Article

Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated

Isabelle J. Neuwald, Daniel Hübner, Hanna L. Wiegand, Vassil Valkov, Ulrich Borchers, Karsten Nödler, Marco Scheurer, Sarah E. Hale, Hans Peter H. Arp, and Daniel Zahn*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) have been a focal point of environmental chemistry and chemical regulation in recent years, culminating in a shift from individual PFAS regulation toward a PFAS group regulatory approach in Europe. PFASs are a highly diverse group of substances, and knowledge about this group is still scarce beyond the well-studied, legacy long-chain, and short-chain perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs). Herein, quantitative and semi-quantitative data for 43 legacy short-chain and ultra-short-chain PFASs (≤ 2 perfluorocarbon atoms for PFCAs, ≤ 3 for PFSAs and other PFASs) in 46 water samples collected from 13 different sources of German drinking water are presented. The PFASs considered include novel compounds like hexafluoroisopropanol, bis(trifluoromethylsulfonyl)imide, and tris(pentafluoroethyl)trifluorophosphate. The ultra-short-chain PFASs trifluoroacetate, perfluoropropanoate, and trifluoromethanesulfonate were ubiquitous and present at the highest concentrations (98% of sum target PFAS concentrations). "PFAS total" parameters like the adsorbable organic fluorine (AOF) and total oxidizable precursor (TOP) assay were found to provide only an incomplete picture of PFAS contamination in these water samples by not capturing these highly prevalent ultra-short-chain PFASs. These ultra-short-chain PFASs represent a major challenge for drinking water production and show that regulation in the form of preventive measures is required to manage them.

KEYWORDS: *monitoring, sum parameters, trifluoroacetate (TFA), trifluoromethanesulfonate (TFMS), perfluoropropanoate (PFPrA), hexafluoroisopropanol (HFIP), bis(trifluoromethylsulfonyl)imide (NTf₂), tris(pentafluoroethyl)trifluorophosphate (FAP)*
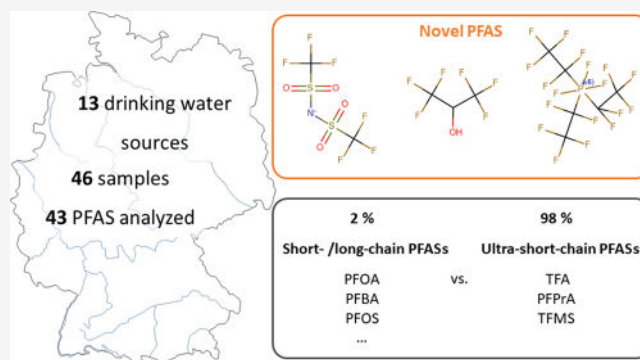
INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are highly fluorinated substances that are widely used in diverse products and processes, such as water-repelling textiles, grease-resistant paper, packaging, aqueous film-forming foams (AFFF), and industrial detergents.[1−4] Consequently, there are many potential environmental entry pathways for PFASs and, once emitted, they are difficult to remove since most PFASs are recalcitrant to common treatment methods.[5] This has led to the detection of PFASs in all environmental compartments throughout the world.[6−11]

The persistence and ubiquitous occurrence of some of the most prevalent PFASs, such as perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluorohexanesulfonate (PFHxS), has resulted in increased attention and their identification as substances of very high concern (SVHC) under REACH [Registration, Evaluation Authorization and Restriction of Chemicals (EC 1907/2006)] within the last 8 years. The phase out of long-chain legacy PFASs has led to their replacement with short-chain fluorinated alternatives,[12,13] such as perfluorobutanoate (PFBA),[14] per-

fluorobutanesulfonate (PFBS),[15] or HFPO-DA [2,3,3,3-tetra-fluoro-2-(heptafluoropropoxy)propanoate/Gen-X].[16] Long-chain PFASs are generally defined as having seven or more perfluorocarbons for perfluorocarboxylates (PFCAs) and six or more for perfluorosulfonates (PFSAs);[1,17] short-chain PFASs are herein defined as those with three to six perfluorocarbons for PFCAs and four to five for PFSAs;[18,19] other PFASs are herein classified analogously to PFSAs for consistency; ultra-short-chain PFASs are those with ≤ 2 perfluorocarbon atoms for PFCAs, ≤ 3 for PFSAs and other PFASs).

The diversity of PFAS subgroups as well as the attention toward non-legacy and unknown fluorinated compounds continues to increase.[20,21] Hence, to reduce production, emissions, and exposure to PFASs, regulatory proposals to

A

manage PFASs as a single substance class[22] and to apply the concept of essential use[23] to PFASs have been made.

The smaller the perfluorinated alkyl chain, the more soluble and the weaker the sorption of the PFAS to environmental media.[24] For example, PFBS was shown to have a significantly smaller fraction (ca. 30%) partitioned to soil than PFOS (ca. 70%).[25] Short-chain and ultra-short-chain PFASs generally fulfill the proposed criteria for persistent, mobile, and toxic (PMT) or very persistent and very mobile (vPvM) substances, established by the German Environment Agency (UBA).[26] They are able to penetrate natural and anthropogenic barriers and eventually reach drinking water sources, where common remediation techniques do not sufficiently remove them.[27,28] However, with the exception of trifluoroacetate (TFA),[29−31] occurrence data for ultra-short-chain PFASs are still very scarce.[27] Broad monitoring programs for PFASs often omit the shortest analogues as they are difficult to analyze,[32] and recent investigations have often focused on screenings at specific point sources.[19] This is exacerbated for PFAS classes besides PFCAs and PFSAs. Thus, the lack of screening and monitoring data[33] is even more pronounced for these analytically challenging ultra-short-chain PFASs that might easily reach raw and drinking water. Methods that facilitate a simultaneous determination of ultra-short-chain and long-chain PFASs have only recently emerged.[34]

To address the ever-increasing number of PFASs on the global market, which is approximately 5000,[17] the revised European Drinking Water Directive (EU DWD) has proposed the introduction of two parameters: "Sum of PFAS" and "PFAS total".[35] "Sum of PFAS" is the sum of PFCAs with 3−12 and PFSAs with 4−13 perfluorocarbons and a limit value of 0.1 $\mu g/$L. "PFAS total" refers to all PFASs in the sample with a limit value of 0.5 $\mu g/$L. A grouping approach is also included in the 2020 EU Chemicals Strategy for Sustainability Towards a Toxic Free Environment;[36] however, it is unclear how definitions of "PFAS total" may vary across different regulations and how they will be analyzed. The revision of the EU DWD inevitably results in a demand for approaches to "PFAS total" analyses. While no true "PFAS total" method exists, the adsorbable organic fluorine (AOF) method and the total oxidizable precursor (TOP) assay are the two most widely used PFAS bulk approaches. However, one limitation with these methods is how well they account for ultra-short-chain PFASs.[37,38] The relevance and impact of this omission are yet largely unknown and are the focus of the current regulatory discussion. Therefore, to deliver context for this discussion, this study presents a monitoring campaign throughout Germany for PFASs, including legacy long-chain, short-chain, ultra-short-chain, and other non-PFSA and non-PFCA PFASs, in various sources of drinking water. Surface water, bank filtrate (water that has passed through a river or lake bank as a method of purification for drinking water production), groundwater, and raw water (water from the exact point of entry into the drinking water production plant) were included. Targeted PFAS analysis and methods to determine "PFAS total" concentrations were used to assess the occurrence and distribution of PFASs. Statistical methods were used to investigate the co-occurrences of PFASs, correlations between them, and ubiquitous or regional presence. Forensic identification of specific emission sources was not within the scope of this study. Results from the work can be used to better account for ultra-short-chain PFASs in fresh water and drinking water sources and to support monitoring campaigns, policy development, and risk assessment of these problematic substances.

■ MATERIALS AND METHODS

Target PFASs and "PFAS Total" Methods. The list of target PFASs included (i) 18 out of the 20 PFAS included in Annex III of the revised EU DWD[35] [for perfluoroundecanesulfonate (PFUnS) and perfluorotridecanesulfonate (PFTrS), there was no analytical standard available at the time of analysis]; (ii) 23 PFAS registered under REACH, which meet the proposed PMT/vPvM criteria,[39] most with production volumes of >10 tons per annum and a limited availability of analytical data; and (iii) two additional ultra-short-chain PFASs, perfluoroethanesulfonate (PFEtS) and perfluoropropanesulfonate (PFPrS). The 23 PFASs registered under REACH were selected based on their prioritization in a previous screening of REACH-registered substances, based on their PMT/vPvM properties,[39] and a subsequent query for additional polar or ionic short-chain PFAS substances that have been registered in 2019, as these were known to be used in Europe. In total, 43 PFASs were analyzed (see Table S1, which also presents all substance abbreviations).

Chemicals and Standards. Water, acetonitrile, methanol [all LiChrosolv ultra-high-performance liquid chromatography−mass spectrometry (UHPLC−MS) grade], and methane sulfonic acid were obtained from Merck KGaA (Darmstadt, Germany). Ammonia (30%) was purchased from Carl Roth GmbH (Karlsruhe, Germany). Ammonium formate (>99% purity) was bought from Fluka (Munich, Germany), and formic acid was purchased from Fisher Chemical (Schwerte, Germany). Sulfuric acid pro analysis (p.a.) was obtained from Merck KGaA (Darmstadt, Germany), and ammonium carbonate (p.a.) was purchased from VWR (Darmstadt, Germany).

A list of all standards used is presented in Table S1 in the Supporting Information (SI).

Water Samples. 46 grab water samples were obtained from 13 water suppliers all over Germany, all representing direct or indirect source waters for drinking water production. These comprised 16 surface water samples, 16 bank filtrate samples, 7 raw water samples, and 7 groundwater samples (see Table S2), covering the river basins Danube, Elbe, Ems, Havel, Main, Neckar, Rhine, and Sieg, among others, and their surroundings. Exact locations cannot be provided by request of anonymity of water suppliers. The samples were stored in 2 L glass bottles in the dark at 6 °C and were analyzed within 8 weeks of sampling. The samples were taken between October 27 and November 4, 2020. All sampling equipment was tested for PFAS contaminations (see quality control).

Sample Preparation. *Liquid Chromatography Sample Preparation.* Trifluoromethanesulfonate (TFMS), tris-(pentafluoroethyl)trifluorophosphate (FAP), bis-(trifluoromethylsulfonyl)imide (NTf2), PFEtS, and perfluoropropanoate (PFPrA) were analyzed using hydrophilic interaction chromatography (HILIC) analysis, and multilayer solid-phase extraction (mlSPE) was used as the enrichment method. Legacy PFAS, 6:2 FTS, HFPO-DA, PFPrS, triflinate, and DPOSA were analyzed with weak anion-exchange SPE in combination with reversed-phase liquid chromatography (RPLC) measurements. Procedural blanks were enriched using the same method as the real samples. Detailed information on the techniques is presented in the Supporting Information (Text S1).

Gas Chromatography Sample Preparation. TFA (evaporative concentration), 1,1,2,2,3,3,4,4-nonafluoro-*N*-(2-hydroxyethyl)-*N*-methyl-1-butanesulfonamide (CAS 34454-97-

2), and trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silane (CAS 78560-45-9) (liquid−liquid extraction) were analyzed by gas chromatography−mass spectrometry (GC−MS). More details can be found in the Supporting Information (Text S2).

The remaining analytes listed in Table S1 (CAS 382-28-5, 75-71-8, 40573-09-9, 15290-77-4, 422-05-9, 920-66-1, 355-93-1, 17527-29-6, 85857-16-5, 2144-53-8, 51851-37-7) were directly analyzed by headspace GC−MS without any further sample preparation.

TOP Assay. The TOP assay method was based on Houtz and Sedlak[40] but with further adaptions and optimizations based on Janda.[41] A sample aliquot of 50 mL was mixed with 1 g of $K_2S_2O_8$ and 0.95 mL of NaOH (10 M) in a 50 mL polypropylene container (Sarstedt, Nümbrecht, Germany). After capping, the batch was incubated at 85 °C for 20 h. After cooling in an ice bath, the pH was adjusted to 5 with formic acid, and a mixture of internal standards (IS) [isotopically labeled PFBA—perfluoro-tridecanoate (PFTrA), PFBS, PFHxS, and PFOS] and 2 mL of methanol were added. The analytes [PFBA—perfluorotetrade-canoate (PFTeA), PFPrS, PFBS, perfluoropentanesulfonate (PFPeS), PFHxS, perfluoroheptanesulfonate (PFHpS), PFOS, perfluorononanesulfonate (PFNS), and perfluorodecanesulfo-nate (PFDS)] were extracted by a weak anion exchanger (Strata X-AW 6 mL, 200 mg; Phenomenex, Aschaffenburg, Germany) using an elution flow rate of 0.8 mL/min. The sorbent was preconditioned with 4 mL of methanol containing 0.1% NH_4OH, 4 mL of methanol, and 2×5 mL of ultrapure water. After extraction, the sorbent was dried for 30 min by N_2, and the analytes were eluted with 2×2 mL of methanol and 3×2 mL of methanol containing 0.1% NH_4OH. After evaporating the extract to dryness with N_2, the residues were redissolved in 0.25 mL of methanol:water (80:20, v:v).

Adsorbable Organic Fluorine (AOF). The AOF was determined as follows. A sample aliquot of 100 mL was mixed with 5 mL of aqueous $NaNO_3$ solution (0.2 mol/L), and the AOF was extracted using 100 mg of activated carbon (AC) adsorbent (Blücher #100043, Erkrath, Germany). The amount of AC was divided into two portions of 50 mg each filled between two polyethylene (PE) frits (10 μm, Biotage, Uppsala, Sweden) in SPE cartridges (3 mL, Phenomenex, Torrance, CA). Two of these cartridges were connected with a Luer-Slip adapter for the analysis of each sample. The flow rate was adjusted to 3 mL/min. After extraction, the cartridges were washed with 25 mL of $NaNO_3$ solution (0.01 mol/L) at the same flow rate to remove adsorbed inorganic fluorine (fluoride, F^-). As shown by spike experiments, fluoride concentrations up to 300 μg/L were efficiently removed. All samples were analyzed for fluoride before AOF analysis, and none of the samples exceeded 300 μg/L.

Analytical Methods. *Liquid Chromatography−Mass Spectrometry Instrumentation.* The liquid chromatography−mass spectrometry (LC−MS) system used was a Shimadzu Nexera X2, consisting of a degassing unit, four pumps, an autosampler, a communication module, and a column oven (Shimadzu, Kyoto, Japan) coupled to a QTrap 5500 tandem-MS (MS/MS) system (AB Sciex, Darmstadt, Germany). HILIC and RPLC measurements are described in detail in the Supporting Information (Text S3 and S4), and scheduled multiple reaction monitoring (sMRM) parameters for each analyte are presented in Table S3.

Gas Chromatography−Mass Spectrometry Instrumenta-tion. Three GC−MS methods and instruments were used for the analysis of PFASs as described in the sections above: derivatized TFA was analyzed with GC method 1 (Text S5), liquid−liquid extracts were analyzed with GC method 2 (Text S6), and headspace analysis was performed with GC method 3 (Text S7). Further MS parameters are summarized in Table S4.

TOP Assay Instrumentation. Instrumental analysis of the TOP assay samples was conducted by LC−MS using a 1260 Infinity II LC System (Agilent, Waldbronn, Germany) connected to a 6500+ MS/MS instrument (Sciex, Darmstadt Germany). The analytical column was a Luna Omega Polar C18 100 × 2.1 mm, 1.6 μm (Phenomenex, Aschaffenburg, Germany). Eluent A was 10% methanol in ultrapure water (+ 0.01 M ammonium acetate), and eluent B was methanol. A flow rate of 0.18 mL/min was applied, and an injection volume of 10 μL was used. The gradient was as follows: starting at 20% B, increasing to 25% B from 0 to 0.5 min, increasing to 70% B from 0.5 to 7.0 min, increasing to 98% B from 7.0 to 14.5 min, holding this condition until 21.5 min, and decreasing to starting conditions within 0.5 min. The equilibration time was 8.0 min. Further MS parameters are summarized in Table S5.

AOF Instrumentation. The determination of AOF was performed using a modified combustion ion chromatography (CIC) system for ultra-trace fluorine analysis, consisting of an automated boat controller (ABC-100), an automatic quick furnace (AQF-100) with a water supply unit (WS-100), and a gas absorption unit (GA-100) (all from Mitsubishi Chemical Analytech Co., LTD, Kanagawa, Japan). The combustion unit was linked to an IC system (ICS-2100, Thermo Fisher Scientific, Waltham, MA, USA). The calibrant for the AOF was NaF (VWR, Darmstadt, Germany) dissolved in deionized water. The calibration range was 0.1−14 μg/L F. For analysis, the adsorbent was transferred to a ceramic sample boat (a1-envirosciences, Düsseldorf, Germany) and combusted in a furnace at 950−1000 °C while delivering 0.1 mL/min of ultrapure water by the WS-100. Using this method, organic fluorine belonging to the adsorbed organic substances is converted into hydrogen fluoride (HF), while the addition of excess water into the combustion tube prevents the formation of silicon tetrafluoride. The HF formed was measured as F^- by IC analysis. The adsorbent of the second cartridge of the same sample was analyzed in the same way. Both results were blank-corrected and summed to give the AOF.

Quality Control. For LC measurements, reproducibility (in triplicates), recovery, matrix effects, trueness (for equations, see Text S8), limit of detection (LOD), and limit of quantification (LOQ) of the methods were determined (Table S6). The ion ratio tolerance between the quantifier and qualifier mass was 20% for analytes with two transitions. To assess the retention time and intensity shifts in LC measurements, a quality control (QC) mix standard of all analytes was measured four times in each batch. Reproducibility of the method was determined by enriching a selection of samples (11%) in duplicates (Table S7). A selection of samples (11% for RPLC, 22% for HILIC) was spiked prior to sample enrichment (Table S8). Procedural blank signals (Table S6) were subtracted from the analyte signal. IS were used where applicable and available (Table S1) and added before enrichment. To compensate for the low trueness of some analytes (<70 and >130%), the concentration of substances was calculated considering recovery and matrix effects obtained from the validation. Since matrix effects in HILIC were shown to be highly sample and analyte specific, chemically similar IS cannot be used,[42] and thus, matrix effects were determined for each analyte and sample individually. Therefore, all samples were split
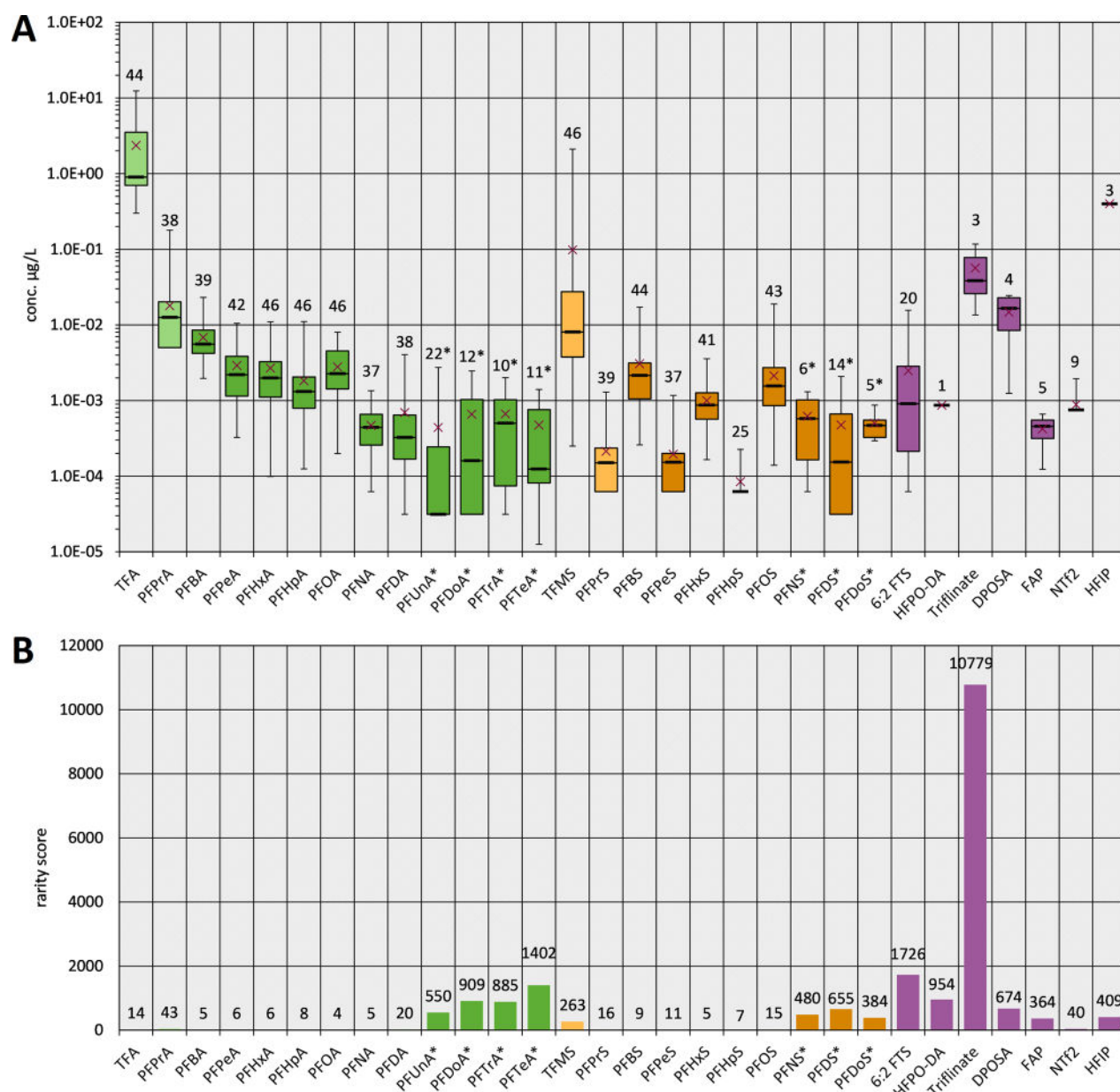
Figure 1. (A) Boxplots of PFAS concentrations over all samples. The number above the bars depicts the number of detects out of 46 samples. X marks the mean concentration, and the horizontal line inside the box depicts the median concentration. <LOQ was included as half its value for each substance. (B) RS of all detected PFASs. <LOQ and <LOD were included as half their value for each substance. Green: PFCA regulated under EU DWD and PFTeA, orange: PFSA regulated under EU DWD, purple: other non-PFCA and PFSA PFAS, compounds in lighter shades are ultra-short-chain PFAS (not regulated under EU DWD). Note: PFCA > PFDA and PFSA > PFOS are marked with a star, indicating semiquantitative data.

after reconstitution, and one part was spiked with a PFAS mix standard.

For GC measurements, trueness, duplicates, LOD, LOQ, and the correlation coefficient (R^2) were determined (Table S6). A QC sample treated in the same way as real samples was analyzed at least once in each batch of GC measurements. Blanks were controlled in each batch by measuring the samples of deionized water, which is prepared in the same way as real samples. In order to monitor the trueness of the method, 17% of samples were spiked before sample preparation (Table S8).

For AOF analysis, the HF formed was absorbed in an aqueous methane sulfonic acid solution (1 mg/L) which was used to correct for deviations of the injection unit of the CIC system. All analyses were performed in duplicates. Relative standard deviations were below 10%. The LOQ for the entire AOF

protocol (SPE-CIC) was calculated according to the blank value method of DIN 32645[43] ($n = 10$) with LOQ $= 10 \times$ SD$/s \times$ FD, where SD is the standard deviation of the procedural blank, s the slope of the calibration function in the low-concentration range, and FD the dilution factor. The LOQ was 1, and 0.5 μg/L was set as the qualitative reporting level. Procedural blank samples (one per day) were included, covering extraction (100 mL of deionized water) and CIC, and were used for blank correction.

QC of the TOP assay was performed by controlling the oxidative conversion of PFCA precursors, in addition to IS. This was ensured by spiking 25 ng of N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) into a QC sample that was treated as real samples. A conversion of at least 70% of N-EtFOSAA into PFOA was set as the minimum value to be able to consider the sample batch as valid. Multiple procedural blanks

were used: One blank covered the whole sample preparation and analysis procedure, a second blank sample was used for the SPE procedure only, and the last blank, the QC sample, was used to ensure that precursors were degraded.

Field blanks were not taken during this sampling campaign since regular validation of the sampling procedure using the same glass bottles than in this study did not show any positive findings for PFASs (Table S12). This validation was limited to 23 PFASs, but frequent non-detects for most other PFASs indicate that there is no relevant contamination through sampling. A similar validation for the TOP assay or AOF was not performed, and thus, the influence of blanks here cannot be excluded.

■ RESULTS AND DISCUSSION

Occurrence in Drinking Water Sources. Among the 46 samples, 43 PFASs were analyzed via HILIC-sMRM, RPLC-sMRM, and GC−MS, and 30 of them were detected at least once above their LOQ. The number of positive detects per sample ranged from 4 to 28 with a median of 17 (see Figure S1A, for concentrations, see Table S9). Since the samples were taken and stored in glass bottles, sorption of longer chain PFAS cannot be excluded, and thus, data for PFCA > PFDA and PFSA > PFOS is only semiquantitative. However, the concentrations detected herein for these longer chain PFAS are in the same order of magnitude as in other studies.[13,44,45]

TFA was the most dominant PFAS, accounting for more than 90% of the total concentration of PFASs analyzed in all samples, with a maximum and median concentration of 12.4 and 0.9 μg/L, respectively, which is in line with previous monitoring programs in German surface waters.[46] TFA is known to be widespread in the aquatic environment and can be introduced into the water cycle through industrial processes and as a transformation product of pharmaceutical and agricultural products[46,47] among others. TFA is also a transformation product of hydrofluorocarbon refrigerants in the atmosphere and may reach the aqueous environment via atmospheric deposition.[30,48,49] Due to its unique environmental exposure pathways and generally high concentrations, a comparison of TFA with other PFAS is not necessarily meaningful.

When omitting TFA, two other ultra-short-chain PFAS, namely, TFMS (median 8.0 ng/L, maximum 2.1 μg/L, Figure 1A) and PFPrA (median 12.6 ng/L, maximum 0.18 μg/L) are the most prevalent, accounting for 59 and 9% of the mean total PFAS concentration across all samples, respectively (see Figure S1B). A similar picture for the ultra-short-chain PFAS was observed by Yeung et al.,[50] where they accounted for more than 40% of the total amount of PFAS in Canadian rivers. The other ultra-short-chain PFSA PFEtS was not detected at all, and perfluoropropanesulfonate (PFPrS) was only present at concentrations well below 0.01 μg/L. The distinct variations in the occurrence of ultra-short-chain PFAS may be related to their use and sources. According to REACH, TFMS is produced at a volume of 100−1000 tons per year and is used for the manufacture of chemicals and electrical, electronic, and optical equipment.[51] It is used in organic syntheses and lithium-ion batteries.[52] Environmental sources of TFMS remain largely unknown. No clear uses of PFPrA could be identified based on information registered under REACH. PFPrA has been reported to be a degradation product of hydrofluorocarbon refrigerants and other intermediates.[52] In contrast, PFEtS and PFPrS, which were infrequently detected in this data set, have previously only been reported in AFFF and groundwater at military training

sites,[53] and no other use could be identified from our literature search. To our knowledge, they are not associated with large emissions.

Short- and long-chain PFASs were predominantly detected at individual concentrations below 0.01 μg/L. The sum of the analyzed 18 (of 20) PFASs listed in the EU DWD "Sum of PFAS" did not exceed the proposed threshold of 0.1 μg/L[35] in any sample. Among the novel or yet scarcely analyzed non-PFCAs and non-PFSAs, the most commonly detected were hexafluoroisopropanol (HFIP), NTf$_2$, and FAP (for structures, see Table S1). HFIP is a fluorinated solvent used in polymer chemistry and organic synthesis that was only detected in three samples but at high concentrations (median 0.4 μg/L, maximum 0.4 μg/L). This is the first report of the environmental detection of this chemical to the best of our knowledge. Since this data is near the LOQ of 0.1 μg/L, a wider distribution at concentrations <LOD (0.03 μg/L) cannot be excluded. NTf$_2$ is a fluorinated anion predominantly used in ionic liquids and was detected in low concentrations (median 0.8 ng/L, maximum 2.0 ng/L) in nine samples. It is mainly used in lithium-ion batteries[54] among other applications. The currently increasing demand for energy storage capacities facilitated by the rise of renewable energy sources may result in increased production and release of chemicals associated with lithium batteries, such as fluorinated ionic liquids including NTf$_2$. Currently, the lack of occurrence data makes it impossible to evaluate if its use in energy storage leads to its environmental release. NTf$_2$ and the infrequently detected FAP (five samples, median 0.5 ng/L, maximum 0.7 ng/L) have only recently been detected in the aquatic environment[55] as a novel class of PFASs. Occurrence data on NTf$_2$ is so far exceedingly scarce and only semiquantitative.[56] Toxicity tests have shown that NTf$_2$ is toxic to aquatic organisms[57] and sludge bacteria,[58] while toxic effects on clinically relevant bacteria have been reported for FAP.[59] Toxicity data for HFIP is, to the best of our knowledge, not available.

While PFAS concentrations reported herein for short- and long-chain PFAS are in line with previous studies,[13,44,45] concentrations of ultra-short-chain PFAS are rare[60,61] as are studies that include TFMS.[19,62] A recent study by Björnsdotter et al.[19] monitored a highly similar set of analytes including the ultra-short-chain homologues in samples near suspected PFAS sources. Comparing their results to the ones presented herein, a substantial shift from long-chain PFAS toward ultra-short-chain homologues in samples with no known contamination (ratio ultra-short-chain vs short and long-chain near sources 1:40[19]) and in samples with no known contamination 5:1 (this study) (both excluding TFA) was determined. This shift toward shorter chain homologues may be explained by an increasing aquatic mobility of the shorter chain PFAS[7,63,64] or additional, yet unknown sources of ultra-short-chain PFAS. Particular identification would, however, require subsequent investigation.

When generalizing the results of such a diverse sample set, the homogeneity of the occurrence data must be considered. To probe this homogeneity, a rarity score (RS) was calculated according to Krauss et al.[65] For this calculation, results <LOD or <LOQ were treated as half of the LOD or LOQ respectively[66] (eq 1):

$$RS = \frac{\text{maximum concentration}}{\text{median concentration}} \cdot \frac{\text{number of samples}}{\text{number of detects}} \quad (1)$$

A low RS indicates a uniform distribution over most if not all samples, while a high RS implies that a detected substance is site-specific, either occurring only in few samples or showing
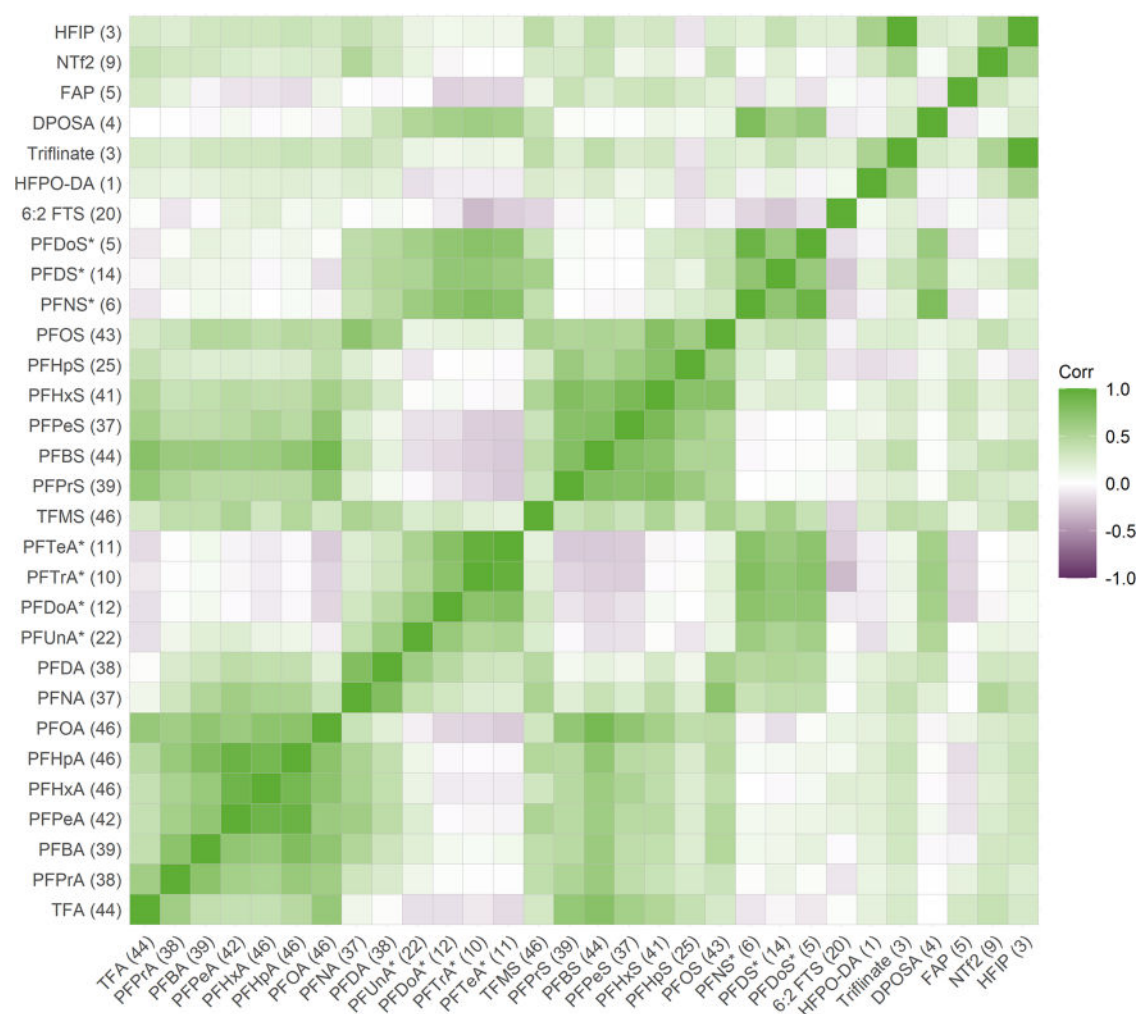
Figure 2. Correlation plot (Spearman correlation, produced using R Studio, version 3.6.3) of all detected PFASs, sorted by type and chain length. Numbers in brackets depict the number of detects. <LOQ and n.d. were included as LOQ/2 and LOD/2 for each substance, respectively. Note: PFCA > PFDA and PFSA > PFOS are marked with a star, indicating semiquantitative data.

pronounced differences in concentrations between sampling sites (Figure 1B). All PFCA < perfluoroundecanoate (PFUnA) and all PFSA between PFBS and PFOS showed exceptionally low RS (RS 4−43), thus demonstrating their uniform distribution within this geographically diverse sample set covering surface water, bank filtrate samples, groundwater samples, and raw water samples. Consequently, results for these substances can likely be extrapolated toward a more general occurrence in these environmental compartments. RS significantly increased for PFCA ≥ PFUnA and PFSA ≥ PFNS (RS 384−1402, note: semiquantitative data). Above these chain lengths, atmospheric transport has been reported to be less relevant,[67,68] and such PFASs are considered to be less mobile with a log $K_{OC} > 3$ (low RS PFASs are below a log K_{OC} of 3, and high RS PFASs are above a log K_{OC} of 3). This is an indicator that the presence of these longer chain PFASs in drinking water sources may be associated with local emissions, though subsequent studies would be needed to confirm this. TFMS (RS 263) was detected in all samples but with significantly elevated concentrations at a few sampling locations. Therefore, TFMS can be considered as a diffusely distributed PFAS, but in certain areas, there could be emission hot-spots in addition. PFASs that were neither PFSA nor PFCA generally showed high RS (364−10,779) in line with their pronounced site specificity

that was either indicated by very few detects (HFPO-DA, triflinate, DPOSA, FAP, and HFIP) or by concentration ranges spanning 2 orders of magnitude (6:2 FTS). NTf$_2$, which was detected in nine samples close to the LOQ, is the only exception with a very low RS of 40. This might imply a ubiquitous presence of NTf$_2$ at low concentrations, which is in line with a recent suspect screening for PMT/vPvM substances that included many ions used in ionic liquids.[56]

Distribution Patterns of PFASs. To study similarities and differences in the occurrence and distribution patterns of the investigated PFASs, the Spearman correlations across all samples and analytes were plotted (Figure 2, for p-values, see Table S10). Ultra-short- and short-chain PFCAs, along with the PFCA PFHpA, PFOA, and PFNA, were positively correlated between one and the other. The correlation coefficients decreased with the decreasing number of perfluorocarbons, down to 0.4 for TFA (p-values <0.05). Similarly, positive correlations for ultra-short- and short-chain PFSAs, along with the long-chain PFHxS, PFHpS, and PFOS, were observed, though with the smallest correlation with TFMS (between 0.3 and 0.5, p-values <0.05 with very few exceptions). Additionally, these two groups of PFCAs and PFSAs were positively correlated between each other as well (Figure 2). The strong correlation particularly for short-chain PFCA and PFSA and
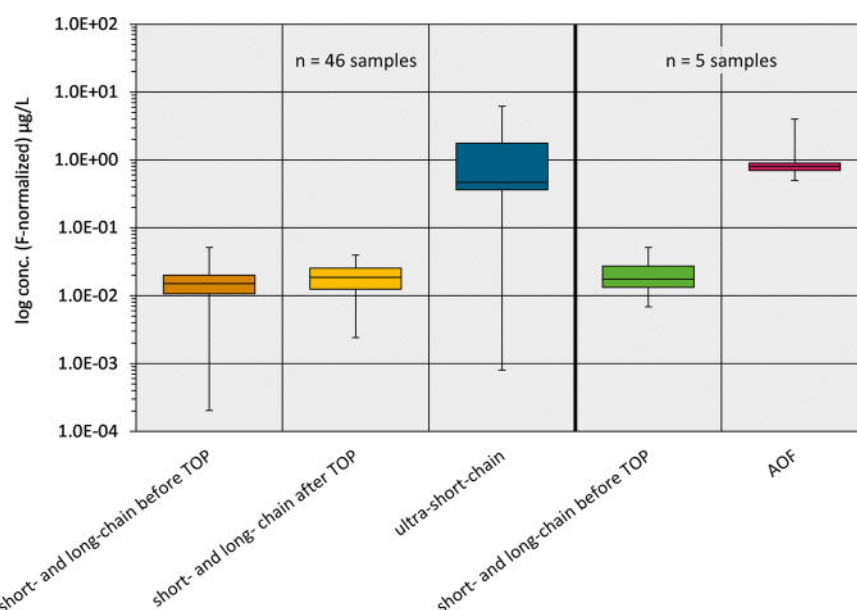
Figure 3. Boxplots of F-normalized sum of short- and long-chain PFASs before the TOP assay (orange, $n = 46$ samples), short- and long-chain PFASs after the TOP assay (yellow, $n = 46$ samples), and ultra-short-chain PFASs (blue, $n = 46$ samples) over all samples. Also shown is the boxplot of short- and long-chain PFASs before the TOP assay for the samples analyzed with AOF (green, $n = 5$ samples) and the AOF of the corresponding five samples (fuchsia, $n = 5$ samples). The horizontal bar in the box depicts the median concentration. Note: only semiquantitative data is available for PFCA > PFDA and PFSA > PFOS.

PFHxS (>0.7, p-values <0.05) may be associated with their similar uses, such as processing aids for Teflon production and in AFFFs.[69] Long-chain PFCAs, starting with PFUnA, and the long-chain PFSAs PFNS, PFDS, and PFDoS correlated strongly among themselves (correlation coefficients >0.6, p-values <0.05, note: semiquantitative data). These substances were shown to be rather site-specific as demonstrated by their elevated RS. This is also expected as they are known to be less readily transported in the environment than their shorter chain homologues; therefore, their occurrence is likely the result of more local, common sources and use patterns. However, given the low detection frequency of these PFASs (<50%), this interpretation must be made with caution. PFNA, PFDA, and DPOSA also have a less pronounced correlation (correlation coefficients 0.3−0.6, p-values <0.05) with each other. The shortest ultra-short-chain PFAS TFA and TFMS correlated weakly to moderately with other PFASs (correlation coefficients −0.2 − 0.6, p-values <0.05 with very few exceptions) and with each other. Despite similar environmental behavior and low RS, this is an indication that these substances may have unique environmental distribution pathways and/or unique point sources that are not common to the other PFAS. Interestingly, the highest concentrations of TFMS coincided with the few detections of HFPO-DA and HFIP, which are both associated with industrial sources. This is a first hint toward industrial hot-spot sources of TFMS and may be a starting point for future studies to confirm or disprove this hypothesis.

From the data presented herein, it is evident that short-chain PFASs and especially the ultra-short-chain PFASs TFA, TFMS, and PFPrA are widespread and dominant in these samples from drinking water sources. AC filtration, which is an effective tool to remove longer chain PFASs during drinking water production, is less effective for both short- and ultra-short-chain PFASs.[27] This renders their removal during drinking water production exceedingly difficult. Consequently, the most prevalent PFASs occurring in the drinking water sources herein are also the ones

that are the most difficult to remove during drinking water production. This raises questions both about the costs of removing these substances and the potential health effects these chemicals might cause. It is expected that ultra-short-chain PFASs have very short half-lives in the body preventing bioaccumulation. TFA, the most well-studied ultra-short-chain PFAS, has a drinking water health guidance value of 60 μg/L and a target value as a plant protection agent metabolite of 10 μg/L[70] in Germany. There are no target values for PFPrA and TFMS. For ultra-short-chain PFASs, little to no data about long-term (chronic) exposure and mixture toxicology exists. PFASs will remain in the environment for decades once released due to their persistent nature;[71] remediation is either unfeasible or exceedingly expensive if adverse effects from these PFASs occur.

Omission of Ultra-Short-Chain PFASs by the TOP Assay/AOF. To support regulatory work that considers PFASs as a group, analytical methods are needed that are able to measure "PFAS total" parameters. While the TOP assay provides a measure of diverse precursors that can be transformed into PFCAs through chemical oxidation (even when some precursors may also be transformed into PFSAs through environmental or in vitro processes), the AOF analysis provides a measure of the concentration of all fluorinated substances in the sample and thus includes targeted and non-targeted PFASs as well as other organic chemicals containing fluorine. Ultra-short-chain PFASs, however, remain a blind spot even for these "PFAS total" parameters. For the TOP assay, this limitation stems from the difficulty to analyze ultra-short-chain PFASs in the high ionic strength reaction mixture, while the sample enrichment in AOF assessment (adsorption to AC) is the discriminating part for very mobile PFASs.[72] Recent efforts to extend the scope of group methods toward more mobile PFASs were successful[73] and managed to include TFA and PFPrA into the TOP assay at the cost of additional sample pretreatment steps and a separate analysis of ultra-short-chain homologues with ion chromatography-MS. In most applications, however,

PFBA remains the shortest chain PFCA included. While the importance of this blind spot remains unknown, a comparison between target analysis results of long-chain, short-chain, and ultra-short-chain PFASs (Figure 3) might be an indicator of its relevance in samples not close to known sources (e.g., chemical industry, military bases, airports, and so forth). The median F-normalized sum of short- and long-chain PFASs (0.015 μg/L) increases only moderately after the TOP assay (0.019 μg/L), which implies that the oxidizable precursors are of minor importance in these samples not close to known sources and have likely already been converted into PFCA and PFSA by biotic or abiotic processes. The AOF was only analyzed in five samples with a high concentration of short- and long-chain PFASs. Here, the discrepancy to the results of the target analysis is much more pronounced (median F-normalized sum of short- and long-chain PFASs from target analysis: 0.015 μg/L; median AOF: 0.8 μg/L, note: semiquantitative data for PFCA > PFDA and PFSA > PFOS), demonstrating that fluorinated chemicals that are neither short- and long-chain PFCAs or PFSAs nor their precursors are prevalent in these samples.

The F-normalized sum of the four ultra-short-chain PFASs TFA, TFMS, PFPrA, and PFPrS (median 0.40 μg/L) exceeds the AOF in 2 out of 5 samples and is more than an order of magnitude higher than the F-normalized sum of short- and long-chain PFASs even after the conversion of oxidizable precursors through the TOP assay. The sum of these four ultra-short-chain PFASs alone exceeds the EU DWD limit for "PFAS total" of 0.5 μg/L[35] in 39 out of 46 samples. This demonstrates that any analytical approach that is ultimately chosen to represent the "PFAS total" has to be extended toward these most mobile PFASs to not miss a substantial part of the PFAS load in the sources of German drinking water.

Environmental Implications. There is a much better general understanding of the environmental occurrence of long- and short-chain PFASs than that of ultra-short-chain PFASs. Knowledge about ultra-short-chain homologues and their sources is scarce and often limited to few well-studied examples like TFA and almost exclusively to the two most extensively studied PFAS classes PFCA and PFSA. Beyond these two classes, very mobile PFASs remain excluded from target sampling campaigns and techniques to measure "PFAS total". Ultra-short-chain PFCA and PFSA homologues may only be the tip of the iceberg for the unexplored variety of very mobile PFASs that escape most current analytical approaches for "PFAS total". The recent revision to the definition of PFAS by the Organization for Economic Co-operation and Development (OECD) to substances with "at least one fully fluorinated methyl or methylene carbon atom"[17] now additionally considers substances with a CF_2 moiety as PFAS. Thus, with such a definition, the number of ultra-short-chain PFASs is quite large.[74] Novel PFASs identified here like HFIP, NTf$_2$, and other fluorinated ionic liquid anions may provide a first glance into this gap. While non-target approaches could be used to identify the presence of other mobile PFASs, the enrichment and chromatographic methods used are often tailored toward less mobile chemicals.[32] Since very few remediation options exist for ultra-short-chain PFASs, the approach of the EU Chemicals Strategy for Sustainability to prevent the use and emissions of PFASs seems to be the most effective way to manage PFASs and especially the most mobile PFAS.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c07949.

Table S2: List of all analyzed samples in anonymized form; Text S1: Liquid chromatography sample preparation; Text S2: Gas chromatography sample preparation; Text S3: Hydrophilic interaction chromatography measurements; Text S4: Reversed-phase liquid chromatography measurements; Table S3: Analytical information on liquid chromatography (LC) electrospray ionization (ESI) negative analytes, including used internal standard (IS) and sMRM parameters; Text S5: GC method 1— derivatization of TFA; Text S6: GC method 2—liquid– liquid extraction; Text S7: GC method 3—headspace GC−MS; Table S4: Analytical information on gas chromatography (GC) electron impact (EI) negative analytes, including manufacturer, mass spectrometry (MS) parameters, enrichment and recovery; Table S5: Tandem mass spectrometry (MS/MS)-parameters (Sciex 6500+) for the determination of PFAS after the TOP assay; Text S8: Equations for calculation in validation; Figure S1: Total concentrations of PFAS and their distribution in the samples (DOCX)

Table S1: General information about the analyzed PFAS, including manufacturer of standard, internal standard (IS) used and its manufacturer, enrichment and chromatographic method; Table S6: Validation parameters and additional information for HILIC, RPLC and GC measurements, where available; Table S7: Information on duplicate samples measured in HILIC and RPLC; Table S8: Trueness data for spiked samples; Table S9: Single concentrations (μg/L) for each analyte detected per sample with target methods, including the sum concentration of analyzed EU DWD PFAS (18/20) and the sum concentration of short-chain PFAS per sample; Table S10: p-values of the respective correlation coefficients for each analyte pair; Table S11: Single concentrations (μg/ L) for each analyte detected per sample after TOP assay; and AOF data; Table S12: Concentrations (μg/L) of 23 analyzed PFAS within the validation check using glass bottles from this study (XLSX)

■ AUTHOR INFORMATION

Corresponding Author

Daniel Zahn − *Hochschule Fresenius gemGmbH, Idstein 65510, Germany;* Present Address: Department of Analytical Chemistry, Helmholtz Centre for Environmental Research - UFZ, Permoserstrasse 15, Leipzig 04318, Germany; ⓞ orcid.org/0000-0003-3038-9371; Email: daniel.zahn@ufz.de

Authors

Isabelle J. Neuwald − *Hochschule Fresenius gemGmbH, Idstein 65510, Germany*

Daniel Hübner − *Hochschule Fresenius gemGmbH, Idstein 65510, Germany*

Hanna L. Wiegand − *IWW Zentrum Wasser, Mülheim an der Ruhr 45476, Germany*

Vassil Valkov − *IWW Zentrum Wasser, Mülheim an der Ruhr 45476, Germany*

Ulrich Borchers − *IWW Zentrum Wasser, Mülheim an der Ruhr 45476, Germany*

Karsten Nödler − *TZW: DVGW-Technologiezentrum Wasser, Karlsruhe 76139, Germany;* ⓘ orcid.org/0000-0002-0209-5037

Marco Scheurer − *TZW: DVGW-Technologiezentrum Wasser, Karlsruhe 76139, Germany*

Sarah E. Hale − *Norwegian Geotechnical Institute, Oslo 0806, Norway;* ⓘ orcid.org/0000-0002-7743-9199

Hans Peter H. Arp − *Norwegian Geotechnical Institute, Oslo 0806, Norway; Norwegian University of Science and Technology (NTNU), Trondheim 7491, Norway*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.est.1c07949

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) 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. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr. Environ. Assess. Manag.* **2011**, *7*, 513−541.

(2) Wang, Z.; DeWitt, J. C.; Higgins, C. P.; Cousins, I. T. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environ. Sci. Technol.* **2017**, *51*, 2508−2518.

(3) Kotthoff, M.; Müller, J.; Jürling, H.; Schlummer, M.; Fiedler, D. Perfluoroalkyl and polyfluoroalkyl substances in consumer products. *Environ. Sci. Pollut. Res.* **2015**, *22*, 14546−14559.

(4) Langberg, H. A.; Arp, H. P. H.; Breedveld, G. D.; Slinde, G. A.; Hoiseter, A.; Gronning, H. M.; Jartun, M.; Rundberget, T.; Jenssen, B. M.; Hale, S. E. Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: Source and historic emission tracking. *Environ. Pollut.* **2020**, *273*, No. 116259.

(5) Ahrens, L. Polyfluoroalkyl compounds in the aquatic environment: A review of their occurrence and fate. *J. Environ. Monit.* **2011**, *13*, 20−31.

(6) Cai, M.; Yang, H.; Xie, Z.; Zhao, Z.; Wang, F.; Lu, Z.; Sturm, R.; Ebinghaus, R. Per- and polyfluoroalkyl substances in snow, lake, surface runoff water and coastal seawater in Fildes Peninsula, King George Island, Antarctica. *J. Hazard. Mater.* **2012**, *209-210*, 335−342.

(7) Alves, A. V.; Tsianou, M.; Alexandridis, P. Fluorinated Surfactant Adsorption on Mineral Surfaces: Implications for PFAS Fate and Transport in the Environment. *Surfaces* **2020**, *3*, 516−566.

(8) Banzhaf, S.; Filipovic, M.; Lewis, J.; Sparrenbom, C. J.; Barthel, R. A review of contamination of surface-, ground-, and drinking water in Sweden by perfluoroalkyl and polyfluoroalkyl substances (PFASs). *Ambio* **2017**, *46*, 335−346.

(9) Kaboré, H. A.; Vo Duy, S.; Munoz, G.; Méité, L.; Desrosiers, M.; Liu, J.; Sory, T. K.; Sauvé, S. Worldwide drinking water occurrence and

levels of newly-identified perfluoroalkyl and polyfluoroalkyl substances. *Sci. Total Environ.* **2018**, *616-617*, 1089−1100.

(10) Fromme, H.; Wockner, M.; Roscher, E.; Volkel, W. ADONA and perfluoroalkylated substances in plasma samples of German blood donors living in South Germany. *Int. J. Hyg. Environ. Health* **2017**, *220*, 455−460.

(11) Ghisi, R.; Vamerali, T.; Manzetti, S. Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: A review. *Environ. Res.* **2019**, *169*, 326−341.

(12) Kotthoff, M.; Bucking, M. Four Chemical Trends Will Shape the Next Decade's Directions in Perfluoroalkyl and Polyfluoroalkyl Substances Research. *Front. Chem.* **2018**, *6*, 103.

(13) Janousek, R. M.; Mayer, J.; Knepper, T. P. Is the phase-out of long-chain PFASs measurable as fingerprint in a defined area? Comparison of global PFAS concentrations and a monitoring study performed in Hesse, Germany from 2014 to 2018. *TrAC, Trend. Anal. Chem.* **2019**, *120*, 115393.

(14) Pickard, H. M.; Criscitiello, A. S.; Persaud, D.; Spencer, C.; Muir, D. C. G.; Lehnherr, I.; Sharp, M. J.; De Silva, A. O.; Young, C. J. Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations. *Geophys. Res. Lett.* **2020**, *47*, 1−11.

(15) Knutsen, H.; Mæhlum, T.; Haarstad, K.; Slinde, G. A.; Arp, H. P. H. Leachate emissions of short- and long-chain per- and polyfluoralkyl substances (PFASs) from various Norwegian landfills. *Environ. Sci. Process. Impacts* **2019**, *21*, 1970−1979.

(16) Gebbink, W. A.; van Asseldonk, L.; van Leeuwen, S. P. J. Presence of Emerging Per- and Polyfluoroalkyl Substances (PFASs) in River and Drinking Water near a Fluorochemical Production Plant in the Netherlands. *Environ. Sci. Technol.* **2017**, *51*, 11057−11065.

(17) *Reconciling terminology of the universe of per- and polyfluoroalkyl substances: Recommendations and practical guidance, Series on Risk Management*; Organisation for Economic Co-operation and Development (OECD): Paris, 2021; https://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV/CBC/MONO(2021)25&docLanguage=En (accessed April 19, 2022).

(18) Brendel, S.; Fetter, E.; Staude, C.; Vierke, L.; Biegel-Engler, A. Short-chain Perfluoroalkyl Acids: Environmental concerns and a regulatory strategy under REACH. *Environ. Sci. Eur.* **2018**, *30*, 9.

(19) Björnsdotter, M. K.; Yeung, L. W. Y.; Kärrman, A.; Jogsten, I. E. Ultra-Short-Chain Perfluoroalkyl Acids Including Trifluoromethane Sulfonic Acid in Water Connected to Known and Suspected Point Sources in Sweden. *Environ. Sci. Technol.* **2019**, *53*, 11093−11101.

(20) Göckener, B.; Fliedner, A.; Rüdel, H.; Fettig, I.; Koschorreck, J. Exploring unknown per- and polyfluoroalkyl substances in the German environment - The total oxidizable precursor assay as helpful tool in research and regulation. *Sci. Total Environ.* **2021**, *782*, No. 146825.

(21) Wang, Y.; Yu, N.; Zhu, X.; Guo, H.; Jiang, J.; Wang, X.; Shi, W.; Wu, J.; Yu, H.; Wei, S. Suspect and Nontarget Screening of Per- and Polyfluoroalkyl Substances in Wastewater from a Fluorochemical Manufacturing Park. *Environ. Sci. Technol.* **2018**, *52*, 11007−11016.

(22) Kwiatkowski, C. F.; Andrews, D. Q.; Birnbaum, L. S.; Bruton, T. A.; DeWitt, J. C.; Knappe, D. R. U.; Maffini, M. V.; Miller, M. F.; Pelch, K. E.; Reade, A.; Soehl, A.; Trier, X.; Venier, M.; Wagner, C. C.; Wang, Z.; Blum, A. Scientific Basis for Managing PFAS as a Chemical Class. *Environ. Sci. Technol. Lett.* **2020**, *7*, 532−543.

(23) Cousins, I. T.; Goldenman, G.; Herzke, D.; Lohmann, R.; Miller, M.; Ng, C. A.; Patton, S.; Scheringer, M.; Trier, X.; Vierke, L.; Wang, Z.; DeWitt, J. C. The concept of essential use for determining when uses of PFASs can be phased out. *Environ. Sci. Process. Impacts* **2019**, *21*, 1803−1815.

(24) Arp, H. P.; Niederer, C.; Goss, K. U. Predicting the Partitioning Behavior of Various Highly Fluorinated Compounds. *Environ. Sci. Technol.* **2006**, *40*, 7298−7304.

(25) Li, F.; Fang, X.; Zhou, Z.; Liao, X.; Zou, J.; Yuan, B.; Sun, W. Adsorption of perfluorinated acids onto soils: Kinetics, isotherms, and influences of soil properties. *Sci. Total Environ.* **2019**, *649*, 504−514.

(26) Neumann, M.; Schliebner, I., *UBA Texte 127/2019: Protecting the sources of our drinking water - The criteria for identifying persistent, mobile,*

and toxic (PMT) substances and very persistent, and very mobile (vPvM) substances under EU REACH regulation (EC) No 1907/2006; German Environment Agency (UBA): Dessau-Roßlau, Germany, 2019.

(27) Ateia, M.; Maroli, A.; Tharayil, N.; Karanfil, T. The overlooked short- and ultrashort-chain poly- and perfluorinated substances: A review. *Chemosphere* **2019**, *220*, 866−882.

(28) Gagliano, E.; Sgroi, M.; Falciglia, P. P.; Vagliasindi, F. G. A.; Roccaro, P. Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. *Water Res.* **2020**, *171*, No. 115381.

(29) Scheurer, M.; Nödler, K. Ultrashort-chain perfluoroalkyl substance trifluoroacetate (TFA) in beer and tea − An unintended aqueous extraction. *Food Chem.* **2021**, *351*, No. 129304.

(30) Freeling, F.; Behringer, D.; Heydel, F.; Scheurer, M.; Ternes, T. A.; Nödler, K. Trifluoroacetate in Precipitation: Deriving a Benchmark Data Set. *Environ. Sci. Technol.* **2020**, *54*, 11210−11219.

(31) Taniyasu, S.; Kannan, K.; Yeung, L. W.; Kwok, K. Y.; Lam, P. K.; Yamashita, N. Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2-C4) in precipitation by liquid chromatography-tandem mass spectrometry: comparison to patterns of long-chain perfluorinated acids (C5-C18). *Anal. Chim. Acta* **2008**, *619*, 221−230.

(32) Zahn, D.; Neuwald, I. J.; Knepper, T. P. Analysis of mobile chemicals in the aquatic environment-current capabilities, limitations and future perspectives. *Anal. Bioanal. Chem.* **2020**, *412*, 4763−4784.

(33) Ng, C.; Cousins, I. T.; DeWitt, J. C.; Glüge, J.; Goldenman, G.; Herzke, D.; Lohmann, R.; Miller, M.; Patton, S.; Scheringer, M.; Trier, X.; Wang, Z. Addressing Urgent Questions for PFAS in the 21st Century. *Environ. Sci. Technol.* **2021**, *55*, 12755−12765.

(34) Montes, R.; Rodil, R.; Placer, L.; Wilms, J. M.; Cela, R.; Quintana, J. B. Applicability of mixed-mode chromatography for the simultaneous analysis of C1-C18 perfluoroalkylated substances. *Anal. Bioanal. Chem.* **2020**, *412*, 4849−4856.

(35) European Commission, 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 *Off. J. Eur. Union* **2020**, L 435/431−435/462.

(36) *Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions - Chemicals Strategy for Sustainability Towards a Toxic-Free Environment*; European Union: Brussels, 2020; https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=COM%3A2020%3A667%3AFIN (accessed April 19, 2022).

(37) Aro, R.; Carlsson, P.; Vogelsang, C.; Karrman, A.; Yeung, L. W. Fluorine mass balance analysis of selected environmental samples from Norway. *Chemosphere* **2021**, *283*, No. 131200.

(38) Koch, A.; Aro, R.; Wang, T.; Yeung, L. W. Y. Towards a comprehensive analytical workflow for the chemical characterisation of organofluorine in consumer products and environmental samples. *TrAC, Trend. Anal. Chem.* **2020**, *123*, 115423.

(39) Arp, H.P.H.; Hale, S.E., *UBA Texte 126/2019: REACH: Improvement of guidance and methods for the identification and assessment of PMT/vPvM substances*; German Environment Agency (UBA): Dessau-Roßlau, Germany, 2019.

(40) Houtz, E. F.; Sedlak, D. L. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environ. Sci. Technol.* **2012**, *46*, 9342−9349.

(41) Janda, J. *Polare Perfluoralkylcarbonsäuren*; Springer Spektrum: Wiesbaden, 2019.

(42) Müller, K.; Zahn, D.; Frömel, T.; Knepper, T. P. Matrix effects in the analysis of polar organic water contaminants with HILIC-ESI-MS. *Anal. Bioanal. Chem.* **2020**, *412*, 4867−4879.

(43) DIN 32645:2008−11. *Chemical analysis - Decision limit, detection limit and determination limit under repeatability conditions - Terms, methods, evaluation*, 2008.

(44) Kotthoff, M.; Fliedner, A.; Rüdel, H.; Göckener, B.; Bücking, M.; Biegel-Engler, A.; Koschorreck, J. Per- and polyfluoroalkyl substances in the German environment - Levels and patterns in different matrices. *Sci. Total Environ.* **2020**, *740*, No. 140116.

(45) Möller, A.; Ahrens, L.; Surm, R.; Westerveld, J.; van der Wielen, F.; Ebinghaus, R.; de Voogt, P. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. *Environ. Pollut.* **2010**, *158*, 3243−3250.

(46) Scheurer, M.; Nödler, K.; Freeling, F.; Janda, J.; Happel, O.; Riegel, M.; Muller, U.; Storck, F. R.; Fleig, M.; Lange, F. T.; Brunsch, A.; Brauch, H. J. Small, mobile, persistent: Trifluoroacetate in the water cycle - Overlooked sources, pathways, and consequences for drinking water supply. *Water Res.* **2017**, *126*, 460−471.

(47) Ellis, D. A.; Mabury, S. A. The Aqueous Photolysis of TFM and Related Trifluoromethylphenols. An Alternate Source of Trifluoroacetic Acid in the Environment. *Environ. Sci. Technol.* **2000**, *34*, 632−637.

(48) Frank, H.; Christoph, E. H.; Holm-Hansen, O.; Bullister, J. L. Trifluoroacetate in Ocean Waters. *Environ. Sci. Technol.* **2002**, *36*, 12−15.

(49) Franklin, J. The atmospheric degradation and impact of 1,1,1,2-tetrafluoroethane (hydrofluorocarbon 134a). *Chemosphere* **1993**, *27*, 1565−1601.

(50) Yeung, L. W. Y.; Stadey, C.; Mabury, S. A. Simultaneous analysis of perfluoroalkyl and polyfluoroalkyl substances including ultrashort-chain C2 and C3 compounds in rain and river water samples by ultra performance convergence chromatography. *J. Chromatogr. A* **2017**, *1522*, 78−85.

(51) ECHA - European Chemicals Agency - Trifluoromethanesulphonic acid. https://echa.europa.eu/de/substance-information/-/substanceinfo/100.014.625 (accessed April 19, 2022),

(52) Björnsdotter, M. K.; Yeung, L. W. Y.; Kärrman, A.; Jogsten, I. E. Challenges in the analytical determination of ultra-short-chain perfluoroalkyl acids and implications for environmental and human health. *Anal. Bioanal. Chem.* **2020**, *412*, 4785−4796.

(53) Barzen-Hanson, K. A.; Field, J. A. Discovery and Implications of C2 and C3 Perfluoroalkyl Sulfonates in Aqueous Film-Forming Foams and Groundwater. *Environ. Sci. Technol. Lett.* **2015**, *2*, 95−99.

(54) Stepniak, I.; Andrzejewska, E.; Dembna, A.; Galinski, M. Characterization and application of N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide ionic liquid−based gel polymer electrolyte prepared in situ by photopolymerization method in lithium ion batteries. *Electrochim. Acta* **2014**, *121*, 27−33.

(55) Neuwald, I. J.; Zahn, D.; Knepper, T. P. Are (fluorinated) ionic liquids relevant environmental contaminants? High-resolution mass spectrometric screening for per- and polyfluoroalkyl substances in environmental water samples led to the detection of a fluorinated ionic liquid. *Anal. Bioanal. Chem.* **2020**, *412*, 4881−4892.

(56) Neuwald, I.; Muschket, M.; Zahn, D.; Berger, U.; Seiwert, B.; Meier, T.; Kuckelkorn, J.; Strobel, C.; Knepper, T. P.; Reemtsma, T. Filling the knowledge gap: A suspect screening study for 1310 potentially persistent and mobile chemicals with SFC- and HILIC-HRMS in two German river systems. *Water Res.* **2021**, *204*, No. 117645.

(57) Ventura, S. P. M.; Gonçalves, A. M. M.; Gonçalves, F.; Coutinho, J. A. P. Assessing the toxicity on [C3mim][Tf2N] to aquatic organisms of different trophic levels. *Aquat. Toxicol.* **2010**, *96*, 290−297.

(58) Gomez-Herrero, E.; Tobajas, M.; Polo, A.; Rodriguez, J. J.; Mohedano, A. F. Toxicity and inhibition assessment of ionic liquids by activated sludge. *Ecotoxicol. Environ. Saf.* **2020**, *187*, No. 109836.

(59) Weyhing-Zerrer, N.; Kalb, R.; Ossmer, R.; Rossmanith, P.; Mester, P. Evidence of a reverse side-chain effect of tris-(pentafluoroethyl)trifluorophosphate [FAP]-based ionic liquids against pathogenic bacteria. *Ecotoxicol. Environ. Saf.* **2018**, *148*, 467−472.

(60) Janda, J.; Nödler, K.; Brauch, H.-J.; Zwiener, C.; Lange, F. T. Robust trace analysis of polar (C2-C8) perfluorinated carboxylic acids by liquid chromatography-tandem mass spectrometry: method development and application to surface water, groundwater and drinking water. *Environ. Sci. Pollut. Res.* **2018**, *26*, 7326−7336.

(61) Chow, S. J.; Ojeda, N.; Jacangelo, J. G.; Schwab, K. J. Detection of ultrashort-chain and other per- and polyfluoroalkyl substances (PFAS) in U.S. bottled water. *Water Res.* **2021**, *201*, No. 117292.

(62) Zahn, D.; Frömel, T.; Knepper, T. P. Halogenated methanesulfonic acids: A new class of organic micropollutants in the water cycle. *Water Res.* **2016**, *101*, 292−299.

(63) Gellrich, V.; Knepper, T.P., Sorption and Leaching Behavior of Perfluorinated Compounds in Soil. In *Polyfluorinated Chemicals and Transformation Products*; Knepper, T. P., Lange, F.T., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2012; pp 63−72.

(64) Sörengård, M.; Östblom, E.; Köhler, S.; Ahrens, L. Adsorption behavior of per- and polyfluoralkyl substances (PFASs) to 44 inorganic and organic sorbents and use of dyes as proxies for PFAS sorption. *J. Environ. Chem. Eng.* **2020**, *8*, No. 103744.

(65) Krauss, M.; Hug, C.; Bloch, R.; Schulze, T.; Brack, W. Prioritising site-specific micropollutants in surface water from LC-HRMS non-target screening data using a rarity score. *Environ. Sci. Eur.* **2019**, *31*, 1−12.

(66) Hites, R. A. Correcting for Censored Environmental Measurements. *Environ. Sci. Technol.* **2019**, *53*, 11059−11060.

(67) Taniyasu, S.; Yamashita, N.; Moon, H. B.; Kwok, K. Y.; Lam, P. K.; Horii, Y.; Petrick, G.; Kannan, K. Does wet precipitation represent local and regional atmospheric transportation by perfluorinated alkyl substances? *Environ. Int.* **2013**, *55*, 25−32.

(68) Yeung, L. W. Y.; Dassuncao, C.; Mabury, S.; Sunderland, E. M.; Zhang, X.; Lohmann, R. Vertical Profiles, Sources, and Transport of PFASs in the Arctic Ocean. *Environ. Sci. Technol.* **2017**, *51*, 6735−6744.

(69) Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z. An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environ. Sci. Process. Impacts* **2020**, *22*, 2345−2373.

(70) Umweltbundesamt Empfehlungen und Stellungnahmen zu Trinkwasser - Ableitung eines gesundheitlichen Leitwertes für Trifluoressigsäure (TFA). https://www.umweltbundesamt.de/sites/default/files/medien/421/dokumente/ableitung_eines_gesundheitlichen_leitwertes_fuer_trifluoressigsaeure_fuer_uba-homepage.pdf (accessed September 22, 2021).

(71) Cousins, I. T.; Ng, C. A.; Wang, Z.; Scheringer, M. Why is high persistence alone a major cause of concern? *Environ. Sci. Process. Impacts* **2019**, *21*, 781−792.

(72) Wagner, A.; Raue, B.; Brauch, H.-J.; Worch, E.; Lange, F. T. Determination of adsorbable organic fluorine from aqueous environmental samples by adsorption to polystyrene-divinylbenzene based activated carbon and combustion ion chromatography. *J. Chromatogr. A* **2013**, *1295*, 82−89.

(73) Janda, J.; Nödler, K.; Scheurer, M.; Happel, O.; Nürenberg, G.; Zwiener, C.; Lange, F. T. Closing the gap - inclusion of ultrashort-chain perfluoroalkyl carboxylic acids in the total oxidizable precursor (TOP) assay protocol. *Environ. Sci. Process. Impacts* **2019**, *21*, 1926−1935.

(74) Barnabas, S. J.; Böhme, T.; Boyer, S. K.; Irmer, M.; Ruttkies, C.; Wetherbee, I.; Kondic, T.; Schymanski, E. L.; Weber, L. Extracting and Comparing PFAS from Literature and Patent Documents using Open Access Chemistry Toolkits - Working Paper. *J. Theor. Comput. Chem.* **2022**, DOI: 10.26434/chemrxiv-2022-nmnnd-v2.