

1 **Ultra-short-chain PFAS in the sources of German drinking water:**
2 **prevalent, overlooked, difficult to remove, and unregulated**

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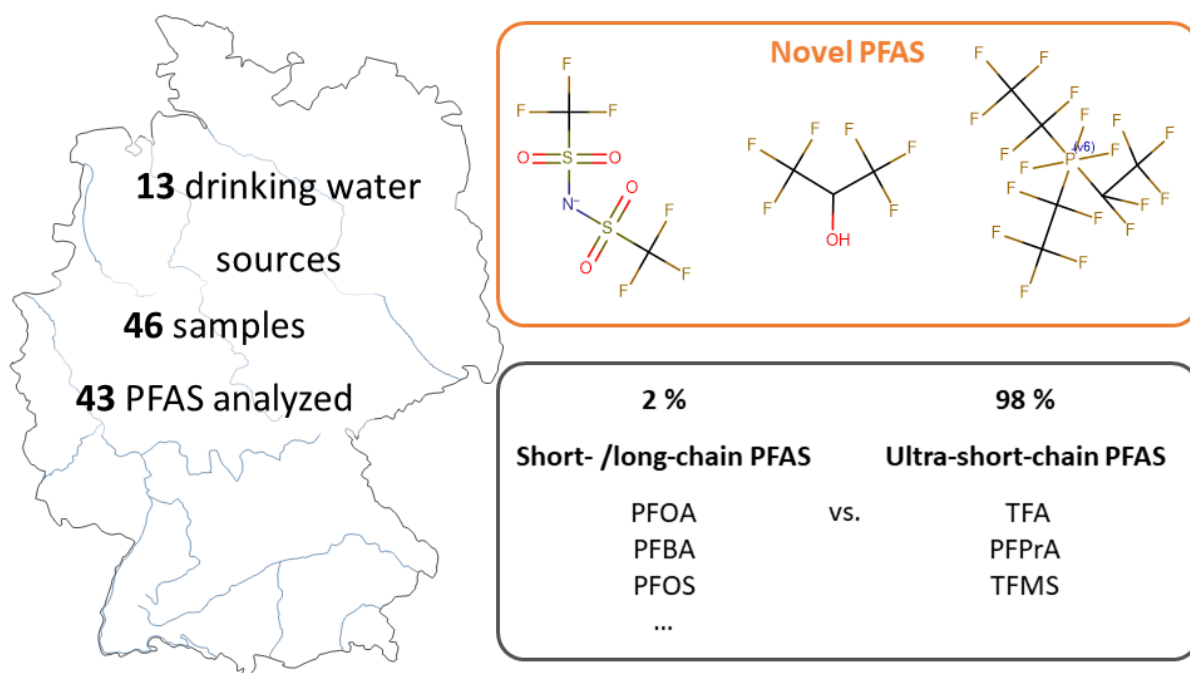
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16 **Keywords**

17 Monitoring, sum parameters, trifluoroacetate (TFA), trifluoromethanesulfonate (TFMS),
18 perfluoropropanoate (PFPrA), hexafluoroisopropanol (HFIP), bis(trifluoromethylsulfonyl)imide (NTf₂),
19 tris(pentafluoroethyl)trifluorophosphate (FAP)

20 Graphical Abstract



21

22 Abstract

23 Per- and polyfluoroalkyl substances (PFAS) have been a focal point of environmental chemistry and
24 chemical regulation in recent years, culminating in a shift from individual PFAS regulation towards a
25 PFAS group regulatory approach in Europe. PFAS are a highly diverse group of substances, and
26 knowledge about this group is still scarce beyond the well-studied, legacy long-chain, and short-chain
27 perfluorocarboxylates (PFCA) and perfluorosulfonates (PFSA). Herein, quantitative and semi-
28 quantitative data for 43 legacy, short-chain and ultra-short-chain PFAS (≤ 2 perfluorocarbon atoms for
29 PFCA, ≤ 3 for PFSA and other PFAS) in 46 water samples collected from 13 different sources of German
30 drinking water are presented. The PFAS considered include novel compounds like
31 hexafluoroisopropanol, bis(trifluoromethylsulfonyl)imide, and
32 tris(pentafluoroethyl)trifluorophosphate. The ultra-short-chain PFAS trifluoroacetate,
33 perfluoropropanoate, and trifluoromethanesulfonate were ubiquitous and present at the highest
34 concentrations (98% of sum target PFAS concentrations). 'PFAS total' parameters like the AOF
35 (absorbable organic fluorine) and TOP assay (total oxidizable precursor) were found to provide only
36 an incomplete picture of PFAS contamination in these water samples by not capturing these highly

37 prevalent ultra-short-chain PFAS. These ultra-short-chain PFAS represent a major challenge for
38 drinking water production and show that regulation in the form of preventive measures is required to
39 manage them.

40 **Synopsis**

41 Ultra-short-chain PFAS were the most dominant and ubiquitous PFAS present in the sources of
42 drinking water throughout Germany.

43 **Introduction**

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

50 The persistence and ubiquitous occurrence of some of the most prevalent PFAS such as
51 perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA) and
52 perfluorohexanesulfonate (PFHxS), has resulted in increased attention and their identification as
53 substances of very high concern (SVHC) under REACH (Registration, Evaluation Authorization and
54 Restriction of Chemicals (EC 1907/2006)) within the last eight years. The phase out of long-chain legacy
55 PFAS has led to their replacement with short-chain fluorinated alternatives [12, 13], such as
56 perfluorobutanoate (PFBA) [14], perfluorobutanesulfonate (PFBS) [15], or HFPO-DA (2,3,3,3-
57 tetrafluoro-2-(heptafluoropropoxy)propanoate/Gen-X) [16]. Long-chain PFAS are generally defined as
58 having seven or more perfluorocarbons for perfluorocarboxylates (PFCA) and six or more for
59 perfluorosulfonates (PFSA)[1, 17]; short-chain PFAS are herein defined as those with three to six
60 perfluorocarbons for PFCA and four to five for PFSA[18, 19]; other PFAS are herein classified

61 analogously to perfluorosulfonates for consistency; ultra-short-chain PFAS are those with ≤ 2
62 perfluorocarbon atoms for PFCA, ≤ 3 for PFSA and other PFAS).

63 The diversity of PFAS sub groups as well as the attention towards non-legacy and unknown fluorinated
64 compounds continues to increase [20, 21]. Hence, to reduce production, emissions and exposure to
65 PFAS, regulatory proposals to manage PFAS as a single substance class [22] and to apply the concept
66 of essential use [23] to PFAS have been made.

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

81 To address the ever increasing number of PFAS on the global market, which is approximately 5000
82 [17], the revised European Drinking Water Directive (EU DWD) has proposed the introduction of two
83 parameters: 'Sum of PFAS' and 'PFAS total' [35]. 'Sum of PFAS' is the sum of PFCA with three to twelve
84 and PFSA with four to thirteen perfluorocarbons and a limit value of 0.1 $\mu\text{g/L}$. 'PFAS total' refers to all
85 PFAS in the sample with a limit value of 0.5 $\mu\text{g/L}$. A grouping approach is also included in the 2020 EU

86 Chemicals Strategy for Sustainability Towards a Toxic Free Environment [36]; though, it is unclear how
87 definitions of 'PFAS total' may vary across different regulations and how they will be analyzed. The
88 revision of the EU DWD inevitably results in a demand for approaches to 'PFAS total' analyses. While
89 no true 'PFAS total' method exists, the adsorbable organic fluorine (AOF) method and the total
90 oxidizable precursor (TOP) assay are the two most widely used PFAS bulk approaches. However, one
91 limitation with these methods is how well they account for ultra-short-chain PFAS [37, 38]. The
92 relevance and impact of this omission is yet largely unknown and is the focus of current regulatory
93 discussion. Therefore, to deliver context for this discussion, this study presents a monitoring campaign
94 throughout Germany for PFAS, including legacy long-chain, short-chain, ultra-short-chain and other
95 non-PFSA and non-PFCA PFAS, in various sources of drinking water. Surface water, bank filtrate (water
96 that has passed through a river- or lake bank as a method of purification for drinking water
97 production), groundwater and raw water (water from the exact point of entry into the drinking water
98 production plant) were included. Targeted PFAS analysis and methods to determine 'PFAS total'
99 concentrations were used to assess the occurrence and distribution of PFAS. Statistical methods were
100 used to investigate the co-occurrences of PFAS, correlations between them and ubiquitous or regional
101 presence. Forensic identification of specific emission sources was not within the scope of this study.
102 Results from the work can be used to better account for ultra-short-chain PFAS in fresh water and
103 drinking water sources, and to support monitoring campaigns, policy development and risk
104 assessment of these problematic substances.

105

106 **Materials and methods**

107 **Target PFAS and 'PFAS total' methods**

108 The list of target PFAS included i) 18 out of the 20 PFAS included in Annex III of the revised EU DWD
109 [35] (for perfluoroundecanesulfonate (PFUnS) and perfluorotridecanesulfonate (PFTrS) there was no
110 analytical standard available at the time of analysis); ii) 23 PFAS registered under REACH, which meet

111 the proposed PMT/vPvM criteria [39], most with production volumes of >10 tons per annum and a
112 limited availability of analytical data; and, 3) two additional ultra-short-chain PFAS,
113 perfluoroethanesulfonate (PFETs) and perfluoropropanesulfonate (PFPrS). The 23 PFAS registered
114 under REACH were selected based on their prioritization in a previous screening of REACH registered
115 substances, based on their PMT/vPvM properties [39], and a subsequent query for additional polar or
116 ionic short-chain PFAS substances that have been registered in 2019, as these were known to be used
117 in Europe. In total, 43 PFAS were analyzed (see Table S1, which also presents all substance
118 abbreviations).

119 **Chemicals and standards**

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

127 A list of all standards used is presented in Table S1 in the supporting information (SI).

128 **Water samples**

129 46 grab water samples were obtained from 13 water suppliers all over Germany, all representing
130 direct or indirect source waters for drinking water production. These comprised 16 surface water
131 samples, 16 bank filtrate samples, 7 raw water samples and 7 groundwater samples (see Table S2),
132 covering the river basins Danube, Elbe, Ems, Havel, Main, Neckar, Rhine, and Sieg, among others, and
133 their surroundings. Exact locations cannot be provided by request of anonymity of water suppliers.
134 The samples were stored in 2 L glass bottles in the dark at 6 °C and were analyzed within 8 weeks of

135 sampling. The samples were taken between October 27th and November 4th, 2020. All sampling
136 equipment was tested for PFAS contaminations (see quality control).

137 **Sample preparation**

138 Liquid chromatography sample preparation

139 Trifluoromethanesulfonate (TFMS), tris(pentafluoroethyl)trifluorophosphate (FAP),
140 bis(trifluoromethylsulfonyl)imide (NTf₂), PFETs and perfluoropropanoate (PFPrA) were analyzed using
141 hydrophilic interaction chromatography (HILIC) analysis, and multi-layer solid phase extraction
142 (mISPE) was used as enrichment method. Legacy PFAS, 6:2 FTS, HFPO-DA, PFPrS, triflinate and DPOSA
143 were analyzed with weak anion-exchange SPE in combination with reversed-phase liquid
144 chromatography (RPLC) measurements. Procedural blanks were enriched using the same method as
145 the real samples. Detailed information on the techniques is presented in the SI (Text S1).

146 Gas chromatography sample preparation

147 TFA (evaporative concentration), 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-hydroxyethyl)-N-methyl-1-
148 butanesulfonamide (CAS 34454-97-2) and Trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,8-
149 tridecafluorooctyl)silane (CAS 78560-45-9) (liquid-liquid extraction) were analyzed by gas
150 chromatography-mass spectrometry (GC-MS). More details can be found in the SI (Text S2).

151 The remaining analytes listed in Table S1 (CAS 382-28-5, 75-71-8, 40573-09-9, 15290-77-4, 422-05-9,
152 920-66-1, 355-93-1, 17527-29-6, 85857-16-5, 2144-53-8, 51851-37-7) were directly analyzed by
153 headspace GC-MS without any further sample preparation.

154 Total oxidizable precursor (TOP) assay

155 The TOP assay method was based on Houtz and Sedlak [40] but with further adaptations and
156 optimizations based on Janda [41]. A sample aliquot of 50 mL was mixed with 1 g K₂S₂O₈ and 0.95 mL
157 NaOH (10 M) in a 50-mL-polypropylene container (Sarstedt, Nümbrecht, Germany). After capping, the
158 batch was incubated at 85°C for 20 h. After cooling in an ice bath, the pH was adjusted to 5 with formic
159 acid and a mixture of internal standards (IS) (isotopically labelled PFBA- perfluorotridecanoate (PFTrA),

160 PFBS, PFHxS, and PFOS) and 2 mL methanol were added. The analytes (PFBA –
161 perfluorotetradecanoate (PFTeA), PFPrS, PFBS, perfluoropentanesulfonate (PFPeS), PFHxS,
162 perfluoroheptanesulfonate (PFHpS), PFOS, perfluorononanesulfonate (PFNS), and
163 perfluorodecanesulfonate (PFDS)) were extracted by a weak anion exchanger (Strata X-AW 6 mL, 200
164 mg; Phenomenex, Aschaffenburg, Germany) using an elution flow rate of 0.8 mL/min. The sorbent
165 was preconditioned with 4 mL methanol containing 0.1% NH₄OH, 4 mL methanol, and 2 × 5 mL
166 ultrapure water. After extraction, the sorbent was dried for 30 min by N₂ and the analytes were eluted
167 with 2 × 2 mL methanol and 3 × 2 mL methanol containing 0.1% NH₄OH. After evaporating the extract
168 to dryness with N₂, the residues were redissolved in 0.25 mL methanol:water (80:20, v:v).

169 Adsorbable organic fluorine (AOF)

170 The AOF was determined as follows. A sample aliquot of 100 mL was mixed with 5 mL aqueous NaNO₃
171 solution (0.2 mol/L) and the AOF was extracted using 100 mg of activated carbon (AC) adsorbent
172 (Blücher #100043, Erkrath, Germany)). The amount of AC was divided into two portions of 50 mg each
173 filled between two polyethylene (PE) frits (10 µm, Biotage, Uppsala, Sweden) in SPE cartridges (3 mL,
174 Phenomenex, Torrance, CA). Two of these cartridges were connected with a Luer-Slip adapter for the
175 analysis of each sample. The flow rate was adjusted to 3 mL/min. After extraction, the cartridges were
176 washed with 25 mL NaNO₃ solution (0.01 mol/L) at the same flow rate to remove adsorbed inorganic
177 fluorine (fluoride, F⁻). As shown by spike experiments, fluoride concentrations up to 300 µg/L are
178 efficiently removed. All samples were analyzed for fluoride before AOF analysis and none of the
179 samples exceeded 300 µg/L.

180 Analytical methods

181 Liquid-chromatography mass spectrometry instrumentation

182 The liquid chromatography mass spectrometry (LC-MS) system used was a Shimadzu Nexera X2,
183 consisting of a degassing unit, four pumps, an autosampler, a communication module and a column
184 oven (Shimadzu, Kyoto, Japan) coupled to a QTrap 5500 tandem-MS (MS/MS) system (AB Sciex,

185 Darmstadt, Germany). HILIC and RPLC measurements are described in detail in the SI (Text S3 and S4)
186 and scheduled multiple reaction monitoring (sMRM) parameters for each analyte are presented in
187 Table S3.

188 Gas chromatography mass spectrometry instrumentation

189 Three GC-MS methods and instruments were used for the analysis of PFAS as described in the sections
190 above: derivatized TFA was analyzed with GC method 1 (Text S5), liquid-liquid extracts were analyzed
191 with GC method 2 (Text S6) and headspace analysis was performed with GC method 3 (Text S7).
192 Further MS parameters are summarized in Table S4.

193 TOP assay instrumentation

194 Instrumental analysis of the TOP assay samples was conducted by LC-MS using a 1260 Infinity II LC
195 System (Agilent, Waldbronn, Germany) connected to a 6500+ MS/MS instrument (Sciex, Darmstadt
196 Germany). The analytical column was a Luna Omega Polar C18 100 × 2.1 mm, 1.6 μm (Phenomenex,
197 Aschaffenburg, Germany). Eluent A was 10% methanol in ultrapure water (+ 0.01 M ammonium
198 acetate) and eluent B was methanol. A flow rate of 0.18 mL/min was applied and an injection volume
199 of 10 μL was used. The gradient was as follows: starting at 20% B, increasing to 25% B from 0–0.5 min,
200 increasing to 70% B from 0.5–7.0 min, increasing to 98% B from 7.0–14.5 min, holding this condition
201 until minute 21.5 and decreasing to starting conditions within 0.5 min. The equilibration time was
202 8.0 min. Further MS parameters are summarized in Table S5.

203 AOF instrumentation

204 The determination of AOF was performed using a modified combustion ion chromatography (CIC)
205 system for ultra-trace fluorine analysis, consisting of an automated boat controller (ABC-100), an
206 automatic quick furnace (AQF-100) with a water supply unit (WS-100), and a gas absorption unit (GA-
207 100) (all from Mitsubishi Chemical Analytech Co., LTD, Kanagawa, Japan). The combustion unit was
208 linked to an IC system (ICS-2100, Thermo Fisher Scientific, Waltham, MA, USA). The calibrant for the
209 AOF was NaF (VWR, Darmstadt, Germany) dissolved in deionized water. The calibration range was

210 0.1–14 µg/L F. For analysis the adsorbent was transferred to a ceramic sample boat (a1-
211 envirosciences, Düsseldorf, Germany) and combusted in a furnace at 950–1000 °C while delivering 0.1
212 mL/min of ultrapure water by the WS-100. Using this method, organic fluorine belonging to the
213 adsorbed organic substances is converted into hydrogen fluoride (HF), while the addition of excess
214 water into the combustion tube prevents the formation of silicon tetrafluoride. The HF formed was
215 measured as F⁻ by IC analysis. The adsorbent of the second cartridge of the same sample was analyzed
216 in the same way. Both results were blank corrected and summed to give the AOF.

217 **Quality control**

218 For LC measurements, reproducibility (in triplicates), recovery, matrix effects, trueness (equations see
219 Text S8), limit of detection (LOD) and LOQ of the methods were determined (Table S6). The ion ratio
220 tolerance between quantifier and qualifier mass was 20% for analytes with two transitions. To assess
221 retention time and intensity shifts in LC measurements, a quality control (QC) mix standard of all
222 analytes was measured four times in each batch. Reproducibility of the method was determined by
223 enriching a selection of samples (11%) in duplicates (Table S7). A selection of samples (11% for RPLC,
224 22% for HILIC) was spiked prior to sample enrichment (Table S8). Procedural blank signals (Table S6)
225 were subtracted from the analyte signal. IS were used where applicable and available (Table S1), and
226 added before enrichment. To compensate for the low trueness of some analytes (<70% and >130%),
227 the concentration of substances was calculated considering recovery and matrix effects obtained from
228 the validation. Since matrix effects in HILIC were shown to be highly sample and analyte specific,
229 chemically similar IS cannot be used [42], and thus, matrix effects were determined for each analyte
230 and sample individually. Therefore, all samples were split after reconstitution and one part was spiked
231 with a PFAS mix standard.

232 For GC measurements, trueness, duplicates, LOD, LOQ, and the correlation coefficient (R²) were
233 determined (Table S6). A QC sample treated in the same way as real samples was analyzed at least
234 once in each batch of GC measurements. Blanks were controlled in each batch by measuring samples

235 of deionized water, which is prepared in the same way as real samples. In order to monitor the
236 trueness of the method, 17% of samples were spiked before sample preparation (Table S8).

237 For AOF analysis, the HF formed was absorbed in an aqueous methane sulfonic acid solution (1 mg/L)
238 which was used to correct for deviations of the injection unit of the CIC system. All analyses were
239 performed in duplicates. Relative standard deviations were below 10%. The LOQ for the entire AOF
240 protocol (SPE-CIC) was calculated according to the blank value method of DIN 32645 [43] ($n = 10$) with
241 $LOQ = 10 \times SD/s \times FD$, where SD is the standard deviation of the procedural blank, s the slope of the
242 calibration function in the low concentration range, and FD the dilution factor. The limit of
243 quantification (LOQ) was 1 $\mu\text{g/L}$ and 0.5 $\mu\text{g/L}$ was set as the qualitative reporting level. Procedural
244 blank samples (one per day) were included, covering extraction (100 mL deionized water) and CIC, and
245 were used for blank correction.

246 QC of the TOP assay was performed by controlling the oxidative conversion of PFCA precursors, in
247 addition to IS. This was ensured by spiking 25 ng *N*-Ethyl perfluorooctane sulfonamido acetic acid (*N*-
248 EtFOSAA) into a quality control sample that was treated as real samples. A conversion of at least 70%
249 of *N*-EtFOSAA into PFOA was set as the minimum value to be able to consider the sample batch as
250 valid. Multiple procedural blanks were used: One blank covered the whole sample preparation and
251 analysis procedure, a second blank sample was used for the SPE procedure only, and the last blank,
252 the quality control sample, was used to make sure that precursors were degraded.

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

258 **Results and discussion**

259 **Occurrence in drinking water sources**

260 Amongst the 46 samples, 43 PFAS were analyzed via HILIC-sMRM, RPLC-sMRM, and GC-MS and 30 of
261 them were detected at least once above their LOQ. The number of positive detects per sample ranged
262 from 4 to 28 with a median of 17 (see Figure S1 A, concentrations see Table S9). Since the samples
263 were taken and stored in glass bottles, sorption of longer chain PFAS cannot be excluded and thus,
264 data for PFCA >PFDA and PFSA >PFOS is only semiquantitative. However, the concentrations detected
265 herein for these longer chain PFAS are in the same order of magnitude as in other studies [13, 44, 45].
266 TFA was the most dominant PFAS, accounting for more than 90% of the total concentration of PFAS
267 analyzed in all samples, with a maximum and median concentration of 12.4 µg/L and 0.9 µg/L,
268 respectively, which is in line with previous monitoring programs in German surface waters [46]. TFA is
269 known to be widespread in the aquatic environment and can be introduced into the water cycle
270 through industrial processes and as a transformation product of pharmaceutical and agricultural
271 products [46, 47] among others. TFA is also a transformation product of hydrofluorocarbon
272 refrigerants in the atmosphere and may reach the aqueous environment via atmospheric deposition
273 [30, 48, 49]. Due to its unique environmental exposure pathways and generally high concentrations,
274 a comparison of TFA with other PFAS is not necessarily meaningful.

275 When omitting TFA, two other ultra-short-chain PFAS, namely TFMS (median 8.0 ng/L, maximum 2.1
276 µg/L, Figure 1 A) and PFPrA (median 12.6 ng/L, maximum 0.18 µg/L) are the most prevalent,
277 accounting for 59% and 9% of the mean total PFAS concentration across all samples, respectively (see
278 Figure S1 B). A similar picture for the ultra-short-chain PFAS was observed by Yeung et al. [50], where
279 they accounted for more than 40% of the total amount of PFAS in Canadian rivers. The other ultra-
280 short-chain PFSA PFEtS was not detected at all and perfluoropropanesulfonate (PFPrS) was only
281 present at concentrations well below 0.01 µg/L. The distinct variations in the occurrence of ultra-
282 short-chain PFAS may be related to their use and sources. According to REACH, TFMS is produced at a

283 volume of 100-1000 tons per year and is used for the manufacture of chemicals and electrical,
284 electronic and optical equipment [51]. It is used in organic syntheses and lithium-ion batteries [52].
285 Environmental sources of TFMS remain largely unknown. No clear uses of PFPrA could be identified
286 based on information registered under REACH. PFPrA has been reported to be a degradation product
287 of hydrofluorocarbon refrigerants and other intermediates [52]. In contrast, PFEtS and PFPrS, which
288 were infrequently detected in this data set, have previously only been reported in AFFF and
289 groundwater at military training sites [53] and no other use could be identified from our literature
290 search. To our knowledge they are not associated with large emissions.

291 Short- and long-chain PFAS were predominantly detected at individual concentrations below 0.01
292 $\mu\text{g/L}$. The sum of the analyzed 18 (of 20) PFAS listed in the EU DWD 'Sum of PFAS' did not exceed the
293 proposed threshold of 0.1 $\mu\text{g/L}$ [35] in any sample. Among the novel or yet scarcely analyzed non-
294 PFCA and non-PFSA, the most commonly detected were hexafluoroisopropanol (HFIP), NTf_2 and FAP
295 (for structures see Table S1). HFIP is a fluorinated solvent used in polymer chemistry and organic
296 synthesis that was only detected in 3 samples but at high concentrations (median 0.4 $\mu\text{g/L}$, maximum
297 0.4 $\mu\text{g/L}$). This is the first report of the environmental detection of this chemical to the best of our
298 knowledge. Since this data is near the LOQ of 0.1 $\mu\text{g/L}$, a wider distribution at concentrations $<\text{LOD}$
299 (0.03 $\mu\text{g/L}$) cannot be excluded. NTf_2 is a fluorinated anion predominantly used in ionic liquids and was
300 detected in low concentrations (median 0.8 ng/L , maximum 2.0 ng/L) in nine samples. It is mainly used
301 in lithium-ion batteries [54] among other applications. The currently increasing demand for energy
302 storage capacities facilitated by the rise of renewable energy sources may result in increased
303 production and release of chemicals associated with lithium batteries, such as fluorinated ionic liquids
304 including NTf_2 . Currently, the lack of occurrence data makes it impossible to evaluate if its use in
305 energy storage leads to its environmental release. NTf_2 and the infrequently detected FAP (5 samples,
306 median 0.5 ng/L , maximum 0.7 ng/L) have only recently been detected in the aquatic environment
307 [55] as a novel class of PFAS. Occurrence data on NTf_2 is so far exceedingly scarce and only semi-
308 quantitative [56]. Toxicity tests have shown that NTf_2 is toxic to aquatic organisms [57] and sludge

309 bacteria [58], while toxic effects on clinically relevant bacteria have been reported for FAP [59].
310 Toxicity data for HFIP is, to the best of our knowledge, not available.

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

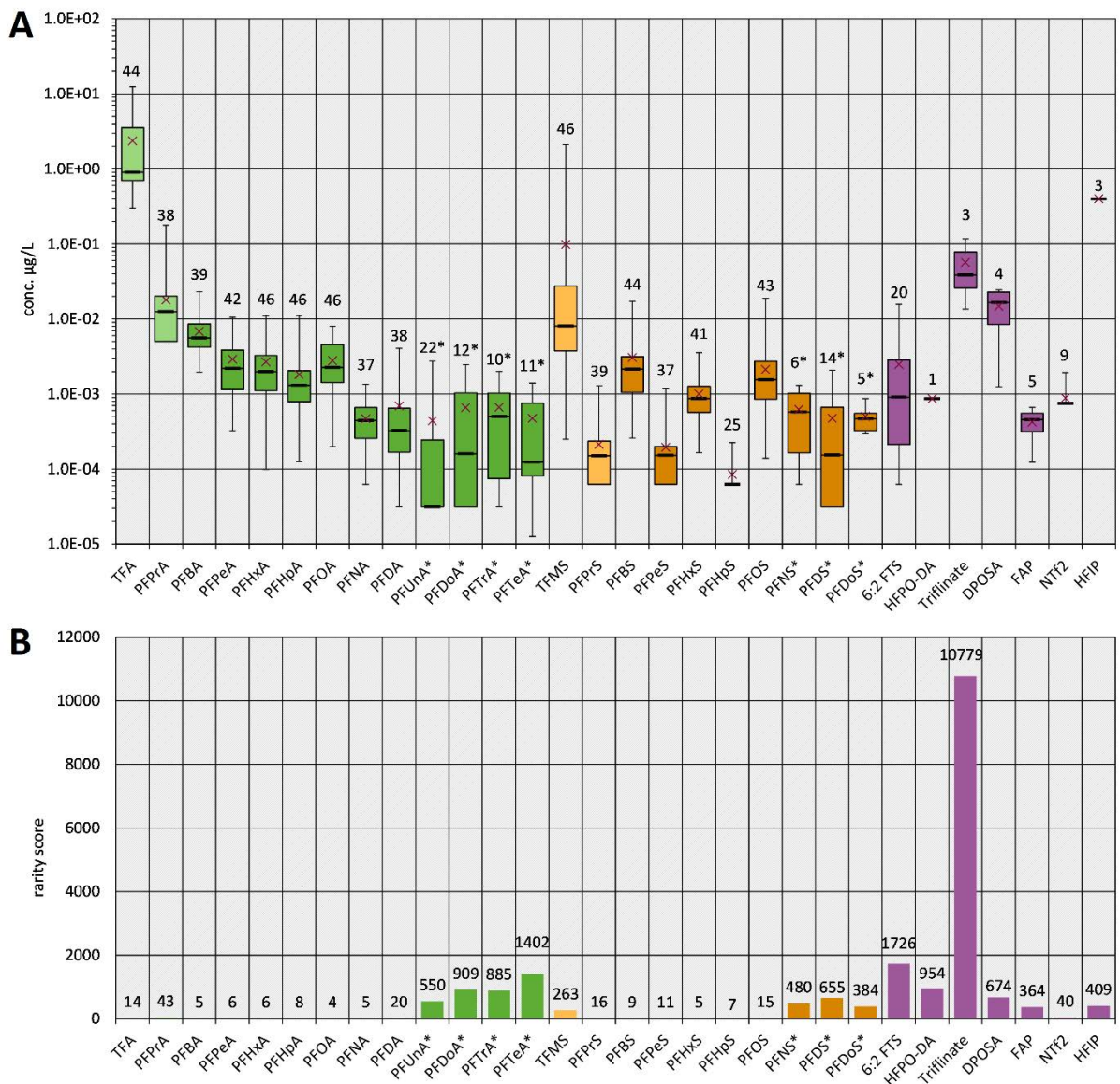
322 When generalizing the results of such a diverse sample set, the homogeneity of the occurrence data
323 must be considered. To probe this homogeneity, a rarity score (RS) was calculated according to Krauss
324 et al. [65]. For this calculation, results <LOD or <LOQ were treated as half of the LOD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

$$326 \quad RS = \frac{\textit{maximum concentration}}{\textit{median concentration}} \cdot \frac{\textit{number of samples}}{\textit{number of detects}}$$

327 Equation 1

328 A low RS indicates a uniform distribution over most if not all samples while a high RS implies that a
329 detected substance is site-specific, either occurring only in few samples or showing pronounced
330 differences in concentrations between sampling sites (Figure 1B). All PFCA <perfluoroundecanoate
331 (PFUnA) and all PFSA between PFBS and PFOS showed exceptionally low RS (RS 4-43), thus
332 demonstrating their uniform distribution within this geographically diverse sample set covering

333 surface water, bank filtrate samples, groundwater samples and raw water samples. Consequently,
334 results for these substances can likely be extrapolated towards a more general occurrence in these
335 environmental compartments. RS significantly increased for PFCA \geq PFUnA and PFSA \geq PFNS (RS 384-
336 1402, note: semiquantitative data). Above these chain lengths atmospheric transport has been
337 reported to be less relevant [67, 68] and such PFAS are considered to be less mobile with a $\log K_{oc} > 3$
338 (low RS score PFAS are below a $\log K_{oc}$ of 3, high RS PFAS are above). This is an indicator that the
339 presence of these longer chain PFAS in drinking water sources may be associated with local emissions,
340 though subsequent studies would be needed to confirm this. TFMS (RS 263) was detected in all
341 samples but with significantly elevated concentrations at a few sampling locations. Therefore, TFMS
342 can be considered as a diffusely distributed PFAS, but in certain areas there could be emission hot-
343 spots in addition. PFAS that were neither PFSA nor PFCA generally showed high RS (364 -10779) in line
344 with their pronounced site specificity that was either indicated by very few detects (HFPO-DA,
345 triflinate, DPOSA, FAP, and HFIP) or by concentration ranges spanning two orders of magnitude (6:2
346 FTS). NTf₂, which was detected in nine samples close to the LOQ, is the only exception with a very low
347 RS of 40. This might imply a ubiquitous presence of NTf₂ at low concentrations, which is in line with a
348 recent suspect screening for PMT/vPvM substances that included many ions used in ionic liquids [56].



349

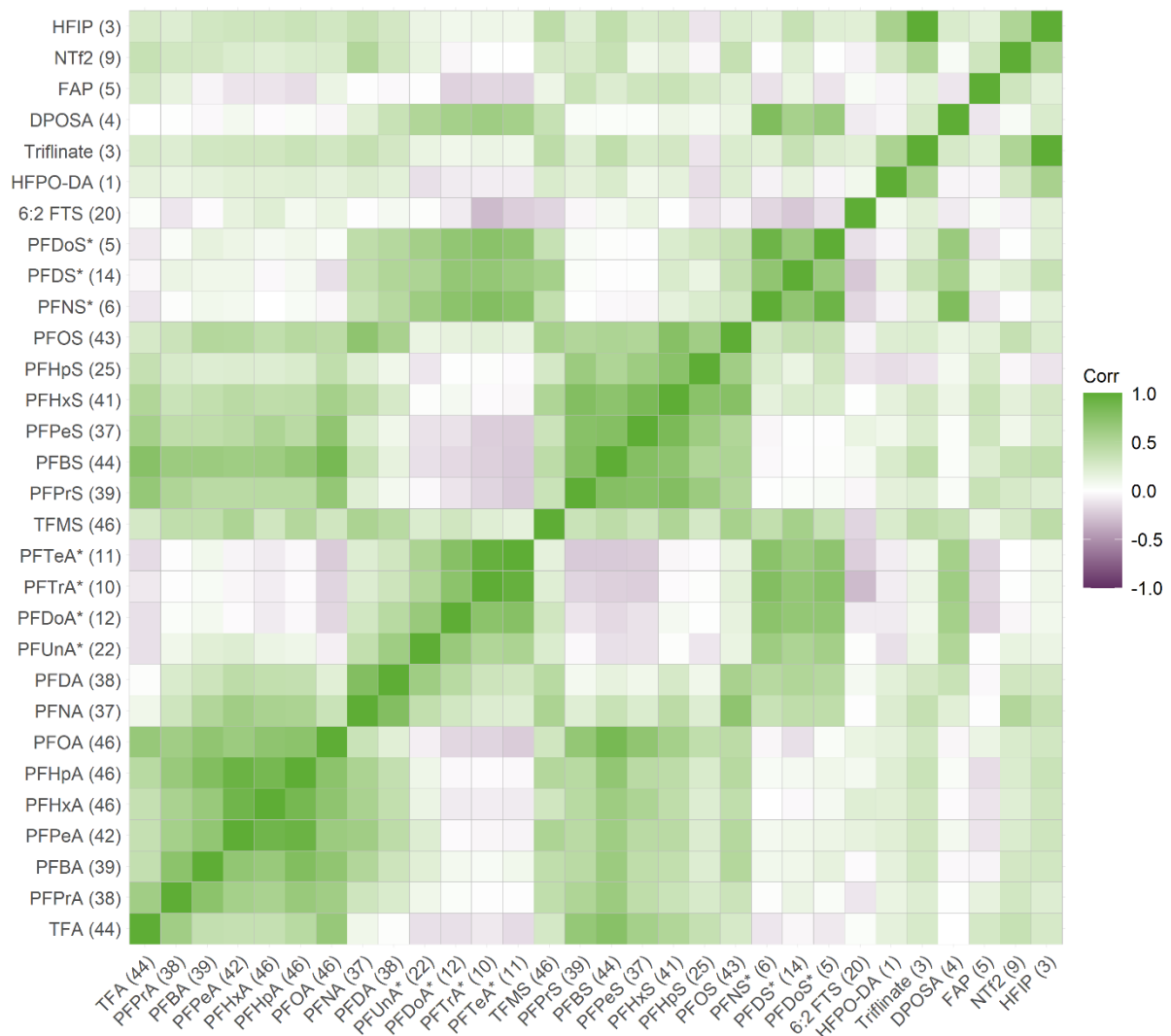
350 *Figure 1: A) Boxplots of PFAS concentrations over all samples. The number above the bars depict the number of*
 351 *detects out of 46 samples. X marks the mean concentration, and the horizontal line inside the box depicts the*
 352 *median concentration. <LOQ was included as half its value for each substance. B) Rarity score of all detected*
 353 *PFAS. <LOQ and <LOD were included as half their value for each substance. Green: PFCA regulated under EU*
 354 *DWD and PFTTeA, orange: PFSA regulated under EU DWD, purple: other non PFCA and PFSA PFAS, compounds in*
 355 *lighter shades are ultra-short-chain PFAS (not regulated under EU DWD). Note: PFCA >PFDA and PFSA >PFOS are*
 356 *marked with a star, indicating semiquantitative data.*

357 **Distribution patterns of PFAS**

358 To study similarities and differences in the occurrence and distribution patterns of the investigated
359 PFAS, the Spearman correlations across all samples and analytes were plotted (Figure 2, p-values see
360 Table S10). Ultra-short- and short-chain PFCA, along with the PFCA PFHpA, PFOA and PFNA were
361 positively correlated between one and other. The correlation coefficients decreased with decreasing
362 number of perfluorocarbons, down to 0.4 for TFA (p-values <0.05). Similarly, positive correlations for
363 ultra-short- and short-chain PFSA, along with the long-chain PFHxS, PFHpS and PFOS were observed,
364 though with the smallest correlation with TFMS (between 0.3 and 0.5, p-values <0.05 with very few
365 exceptions). Additionally, these two groups of PFCAs and PFSAs were positively correlated between
366 each other as well (Figure 2). The strong correlation particularly for short-chain PFCA and PFSA and
367 PFHxS (>0.7, p-values <0.05) may be associated with their similar uses, such as processing aids for
368 Teflon production and in AFFFs [69]. Long-chain PFCA, starting with PFUnA, and the long-chain PFSA
369 PFNS, PFDS and PFDoS correlated strongly among themselves (correlation coefficients >0.6, p-values
370 <0.05, note: semiquantitative data). These substances were shown to be rather site specific as
371 demonstrated by their elevated RS. This is also expected as they are known to be less readily
372 transported in the environment than their shorter chain homologues; therefore, their occurrence is
373 likely the result of more local, common sources and use patterns. However, given the low detection
374 frequency of these PFAS (<50%), this interpretation must be made with caution. PFNA, PFDA, and
375 DPOSA also have a less pronounced correlation (correlation coefficients 0.3 – 0.6, p-values <0.05) with
376 each other. The shortest ultra-short-chain PFAS TFA and TFMS correlated weakly to moderately with
377 other PFAS (correlation coefficients -0.2 – 0.6, p-values <0.05 with very few exceptions) and with each
378 other. Despite similar environmental behavior and low RS, this is an indication that these substances
379 may have unique environmental distribution pathways and/or unique point sources that are not
380 common to the other PFAS. Interestingly, the highest concentrations of TFMS coincided with the few
381 detections of HFPO-DA and HFIP, which are both associated with industrial sources. This is a first hint

382 towards industrial hot-spot sources of TFMS and may be a starting point for future studies to confirm
 383 or disprove this hypothesis.

384



385

386 *Figure 2: Correlation plot (Spearman correlation, produced using R Studio, version 3.6.3) of all detected PFAS,*
 387 *sorted by type and chain length. Numbers in brackets depict the number of detects. <LOQ and n.d. were*
 388 *included as LOQ/2 and LOD/2 for each substance, respectively. Note: PFCA >PFDA and PFSA >PFOS are marked*
 389 *with a star, indicating semiquantitative data.*

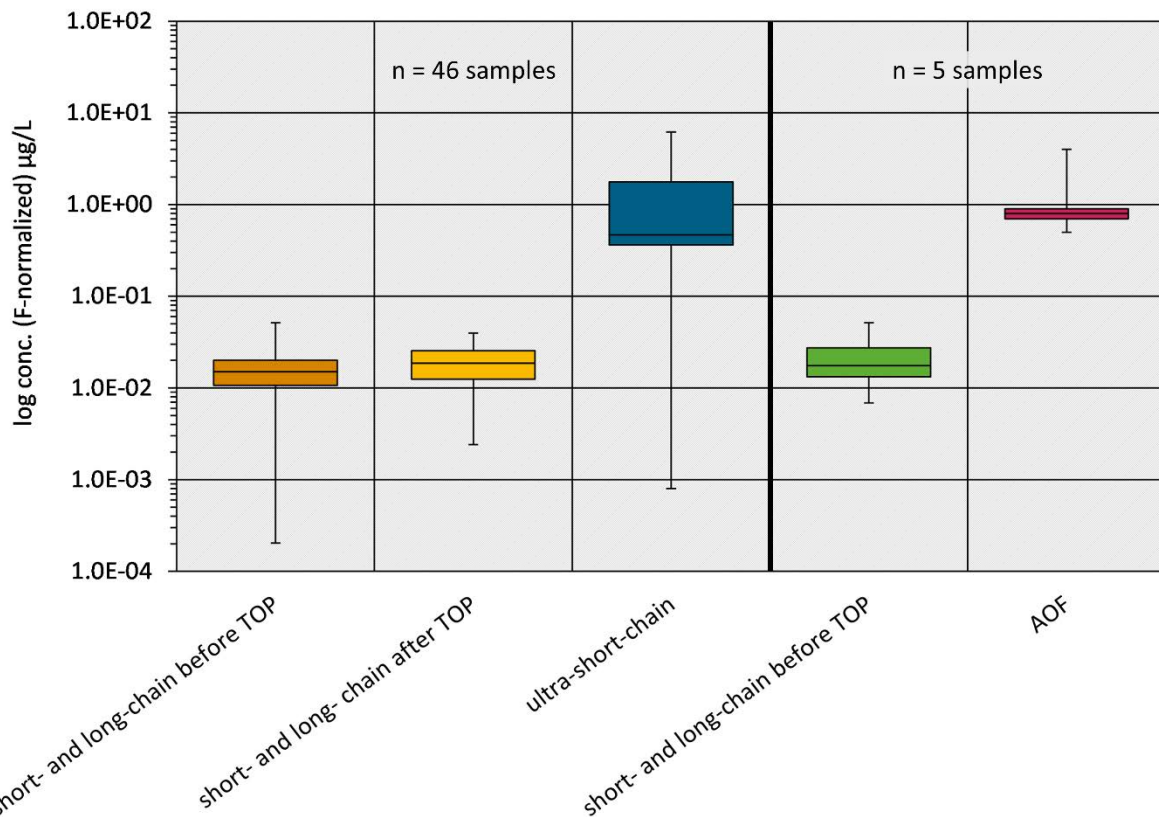
390 From the data presented herein, it is evident that short-chain PFAS and especially the ultra-short-chain
391 PFAS TFA, TFMS, and PFPrA are widespread and dominant in these samples from drinking water
392 sources. AC filtration, which is an effective tool to remove longer chain PFAS during drinking water
393 production is less effective for both short and ultra-short-chain PFAS [27]. This renders their removal
394 during drinking water production exceedingly difficult. Consequently, the most prevalent PFAS
395 occurring in the drinking water sources herein are also the ones that are the most difficult to remove
396 during drinking water production. This raises questions both about the costs of removing these
397 substances, and the potential health effects these chemicals might cause. It is expected that ultra-
398 short-chain PFAS have very short half-lives in the body preventing bioaccumulation. TFA, the most
399 well-studied ultra-short-chain PFAS, has a drinking water health guidance value of 60 µg/L and a target
400 value as a plant protection agent metabolite of 10 µg/L [70] in Germany. There are no target values
401 for PFPrA and TFMS. For ultra-short-chain PFAS, little to no data about long term (chronic) exposure
402 and mixture toxicology exists. PFAS will remain in the environment for decades once released due to
403 their persistent nature [71]; remediation is either unfeasible or exceedingly expensive if adverse
404 effects from these PFAS occur.

405 **Omission of ultra-short-chain PFAS by TOP Assay/AOF**

406 To support regulatory work that considers PFAS as a group, analytical methods are needed that are
407 able to measure 'PFAS total' parameters. While the TOP assay provides a measure of diverse
408 precursors that can be transformed into PFCA through chemical oxidation (even when some
409 precursors may also be transformed into PFSA through environmental or in vitro processes), the AOF
410 analysis provides a measure of the concentration of all fluorinated substances in the sample and thus
411 includes targeted and non-targeted PFAS as well as other organic chemicals containing fluorine. Ultra-
412 short-chain PFAS, however, remain a blind spot even for these 'PFAS total' parameters. For the TOP
413 assay, this limitation stems from the difficulty to analyze ultra-short-chain PFAS in the high ionic
414 strength reaction mixture, while the sample enrichment in AOF assessment (adsorption to AC) is the
415 discriminating part for very mobile PFAS [72]. Recent efforts to extend the scope of group methods

416 towards more mobile PFAS were successful [73] and managed to include TFA and PFPrA into the TOP
417 Assay at the cost of additional sample pre-treatment steps and a separate analysis of ultra-short chain
418 homologues with ion chromatography-MS. In most applications, however, PFBA remains the shortest
419 chain PFCA included. While the importance of this blind spot remains unknown, a comparison
420 between target analysis results of long-chain, short-chain and ultra-short chain PFAS (Figure 3) might
421 be an indicator of its relevance in samples not close to known sources (e.g. chemical industry, military
422 bases, airports, etc.). The median F-normalized sum of short- and long-chain PFAS (0.015 µg/L)
423 increases only moderately after the TOP assay (0.019 µg/L), which implies that the oxidizable
424 precursors are of minor importance in these samples not close to known sources, and have likely
425 already been converted into PFCA and PFSA by biotic or abiotic processes. The AOF was only analyzed
426 in five samples with a high concentration of short- and long- chain PFAS. Here the discrepancy to the
427 results of the target analysis is much more pronounced (median F-normalized sum of short- and long-
428 chain PFAS from target analysis: 0.015 µg/L; median AOF: 0.8 µg/L, note: semiquantitative data for
429 PFCA >PFDA and PFSA >PFOS) demonstrating that fluorinated chemicals that are neither short- and
430 long-chain PFCA or PFSA nor their precursors are prevalent in these samples.

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



440

441 *Figure 3: Boxplots of F-normalized sum of short- and long-chain PFAS before TOP assay (orange, n=46 samples),*
 442 *short- and long-chain PFAS after TOP assay (yellow, n=46 samples), ultra-short-chain PFAS (blue, n=46 samples)*
 443 *over all samples. Also shown is the boxplot of short- and long-chain PFAS before TOP assay for the samples*
 444 *analyzed with AOF (green, n=5 samples) and the AOF of the corresponding five samples (fuchsia, n=5 samples).*
 445 *The horizontal bar in the box depicts the median concentration. Note: only semiquantitative data is available*
 446 *for PFCA >PFDA and PFSA >PFOS.*

447 **Environmental implications**

448 There is a much better general understanding of the environmental occurrence of long-and short-
 449 chain PFAS than of ultra-short-chain PFAS. Knowledge about ultra-short-chain homologues and their
 450 sources is scarce and often limited to few well-studied examples like TFA and almost exclusively to the
 451 two most extensively studied PFAS classes PFCA and PFSA. Beyond these two classes, very mobile
 452 PFAS remain excluded from target sampling campaigns and techniques to measure 'PFAS total'. Ultra-

453 short-chain PFCA and PFSA homologues may only be the tip of the iceberg for the unexplored variety
454 of very mobile PFAS that escape most current analytical approaches for 'PFAS total'. The recent
455 revision to the definition of PFAS by the Organisation for Economic Co-operation and Development
456 (OECD) to substances with 'at least one fully fluorinated methyl or methylene carbon atom' [17] now
457 additionally considers substances with a CF₂ moiety as PFAS. Thus, with such a definition, the number
458 of ultra-short-chain PFAS is quite large [74]. Novel PFAS identified here like HFIP, NTF₂ and other
459 fluorinated ionic liquid anions may provide a first glance into this gap. While non-target approaches
460 could be used to identify the presence of other mobile PFAS the enrichment and chromatographic
461 methods used are often tailored towards less mobile chemicals [32]. Since very few remediation
462 options exist for ultra-short-chain PFAS, the approach of the EU Chemicals Strategy for Sustainability
463 to prevent the use and emissions of PFAS, seems to be the most effective way to manage PFAS and
464 especially the most mobile PFAS.

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472 **Supporting Information**

473 Supporting Information contains two parts, one Word file and one Excel file, including eight text
474 passages, eleven tables and one figure. Details on analytes, sample pretreatment, instrumental
475 analysis, validation parameters and concentrations are presented.

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