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PFAS screening in municipal wastewater effluents and mixed liquor – using TOP assay as a sum parameter

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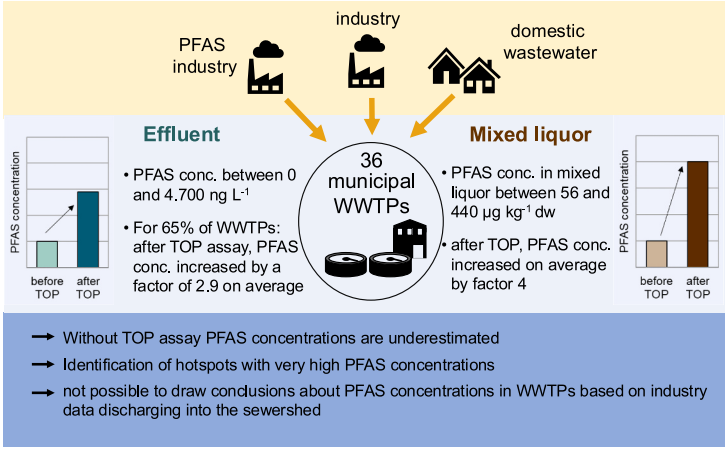
HIGHLIGHTS

- TOP assay as a sum parameter for PFAS concentration in wastewater effluent and sewage sludge samples.
- Impact of the industries on PFAS concentration in municipal WWTPs was investigated.
- PFAS concentrations in effluent and mixed liquor samples are underestimated without TOP assay.
- Identification of hotspots with very high PFAS concentrations in wastewater treatment plants.

GRAPHICAL ABSTRACT



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ABSTRACT

Wastewater treatment plants (WWTPs) are a point source for the release of per- and polyfluorinated alkyl substances (PFAS) into the environment. In our study we investigated wastewater effluent and mixed liquor samples for PFAS in order to obtain information on the current PFAS contamination in municipal WWTPs in Bavaria, Germany. In addition to PFAS target analysis, the total oxidizable precursor (TOP) assay was used as a PFAS sum parameter to obtain information on the precursor concentration in the samples. The sewersheds of the investigated wastewater treatment plants were characterized according to the industrial sectors that discharge into the public sewer system using the Statistical Classification of Economic Activities in the European Community (NACE) code. Known PFAS were detected in all effluent samples, except one, and in concentrations up to 4.700 ng L^{-1}. The concentrations in effluent samples varied widely between the different sampling dates at the individual WWTPs and also between the different WWTPs. The PFAS concentration in the effluent of 65 % of the WWTPs investigated increased significantly by a factor of 2.9 on average after the TOP assay. In the mixed liquor

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samples, the PFAS concentration ranged between 56 and 440 μg kg^{-1} dw. The concentration varied less than in the effluent samples. After the TOP assay the PFAS concentration in the mixed liquor samples increased on average by a factor of 4. The NACE codes alone cannot be used to determine whether low or high PFAS concentrations are to be expected in a municipal WWTP. However, they can provide an indication of PFAS dischargers and help to prioritize further investigations. Without the TOP assay, the PFAS concentration in the effluent and the mixed liquor samples is clearly underestimated. Our investigations identified hotspots with very high PFAS concentrations in the WWTP effluents. Measures must be taken at the sources to prevent the further release of PFAS into the environment via municipal WWTPs.

1. Introduction

PFAS are anthropogenic chemicals containing at least one perfluorinated methyl (-CF_3) or perfluorinated methylene group (–CF_2–) (Wang et al., 2021). Due to the C–F bond they are thermally, biologically and chemically very stable. PFAS are used in numerous industrial applications and consumer products like firefighting foams, electronics, plastics, metal plating fluids, cleaning agents and surface coating for paper, leather and textiles (Glüge et al., 2020; Lindstrom et al., 2011). They are detected in all environmental matrices because of their widespread use, stability and mobility. PFAS can enter municipal wastewater during production, application and leaching from PFAS-containing products (Lenka et al., 2021). The majority of PFAS are not or only partially degraded in conventional WWTPs and either adsorb to the sewage sludge or remain in the water phase and enter the surface waters via the effluent (Bossi et al., 2008; Boulanger et al., 2005; Gobelius et al., 2023; Lenka et al., 2021; Schultz et al., 2006; Sinclair and Kannan, 2006). PFAS-contaminated sewage sludge used for soil amendment leads to high PFAS levels in soils (Chu and Letcher, 2017; Strynar et al., 2012; Washington et al., 2010). Consequently, WWTPs are an important source for the release of PFAS into the environment (Chen et al., 2022; Cookson and Detwiler, 2022; Müller et al., 2023).

The number of individual PFAS compounds developed by industry or produced as by-products and degradation products now exceeds 12,000 substances (CompTox Chemicals Dashboards, 2023). This multitude of compounds cannot be detected using standard target analysis, which usually comprises 20 to 50 individual PFAS compounds. Therefore, it can be assumed that the actual PFAS concentrations in the environment is underestimated. For this reason, sum or group parameters, like the total oxidizable precursor (TOP) assay, extractable organic fluorine (EOF), or adsorbable organic fluorine (AOF) are increasingly being used in order to detect a larger number of PFAS in environmental samples (Abercron et al., 2019; Aro et al., 2021; Joerss et al., 2020; Nxumalo et al., 2023; Willach et al., 2016). Among these sum parameters, the TOP assay has the advantage that PFAS concentrations can be detected even at very low concentrations in the ng L^{-1} range. The polyfluorinated precursor compounds are degraded by hydroxyl radicals to the analytically measurable perfluoro carboxylic acids (PFCA) and perfluorinated ether compounds (Houtz and Sedlak, 2012; Zhang et al., 2019). However, the so-called non-precursors like HDPO-DA are not degraded during the TOP assay (Zhang et al., 2019). The proportion of unknown PFAS precursors can be estimated by comparing the molar PFAS concentration before the TOP assay with the molar PFAS concentration after the TOP assay.

Up to now, only a few studies have used the TOP assay to investigate PFAS contaminations in the effluent and sludge samples of municipal WWTPs (Houtz et al., 2016; Müller et al., 2023; Schaefer et al., 2023). In these studies, only a small number of 2–9 WWTPs were investigated. In our study a total of 36 municipal WWTPs, which cover 35 % of the treatment capacity in the state of Bavaria, were examined in the period of 2017–2022 to obtain information on current PFAS pollution in municipal WWTPs. Effluent samples and mixed liquor samples were both analyzed by PFAS target analysis and TOP assay.

In addition, the sewersheds of the investigated WWTPs were characterized according to industries discharging to the public sewer. For this assessment, industry sectors likely contributing PFAS contamination in wastewater published by Salvatore et al. (2022) were used. The aim was to investigate whether the information on the sectors is a useful tool for the identification of municipal WWTPs where high PFAS concentrations in the wastewater effluents and sewage sludge ca be expected.

2. Material and methods

2.1. Sampling area, sample collection and categorization of the sewershed

In total, 36 municipal WWTPs in the state of Bavaria (Germany) were selected for the investigation of the wastewater and mixed liquor samples. The criteria for selecting the targeted facilities were high PFAS loads in sewage sludge reported in a previous study (Ulrich et al., 2016) and representing facilities with large treatment capacities. The targeted WWTPs have a treatment capacity between 3100 and 1,950,000 population equivalents (PE), whereby mainly large plants with PE > 10,000 were examined (see Table S1 in the SI). The investigated WWTPs are distributed throughout Bavaria and cover 35 % of the treatment capacity in the state of Bavaria (see Fig. S1 and Table S2). The selected WWTPs are receiving either only domestic wastewater or a blend of both domestic and industrial wastewater. The latter in some cases from many different industry sectors.

The effluent and the mixed liquor from activated sludge basins were sampled at 6 WWTPs, only effluent was sampled at 25 WWTPs and only mixed liquor at 5 WWTPs (see Table S1). The effluent samples were taken as 2 h composite samples or qualified random samples during weekdays as part of the official wastewater monitoring program. They were collected in polypropylene (PP) or Polyethylene (PE) bottles, shipped to the laboratory within 24 h and stored at −18 °C pending analysis. The effluents of the WTTPs were sampled with varying frequency (1–4 times, with at least a quarterly interval) between March 2021 and November 2022. Detailed information on the sampling method and the standard parameters measured in the effluent samples are given in S1.1 and Table S3.

The mixed liquor samples were obtained from the sewage sludge archive of the Bavarian Environment Agency. The samples were taken for radioactivity monitoring in Bavaria. Thereby, the mixed liquor samples are taken in PP-bottles, shipped to the laboratory and dried at 105 °C, before they are stored at room temperature in the archive. The drying of the samples at 105 °C does not comply with the specifications of the German national standard method DIN 38414-14:2011-08 for the investigation of PFAS in sludge samples. Here, freeze-drying or drying at 40 °C is preferred. Nevertheless, these samples were used for the PFAS screening campaign, as degradation at 105 °C is not to be expected due to the high thermal stability of PFAS. However, the higher drying temperature can result in a higher volatilization rate of certain PFAS compounds. McNamara et al. (2025) demonstrated that the drying at 105 °C decreased the PFAS concentration on average by 16 % compared to drying at 30 °C, while the PFAS composition remained the same. Therefore, the PFAS concentrations determined are representing a conservative estimate. The actual PFAS levels in the mixed liquor samples could be even higher.

The North American Industry Classification System (NAICS) codes, which are considered likely sources of PFAS contamination according to

Salvatore et al. (2022), were used to characterize the sewershed of the investigated WWTPs. Therefore, the NAICS were translated into the Statistical Classification of Economic Activities in the European Community (NACE) codes and complemented by additional NACE codes of industries known to use PFAS in their industrial processes (see Table S4. The information on the NACE codes was retrieved from the Bavarian Wastewater Data Network (DABay; not publicly accessible). The WWTPs sampled were divided into three groups: 1. WWTPs not impacted by industrial wastewater (no indirect discharger), 2. WWTPs receiving industrial wastewater from sectors not considered to use PFAS (no PFAS NACE) and, 3. WWTPs receiving wastewater from industry considered to use PFAS (PFAS NACE).

2.2. PFAS analysis

The PFAS analysis was carried out by three different laboratories. All of these laboratories are accredited according to DIN EN ISO/IEC 17025:2018-03. In addition, the laboratories are accredited for the analytical methods used for the determination of PFAS in wastewater (according to the German standard method DIN 38407-42:2011-03 and sludge samples (according to the German standard method DIN 38414-14:2011-08). Moreover, the laboratories have to participate successfully in inter-laboratory tests for DIN 38407-42:2011-03 and DIN 38414-14:2011-08 within two years. This ensures that different laboratories deliver comparable analytical results. The laboratories are permitted to use different measurement methods. Laboratory A and B analyzed the wastewater samples. The mixed liquor samples were analyzed by laboratory C.

2.2.1. Wastewater

Wastewater samples were analyzed for 40 quantifiable PFAS compounds listed in Table S7according to DIN 38407-42:2011-03 using solid phase extraction (SPE) followed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). The 40 PFAS include perfluoroalkyl carboxylic acids (PFCA), perfluoroalkyl sulfonic acids (PFSA), perfluoroalkane sulfonyl fluoride based substances (PASF--based), H-substituted PFCA (H-PFCA), a H-substituted unsaturated carboxylic acid (n:2 FTUCA), fluorotelomer sulfonic acids (n:2 FTS), per- and polyfluorinated ether compounds (PFECA and H-PFECA), a Cl-substituted perfluoroalkyl ether sulfonic acid (Cl-PFESA) and the fluorotelomer-based substances, N,N-Dimethyl-3-((perfluorohexyl) ethylsulfonyl)amino-propanamine N-oxide (DPOSA) and 6:2 Fluorotelomer sulfonamide betaine (6:2 FTAB). The limit of quantitation was 1 ng L^{-1} for all PFAS. Further details on chemicals and analysis are given in Sections S1.2.

A slightly modified TOP assay developed by Houtz and Sedlak (2012) was used for the oxidation of the precursor compounds. Details of the TOP assay and the preliminary tests with spiked ultrapure water and synthetic wastewater are given in S1.2.2.2.

2.2.2. Mixed liquor samples

The mixed liquor samples were analyzed according to the German standard method DIN 38414-14:2011-08. In total, 52 quantifiable PFAS compounds listed in Table S10 were determined in the samples. In addition to the PFAS classes analyzed in the wastewater samples, fluorotelomer phosphate diesters (n:2 diPAPs) were analyzed. Details on the target analysis are given in Section S1.2.3.1.

The TOP assay of the mixed liquor samples was performed according to the draft of the German national standard method DIN 3608:2024-08. Details on the procedure and the quality assurance are given in S1.2.3.2.

2.3. Assessment of the detected PFAS concentrations

So far, there are no discharge values for PFAS concentrations in wastewater in Germany. Therefore, the maximum contaminant values of the Drinking Water Ordinance (TrinkwV, 2023) of 100 ng L^{-1} (for the sum of 20 PFAS) and 20 ng L^{-1} (for the sum of PFHxS, PFOA, PFOS and PFNA) were used to evaluate the PFAS concentrations in the effluent samples (see Table S11).

In addition, the detected PFAS concentrations in the effluent samples were compared with the proposal for an environmental quality standard for PFAS for surface waters (European Commission, 2022). The proposed EQS is 4.4 ng L^{-1} for the sum of 24 PFAS. Further details are given in chapter S1.3.

For the assessment of mixed liquor, there is currently only a limit value of 100 µg kg^{-1} dw for the sum of PFOA and PFOS (Fertiliser Ordinance, 2019). This limit value must be complied with if sewage sludge is to be used for agricultural or landscaping purposes. If the PFOS and PFOA concentration in the sludge exceeds 100 µg kg^{-1}, the sludge must be incinerated.

3. Results and discussion

3.1. PFAS concentrations and occurrence patterns in wastewater effluents

The total PFAS concentration in the secondary effluent of the investigated WWTPs varied between < LOQ and 4700 ng L^{-1}, with an average of 287 ng L^{-1} (see Fig. 1 and Table S12). For the majority of the WWTPs (84 %), the PFAS contamination varied in a range between < LOQ and 500 ng L^{-1}. These PFAS concentrations are in good accordance with previous studies from the USA, Australia, Austria and China where wastewater effluent concentrations up to 560 ng L^{-1} were detected (Coggan et al., 2019; Gallen et al., 2018; Lenka et al., 2021; Pan et al., 2016; Schaefer et al., 2023). When comparing the findings to other studies, it must be considered that the samples were taken differently (as mixed or grab samples), different analysis methods were employed, and the number of PFAS analyzed was not the same. In addition, some of the samples were taken more than 10 years ago (Gallen et al., 2018; Pan et al., 2016). Wastewater treatment plant technologies and wastewater composition can also differ significantly between different countries.

20 of 40 PFAS analyzed were detected in the effluent samples in concentrations above the LOQ (see Fig. 1). In decreasing order, PFHxA (75 ng L^{-1}), 6:2 FTAB (74 ng L^{-1}), 6:2 FTS (55 ng L^{-1}) and PFPeA (38 ng L^{-1}) were detected in the highest average concentrations (see Table S12). C_4 to C_8 PFCA, PFBS, PFOS and 6:2 FTAB were detected most frequently with a detection frequency greater than 82 % (see Table S12). The proportion of known precursor substances in the total concentration of PFAS was 37 % on average. Consequently, the short-chain PFCA and the known precursors, 6:2 FTAB and 6:2 FTS, account for the majority of the total PFAS concentration in the effluent of the investigated WWTPs. Despite the restrictions and regulations for the long-chain PFAS at national and international level, PFOA and PFOS were still detected in 95 % and 89 % of the wastewater samples analyzed, respectively. The average concentration for PFOA and PFOS was 5.1 ng L^{-1} and 6.2 ng L^{-1}, respectively.

The detection frequency and the median for the individual PFAS are in good accordance with the values published by the German Environment Agency in 2020 (Toshovski et al., 2020; see Table S13). Only PFNA and 6:2 FTS were detected more frequently in the present study. The mean values of the short chain PFAS were lower in the German Environment Agency study. Whereby, the mean values of the long-chain PFAS, PFOA and PFDA were higher. The German Environment Agency study was carried out between 2017 and 2019. In our study, the sampling campaign took place between 2021 and 2022. The lower concentration of long-chain PFCAs can possibly be attributed to the ban on these compounds, which might had a greater impact on the more recent sampling results. The fact that the short-chain PFAS are used as substitutes for the long-chain PFAS can possibly explain the higher concentrations of the short-chain PFAS in the present study. However, to clearly prove this, the same WWTPs would have to be sampled again using the same methods. The maximum values of the single compounds in our study were much greater than in the German Environment Agency

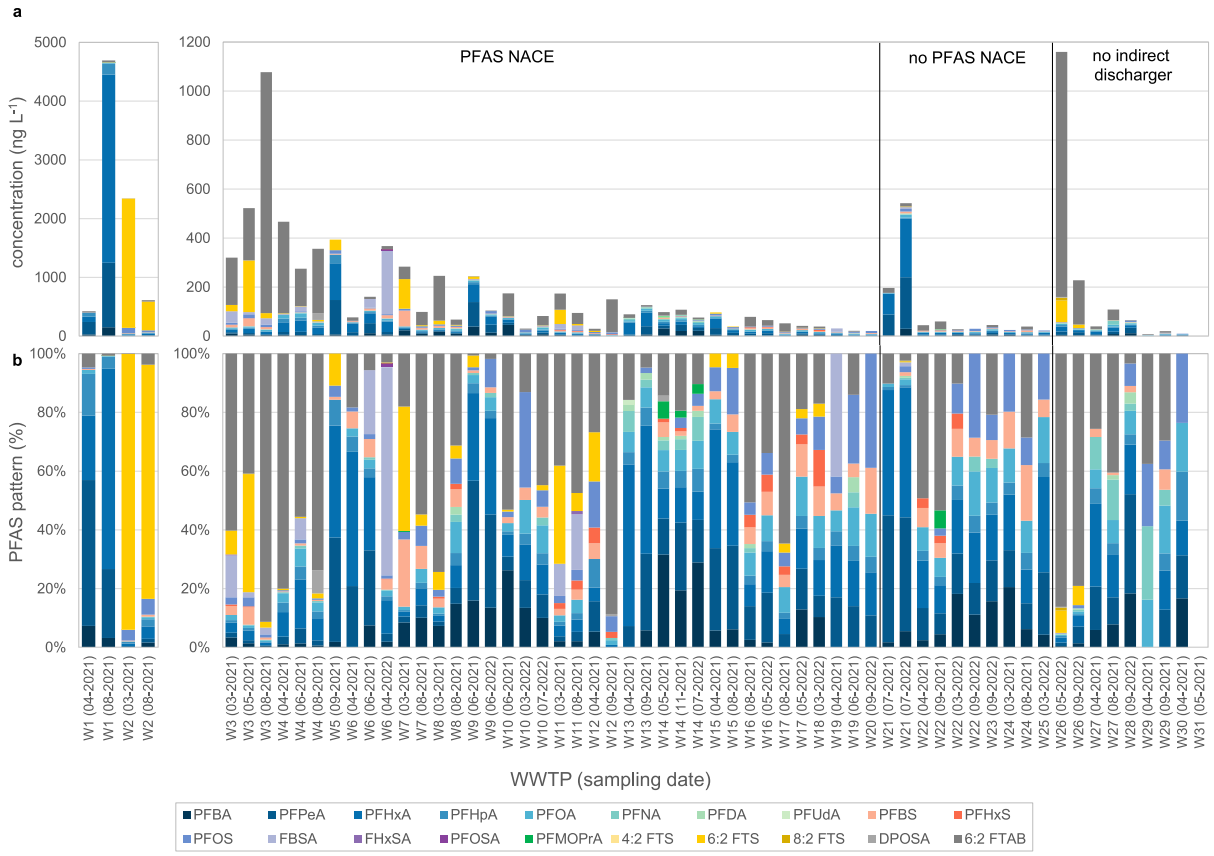

Fig. 1. Concentrations of PFAS (a) and PFAS pattern (b) in effluent samples of 31 municipal WWTPs. PFAS that were not determined in any sample greater than the LOQ are not shown in the figure. Single WWTPs were sampled between 1 and 4 times during the sampling period from March 2021 to September 2022.

study. This is because the present study specifically sampled WWTPs that were known to have high levels of PFAS contamination in their mixed liquor.

3.1.1. *Influence of the sewershed on PFAS concentrations in WWTPs*

Very high PFAS concentrations exceeding 500 ng L^{-1} were detected in the effluent samples of five WWTPs. Three of these plants (W1, W2, and W3) receive wastewater from industrial dischargers which are likely using PFAS (PFAS NACE). One facility (W 21) receives wastewater from industrial dischargers not considered to use PFAS (no PFAS NACE) and one facility (W26) does not receive industrial wastewater at all. Here, very high 6:2 FTAB concentrations were detected. The highest PFAS sum concentration was detected in the effluent of the WWTP W1 with 4700 ng L^{-1}. This WWTP receives wastewater from chemical and metal plating industries (NACE Code '20 Manufacture of chemicals and chemical products' and '25.61 Treatment and coating of metals'). The second highest PFAS concentrations were detected in the effluent of WWTP W2 with 2300 ng L^{-1}. In the sewershed of this WWTP a plastic producing industry (NACE code '22.2 Manufacture of plastic products') is located. PFAS concentrations up to 1000 ng L^{-1} were measured in the effluent of WWTP W3, which receives wastewater from a metal plating industry ('25.61 Treatment and coating of metals') and wastewater disposal ('37. Sewerage').

PFHxS, FBSA and PFMoPrA were only detected in WWTP effluents influenced by industrial dischargers. Furthermore, PFUdA, 4:2 FTS, FHxSA and PFOSA were only detected in effluent samples of WWTPs receiving wastewater from PFAS NACE facilities (see Table S12). According to Glüge et al. (2020), FBSA is used in semiconductor industry (with the NACE code 26.11 Manufacture of electronic components), whereas FHxSA is used in electroplating and metal plating industry and in firefighting foams. This knowledge can help to identify the polluters, as these substances indicate an industrial discharger. In addition, the PFAS concentrations measured in the effluent of WWTPs with PFAS-NACE plants in the catchment area are much more scattered, especially the extreme values. PFAS are often used in batch processes and therefore enter the wastewater discontinuously with high fluctuations in concentration (Szabo et al., 2023).

6:2 FTAB is used as a PFOS substitute in fluorine-containing foam agents (Glüge et al., 2020). This may also be the reason for the high 6:2 FTAB concentration in the effluent from WWTP W26, which does not receive any wastewater from industrial dischargers (no PFAS NACE). This is also supported by the significantly lower 6:2 FTAB concentration of the 2nd sampling date (09–2022). Thus, fire events or the maintenance of sprinkler systems with fluorine-containing foam agents represent a possible cause for the frequent detections of 6:2 FTAB in wastewater. Nevertheless, 6:2 FTAB is also used as a flame retardant and in the chemical industry for the production of chemicals and chemical products (Glüge et al., 2020). Also, 6:2 FTS is used as a substitute for PFOS in fluorine-containing foaming agents, but also in electroplating for hard chrome plating. PFPeA and PFHxA are used in a variety of consumer and industrial products. These include surface treatment of leather, paper and textiles, cosmetic products, outdoor and sporting goods, semiconductor industry and extinguishing foam agents (Glüge et al., 2020). Therefore, identifying the source of PFCA contamination in wastewater is very difficult.

The PFAS NACE codes alone are not sufficient to conclude that there are high concentrations of PFAS in the effluents of municipal WWTPs. High PFAS concentrations were also detected in the effluents of WWTPs without known industrial dischargers or with industrial dischargers not suspected of using PFAS. NACE codes are too ambiguous, as only one industry classification is provided in the wastewater database, even though different industries may be applied in one company. For

example, vehicle manufacturers (with NACE '29. Manufacture of motor vehicles, trailers and semi-trailers') may operate their own electroplating facilities (NACE 25.6 'Treatment and coating of metals; machining' or 25.61 'Treatment and coating of metals') in certain plants. However, these plants are only listed as NACE '29. Manufacture of motor vehicles, trailers and semi-trailers' in the wastewater database. Furthermore, small industrial dischargers do not have a wastewater discharge permit and therefore do not appear in the wastewater database. In addition, extinguishing foam inputs, which cause high 6:2 FTS or 6:2 FTAB concentrations in the WWTP, occur independently of the industrial discharger situation. However, individual PFAS compounds that are only used in certain industries like the perfluoroalkane sulfonyl fluoride (PASF)-based substances, FBSA and FHxSA, and strong fluctuations in concentration might give a hint to industrial discharges. Here, the PFAS NACE codes can be used to prioritize the industries located in the sewershed and to identify the source of the inputs.

3.1.2. Evaluation of PFAS concentrations in the effluent samples and temporal trends

Nine plants exceed the maximum contaminant value of 100 ng L^{-1} for the sum of 20 PFAS, if the PFAS concentrations detected in the wastewater effluents are assessed on the basis of the drinking water regulation (see Fig. S2). The exceedances are mainly caused by high PFPeA and PFHxA concentrations in the secondary effluents. In addition, the number of WWTPs exceeding the drinking water maximum contaminant value increases by 2 (W4 and W27) if the value for the sum of 4-PFAS (PFHXs, PFOA, PFNA and PFOS) of 20 ng L^{-1} is also considered (see Fig. S3). Both WWTPs with industrial dischargers in the sewershed and WWTPs without industrial dischargers exceed the limit value for drinking water in the effluent.

If the proposal for the environmental quality standard (EQS) of 4.4 ng L^{-1} for the sum of 24 PFAS is taken into account for the assessment, 30 WWTPs exceed this value (see Fig. S4). The exceedance is mainly caused by the long-chain PFAS, PFOA, PFNA, PFDA and PFOS. In contrast, the short-chain PFAS, which were detected in almost all wastewater samples in high concentrations, only play a minor role. Since PFAS are not or only poorly removed in municipal biological WWTPs, industrial wastewater containing high concentrations of long-chain PFAS should be treated onsite before being discharged to the public sewer system.

Six WWTPs (W4, W11, W13, W19, W20 and W24) were sampled between 3 and 4 times at intervals of several months to obtain information on temporal fluctuations (see Fig. S5). The PFAS concentration and composition varied widely over the sampling period in the effluent samples of four WWTPs. In the effluent of WWTP W11 and W19 both the concentration and the composition remain constant over the three sampling dates. Therefore, the high fluctuations in the PFAS concentration demonstrate that 2 h-grab samples are of little significance for determining the actual PFAS concentration in the effluent. Consequently, 24-h or 48-h composite samples taken on weekdays and weekends (e.g., monthly and over a period of several months) should be more meaningful, with the disadvantage that concentration peaks can be detected less clearly and sampling becomes more elaborate.

However, specific risks for drinking water and organisms in the receiving streams could not be comprehensively assessed based on the PFAS concentrations in the wastewater secondary effluents. This is because the wastewater is diluted in the receiving streams and, in the case of bank filtration for drinking water use, is additionally diluted by groundwater and further altered during post-treatment. As neither the discharge of the receiving waters nor the dilution by the groundwater are known, no assessment on adverse health effects could be carried out as part of this study.

3.1.3. TOP assay - wastewater

The TOP assay was used to estimate the proportion of unknown precursors. The results of the validation experiments with synthetic wastewater and detailed information on the robustness of the TOP assay for are described in S2.1.2.

In the oxidized wastewater effluent samples, the average molar PFAS concentration increased from 0.78 nmol L^{-1} to 1.3 nmol L^{-1} (see Table S16). The PFAS concentration in the effluent of 20 WWTPs, which corresponds to 65 % of the WWTPs investigated, clearly increased by a factor between 1.4 and 5.5 (on average by 2.9) after the oxidative treatment (see Table S17). Here, the mean value was used for WWTPs for which several measurement results were available at different sampling times. A significant increase could be demonstrated for the short-chain PFCA, PFBA, PFPeA, PFHxA and PFHpA (see Table S16). The PFOA concentration also increased significantly after oxidation, indicating that PFOA precursors are still present in wastewater samples despite the regulations on this compound.

Consequently, unknown precursor compounds must be present in the wastewater samples in relevant concentrations in addition to the precursors already detected by target analysis. Very high increases were observed in the effluent of the WWTPs W1, W13 and W29 (see Fig. 2). There was no influence of the sewershed (described by NACE code) on the concentration increase after the TOP assay.

In nine WWTPs (W2, W3, W4, W7, W8, W11 and W28) no increase in concentrations after the TOP assay was found. For single sampling dates even a decrease in PFAS concentration after the TOP assay was detected (see Fig. 2). This could be caused by a suppression of the measurement signal due to matrix effects. Furthermore, the precursors are possibly not completely degraded to the PFCA during the oxidation due to insufficient amount of oxidant added or degradation products are formed not detectable by target analysis. These results are in agreement with the results of the validation experiments with synthetic wastewater (see chapter S2.1.2.2) and literature (Chen et al., 2022; Müller et al., 2023).

In addition, the precursors 6:2 FTS and FOSA were still detectable at very low concentrations in some oxidized effluent samples. FOSA was detected in one effluent sample with 1 ng L^{-1} after the TOP assay. 6:2 FTS was detected in four effluent samples after the oxidation in concentrations between 1 and 3 ng L^{-1}. These trace levels of precursor compounds demonstrate that the precursors were not always completely degraded during the TOP assay. This indicates that radical scavengers may be present in some wastewater samples competing with the PFAS for OH radicals. The precursor concentration after the TOP assay showed no correlation with the COD concentration in the untreated samples (see Fig. S7 a). Therefore, the COD concentration may not be sufficient to indicate whether precursors are completely oxidized during TOP assay in a complex matrix or not. Also, no correlation was detectable between precursor concentration before and after TOP (see Fig. S7 b). Further studies are needed to obtain more information on the influence of other substances on the TOP assay of PFAS in complex matrices.

3.2. Occurrence of PFAS in mixed liquor samples

The total PFAS concentration in the mixed liquor samples of the 11 WWTPs was between 56 and 440 µg kg^{-1} dw, with a median of 112 µg kg^{-1} dw (see Fig. 3 and Table S18). The limit of 100 µg kg^{-1} dw for the sum of PFOS and PFOA in the Fertilizer Ordinance was clearly complied with in all the mixed liquor samples analyzed.

All 11 investigated WWTPs receive wastewater from industrial discharges characterized by PFAS NACE code. The PFAS concentrations in the mixed liquor samples differ less between the various WWTPs than the concentrations in the effluent. In addition, the concentration in the mixed liquor samples of the individual WWTPs also fluctuates only slightly over time. Thus, the mixed liquor concentrations provide time-integrating information on the PFAS load to WWTPs due to the longer retention time of the sludge in the biological treatment step.

28 of the 50 PFAS analyzed were detected in concentrations above the limit of quantification. PFHxA, PFDA, PFOS, N-MeFOSAA, N-EtFOSAA, 5:3 FTCA and 10:2 FTS were detected in every sludge sample (see Table S18). In decreasing order 5:3 FTCA (mean 39 µg kg^{-1} dw), PFOS

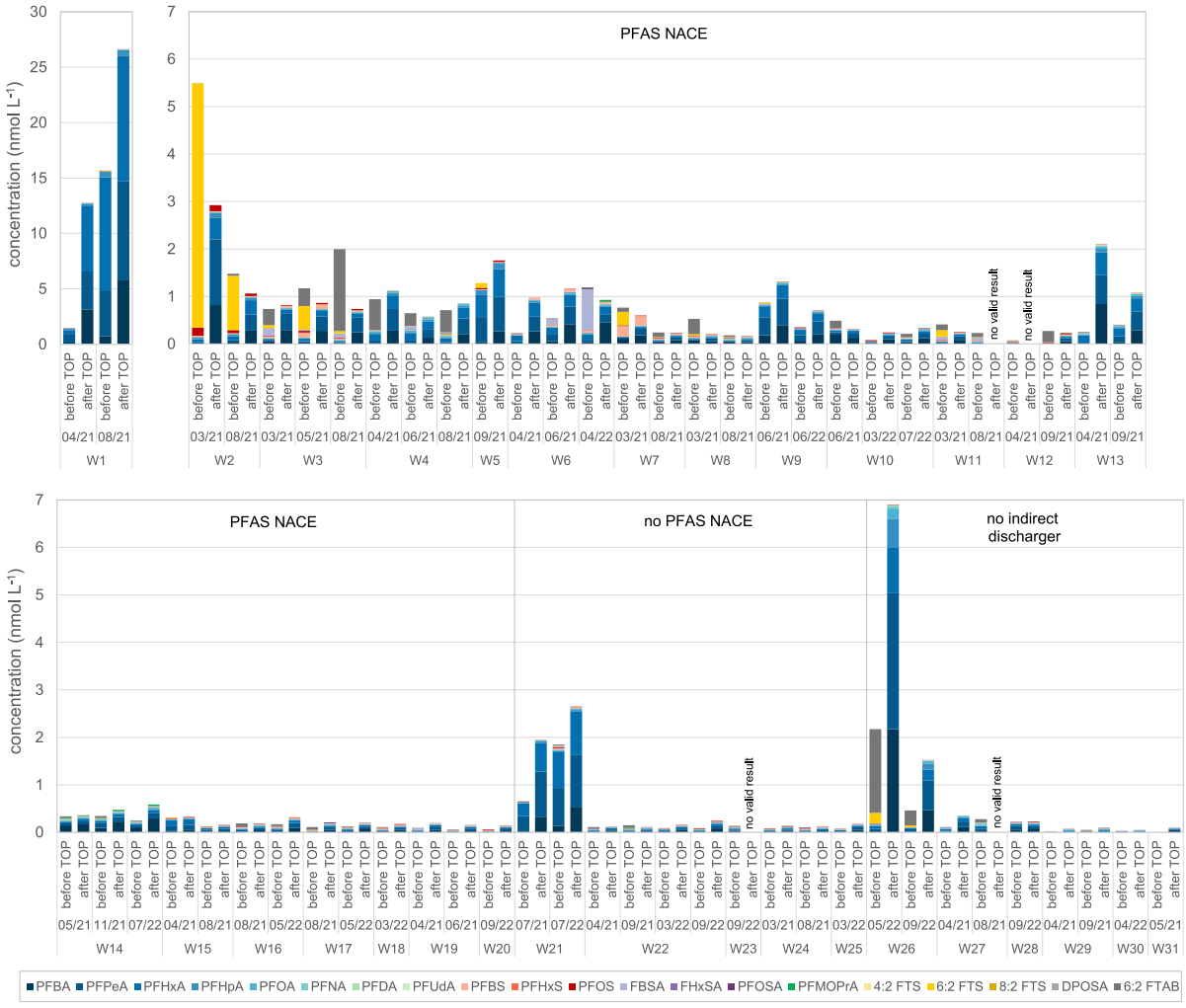

Fig. 2. Total PFAS concentration in the effluent of the investigated WWTPs before and after oxidative treatment ('no valid result': deviation between the duplicate measurements for individual parameters was >40 %).

(mean 17 μg kg^{-1} dw), 6:2 FTAB (mean 14 μg kg^{-1} dw) and N-EtFOSAA (mean 8.5 μg kg^{-1} dw) were analyzed in the highest mean concentrations. These findings are in good accordance with studies in Canada, where high 5:3 FTCA and PFOS concentrations were detected in biosolids of municipal WWTPs and PFHxA, 5:3 FTCA, long-chain PFCA, PFOS, N-MeFOSAA and N-EtFOSAA were detected most frequently (Gewurtz et al., 2024). The high amount of precursors detected in the sludge samples is in good according to the findings of a Swedish study (Fredriksson et al., 2022).

The high detection frequency of 5:3 FTCA, N-MeFOSAA and N-EtFOSAA can be explained by the fact that these compounds are degradation products of precursors, which are used in numerous industrial sectors. 5:3 FTCA is a degradation product of 6:2 FTS, 6:2 FTOH and 6:2 FTAB (Shaw et al., 2019; Zhang et al., 2021). N-MeFOSE (CAS 24448-09-7) and N-EtFOSE (CAS 1691-99-2) are the precursor substances of N-MeFOSAA and N-EtFOSAA, which are further degraded to PFOS (Mejia Avendaño and Liu, 2015; Zhang et al., 2021). These precursors are used in numerous industrial and consumer applications, including leather, textile, photographic and semiconductor industry (Glüge et al., 2020; Mejia Avendaño and Liu, 2015; Zhang et al., 2021). They are also used in cleaning compositions, for coatings, paints, varnishes and cosmetics, etc. Since all of these compounds were detected in all mixed liquor samples and are used in many different consumer and industrial products, it can be assumed that many different sources cause the increased concentrations in the mixed liquor. Furthermore, 6:2 diPAP and 8:2 diPAP, PFAS that are used for food-contact papers and packaging and for personal care products and cosmetics, were detected in almost all mixed liquor samples, with the exception of W19. The mean concentrations of 6:2 diPAP and 8:2 diPAP were 2.3 and 1.0 μg kg^{-1} dw, respectively. These substances are leaching out during the usage of treated paper, personal care products and cosmetics into wastewater and accumulate in the mixed liquor due to their high adsorption tendency (Fredriksson et al., 2022; Glüge et al., 2020). However, the industry that uses these substances, e.g., for paper production or cosmetics, also contributes to the emission of these substances into the wastewater. It is remarkable that N-MeFOSAA, N-EtFOSAA and PFOS were detected in all mixed liquor samples analyzed, in some cases even at high concentrations, although PFOS and its precursors were regulated by the Stockholm Convention more than 10 years ago (UNEP, 2009).

The PFAS composition in the mixed liquor samples differs significantly from the PFAS composition in the effluent samples. In the effluent, mainly short-chain PFCA were detected, whereas in the mixed liquor, mainly long-chain PFAS and transformation products were detected. This is because the long-chain PFAS have a higher tendency to adsorb to the mixed liquor than shorter-chain PFAS and the transformation processes mainly take place during secondary wastewater treatment (Arvaniti et al., 2012; Coggan et al., 2019; Guerra et al., 2014; Sinclair and Kannan, 2006; Yu et al., 2009).

Fig. 3. PFAS concentration (a) and PFAS pattern (b) in the mixed liquor samples of 11 municipal WWTPs. Single WWTPs were sampled between 1 and 10 times between 2017 and 2022.

3.2.1. Temporal variability in PFAS concentrations and influence of the sewersheds on PFAS concentration in the mixed liquor samples

The PFAS concentration in the mixed liquor samples from WWTP W12, W14 and W33 was analyzed from four different years. In the mixed liquor from all four plants, the total PFAS concentration decreased over the sampling period (see Fig. 3). However, this cannot be attributed to the same PFAS. At WWTP W12, the decrease is mainly due to a decline in the concentrations of the long-chain PFCA and 5:3 FTCA. At WWTP W14, the concentrations of PFOS and N-EtFOSAA decreased, and at W33, the concentrations of 5:3 FTCA and 6:2 FTS decreased. This decrease could indicate a reduced use of PFAS. However, it is likely that short-chain PFAS are increasingly used instead of long-chain PFAS (Wang et al., 2013, 2017), which have a lower tendency to adsorb to mixed liquor. Also, Fredriksson et al. (2022) observed a declining trend between the years 2004 and 2017 in the total PFAS concentration and a shift from long-chain to shorter-chain PFAS in sewage sludge samples from Swedish WWTPs. However, further analyses of mixed liquor and wastewater samples are needed to better understand the trends.

The PFAS pattern in the mixed liquor samples from the investigated WWTPs is very similar. Nevertheless, in the sludge samples of WWTP W12 high PFPrA concentrations were detected. Whereas, in the sludge samples of WWTP W14 high concentrations of the long-chain C_{10} to C_{14} PFCA were analyzed. WWTP W 12 receives wastewater from paper, textile, dyes and pigments industry, treatment and coating of metals and plastic production (see Table S1). According to Glüge et al. (2020), PFPrA is only used in textile and upholstery industry. It is therefore likely that the textile industries in the sewershed cause the high concentrations of PFPrA in the mixed liquor samples. WWTP W14 is impacted by chemical and electronic industry. However, as the long-chain PFCA compounds are used in numerous industrial and consumer products (Glüge et al., 2020) and the NACE codes are ambiguous, further investigations would be needed to identify the sources of the high concentrations.

3.2.2. TOP assay and evaluation – mixed liquor samples

In the blanks of the mixed liquor sample sets no PFAS were detected in concentrations above LOQ. The intraday standards were completely degraded to the expected PFCA within the accepted deviation of ±40 %.

After the oxidative treatment a high increase in PFAS concentration was detectable for all mixed liquor samples (see Fig. S8). The median PFAS concentration in the oxidized samples increased by a factor of 4.2 from 261 to 1098 nmol kg^{-1} dw. Similar to the results of the wastewater effluent samples, a significant increase was exhibited by short-chain PFCA, PFBA, PFPeA, PFHxA and PFHpA and for PFOA (see Fig. S9).

Also, in the oxidized mixed liquor samples from the individual WWTPs, neither the PFAS concentration nor the composition varied greatly. However, W3 and W33 are an exception. Here, the PFAS concentration increased significantly after the TOP assay in individual mixed liquor samples. Since the 6:2 FTAB, 6:2 FTS and 5:3 FTCA concentrations were very high in the unoxidized samples, the large increases in concentration after to the TOP assay could be due to the entry of AFFF-containing extinguishing water.

The mixed liquor samples comply with the limit values set in the Fertilizer Ordinance for the sum of PFOS and PFOA. Therefore, the investigated mixed liquor can be applied on agricultural land despite a median PFAS concentration of 112 μg kg^{-1} dw. Furthermore, the PFAS concentration in all mixed liquor samples increased significantly after the TOP assay. Mixed liquor that is not incinerated but applied to agricultural land thus represents another source of PFAS to the environment.

4. Conclusion

The results of the comprehensive wastewater effluent screening demonstrate that individual hotspots with very high PFAS concentrations >500 μg L^{-1} could be identified. There is an urgent need for action to reduce the discharge of PFAS from these WWTPs into the aquatic environment. Since PFAS are not or only slightly removed in municipal WWTPs, industrial wastewater containing high concentrations of PFAS should be treated directly at the source, e.g., by ion exchange resins or activated carbon to remove them before being discharged into the public sewer system. In addition, the concentration of PFAS in wastewater and sewage sludge could be significantly reduced by banning PFAS, e.g., in consumer products. The results of the TOP assay demonstrate that PFAS concentrations are higher in a large proportion of the WWTPs studied than the target analyses suggest. Furthermore, individual high PFAS concentrations could only be detected using TOP assay. Therefore, it is important to regulate the whole group of PFAS and not only specific compounds.

The TOP assay is an important analytical tool. Nevertheless, further method development is needed, as for some wastewater samples the PFAS concentration decreased after oxidation and thus, a complete recovery was not achieved. A higher quantity of oxidizing agent can possibly improve degradation. However, it must then also be considered that this is accompanied by an increased salt load in the samples, which interferes with the subsequent measurement. Further method developments are therefore necessary and efforts should be made to standardize the TOP assay so that different study results can be better compared with each other.

In future studies, composite samples over extended time periods should be taken for determining the actual PFAS concentration in the effluent samples. In addition, the wastewater and sewage sludge sampling should also be extended to smaller WWTPs and repeated at regular intervals to obtain a more complete picture of the PFAS concentrations in municipal WWTPs.

CRediT authorship contribution statement

H. Ulrich: Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **A.-S. Heldele:** Writing – review & editing, Resources, Methodology, Investigation, Data curation. **M. Gierig:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis, Conceptualization. **T. Letzel:** Writing – review & editing, Supervision, Methodology, Conceptualization. **J.E. Drewes:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jorg E. Drewes reports financial support, administrative support, equipment, drugs, or supplies, and travel were provided by Technical University of Munich. Jorg E. Drewes reports a relationship with Technical University of Munich that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2025.144612.

Data availability

Data will be made available on request.

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