the aggregate parameters (SCHEER (Scientific Committee on Health, Environmental and Emerging Risks), 2025) will likely lead to an overwhelming exceedance of the threshold, due to TFA's high concentration.

4.2. PFAS co-occurrence and common emission sources

PCA and hotspot analysis reveal that PFAS contamination profiles in European surface waters are governed by local industrial activity, transformation processes, and physicochemical properties. The co-loading of 6:2 FTS with the short-chain PFCAs fingerprint is consistent with a potential association between the substances, including precursor transformation. PFHpA, PFPeA, PFHxA, and PFBA were identified as late-stage transformation products of 6:2 FTS in landfill leachate, sediments, and soils (Hamid et al., 2020; Wang et al., 2011; Yan et al., 2024) indicating, that biotic transformation is a significant secondary source contributing to the observed concentration profiles of short-chain PFCAs. 6:2 FTS is associated with AFFF-usage and industrial activities (Krlovic et al., 2024a; Houtz et al., 2013), and more specifically with the production

and usage of telomer-based AFFF (Adamson et al., 2022; Houtz et al., 2013). Moreover, PFHxA and PFHpA are metabolites of PFOA (Tang et al., 2024), taking account of evidence regarding overlapping degradation pathways. These findings support the interpretation that the first fingerprint not only reflects primary emissions from industrial and consumer sources but also the secondary formation of stable PFCAs from the degradation of precursors like 6:2 FTS and PFOA itself. Accordingly, the first fingerprint is interpreted as representing emissions linked to fluorochemical industry activities and the release of associated consumer products through waste streams as well as a complex web of transformation processes.

The absence of co-loading between these sulfonates and 6:2 FTS suggests that the observed AFFF and industrial signatures are predominantly legacy ECF-based formulations rather than modern telomer-based alternatives. Due to historical PFOS production via ECF, fluorochemical production facilities represent major primary sources of environmental contamination (Ohoro et al., 2024). The occurrence of PFHpS and PFPeS alongside PFOS and PFHxS is consistent with similar use patterns but may also reflect their presence as impurities in ECF-derived products (Glüge et al., 2020; Paul et al., 2009). Therefore, this fingerprint is interpreted as being associated with ECF-derived PFSA emissions, with contributions from AFFF-related sources and additional influence from industrial applications.

The occasional co-loading of PFOA with PFOS suggests overlapping historical uses, including applications in firefighting foams and surface treatments (Glüge et al., 2020). While this could further indicate a mixture of ECF- and telomer-based AFFF formulations (Adamson et al., 2022), the absence of co-loading between the two PFSA, PFOS and PFHxS, and 6:2 FTS argues against a dominant contribution from telomer-based AFFF in the analysed samples. Like PFOA, PFOS was phased out in the early 2000s and subsequently replaced by shorter-chain homologues in many applications (Paul et al., 2009). Contamination with PFOA and PFOS remains an issue, with hotspots identified in Belgium, Germany, and Italy. Switzerland also emerges as a hotspot specifically for PFOS, indicating historical sources, likely from industrial use or AFFF applications.

The strong and isolated loading of several substances may indicate dominant, localised point sources of modern PFAS rather than diffuse, legacy contamination. Short-chain substances (PFBA, PFBS, PFHxA) and replacement compounds (6:2 FTS and HFPO-DA) were responsible for many of the identified hotspots across Belgium, Germany, and Italy. In Germany, elevated concentrations were observed in urban areas and notably downstream of a chemical park in Bavaria. Scheurer et al. found elevated TFA concentrations downstream of the same chemical park, suggesting a broader PFAS emission profile (Scheurer et al., 2017). The dominance of PFBS and PFBA in this fingerprint indicates a distinct fingerprint of modern PFAS usage as opposed to long-chain legacy substances.

Strong and isolated loadings of PFOA likely point to dominant point sources with distinct localised inputs. Additionally, the continued detection of PFOA

with its replacements suggests releases from a combination of legacy and modern product waste streams entering WWTPs, which are established sources of PFAS to surface waters (Kurwadkar et al., 2022). PFOA-dominated components are concerning, as the substance is strictly regulated in Europe. However, our findings provide evidence for ongoing emissions of PFOA or its precursors in Belgium and the Netherlands. Furthermore, the isolated loadings for multiple substances in several basins suggest that specific manufacturing processes may be decoupled from the broader industrial PFAS mix, representing unique, site-specific emission profiles.

4.3. Environmental partitioning affected by physicochemical properties

The independent co-loading of PFNA, PFDA, and other long-chain substances from short-chain substances proposes a chain-length-based differentiation. This separation was consistent with the physicochemical properties of PFAS, as water solubility decreases with increasing carbon-chain length (Ohero et al., 2024). An increasing perfluoroalkyl tail length generally leads to higher sorption to organic carbon in soils, sediment, and biota due to the hydrophobicity of the carbon-fluorine bond (Brunn et al., 2023; Higgins and Luthy, 2006; Catherine et al., 2019; Chen et al., 2018; Behnami et al., 2024; Abou-Khalil et al., 2026), which in turn leads to higher mobility and prevalence of short-chain homologues in the aqueous phase. Contrasting the third and fourth fingerprint revealed that concentration patterns were not solely governed by emission sources, but also by environmental partitioning processes due to chain length differences. While the third fingerprint reflected mobile, short-chain PFAS associated with contemporary usage and wastewater-related pathways, the fourth represented the accumulation and retention of less soluble, long-chain PFAS in environmental compartments.

In contrast to long-chain substances, many of the high median concentration substances contain eight or fewer carbon atoms, which might be caused by their lower sorptive strength to particulates compared to longer-chain PFAS (Brunn et al., 2023; Higgins and Luthy, 2006; Catherine et al., 2019; Chen et al., 2018). However, long-chain PFAS such as PFDA, PFNA, and PFUnDA showed fewer hotspots, as these substances are more likely to adsorb to sediment and organic matter, making them less prevalent at high concentrations in the aqueous phase of surface waters (Ahrens and Bundschuh, 2014). Their detection above the LOQ, even without forming hotspots, still indicates widespread, low-level contamination.

Notably, for long-chain PFCAs, a trend of higher bioaccumulation has been observed for odd-carbon-numbered substances compared to their respective adjacent shorter even-numbered substances (i.e. PFTrDA was found to have higher concentrations in biota than PFDoDA) (Lu et al., 2024; Sturm and Ahrens, 2010; Kesic et al.). This effect, previously reported as the "odd-even" effect, is suggested to be the result of higher production of odd-carbon-numbered PFCAs via atmospheric oxidation of x:2 fluorotelomer alcohols (FTOHs) (x refers to the number of fluorinated carbon atoms) (Lu et al., 2024; Kesic et al.). Contrary, Sturm and Ahrens (2010) suggest, that FTOHs degrade to equal amounts of

odd- and even-numbered PFCAs, and odd-numbered PFCAs are more bioaccumulative than their even-numbered counterparts (Sturm and Ahrens, 2010). Our results showed no significant higher concentrations of odd-numbered over even-numbered PFCAs, supporting higher bioaccumulation of odd-numbered PFCAs. Furthermore, comparatively high concentrations of long-chain PFCAs, such as PFOA, PFTrDA, PFTeDA, PFHxDA, and PFODA, might be linked to specific sources located in the sampling areas, and reflect a broader shift to longer-chain substances and their precursors (Catherine et al., 2019; Lu et al., 2024).

Finally, PFSAAs tend to be more sorptive to organic carbon than their equal-chain PFCAs counterparts (Higgins and Luthy, 2006), however, sorption mechanics of PFAS cannot be simplified to their respective function acid group (Pereira et al.). For example, the high detection rate of PFOS might be explained by the selection of sample locations and uses, as historical applications of PFOS-based AFFFs remain an ongoing source of this compound in surface waters (Glüge et al., 2020; Houtz et al., 2013; Ankley et al., 2020).

Notably, negligible association between HFPO-DA and PFHxA or PFOA was unexpected, since these substances are used in the fluorochemical industry, for example as processing aid (Dalmijn et al., 2025). The lack of positive correlation implies different specific applications or release pathways, suggesting that the sources of HFPO-DA are distinct from those of other PFAS.

The high prevalence of TFA in the aqueous phase may be due to its ultra-short perfluorocarbon chain. While TFA monitoring carried out in studies or by authoritative institutions in surface waters is sparse, when monitored, its detection frequencies as well as concentrations are usually high, aligning with our findings (Röhrig et al., 2026; Björnsdotter et al., 2019). TFA shares common sources with other PFAS, such as industrial facilities, WWTPs, and landfills (Kurwadkar et al., 2022; Freeling and Björnsdotter, 2023). However, TFA has substance-specific diffuse emissions from atmospheric formation and agricultural runoff (Arp et al., 2024; Henne et al., 2025). Main precursors of TFA are volatile fluorinated gases (F-gases) and a wide range of modern pesticides and pharmaceuticals containing a $-CF_3$ moiety (Arp et al., 2024; Freeling and Björnsdotter, 2023). The application and subsequent degradation of certain modern pesticides represent a significant and seasonally variable source of TFA to surface waters in agricultural regions, a pathway that is less characteristic for many other PFAS (Freeling and Björnsdotter, 2023). In contrast, many other regulated PFAS are formed from precursors like FTOHs and FTSs or are released directly (Glüge et al., 2020).

Several substances, including precursors (EtFOSAA, N-MeFOSAA, FOSA) and long-chain compounds (PFDS, PFDoDA, PFTeDA, PFTrDA), were detected across multiple countries and basins, while the proportion of the highest 15th percentile was well balanced (Figure A.19, Figure A.20, Figure A.22, Figure A.25, Figure A.26, Figure A.34, Figure A.35). This may be due to lower usage volumes, different environmental transport pathways, or rapid transformation into other terminal PFAS.

The underlying data reveals that PFAS hotspots are predominantly located

in highly industrialised and densely populated regions, including Antwerp, Brussels, Ghent, the Veneto region, the Paris metropolitan area, and the Danube, Seine, and Rhine river basins. This spatial pattern aligns with and reinforces earlier research findings (Lindim et al., 2015; Giglioli et al., 2023; Röhrig et al., 2026).

4.4. *Ecological implications of PFAS pollution*

Ecological risk evaluations have been carried out for several European rivers since the 2000s, and their findings underscore the ongoing environmental risk from long-chained legacy PFAS. Notably, PFOS exhibited the largest area of "high ecological risk" (Figure A.3) and was most frequently cited as a major threat, for example, in the Oder and Elbe rivers as well as multiple regions in Italy (Zarebska et al., 2024; Castellani et al., 2023; Giglioli et al., 2023). In Italy, high ecological risk has been reported for the Umbria region (Castellani et al., 2023), moreover in the Veneto region (Northern Italy), PFOS contamination has been documented as a serious environmental issue stemming from industrial pollution (Giglioli et al., 2023). For the Elbe and its tributaries, Röhrig et al. (2026) found that PFOS and long-chain PFCAs presented the highest ecological risk (Röhrig et al., 2026).

Despite its comparatively high concentrations, TFA contamination posed a negligible to low ecological risk due to its high PNEC of $110 \mu\text{gL}^{-1}$. Importantly, Danish drinking water guidelines established an advisory threshold value of $9 \mu\text{g}_{\text{TFA}}\text{L}^{-1}$ (Miljøministeriet, 2025). This lowered threshold was exceeded 50 times in surface waters (0.7 %, $n = 7,117$). The potential ecological risk of TFA should not be underestimated due to its high mobility and persistence in the water cycle (Lange et al., 2025), which currently makes effective drinking water treatment not yet possible (Brunn et al., 2023; Scheurer et al., 2017). If TFA were to be included in a sum parameter for surface water or drinking water, as advised by SCHEER (2025), it would likely trigger widespread exceedances of thresholds applicable to other PFAS.

4.5. *Limitations and future perspective*

Analysis of large-scale concentration data compiled from multiple sources presents certain limitations. Regarding the state of monitoring, it was infeasible to distinguish the exact water body for each sampling location due to the dataset's large size. This is also reflected in the fact that data on discharge was mostly not available and thus not considered. Future studies should aim to integrate hydrological data to account for dilution effects, thereby enabling mass flux calculations that would provide a more robust assessment of PFAS transport and associated emission sources.

The findings highlight biased monitoring focussing on historically contaminated areas. Targeted sampling in known hotspots, such as the Veneto region (Giglioli et al., 2023), and Antwerp, likely elevated reported median concentrations, a tendency further compounded by the high costs of PFAS analysis. Consequently, broad spatial and temporal monitoring frameworks often fail to

capture episodic, short-term releases of PFAS from industrial production sites (Dalmijn et al., 2025).

While PCA successfully identified co-occurrence patterns, source attribution remains inferential, and the exclusion of non-detects as well as variability in group composition may influence the components. Nevertheless, the consistent fingerprint patterns demonstrate that PFAS occurrence in European surface waters reflects a combined signature of historical and ongoing emissions, precursor transformation, and environmental partitioning based on physicochemical properties. Several analytes had limited spatial coverage (e.g. PFTrDA, PFTeDA, DONA, 8:2 fluorotelomer sulfonic acid (8:2 FTS)), which constrains source inference.

The interpretation of the ecological risk evaluation was constrained by the availability and quality of ecotoxicity data, as the use of limited or data-poor ecotoxicological thresholds can lead to inaccurate PNEC estimations (Wang et al., 2024). The usage of suboptimal ecotoxicity data can lead to an inaccurate estimation of PNECs (Wang et al., 2024). Thus, findings from the RQ-approach used in this study may only indicate PFAS pollution and potential ecological risk (Röhrig et al., 2026). Again, the inclusion of targeted measuring campaigns in known contaminated areas could lead to a bias towards higher RQs. Nonetheless, potential ecological risk from PFAS contamination is still widespread across Europe, with high concentrations often occurring in smaller streams due to reduced dilution. Additionally, PFAS often occur in a mixture of multiple substances. Although concentrations of single substances may be too low to cause adverse effects, their mixtures can pose environmental and human health concerns (Bil et al., 2021; Hong et al., 2025). Adverse effects of PFAS mixtures are not simply additive, and the sensitivity of immune responses to PFAS varies by organism and mixture (Arnesdotter et al., 2025). Thus, not only single substances should be assessed for risk, but also mixtures of multiple substances (Ankley et al., 2020).

5. Conclusions

This study presents a comprehensive, large-scale analysis of PFAS measurements in European surface waters, encompassing a diverse range of substances including legacy compounds, emerging alternatives, and ultrashort-chain substances like TFA. The analysis revealed distinct PFAS fingerprint patterns across European surface waters, reflecting both historical contamination and emerging pollution sources. Our findings demonstrate that while legacy PFAS, such as PFOA and PFOS, remain significant environmental concerns, frequently exceeding safety thresholds, the pollution landscape is increasingly dominated by emerging substances. These emerging PFAS, including HFPO-DA, 6:2 FTS, and TFA, exhibit unique source signatures across Europe.

The continued environmental presence of legacy PFAS, particularly PFOA and PFOS, remains a concern. Despite restrictions on their use, these substances are still detected in European rivers. Alongside these legacy contaminants,

elevated concentrations of short-chain TFA underscore the need for stringent monitoring due to high mobility and environmental persistence.

The detection of numerous unregulated emerging PFAS, including various fluorotelomer sulfonates, HFPO-DA, and TFA, revealed a critical gap in environmental oversight. Currently, large portions of the European Union's freshwater systems remain either unmonitored or suffer from a lack of accessible PFAS data. This highlights the need for coordinated European monitoring with consistent methods, and broad coverage of legacy, emerging, and ultrashort-chain compounds, and the systematic integration of hydrological data, such as river discharge. Further work combining these comprehensive datasets with source-specific information will be needed to test the potential origins and pathways suggested by these co-occurrence patterns. Finally, this research provides the necessary foundation for future environmental modelling, impact assessment and regulatory action to address the persistent threat of PFAS contamination.

CRedit authorship contribution statement

Robin Schröder: Writing - Original Draft, Writing - review & editing, Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Software, Visualization. **Jens Prothmann:** Writing - review & editing. **Tobias Licha:** Writing - review & editing. **Hans H. Dürr:** Writing - review & editing, Supervision. **Martina Flörke:** Writing - review & editing, Supervision, Project administration.

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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Code and data availability

The research code to create the "PFAS concentrations in European surface waters, 2018-July 2026" dataset and conduct the analyses presented in this article as well as the data is available at <https://zenodo.org/records/23321966> (Schröder, 2026).

The HydroBASINS (version 1) product is available at <https://www.hydrosheds.org/products/hydrobasins>.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the authors used ChatGPT (OpenAI) to assist with code refactoring and software development tasks. ScienceOS (scienceOS) was used to assist in literature research. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

References

- Abou-Khalil, C., Jiang, M., Gerges, F., Curtis, E.G., Chernysheva, L., Kim, J., Doudrick, K., 2026. A Critical Review and Meta-Analysis of the Occurrence and Fate of Per- and Polyfluoroalkyl Substances in Global Wastewater Treatment Plants. ACS ES&T Engineering URL: <https://doi.org/10.1021/acsestengg.5c00648>, doi:10.1021/acsestengg.5c00648.
- Ackerman Grunfeld, D., Gilbert, D., Hou, J., Jones, A.M., Lee, M.J., Kibbey, T.C.G., O’Carroll, D.M., 2024. Underestimated burden of per- and polyfluoroalkyl substances in global surface waters and groundwaters. Nature Geoscience 17, 340–346. URL: <https://www.nature.com/articles/s41561-024-01402-8>, doi:10.1038/s41561-024-01402-8.
- Adamson, D.T., Kulkarni, P.R., Nickerson, A., Higgins, C.P., Field, J., Schwichtenberg, T., Newell, C., Kornuc, J.J., 2022. Characterization of relevant site-specific PFAS fate and transport processes at multiple AFFF sites. Environmental Advances 7, 100167. URL: <https://www.sciencedirect.com/science/article/pii/S2666765722000035>, doi:10.1016/j.envadv.2022.100167.
- Ahrens, L., Bundschuh, M., 2014. Fate and effects of poly- and perfluoroalkyl substances in the aquatic environment: A review. Environmental Toxicology and Chemistry 33, 1921–1929. URL: <https://doi.org/10.1002/etc.2663>, doi:10.1002/etc.2663.
- Ankley, G.T., Cureton, P., Hoke, R.A., Houde, M., Kumar, A., Kurias, J., Lanno, R., McCarthy, C., Newsted, J., Salice, C.J., Sample, B.E., Sepúlveda, M.S., Steevens, J., Valsecchi, S., 2020. Assessing the Ecological Risks of Per- and Polyfluoroalkyl Substances: Current State-of-the Science and a Proposed Path Forward. Environmental Toxicology and Chemistry 40, 564–605. URL: <https://academic.oup.com/etc/article/40/3/564/7734567>, doi:10.1002/etc.4869.

- Arnesdotter, E., Stoffels, C.B.A., Alker, W., Gutleb, A.C., Serchi, T., 2025. Per- and polyfluoroalkyl substances (PFAS): Immunotoxicity at the primary sites of exposure. *Critical Reviews in Toxicology* 55, 484–504. URL: <https://doi.org/10.1080/10408444.2025.2501420>, doi:10.1080/10408444.2025.2501420.
- Arp, H.P.H., Gredelj, A., Glüge, J., Scheringer, M., Cousins, I.T., 2024. The Global Threat from the Irreversible Accumulation of Trifluoroacetic Acid (TFA). *Environmental Science & Technology* 58, 19925–19935. URL: <https://doi.org/10.1021/acs.est.4c06189>, doi:10.1021/acs.est.4c06189.
- Ateia, M., Maroli, A., Tharayil, N., Karanfil, T., 2019. The overlooked short- and ultrashort-chain poly- and perfluorinated substances: A review. *Chemosphere* 220, 866–882. URL: <https://www.sciencedirect.com/science/article/pii/S0045653518325281>, doi:10.1016/j.chemosphere.2018.12.186.
- Bartlett, M.S., 1937. Properties of Sufficiency and Statistical Tests. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* 160, 268–282. URL: <https://www.jstor.org/stable/96803>, arXiv:96803.
- Beggs, C., Mackie, R., Vrana, B., Prokeš, R., Gorji, S.G., Schulze, B., Thomas, K.V., Mueller, J.F., Kaserzon, S.L., 2023. Estimation of per- and poly-fluoroalkyl substances mass loads in the Danube River using passive sampling. *Science of the Total Environment* 892. URL: <https://www.scopus.com/inward/record.uri?eid=2-s2.0-85161019309&doi=10.1016%2fj.scitotenv.2023.164458&partnerID=40&md5=ccf83a4753e76f54fc1a53e1bc7a6c8f>, doi:10.1016/j.scitotenv.2023.164458.
- Behnami, A., Zoroufchi Benis, K., Pourakbar, M., Yeganeh, M., Esrafil, A., Gholami, M., 2024. Biosolids, an important route for transporting poly- and perfluoroalkyl substances from wastewater treatment plants into the environment: A systematic review. *Science of The Total Environment* 925, 171559. URL: <https://www.sciencedirect.com/science/article/pii/S0048969724017005>, doi:10.1016/j.scitotenv.2024.171559.
- Biggs, J., Madnani, N., 2022. Factor_analyzer. Educational Testing Service. URL: <https://factor-analyzer.readthedocs.io/en/latest/index.html>.
- Bil, W., Zeilmaker, M., Fragki, S., Lijzen, J., Verbruggen, E., Bokkers, B., 2021. Risk Assessment of Per- and Polyfluoroalkyl Substance Mixtures: A Relative Potency Factor Approach. *Environmental Toxicology and Chemistry* 40, 859–870. URL: <https://doi.org/10.1002/etc.4835>, doi:10.1002/etc.4835.
- Björnsdotter, M.K., Yeung, L.W.Y., Kärrman, A., Jogsten, I.E., 2019. Ultra-Short-Chain Perfluoroalkyl Acids Including Trifluoromethane Sulfonic Acid in

- Water Connected to Known and Suspected Point Sources in Sweden. *Environmental Science & Technology* 53, 11093–11101. URL: <https://doi.org/10.1021/acs.est.9b02211>, doi:10.1021/acs.est.9b02211.
- Björnsdotter, M.K., Yeung, L.W.Y., Kärrman, A., Jogsten, I.E., 2022. Mass Balance of Perfluoroalkyl Acids, Including Trifluoroacetic Acid, in a Freshwater Lake. *Environmental Science & Technology* 56, 251–259. URL: <https://doi.org/10.1021/acs.est.1c04472>, doi:10.1021/acs.est.1c04472.
- den Bossche, J.V., Jordahl, K., Fleischmann, M., Richards, M., McBride, J., Wasserman, J., Badaracco, A.G., Snow, A.D., Roggemans, P., Ward, B., Tratner, J., Gerard, J., Taves, M., Perry, M., carsonfarmer, Hjelle, G.A., Tan, N.Y., Bell, R., rraymondgh, Cochran, M.D., Caria, G., ter Hoeven, E., Chai, C.P., Culbertson, L., Bartos, M., Eubank, N., sangarshanan, Flavin, J., Rey, S., 2026. Geopandas/geopandas: Version 1.1.4. Zenodo. URL: <https://zenodo.org/records/20938197>.
- Brunn, H., Arnold, G., Körner, W., Rippen, G., Steinhäuser, K.G., Valentin, I., 2023. PFAS: Forever chemicals—persistent, bioaccumulative and mobile. Reviewing the status and the need for their phase out and remediation of contaminated sites. *Environmental Sciences Europe* 35, 20. URL: <https://doi.org/10.1186/s12302-023-00721-8>, doi:10.1186/s12302-023-00721-8.
- Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., De Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A., Van Leeuwen, S.P., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management* 7, 513–541. URL: <https://academic.oup.com/ieam/article/7/4/513/7741313>, doi:10.1002/ieam.258.
- Buck, R.C., Korzeniowski, S.H., Laganis, E., Adamsky, F., 2021. Identification and classification of commercially relevant per- and poly-fluoroalkyl substances (PFAS). *Integrated Environmental Assessment and Management* 17, 1045–1055. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/ieam.4450>, doi:10.1002/ieam.4450.
- Byns, C., Teunen, L., Groffen, T., Lasters, R., Bervoets, L., 2022. Bioaccumulation and trophic transfer of perfluorinated alkyl substances (PFAS) in marine biota from the Belgian North Sea: Distribution and human health risk implications. *ENVIRONMENTAL POLLUTION* 311. doi:10.1016/j.envpol.2022.119907.
- Calore, F., Guolo, P.P., Wu, J., Xu, Q., Lu, J., Marcomini, A., 2023. Legacy and novel PFASs in wastewater, natural water, and drinking water: Occurrence in Western Countries vs China. *Emerging Contaminants* 9, 100228. URL: <https://www.sciencedirect.com/science/article/pii/S2405665023000264>, doi:10.1016/j.emcon.2023.100228.

- Castellani, F., Galletti, M., Charavgis, F., Cingolani, A., Renzi, S., Nucci, M., Protano, C., Vitali, M., 2023. Perfluorinated Compounds (PFCs) in River Waters of Central Italy: Monthly Variation and Ecological Risk Assessment (ERA). *Archives of Environmental Contamination and Toxicology* 84, 332–346. URL: <https://doi.org/10.1007/s00244-023-00993-4>, doi:10.1007/s00244-023-00993-4.
- Catherine, M., Nadege, B., Charles, P., Yann, A., 2019. Perfluoroalkyl substances (PFASs) in the marine environment: Spatial distribution and temporal profile shifts in shellfish from French coasts. *CHEMOSPHERE* 228, 640–648. doi:10.1016/j.chemosphere.2019.04.205.
- Chen, H., Yao, Y., Zhao, Z., Wang, Y., Wang, Q., Ren, C., Wang, B., Sun, H., Alder, A.C., Kannan, K., 2018. Multimedia Distribution and Transfer of Per- and Polyfluoroalkyl Substances (PFASs) Surrounding Two Fluorochemical Manufacturing Facilities in Fuxin, China. *Environmental Science & Technology* 52, 8263–8271. URL: <https://doi.org/10.1021/acs.est.8b00544>, doi:10.1021/acs.est.8b00544.
- Codling, G., Yuan, H., Jones, P.D., Giesy, J.P., Hecker, M., 2020. Metals and PFAS in stormwater and surface runoff in a semi-arid Canadian city subject to large variations in temperature among seasons. *Environmental Science and Pollution Research* 27, 18232–18241. URL: <https://doi.org/10.1007/s11356-020-08070-2>, doi:10.1007/s11356-020-08070-2.
- Conder, J.M., Hoke, R.A., de Wolf, W., Russell, M.H., Buck, R.C., 2008. Are PFCAs Bioaccumulative? A Critical Review and Comparison with Regulatory Criteria and Persistent Lipophilic Compounds. *Environmental Science & Technology* 42, 995–1003. URL: <https://doi.org/10.1021/es070895g>, doi:10.1021/es070895g.
- Cordner, A., Brown, P., Cousins, I.T., Scheringer, M., Martinon, L., Dagorn, G., Aubert, R., Hosea, L., Salvidge, R., Felke, C., Tausche, N., Drepper, D., Liva, G., Tudela, A., Delgado, A., Salvatore, D., Pilz, S., Horel, S., 2024. PFAS Contamination in Europe: Generating Knowledge and Mapping Known and Likely Contamination with “Expert-Reviewed” Journalism. *Environmental Science & Technology* 58, 6616–6627. URL: <https://doi.org/10.1021/acs.est.3c09746>, doi:10.1021/acs.est.3c09746.
- Cousins, I.T., DeWitt, J.C., Gluege, J., Goldenman, G., Herzke, D., Lohmann, R., Ng, C.A., Scheringer, M., Wang, Z., 2020. The high persistence of PFAS is sufficient for their management as a chemical class. *ENVIRONMENTAL SCIENCE-PROCESSES & IMPACTS* 22, 2307–2312. doi:10.1039/d0em00355g.
- Dalmijn, J., Shafer, J.J., Benskin, J.P., Salter, M.E., Johansson, J.H., Cousins, I.T., 2025. HFPO-DA and Other PFAS in Air Downwind of a Fluoropolymer

- Production Plant in the Netherlands: Measurements and Modeling. *Environmental Science & Technology* 59, 8662–8672. URL: <https://doi.org/10.1021/acs.est.4c13943>, doi:10.1021/acs.est.4c13943.
- Directive (EU) 2020/2184, 2020. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast) (Text with EEA relevance). URL: <http://data.europa.eu/eli/dir/2020/2184/oj/eng>.
- Evich, M.G., Davis, M.J.B., McCord, J.P., Acrey, B., Awkerman, J.A., Knappe, D.R.U., Lindstrom, A.B., Speth, T.F., Tebes-Stevens, C., Strynar, M.J., Wang, Z., Weber, E.J., Henderson, W.M., Washington, J.W., 2022. Per- and polyfluoroalkyl substances in the environment. *SCIENCE* 375, 512+. doi:10.1126/science.abg9065.
- Fabrigar, L.R., Wegener, D.T., MacCallum, R.C., Strahan, E.J., 1999. Evaluating the use of exploratory factor analysis in psychological research. *Psychological Methods* 4, 272–299. URL: <https://doi.apa.org/doi/10.1037/1082-989X.4.3.272>, doi:10.1037/1082-989X.4.3.272.
- Freeling, F., Björnsdotter, M.K., 2023. Assessing the environmental occurrence of the anthropogenic contaminant trifluoroacetic acid (TFA). *Current Opinion in Green and Sustainable Chemistry* 41, 100807. URL: <https://www.sciencedirect.com/science/article/pii/S2452223623000561>, doi:10.1016/j.cogsc.2023.100807.
- Gebbink, W.A., van Asseldonk, L., van Leeuwen, S.P., 2017. Presence of Emerging Per- and Polyfluoroalkyl Substances (PFASs) in River and Drinking Water near a Fluorochemical Production Plant in the Netherlands. *Environmental Science & Technology* 51, 11057–11065. URL: <https://doi.org/10.1021/acs.est.7b02488>, doi:10.1021/acs.est.7b02488.
- Ghisi, R., Vamerali, T., Manzetti, S., 2019. Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: A review. *Environmental Research* 169, 326–341. URL: <https://www.sciencedirect.com/science/article/pii/S0013935118305577>, doi:10.1016/j.envres.2018.10.023.
- Giglioli, S., Colombo, L., Azzellino, A., 2023. Cluster and multivariate analysis to study the diffuse contamination of emerging per- and polyfluoroalkyl substances (PFAS) in the Veneto Region plain (North-eastern Italy). *Chemosphere* 319, 137916. URL: <https://www.sciencedirect.com/science/article/pii/S0045653523001832>, doi:10.1016/j.chemosphere.2023.137916.
- Glüge, J., Scheringer, M., Cousins, I.T., Dewitt, J.C., Goldenman, G., Herzke, D., Lohmann, R., Ng, C.A., Trier, X., Wang, Z., 2020. An overview of the uses of per- And polyfluoroalkyl substances (PFAS). *Environmental Science: Processes and Impacts* 22, 2345–2373. URL: <https://www.scopus.com/inward/record.uri?eid=2-s2.0-85098451345&doi=10.1039/>

- 2fd0em00291g&partnerID=40&md5=a41767dfe4f112739e8dd1aa278dcc21,
doi:10.1039/d0em00291g.
- Gobelius, L., Hedlund, J., Dürig, W., Tröger, R., Lilja, K., Wiberg, K., Ahrens, L., 2018. Per- and Polyfluoroalkyl Substances in Swedish Groundwater and Surface Water: Implications for Environmental Quality Standards and Drinking Water Guidelines. *Environmental Science & Technology* 52, 4340–4349. URL: <https://pubs.acs.org/doi/10.1021/acs.est.7b05718>, doi:10.1021/acs.est.7b05718.
- Göckener, B., Fliedner, A., Rüdell, H., Fettig, I., Koschorreck, J., 2021. Exploring unknown per- and polyfluoroalkyl substances in the German environment – The total oxidizable precursor assay as helpful tool in research and regulation. *Science of the Total Environment* 782. URL: <https://www.scopus.com/inward/record.uri?eid=2-s2.0-85103761499&doi=10.1016%2fj.scitotenv.2021.146825&partnerID=40&md5=1b43955c331f00aab6be69a77a37bf31>, doi:10.1016/j.scitotenv.2021.146825.
- Grung, M., Hjermann, D.O., Rundberget, T., Baek, K., Thomsen, C., Knutsen, H.K., Haug, L.S., 2024. Low levels of per- and polyfluoroalkyl substances (PFAS) detected in drinking water in Norway, but elevated concentrations found near known sources. *SCIENCE OF THE TOTAL ENVIRONMENT* 947. doi:10.1016/j.scitotenv.2024.174550.
- Hair, J.F., Black, W.C., Babin, B.J., Anderson, R.E., 2019. *Multivariate Data Analysis*. Eighth edition ed., Cengage, Australia Brazil Mexico South Africa Singapore United Kingdom United States.
- Hamid, H., Li, L.Y., Grace, J.R., 2020. Aerobic biotransformation of fluorotelomer compounds in landfill leachate-sediment. *Science of The Total Environment* 713, 136547. URL: <https://www.sciencedirect.com/science/article/pii/S0048969720300577>, doi:10.1016/j.scitotenv.2020.136547.
- Henne, S., Storck, F.R., Wöhrnschimmel, H., Leuenberger, M., Vollmer, M.K., Reimann, S., 2025. Trifluoroacetate (TFA) in Precipitation and Surface Waters in Switzerland: Trends, Source Attribution, and Budget. *EGU-sphere*, 1–43 URL: <https://egusphere.copernicus.org/preprints/2025/egusphere-2025-2861/>, doi:10.5194/egusphere-2025-2861.
- Higgins, C.P., Luthy, R.G., 2006. Sorption of Perfluorinated Surfactants on Sediments. *Environmental Science & Technology* 40, 7251–7256. URL: <https://pubs.acs.org/doi/10.1021/es061000n>, doi:10.1021/es061000n.
- Hong, M.S., Lee, J.S., Lee, M.C., Lee, J.S., 2025. Ecotoxicological effects of per- and polyfluoroalkyl substances in aquatic organisms: A review. *Marine Pollution Bulletin* 214, 117678. URL: <https://www>.

- sciencedirect.com/science/article/pii/S0025326X25001535, doi:10.1016/j.marpolbul.2025.117678.
- Hotelling, H., 1933. Analysis of a complex of statistical variables into principal components. *Journal of Educational Psychology* 24, 417–441. doi:10.1037/h0071325.
- Houtz, E.F., Higgins, C.P., Field, J.A., Sedlak, D.L., 2013. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environmental Science & Technology* 47, 8187–8195. URL: <https://doi.org/10.1021/es4018877>, doi:10.1021/es4018877.
- Kaiser, H.F., 1958. The Varimax Criterion for Analytic Rotation in Factor Analysis. *Psychometrika* 23, 187–200. URL: <https://www.cambridge.org/core/journals/psychometrika/article/abs/varimax-criterion-for-analytic-rotation-in-factor-analysis/88F99AA31F472BF854B01B6B92F4212B>, doi:10.1007/BF02289233.
- Kaiser, H.F., 1970. A second generation little jiffy. *Psychometrika* 35, 401–415. URL: <https://doi.org/10.1007/BF02291817>, doi:10.1007/BF02291817.
- Kali, S.E., Österlund, H., Viklander, M., Blecken, G.T., 2025. Stormwater discharges affect PFAS occurrence, concentrations, and spatial distribution in water and bottom sediment of urban streams. *Water Research* 271, 122973. URL: <https://www.sciencedirect.com/science/article/pii/S0043135424018736>, doi:10.1016/j.watres.2024.122973.
- Kärrman, A., Elgh-Dalgren, K., Lafossas, C., Mørskeland, T., 2011. Environmental levels and distribution of structural isomers of perfluoroalkyl acids after aqueous fire-fighting foam (AFFF) contamination. *Environmental Chemistry* 8, 372–380. URL: <https://connectsci.au/en/article/8/4/372/24133/Environmental-levels-and-distribution-of>, doi:10.1071/EN10145.
- Kesic, R., Elliott, J.E., Elliott, K.H., Lee, S.L., Maisonneuve, F., . Perfluoroalkyl Substances in Seabird Eggs from Canada’s Pacific Coast: Temporal Trends (1973–2019) and Interspecific Patterns. *Environmental Science & Technology* 57, 10792–10803. doi:10.1021/acs.est.3c02965.
- Kim, K.Y., Ndabambi, M., Choi, S., Oh, J.E., 2021. Legacy and novel perfluoroalkyl and polyfluoroalkyl substances in industrial wastewater and the receiving river water: Temporal changes in relative abundances of regulated compounds and alternatives. *Water Research* 191, 116830. URL: <https://www.sciencedirect.com/science/article/pii/S0043135421000282>, doi:10.1016/j.watres.2021.116830.
- Kotthoff, M., Müller, J., Jürling, H., Schlummer, M., Fiedler, D., 2015. Perfluoroalkyl and polyfluoroalkyl substances in consumer products. *Environmental Science and Pollution Research* 22, 14546–14559. URL: <http://link.springer.com/10.1007/s11356-015-4202-7>, doi:10.1007/s11356-015-4202-7.

- Krlovic, N., Saracevic, E., Derx, J., Gundacker, C., Krampe, J., Kreuzinger, N., Zessner, M., Zoboli, O., 2024a. Exploring the variability of PFAS in urban sewage: A comparison of emissions in commercial versus municipal urban areas. *ENVIRONMENTAL SCIENCE-PROCESSES & IMPACTS* 26, 1868–1878. doi:10.1039/d4em00415a.
- Krlovic, N., Saracevic, E., Derx, J., Gundacker, C., Krampe, J., Zessner, M., Zoboli, O., 2024b. A source-based framework to estimate the annual load of PFAS in municipal wastewater. *SCIENCE OF THE TOTAL ENVIRONMENT* 920. doi:10.1016/j.scitotenv.2024.170997.
- Kurwadkar, S., Dane, J., Kanel, S.R., Nadagouda, M.N., Cawdrey, R.W., Ambade, B., Struckhoff, G.C., Wilkin, R., 2022. Per- and polyfluoroalkyl substances in water and wastewater: A critical review of their global occurrence and distribution. *SCIENCE OF THE TOTAL ENVIRONMENT* 809, 151003. URL: <https://www.webofscience.com/api/gateway?GWVersion=2&SrcAuth=DOI&Source&SrcApp=WOS&KeyAID=10.1016%2Fj.scitotenv.2021.151003&DestApp=DOI&SrcAppSID=EUW1ED0B63P9IZv72wVzWvLJIuYYe&SrcJTitle=SCIENCE+OF+THE+TOTAL+ENVIRONMENT&DestDOIRegistrantName=Elsevier>, doi:10.1016/j.scitotenv.2021.151003.
- Lange, J., Bulka, L., Nöltge, D., Freeling, F., Ilgen, K., Külls, C., Müller, M., 2025. Trifluoroacetate (TFA) – Potentials and limits of a new hydrological pollution tracer. *Science of The Total Environment* 997, 180175. URL: <https://www.sciencedirect.com/science/article/pii/S0048969725018157>, doi:10.1016/j.scitotenv.2025.180175.
- Lehner, B., Grill, G., 2013. Global river hydrography and network routing: Baseline data and new approaches to study the world’s large river systems. *Hydrological Processes* 27, 2171–2186. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/hyp.9740>, doi:10.1002/hyp.9740.
- Li, H., Zhu, X., Zhang, J., Wang, Z., Li, R., 2023. Characterizing the long-term occurrence and anthropogenic drivers of per- and polyfluoroalkyl substances in surface water of the Rhine River. *Water Research* 245, 120528. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0043135423009685>, doi:10.1016/j.watres.2023.120528.
- Lindim, C., Cousins, I.T., vanGils, J., 2015. Estimating emissions of PFOS and PFOA to the Danube River catchment and evaluating them using a catchment-scale chemical transport and fate model. *Environmental Pollution* 207, 97–106. URL: <https://www.sciencedirect.com/science/article/pii/S0269749115300440>, doi:10.1016/j.envpol.2015.08.050.
- Lu, R., Colomer-Vidal, P., Munoz-Arnanz, J., Garcia-Barcelona, S., Zheng, X., Mai, B., Gonzalez-Solis, J., Jimenez, B., 2024. A 20-year study reveal decrease in per- and polyfluoroalkyl substances (PFAS) in a pelagic seabird

- from the Western Mediterranean Sea. ENVIRONMENTAL POLLUTION 362. doi:10.1016/j.envpol.2024.125025.
- Miljøministeriet, 2025. Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg. URL: <https://www.retsinformation.dk/eli/lta/2025/1272?id2af08e5a-33e1-4439-9302-f3c159f3136d>.
- Moneta, B.G., Feo, M.L., Torre, M., Tratzi, P., Aita, S.E., Montone, C.M., Taglioni, E., Mosca, S., Balducci, C., Cerasa, M., Guerriero, E., Petracchini, F., Cavaliere, C., Lagana, A., Paolini, V., 2023. Occurrence of per- and polyfluorinated alkyl substances in wastewater treatment plants in Northern Italy. SCIENCE OF THE TOTAL ENVIRONMENT 894. doi:10.1016/j.scitotenv.2023.165089.
- Moody, C.A., Field, J.A., 2000. Perfluorinated Surfactants and the Environmental Implications of Their Use in Fire-Fighting Foams. Environmental Science & Technology 34, 3864–3870. URL: <https://doi.org/10.1021/es991359u>, doi:10.1021/es991359u.
- Navarro, I., De La Torre, A., Sanz, P., Martínez, M.D.L.Á., 2020. Perfluoroalkyl acids (PFAAs): Distribution, trends and aquatic ecological risk assessment in surface water from Tagus River basin (Spain). Environmental Pollution 256, 113511. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0269749119339533>, doi:10.1016/j.envpol.2019.113511.
- Neuwald, I.J., Hübner, D., Wiegand, H.L., Valkov, V., Borchers, U., Nödler, K., Scheurer, M., Hale, S.E., Arp, H.P.H., Zahn, D., 2022. Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated. Environmental Science & Technology 56, 6380–6390. URL: <https://doi.org/10.1021/acs.est.1c07949>, doi:10.1021/acs.est.1c07949.
- Ng, K., Alygizakis, N., Androulakakis, A., Galani, A., Aalizadeh, R., Thomaidis, N.S., Slobodnik, J., 2022. Target and suspect screening of 4777 per- and polyfluoroalkyl substances (PFAS) in river water, wastewater, groundwater and biota samples in the Danube River Basin. Journal of Hazardous Materials 436, 129276. URL: <https://www.sciencedirect.com/science/article/pii/S0304389422010664>, doi:10.1016/j.jhazmat.2022.129276.
- Nguyen, T.M.H., Bräunig, J., Thompson, K., Thompson, J., Kabiri, S., Navarro, D.A., Kookana, R.S., Grimison, C., Barnes, C.M., Higgins, C.P., McLaughlin, M.J., Mueller, J.F., 2020. Influences of Chemical Properties, Soil Properties, and Solution pH on Soil–Water Partitioning Coefficients of Per- and Polyfluoroalkyl Substances (PFASs). Environmental Science & Technology 54, 15883–15892. URL: <https://doi.org/10.1021/acs.est.0c05705>, doi:10.1021/acs.est.0c05705.
- NORMAN Database System, 2026. NORMAN Ecotoxicology Database. URL: <https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php>.

- OECD, . Synthesis Paper on per and Polyfluorinated Chemicals. OECD Series on Risk Management of Chemicals, OECD. doi:10.1787/0bc75123-en.
- Ohoro, C.R., Amaku, J.F., Conradie, J., Olisah, C., Akpomie, K.G., Malloum, A., Akpotu, S.O., Adegoke, K.A., Okeke, E.S., Omotola, E.O., 2024. Effect of physicochemical parameters on the occurrence of per- and polyfluoroalkyl substances (PFAS) in aquatic environment. MARINE POLLUTION BULLETIN 208. doi:10.1016/j.marpolbul.2024.117040.
- Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate. Environmental Science & Technology 43, 386–392. URL: <https://doi.org/10.1021/es802216n>, doi:10.1021/es802216n.
- Pedregosa, F., Varoquaux, G., Gramfort, A., Michel, V., Thirion, B., Grisel, O., Blondel, M., Prettenhofer, P., Weiss, R., Dubourg, V., Vanderplas, J., Passos, A., Cournapeau, D., Brucher, M., Perrot, M., Duchesnay, É., 2011. Scikit-learn: Machine Learning in Python. Journal of Machine Learning Research 12, 2825–2830. URL: <http://jmlr.org/papers/v12/pedregosa11a.html>.
- Pereira, H.C., Ullberg, M., Kleja, D.B., Gustafsson, J.P., Ahrens, L., . Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon - Effect of cation composition and pH. Chemosphere 207, 183–191. doi:10.1016/j.chemosphere.2018.05.012.
- Python Software Foundation, . Python Language Reference (version 3.14). URL: <http://www.python.org>.
- Röhrig, A., Grasse, N., Krauss, M., Bücher, D., Brack, W., Kamjunke, N., Matousu, A., Sanders, T., Bussmann, I., Achterberg, E.P., Reemtsma, T., Fu, Q., 2026. Beyond Legacy PFAS: Dominant Role of Ultrashort-Chain and Emerging PFAS in the Elbe River-Sea Continuum. ACS Environmental Au , acsenvironau.5c00219URL: <https://pubs.acs.org/doi/10.1021/acsenvironau.5c00219>, doi:10.1021/acsenvironau.5c00219.
- Rüdel, H., Körner, W., Letzel, T., Neumann, M., Nödler, K., Reemtsma, T., . Persistent, mobile and toxic substances in the environment: A spotlight on current research and regulatory activities. Environmental Sciences Europe 32, 5. doi:10.1186/s12302-019-0286-x.
- Sánchez-Bayo, F., Baskaran, S., Kennedy, I.R., 2002. Ecological relative risk (EcoRR): Another approach for risk assessment of pesticides in agriculture. Agriculture, Ecosystems & Environment 91, 37–57. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0167880901002584>, doi:10.1016/S0167-8809(01)00258-4.
- SCHEER (Scientific Committee on Health, Environmental and Emerging Risks), 2025. Scientific Opinion on "DRAFT ENVIRONMENTAL QUALITY STANDARD FOR PFAS TOTAL UNDER THE WATER

- FRAMEWORK DIRECTIVE". Technical Report. European Commission. URL: https://health.ec.europa.eu/document/download/7f645d23-3d53-47fc-bf76-4067039a8468_en?filename=scheer_o_065.pdf.
- Scheurer, M., Nödler, K., Freeling, F., Janda, J., Happel, O., Riegel, M., Müller, U., Storck, F.R., Fleig, M., Lange, F.T., Brunsch, A., Brauch, H.J., 2017. Small, mobile, persistent: Trifluoroacetate in the water cycle – Overlooked sources, pathways, and consequences for drinking water supply. *Water Research* 126, 460–471. URL: <https://www.sciencedirect.com/science/article/pii/S0043135417307996>, doi:10.1016/j.watres.2017.09.045.
- Schmidt, N., Fauvelle, V., Castro-Jiménez, J., Lajaunie-Salla, K., Pinazo, C., Yohia, C., Sempéré, R., 2019. Occurrence of perfluoroalkyl substances in the bay of marseille (NW mediterranean sea) and the rhône river. *Marine Pollution Bulletin* 149. URL: <https://www.scopus.com/inward/record.uri?eid=2-s2.0-85070223800&doi=10.1016%2fj.marpolbul.2019.110491&partnerID=40&md5=e584e04b4cbe559deb95c9ceff65ba50>, doi:10.1016/j.marpolbul.2019.110491.
- Schröder, R., 2026. PFAS assessment in European surface waters: Code and data. Zenodo. doi:10.5281/ZENODO.23321966.
- Sha, B., Johansson, J.H., Tunved, P., Bohlin-Nizzetto, P., Cousins, I.T., Salter, M.E., 2022. Sea Spray Aerosol (SSA) as a Source of Perfluoroalkyl Acids (PFAAs) to the Atmosphere: Field Evidence from Long-Term Air Monitoring. *Environmental Science & Technology* 56, 228–238. URL: <https://doi.org/10.1021/acs.est.1c04277>, doi:10.1021/acs.est.1c04277.
- Souza, M.C.O., Domingo, J.L., 2025. Levels of *per*- and polyfluoroalkyl substances (PFAS) in foodstuffs: A review of dietary exposure, health risks, and regulatory challenges. *Food Research International* 221, 117494. URL: <https://www.sciencedirect.com/science/article/pii/S0963996925018320>, doi:10.1016/j.foodres.2025.117494.
- Stoiber, T., Evans, S., Naidenko, O.V., 2020. Disposal of products and materials containing *per*- and polyfluoroalkyl substances (PFAS): A cyclical problem. *Chemosphere* 260, 127659. URL: <https://www.sciencedirect.com/science/article/pii/S0045653520318543>, doi:10.1016/j.chemosphere.2020.127659.
- Sturm, R., Ahrens, L., 2010. Trends of polyfluoroalkyl compounds in marine biota and in humans. *Environmental Chemistry* 7, 457–484. URL: <https://connectsci.au/en/article/7/6/457/24103/Trends-of-polyfluoroalkyl-compounds-in-marine>, doi:10.1071/EN10072.
- Sunderland, E.M., Hu, X.C., Dassuncao, C., Tokranov, A.K., Wagner, C.C., Allen, J.G., 2019. A review of the pathways of human exposure to poly-

- and perfluoroalkyl substances (PFASs) and present understanding of health effects. *JOURNAL OF EXPOSURE SCIENCE AND ENVIRONMENTAL EPIDEMIOLOGY* 29, 131–147. doi:10.1038/s41370-018-0094-1.
- Tang, Z., Vogel, T.M., Wang, Q., Wei, C., Ali, M., Song, X., 2024. Microbial defluorination of TFA, PFOA, and HFPO-DA by a native microbial consortium under anoxic conditions. *Journal of Hazardous Materials* 465, 133217. URL: <https://www.sciencedirect.com/science/article/pii/S0304389423025013>, doi:10.1016/j.jhazmat.2023.133217.
- Teymoorian, T., Delon, L., Munoz, G., Sauvé, S., 2025. Target and Suspect Screening Reveal PFAS Exceeding European Union Guideline in Various Water Sources South of Lyon, France. *Environmental Science & Technology Letters* 12, 327–333. URL: <https://pubs.acs.org/doi/10.1021/acs.estlett.4c01126>, doi:10.1021/acs.estlett.4c01126.
- The pandas development team, 2026. Pandas-dev/pandas: Pandas. Zenodo. URL: <https://zenodo.org/records/21500199>.
- Virtanen, P., Gommers, R., Oliphant, T.E., Haberland, M., Reddy, T., Cournapeau, D., Burovski, E., Peterson, P., Weckesser, W., Bright, J., Van Der Walt, S.J., Brett, M., Wilson, J., Millman, K.J., Mayorov, N., Nelson, A.R.J., Jones, E., Kern, R., Larson, E., Carey, C.J., Polat, İ., Feng, Y., Moore, E.W., VanderPlas, J., Laxalde, D., Perktold, J., Cimrman, R., Henriksen, I., Quintero, E.A., Harris, C.R., Archibald, A.M., Ribeiro, A.H., Pedregosa, F., Van Mulbregt, P., SciPy 1.0 Contributors, Vijaykumar, A., Bardelli, A.P., Rothberg, A., Hilboll, A., Kloeckner, A., Scopatz, A., Lee, A., Rokem, A., Woods, C.N., Fulton, C., Masson, C., Häggström, C., Fitzgerald, C., Nicholson, D.A., Hagen, D.R., Pasechnik, D.V., Olivetti, E., Martin, E., Wieser, E., Silva, F., Lenders, F., Wilhelm, F., Young, G., Price, G.A., Ingold, G.L., Allen, G.E., Lee, G.R., Audren, H., Probst, I., Dietrich, J.P., Silterra, J., Webber, J.T., Slavič, J., Nothman, J., Buchner, J., Kulick, J., Schönberger, J.L., De Miranda Cardoso, J.V., Reimer, J., Harrington, J., Rodríguez, J.L.C., Nunez-Iglesias, J., Kuczynski, J., Tritz, K., Thoma, M., Newville, M., Kümmerer, M., Bolingbroke, M., Tartre, M., Pak, M., Smith, N.J., Nowaczyk, N., Shebanov, N., Pavlyk, O., Brodtkorb, P.A., Lee, P., McGibbon, R.T., Feldbauer, R., Lewis, S., Tygier, S., Sievert, S., Vigna, S., Peterson, S., More, S., Pudlik, T., Oshima, T., Pingel, T.J., Robitaille, T.P., Spura, T., Jones, T.R., Cera, T., Leslie, T., Zito, T., Krauss, T., Upadhyay, U., Halchenko, Y.O., Vázquez-Baeza, Y., 2020. SciPy 1.0: Fundamental algorithms for scientific computing in Python. *Nature Methods* 17, 261–272. URL: <https://www.nature.com/articles/s41592-019-0686-2>, doi:10.1038/s41592-019-0686-2.
- Wang, L., Yang, T., Liu, X., Liu, J., Liu, W., 2024. Critical Evaluation and Meta-Analysis of Ecotoxicological Data on Per- and Polyfluoroalkyl Substances (PFAS) in Freshwater Species. *Environmental Science & Technol-*

- ogy 58, 17555–17566. URL: <https://doi.org/10.1021/acs.est.4c04818>, doi:10.1021/acs.est.4c04818.
- Wang, N., Liu, J., Buck, R.C., Korzeniowski, S.H., Wolstenholme, B.W., Folsom, P.W., Sulecki, L.M., 2011. 6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants. *Chemosphere* 82, 853–858. URL: <https://www.sciencedirect.com/science/article/pii/S0045653510012634>, doi:10.1016/j.chemosphere.2010.11.003.
- Wilcoxon, F., 1945. Individual Comparisons by Ranking Methods. *Biometrics Bulletin* 1, 80. URL: <https://www.jstor.org/stable/10.2307/3001968?origin=crossref>, doi:10.2307/3001968, arXiv:10.2307/3001968.
- Yan, P.F., Dong, S., Woodcock, M.J., Manz, K.E., Garza-Rubalcava, U., Abriola, L.M., Pennell, K.D., Cápiro, N.L., 2024. Biotransformation of 6:2 fluorotelomer sulfonate and microbial community dynamics in water-saturated one-dimensional flow-through columns. *Water Research* 252, 121146. URL: <https://www.sciencedirect.com/science/article/pii/S0043135424000460>, doi:10.1016/j.watres.2024.121146.
- Yeo, I.K., Johnson, R.A., 2000. A New Family of Power Transformations to Improve Normality or Symmetry. *Biometrika* 87, 954–959. URL: <https://www.jstor.org/stable/2673623>, arXiv:2673623.
- Zarebska, M., Bajkacz, S., Hordyjewicz-Baran, Z., 2024. Assessment of legacy and emerging PFAS in the Oder River: Occurrence, distribution, and sources. *Environmental Research* 251, 118608. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0013935124005127>, doi:10.1016/j.envres.2024.118608.
- Zhang, J., Zhang, S., Lu, C., Wang, X., Du, Z., Wang, J., Li, B., Wang, J., Zhu, L., 2025. Comparison of the combined toxicity of PFOA and emerging alternatives: A comprehensive evaluation of oxidative damage, apoptosis and immunotoxicity in embryonic and adult zebrafish. *Water Research* 273, 123028. URL: <https://www.sciencedirect.com/science/article/pii/S0043135424019286>, doi:10.1016/j.watres.2024.123028.
- Zhao, L., Chen, J., Wen, J., Li, Y., Zhang, Y., Wu, Q., Yu, G., 2025. Unveiling PFAS hazard in European surface waters using an interpretable machine-learning model. *Environment International* 199, 109504. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0160412025002557>, doi:10.1016/j.envint.2025.109504.

Supplementary Information A

Fingerprinting PFAS pollution in European surface waters

Robin Schröder^{a,*}, Jens Prothmann^b, Tobias Licha^b, Hans H. Dürr^a, Martina Flörke^a

^a *Engineering Hydrology and Water Resources Management, Faculty of Civil and Environmental Engineering, Ruhr University Bochum, Universitätsstraße 150, 44801 Bochum, Germany*

^b *Hydrogeochemistry & Hydrogeology, Institute of Geosciences, Ruhr University Bochum, Universitätsstraße 150, 44801 Bochum, Germany*

*Corresponding author

Email address: robin.schroeder@hydrology.ruhr-uni-bochum.de (Robin Schröder)

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A. Supplementary Information

Table A.1: Included PFAS and their commonly used abbreviations. Carbon atoms are reported as the sum of perfluorinated methyl (-CF₃) and perfluorinated methylene (-CF₂-) group(s) + the remaining carbon atom(s).

Substance ^a	Abbreviation ^a	CASID	Carbon Atoms ^a
Perfluoroalkyl carboxylic acids (PFCAs)			
Trifluoroacetic acid	TFA	76-05-1	C1+1
Perfluorobutanoic acid	PFBA	375-22-4	C3+1
Perfluoropentanoic acid	PFPeA	2706-90-3	C4+1
Perfluorohexanoic acid	PFHxA	307-24-4	C5+1
Perfluoroheptanoic acid	PFHpA	375-85-9	C6+1
Perfluorooctanoic acid	PFOA	335-67-1	C7+1
Perfluorononanoic acid	PFNA	375-95-1	C8+1
Perfluorodecanoic acid	PFDA	335-76-2	C9+1
Perfluoroundecanoic acid	PFUnDA	2058-94-8	C10+1
Perfluorododecanoic acid	PFDoDA	307-55-1	C11+1
Perfluorotridecanoic acid	PFTTrDA	72629-94-8	C12+1
Perfluorotetradecanoic acid	PFTeDA	376-06-7	C13+1
Perfluorohexadecanoic acid	PFHxDA	67905-19-5	C15+1
Perfluorooctadecanoic acid	PFODA	16517-11-6	C17+1
Perfluoroalkane sulfonic acids (PFSAAs)			
Perfluorobutane sulfonic acid	PFBS	375-73-5	C4
Perfluoropentane sulfonic acid	PFPeS	2706-91-4	C5
Perfluorohexane sulfonic acid	PFHxS	355-46-4	C6
Perfluoroheptane sulfonic acid	PFHpS	375-92-8	C7
Perfluorooctane sulfonic acid	PFOS	1763-23-1	C8
Perfluorononane sulfonic acid	PFNS	68259-12-1	C9
Perfluorodecane sulfonic acid	PFDS	335-77-3	C10
Perfluoroundecane sulfonic acid	PFUnDS	749786-16-1	C11
Perfluorododecane sulfonic acid	PFDoDS	79780-39-5	C12
Perfluorotridecane sulfonic acid	PFTTrDS	791563-89-8	C13
Fluorotelomer-based substances			
6:2 Fluorotelomer carboxylic acid	6:2 FTCA	53826-12-3	C6+2
4:2 Fluorotelomer sulfonic acid	4:2 FTS / H4PFHxS	757124-72-4	C4+2
6:2 Fluorotelomer sulfonic acid	6:2 FTS / H4PFOS	27619-97-2	C6+2
8:2 Fluorotelomer sulfonic acid	8:2 FTS / H4PFDS	39108-34-4	C8+2
Perfluoroalkylether carboxylic acids (PFECAs)			
Perfluoro-2-methyl-3-oxahexanoic acid / Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	C4+2
4,8-dioxa-3H-perfluorononanoic acid	DONA	919005-14-4	C5+2
Perfluoroalkane sulfonyl fluoride (PASF)-based substances			
Perfluorooctanesulfonamide ^b	FOSA	754-91-6	C8
N-Ethylperfluorooctanesulfonamide ^c	N-Et-FOSA	4151-50-2	C8+2
N-Methyl perfluorooctane sulfonamidoacetic acid ^d	N-MeFOSAA	2355-31-9	C8+3
N-Ethyl perfluorooctane sulfonamidoacetic acid ^e	EtFOSAA	2991-50-6	C8+4

^a Information derived from <https://comptox.epa.gov/dashboard> and Glüge et al. (2020) based on CASID

^b Subgroup: Perfluoroalkane sulfonamides (FASAs)

^c Subgroup: N-Ethyl perfluoroalkane sulfonamides (EtFASAs)

^d Subgroup: N-Methyl perfluoroalkane sulfonamidoacetic acids (MeFASAs)

^e Subgroup: N-Ethyl perfluoroalkane sulfonamidoacetic acids (EtFASAs)

A.1. PFAS ratios

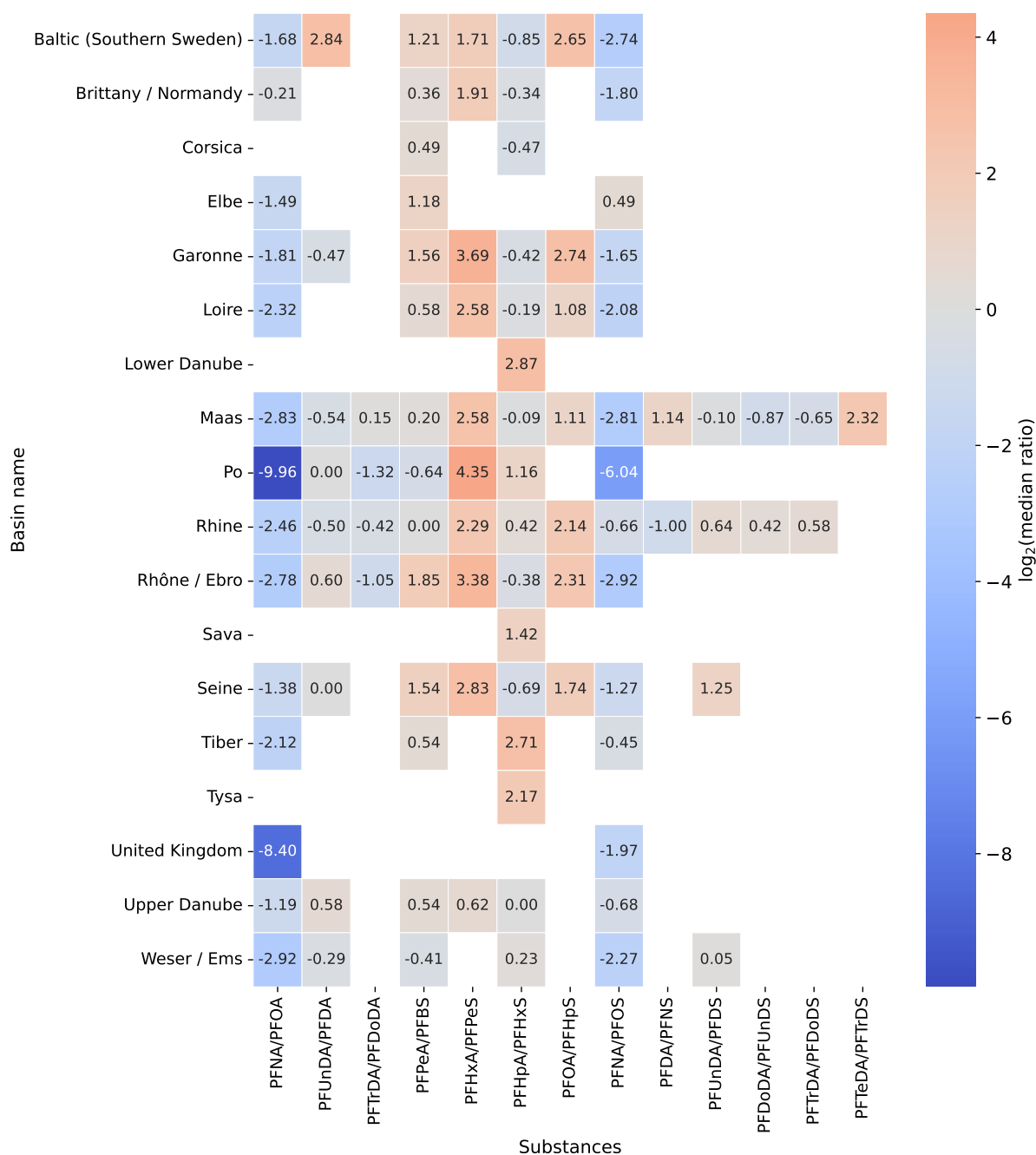


Figure A.1: Heatmap of the log₂ transformed median ratios of PFAS concentrations by basins as defined in Figure 1. Ratios were calculated based on substance pairs for a given sampling site and day. Values of 0 mean equal concentrations, while +1 denote that the numerator is twice the denominator and vice versa for -1. Counts for each ratio-basin pair are reported in Table B.1.

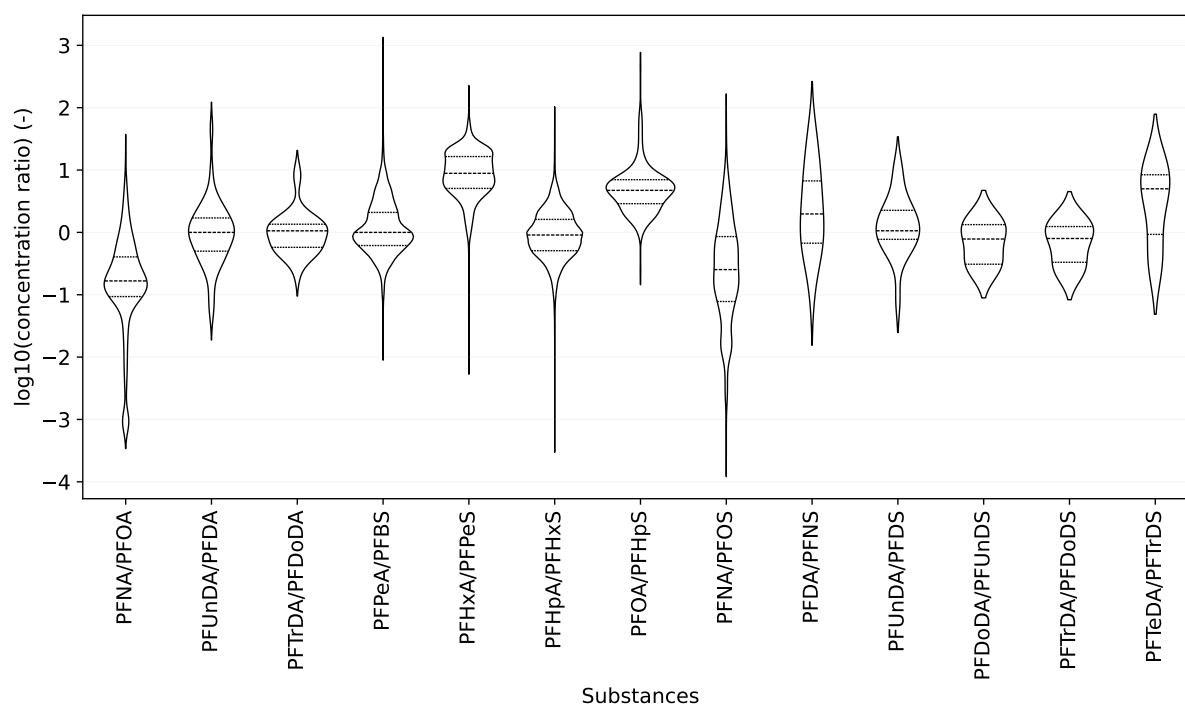


Figure A.2: Violinplot of the log₁₀ transformed concentrations ratios of two PFAS. Quartiles of the data are shown as dotted lines in the interior of the plots. Ratios were calculated based on substance pairs for a given sampling site and day. Counts for each ratio are reported in Table B.1.

A.2. Sum parameters

Table A.2: Common sum parameters and their associated substances. The X indicates that a substance belongs to the sum parameter. For abbreviations refer to [Table A.1](#).

Abbreviation	PFAS 4	PFAS 7	PFAS 11	PFAS 18	Sum of PFAS / PFAS 20 ^a
PFBA			X	X	X
PFPeA		X	X	X	X
PFHxA		X	X	X	X
PFHpA		X	X	X	X
PFOA	X	X	X	X	X
PFNA	X		X	X	X
PFDA			X	X	X
PFUnDA				X	X
PFDoDA				X	X
PFTTrDA				X	X
PFBS		X	X	X	X
PFPeS				X	X
PFHxS	X	X	X	X	X
PFHpS				X	X
PFOS	X	X	X	X	X
PFNS				X	X
PFDS				X	X
PFUnDS					X
PFDoDS					X
PFTTrDS					X
6:2 FTS			X	X	

^a Sum parameter used in this study

A.3. Environmental risk evaluation

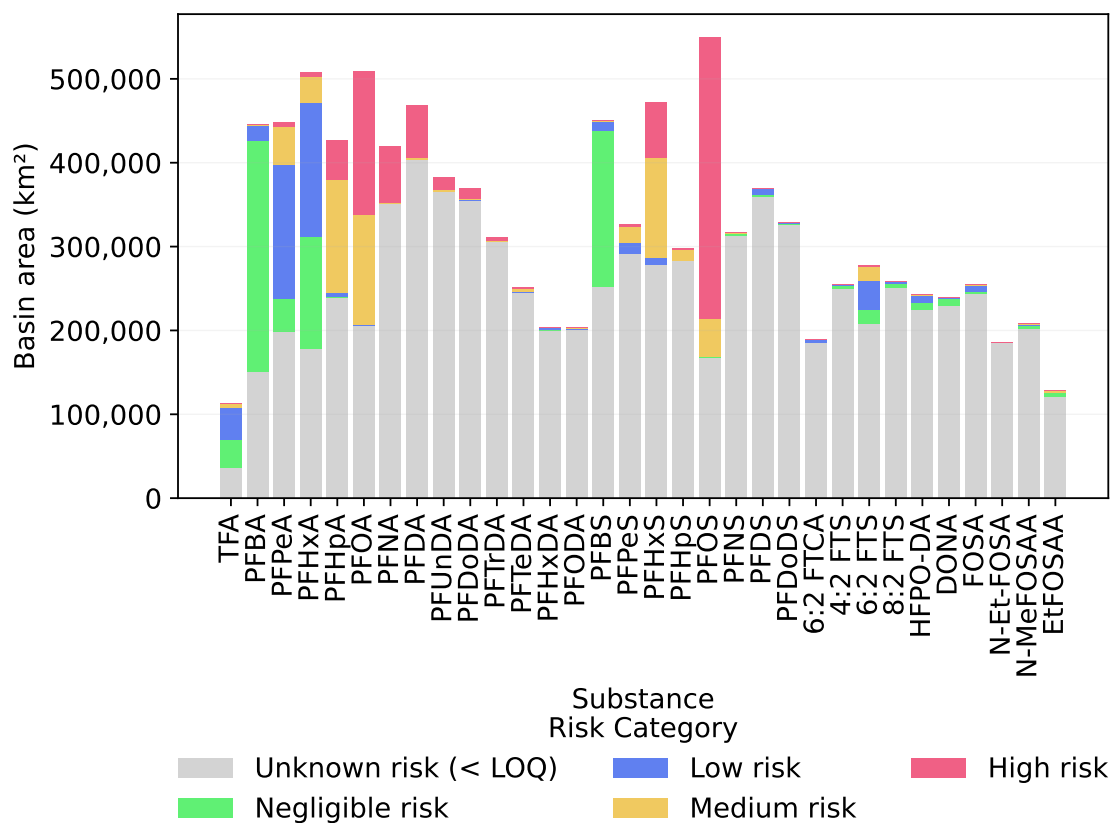


Figure A.3: Area-based risk categories computed for various PFAS for the period 2019-2026.

A.4. PCA/FA Consensus Matrix and Bi-plots

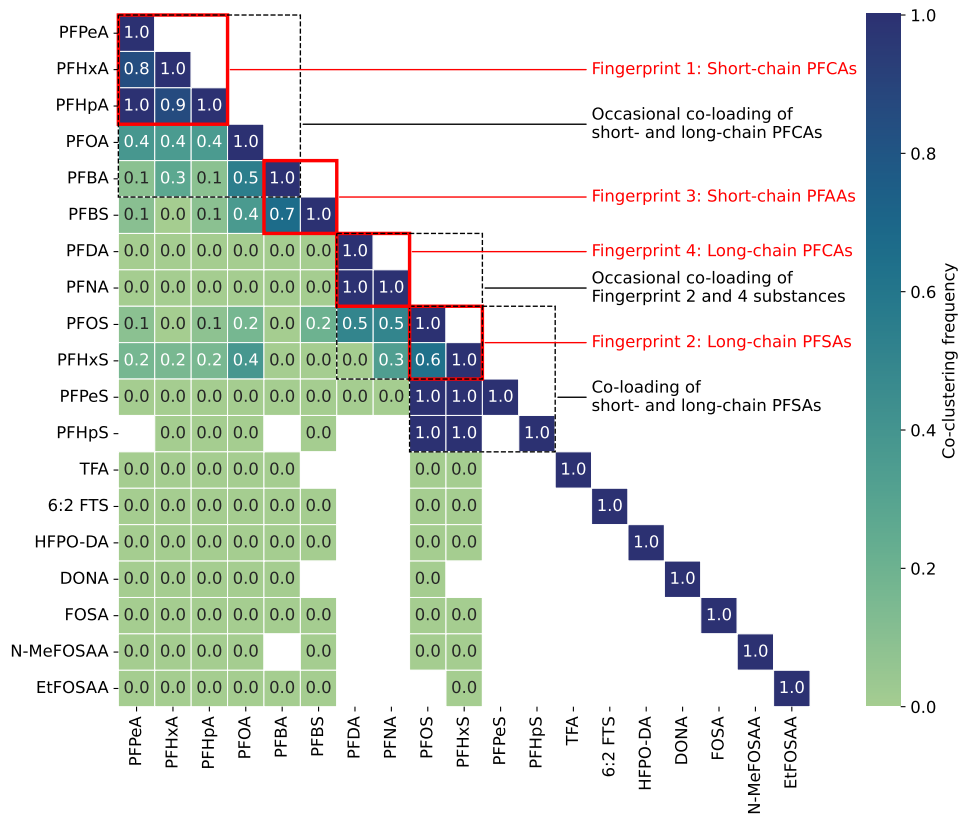


Figure A.4: Consensus matrix across all clustering runs. Co-clustering frequency is normalized to the number of clustering runs carried out for each substance combination. Empty fields denote substance combinations that have not been evaluated together in any run.

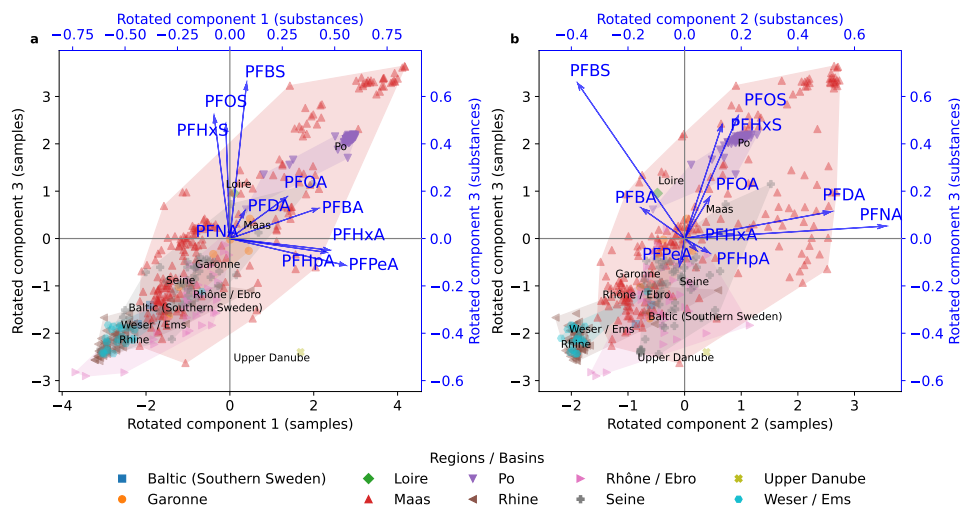


Figure A.5: Bi-plot of varimax-rotated principal components (RCs) of Group A1 substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

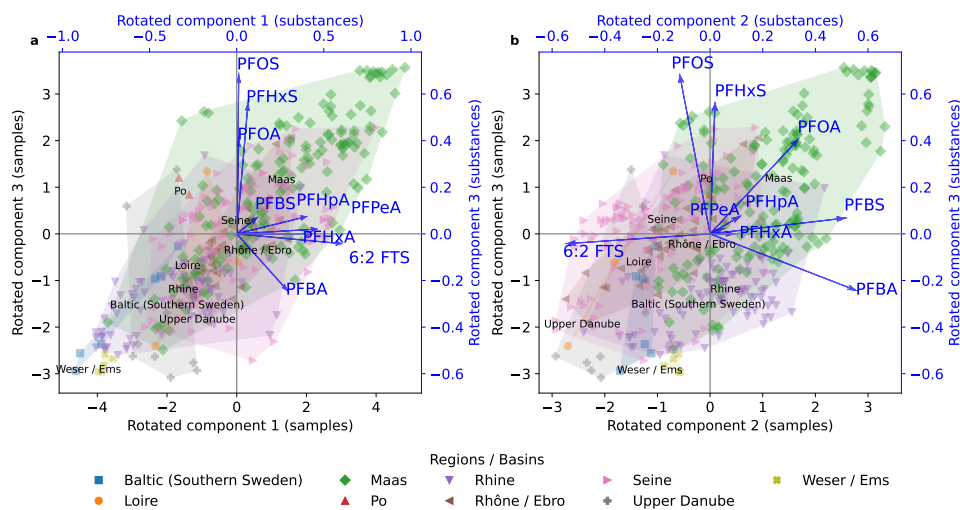


Figure A.6: Bi-plot of varimax-rotated principal components (RCs) of Group A2 substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

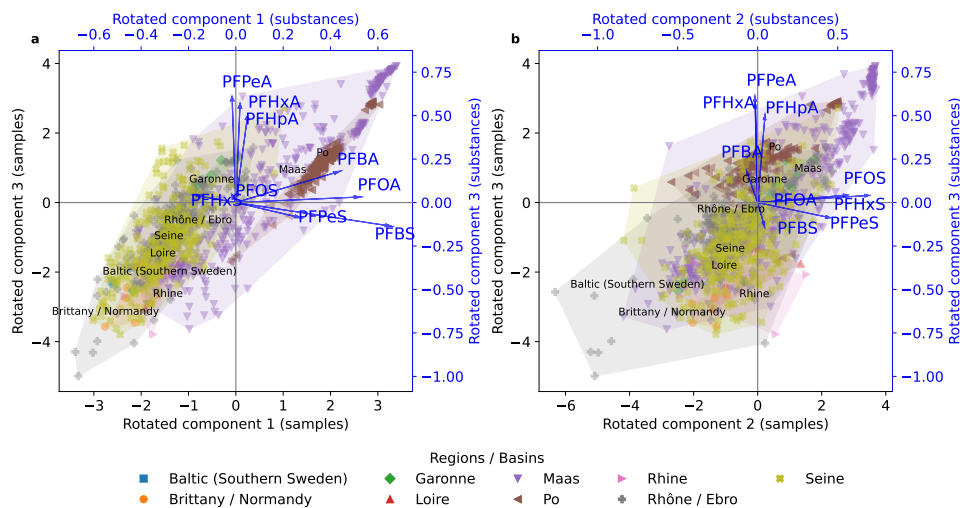


Figure A.7: Bi-plot of varimax-rotated principal components (RCs) of Group A3 substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

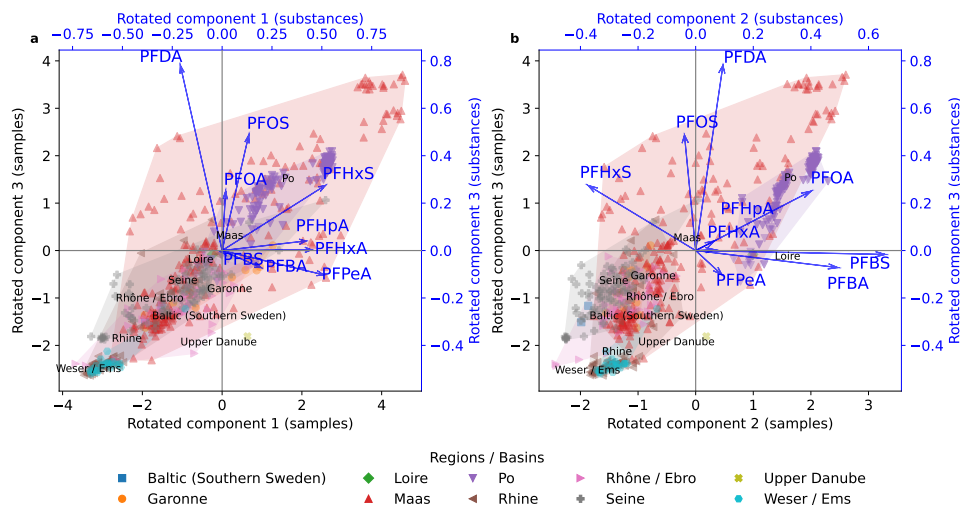


Figure A.8: Bi-plot of varimax-rotated principal components (RCs) of Group A4 substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

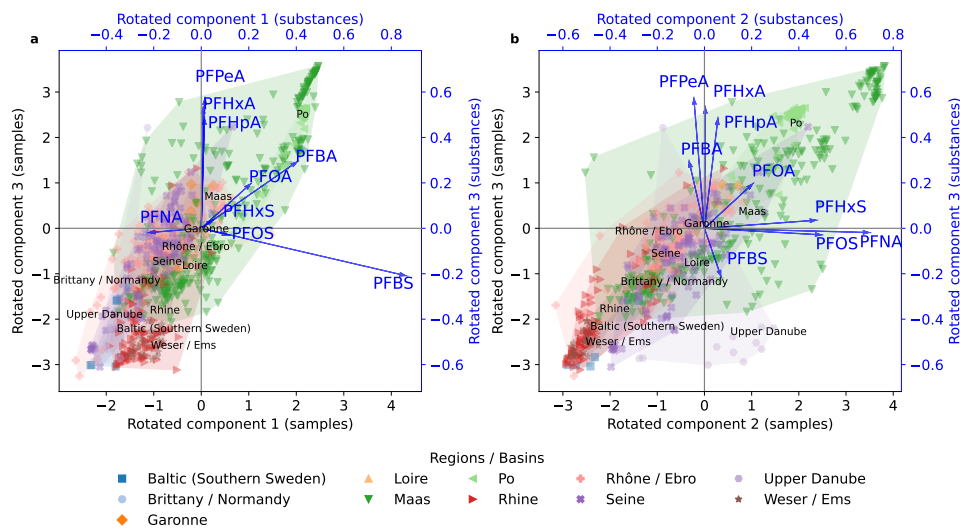


Figure A.9: Bi-plot of varimax-rotated principal components (RCs) of Group A5 substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

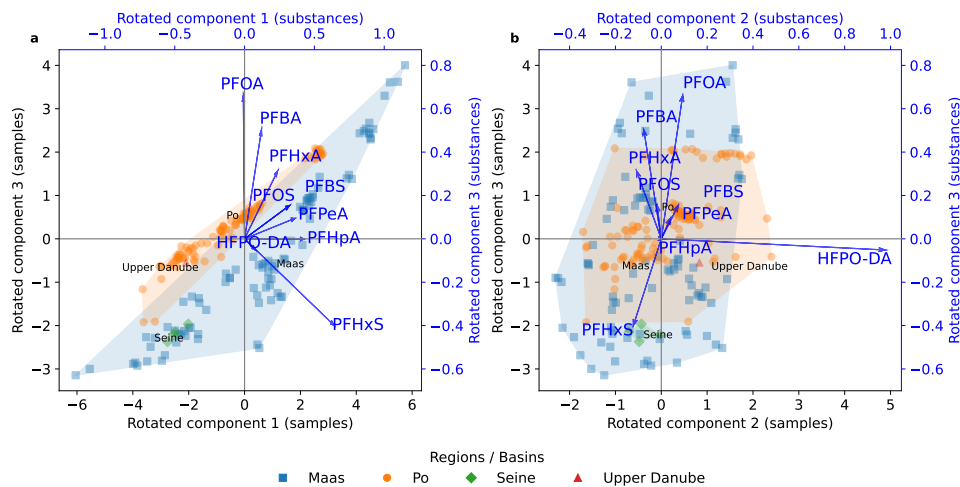


Figure A.10: Bi-plot of varimax-rotated principal components (RCs) of Group A6 substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

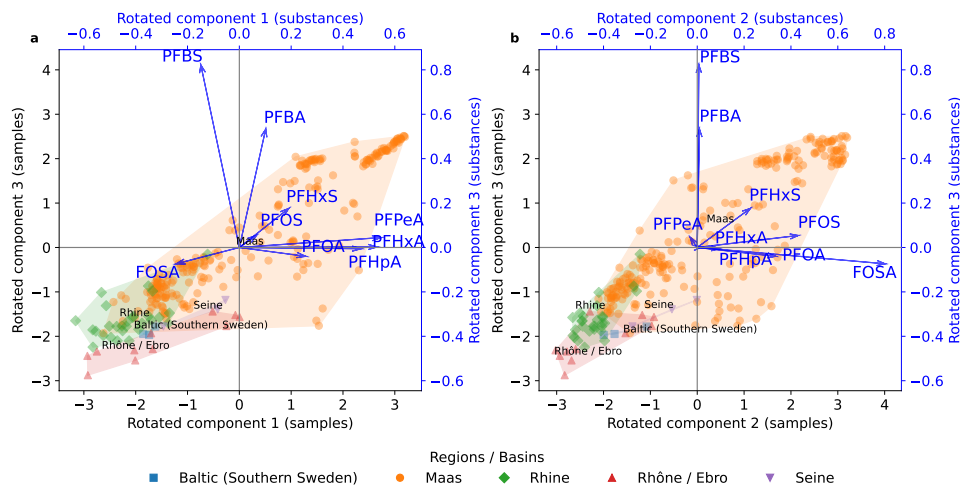


Figure A.11: Bi-plot of varimax-rotated principal components (RCs) of Group A7 substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

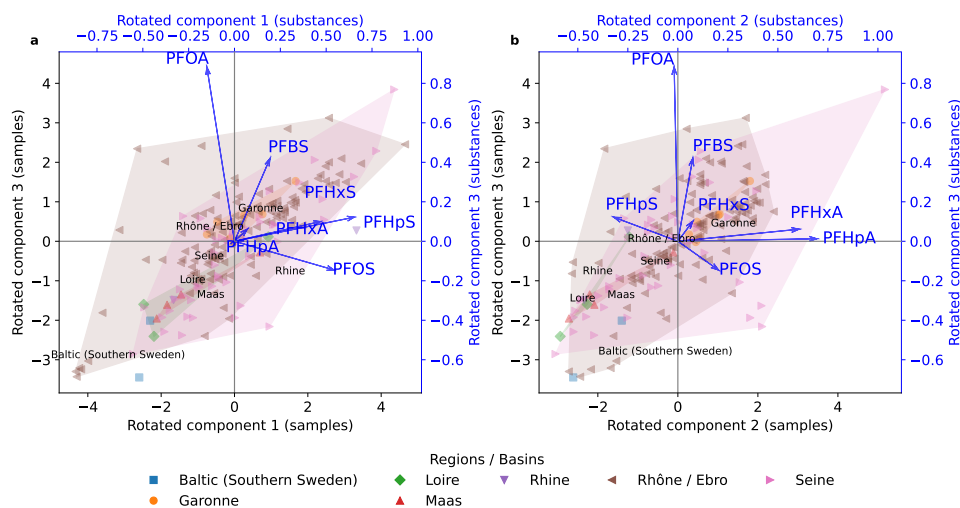


Figure A.12: Bi-plot of varimax-rotated principal components (RCs) of Group B substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

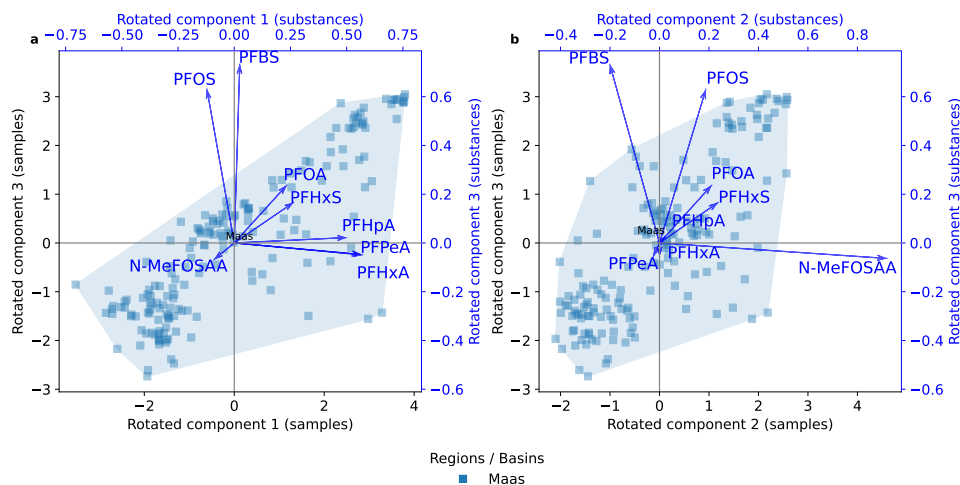


Figure A.13: Bi-plot of varimax-rotated principal components (RCs) of Group C substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

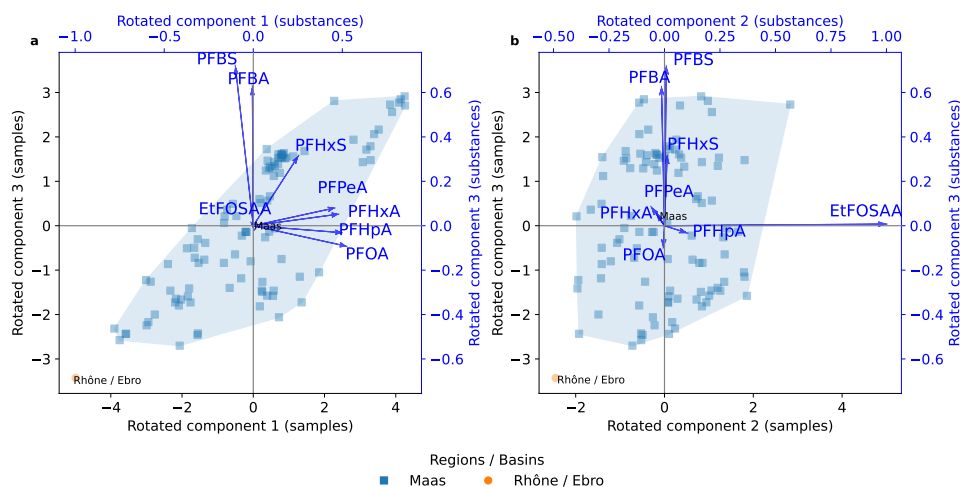


Figure A.14: Bi-plot of varimax-rotated principal components (RCs) of Group D substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

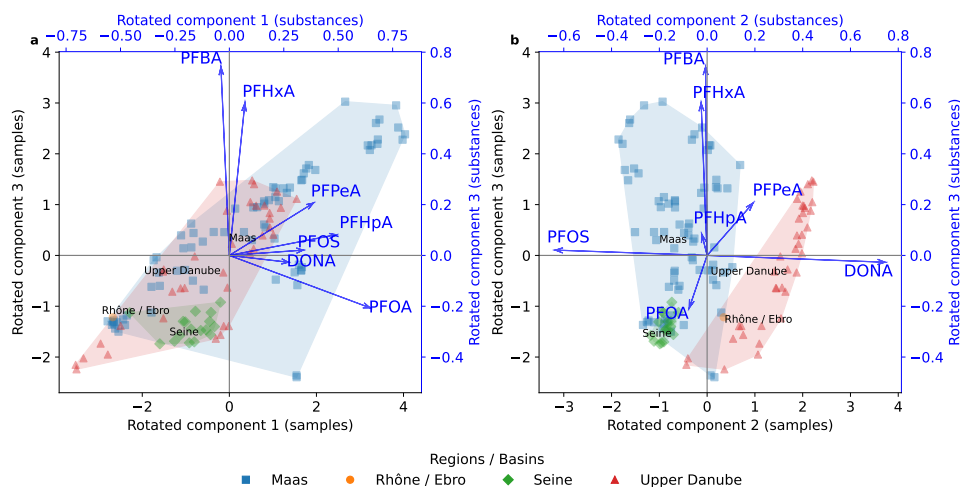


Figure A.15: Bi-plot of varimax-rotated principal components (RCs) of Group E substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

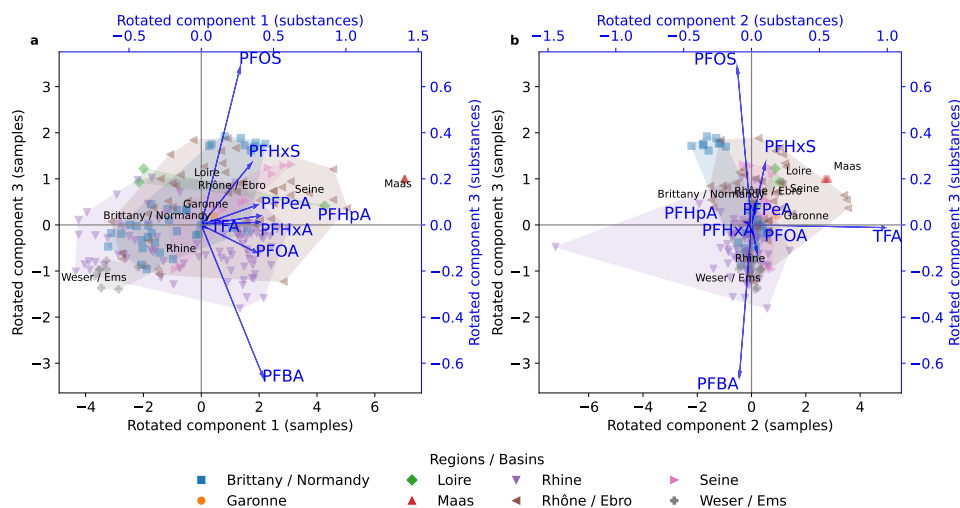


Figure A.16: Bi-plot of varimax-rotated principal components (RCs) of Group F substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

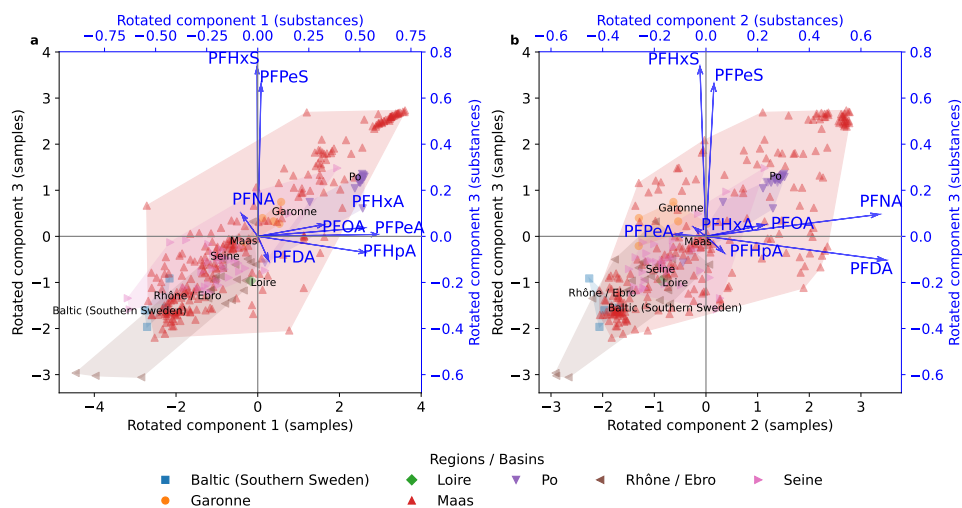


Figure A.17: Bi-plot of varimax-rotated principal components (RCs) of Group G substances. Colours denote geographic region / river basin, including convex hulls for sample sizes > 3. Region names are plotted at the respective centre. Substance loadings are scaled according to the secondary x and y axes, as denoted in blue. (a) RCs 1 and 3. (b) RCs 2 and 3.

A.5. Hotspots

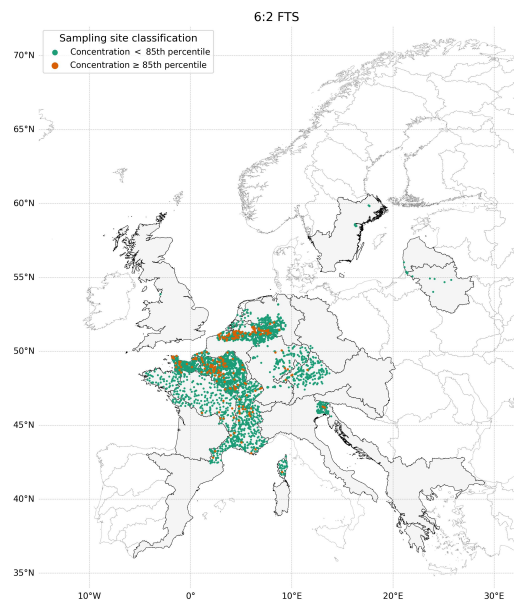


Figure A.18: 6:2 FTS sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

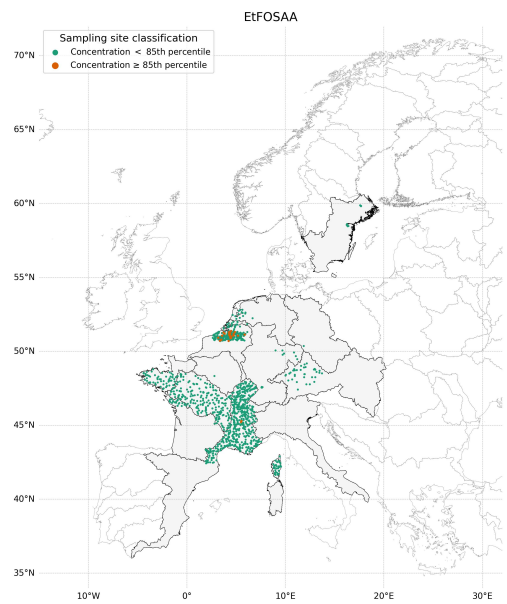


Figure A.19: EtFOSAA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

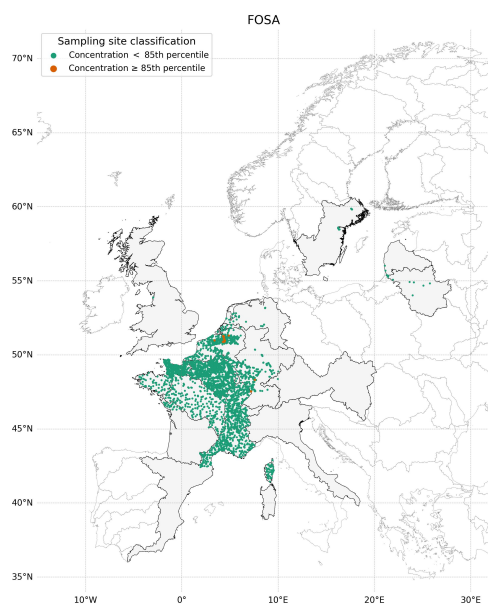


Figure A.20: FOSA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

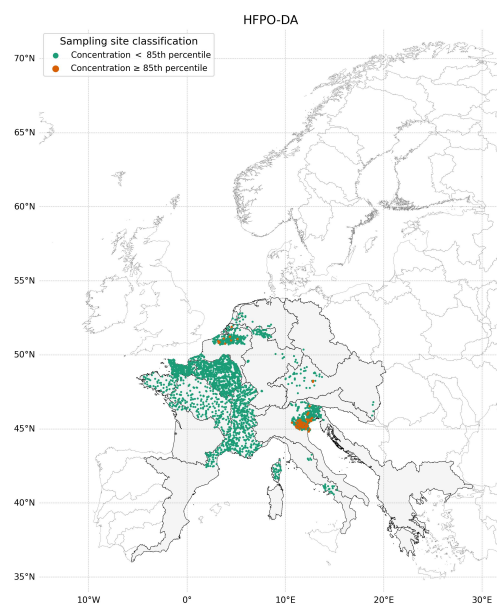


Figure A.21: HFPO-DA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

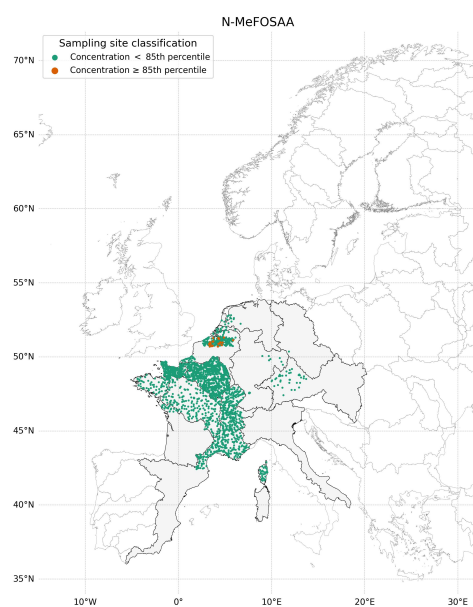


Figure A.22: N-MeFOSAA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

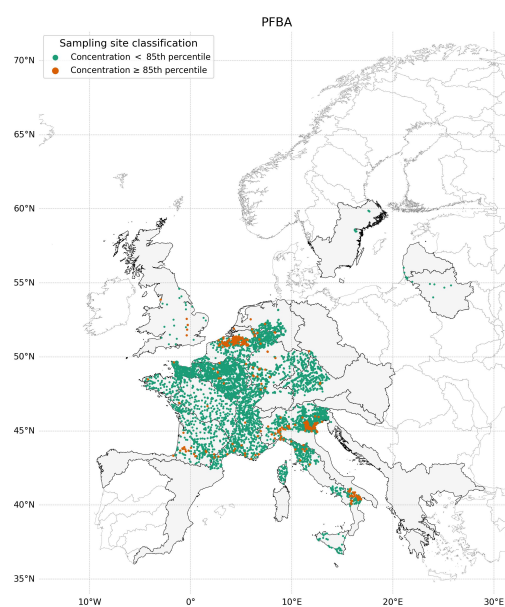


Figure A.23: PFBA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

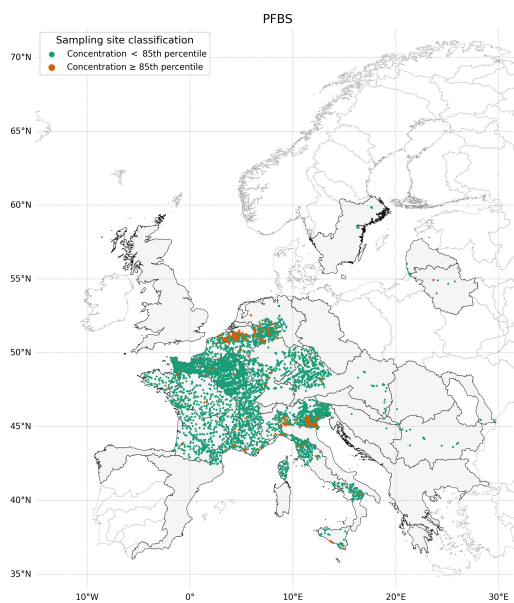


Figure A.24: PFBS sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

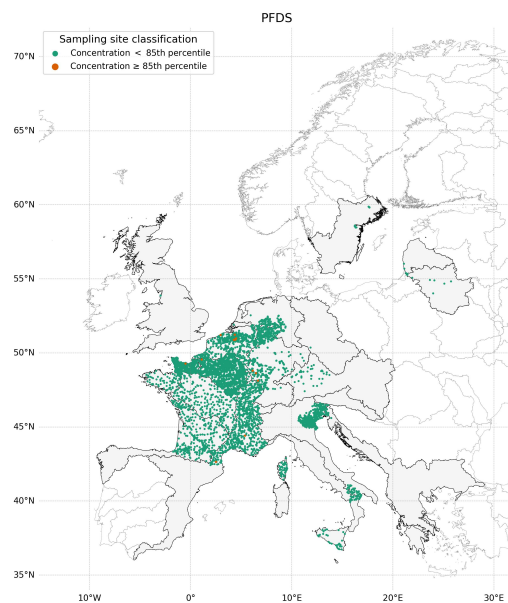


Figure A.25: PFDS sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

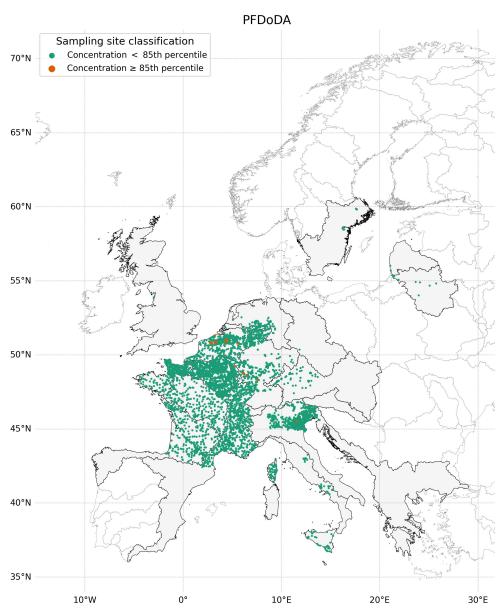


Figure A.26: PFDoDA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

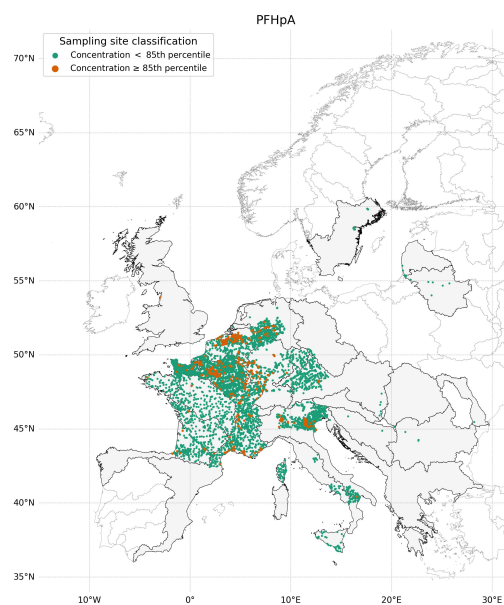


Figure A.27: PFHpA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

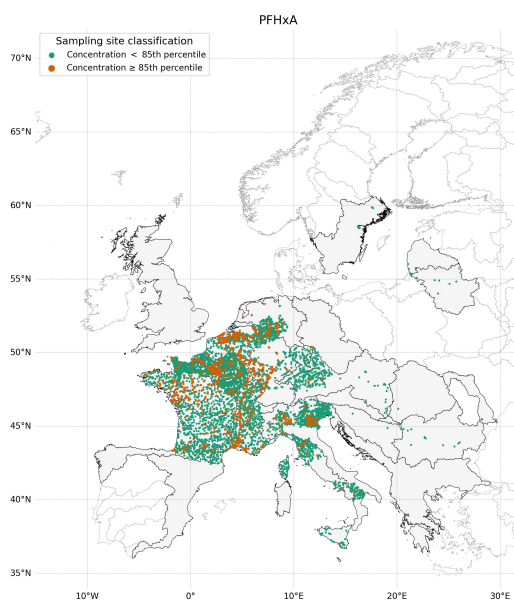


Figure A.28: PFHxA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

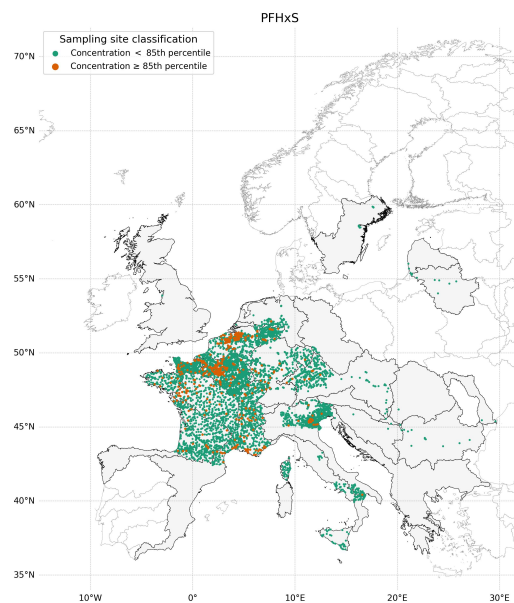


Figure A.29: PFHxS sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

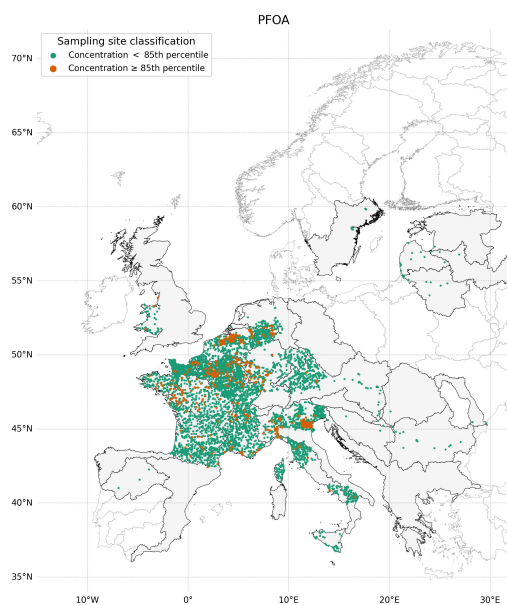


Figure A.30: PFOA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

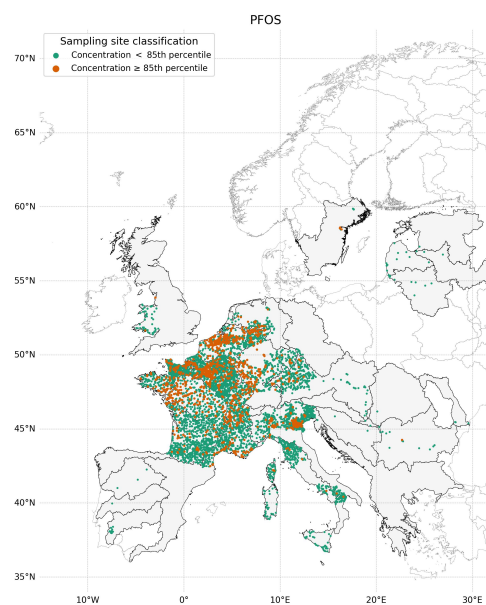


Figure A.31: PFOS sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

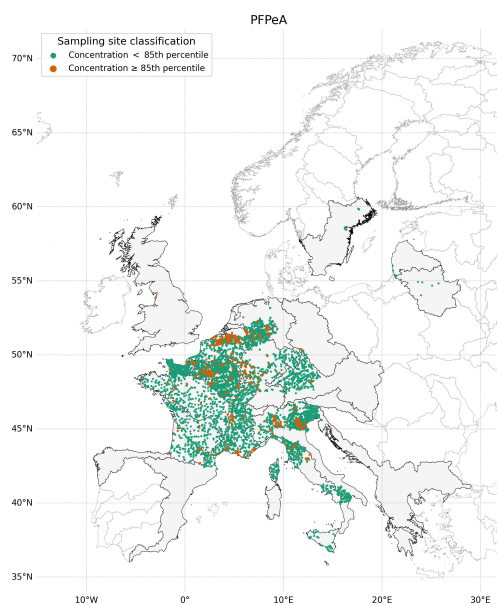


Figure A.32: PFPeA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

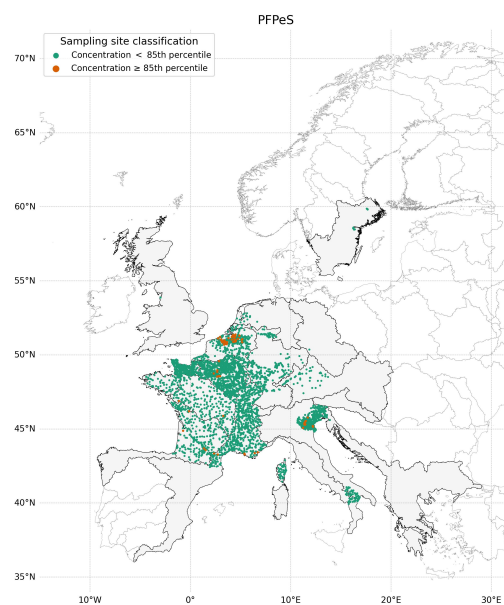


Figure A.33: PFPeS sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

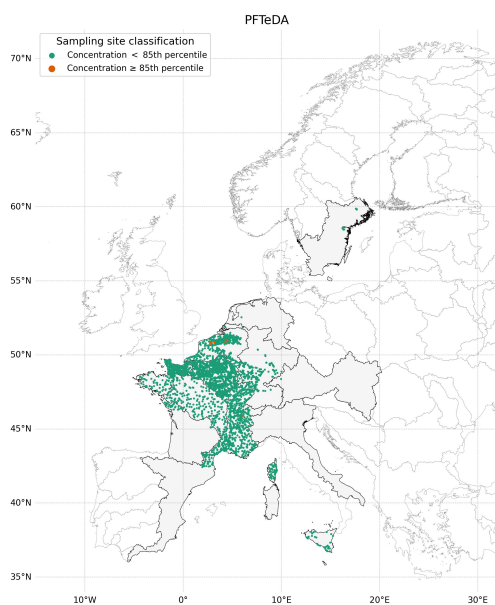


Figure A.34: PFTeDA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

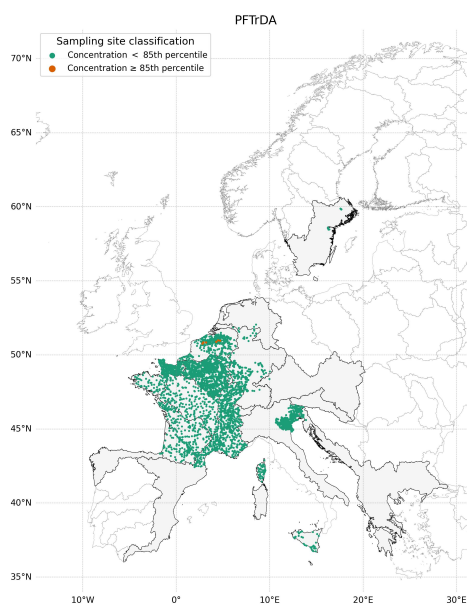


Figure A.35: PFTrDA sampling sites with measured concentrations above and below the substance's 85th percentile. Highlighted basins contain sampling locations.

References Supplementary Information A

Glüge, J., Scheringer, M., Cousins, I. T., Dewitt, J. C., Goldenman, G., Herzke, D., Lohmann, R., Ng, C. A., Trier, X., & Wang, Z. (2020). An overview of the uses of per- And polyfluoroalkyl substances (PFAS). *Environmental Science: Processes and Impacts*, 22(12), 2345–2373. <https://doi.org/10.1039/d0em00291g>

Title	Supplementary Information B Fingerprinting PFAS pollution in European surface waters
Authors	Robin Schröder ^a Jens Prothmann ^b Tobias Licha ^b Hans H. Dürr ^a Martina Flörke ^a
Affiliations	^a Engineering Hydrology and Water Resources Management, Faculty of Civil and Environmental Engineering, Ruhr University Bochum, Universitätsstraße 150, 44801 Bochum, Germany ^b Hydrogeochemistry & Hydrogeology, Institute of Geosciences, Ruhr University Bochum, Ruhr University Bochum, Universitätsstraße 150, 44801 Bochum, Germany
Contents	Ratio counts - Table B.1: Number of observations per PFAS ratio and basin. Total counts are given for the respective row and column. Wilcoxon test - Table B.2: Results from one-sided, paired Wilcoxon signed-rank test of PFAS concentrations Substance statistics - Table B.3: General statistics of the used PFAS dataset collection. Concentrations in ng/L. Time period: 2019-2026. Fc PNEC - Table B.4: Predicted no-effect concentrations (PNEC) of respective substances as used in this study. In the NORMAN Database, PNEC of PFBA is given as 0.0044 ng/L, which was adjusted in our study. LOQ - Table B.5: Inferred minimum and maximum limits of quantification of the respective substances for 2019-2026. PFAS20 dependency - Table B.6: Dependency of the 'Sum of 20 PFAS' parameter on the minimum number of included substances. PCAFA - Table B.7: Group definitions, test statistics and results from the PCA/FA.
Contact	robin.schroeder@hydrology.ruhr-uni-bochum.de

or abbreviations refer to Table A.1.

Table B.1: Number of observations per PFAS ratio and basin. Total counts are given for the respective row and column.

Basin	PFNA / PFOA	PFUnDA / PFDA	PFTTrDA / PFDoDA	PFPeA / PFBS	PFHxA / PFPeS	PFHpA / PFHxS
Baltic (Southern Sweden)	37	9	0	16	21	69
Brittany / Normandy	4	0	0	132	14	201
Corsica	0	0	0	1	0	2
Elbe	3	0	0	20	0	0
Garonne	18	1	0	44	12	60
Loire	11	0	0	167	20	152
Lower Danube	0	0	0	0	0	3
Maas	672	48	28	1443	654	1914
Po	180	5	2	3248	354	1148
Rhine	668	14	1	2756	16	1524
Rhône / Ebro	160	5	1	870	432	3457
Sava	0	0	0	0	0	2
Seine	311	16	0	1156	354	3044
Tiber	1	0	0	133	0	1
Tysa	0	0	0	0	0	1
United Kingdom	1	0	0	0	0	0
Upper Danube	80	29	0	261	2	98
Weser / Ems	84	2	0	122	0	61
Total	2230	129	32	10369	1879	11737

PFOA / PFHpS	PFNA / PFOS	PFDA / PFNS	PFUnDA / PFDS	PFDoDA / PFUnDS	PFTTrDA / PFDoDS	PFTeDA / PFTTrDS	Total
3	37	0	0	0	0	0	192
0	5	0	0	0	0	0	356
0	0	0	0	0	0	0	3
0	3	0	0	0	0	0	26
8	18	0	0	0	0	0	161
4	10	0	0	0	0	0	364
0	0	0	0	0	0	0	3
6	591	18	10	4	5	7	5400
0	179	0	0	0	0	0	5116
15	499	1	5	1	1	0	5501
250	156	0	0	0	0	0	5331
0	0	0	0	0	0	0	2
47	312	0	2	0	0	0	5242
0	1	0	0	0	0	0	136
0	0	0	0	0	0	0	1
0	1	0	0	0	0	0	2
0	91	0	0	0	0	0	561
0	35	0	1	0	0	0	305
333	1938	19	18	5	6	7	28702

Table B.2: Results from one-sided, paired Wilcoxon signed-rank test of PFAS concentrations

Comparison	Observations	Test statistic	p value
PFNA > PFOA	2230	188808	1
PFUnDA > PFDA	129	3622	0,445155441
PFTTrDA > PFDoDA	32	219	0,800014503
PFPeA > PFBS	10369	21059512	1
PFHxA > PFPeS	1879	1735597,5	1,1078E-296
PFHpA > PFHxS	11737	27000102,5	1
PFOA > PFHpS	333	55105,5	8,42812E-56
PFNA > PFOS	1938	289550,5	1
PFDA > PFNS	19	127,5	0,095436094
PFUnDA > PFDS	18	60	0,660467478
PFDoDA > PFUnDS	5	3	0,90625
PFTTrDA > PFDoDS	6	3	0,90625
PFTeDA > PFTTrDS	7	15	0,46875
PFOA > PFNA	2230	2203770	2,3952E-255
PFDA > PFUnDA	129	3518	0,554844559
PFDoDA > PFTTrDA	32	309	0,199985497
PFBS > PFPeA	10369	27132141	1,48877E-27
PFPeS > PFHxA	1879	15658,5	1
PFHxS > PFHpA	11737	36929675,5	1,03629E-46
PFHpS > PFOA	333	172,5	1
PFOS > PFNA	1938	1522105,5	4,9643E-146
PFNS > PFDA	19	62,5	0,904563906
PFDS > PFUnDA	18	76	0,339532522
PFUnDS > PFDoDA	5	12	0,15625
PFDoDS > PFTTrDA	6	12	0,15625
PFTTrDS > PFTeDA	7	13	0,59375

Table B.3: General statistics of the used PFAS dataset collection. Concentrations in ng/L. Time period: 2019-2026. For abbreviations refer to Table A.1.

Substance	Sites	Samples	Detection frequency	Median	Mean	Standard deviation
TFA		1080	7117	0,360826191	1100	4903,735592
PFBA		6944	77604	0,27801402	4	67,7508285
PFPeA		7090	64672	0,316149184	4	42,76534813
PFHxA		8215	124090	0,333572407	4	47,67554928
PFHpA		7266	104101	0,174570849	3	37,47619962
PFOA		7487	115248	0,29769714	4	205,385241
PFNA		6696	80739	0,030270377	2,5	12,29358022
PFDA		7660	117190	0,017373496	2,6	9,631192423
PFUnDA		6176	75679	0,003078793	4	13,28808569
PFDoDA		5627	72459	0,002083937	3,7	11,78287554
PFTTrDA		4677	54318	0,001104606	9,7	30,81914582
PFTeDA		3394	39128	0,001533429	8,5	14,8295
PFHxDA		2851	18639	0,002199689	10,3	14,21121951
PFODA		2857	18890	0,000952885	22	33,73333333
PFBS		7049	79173	0,213785002	4	66,48921714
PFPeS		4947	46678	0,09539826	0,45	140,041854
PFHxS		7422	117485	0,16614887	3,1	183,5101411
PFHpS		4104	52143	0,006942447	1,7	2,456150438
PFOS		8039	134841	0,444634792	2,2	113,1026337
PFNS		4810	44236	0,001017271	2,3	25,97566
PFDS		6310	87916	0,001035079	3	9,669494505
PFUnDS		4444	38813	0,000592585	3	16,10869565
PFDoDS		4897	40266	0,000447027	4,5	44,72222222
PFTTrDS		4314	37876	0,000343225	2	24,24615385
6:2 FTCA		2317	16606	0,001204384	7	10,45
4:2 FTS		4135	26899	0,002676679	6,55	65,03902778
6:2 FTS		4260	33415	0,103486458	5,7	48,45456709
8:2 FTS		4174	29608	0,007599297	0,117	15,85723022
HFPO-DA		4030	32378	0,029989499	5,5	62,96337796

DONA	3044	19338	0,016289172	5,8	308,1474603
FOSA	3484	51825	0,018909793	1,2	85,69121204
N-Et-FOSA	2518	19476	0,000256726	7	47,8
N-MeFOSAA	2717	16924	0,032616403	1,1	21,77560879
EtFOSAA	1518	11539	0,073749892	0,19	16,63489423

Table A.1.

85%-percentile	Maximum
2449,5	5000000
27	26000
19	24000
14	66000
10	29000
18	170000
8,655	1000
15	1490
28,84	1000
12	1000
32,9	2000
25	1000
26	10000
54,15	10000
26	48000
4	360000
11	130000
3,2	200
7,346	560000
22,4	1000
9,3	1000
9,5	2500
60,975	1000
29,84	2500
18,15	100
34	1000
32	17000
3,56	2310
42	6461

344	4400
45,27	23000
94,4	1000
6,48	8500
0,9985	4000

Table B.4: Predicted no-effect concentrations (PNEC) of respective substances as used in this study. In the NORMAN Database, PNEC of PFBA is given :

Substance	PNEC (ng/L)
4:2 FTS	2970,01
6:2 FTCA	433,34
6:2 FTS	621,84
8:2 FTS	252,69
DONA	1746,02
EtFOSAA	300,8
FOSA	166,74
HFPO-DA	1351,22
N-Et-FOSA	191,29
N-MeFOSAA	410,93
PFBA	4400
PFBS	4400
PFDA	0,628571429
PFDS	162,34
PFDoDA	1,466667
PFDoDS	116,73
PFHpA	8,712871287
PFHpS	3,384615385
PFHxA	440
PFHxDA	220
PFHxS	7,33333
PFNA	0,44
PFNS	216,39
PFOA	4,4
PFODA	220
PFOS	0,65
PFPeA	146,666667
PFPeS	14,6422649
PFTeDA	14,66667

PFTTrDA	2,66667
PFUnDA	1,1
TFA	109797,44

as 0.0044 ng/L, which was adjusted in our study.

Table B.5: Inferred minimum and maximum limits of quantification of the respective substances for 2019-2026.

Substance	Minimum (ng/L)	Maximum (ng/L)
4:2 FTS	0,25	1000
6:2 FTCA	1	100
6:2 FTS	0,1	1000
8:2 FTS	0,05	1000
DONA	0,1	2000
EtFOSAA	0,1	1000
FOSA	0,04	23000
HFPO-DA	0,2	2000
N-Et-FOSA	0,25	1000
N-MeFOSAA	0,05	1000
PFBA	0,2	2000
PFBS	0,2	500
PFDA	0,1	1000
PFDS	0,1	1000
PFDoDA	0,05	1000
PFDoDS	0,3	1000
PFHpA	0,2	500
PFHpS	0,3	200
PFHxA	0,2	500
PFHxDA	0,25	10000
PFHxS	0,12	500
PFNA	0,2	1000
PFNS	0,05	1000
PFOA	0,039	100
PFODA	1	10000
PFOS	0,039	224
PFPeA	0,2	980
PFPeS	0,1	1000
PFTeDA	0,2	1000

PFTrDA	0,25	2000
PFTrDS	0,5	2500
PFUnDA	0,1	1000
PFUnDS	0,5	2500
TFA	200	5000000

Table B.6: Dependency of the 'Sum of 20 PFAS' parameter on the minimum number of included substances.

Included substances	Number of matching samples	Median (ng/L)	Mean (ng/L)	Number of 100ng/L exceedance
1	76941	6,78	314,6581749	4947
2	51632	13	466,5483449	4861
3	36026	20,4	563,7649579	4689
4	27493	26,72	730,9232003	4556
5	19948	34,1	993,5695772	4391
6	13449	47,18	1453,684683	4010
7	8197	60,9	2341,248134	3083
8	4860	81,3	3870,617935	2186
9	2236	138,075	7638,688913	1285
10	946	171,25	14701,36724	597
11	354	213,9	22008,75798	260
12	70	305,85	23057,69024	50
13	27	793,5	22237,63622	21
14	15	7955,1	39414,58067	13
15	12	8011,6	47731,54083	11
16	7	57511,7	68918,48571	7
17	6	65497,55	70819,61667	6
18	2	1317,5	1317,5	2
19	2	1317,5	1317,5	2
20	0 -	-	-	0

Table B.7: Group definitions, test statistics and results from the PCA/FA.

Group ID	Substances	Sampling sites	Samples	KMO criterion
A	PFBA, PFBS, PFHpA, PFHxS, PFHxA, PFOA, PFOS, PFPeA	777	3876	0,918
A1	PFBA, PFBS, PFHpA, PFHxS, PFHxA, PFOA, PFOS, PFPeA, PFNA, PFDA	171	541	0,921
A2	PFBA, PFBS, PFHpA, PFHxS, PFHxA, PFOA, PFOS, PFPeA, 6:2 FTS	176	428	0,877
A3	PFBA, PFBS, PFHpA, PFHxS, PFHxA, PFOA, PFOS, PFPeA, PFPeS	311	1329	0,906
A4	PFBA, PFBS, PFHpA, PFHxS, PFHxA, PFOA, PFOS, PFPeA, PFDA	213	751	0,923
A5	PFBA, PFBS, PFHpA, PFHxS, PFHxA, PFOA, PFOS, PFPeA, PFNA	252	843	0,922
A6	PFBA, PFBS, PFHpA, PFHxS, PFHxA, PFOA, PFOS, PFPeA, HFPO-DA	73	214	0,892
A7	PFBA, PFBS, PFHpA, PFHxS, PFHxA, PFOA, PFOS, PFPeA, FOSA	89	288	0,923
B	PFOA, PFOS, PFHxA, PFBS, PFHpA, PFHxS, PFHpS	69	192	0,864
C	N-MeFOSAA, PFBS, PFHpA, PFHxA, PFHxS, PFOA, PFOS, PFPeA	55	180	0,892
D	EtFOSAA, PFBA, PFBS, PFHpA, PFHxA, PFHxS, PFOA, PFPeA	52	101	0,837
E	DONA, PFBA, PFHpA, PFHxA, PFOA, PFOS, PFPeA	41	129	0,815
F	PFBA, PFOS, PFHxS, PFOA, PFHxA, PFPeA, PFHpA, TFA	64	195	0,888
G	PFDA, PFHpA, PFHxA, PFHxS, PFNA, PFOA, PFPeA, PFPeS	135	353	0,897

Bartlett's p	Explained Variance 1	Explained Variance 2	Explained Variance 3	Sum Explained Variance
<0.05	0,842	0,079	0,031	0,952
<0.05	0,9	0,044	0,019	0,963
<0.05	0,695	0,118	0,064	0,876
<0.05	0,801	0,098	0,035	0,934
<0.05	0,907	0,032	0,025	0,964
<0.05	0,885	0,043	0,027	0,955
<0.05	0,759	0,08	0,055	0,894
<0.05	0,897	0,038	0,026	0,961
<0.05	0,725	0,104	0,066	0,895
<0.05	0,83	0,066	0,048	0,945
<0.05	0,752	0,142	0,046	0,94
<0.05	0,64	0,185	0,066	0,892
<0.05	0,664	0,119	0,078	0,861
<0.05	0,869	0,074	0,022	0,965

Max absolute factor correlation

- 0,105
- 0,1
- 0,108
- 0,056
- 0,095
- 0,078
- 0,184
- 0,105
- 0,061
- 0,072
- 0,054
- 0,038
- 0,199
- 0,042