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Original Research Article

Screening for 26 per- and polyfluoroalkyl substances (PFAS) in German drinking waters with support of residents

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ABSTRACT

The occurrence of per- and polyfluoroalkyl substances (PFAS) in water cycles poses a challenge to drinking water quality and safety. In order to counteract the large knowledge gap regarding PFAS in German drinking water, 89 drinking water samples from all over Germany were collected with the help of residents and were analyzed for 26 PFAS by high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). The 20 PFAS recently regulated by sum concentration (PFAS_{Σ20}), as well as six other PFAS, were quantified by targeted analysis. In all drinking water samples, PFAS_{Σ20} was below the limit of 0.1 µg/L, but the sum concentrations ranged widely from below the limit of quantification up to 80.2 ng/L. The sum concentrations (PFAS_{Σ4}) of perfluorohexanesulfonate (PFHxS), perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and perfluorononanoate of 20 ng/L were exceeded in two samples. The most frequently detected individual substances were PFOS (in 52% of the samples), perfluorobutanesulfonate (52%), perfluorohexanoate (PFHxA) (44%), perfluoropentanoate (43%) and PFHxS (35%). The highest single concentrations were 23.5 ng/L for PFHxS, 15.3 ng/L for PFOS, and 10.1 ng/L for PFHxA. No regionally elevated concentrations were identified, but some highly urbanized areas showed elevated levels. Concentrations of substitution PFAS, including 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate and 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]-propanoate (anion of ADONA), were very low compared to regulated PFAS. The most frequently detected PFAS were examined for co-occurrences, but no definite correlations could be found.

1. Introduction

Per- and polyfluorinated substances (PFAS) have attracted increasing attention in recent years [1,2]. Despite their unique and valuable properties [3], PFAS were noticed as “forever-chemicals” [4] due to their pronounced persistency, which also causes a spread throughout the environment even to rather remote areas [5–7]. Once distributed in an environmental compartment, there is no way of recollecting PFAS. With very long half-lives, PFAS may impact interconnected ecosystems in the long term, which underlines the necessity of respective regulations by authorities.

Legislation, however, often struggles with the multitude of compounds [8], mostly due to the lack of sufficiently sensitive routine analytical methods. Therefore, a very limited number of PFAS is currently covered by particular regulatory documents. For example, the European environmental quality standard directive only refers to

perfluorooctanesulfonate (PFOS) [9] that has then been included in the directive on persistent organic pollutants [10]. Further, in a rolling revision process of the guidelines for drinking water quality, the World Health Organization has recently published a document for a public-review process that only lists PFOS and perfluorooctanoate (PFOA) as PFAS representatives [11].

As a compromise, it comes down to a selection of compounds, i.e., subgroups of the unmanageable PFAS, that are considered representatives, presuming the focus on relevant derivatives. For drinking water in particular, the regulation of PFAS appears to be overdue as drinking water might pose a direct exposure pathway [12–15].

In terms of European legislation, the drinking water directive [16] includes, for the first time, limit values for PFAS in drinking water. To date, no routine applicable analytical method comprises the entire PFAS family in a required sensitive manner. For drinking water surveillance, a sum parameter PFAS_{Σ20} of 20 selected PFAS (i.e., C₄–C₁₃ perfluorinated

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carboxylates and sulfonates) has to be determined by targeted analyses [17]. The sum of the concentrations of these 20 individual compounds must not exceed 100 ng/L. Compounds are only considered for summarization when their concentration exceeds the limit of quantification (LoQ). According to the drinking water directive [16], individual compounds have to be analyzed with LoQ below 30% of the limit value. In the case of PFAS Σ_{20} , this requires LoQ values of 1.5 ng/L or lower for each compound for sum value calculation.

Severe concerns arose from potential adverse health risks associated with PFAS [18,19], even at low concentrations [20] in environmental media that might result in elevated concentrations in biota (including humans) due to bioaccumulation [21–23]. Along food chains, top predators are prone to pronounced exposure [24,25]. Toxicological considerations suggest even lower threshold values for a further subset PFAS Σ_4 , consisting of the four individual substances [perfluorohexanesulfonate (PFHxS), PFOS, PFOA, and perfluorononanoate (PFNA)] that have been evaluated as a group [20]. Interestingly, this group includes some of the most frequently applied PFAS.

To date, only limited data about PFAS concentrations and their relative levels regarding the new multi-national regulatory limits exist. Domingo and Nadal [14] reviewed available data on PFAS in drinking water, but no study has addressed all 20 PFAS so far. Concentrations of PFAS in German drinking water at selected locations were reported by Gellrich et al. [26] and Llorca et al. [27] for the German federal state of Hesse and by Skutlarek et al. [28] for North Rhine-Westphalia and other locations in Germany. Borchers et al. [29] compiled large data sets of anonymized origin to estimate the percentages of exceedances of PFAS Σ_{20} and PFAS Σ_4 . Drinking water in Germany mainly stems from different resources such as groundwater, surface water, and bank filtrate, but the impact of the type of drinking water resource has not been addressed yet. Very little is known about substitute PFAS in drinking water.

In the present investigation, drinking water samples from 89 locations were taken by voluntary residents following a defined protocol and were sent to the laboratory for analyses to address knowledge gaps concerning PFAS occurrences. The involvement of residents was chosen as the only feasible way to obtain such a large set of samples since sampling by water surveillance professionals was impossible with the limited available resources. In total, 26 PFAS compounds were quantified to obtain an overview of the most relevant compounds in Germany, concentration ranges, sum concentrations and their levels relative to the new regulatory limits, potential regional differences, potential relation to the underlying resources, and potentially connected co-occurrences of individual PFAS.

2. Materials and methods

2.1. Sampling locations

Volunteering residents were gathered to sample 89 drinking waters at the tap in different locations, including the largest water supply areas (above 400,000 supplied residents) and all federal state capitals. Additionally, samples from rural water supplies were taken in most federal states depending on the availability of volunteers (from professional and private networks). Furthermore, different raw water resources were covered and distinguished between three categories: groundwater (48% or 54%), surface water (6% or 7%), and combinations of groundwater and/or surface water and/or managed aquifer recharge (bank filtration or artificial groundwater recharge) (34% or 38%). One drinking water supply system (1%) (Heligoland) uses seawater and brackish water with reverse osmosis treatment. In some supply areas where the use of different resources was assumed (all sample locations are listed in Table S1), more than one sample was taken. Incorrect assignment of the partly complex drinking water distribution systems (with several waterworks) to the respective categories based on publicly available information cannot be fully excluded.

2.2. Sampling procedure

Voluntary residents received a parcel (with return postage) containing dried 1-L high-density polyethylene (HDPE) flasks (NALGENE®, Thermo Fischer Scientific Inc., USA) that were pre-rinsed with methanol. Travelling to all locations to professionally collect samples was not affordable. The drinking water samples were collected once by the residents (in December 2021 or January 2022), mainly in private households (and partly in public buildings, cafes, or restaurants), following a well-described and illustrated protocol. The step-by-step instruction adopted from a published procedure [30] included the draining of tap water (cold) for 1 min before taking the sample, as well as a detailed description of sample handling. The volunteers were not sampling professionals, and slight deviations from the targeted procedure and background contaminations cannot be fully excluded.

The HDPE flasks were filled after the tap water was drained for 1 min and were then sent back to the laboratory for analyses. After arrival, all samples were filtered with membranes (0.45 μ m pore size, regenerated cellulose, CHROMAFIL®, Macherey–Nagel GmbH, Germany). Field blanks were obtained by filling HDPE flasks with ultra-pure water and were stored for one month (the longest travel time of samples) in identical sampling flasks. Since the target compounds are not volatile, contamination by diffusive mass transfer via the gas phase is not likely.

2.3. Solid phase extraction

Analyses were carried out according to a standardized method [31], including a solid phase extraction procedure taken from standard [32]. The 5% methanol and 50 μ L of a solution containing isotopically labelled standards (13 C for C₄ to C₁₂ carbonic acids and C₄, C₆, and C₈ sulfonic acids, MPFAC-24ES Wellington Laboratories, Canada) were added to 100 mL sample, and the flasks were sonicated for 5 min. A volume of 100 mL sample was then enriched with a pre-conditioned [2 mL of each i) 0.1% ammonia in methanol, ii) methanol, and iii) ultra-pure water] weak ion exchange resin (Phenomenex, Strata X-AW 33 μ m, 100 mg/3 mL). Subsequently, the column was washed with 2 mL of water, 2 mL of a washing solution (containing acetone, acetonitrile, and formic acid with shares of 50:50:1 by volume), and 2 mL of methanol. Afterwards, analytes were eluted with 2 mL of 0.1% ammonia in methanol. Extracts were brought to dryness by a gentle stream of nitrogen at 30 °C and were re-dissolved in 1.0 mL of a mixture of methanol and water (1:1).

2.4. Quantification and quality assurance

A volume of 10 μ L of the extract was injected for HPLC separation (Agilent Infinity 1260 with a Phenomenex Synergi Fusion RP80A column, 50 mm \times 2 mm \times 4 μ m, 350 μ L/min) connected to MS/MS detection (QTRAP 6500+, AB Sciex). Two eluents were used: eluent A (5 mM ammonium acetate in water) and eluent B [0.05 vol. % acetic acid in a mixture of methanol and acetonitrile (90:10 by volume)]. The gradient program consisted of i) constant 60% eluent A until 0.5 min, ii) linear decrease of eluent A between 0.5 and 15.0 min from 60% to 5%, iii) constant 5% eluent A between 15.0 and 20.0 min, iv) linear increase of eluent A from 5% to 60% between 20.0 and 20.5 min, and v) constant 60% eluent between 20.5 and 25.0 min. A solution containing a standard mixture (PFT-Mix20, Neochema, Germany) and additional analytes [11-chloroeicosfluoro-3-oxaundecane-1-sulfonate (11-Cl-PF30UnDS), 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]-propanoate (ADONA), 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (HPFO-DA), 1H,1H,2H,2H-perfluorooctanesulfonate (6:2-FTS), 1H,1H,2H,2H-perfluorodecanesulfonate (8:2-FTS), and perfluoro-3-methoxypropanoate (PFMPA)] was used for calibration in ranges between 0.02 ng/mL and 5.0 ng/mL. The LoQ ranging from 0.2 to 1.0 ng/L (individual LoQ are listed in Table S2) were determined and validated according to a standard procedure [33]. Analyte concentrations were corrected by the recovery rates for each individual compound determined on certified reference

materials (as continuous calibration verification: IRMM428, JRC, Belgium; as initial calibration verification: PFAC-24PAR, Wellington Laboratories, Canada). Recovery rates were remeasured and analyzed during each acquisition batch and are given in Table S3. Blank samples of ultra-pure water and recovery rates are redetermined after ten samples. Field blanks were treated the same as samples. External quality assurance of the applied analytical method was acquired by successful participation in a round-robin test for PFAS in drinking water (AQS BW, Germany, 2022, RV 7/22 TW S4).

3. Results and discussion

3.1. Concentration of regulated PFAS

The frequencies of PFAS detections above LoQ differ within a broad range, as shown in Fig. 1a. PFOS and perfluorobutanesulfonate (PFBS) were detected above LoQ most frequently in 46 samples, which corresponds to 51.7%. PFHxS was detected in 34.8% of the samples. The most frequently detected perfluorocarbonic acids were perfluorohexanoate (PFHxA), perfluoropentanoate (PFPeA), and perfluorododecanoate (PFDoDA) in 43.8%, 42.7% and 22.5%, respectively. The detection frequencies show that PFAS of a wide range of chain lengths were found in the drinking water samples. PFDoDA, one of the largest analyzed PFAS, was quantified above LoQ more often than other PFAS with shorter chain lengths, e.g., PFOA and perfluorobutanoate (PFBA). No relation between chain length and detection frequency could be identified. These findings suggest that a mix of PFAS of different origins and times of emission can be found in the drinking water. For example, PFOS production and emissions might have occurred in the past, but their passage to the aquifers is reported to be slow according to their hydrophobicity [34]. PFBS, PFHxA, and PFPeA are likely to be recent PFAS emissions or end-stage metabolites of currently used PFAS [35,36].

The majority of PFAS concentrations were below 9 ng/L, as shown in Fig. 1b. The three highest individual concentrations (not included in Fig. 1b for better resolution) were 23.5 ng/L PFHxS (Cologne 2), 15.3 ng/L PFOS (Berlin 1), and 10.1 ng/L PFHxS (Berlin 1). PFNA and perfluorotridecanesulfonate (PFTrDS) were not detected above LoQ. High numbers of detections within one sample coincide with higher PFAS single substance concentrations, which was also observed by Guelfo and

Adamson [37]. All individual PFAS concentrations are provided in Table S4.

Although concentrations of individual PFAS showed significant variation, most median values were close to the LoQ. Upper quartile values were highest for PFOS (2.0 ng/L), while median values of PFOS and PFBS were at 0.3 ng/L (Fig. 1b). For the analyses of concentration distributions, results below LoQ were set to the respective LoQ.

Individual substance concentrations of PFOA found in this study in Mainz and Frankfurt/Main are consistent with other studies at approximately 2 ng/L [27,38]. In Hesse and Rhineland-Palatinate, PFOS concentrations at 3 ng/L were similar to the findings of Gellrich et al. [26]. The findings of PFPeA, perfluoroheptanoate (PFHpA), PFOA, PFBS, and PFOS in Münster, Koblenz, Dresden, Bad Elster, Munich, and Freiburg were consistent with the study of Skutlarek et al. [28]. Higher concentrations of PFOA, PFOS, and PFHxA were found by others in North Rhine-Westphalian cities, with most significant deviations in Dortmund, with concentrations at 152 ng/L (PFOA), 11 ng/L (PFOS), and 26 ng/L (PFHxA) [28], compared to 4.1 ng/L, 2.3 ng/L, and 1.7 ng/L, respectively, in the present study. Maximum PFOA, PFBS, and PFHxA findings in Hesse and Rhineland-Palatinate of 6.1 ng/L, 5.8 ng/L, and 6.4 ng/L [26], respectively, were roughly twice as high as the results of this study (2.6 ng/L PFOA, 2.2 ng/L PFBS, 2.4 ng/L PFHxA). These results might indicate a reduction in PFAS emissions in the meanwhile.

Lower concentrations were found in Bonn, where no PFAS were found [28], differing from the findings of this study (3.0 ng/L PFOA, 6.9 ng/L PFOS, 5.6 ng/L PFBS). The maximum concentration of PFOS detected in Berlin (15.3 ng/L PFOS in Berlin 1) exceeds the PFOS concentration measured by Skutlarek et al. [28] in Berlin by more than a double (6.0 ng/L). PFOS concentrations were below the LoQ in Frankfurt/Main and in Wiesbaden [27], whereas in the present study, corresponding PFOS concentrations were at 2.3 ng/L and 3.2 ng/L, respectively. The PFHxA concentration of 0.71 ng/L in Frankfurt/Main found by Llorca et al. [27] was below the findings of this study (3.2 ng/L).

3.2. Sum of 20 PFAS

All sum concentrations of PFAS_{Σ20}, as the first multi-national (European) regulatory limit, were below the limit value of 100 ng/L (Fig. 2). However, PFAS_{Σ20} varied widely over a range from zero (all individual concentrations below the LoQ) to 56.7 ng/L (Berlin 1), 66.7 ng/L (Cologne 1), and 80.2 ng/L (Cologne 2). Most PFAS_{Σ20} concentrations above 20 ng/L were found in larger cities. However, not all drinking water samples taken from densely populated areas contained high PFAS_{Σ20} values, as seen in the samples from Hamburg (1.0 ng/L PFAS_{Σ20}) or Munich (6.7 ng/L PFAS_{Σ20}). In 22% of the samples, all PFAS concentrations were below the LoQ, such as in the samples from Schwerin, Gera, Jena, and Ludwigshafen.

PFAS_{Σ20} in samples from the same city partly diverged both in the composition and contribution of individual PFAS. For example, the sample from Berlin 1 and Berlin 3 ranged from 56.7 ng/L to 5.4 ng/L with one order of magnitude between them. A PFAS_{Σ20} sum concentration of 32.3 ng/L was detected in Frankfurt/Main 1, whereas no concentration above the LoQ was detected in the samples from Frankfurt/Main 2. Thus, PFAS concentrations in drinking water can significantly vary within a limited radius.

The determination of PFAS with chain lengths of C₁₁ to C₁₃ (and higher) bears particular challenges due to the pronounced adsorptive properties of the analytes. Concentrations reported in this study were obtained following strict quality-control protocols. During all analyses, independent reference materials with certified concentrations were analyzed in parallel with good recovery. However, possible elevated uncertainties of measurement for C₁₁ to C₁₃ PFAS are not negligible and are not neglected for the calculation of PFAS_{Σ20} as they contribute significantly in some cases (e.g., Cologne 1 and 2).

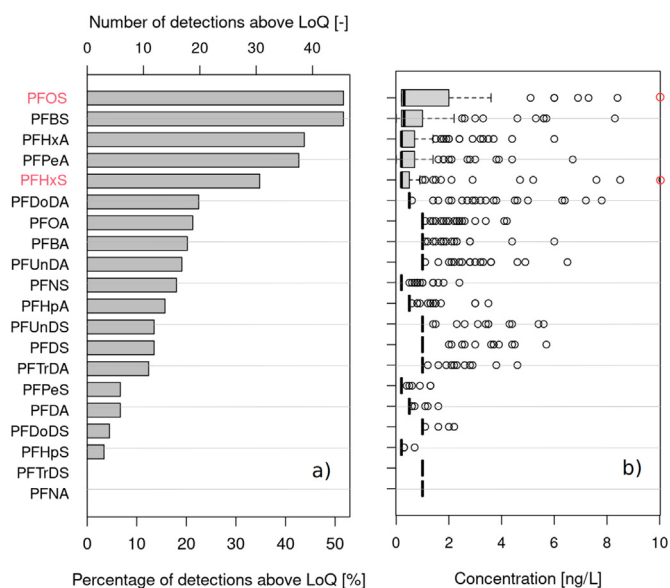


Fig. 1. Detection frequencies (a) and concentration distributions of individual per- and polyfluoroalkyl substances (PFAS) (b). Red labels and dots in (b) indicate values above the shown range [15.3 ng/L perfluorooctanesulfonate (PFOS) and 23.5 and 10.1 ng/L perfluorohexanesulfonate (PFHxS)].

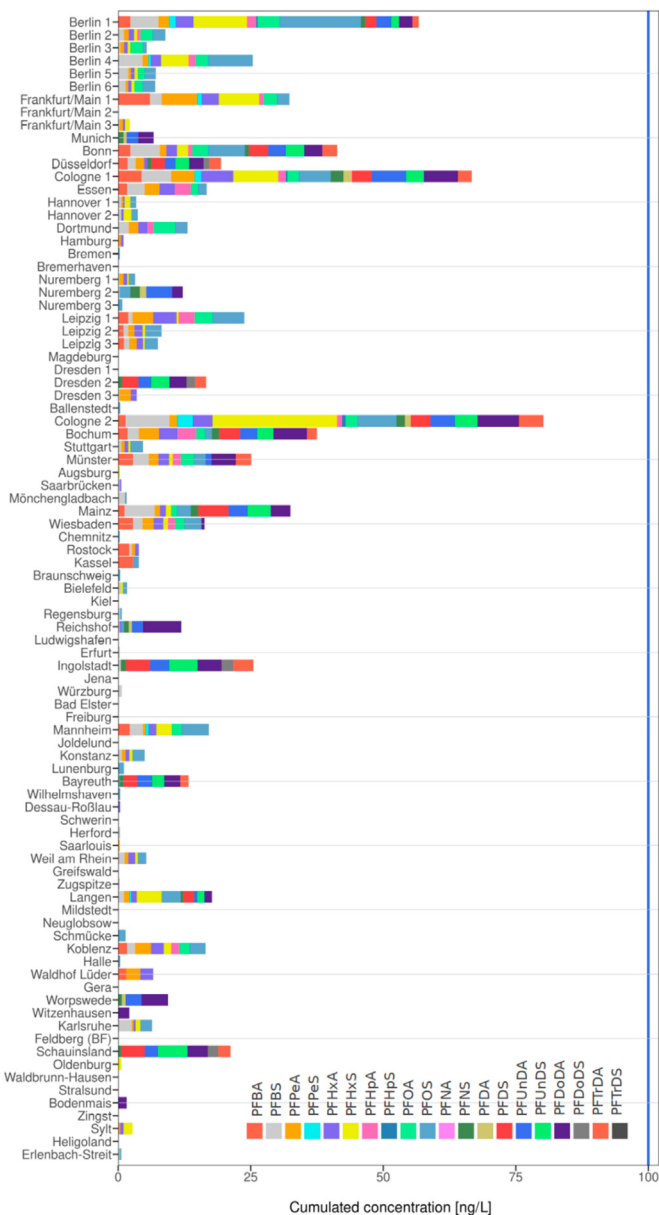


Fig. 2. Sum concentration of PFAS_{Σ20} regulated in the European drinking water directive calculated with concentrations above the respective limit of quantification (LoQ). The regulator limit of 100 ng/L is indicated by the blue vertical line, and samples are listed according to the descending size of the respective water supply area.

3.3. Sum of four PFAS

Two samples exceeded the novel national limit value that German water suppliers have to comply with from 2028, including the sum concentration PFAS_{Σ4} of 20 ng/L (Fig. 3) with 29.6 ng/L (Berlin 1) and 33.1 ng/L (Cologne 2). PFAS_{Σ4} concentrations above 10 ng/L were found in the samples from Cologne 1 (16.7 ng/L), Berlin 4 (16.0 ng/L), Frankfurt/Main 1 (12.5 ng/L), and Bonn (12.0 ng/L).

High PFAS_{Σ4} values are mostly consistent with high PFAS_{Σ20} values, reflected by the order of samples according to descending PFAS_{Σ4} and descending PFAS_{Σ20} values (Cologne 2, Berlin 1, Cologne 1). PFOS, PFHxS, and PFOA account for relevant contributions to PFAS_{Σ20} in accordance with the high numbers of detections above the LoQ. The parallel orders also indicate that PFOS, PFHxS, and PFOA mostly occur with other PFAS. However, e.g., Mannheim (9.9 ng/L PFAS_{Σ4}) and

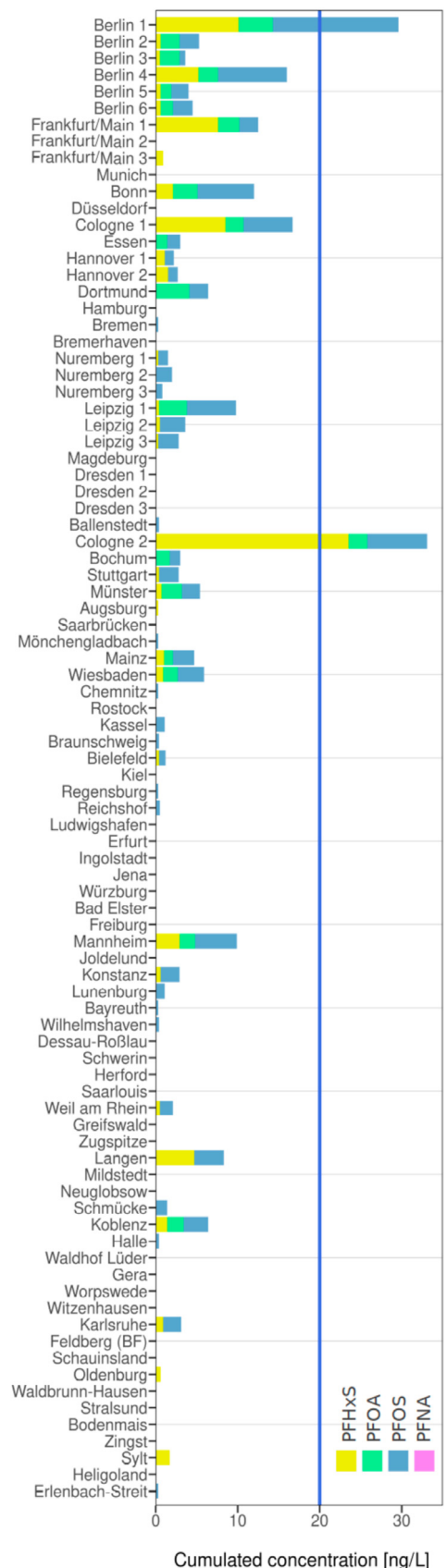


Fig. 3. Cumulated concentrations of perfluorohexanesulfonate (PFHxS), perfluorooctanoate (PFOA), PFOS, and perfluorononanoate (PFNA) with concentration above the LoQ. The potential regulatory value for Germany of 20 ng/L is indicated by a blue vertical line.

Leipzig 1 (9.8 ng/L PFAS $_{\Sigma 4}$) show comparably high PFAS $_{\Sigma 4}$ values and unnoticeable PFAS $_{\Sigma 20}$ values. Overall, the prospective limit for PFAS $_{\Sigma 4}$ is more critical since a larger number of drinking water samples is close to it.

3.4. Regional distribution of PFAS concentrations

The geographical positions of all sample locations are marked and coloured, according to their PFAS $_{\Sigma 20}$ and PFAS $_{\Sigma 4}$ values, on the map of Germany (Fig. 4). In supply areas with multiple sample locations, sum concentrations are represented as overlapping dots (e.g., Berlin). Samples without any PFAS above the LoQ (indicated by blue dots) are almost homogeneously distributed over Germany. However, samples with significant PFAS concentrations are not equally distributed among the federal states.

Elevated PFAS $_{\Sigma 20}$ and PFAS $_{\Sigma 4}$ values occur in the Rhine catchment in the federal states North Rhine-Westphalia, Rhineland-Palatinate, and Hesse, as well as in the federal state of Berlin. Higher PFAS sum concentrations tend to correspond with higher population densities (e.g., 2,675 inhabitants/km² in Cologne, 4,112 inhabitants/km² in Berlin, 135 inhabitants/km² in Schwerin, 62 inhabitants/km² in Zingst) [39]. Prominent PFAS contaminations reported for, e.g., Rastatt (Baden-Württemberg) [40,41] or Altötting in Bavaria [42] represent local hot-spots and are not connected with regional drinking water contaminations. Since the PFAS data collected in this study are based on a single sampling campaign, temporal changes, and eventual peak concentrations could not be covered.

3.5. Non-regulated PFAS

The other PFAS (11-Ch-PF2OU_nDS, ADONA, 6:2 FTS, and 8:2 FTS) often discussed as substitution PFAS were only detected at low concentrations and at frequencies far lower than those of regulated PFAS (Fig. S1 and Table S5 with the LoQ of the individual substances).

11-Cl-PF3OU_nDS was detected above the LoQ in 11 samples (14%), ranging from 1.6 ng/L (Langen) to 3.9 ng/L (Schauinsland, Black Forest). ADONA (seven samples above the LoQ) occurred in concentrations around 5 ng/L in the samples from Nuremberg 1, Bochum, and Dortmund and at very low concentrations in Münster, Nuremberg 2, Kassel, and Mönchengladbach.

The substance 6:2 FTS was found twice in samples from Joldelund (0.8 ng/L) and Stuttgart (0.6 ng/L), whereas 8:2 FTS was also found twice in Cologne 1 (1.2 ng/L) and Nuremberg 2 (1.1 ng/L) at low concentrations close to the LoQ in each case. PFMPA and HFPO-DA were not found in any of the drinking water samples. Other studies reported HFPO-DA concentrations ranging from 0.25 ng/L to 11 ng/L in drinking water close to fluorocemical plants in the Netherlands [43] and average concentrations of 631 ng/L in North Carolina (USA) [44].

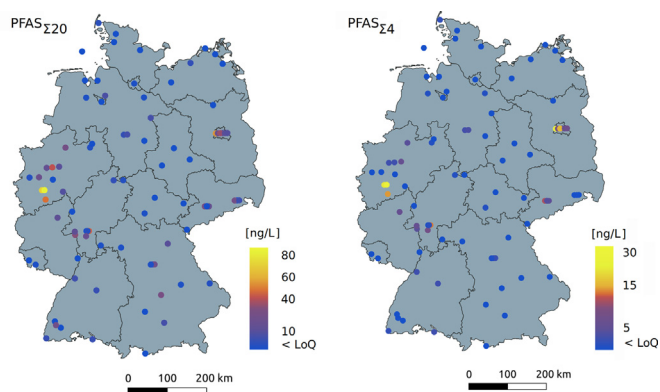


Fig. 4. Regional distributions of PFAS $_{\Sigma 20}$ and PFAS $_{\Sigma 4}$ on the map of Germany with sum concentrations presented in a colour gradient from blue (below the LoQ) to yellow.

3.6. Influence of the drinking water resource

PFAS concentrations vary within all raw water (resource) categories, and the highest average PFAS $_{\Sigma 20}$ concentrations were found in drinking water that stems from two or more different resources. This category consists mainly of combinations of groundwater and bank filtration or recharged groundwater, partly from different water works contributing to one drinking water distribution system. The combination of two waters might increase the risk of PFAS occurrences just because of the number of resources but might also dilute a partial contribution of contaminated drinking water. The fewest findings and lowest PFAS $_{\Sigma 20}$ average concentrations occur in drinking water from surface water origin, including reservoirs, rivers, and lakes (Fig. 5). This agrees with the study of Guelfo and Adamson [37], who analyzed numerous drinking water samples from different water source types in the USA. They found the highest PFAS sum concentrations (PFBS, PFHxS, PFOS, PFHpA, PFOA, and PFNA) in drinking water samples from groundwater. The average PFAS $_{\Sigma 20}$ concentration in groundwater in the present study was comparably low (3.6 ng/L), close to the category surface water (2.4 ng/L). Considering not sum concentrations but single substances, PFPeA and PFHxA average concentrations are highest in samples from the category groundwater (both 0.2 ng/L).

The average concentrations of PFOS and PFBS were the highest in the category combinations (2.9 and 2.2 ng/L), followed by surface water (0.9 and 0.3 ng/L). Also, the highest individual concentrations of PFOS and PFBS (15.3 and 8.3 ng/L) were found in combinations. The PFHxS mean concentration was highest in combinations (2.4 ng/L), followed by groundwater (0.3 ng/L).

Generally, it must be considered that not only raw water resources might influence PFAS concentrations but also treatment processes for drinking water production. Drinking water treatment processes differ in all categories, and thus, influences of the resources and the treatments cannot be differentiated. However, the majority of the samples originate from water supply areas with conventional treatment steps (e.g., aeration, sand filtration), which are not effective for PFAS removal [15].

PFAS concentrations in drinking water might, to some extent, reflect PFAS concentrations in the respective raw waters. However, to fully understand the individual influences of the respective resources on PFAS concentrations in drinking water, the treatment processes have to be investigated and analyzed in more detail with samples directly obtained after the waterworks.

3.7. Co-occurrences of PFAS

Concentrations of the most frequently found PFAS were mutually compared to search for potential indicator substances [45] within the group of 20 PFAS. Impurities of compounds with non-targeted chain length in applied pure substances and combinations of PFAS in commercial products might cause connected occurrences of the main compound and potential impurities, but the results show little evidence of co-occurrences among the investigated PFAS. Partial relations were found for PFBS and PFOS, for PFHxS and PFBS, for PFHxA and PFBS, and for PFHxA and PFOS, with Pearson correlation coefficients (R) of 0.78, 0.75, 0.72, and 0.69, respectively, and p -values below 0.05 (Fig. 6).

The other PFAS showed rather diverging or independent occurrences in the drinking water samples. While PFOS and PFHxS show only a weak correlation ($R = 0.66$) in this study, a significant correlation between PFOS and PFHxS, as well as between PFOS and PFOA, PFOS and PFHpA, PFOA and PFHxS, PFOA and PFHpA, and PFBS and PFHpA were reported for another region [37]. Co-occurrences of PFHxA, PFNA, and PFOA were reported in drinking water from groundwater wells close to fluoropolymer manufacturers [46].

Very little is known about co-occurrences of PFAS in drinking water, and more research needs to be done in order to better understand PFAS occurrences. Moreover, the knowledge about PFAS co-occurrence could

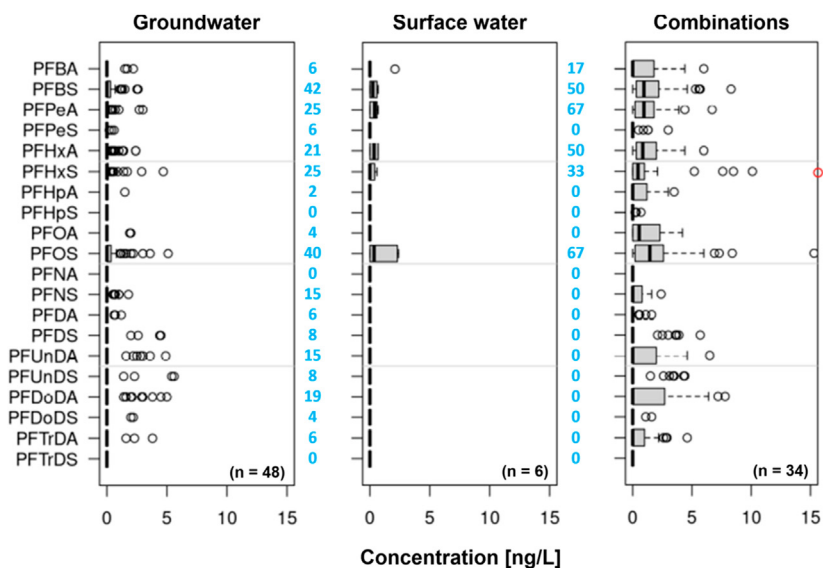


Fig. 5. Concentrations of regulated PFAS in drinking water from groundwater, surface water, and combinations of two or more sources (compare Table S1), with numbers in blue indicating the respective percentages of detections above the LoQ within each category. Due to the complexities of water supply systems fed by several water works, it cannot be excluded that assignments to the categories based on publicly available information might be incorrect. The red data point indicates a concentration of 23.5 ng/L outside the given range.

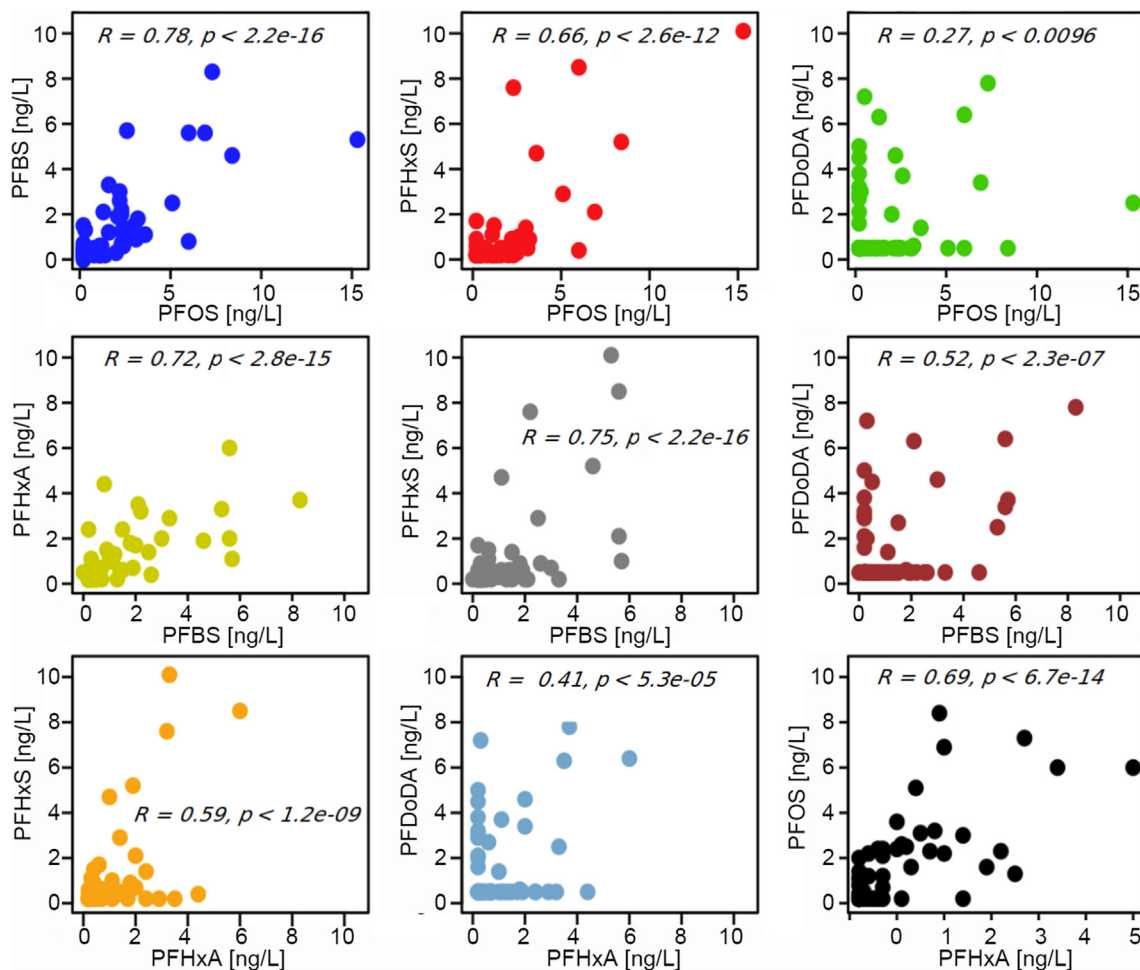


Fig. 6. Co-occurrences of the five most frequently detected PFAS with mutual relations between pairs of individual compounds, including Pearson correlation coefficients (R) and corresponding p-values.

help to find indicator PFAS, which could be beneficial in identifying contaminated sites.

4. Conclusions

1) A large set of valuable drinking water samples can be obtained with the support of voluntary residents, even if there is no official monitoring campaign with huge financial resources.

2) Regulated PFAS were below the sum threshold of 0.1 µg/L in 89 drinking water samples from all over Germany.

3) PFOS, PFBS, PFHxA, PFPeA, and PFHxS were the most frequently found individual compounds (in decreasing order). The highest observed concentrations were 23.5 ng/L (PFHxS), 15.3 ng/L (PFOS), and 10.1 ng/L (PFHxA). High numbers of PFAS detections coincide with higher PFAS concentrations.

4) The sum concentration of PFOS, PFOA, PFHxS, and PFNA (PFAS_{Σ4}) exceeded the new German limit value of 20 ng/L in two samples.

5) Substitution PFAS were found in a few samples with very low concentrations of around 5 ng/L (Adona) and below (11-Cl-PF3OUndS) and close to LoQ for 6:2 FTS and 8:2 FTS. HFPO-DA, and PFMPA were not detected above the LoQ at all.

6) The average PFAS_{Σ20} concentration was the lowest in samples from surface water origin and the highest in drinking water from combined resources. Average single substance concentrations of PFPeA and PFHxA were the highest in samples from groundwater, whereas those of PFOS, PFBS, and PFHxA were the highest in samples from combinations. The highest number of PFAS was detected in samples from combined resources, followed by samples from groundwater.

7) Slight tendencies of co-occurrences were found for PFBS and PFOS, for PFHxS and PFBS, for PFHxA and PFBS, and for PFHxA and PFOS with Pearson correlation coefficients (R) of 0.78, 0.75, 0.72, and 0.69, respectively, and *p*-values below 0.05, but no useful indicator could be identified.

Author contributions

V.I., A.K. and A.S.R.: conceptualization, investigation and methodology, data curation and formal analysis, validation, writing – original draft, review, and editing. A.S.R.: funding acquisition, project administration, and supervision; V.I. and A.S.R.: visualization.

Declaration of competing interests

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Aki Sebastian Ruhl reports financial support was provided by German Federal Ministry of Health.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eehl.2023.08.004>.

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