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Investigations on the presence and behavior of precursors to perfluoroalkyl substances in the environment as a preparation of regulatory measures

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Investigations on the presence and behavior of precursors to perfluoroalkyl substances in the environment as a preparation of regulatory measures

by

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Abstract

Wastewater treatment plants (WWTPs) have been identified as a significant pathway for the introduction of perfluoroalkyl and polyfluoroalkyl substances (PFASs) to natural waters. It was observed in several studies that the concentration of certain PFASs were higher in the WWTP effluent compared to the corresponding influent. The objective of the present study was the identification of potential precursor substances of persistent perfluoroalkyl acids (PFAAs) in WWTPs and indoor rooms in order to support the preparation of regulatory measures.

Following the development of robust and validated analytical methods for 65 PFASs, which included persistent PFASs and their potential precursors, sampling campaigns in six WWTPs (industrial and municipal, located in Europe) over a period of four weeks each were realized. The influent water and effluent water, the air above the influent and the sludge of the WWTPs as well as dust and air from three indoor rooms were sampled and analyzed.

Due to the differences between the WWTPs sampled, above all the share of industrial wastewater, the concentrations of detected PFASs in the aqueous samples varied within five orders of magnitude and were in the range of low ng/L up to high µg/L. Several transformation products of fluorotelomer alcohols (FTOHs) e.g. unsaturated fluorotelomer carboxylic acids (FTUCAs), fluorotelomer carboxylic acids (FTCAs) and x:3-acids could be determined, particularly in the aqueous phase of the industrial WWTPs. Further biotransformation of these intermediates led to an increased concentration of perfluoroalkyl carboxylic acids (PFCAs) in the effluent of WWTPs. FTOHs were the dominant substance class in the air samples collected above the influent and were detected in all WWTP air samples (with one exception) and in indoor air samples. Precursors of perfluoroalkane sulfonic acids (PFSAs), e.g. perfluorooctane sulfonamidoethanols (FOSEs) and perfluorooctane sulfonamidoacetic acids (FOSAA) were rarely detected and mainly so in indoor air and dust samples, respectively. Based on the frequency of detection and concentration of FTOHs, biotransformation intermediates (e.g. FTUCAs and FTCAs) and persistent biotransformation products (e.g. x:3 acids and PFCAs), fluorotelomer-based substances were identified as the most relevant precursors of PFCAs. Data for several corresponding WWTP influent, air and effluent samples suggests that FTOHs could be present as a residual synthetic intermediate of non-targeted PFASs, such as fluorinated polymers or other unknown low molecular weight fluorotelomer-based chemicals. This aspect should be investigated in future studies.

Kurzbeschreibung

Kläranlagen konnten als wichtiger Eintragsweg für perfluorierte und polyfluorierte Alkylsubstanzen (PFASs) in natürliche Gewässer identifiziert werden. In verschiedenen Studien wurde festgestellt, dass die Konzentrationen bestimmter PFASs im Ablauf der Kläranlage höher sind als in dem korrespondierenden Zulauf. Das Ziel dieser Studie war die Identifikation von potenziellen Vorläufersubstanzen von persistenten PFASs in Kläranlagen und Innenräumen, um die Vorbereitung regulatorischer Maßnahmen zu unterstützen.

Nach der Entwicklung von robusten und validierten Analysemethoden für 65 PFASs, welche persistente PFASs und deren potentielle Präkursoren beinhalteten, wurden in sechs Kläranlagen (industrielle und kommunale innerhalb Europas) vierwöchige Probenkampagnen durchgeführt. Der Zulauf, der Ablauf, die Luft über dem Zulauf und der Schlamm der Kläranlagen sowie Staub und Luft von drei Innenräumen wurden beprobt und analysiert,.

Aufgrund der Unterschiede zwischen den Kläranlagen, allen voran der Anteil von industriellem Abwasser, unterschieden sich die Konzentrationen der in der wässrigen Phase festgestellten PFASs um fünf Größenordnungen und reichten vom niedrigen ng/L-Bereich bis zum hohen µg/L-Bereich. Gerade in der wässrigen Phase der industriellen Kläranlagen konnten verschiedene Transformationsprodukte von Fluortelomeralkoholen (FTOHs), wie z.B. ungesättigte Fluortelomercarbonsäuren (FTUCAs), Fluortelomercarbonsäuren (FTCAs) und die x:3-Säuren, bestimmt werden. Die weitere Biotransformation dieser Zwischenprodukte führte im Ablauf der Kläranlagen zu einer Konzentrationserhöhung der Perfluoralkylcarbonsäuren (PFCAs). In den über dem Zulauf genommenen Luftproben waren die FTOHs die dominierende Substanzklasse und wurden sowohl in allen Kläranlagenproben (bis auf eine Ausnahme) wie auch in allen Innenraumproben gefunden. Präkursoren von perfluorierten Alkansulfonsäuren (PFSAs), wie z.B. Perfluoroctansulfonamidoethanole (FOSEs) und Perfluoroctansulfonamidoessigsäuren (FOSAAs) wurden deutlich seltener und hauptsächlich in den Innenraumproben detektiert. Aufgrund der Häufigkeit und der Konzentration der FTOHs, der Biotransformationsintermediate (z.B. FTUCAs und FTCAs) und persistenter Biotransformationsprodukte (z.B. x:3-Säuren und PFCAs) konnten fluortelomerbasierte Substanzen als relevante Präkursoren von PFCAs identifiziert werden. Die Daten von vielen korrespondierenden Kläranlagenzuläufen, Luft- und Ablaufproben lassen vermuten, dass die FTOHs als Rückstand von synthetischen Zwischenprodukten, nicht untersuchter PFASs, wie z.B. fluorierte Polymere oder anderen unbekannte, auf Fluortelomerbasis hergestellten Chemikalien, vorhanden sind. Dieses könnte ein weiterer Grund für die Häufigkeit der Detektion sein und sollte in zukünftigen Studien untersucht werden.

Summary

Following numerous studies carried out in the last years in order to determine the fate and effects of perfluoroalkyl and polyfluoroalkyl substances (PFASs), mainly their most relevant substance classes perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), this study aimed at identifying relevant precursors to these persistent perfluoroalkyl acids (PFAAs) in environmental samples. This is reasoned by several investigations showing biotic and abiotic transformation ending up in PFCAs or PFSAs. Furthermore, higher concentrations of perfluoroalkyl acids PFAAs in effluent samples compared to corresponding

influent samples had been observed during investigations on the presence of PFASs in wastewater treatment plants (WWTPs) indicating transformation of untargeted PFAS precursors along the wastewater treatment chain. However, the occurrence of the PFAS precursors known to yield PFCAs and PFSAs in real samples has only been studied sporadically causing a knowledge gap for the scientific community and regulatory authorities.

Upon a literature search and availability check of suitable reference materials, 65 PFASs were selected comprising persistent PFASs such as PFCAs and PFSAs, fluorotelomer-based compounds (marketed products, synthetic intermediates, biotransformation intermediates and persistent biotransformation products) and perfluorooctane sulfonamide derivatives (synthetic intermediates and biotransformation intermediates). Three instrumental methods based on HPLC-MS/MS and GC-MS as well as several sample pretreatment methods for different sample matrices were developed and validated.

These methods were used to determine the concentration of the selected PFASs in water and air samples from six WWTPs of municipal and industrial character during a period of four weeks as well as air and dust from three indoor rooms. The WWTPs were chosen based on previous PFAS data and comprised three ‘industrial’ WWTPs, where impact of fluorochemical-producing or fluorochemical-using industry was known or expected as well as three ‘municipal’ WWTPs, where this was not the case. Influent, effluent, sludge and air samples above the influent were taken to capture the broadest PFAS spectrum possible. The indoor rooms were chosen in a way that products known to contain PFASs, such as freshly laid carpets, were present, except for one indoor room which served as a comparison with low expected PFASs concentrations.

WWTPs exhibited a different set of PFASs as well as drastically different concentrations between industrial and municipal WWTPs. Samples from industrial WWTPs exhibited 32 (influent), 20 (effluent), and 34 (air above influent) PFASs of the 65 PFASs under investigation, whereas samples from municipal WWTPs only contained 9 (influent), 10 (effluent) and 7 (air) compounds, respectively. Apart from PFCAs and PFSAs, which were frequently detected, fluorotelomer alcohols (FTOHs) and fluorotelomer (meth)acrylates (FT(M)ACs) dominated the PFAS spectrum in industrial WWTPs. One WWTP showed extremely high PFAS concentrations reaching up to 986 µg/L for 6:2-FTOH in an influent sample and 4.40 µg/L for 6:2-FTMAC in an air sample above the influent. All other WWTPs exhibited significantly lower concentrations of all detected PFASs which were mostly in the ng/L range (aqueous samples) and in the ng/m^3 range (air samples). The most frequently detected PFAS precursors in WWTPs were FTOHs, mainly 6:2-FTOH, and 6:2-fluorotelomer sulfonate (6:2-FTS), both of which were detected in five of six WWTPs. To the best of our knowledge, the x:3-acids, namely 5:3-acid and 7:3-acid were detected in real samples for the first time and their detection indicates the occurrence of fluorotelomer-based compounds in corresponding influents. For WWTPs, a dominance of C_6-based chemistry was observed with respect to the perfluoroalkyl chain length.

Non-target screening by HPLC coupled to high-resolution mass spectrometry (HRMS) revealed the presence of a whole homologous series of 2H-PFCAs in several industrial WWTP samples, which underlines the importance of expanding the target PFAS list in monitoring campaigns. 2H-PFCAs are known persistent biotransformation products of fluorotelomer-based compounds.

The indoor samples exhibited fewer compounds than WWTP samples, with 8:2-FTOH and 6:2-FTOH dominating the air samples. Contrarily to WWTPs, concentrations of 8:2-FTOH were generally higher than 6:2-FTOH concentrations. Furthermore, N-MeFOSE and N-EtFOSE were

detected in most of the samples. Accordingly, the biotransformation intermediate of N-EtFOSE, namely N-EtFOSAA, was detected in corresponding dust samples.

The present study underlines the significance of fluorotelomer-based compounds as precursors of PFCAs. Especially FTOHs were detected very frequently, but these might be present only as synthetic residuals to other non-targeted PFASs. Such compounds could be fluorinated polymers or other unknown low molecular weight fluorotelomer-based chemicals. This issue should be addressed in future studies.

Zusammenfassung

Nach einer Vielzahl von Studien, die den Verbleib und die Effekte von perfluorierten und polyfluorierten Alkylverbindungen (PFASs), hauptsächlich der relevantesten Verbindungsklassen Perfluoralkylcarbonsäuren (PFCAs) und Perfluoralkansulfonsäuren (PFSAs) untersuchten, sollten in dieser Studie relevante Vorläuferverbindungen dieser persistenten PFASs in Umweltproben ermittelt werden. Die Notwendigkeit dazu begründet sich in der Tatsache, dass einige PFASs bekanntermaßen durch biotische und abiotische Prozesse zu Perfluoralkylsäuren (PFAAs) transformiert werden können. Des Weiteren wurde in mehreren Studien gezeigt, dass die Konzentration einzelner PFAAs in Kläranlagenabläufen höher waren als in korrespondierenden Zulaufproben, was auf eine Biotransformation nicht gemessener PFASs während der Abwasserbehandlung hindeutet. Das Vorkommen bekannter Vorläuferverbindungen in Realproben wurde jedoch bislang nur sporadisch untersucht, was eine Wissenslücke für die wissenschaftliche Gemeinschaft und regulatorische Behörden nach sich zieht.

Nach einer Literaturstudie und Überprüfung der Verfügbarkeit geeigneter Referenzverbindungen wurden 65 PFASs ausgewählt, darunter persistente PFASs wie PFCAs und PFSAs, fluortelomer-basierte Substanzen (Endprodukte, Biotransformationsintermediate und persistente Biotransformationsprodukte) und Perfluoroctansulfonamid-Derivate (synthetische Zwischenprodukte und Biotransformationsintermediate). Drei instrumentelle Methoden basierend auf HPLC-MS/MS und GC-MS, sowie mehrere Probebenvorbereitungsmethoden für verschiedenste Probenmatrizes wurden entwickelt und validiert.

Mithilfe dieser Methoden wurden die Konzentrationen der ausgewählten PFASs in Proben von insgesamt sechs kommunalen und industriellen Kläranlagen bestimmt. Zudem wurden drei Innenräume beprobt, in denen Luft- und Staubproben genommen wurden. Dabei wurden die Kläranlagen nach vorherigen PFAS-Untersuchungen ausgewählt, so dass drei „industrielle“ Kläranlagen ausgewählt wurden, in denen PFAS-produzierende oder –applizierende Industrie einleitet, und drei „kommunale“, bei denen keine solchen industriellen Einflüsse bekannt oder offensichtlich waren. Zulauf, Ablauf, Schlamm und die Luft über dem Zulauf wurden beprobt, um ein möglichst großes Spektrum an PFASs zu erfassen. Die Innenräume wurden dahingehend ausgewählt, dass PFAS-enthaltende Produkte, wie frisch verlegte Teppiche, vorhanden waren. Ein weiterer Innenraum diente als Vergleichsraum, in dem geringe PFAS-Konzentrationen erwartet wurden.

Zwischen den industriellen und kommunalen Kläranlagen konnte ein deutlicher Unterschied der Konzentrationen und des nachweisbaren Analytenspektrums festgestellt werden. So konnten in industriellen Kläranlagen 32 (Zulauf), 20 (Ablauf) bzw. 34 (Luft über dem Zulauf) der 65 untersuchten PFASs detektiert werden, wohingegen in kommunalen Kläranlagenproben lediglich 9 (Zulauf), 10 (Ablauf) bzw. 7 (Luft über dem Zulauf) Verbindungen detektiert wurden. Abgesehen von PFCAs und PFSAs, die häufig nachgewiesen werden konnten, dominierten Fluortelomeralkohole (FTOHs) und Fluortelomer(meth)acrylate (FT(M)ACs) das Analytenspektrum in industriellen Kläranlagen. Dabei wies eine Kläranlage enorm hohe PFAS-Konzentrationen auf mit 986 µg/L für 6:2-FTOH im Zulauf und 4,40 µg/L für 6:2-FTMAC in der Luft über dem Zulauf. Alle weiteren Kläranlagen wiesen deutlich geringere Konzentrationen aller Substanzen auf. Die relevantesten Vorläufer waren dabei die FTOHs, vor allem 6:2-FTOH und 6:2-Fluortelomersulfonat (6:2-FTS), welche jeweils in Proben aus fünf von sechs Kläranlagen

nachgewiesen werden konnten. Nach unserem Wissensstand wurden zudem die x:3-Säuren, genauer 5:3-Säure und 7:3-Säure, zum ersten Mal in Umweltproben nachgewiesen werden. Dies deutet auf eine Biotransformation im Zulauf enthaltener FTOHs bzw. weiterer Fluortelomer-basierter Verbindungen hin. In Kläranlagenproben wurde generell eine Tendenz zu C6-basierten Verbindungen bezogen auf die Perfluoralkyl-Kettenlänge ermittelt.

Mittels HPLC und hochauflösender Massenspektrometrie wurden weitere nicht im Messprogramm enthaltene PFASs in mehreren industriellen Kläranlagenproben identifiziert. Dies war die homologe Reihe der 2H-PFCAs, welche bekannte persistente Biotransformationsprodukte Fluortelomer-basierter Verbindungen sind.

In Innenraumproben wurden insgesamt deutlich weniger Verbindungen detektiert als in Kläranlagenproben, wobei 8:2-FTOH und 6:2-FTOH die relevantesten Verbindungen in Luftproben darstellten. Im Gegensatz zu Kläranlagenproben wies 8:2-FTOH in der Innenraumluft jedoch generell höhere Konzentrationen als 6:2-FTOH auf. Zudem wurden N-Methyl-perfluoroctansulfonamidoethanol (N-MeFOSE) und N-Ethyl-perfluoroctansulfonamidoethanol (N-EtFOSE) in den meisten Proben detektiert sowie das Biotransformationsintermediat von N-EtFOSE N-Ethyl-perfluorctansulfonamid-essigsäure, welches in den korrespondierenden Staubproben bestimmt wurde.

Die vorliegende Studie unterstreicht die Bedeutung der Fluortelomer-basierten Verbindungen als relevante Vorläufer der PFCAs. Insbesondere die FTOHs wurden im Großteil der Proben detektiert, jedoch könnten diese Begleitsubstanzen weiterer noch unbekannter Fluortelomerverbindungen darstellen, zu denen die FTOHs als synthetische Zwischenprodukte fungieren könnten. Solche Substanzen könnten fluorierte Polymere oder andere Substanzen geringeren Molekulargewichts sein. Dieser Fragestellung sollten sich zukünftige Untersuchungen widmen.

Table of Content

List of Figures

List of Tables

List of Abbreviations

10:2-FTCA	2-Perfluorodecyl ethanoic acid
10:2-FTI	1H,1H,2H,2H-Perfluorododecyl iodide
10:2-FTO	1H,1H,2H,2H-Perfluorododec-1-ene
10:2-FTOH	1H,1H,2H,2H-Perfluoro-1-dodecanol
10:2-FTUCA	2H-Pefluoro-2-dodecenoic acid
2H-PFCA	2H-Perfluoroalkyl carboxylic acid
3:3-acid	2H,2H,3H,3H-Perfluorohexanoic acid
4:2-FTS	1H,1H,2H,2H-Perfluorohexane sulfonate
4:3-acid	2H,2H,3H,3H-Perfluoroheptanoic acid
5:3-acid	2H,2H,3H,3H-Perfluorooctanoic acid
6:2-diPAP	Bis(1H,1H,2H,2H-perfluorooctyl) phosphate
6:2-FTCA	2-Pefluorohexyl ethanoic acid
6:2-FTAC	1H,1H,2H,2H-Perfluorooctyl acrylate
6:2-FTEO1C	1H,1H,2H,2H-Perfluorooctoxy acetic acid
6:2-FTI	1H,1H,2H,2H-Perfluorooctyl iodide
6:2-FTMAC	1H,1H,2H,2H-Perfluorooctyl methacrylate
6:2-FTO	1H,1H,2H,2H-Perfluorooct-1-ene
6:2-FTOH	1H,1H,2H,2H-Perfluoro-1-octanol
6:2-FTS	1H,1H,2H,2H-Perfluorooctane sulfonate
6:2-FTUCA	2H-Perfluoro-2-octenoic acid
6:2-PAP	1H,1H,2H,2H-Perfluorooctylphosphate
6:3-acid	2H,2H,3H,3H-Perfluorononanoic acid
7:1 FTAC	1H,1H-Perfluorooctyl acrylate
7:3-acid	2H,2H,3H,3H-Perfluorodecanoic acid
7H-6:1-FTI	1H,1H,7H-Dodecafluoroheptyl iodide
7Me-6:2-FTI	1H,1H,2H,2H-Perfluoro-7-methyloctyl iodide
8:2-diPAP	Bis(1H,1H,2H,2H-Perfluorodecyl) phosphate
8:2-FTCA	2-Pefluorooctyl ethanoic acid
8:2-FTAC	1H,1H,2H,2H-Perfluorodecyl acrylate
8:2-FTEO1C	1H,1H,2H,2H-Perfluorodecoxy acetic acid
8:2-FTI	1H,1H,2H,2H-Perfluorodecyl iodide
8:2-FTMAC	1H,1H,2H,2H-Perfluorodecyl methacrylate
8:2-FTO	1H,1H,2H,2H-Perfluorodec-1-ene
8:2-FTOH	1H,1H,2H,2H-Perfluoro-1-decanol
8:2-FTS	1H,1H,2H,2H-Perfluorodecane sulfonate
8:2-FTUCA	2H-Pefluoro-2-decenoic acid
8:2-PAP	1H,1H,2H,2H-Perfluorodecylphosphate
Ac	Acetate
ACN	Acetonitrile
AFFF	Aqueous firefighting foam

$Ca(OH)_2$	Calcium hydroxide
CCA	Canonical correlations analysis
CI	Chemical ionization
CID	Collision-induced dissociation
diPAP	Fluorotelomer phosphate diester)
ECNI	Electron capture negative ionization
EEC	European Economic Community
EFF	Effluent
EI	Electron ionization
ESI	Electrospray ionization
FASA	Perfluoroalkane sulfonamide
FASAA	Perfluoroalkane sulfonamidoacetic acid
FASE	Perfluoroalkane sulfonamidoethanol
FOSA	Perfluoro-1-octanesulfonamide
FOSAA	Perfluoro-1-octanesulfonamidoacetic acid
FTAC	Fluorotelomer acrylate
FTAL	Fluorotelomer aldehyde
FTCA	Fluorotelomer carboxylic acid
FTEO	Fluorotelomer ethoxylate
FTI	Fluorotelomer iodide
FTMAC	Fluorotelomer methacrylate
FTO	Fluorotelomer olefin
FTOH	Fluorotelomer alcohol
FTS	Fluorotelomer sulfonate
FTUCA	Unsaturated fluorotelomer carboxylic acid
GC	Gas chromatography
HCl	Hydrogen chloride
HDPE	High density polyethylene
HLB	Hydrophilic-lipophilic balance
HPLC	High pressure liquid chromatography
HRMS	High-resolution mass spectrometry
INF	Influent
IS	Internal standard
LC	Liquid chromatography
LOD	Limit of detection
LOQ	Limit of quantification
M-10:2-FTUCA	2H-Pefluoro-[1,2-$^{13}C_2$]-2-dodecenoic acid
M-6:2-FTCA	2-Perfluorohexyl-[1,2-$^{13}C_2$]-ethanoic acid
M-6:2-FTOH	1H,1H,2H,2H-Perfluoro[^{13}C,D_4]-1-octanol
M-6:2-FTS	1H,1H,2H,2H-perfluoro-[1,2-$^{13}C_2$]-octane sulfonate
M-6:2-FTUCA	2H-Pefluoro-[1,2$^{13}C_2$]-2-octenoic acid

M-8:2-diPAP	Sodium bis(1H,1H,2H,2H-[1,2$^{13}C_2$]-perfluorodecyl) phosphate
M-8:2-FTCA	2-Pefluorooctyl-[1,2-$^{13}C_2$]-ethanoic acid
M-8:2-FTOH	2-Perfluorooctyl-[1,1-$^{2}H_2$]-[1,2-$^{13}C_2$]-ethanol
M-8:2-FTUCA	2H-Pefluoro-[1,2-$^{13}C_2$]-2-decenoic acid
M-8:2-PAP	1H,1H,2H,2H-[1,2-$^{13}C_2$]-Perfluorodecyl phosphate
MeOH	Methanol
M-N-EtFOSA	N-Ethyl-d_5-perfluoro-1-octanesulfonamide
M-N-EtFOSAA	N-Ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid
M-N-MeFOSA	N-Methyl-d_3-perfluoro-octanesulfonamide
MPFBA	Perfluoro-n-[$^{13}C_4$]butanoic acid
MPFDA	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid
MPFDoA	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid
MPFHpA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid
MPFHxA	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid
M-PFHxPA	Chloroperfluorohexylphosphonic acid
MPFHxS	Perfluoro-1-hexane[$^{18}O_2$]sulfonate
MPFNA	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid
MPFOA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid
MPFOS	Perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonate
MPFPeA	Perfluoro-n-[$^{13}C_5$]pentanoic acid
MPFUnA	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid
MRM	Multiple reaction monitoring
MS	Mass spectrometer
MW	Molecular weight
n.a.	Not analyzed
n.c.	Not calculated
n.d.	Not detected
NaOH	Sodium hydroxide
N-EtFOSA	N-Ethylperfluoro-1-octanesulfonamide
N-EtFOSAA	N-Ethylperfluoro-1-octanesulfonamidoacetic acid
N-EtFOSE	2-(N-Ethylperfluoro-1-octanesulfonamido)-ethanol
N-MeFOSA	N-Methylperfluoro-1-octanesulfonamide
N-MeFOSAA	N-Methylperfluoro-1-octanesulfonamidoacetic acid
N-MeFOSE	2-(N-Methylperfluoro-1-octanesulfonamido)-ethanol
OECD	Organisation for Economic Co-operation and Development
PAP	Fluorotelomer phosphate monoester
PBT	Persistent, bioaccumulative, toxic
PCA	Principal component analysis
PCI	Positive chemical ionization
PE	Population equivalent
PFAA	Perfluoroalkyl acids
PFAI	Perfluoroalkyl iodide

PFASs	Perfluoroalkyl and polyfluoroalkyl substances
PFBA	n-Perfluorobutanoic acid
PFBI	Perfluorobutyl iodide
PFBS	Perfluoro-1-butane sulfonate
PFCA	Perfluorinated carboxylic acid
PFDA	n-Perfluorodecanoic acid
PFDoA	n-Perfluorododecanoic acid
PFDPA	Perfluorodecylphosphonic acid
PFDS	Perfluoro-1-decane sulfonate
PFDUnA	n-Perfluoroundecanoic acid
PFHpA	n-Perfluoroheptanoic acid
PFHpS	Perfluoro-1-heptane sulfonate
PFHxA	n-Perfluorohexanoic acid
PFHxI	Perfluorohexyl iodide
PFHxPA	Perfluorohexylphosphonic acid
PFPrA	Perfluoropropionic acid
PFHxS	Perfluoro-1-hexane sulfonate
PFNA	n-Perflouorononanoic acid
PFOA	n-Perflouorooctanoic acid
PFOI	Perfluorooctyl iodide
PFOPA	Perfluorooctylphosphonic acid
PFOS	Perfluoro-1-octane sulfonate
PFPA	Perfluoroalkyl phosphonic acid
PFPeA	n-Perfluoropentanoic acid
PFPrA	Perfluoropropionic acid
PFSA	Perfluoroalkanesulfonic acids
PFTeA	n-Perfluorotetradecanoic acid
PFTrA	n-Perfluorotridecanoic acid
POP	Persistent organic pollutants
PTFE	Polytetrafluoroethylene
QCS	Quality control standard
RCC	Regularized canonical correlations analysis
RCF	Relative centrifugal force
REACH	Regulation, evaluation, authorisation and restriction of chemicals
RF	Radio frequency
RSD	Relative standard deviation
SD	Standard deviation
SIM	Single ion monitoring
SPE	Solid phase extraction
TFE	Tetrafluoroethylene

t_R	Retention time
WWTP	Wastewater treatment plant

1 Introduction

1.1. Definition, use and effects of PFASs

During the last decade, perfluoroalkyl and polyfluoroalkyl substances (PFASs) have become a notorious group of micropollutants due to their various detrimental effects and properties. PFASs are characterized by an aliphatic structure containing a perfluoroalkyl group (C_nF_{2n+1}). They are subdivided into perfluoroalkyl substances, in which all H atoms in the molecule are formally exchanged by F, and polyfluoroalkyl substances, which contain at least one C-H bond. This definition refers solely to the aliphatic chain not considering functional groups.

The most thoroughly investigated classes of PFASs are perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), especially their C_8 homologs perfluorooctanoic acid (PFOA) and perfluoroalkane sulfonic acid (PFOS). Both PFCAs and PFSAs belong to the group of perfluoroalkyl acids (PFAAs).

Many PFASs exhibit extreme chemical and heat stability and they provide an unrivalled decrease of surface tension as a result of the very strong C-F bond (Krafft and Riess, 2015). These properties have entailed use of PFASs in specialty products since the 1950s and their mix of unique properties render them hard to replace by non-fluorinated substances. However, their stability is also reflected by the persistence of several PFASs congeners, especially PFAAs, in terms of biotransformation and photodegradation, which is further explained in chapter 1.2.

The adverse properties are extended by diverse toxicological and ecotoxicological effects as well as bioaccumulation, which has been well compiled for PFOA and PFOS, but also for other PFAS congeners (Lau et al., 2004, Lau et al., 2007, Suja et al., 2009, Buck et al., 2011, DeWitt et al., 2012, Grandjean and Budtz-Jorgensen, 2013).

As a result of the aforementioned properties, PFOS was amended to Annex B of the Stockholm Convention on Persistent Organic Pollutants (2010) and PFOA as well as C_{11}-C_{14} PFCAs were added to the Candidate List of Substances of Very High Concern within REACH Regulation (ECHA, 2013). Furthermore, a restriction proposal for PFOA has been submitted to ECHA (ECHA, 2015).

1.2. Environmental occurrence and fate of PFASs

While PFCAs and PFSAs are considered non-biodegradable (Key et al., 1998, Saez et al., 2008), several PFASs from different classes have been shown to be transformed biotically or abiotically to PFCAs and PFSAs during the last decade. These compounds can be distinguished between fluorotelomer-based compounds, such as n:2-fluorotelomer alcohols (n:2-FTOHs), and non-fluorotelomer-based compounds, e.g. perfluoroalkane sulfonamides (FASAs) and their derivatives (see Figure 1). In this report, three types of substances will be referred to as precursors:

1. Substances known to yield either PFCAs or PFSAs upon hydrolysis, biotransformation, atmospheric reactions or a combination thereof as a result of scientific investigations.

2. Homologs of substances in 1) with regard to their perfluoroalkyl chain length (e.g. 10:2-FTOH vs 8:2-FTOH). No scientific proof for transformation has been established yet. However, these substances are expected to be transformed to PFCAs or PFSAs as the chemical functional groups mainly govern biotic and abiotic reactions.
3. Chemical derivatives of substances in 1) if these modifications are not considered to alter the processes mentioned in 1) significantly (e.g. exchange of an ethyl group by a methyl group) as well as chemical derivatives of substances in 2).

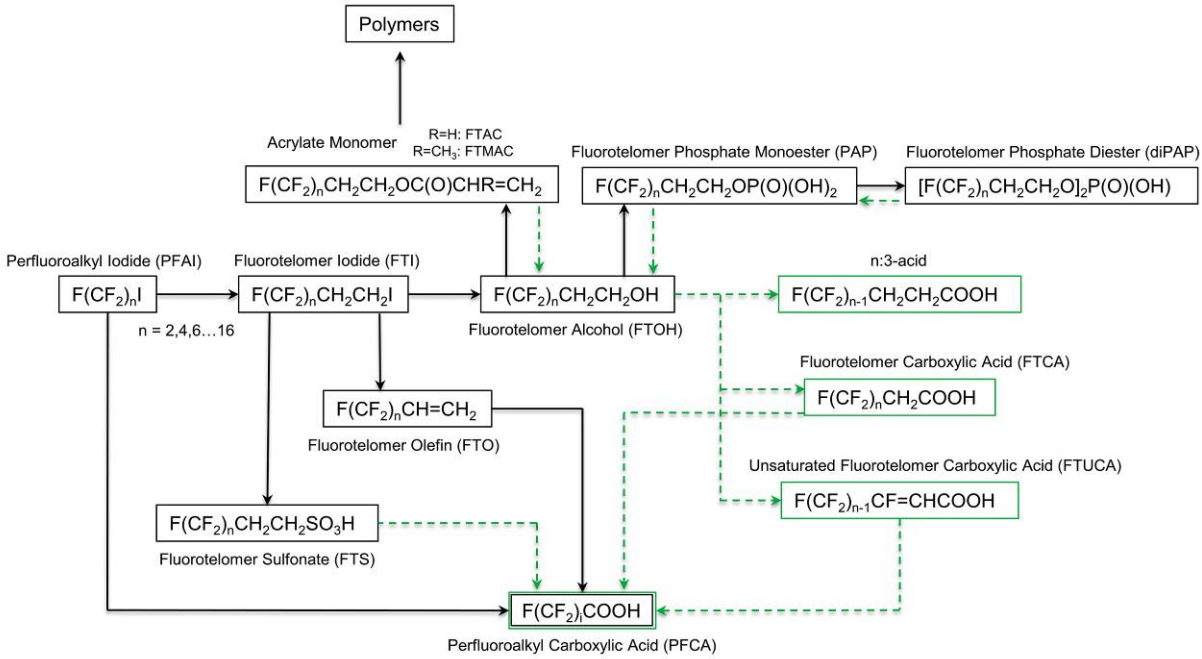


Figure 1: Synthetic pathway (black solid arrows) and biotransformation (dashed green arrows) of fluorotelomer-based PFASs. PFAIs are synthesized by telomerization of tetrafluoroethylene. PFCA chain length is given as "i" as PFCAs of different alkyl chain lengths are formed by biotransformation of fluorotelomer-based PFASs of one specific chain length n (see also Figure 2).

Comprehensive compilations on biotransformation of PFASs can be found in literature reviews (Frömel and Knepper, 2010a, Liu and Mejia Avendano, 2013, Butt et al., 2014, Ruan et al., 2015).

Among the fluorotelomer-based precursor substances, FTOHs have been studied most thoroughly. In several studies 8:2-FTOH has been shown to be degraded to, among other substances, PFOA as well as PFHxA by microbial transformation with different molar conversion rates depending on the inoculum used (Dinglasan et al., 2004, Wang et al., 2005, Wang et al., 2009). Besides PFCAs, a number of other transformation products are formed by FTOH biotransformation (Figure 2). These substances include fluorotelomer aldehydes (FTALs), fluorotelomer carboxylic acids (FTCAs), unsaturated fluorotelomer carboxylic acids (FTUCAs) and x:3-acids (see Figure 1). Similarly, atmospheric transformation of FTOHs leads to several PFCAs (Andersen et al., 2005, Wallington et al., 2006). The carboxylic acid biotransformation products can be considered indicative for biotransformation of FTOHs and possibly for other FTOH derivatives such as fluorotelomer acrylates (FTACs), fluorotelomer methacrylates (FTMACs), polyfluoroalkyl phosphates (PAPs) etc. Since FTOH analysis in aqueous matrices can be defective due to their

complicating physico-chemical properties, verification of FTOH transformation via significant transformation products is believed to be a helpful tool when assessing different sources to PFCA formation.

Besides FTOHs, several other intermediates in fluorotelomer (meth)acrylate synthesis are potential precursors to PFCAs, which may be contained in products as synthetic residuals. Among these, 6:2-fluorotelomer iodide (6:2-FTI) has been investigated so far in terms of biotransformation (Ruan et al., 2013), which yields mainly perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), 5:3-acid and 4:3-acid. The list of fluorotelomer production intermediates analyzed in this study comprises FTIs, perfluoroalkyl iodides (PFAIs) and fluorotelomer olefins (FTOs). Although they do not contain the typical fluorotelomer structure (i.e. perfluoroalkyl moiety and at least one non-fluorinated carbon atom), PFAIs will be covered as fluorotelomer-based as they are synthetic intermediates of these compounds.

Besides FTACs, their methacrylic acid ester analogs FTMACs were appended to the list of target substances, since both FTACs and FTMACs are used to produce polymers (Buck et al., 2011). At least for 8:2-FTAC and 8:2-FTMAC, it was shown that these substances yield PFOA to an extent of 10-15% (Royer et al., 2015).

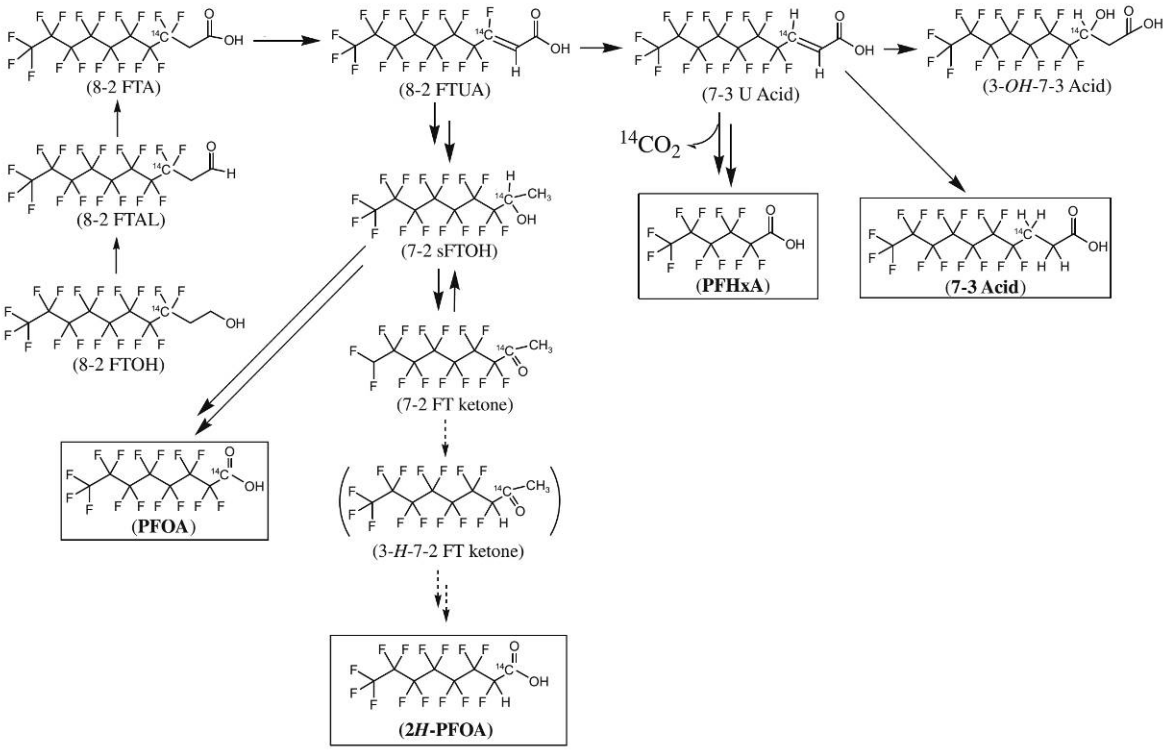


Figure 2: Biotransformation scheme of 8:2-FTOH (reprinted from Wang et al. (2009) with permission).

As has been investigated in our laboratories, fluorotelomer ethoxylates (FTEOs), a group of commercially used fluorotelomer-based compounds, can contribute to the burden of PFCAs (Frömel, 2012). Depending on the biotransformation conditions, ω-oxidized carboxylic acid transformation products (fluorotelomer ethoxycarboxylates, FTEOCs) can occur as biotransformation products (Frömel and Knepper, 2010b). Thus, a set of FTEOs

and FTEOCs was analyzed in the wastewater treatment plant (WWTP) samples and indoor rooms.

Fluorotelomer sulfonates (FTSs) which belong to the fluorotelomer-based PFASs were appended to the list of chemicals, since it was shown that 6:2-FTS can be biotransformed in WWTP activated sludge yielding – among others – PFCAs (Wang et al., 2011).

As mentioned above, PAPs, namely fluorotelomer phosphate monoesters (mono-PAPs) and fluorotelomer phosphate diesters (diPAPs), were investigated in this study. These substances are used mainly food contact paper products (Trier et al., 2011) and have been shown to yield PFCAs upon biotransformation (Lee et al., 2010).

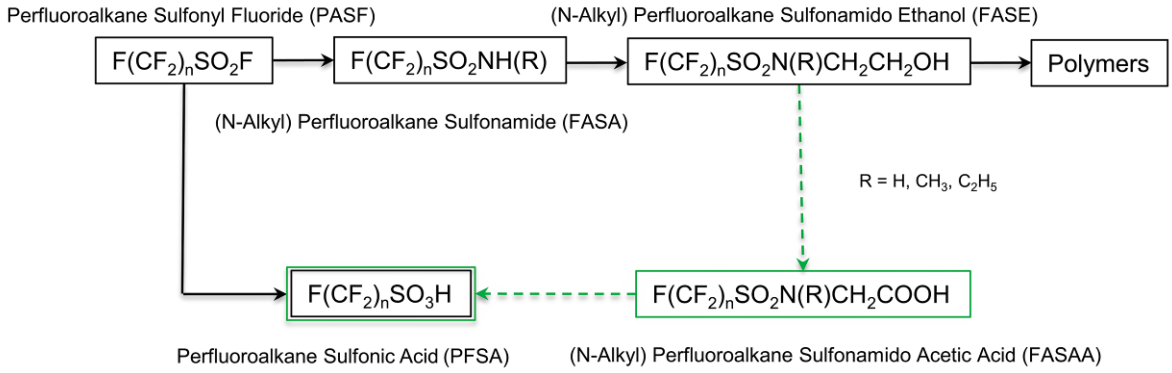


Figure 3: Synthetic pathway (black solid arrows) and biotransformation (dashed green arrows) of sulfonamide-based PFASs. PASF are synthesized by electrochemical fluorination, which is not depicted here.

Several precursors of PFSAs (and partially of PFCAs) were analyzed for in this study (see Figure 3). Among these were perfluorooctane sulfonamide (FOSA) and its N-methyl and N-ethyl derivative as well as N-methyl and N-ethyl perfluorooctane sulfonamidoethanols (N-MeFOSE, N-EtFOSE) which are synthetic intermediates en route to polymers (3M, 1999). The list of PFSA precursors was extended by biotransformation intermediates of FOSEs, namely their oxidized transformation products perfluorooctane sulfonamidoacetic acids (FOSAAs), including the N-methyl and N-ethyl derivatives (Rhoads et al., 2008, Benskin et al., 2013). This ensures the monitoring of FOSE-related biotransformation processes along the WWTP processes.

Substances that might further contribute to the PFCA and PFSA burden in the environment are fluorinated polymers, notably side-chain fluorinated polymers. Such polymers consist of a non-fluorinated backbone such as polyacrylates and polymethacrylates and fluorotelomer or perfluoroalkane sulfonamide-based side-chains connected to the backbone via ester bonds (Russell et al., 2008, Washington et al., 2009, Buck et al., 2011, Rankin and Mabury, 2015). It is still under scientific debate whether such polymers may release FTOHs or perfluoroalkane sulfonamidoethanols (FASAs) into the environment (Russell et al., 2008, Washington et al., 2009) and by which processes such as biotransformation, hydrolysis or photodegradation this might occur. If this was the case, these substances would be transformed to PFCAs and PFSAs, respectively. Polymers were not included in the list of analytes in real samples due to chemical complexity of this class and as no methods exist that could determine these compounds at very low concentrations. Characterization of fluorinated polymer samples was performed in the context of this study (Dimzon et al., 2015). However, another issue regarding fluorinated polymers are unreacted residuals from synthesis of these polymers,

such as the abovementioned FTOHs, FT(M)ACs, FTOs etc., which have been investigated in this study.

The chemical formula for all substances under investigation is presented in 2.1.2, Table 3.

1.3. Occurrence of PFCA and PFSA precursors in the environment

Several of the substances known to be precursors for PFCAs and PFSAs from laboratory experiments have been detected in different kinds of environmental matrices. However, a broad picture representing the relevance of these precursors in real samples has not yet been compiled as most of the articles in scientific literature focus on PFCAs and PFSAs. Precursors, however, have been investigated and detected only sporadically, thus no comprehensive data as to the significance and distribution of these substances is available so far. Therefore, the present study focusses on detection of PFAS precursors rather than traditional PFCAs and PFSAs in order to 0assess the extent to which the precursors contribute to environmental PFAS concentrations.

A review covering the detection of precursors has been published by Ahrens (2011). A compilation of these findings amended by more recent data is summarized in Table 3. For chemical structures, please refer to Table 3.

Table 1: Overview of precursor substances detected in environmental matrices. Chain length refers to the perfluoroalkyl chain length only (Me=methyl, Et=ethyl, PFSI=Perfluoroalkyl sulfinates).

Compound Class	Compartment	Chain Length (and other modifications)	Reference
FTOH	Outdoor air (Northwest Europe)	4, 6, 8, 10, 12	(Barber et al., 2007)
	Urban and rural air (Germany)	4, 6, 8, 10	(Jahnke et al., 2007a)
	Air (North Sea)	6, 8, 10, 12	(Xie et al., 2013)
	Remote air (Asia and West US)	6, 8, 10	(Piekarz et al., 2007)
	Atmosphere (Canadian Arctic)	6, 8, 10	(Ahrens et al., 2011a)
	Atmosphere (Asia)	4, 6, 8, 10, 12	(Li et al., 2011)
	Air above WWTP (Canada)	6, 8, 10	(Ahrens et al., 2011b)
	Air above landfill (Canada)	6, 8, 10	
FTO	Outdoor air (Northwest Europe)	6, 8, 10, 12	(Barber et al., 2007)
	Atmosphere (Asia)	8	(Li et al., 2011)

Compound Class	Compartment	Chain Length (and other modifications)	Reference
FTCA	Urban rain water (Canada)	8, 10	(Loewen et al., 2005)
	Precipitation (North American)	8, 10	(Scott et al., 2006)
	Treated leachate (Germany)	6	(Busch et al., 2010)
FTUCA	Urban rain water (Canada)	8, 10	(Loewen et al., 2005)
	Precipitation (North American)	8, 10	(Scott et al., 2006)
	River water (Elbe, Germany)	8, 10	(Ahrens et al., 2009)
	Treated leachate (Germany)	6, 8	(Busch et al., 2010)
FASA	Outdoor air (Northwest Europe)	C_4, R=Me C_8, R=H, Me, Et	(Barber et al., 2007)
	Urban and rural air (Germany)	C_8, R=Me, Et	(Jahnke et al., 2007a)
	Air (US)	C_8, R=H	(Kim and Kannan, 2007)
	Remote air (Asia and West US)	C_8, R=Et	(Piekarz et al., 2007)
	Air (North Sea)	C_4, R=Me C_8, R=Me, Et	(Xie et al., 2013)
	Air above WWTP	C_8, R=Me/Et	(Ahrens et al., 2011b)
	Air above landfill	C_8, R=Me/Et	(Ahrens et al., 2011b)
	Atmosphere (Asia)	C_8, R=Me, Et	(Li et al., 2011)
	Air (WWTP aeration tank and secondary clarifier (Canada)	C_8, R=H	(Vierke et al., 2013)
	Rain surface runoff water (US)	C_8, R=H	(Kim and Kannan, 2007)
	River water (Japan)	C_8, R=H	(Murakami et al., 2008)
	River water (Elbe, Germany)	C_8, R=H	(Ahrens et al., 2009)
	Sea water (Arctic Ocean)	C_8, R=H	(Cai et al., 2012b)
	Coastal water (East to South China)	C_8, R=Et	(Cai et al., 2012a)
	WWTP effluent (US)	C_8, R=H	(Plumlee et al., 2008)
	WWTP effluent (Germany)	C_4, R=Me C_8, R=Me	(Ahrens et al., 2009)
	Treated leachate (Germany)	C_8, R=H	(Busch et al., 2010)
	Ice (Arctic Sea)	C_8, R=H	(Cai et al., 2012b)

Compound Class	Compartment	Chain Length (and other modifications)	Reference
FASAA	WWTP effluent (US)	C_8, R=Et	(Plumlee et al., 2008)
FASE	Outdoor air (Northwest Europe)	C_4, R=Me C_8, R=Me/Et	(Barber et al., 2007)
	Urban and rural air (Germany)	C_8, R=Me/Et	(Jahnke et al., 2007a)
	Air (North Sea)	C_4, R=Me	(Xie et al., 2013)
	Remote air (Asia and West US)	C_8, R=Me/Et	(Piekarz et al., 2007)
	Atmosphere (Asia)	C_4, R=Me C_8, R=Me/Et	(Li et al., 2011)
	Air above WWTP (Canada)	C_8, R=Me/Et	(Ahrens et al., 2011b)
	Air above landfill (Canada)	C_8, R=Me/Et	
	Sea water (Arctic Ocean)	C_8, R=Me	(Cai et al., 2012b)
	WWTP effluent (Germany)	C_4, R=Me	(Ahrens et al., 2009)
	Treated leachate (Germany)	C_4, R=Me C_8, R=Me	(Busch et al., 2010)
	Ice (Arctic Sea)	C_4, R=Me	(Cai et al., 2012b)
FTS	Urban rain water (US)	6, 8	(Kim and Kannan, 2007)
	Snow (US)	8	(Kim and Kannan, 2007)
	Lake water (US)	8	(Kim and Kannan, 2007)
	Snow surface runoff water(US)	6, 8	(Kim and Kannan, 2007)
	Rain surface runoff water (US)	6, 8	(Kim and Kannan, 2007)
	River water (Elbe, Germany)	6	(Ahrens et al., 2009)
	WWTP effluent (US)	6	(Plumlee et al., 2008)
	WWTP effluent (Germany)	6	(Ahrens et al., 2009)
	Treated leachate (Germany)	6	(Busch et al., 2010)
diPAP	WWTP sludge (Canada)	6, 8, 10 (+ mixed)	(D'eon et al., 2009a)
PFPA	Surface water, creek water, WWTP effluent (Canada)	6, 8, 10	(D'eon et al., 2009b)
	Treated leachate (Germany)	6, 8, 10	(Busch et al., 2010)
	WWTP effluents (Germany)	6, 8, 10	(Llorca et al., 2012)

Compound Class	Compartment	Chain Length (and other modifications)	Reference
PFAI	Soil (proximity to fluorotelomer manufacturing plant, China)	8, 10, 12	(Ruan et al., 2010)
	Air (proximity to fluorotelomer manufacturing plant, China)	6, 8, 10, 12	
FTI	Soil (proximity to fluorotelomer manufacturing plant, China)	6, 8, 10	(Ruan et al., 2010)
	Air (proximity to fluorotelomer manufacturing plant, China)	6, 8, 10	
PFSI	WWTP effluent (Germany)	6, 8	(Ahrens et al., 2009)
	River water (Elbe, Germany)	8	
	Treated leachate (Germany)	6, 8	(Busch et al., 2010)

So far, physico-chemical properties of the analytes determine in which compartments PFAS precursors were analyzed. Thus, volatile substances such as FTOHs were measured and detected in various kinds of gaseous samples, such as atmospheric air and air above WWTPs and landfills as well as indoor air. Indeed, there is currently no evidence for occurrence of FTOHs in aqueous samples. Contrarily, non-volatile precursors such as FTSs were only analyzed in aqueous samples.

1.4. Scope of the study

Many studies have been carried out exploring the occurrence and sources of PFCAs and PFSAs in the environment. In addition to sources resulting from the use of these chemicals, named ‘direct sources’ (Prevedouros et al., 2006), transformation of fluorinated precursor compounds to PFCAs and PFSAs was observed in numerous laboratory experiments, where reactions may involve abiotic, especially atmospheric reactions, as well as biotic transformation by microorganisms (Buck et al., 2011) as delineated in chapter 1.3.

In several studies, it was observed that concentrations of certain PFAAs were higher in WWTP effluents than in the corresponding influents suggesting transformation of precursor substances as a source of the PFASs investigated (Sinclair and Kannan, 2006, Kunacheva et al., 2011, Pan et al., 2011, Chen et al., 2012). However, the occurrence of individual precursor substances has been rarely determined so far or only a small subset of potential precursors were included in these studies as shown in chapter 1.3. Therefore, the present study aims at the identification of relevant precursor substances of PFAAs in WWTPs, which are an important environmental source for micropollutants in general (Reemtsma and Jekel, 2006) and for PFASs specifically (Sinclair and Kannan, 2006, Buck et al., 2011, Arvaniti and Stasinakis, 2015). Furthermore, indoor rooms, where PFAS-containing consumer products can be present, were sampled and (Jahnke et al., 2007a, Goosey and Harrad, 2011, Haug et al., 2011, Schlummer et al., 2013).

In the present study, a set of 65 PFAS congeners were monitored in terms of a comprehensive investigation of WWTPs as well as indoor air and dust. By screening for

such a large set of PFAAs and their precursors, relevant substances should be assessed and at the same time, the current levels of PFAAs can be determined. Inclusion of industrial WWTPs with presumably higher levels of PFASs allows identification of relevant precursors near the source, which has not yet been studied to our knowledge. Additional non-target screening should allow detection and identification of further compounds completing the assessment of relevant PFASs in the environment.

2 Materials and Methods

2.1 Chemicals used during the study

2.1.1 Chemicals

The chemicals that were used in this study are listed in Table 2.

Table 2: List of chemicals used.

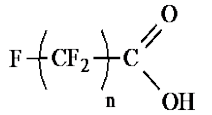
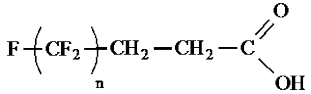
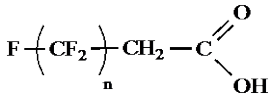
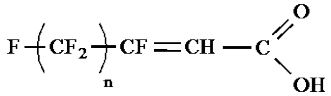
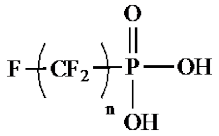
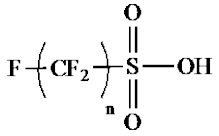
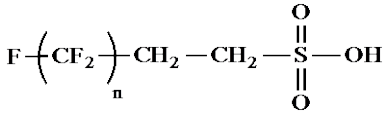
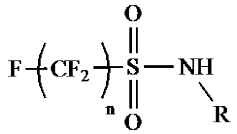
Chemical	Purity	Manufacturer
Acetone	SupraSolv® ≙ 99.8%	Merck, Darmstadt, Germany
Acetonitrile	Ultra LC-MS ≙ 99.98%	Carl Roth, Karlsruhe, Germany
Ammonium acetate	p.a. ≙ 99.0%, LC-MS grade	Sigma Aldrich, Buchs, Switzerland
Methanol	Ultra LC-MS ≙ 99.98%	Carl Roth, Karlsruhe, Germany
Methanol	ULC/MS grade, 99.98%	Biosolve, Dieuze, France
Isopropanol	SupraSolv® ≙ 99.8%	Merck, Darmstadt, Germany
Glacial acetic acid	≙ 99%	Roth, Karlsruhe, Germany
Ammonia	30%	Roth, Karlsruhe, Germany
EnviCarb	-	Sulpelco, Bellefonte, United States
n-Pentane	HPLC grade, 99%	Biosolve, Dieuze, France

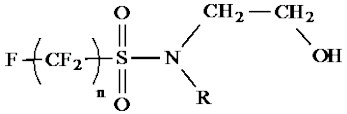
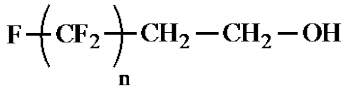
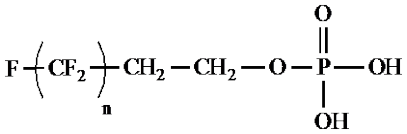
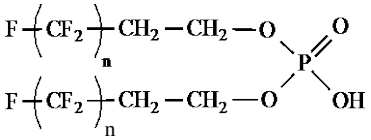
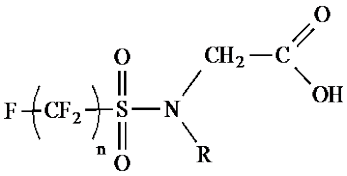
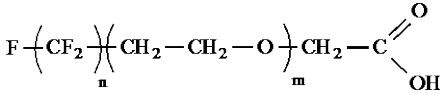
Milli-Q-water was prepared using a Millipore Direct-Q3 system with a SmartPak® Cartridge (Millipore, Milford, USA).

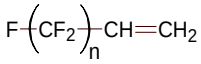
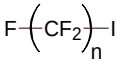
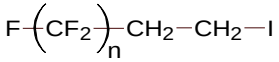
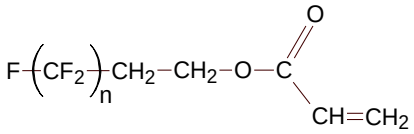
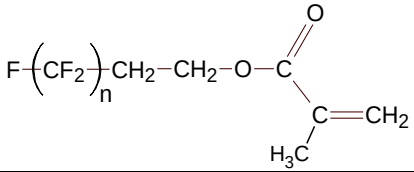
2.1.2 Analytes

During this study, 65 compounds were analyzed in addition of 26 ^{2}H, ^{18}O and ^{13}C labelled internal standards and two non-mass-labelled internal standards. Table 3 and Table 4 show the structures of these compounds, their acronyms and the acronyms for the different number of carbon atoms in the substances.

Table 3: Structures and acronyms of analytes (Me=Methyl, Et=Ethyl).

Structure	Acronym substance class	Acronym single compounds	Variations	Instrumental method
	PFCA (Perfluoroalkyl carboxylic acid)	PF*X*A	n=3-13	HPLC-MS-a
	x:3-Acid	n:3-acid	n=3-7	HPLC-MS-a
	n:2-FTCA (n:2-Fluorotelomer acid)	n:2-FTCA	n=6,8,10	HPLC-MS-a
	FTUCA (Unsaturated fluorotelomer acid)	n:2-FTUCA	n=6,8,10	HPLC-MS-a
	PFPA (Perfluoroalkyl phosphonic acid)	PF*X*PA	n=6, 8, 10	HPLC-MS-a
	PFSA (Perfluoroalkane sulfonic acid)	PF*X*S	n=4, 6, 7, 8, 10	HPLC-MS-a
	FTS (Fluorotelomer sulfonic acid)	n:2-FTS	n=4, 6, 8	HPLC-MS-a
	FASA (Perfluoroalkane sulfonamide)	N-Me/N-EtF*X*SA	n=8 R=H, Me, Et	HPLC-MS-a

Structure	Acronym substance class	Acronym single compounds	Variations	Instrumental method
	FASE (Perfluoroalkane sulfonamidoethanol)	N-Me/N-EtFχSE	n=8 R=Me, Et	HPLC-MS-n
	FTOH (Fluorotelomer alcohol)	n:2-FTOH	n=6, 8, 10	HPLC-MS-n
	mono-PAP (Monoalkylated fluorotelomer phosphate)	n:2-PAP	n=6, 8	HPLC-MS-a
	di-PAP (Dialkylated fluorotelomer phosphate)	n:2-diPAP	n=6, 8	HPLC-MS-a
	FASAA (Perfluoroalkane sulfonamidoacetic acid)	FχSAA	n=8 R=H, Me, Et	HPLC-MS-a
	FTEOC (Fluorotelomer ethoxycarboxylate)	n:2-FTEO$_m$C	n=6, 8 m=1	HPLC-MS-a

Structure	Acronym substance class	Acronym single compounds	Variations	Instrumental method
	FTO (Fluorotelomer olefin)	n:2-FTO	n=6, 8, 10	GC-MS
	PFAI (Perfluoroalkyl iodide)	PF*X*I	n=4, 6, 8, 10	GC-MS
	FTI (Fluorotelomer iodide)	n:2-FTI	n=4, 6, 8	GC-MS
	FTAC (Fluorotelomer acrylate)	n:2-FTAC	n=6, 8	GC-MS
	FTMAC (Fluorotelomer methacrylate)	n:2-FTMAC	n=6, 8	GC-MS

R: Methyl group, ethyl group; n/m: number of perfluorinated carbon atoms; *X*: acronym of carbon atoms, shown in Table 4; m: number of repeating units

Table 4: Acronyms for alkyl chain lengths in non-fluorotelomer-based compounds as well as for PFAIs.

Number of carbon atoms	Acronym	Number of carbon atoms	Acronym
3	Pr	9	N
4	B	10	D
5	Pe	11	Un
6	Hx	12	Do
7	Hp	13	Tr
8	O	14	Te

2.1.3 Reference materials

For calibration and validation several mixtures and individual substances of PFASs, which were obtained by the suppliers Neochema (Bodenheim, Germany), Wellington (Ontario, Canada) and DuPont (Wilmington, DE, USA) were used. Two compounds were synthesized by the Institute For Analytical Research (IFAR, Idstein, Germany). A list of these compounds is shown in Table 5.

For the internal standards the mixtures MPFAX-M, MFOET from Wellington that contain only ^{13}C, ^{18}O and ^{2}H labelled compounds were applied in addition of 13 individual substances from Wellington and one compound from DuPont. Spiking solutions of these compounds were prepared in methanol (MeOH).

Table 5: List of PFAS reference materials purchased in solution.

(Brand) Name (Supplier)	Compound	Acronym	Concentration [µg/mL]
PFT-Mix 11 (Neochema)	n-Perfluorobutanoic acid	PFBA	10
	n-Perfluoropentanoic acid	PFPeA	
	n-Perfluorohexanoic acid	PFHxA	
	n-Perfluoroheptanoic acid	PFHpA	
	n-Perfluorooctanoic acid	PFOA	
	n-Perfluorononanoic acid	PFNA	
	n-Perfluorodecanoic acid	PFDA	
	n-Perfluoroundecanoic acid	PFDUnA	
	n-Perfluorododecanoic acid	PFDoA	
	n-Perfluorotridecanoic acid	PFTrA	
	n-Perfluorotetradecanoic acid	PFTeA	
6:2-FTCA (Wellington)	2-Pefluorohexyl ethanoic acid	6:2-FTCA	50
8:2-FTCA (Wellington)	2-Pefluorooctyl ethanoic acid	8:2-FTCA	50
10:2-FTCA	2-Perfluorodecyl ethanoic acid	10:2-FTCA	50

(Brand) Name (Supplier)	Compound	Acronym	Concentration [μg/mL]
(Wellington)			
6:2-FTUCA (Wellington)	2H-Pefluoro-2-octenoic acid	6:2-FTUCA	50
8:2-FTUCA (Wellington)	2H-Pefluoro-2-Decenoic acid	8:2-FTUCA	50
10:2-FTUCA (Wellington)	2H-Pefluoro-2-dodecenoic acid	10:2-FTUCA	50
PFHxPA (Wellington)	Perfluorohexylphosphonic acid	PFHxPA	50
PFOPA (Wellington)	Perfluorooctylphosphonic acid	PFOPA	50
PFDPA (Wellington)	Perfluorodecylphosphonic acid	PFDPA	50
3:3-acid (DuPont)	2H,2H,3H,3H-Perfluorohexanoic acid	3:3-acid	3010
4:3-acid (DuPont)	2H,2H,3H,3H-Perfluoroheptanoic acid	4:3-acid	2900
5:3-acid (DuPont)	2H,2H,3H,3H-Perfluorooctanoic acid	5:3-acid	1020
6:3-acid (DuPont)	2H,2H,3H,3H-Perfluorononanoic acid	6:3-acid	1040
7:3-acid (DuPont)	2H,2H,3H,3H-Perfluorodecanoic acid	7:3-acid	1220
PFS-MXA (Wellington)	Potassium perfluoro-1-butanesulfonate Sodium perfluoro-1-hexanesulfonate Sodium perfluoro-1-heptanesulfonate Sodium perfluoro-1-octanesulfonate Sodium perfluoro-1-decanesulfonate	PFBS PFHxS PFHpS PFOS PFDS	2
4:2-FTS (Wellington)	Sodium 1H,1H,2H,2H-perfluorohexane sulfonate	4:2-FTS	50
6:2-FTS (Wellington)	Sodium 1H,1H,2H,2H-perfluorooctane sulfonate	6:2-FTS	50
8:2-FTS (Wellington)	Sodium 1H,1H,2H,2H,-perfluorodecane sulfonate	8:2-FTS	50
FOSAA (Wellington)	Perfluoro-1-octanesulfonamidoacetic acid	FOSAA	50

(Brand) Name (Supplier)	Compound	Acronym	Concentration [μg/mL]
N-MeFOSAA (Wellington)	N-Methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA	50
N-EtFOSAA (Wellington)	N-Ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	50
6:2-FTEO1C (IFAR)	1H,1H,2H,2H-Perfluorooctoxy acetic acid	6:2-FTEO$_1$C	1240
8:2-FTEO1C (IFAR)	1H,1H,2H,2H-Perfluorodecoxy acetic acid	8:2-FTEO$_1$C	1140
6:2-PAP (Wellington)	Sodium 1H,1H,2H,2H-perfluorooctylphosphate	6:2-PAP	50
8:2-PAP (Wellington)	Sodium 1H,1H,2H,2H-perfluorodecylphosphate	8:2-PAP	50
6:2-diPAP (Wellington)	Sodium bis(1H,1H,2H,2H-perfluorooctyl) phosphate	6:2-diPAP	50
8:2-diPAP (Wellington)	Sodium bis(1H,1H,2H,2H-perfluorodecyl) phosphate	8:2-diPAP	50
6:2-FTOH (Neochema)	1H,1H,2H,2H-Perfluoro-1-octanol	6:2-FTOH	50
8:2-FTOH (Neochema)	1H,1H,2H,2H-Perfluoro-1-decanol	8:2-FTOH	50
10:2-FTOH (Neochema)	1H,1H,2H,2H-Perfluoro-1-dodecanol	10:2-FTOH	50
FOSA-M (Wellington)	Perfluoro-1-octanesulfonamide	FOSA	50
N-MeFOSA-M (Wellington)	N-methylperfluoro-1-octanesulfonamide	N-MeFOSA	50
N-EtFOSA-M (Wellington)	N-ethylperfluoro-1-octanesulfonamide	N-EtFOSA	50
N-MeFOSE-M (Wellington)	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	N-MeFOSE	50
N-EtFOSE-M (Wellington)	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	N-EtFOSE	50

(Brand) Name (Supplier)	Compound	Acronym	Concentration [μg/mL]
PFAX-MXA (Wellington)	Sodium perfluoro-1-hexane[$^{18}O_2$]sulfonate	MPFHxS	2
	Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	MPFOS	
	Perfluoro-n-[$^{13}C_4$]butanoic acid	MPFBA	
	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	MPFHxA	
	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	MPFOA	
	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	MPFNA	
	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	MPFDA	
	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	MPFUnA	
	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	MPFDoA	
MPFPeA (Wellington)	Perfluoro-n-[$^{13}C_5$]pentanoic acid	MPFPeA	50
MPFHpA (Wellington)	Perfluoro-n-[1,2,3,4$^{13}C_4$]heptanoic acid	MPFHpA	50
M-6:2-FTCA (Wellington)	2 Perfluorohexyl [1,2 $^{13}C_2$] ethanoic acid	M-6:2-FTCA	50
M-8:2-FTCA (Wellington)	2-Pefluorooctyl-[1,2 $^{13}C_2$]-ethanoic acid	M-8:2-FTCA	50
M-6:2FTUCA (Wellington)	2H-Pefluoro-[1,2$^{13}C_2$]-2-octenoic acid	M-6:2-FTUCA	50
M-8:2-FTUCA (Wellington)	2H-Pefluoro-[1,2$^{13}C_2$]-2-decenoic acid	M-8:2-FTUCA	50
M-10:2-FTUCA (Wellington)	2H-Pefluoro-[1,2$^{13}C_2$]-2-dodecenoic acid	M-10:2FTUCA	50
M-8:2-PAP (Wellington)	Sodium 1H,1H,2H,2H-[1,2$^{13}C_2$]-perfluorodecylphosphate	M-8:2-PAP	50
M-8:2-diPAP (Wellington)	Sodium bis(1H,1H,2H,2H-[1,2$^{13}C_2$]-perfluorodecyl) phosphate	M-8:2-diPAP	50
M-6:2-FTS (Wellington)	Sodium 1H,1H,2H,2H-perfluoro-[1,2 $^{13}C_2$]-octane sulfonate	M-6:2-FTS	50
M-N-MeFOSA (Wellington)	N-methyl-$^2H_3$-perfluoro-octanesulfonamide	M-N-MeFOSA	50
M-N-EtFOSA (Wellington)	N-ethyl-$^2H_3$-perfluoro-1-octanesulfonamide	M-N-EtFOSA	50

(Brand) Name (Supplier)	Compound	Acronym	Concentration [μg/mL]
M-N-EtFOSAA (Wellington)	N-ethyl-$^{2}H_3$-perfluoro-1-octanesulfonamidoacetic acid	M-N-EtFOSAA	50
M-N-EtFOSAA (Wellington)	N-ethyl-$^{2}H_5$-perfluoro-1-octanesulfonamidoacetic acid	M-N-EtFOSAA	50
M-6:2-FTOH (DuPont)	1H,1H,2H,2H-Perfluoro[^{13}C,$^{2}H_4$]-1-octanol	M-6:2-FTOH	333
MFOET (Wellington)	2-Perfluorooctyl-[1,1,-$^{2}H_2$]-[1,2-$^{13}C_2$]-ethanol	M-8:2-FTOH	50

Another set of substances was purchased from ABCR as pure solids or liquids with purities ranging from 95% to 99%. These compounds are summarized in Table 6.

Due to a lack of mass-labeled internal standards for these substances, three structurally similar compounds were purchased and used as internal standards. These two substances exhibit structural features that are synthetically challenging and thus not expected to be used in industrial processes. These features are an exchange of fluorine by hydrogen in position 7 (7H-6:1-FTI), trifluoromethyl branching in position 7 (7Me-6:2-FTI) and an odd carbon number in a fluorotelomer-based substance (7Me-6:2-FTI and 7:1-FTAC; fluorotelomer compounds usually exhibit an even number of perfluorinated carbon atoms (Buck et al., 2011)).

Table 6: List of PFAS reference materials purchased as pure solid or liquid materials. Substances labeled with * were used as internal standards.

Substance class	Compound	Acronym
FTO	1H,1H,2H-Perfluoro-1-octene	6:2-FTO
	1H,1H,2H-Perfluoro-1-decene	8:2-FTO
	1H,1H,2H-Perfluoro-1-dodecene	10:2-FTO
PFAI	Perfluoro-n-butyl iodide	PFBI
	Perfluoro-n-hexyl iodide	PFHxI
	Perfluorooctyl iodide	PFOI
	Perfluorodecyl iodide	PFDI
FTI	1H,1H,2H,2H-Perfluorohexyl iodide	4:2-FTI
	1H,1H,2H,2H-Perfluorooctyl iodide	6:2-FTI
	1H,1H,2H,2H- Perfluorodecyliodide	8:2-FTI
	1H,1H,7H-Dodecafluoroheptyl iodide	7H-6:1-FTI*
	1H,1H,2H,2H-Perfluoro-7-methyloctyl iodide	7Me-6:2-FTI*
FTAC	1H,1H,2H,2H-Perfluorooctyl acrylate	6:2-FTAC
	1H,1H-Perfluorooctyl acrylate	7:1-FTAC*
	1H,1H,2H,2H-Perfluorodecyl acrylate	8:2-FTAC
FTMAC	1H,1H,2H,2H-Perfluorooctyl methacrylate	6:2-FTMAC
	1H,1H,2H,2H-Perfluorodecyl methacrylate	8:2-FTMAC

2.1.4 Other materials

- Plastic pipettes (10 µL, 200 µL, 1000 µL, 5000 µL, 10,000 µL) (Thermo Scientific, Waltham, USA)
- Pipette tips (10 µL, 50 µL, 100 µL, 1000 µL, 5000 µL, 10,000 µL) (Thermo Scientific, Waltham, USA)
- Micro test tubes, 1.5 mL (Eppendorf, Hamburg, Germany)
- Conical centrifugation tubes, 15 mL (Kartell S.p.A., Noviglio, Italy)
- Oasis WAX SPE cartridge, 60 mg, 3 cm^3 (Waters Corporation, Milford, United States)
- Oasis HLB SPE cartridges, 60 mg, 3 cm^3 (Waters Corporation, Milford, United States)
- Centrifuge 5810 R (Eppendorf, Hamburg, Germany)
- Analytical balance: Type A 200 S, range: 0 – 200 mg, e = 0.1 mg (Sartorius, Göttingen, Germany)
- Disposable weighing pans, 50 mL (Roth, Karlsruhe, Germany)
- Scout® Pro SP6000, range: 1 g-6,000 g, e = 1.0 g (Ohaus, Pine Brook, USA)

- Orbital shaker KL 2 (Edmund Bühler, Tübingen, Germany)
- Syringe filter: Spartan® 13/0,45 RC, 0.45 µm, brown ring L (Schleicher & Schuell, Dassel, Germany)
- Single-use fine dosage syringes Omnifix®-F 1 mL (B.Braun, Melsungen, Germany)
- Cannula: Sterican®, diameter: 0.80, 40 mm (B.Braun, Melsungen, Germany)
- Glass vials 24 mL, clear, 86 x 23 mm, with screw caps (A-Z Analysenzubehör, Langen, Germany)
- LC thread polypropylene vials 500 µL (A-Z Analysenzubehör, Langen, Germany)
- LC thread glass vials 1.5 mL, clear, with screw caps (A-Z Analysenzubehör, Langen, Germany)
- 2 mL PP cryo vial (VWR, Radnor, United States)
- Glass Pasteur pipettes, open jet, length: 150 mm / 230 mm (VWR, Darmstadt, Germany)
- Sample concentrator SC 3 (Barkey, Leopoldshöhe, Germany), connected to nitrogen 5.0
- Syringe filter (degenerated cellulose, pore size of 0.45 µm, Schleicher & Schuell (Dassel, Germany)

2.2 Instrumental methods

2.2.1 HPLC-MS/MS

2.2.1.1 General setup

A device of Perkin Elmer Series 200 liquid chromatograph combined with a reversed-phase column was used for separation of the analytes by HPLC. The analytical C_{18} column (MZ-Aqua Perfect®, 50 x 2.1 mm, 5 µm) was protected by a C_{18} precolumn (MZ-Aqua Perfect® precolumn, 5 µm, MZ Analysentechnik, Mainz, Germany). Eluent A was H_2O with 5% MeOH and 5 mM ammonium acetate and eluent B contained 95% MeOH with 5% H_2O and 5 mM ammonium acetate. The injection volume in both methods was 50 µL.

The HPLC system was coupled to a hybrid triple quadrupole/linear ion trap mass spectrometer (Applied Biosystems 3200 Q TRAP, software Analyst®, version 1.5.1, AB Sciex, Framingham, MA, USA) in MRM and sMRM mode and negative ESI was used for determination of PFASs. Nitrogen for spray gas, desolvation gas and collision-induced dissociation was supplied by an SF 4 FF oil-free orbiting scroll compressor (Atlas Corpo, Stockholm, Sweden) and a membrane nitrogen generator NGM-22-LC/MS (CMC, Eschborn, Germany).

Two HPLC-MS/MS methods were used during this study. The HPLC-MS-a includes 47 analytes and was applied to measure substances that can be measured as their deprotonated molecule after ESI, where ‘a’ stands for ‘acidic’. The method is described in detail in chapter 2.2.1.2.

The HPLC-MS-n ('n' indicating neutral substances, which are ionized as their acetate adduct in negative ESI) method was used for the experiments, which includes the FTOHs (6:2, 8:2, 10:2-FTOH) and FOSEs (N-MeFOSE and N-EtFOSE) and is explained in chapter 2.2.1.3.

The assignment of substance classes to the instrumental methods used to measure them is depicted in Figure 7 in 2.4.2.1.

2.2.1.2 HPLC-MS-a method

The HPLC-MS-a method was used for the determination of PFASs which can be measured as the respective $[M-H]^-$ ion after negative ESI. An overview of these substances is shown in Table 8.

The HPLC flow rate was 300 µL/min using the gradient shown in

Table 7.

Table 7: HPLC gradient of the HPLC-MS-a method.

Total Time [min]	A [%]	B [%]
0	100	0
0.5	100	0
2	35	65
10	0	100
15	0	100
17	100	0
27	100	0

Due to the large number of transitions within this method, the MS was operated in 'scheduled MRM' (sMRM) mode, i.e. transitions of the substances were monitored only around the retention time of the individual substance. The sMRM window was set to 120 s. The sMRM parameters of the MS/MS method, as well as the assigned internal standards and the retention time of all substances are shown in Table 8. MRM transitions and their individual optimized voltages are presented in Table 72 in the annex and the instrumental non-compound dependent parameters are shown in Table 71 in the annex.

Table 8: Overview of the MS/MS method, MRM transition and retention time of the HPLC-MS-a method.

Substance	MW [g/mol]	MRM transition [*m/z*, $[M-H]^-$]		Internal Standard	t_R [min]
		Quantifier	Qualifier		
PFBA	214	213 > 169	-	MPFBA	3.9
PFPeA	264	263 > 219	-	MPFPeA	4.3
PFHxA	314.1	313 > 269	313 > 119	MPFHxA	4.6
PFHpA	364.1	363 > 319	363 > 169	MPFHpA	5
PFOA	414.1	413 > 369	413 > 169	MPFOA	5.4
PFNA	464.1	463 > 419	463 > 169	MPFNA	6
PFDA	514.1	513 > 469	513 > 269	MPFDA	6.9
PFUnA	564.1	563 > 519	563 > 319	MPFUnA	7.7
PFDoA	614.1	613 > 569	613 > 219	MPFDoA	8.5
PFTrA[1]	664.1	663 > 619	663 > 169	MPFDoA	9.1
PFTeA[1]	714.1	713 > 669	713 > 169	MPFDoA	9.8
6:2-FTCA	378	377 > 243	377 > 63	M-6:2-FTCA	5.1
8:2-FTCA	478	477 > 63	477 > 393	M-8:2-FTCA	6.4
10:2-FTCA[1]	578	577 > 63	577 > 493	M-8:2-FTCA	8
6:2-FTUCA	358	357 > 293	-	M-6:2-FTUCA	5.1
8:2-FTUCA	458	457 > 393	-	M-8:2-FTUCA	6.3
10:2-FTUCA	558	557 > 493	-	M-10:2-FTUCA	8
PFHxPA	400	399 > 79	-	M-(CI)PFHxPA	4.3
PFOPA[1]	500	499 > 79	-	M-(CI)PFHxPA	5
PFDPA[1]	600	599 > 79	-	M-(CI)PFHxPA	6.2
3:3-acid[1]	242.1	241 > 117	241 > 177	MPFHxA	4.3
4:3-acid[1]	292.1	291 > 167	291 > 187	MPFHxA	4.7
5:3-acid[1]	342.1	341 > 217	341 > 237	MPFHxA	5.1
6:3-acid[1]	392.1	391 > 267	391 > 287	MPFOA	5.6
7:3-acid[1]	442.1	441 > 317	441 > 337	MPFOA	6.2
PFBS[1]	300.1	299 > 80	299 > 99	MPFHxA	4.3
PFHxS	400.1	399 > 80	399 > 99	MPFHxS	5
PFHpS[1]	450. 1	449 > 80	449 > 99	MPFOA	5.4
PFOS	500.1	499 > 80	499 > 99	MPFOS	6
PFDS[1]	600.1	599 > 80	599 > 99	MPFUnA	7.6
4:2-FTS[1]	328.1	327 > 81	327 > 307	M-6:2-FTS	4.6
6:2-FTS	428.2	427 > 81	-	M-6:2-FTS	5.4
8:2-FTS[1]	528.2	527 > 81	-	M-6:2-FTS	6.8
FOSAA[1]	557	556 > 498	556 > 78	M-N-MeFOSAA	6.7
N-MeFOSAA	571	570 > 169	570 > 219	M-N-MeFOSAA	7.3
N-EtFOSAA	585	584 > 419	584 > 169	M-N-EtFOSAA	7.8

Substance	MW [g/mol]	MRM transition [*m/z*, $[M-H]^-$]		Internal Standard	t_R [min]
		Quantifier	Qualifier		
6:2-FTE01C[1]	422	421 > 75	421 > 255	MPFOA	5.6
8:2-FTE01C[1]	522	521 > 75	521 > 355	MPFDA	7.2
6:2-PAP[1]	444	443 > 79	443 > 97	M-8:2-PAP	-
8:2-PAP	544	543 > 97	543 > 79	M-8:2-PAP	-
6:2-diPAP[1]	790	789 > 97	789 > 79	M-8:2-diPAP	9.4
8:2-diPAP	990	989 > 97	989 > 79	M-8:2-diPAP	11
FOSA[1]	499.2	498 > 78	-	M-N-MeFOSA	6.7
N-MeFOSA	513.2	512 > 169	512 > 219	M-N-MeFOSA	7.3
N-EtFOSA	527.2	526 > 219	527 > 219	M-N-EtFOSA	7.8
6:2/8:2-diPAP	890	889 > 97	889 > 79	-	-
8:2/10:2-diPAP	1090	1089 > 97	1098 > 79	-	-

No internal standard was available for the substances with an index [1]. Instead, mass-labelled standards with similar structure and/or retention time were used. No qualifier transition was determined for PFBA, PFPeA, FTUCAs, PFPAs, 6:2-FTS, 8:2-FTS and FOSA.

The internal standard mix used for the HPLC-MS-a method is shown in Table 9.

Table 9: List of internal standards and the concentration of the spiking solution used for the HPLC-MS-a method.

Internal standard	Concentration [ng/µL]	Internal standard	Concentration [ng/µL]
MPFBA	0.1	M-8:2-FTUCA	0.1
MPFPeA	0.1	M-10:2-FTUCA	0.1
MPFHxA	0.1	M-PFHxPA	1
MPFHpA	0.1	MPFHxS	0.1
MPFOA	0.1	MPFOS	0.1
MPFNA	0.1	M-6:2-FTS	0.1
MPFDA	0.1	M-N-MeFOSA	0.5
MPFUnA	0.1	M-N-EtFOSA	0.5
MPFDoA	0.1	M-N-MeFOSAA	0.5
M-6:2-FTCA	0.5	M-N-EtFOSAA	0.5
M-8:2-FTCA	0.5	M-8:2-PAP	1
M-6:2-FTUCA	0.1	M-8:2-diPAP	0.5

2.2.1.3 HPLC-MS-n method

The HPLC-MS-n method was used for determination of substances measures as acetate adducts after negative ESI, namely FTOHs (6:2, 8:2- and 10:2-FTOH) and FOSEs (N-MeFOSE and N-EtFOSE). The same chromatographic system was used as for HPLC-MS-a method, only the HPLC flow rate was changed to 200 µL/min. The gradient is presented in Table 10.

Table 10: HPLC gradient of the HPLC-MS-n method.

Total Time [min]	A [%]	B [%]
0	50	50
2	50	50
8	0	100
10	0	100
12	50	50
25	50	50

An overview of the MS parameters, internal standards and retention times is shown in

Table 11. Detailed MRM parameters of this method are shown in the annex (Table 74) and the compound-independent parameters are shown in Table 73 in the annex.

Table 11: Overview of the MS/MS parameters, MRM transition and retention time of the HPLC-MS-n method.

Substance	MW [g/mol]	MRM transition [*m/z*, $[M+Ac]^-$]	Internal standard	Retention time [min]
6:2-FTOH	364.1	423 > 59	M-6:2-FTOH	8.7
8:2-FTOH	464.12	523 > 59	M-8:2-FTOH	9.9
10:2-FTOH[1]	564.14	623 > 59	M-8:2-FTOH	10.7
N-MeFOSE[1]	557.23	616 > 59	M-8:2-FTOH	10.0
N-EtFOSE[1]	571.25	630 > 59	M-8:2-FTOH	10.3

No internal standard was available for the substances with an index [1]. Instead, mass-labelled internal standards were chosen by similar retention time.

2.2.2 GC-MS method

A gas chromatography (GC) method was developed to separate selected volatile precursor compounds. A Trace GC 2000 with Trace MS single quadrupole (Thermo Fisher, Waltham, USA) was used for the analysis. Electron ionization (EI) was used as the ionization mode.

Prior to injection, all solutions were spiked with 7Me-6:2-FTI as a GC injection IS. 1 µL of the eluate or calibration standard solution is injected into the splitless injector port that is set at 180 °C. The injector port is splitless for 0.5 min and with a surge pressure of 200 kPa. PAL Combi-xt autosampler (CTC Analytics, Zwingen, Switzerland) was used to introduce the sample and standard. The helium carrier gas is maintained at a constant flow rate of 1.8 mL/min. The separation of the analytes is carried-out in a Restek VMS fused silica column (30 m length, 0.25 mm i.d., 3.0 µm film thickness, Restek Corporation, Bellefonte, USA) from 35 °C to 200 °C. Prior to every run, the oven initial temperature is equilibrated for 0.5 min.

The following oven temperature program was used: 1) 35 °C for 2 min; 2) Ramp the temperature to 45 °C at a speed of 2 °C/min; 3) Ramp again the temperature to 100 °C at 10 °C/min; 4) Ramp slowly at 1 °C/min to 110 °C; Ramp to 240 °C at 30 °C/min and hold at that final temperature for 1 min.

The GC was coupled to an EI source at 70 eV in the selected ion monitoring (SIM) acquisition as indicated in Table 12. Prior to analysis of an analytical batch, the instrument is tuned using perfluorotributylamine.

Table 12: SIM Acquisition Parameters (GC-MS).

Retention Window	Start Time (min)	End Time (min)	Dwell time per Mass (s)	Points per second	*m/z* acquired
1	3.10	8.80	0.080	2.50	69; 77; 131; 177; 319
2	8.80	12.00	0.057	2.50	69; 77; 131; 177; 227; 374; 419
3	12.00	15.50	0.057	2.50	55; 69; 85; 177; 327; 474; 519
4	15.50	17.60	0.100	2.50	191; 377; 442; 524
5	17.60	19.00	0.100	2.50	55; 99; 427; 574
6	19.00	26.00	0.080	2.50	55; 69; 99; 432; 532

Xcalibur software was used to detect and integrate peaks. The ions selected for quantification and for the qualification are shown in Table 13.

Table 13: Ions used to quantify and qualify the volatile compounds.

Analytes	Quantifier [*m/z*]	Qualifier [*m/z*]
6:2-FTO	77	131
8:2-FTO	77	131
10:2-FTO	77	131
PFHxI	319	69
PFOI	69	419
PFDI	69	519
4:2-FTI	374	227
6:2-FTI	474	327
8:2-FTI	574	427
7H-6:1-FTI*	191	442
7Me-6:2-PFAI*	524	377
6:2-FTAC	55	99
7:1-FTAC*	55	85
8:2-FTAC	55	99
6:2-FTMAC	432	69
8:2-FTMAC	532	69

Substances labeled with * were used as internal standards.

2.2.3 HPLC-HRMS screening method

Samples showing high concentration of target PFASs were screened for further unknown PFASs employing high-resolution mass spectrometry (HRMS) in combination with HPLC. Separation was carried out on a Thermo Surveyor Plus system and detection was performed by a Thermo Orbitrap Velos Pro system (Thermo, Dreieich, Germany). The chromatographic method was the same as for the HPLC-MS-a method already explained in chapter 2.2.1.1 and 2.2.1.2.

MS was run in data-dependent acquisition, where Orbitrap full scans in the range of *m/z* 100-2000 were measured at a nominal resolution setting of 60,000 (at *m/z* 400) and data-dependent MS/MS scans of the five most intense ions per scan were recorded in 'higher energy collision-induced dissociation' (HCD) mode at a nominal resolution setting of 15,000 (at *m/z* 400) and stepped normalized collision energy of 40% ± 20% in three steps. For all measurements, deprotonated trifluoroacetic acid (*m/z* 112.9856) was used as 'lock mass', i.e. for continuous internal per-scan mass calibration. Initial evaluation of the data was performed in form of peak picking using the software Compound Discoverer 1.0 (Thermo, Dreieich, Germany) and its module 'Unknown Extractor' and further data evaluation was performed using Qual Browser 3.0.63 (Thermo, Dreieich, Germany).

2.3 Calibration and validation

2.3.1 HPLC-MS-a method

2.3.1.1 Calibration of the HPLC-MS-a method

Two series of standards in a range of 0.05 ng/mL to 48 ng/mL with ten concentration levels were prepared in MeOH/H_2O (1:1, V:V) and measured with the HPLC-MS-a sMRM method. The first series of standards was measured two times on two different days and the second series of standards was measured three times on two different days. The results were used to determine the limit of detection (LOD) and the limit of quantification (LOQ) as well as the linearity of the method.

The software Analyst® 1.5.1 (AB Sciex) was used for the determination of the signal to noise ratio of the LOQ as well as for the limit of detection (LOD) with a signal to noise ratio of > 3. The software MultiQuant® 2.1 (AB Sciex) was used for the determination of accuracy, ratio of response as well as the calibration with a weighting by 1/x.

2.3.1.2 Repeatability and precision of the HPLC-MS-a method

Six individual standards with a concentration of 3 ng/mL and six individual standards with a concentration of 0.5 ng/mL were prepared in MeOH/H_2O (1:1, V:V) and measured with the developed HPLC-MS-a method to determine the repeatability and precision of the method.

2.3.1.3 Robustness of the HPLC-MS-a method

Six individual standards with a concentration 3 ng/mL were prepared in MeOH/H_2O (1:1, V:V). Effluent water from a municipal WWTP located in Germany was used instead of milli-Q-water. The effluent sample was collected on March 4th of 2013 and stored at 4 °C. The effluent water was filtered by using a syringe filter (regenerated cellulose, pore size 0.45 µm) during the standard preparation.

2.3.1.4 Trueness of the HPLC-MS-a method

Two influent samples of WWTP-I1 (INF from May 13th and 27th 2013) and the two corresponding effluent samples (EFF from May 15th and 29th 2013) were spiked with a spiking solution that contains all standards. The concentration of each used standard in the spiking solution was 3 ng/mL. The influent samples from May 27th 2013 and the effluent sample from May 29th 2013 were prepared and measured in duplicate during the analysis of the sample campaign.

2.3.2 HPLC-MS-n method

2.3.2.1 Calibration of the HPLC-MS-n method

Three series of standards in a range of 0.1 ng/mL to 500 ng/mL with eight concentration levels were prepared in MeOH/H_2O (1:1, V:V) and measured with the enhanced HPLC-MS-n MRM method. Each individual standard was prepared immediately before analyzing with the HPLC-MS/MS system. The results are used to determine the limit of detection (LOD) and the limit of quantification (LOQ) as well as the linearity of the method.

2.3.2.2 Repeatability and precision of the HPLC-MS-n method

Six individual standards with a concentration of 100 ng/mL were prepared in MeOH/H_2O (1:1, V:V) and measured with the developed HPLC-MS-n MRM method to determine the repeatability and precision of the method. The individual standards were prepared immediately before the measurements.

2.3.2.3 Robustness of the HPLC-MS-n method

Three standards with a concentration of 100 ng/mL were prepared in MeOH/H_2O (1:1, V:V). Effluent water from a municipal WWTP located in Germany was used instead of milli-Q-water. The effluent sample was collected on March 4th of 2013 and stored at 4 °C. The effluent water was filtrated by using a syringe filter (regenerated cellulose, pore size 0.45 µm) during the standard preparation.

2.3.2.4 Trueness of the HPLC-MS-n method

Two influent samples (of WWTP-I1) and the two corresponding effluent samples (of WWTP-I1) were spiked with a spiking solution that contains all standards. The concentration of the spike was 100 ng/mL, respectively. The influent samples from May 27th and the effluent sample from May 29th were prepared and measured in duplicates during the analysis of the sample campaign.

2.3.3 GC-MS method

2.3.3.1 Calibration and LOD/LOQ

The LODs were calculated by analyzing the signal to noise ratios. A 1 µL portion of the 20 ng/mL standard solution (20 pg absolute amount of each analyte) was injected into the GC-MS. The height of the generated peaks were compared to the corresponding average baseline noise near the peak and the s/n was calculated. Using the signal-to-noise ratio value for 20 pg, the LOD was calculated as the amount of the analyte that will give a signal-to-noise ratio of 3. The values are in the subpicogram range and are shown in Table 14.

Table 14. Summary of the GC-EI-MS instrumental figures of merit.

Analyte	Selectivity Area Ratio Criterion		Absolute LOD (pg)	R^2 (1–20 pg) with IS	R^2 (1-20 pg) without IS	Sensitivity (slope of calibration curve without IS, pg^{-1})
	Area Ratio	RSD (%)				
6:2-FTO	0.029	27	0.3	0.9972	0.9988	5.4E+04
8:2-FTO	0.038	5	0.3	0.9971	0.9985	8.1E+04
10:2-FTO	0.046	7	0.3	0.9971	0.9983	9.1E+04
PFHxI	2.6	10	0.6	0.9976	0.9979	6.5E+03
PFOI	0.18	18	1	0.9954	0.9973	2.0E+04
PFDI	0.054	8	1	0.9900	0.9896	2.3E+04
4:2-FTI	0.46	5	0.3	0.9979	0.9988	1.1E+04
6:2-FTI	0.32	4	0.3	0.9965	0.9977	9.4E+03
8:2-FTI	0.39	13	1	0.9970	0.9982	5.9E+03
6:2-FTAC	0.10	12	1	0.9996	0.9988	4.5E+03
8:2-FTAC	0.10	8	0.6	0.9947	0.9976	3.8E+04
6:2-FTMAC	7.4	10	1	0.9974	0.9966	4.9E+03
8:2-FTMAC	10	17	0.6	0.9950	0.9984	3.9E+03

Table 15. Average coefficients of determination and slopes of the calibration curves for GC-EIMS for each analyte (n=5).

Analyte	R^2	Slope	RSD
6:2-FTO	0.9962	3.24E+04	5.9
8:2-FTO	0.9966	5.05E+04	6.4
10:2-FTO	0.9951	5.57E+04	5.4
PFHxI	0.9950	4.93E+03	7.1
PFOI	0.9922	1.41E+03	6.2
PFDI*	0.9939	5.76E+02	9.5
4:2-FTI	0.9955	6.87E+03	6.0
6:2-FTI	0.9947	5.04E+03	5.8
8:2-FTI	0.9929	2.12E+03	5.8
6:2-FTAC	0.9972	3.11E+04	5.3
8:2-FTAC	0.9946	2.58E+04	4.4
6:2-FTMAC	0.9907	1.95E+03	4.2
8:2-FTMAC	0.9956	1.43E+03	4.2

*The lowest concentration in the calibration curve was 5 pg/μL.

Table 16. Average % residuals in the estimation of concentration using the external standard method and GC-EIMS (n=5).

Compound	2 pg/μL	5 pg/μL	10 pg/μL	20 pg/μL	40 pg/μL	60 pg/μL
6:2-FTO	32.7	4.3	-2.2	-4.2	-0.7	0.8
8:2-FTO	23.5	4.5	-0.7	-3.4	-1.1	0.8
10:2-FTO	22.0	5.3	0.4	-3.2	-2.1	1.2
PFHxI	50.3	3.9	-4.1	-4.2	-1.8	1.3
PFOI	58.1	23.4	-4.9	-10.2	-3.2	2.5
PFDI	-19.6	5.5	6.3	-4.1	-3.0	1.6
4:2-FTI	22.7	3.8	2.1	-3.7	-2.2	1.3
6:2-FTI	29.7	0.5	1.9	-2.9	-2.7	1.4
8:2-FTI	40.3	-1.1	1.4	-3.8	-2.5	1.5
6:2-FTAC	18.3	5.4	-0.3	-2.4	-1.9	1.1
8:2-FTAC	25.7	6.6	0.1	-4.0	-2.1	1.3
6:2-FTMAC	64.4	28.4	-9.7	-10.4	-2.7	2.3
8:2-FTMAC	25.8	4.1	-0.9	-2.8	-1.7	1.1

The average slope of the calibration curve and the corresponding RSD in Table 15 can be used to compare the sensitivity of the method towards the different analytes. With the exception of the FTOs, generally, within a group, as the carbon number is increased, the slope and sensitivity are decreased. The reproducibility of the calibration curve is also good as shown in the low RSD in the slopes of calibration curves.

The LODs and LOQs were calculated by analyzing the signal to noise ratios. The values are in the subpicogram range and are shown in Table 14.

2.4 Sample preparation

This chapter is subdivided into methods that were carried out during the process of method development (subchapters of 2.4.1) and methods that were finally used for sample preparation to determine concentrations in samples related to this study (subchapters of 2.4.2).

2.4.1 Development of sample pretreatment methods

2.4.1.1 Development of a SPE method for municipal WWTP samples

The SPE method was developed with effluent water from a municipal WWTP (Beuerbach, Germany). It was not integral part of this study, but only used for method development purposes. 200 g of the collected effluent water was transferred into 1000 mL narrow neck HDPE bottle, which were washed three times with methanol and dried prior to use. 50 µL of a PFAS-a spiking solution was added to the sample. The spiking solutions contained all analytes of the HPLC-MS-a method in a concentration of 0.1 ng/µL. 40 µL of a spiking solution, which contained the FTOHs and FOSEs with a concentration of 1 ng/µL, was added to the sample as well as two internal standard solutions. 10 µL of the PFAS-a internal standard solution (see

Table 9) and 40 µL of a internal standard solution, which included M-6:2-FTOH and M-8:2-FTOH at a concentration of 0.5 ng/µL, were added to the sample. The bottle was closed with screw caps and shaken for 1 min vigorously. The sample was prepared in triplicate and enriched on an Oasis WAX (60 mg, 3 cm^3) SPE cartridge (Waters Corporation, Milford, United States). The cartridge was conditioned with 2 mL MeOH + 0.1% NH_3, 2 x 2 mL MeOH and 3 x 2 mL H_2O by gravitational flow. The samples were passed through the cartridges with a flow rate of approximately 1 drop/s by vacuum assist using a membrane pump. Afterwards, the cartridges were washed with 3 mL H_2O/MeOH (80:20; V:V) and dried for 10 min by gentle nitrogen stream. The target compounds were eluted in 2 mL MeOH into a special glass vial showing marks at 200 µL by gravitational flow and were concentrated under nitrogen to a final volume of 200 µL and transferred into a 1.5 mL micro test tube. 200 µL milli-Q-H_2O was added and mixed for 30 s by using a vortex mixer. The sample was filtered by a syringe filter, transferred into 500 µL polypropylene (PP) HPLC vial and measured directly by using the corresponding HPLC-MS-n method. The target compounds (acidic PFASs) were eluted in 2 mL MeOH that contained 1% NH_3 into a 2 mL PP cryo vial by gravitational flow. 1.9 mL of the eluate was transferred into 24 mL glass vials and evaporated to dryness at 50°C under gentle nitrogen stream. The residues were dissolved in 250 µL MeOH and mixed for 1 min by using a vortex mixer. 250 µL milli-Q-H_2O was added, mixed and incubated for 2 min. The sample was filtrated with a syringe filter, transferred into a HPLC vial and measured with the corresponding HPLC-MS-a method. Three samples

with 200 g milli-Q-H_2O instead of effluent water were prepared with this procedure and analyzed. Three blanks, which contained only the internal standards, were treated simultaneous with effluent water and milli-Q-H_2O, respectively.

A clean up procedure with activated carbon was tested during the SPE method. Therefore, three additional spiked samples with effluent water and three unspiked samples with effluent water, which contained only the internal standards, were prepared with the SPE method described. For this clean up, the MeOH/NH_3 eluate was transferred into 10 mL centrifuge tubes and 50 mg EnviCarb in addition of 100 µL glacial acetic acid was added and mixed thoroughly for 1 min by using a vortex mixer. The suspension was centrifuged at 20,000 rpm for 10 min. 1.9 mL of the supernatant was transferred into a 24 mL glass vial, evaporated to dryness at 50°C under gentle nitrogen stream and the residues were dissolved in 250 µL MeOH. After the addition of 250 µL milli-Q-H_2O and incubation time of 2 min, the sample was filtrated with a syringe filter and transferred into a HPLC vial and measured with the corresponding HPLC-MS-a method.

2.4.1.2 Development of an analytical method for selected volatile PFASs in air samples

Adding to the substances measured by HPLC-MS, several volatile PFAS classes were measured by GC-MS. The substances under investigation include n:2-FTOs, PFAIs, n:2-FTIs; n:2-FTACs and n:2-FTMACs. Methods were developed to determine these compounds in air and water samples. Figure 4A shows the set-up in the sampling of air samples. The air was passed through the HLB cartridge with the aid of a vacuum pump. Moisture trap and particle filters were also put in the air sample line prior to reaching the pump. The HLB cartridges were conditioned using three portions of 2 mL MeOH and then dried using N_2 gas.

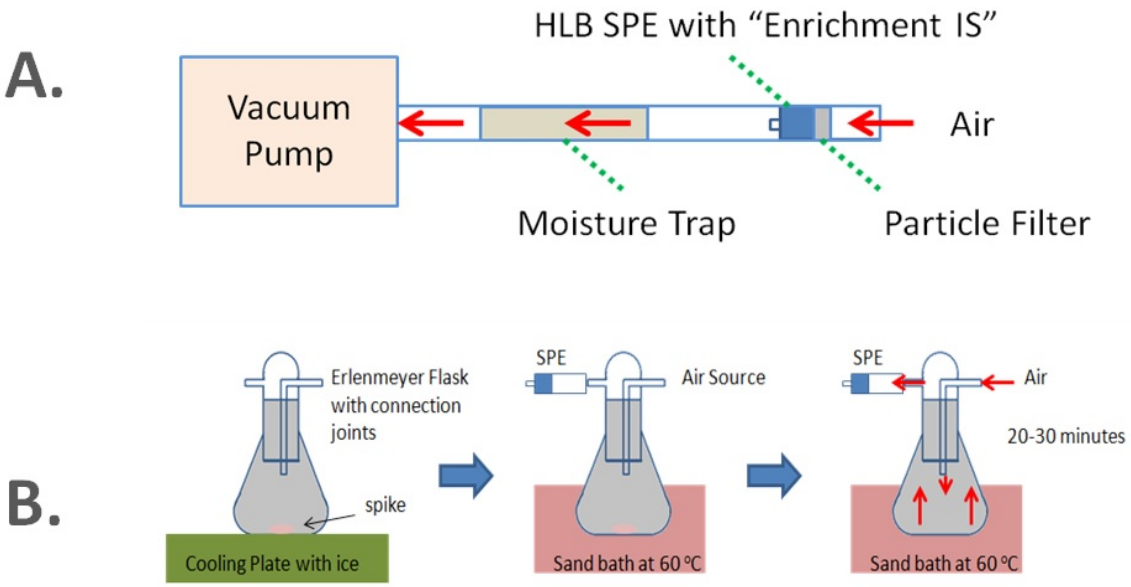


Figure 4: Set-up for the air sampling: A. Sampling using hydrophilic-lipophilic balance (HLB) solid-phase extraction (SPE) and B. Spiking of the analytes to determine the performance of the SPE. IS=Internal standard

To determine the efficiency of the HLB stationary phase (60 mg, 3 cm^3), a recovery experiment was done using the set-up shown in Figure 4B. An Erlenmeyer flask was initially put rested on top of a cooling plate. Known amount of the standard working solution was then spiked into the bottom of the Erlenmeyer flask and then closed with a stopper that has entrance and exit point for air. An HLB cartridge was attached at the exit point for air. The flask was then put in a sand bath that was maintained at 60 °C and the air was passed through the flask and the HLB at a flow rate of 100 mL/min for 20 to 30 min.

The HLB cartridges used in the enrichment were then dried using a stream of N_2 gas. Known amount of internal standard was then spiked into the cartridges. The analytes were then eluted out using 1 mL n-pentane. 1 µL of the solution was then injected into the GC-MS.

2.4.1.3 Liquid-liquid extraction of selected volatile GC-compatible PFASs

Liquid-liquid extraction was initially tested as a method to extract and enrich the volatile PFAS in water samples. Prior to SPE, water samples were first filtered in a glass membrane filter, 0.45 µm pore size. A 100 mL aliquot of distilled water was transferred into a 120 mL separatory funnel. The water was then spiked with 200 ng of each of the analytes and IS. The extraction was then carried out two times with 4.5 mL pentane. The pentane layers were collected in a 10 mL volumetric flask. Another IS to check for the reproducibility of the injection was added prior to dilution to mark. A standard solution with concentration of 20 ng/mL was prepared separately and was directly injected into the GC.

2.4.2 Final methods for sample collection and preparation

2.4.2.1 Overview

The methods finally applied to air samples and aqueous samples are summarized in Figure 5 and Figure 6, respectively.

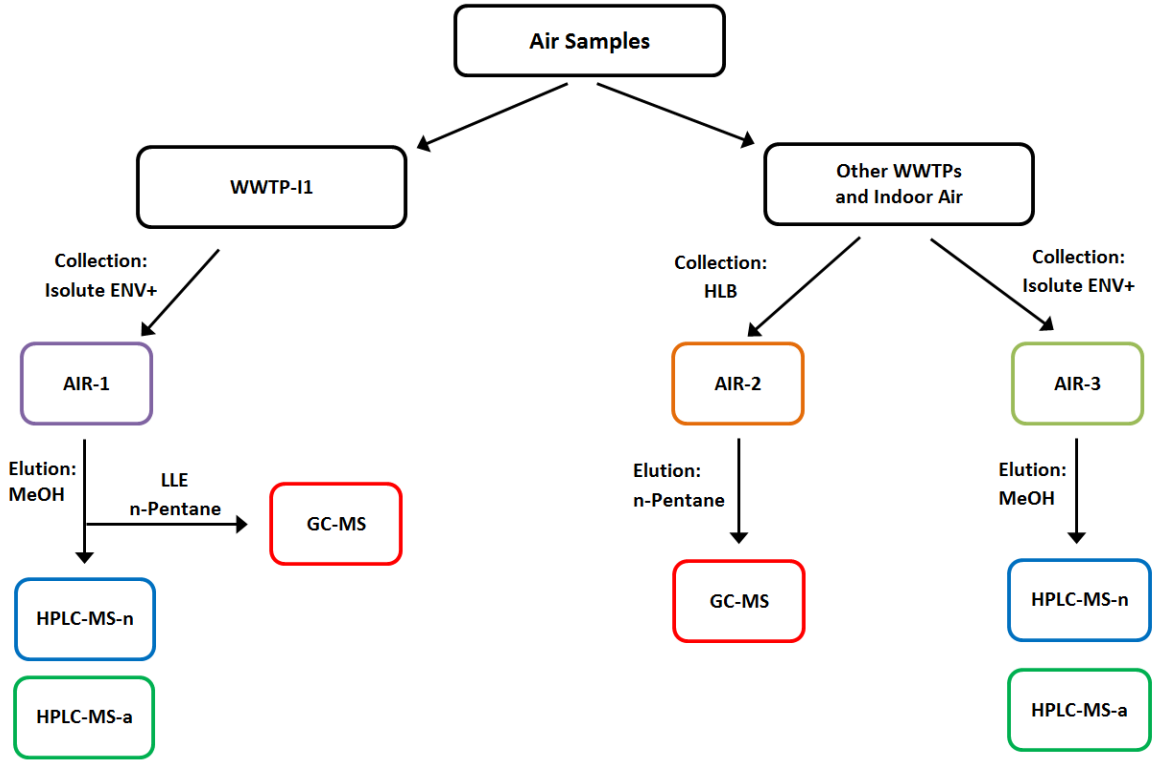


Figure 5: Overview of sample preparation and instrumental methods applied to air samples. Air samples for WWTP-I1 were collected at lower flow rate due to expected high PFAS concentrations. LLE: liquid-liquid extraction.

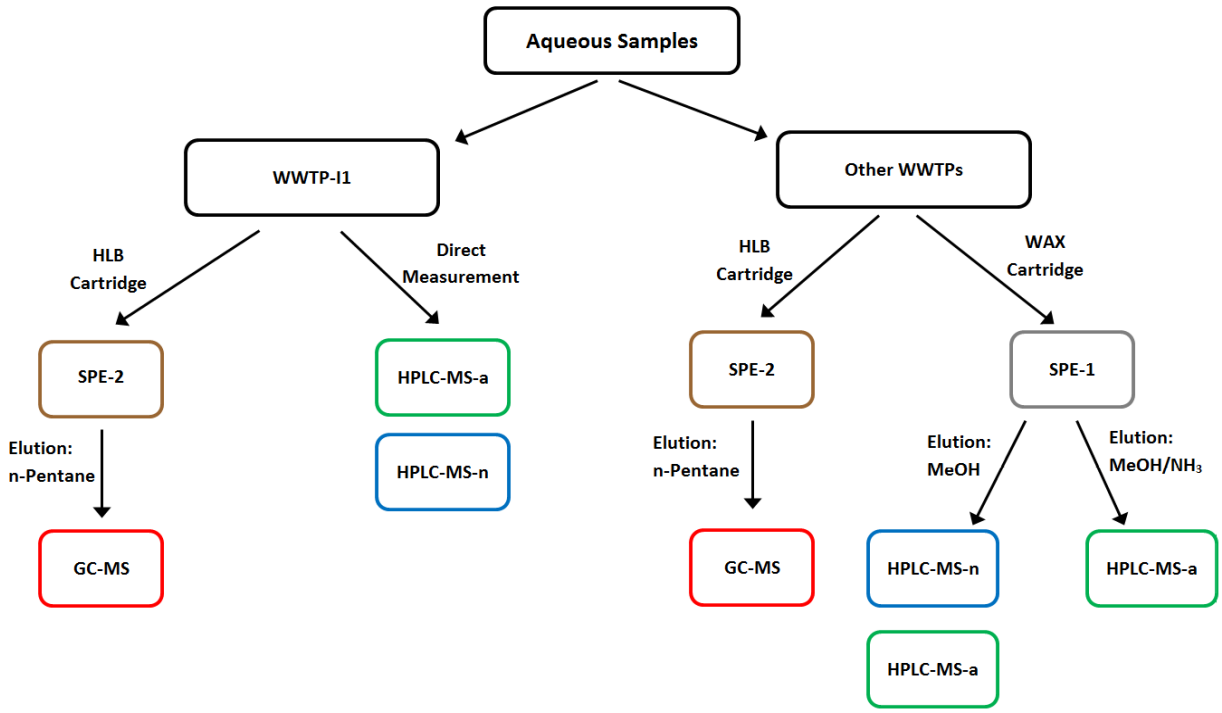


Figure 6: Overview of sample preparation and instrumental methods applied to aqueous WWTP samples.

To summarize the instrumental methods used and shown in Figure 5 and Figure 6, an assignment of analytes to instrumental methods is depicted in Figure 7.

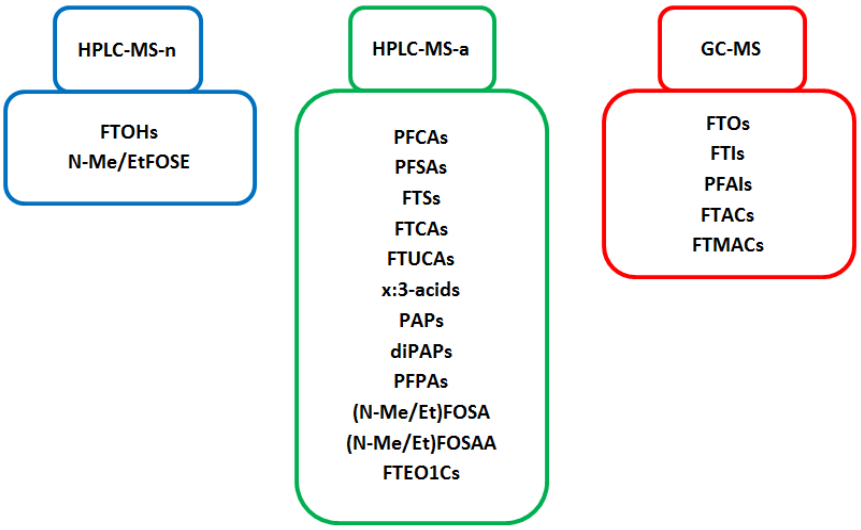


Figure 7: Assignment of instrumental methods to PFAS classes as depicted in Figure 5 and Figure 6.

For sludge and dust samples, only one set of methods was applied (see chapter 2.4.2.8 and 2.4.2.10, respectively), therefore these are not shown in a figure here.

2.4.2.2 Sample preparation for direct injection HPLC-MS of aqueous samples

For samples with expected individual PFAS concentrations > 1 µg/L (aqueous samples from WWTP-I1), no enrichment or clean-up was necessary for determination. The frozen water samples were thawed and shaken vigorously. For the HPLC-MS-a determination, 250 µL of the water sample was transferred into a 1.5 mL Eppendorf reaction tube. Afterwards, 240 µL MeOH and 10 µL of the internal standard spiking solution (shown in

Table 9) were added. The sample was mixed for 20 s by using a vortex mixer. After filtration with a syringe filter (degenerated cellulose, pore size 0.45 µm, Schleicher & Schuell, Dassel, (Germany) the sample was transferred into a HPLC vial, caped and measured with the developed HPLC-MS-a sMRM method. For the HPLC-MS-n determination, 250 µL of the water sample was transferred into a 1.5 mL Eppendorf reaction tube. 240 µL MeOH and 10 µL of the internal standard spiking solution (5 ng/µL) were added. The sample was mixed for 20 s by using a vortex mixer. After filtration with a syringe filter the sample was transferred into a HPLC vial, caped and measured directly with the developed HPLC-MS-n method.

2.4.2.3 SPE of aqueous samples for HPLC-MS analysis (SPE-1)

The method SPE-1 was used to enrich HPLC-MS compatible substances (anionic PFASs including FOSA and derivatives as well as FTOHs and FOSEs) from aqueous WWTP samples (except for WWTP-I1) and was adapted with minor modifications from literature (Taniyasu

et al., 2005). A defined volume (100 mL for influent samples, 200 mL of effluent samples) of the collected water sample was filtered through a 0.45 µm glass fiber filter, transferred into a 500 mL narrow neck HDPE bottle, which was washed three times with methanol and dried prior to use. 10 µL of the PFAS-a internal standard solution (see

Table 9) and 40 µL of an internal standard solution, which included M-6:2-FTOH and M-8:2-FTOH at a concentration of 0.5 ng/µL, were added to the sample. The bottle was closed with screw caps and shaken vigorously for 1 min. An Oasis WAX (60 mg, 3 cm^3) SPE cartridge (Waters Corporation, Milford, United States) was conditioned with 2 mL MeOH + 0.1% NH_3, 2 x 2 mL MeOH and 3 x 2 mL H_2O by gravitational flow. The samples were passed through the cartridges with a flow rate of approximately 1 drop/s under slight vacuum using a membrane pump. Afterwards, the cartridges were washed with 3 mL H_2O/MeOH (80:20; V:V) and dried for 10 min by a gentle nitrogen stream. The non-acidic target compounds (FTOHs, FOSA, N-MeFOSA, N-EtFOSA and FOSEs) were eluted with 2 mL MeOH into a 10 mL glass vial with 200 µL mark by gravitational flow and were concentrated under nitrogen to a final volume of 200 µL and transferred into a 1.5 mL micro test tube (Eppendorf, Hamburg, Germany). 200 µL milli-Q-H_2O was added and mixed for 30 s using a vortex mixer. The sample was filtered by a syringe filter (regenerated cellulose, pore size of 0.45 µm, Schleicher & Schuell (Dassel, Germany), transferred into a 500 µL polypropylene (PP) HPLC vial and measured directly by using the corresponding HPLC-MS-n method.

The acidic compounds were eluted in 2 mL MeOH containing 1% NH_3 into 24 mL glass vials (A-Z Analysenzubehör, Langen, Germany) by gravitational flow and evaporated to dryness at 50 °C under a gentle nitrogen stream. The residues were dissolved in 250 µL MeOH and mixed for 1 min by using a vortex mixer. 250 µL milli-Q-H_2O was added, mixed and incubated for 2 min. The sample was filtered with a syringe filter (regenerated cellulose, 0.45 µm), transferred into a HPLC vial and measured with the corresponding HPLC-MS-a method.

2.4.2.4 SPE of analytes from water samples for GC-MS analysis (SPE-2)

This method was used to enrich GC-MS-compatible substances from aqueous samples of all WWTPs under investigation. Prior to enrichment, water samples were first filtered in a glass membrane filter with 0.45 µm pore size. A volume of 250 mL water sample was enriched on HLB cartridges attached to a vacuum manifold. Prior to enrichment, 20 ng of 7:1-FTAC and 7H-6:1-FTI were added to the aqueous sample. Enrichment was performed using Oasis HLB cartridges (60 mg, 3 cm^3, Waters Corporation, Milford, United States) previously conditioned with 2 mL MeOH and dried under N_2 gas. Before elution, 20 ng of 7Me-6:2-FTI was added on top of the cartridge. Elution was carried out with 1 mL n-pentane. 1 µL of this eluate was then injected into the GC-MS.

2.4.2.5 Low-volume air sampling for WWTP-I1 (AIR-1)

This method was used for enrichment of all analytes from air above the influent of WWTP-I1. A low volume air sampler (type GS 312, DESAGA, Germany, Heidelberg) was used to collect air samples for 24 h with a flow rate of 2 L/min. Air samples were enriched on a

commercially available SPE column as suggested by Jahnke et al. (2007b) and Jogsten et al. (2012)(ISOLUTE ENV+, 1 g, 6 mL, Biotage, Uppsala, Sweden). A regenerated cellulose filter with a pore size of 0.45 µm (Syringe filter: Spartan® 13/0,45 RC, 0.45 µm, brown ring L (Schleicher & Schuell, Dassel, Germany) was installed on the SPE column to remove solids such as dust after the sampling. The SPE cartridges were stored in 50 mL centrifugation tubes to protect them from potential contamination after the installation of the cellulose filter.

The regenerated cellulose filters of the prepared cartridges were removed, extracted with 1 mL MeOH and spiked with the mass labelled internal standards. For the elution of PFASs from the SPE cartridges, 10 mL MeOH was passed through the cartridge by gravitational flow. An aliquot of each eluate was diluted 1:200 and 1:2000, respectively, spiked with mass labelled internal standard and filtrated by using a syringe filter. The extracts were analyzed using the HPLC-MS-a and HPLC-n methods and by the GC-MS methods after the MeOH extract had been diluted 1:10 with n-pentane.

2.4.2.6 Low-volume air sampling for WWTPs (AIR-2)

Due to differences in the detection system between FTOHs (LC-MS) and the rest of the volatile PFASs (GC-MS), there was a need to develop separate air sampling methods for the stated compounds. The method AIR-2 was used to enrich volatile PFASs measured by GC-MS (FTOs, FT(M)ACs, PFAIs and FTIs) from air of all WWTPs except for WWTP-I1 as well as from indoor air. A low volume air sampler (type GS 312, DESAGA, Germany, Heidelberg) was used to collect air samples for 24 h with a flow rate of 1 L/min. It involved the use of HLB cartridges (30 mg, 3 cm^3, Waters Corporation, Milford, US) as shown in Figure 4A. The HLB cartridges were conditioned using three portions of 2 mL MeOH and then dried using N_2 gas. They were then spiked with the enrichment IS by means of the set-up shown in Figure 4B. An Erlenmeyer flask was initially put rested on top of a cooling plate. Known amount of the enrichment IS working solution (20 ng total amount of each IS) was then spiked into the bottom of the Erlenmeyer flask and then closed with a stopper that has entrance and exit point for air. An HLB cartridge was attached at the exit point for air. The flask was then put in a sand bath that was maintained at 60 °C and the air was passed through the flask and the HLB at a flow rate of 100 mL/min for 20 to 30 min. The HLB cartridges with enrichment standard were stored in 50 mL tubes and were stored at -20 °C until the time they would be used. On sampling, the mouth of the cartridge was fitted with a cut 0.45 µm Whatman glass fiber membrane filter (GE Healthcare Bio-Sciences AB, Uppsala, Sweden), to exclude the dust particles. The other end of the cartridge was connected to a silica gel moisture trap and then to the low volume air sampler (type GS 312, DESAGA, Germany, Heidelberg). The air was pumped in through the SPE cartridge at an average flow rate of 1L/min for a period of 24 h. After sampling, the glass membrane filter was separated and was stored for subsequent analysis. The HLB cartridges were stored back in the centrifuge tube and were kept at -20 °C until elution, which was carried out with 1 mL n-pentane.

2.4.2.7 High-volume air sampling for WWTPs (AIR-3)

The method AIR-3 was used to enrich non-volatile and volatile PFASs measured by HPLC-MS (anionic PFASs including FOSA and derivatives; FTOHs and FOSEs) from air of all WWTPs except for WWTP-I1 as well as from indoor air. It was similar to AIR-1, but using higher air flow rates to pass sufficient air to allow quantification of PFASs in the concentration range of ng/m^3. A custom-made high volume air sampler (assembled by the University of Applied Sciences Fresenius) was used to collect air samples for 24 h with a flow rate of approximately 8 L/min. It consists of a membrane vacuum pump (MZ 2, Vacuubrand GmbH + CO KG, Wertheim, Germany), a flow meter (Vision 2000, B.I.O-Tech e.K., Vilshofen, Germany) in combination with a signal processor (DFM 100, ELV Elektronik AG, Leer, Gemany) and a temperature controller (TS 125, H-TRONIK GmbH, Hirschau, Germany). The air samples were enriched on a commercially available SPE column (ISOLUTE ENV+, 1 g, 6 mL, Biotage, Uppsala, Sweden). The SPE columns were stored in 50 mL centrifugation tubes to protect them from potential contamination, which were stored at -20 °C prior to elution. No filter was placed in front of the cartridge. This was initially tested for WWTP-I1, but the flow was reduced so drastically that the volume of air sampled was too low for quantification of the compounds of interest in air samples. In particles collected via the syringe filter at WWTP-I1, none of the target analytes was measured after elution with MeOH (data not shown).

For the elution of PFASs from the SPE cartridges, 10 mL MeOH was passed through the column by gravitational flow. The eluates were spiked with the internal standards of the HPLC-MS-a and HPLC-MS-n methods and evaporated to 500 µL by using a gentle stream of nitrogen respectively. The eluates were filtered by using a syringe filter (regenerated cellulose, 0.45 µm) and analyzed using the HPLC-MS-a and HPLC-MS-n method.

2.4.2.8 Extraction of PFASs from activated sludge

The sludge samples were predried by filtering with filter paper (MN 616, Macherey-Nagel, Düren, Germany) using a water-jet vacuum pump. The samples were dried at 115 °C for 24 h and extracted using accelerated solvent extraction (ASE, Dionex Corporation, Sunnyvale, Canada) similarly to the method described by Kallenborn et al. (2004). A stainless steel ASE vial (11 mL) was used for the extraction. 1 g diatomaceous earth was filled in the bottom of the cell and 0.25 g of the dried sludge sample was added. The sample was spiked with 10 µL spiking solution, which contains the 24 mass labeled internal standards of the HPLC-MS-a method (see

Table 9). The ASE cell was filled with diatomaceous earth. A blank, containing only diatomaceous earth was treated simultaneously. Accelerated solvent extraction was performed with methanol (8 min static, 40% flush, two cycles, 150 °C, 2,000 psi). The extract was transferred into 15 mL centrifuge polypropylene vials and evaporated until dryness using a vacuum concentrator (SpeedVac, Thermo Scientific, Waltham, USA) at 50 °C. The residues were dissolved in 2 mL MeOH and mixed for 2 min by using a vortex mixer. 50 mg super clean activated carbon (EnviCarb, Supelco, Bellefonte, USA) and 25 µL glacial acetic acid were added to the samples to reduce the matrix. The samples were mixed for 2 min by

using a vortex mixer and centrifuged for 10 min at 18,500 rcf. 1.8 mL of the supernatant was transferred into 24 mL glass vial and evaporated to dryness at 50 °C under gentle stream of nitrogen and the residues were dissolved in 250 µL MeOH. After addition of 250 µL milli-Q-water and incubation time of 2 min, the samples were filtered with a syringe filter and transferred into a HPLC vial and measured with the corresponding HPLC-MS-a method.

2.4.2.9 Extraction of PFASs from the particulate phase of WWTP influent and effluent samples

Prior to extraction, the influent samples (approximately 300 mL) were filtered using a 0.45 µm glass fiber filter. A stainless steel ASE vial (11 mL) was used for the extraction. 1 g diatomaceous earth was filled in the bottom of the cell and 500 mg (wet weight) of the particulate phase was added. The sample was spiked with 20 µL spiking solution, which contains the 24 isotopically labeled internal standards of the HPLC-MS-a method. The sample was also spiked with 10 µL of the internal standard solution used for the HPLC-MS-n method. The ASE cell was filled with diatomaceous earth. Accelerated solvent extraction was performed with methanol (8 min static, 40% flush, two cycles, 150 °C, 2000 psi). The extract was transferred into 15 mL centrifuge polypropylene vials respectively and evaporated until 2 mL by using a gentle stream of nitrogen. 50 mg activated super clean carbon (EnviCarb, Supelco, Bellefonte, USA) and 25 µL glacial acetic acid were added to the samples to reduce the matrix. The samples were mixed for 2 min by using a vortex mixer and centrifuged for 15 min at 18,500 rcf. The supernatant was transferred into a glass vial and evaporated until 500 µL under gentle stream of nitrogen. 200 µL of the extract was filtrated with a syringe filter and measured with the HPLC-MS-n method. 250 µL of the extract was mixed with 250 µL milli-Q-H_2O, mixed and incubated for 2 min. The samples were filtered with a syringe filter, transferred into a HPLC vial and measured with the corresponding HPLC-MS-a method.

2.4.2.10 Collection and extraction of PFASs from indoor dust

The dust samples were collected manually into 50 mL PP centrifuge vials using disposable spatula and gloves. Large particles > 10 mm and visible hairs, grains etc. were excluded from the samples. Sample extraction was adopted from Jogsten et al. (2012) and Moriwaki et al. (2003). 50-70 mg of the dust was weighed in and placed in a 15 ml centrifuge vial. 2 mL spiked with 20 µL HPLC-MS-a internal standard mix (see

Table 9) and 10 µL of a solution containing 5 ng/µL M-6:2-FTOH and M-8:2-FTOH were added and ultrasonicated for 15 min. The suspension was centrifuged for 20 min at 18,500 rcf. The supernatant was evaporated to 500 µL under a gentle stream of nitrogen, filtrated using a syringe filter and transferred into a HPLC vial for measurement with the HPLC-MS-n method. An aliquot of 100 µL had been previously mixed with 100 µL ultrapure water, vortexed for 30 s and analyzed with HPLC-MS-a method.

2.5 Quality assurance

During all experiments and sample campaigns, solvent and method blanks were prepared simultaneously to the samples. The blanks were analyzed with the same respective methods

as the samples. Furthermore, reference control standards with a defined concentration of the analytes were measured in between samples to verify the retention time and intensity.

If not explicitly stated otherwise, all aqueous samples were measured in duplicate. Only the average value will be shown in the results and discussion section. Deviations were generally below 15%. Only for samples with high matrix content or when concentrations were close to the respective LOQs, deviations of up to 40% were reached.

Method LODs and LOQ were calculated differently for GC-MS methods and HPLC-MS methods. For GC-MS, LODs and LOQs were calculated as follows:

$$\text{Method Limit} = \text{Instrumental Limit} \cdot F$$

where the instrumental limit is shown in Table 14 in chapter 2.3.3.1 and F is a conversion factor combining the respective volume or amount of sample measured and the enrichment factor. The instrumental LOD was calculated analyzing the signal to noise ratio as discussed in section 3.5.2. The instrumental LOD for each compound is shown in Table 14 in chapter 2.3.3.1.

As a quality control procedure, the ratio of the areas of the enrichment control standards to the elution IS was calculated. The area ratio was then plotted in a n x-bar (mean) control chart. The analysis would be rejected if the value of the area ratio is outside the critical limits set by the formula: mean ± 3SD. The mean and the SD were calculated from the previously analyzed samples. It can be noted that during the time of the analysis, the calculation and evaluation was limited by the fact that the sample size (n) to calculate the mean and SD was still small.

For HPLC-MS methods, LODs and LOQ were calculated by the following formula:

$$\text{Method Limit} = \text{Instrumental Limit} \cdot F \,/\, \text{Recovery of Internal Standard}$$

Where the instrumental limits are shown in Table 18 and Table 24. Thus, calculation was similar to the calculation for GC-MS but taking into account the recovery of the respective internal standard used for each substance. This measure has to be done in order to counteract both losses during enrichment as well as ion suppression or ion enhancement effects, which are common in ESI-MS (King et al., 2000, Taylor, 2005). The recovery of the internal standard was calculated for each individual internal standard in each sample set by dividing the average internal standard peak area for one set of samples (e.g. all influent samples of one WWTP) by the average internal standard peak area in solvent standards measured in the same sample set. Therefore, different LODs and LOQs will be shown for different sample types and for different WWTPs and indoor air and dust samples.

2.6 Water-air partitioning of PFASs

To study the behavior of the volatile PFASs in water, a pseudo-partitioning experiment was done. As the name implies, it is not the aim of this experiment to derive an accurate partitioning coefficient for each volatile PFAS, but rather to gain insight as to the percentage of each volatile PFAS that partitions into the air. The data can be used to explain the

difficulty in achieving near 100% recoveries for the volatile compounds. The set-up of the experiment is shown in

Figure 8. A 4 L jar (bottle 1) is filled half-way with 2 L of water. Known amount of the volatile PFASs solution in methanol is spiked into the water. The pipet tip was intentionally submerged in the water during the spiking. The bottle was then closed and was allowed to equilibrate for 24 h. The 24 h period is not enough time for the equilibrium to be reached. The distribution ratio after the 24 h period is not a partition coefficient. Nonetheless, this ratio can be helpful in understanding the process involved. After 24 h, the water was forced towards bottle 2 by introducing air in bottle 1 via pump 1. When all the water was transferred into bottle 2, the connection between the two bottles were immediately closed so that no gas is transferred to bottle 2 from bottle 1. Pump 1 still introduces air in bottle 1 while the connection towards cartridge 1 is opened. The air from pump 1 forces the gases to go out while the PFASs that partitioned in the air are trapped in cartridge 1. Meanwhile, bottle 2 was heated up to 60 ^{o}C. Air was bubbled through the water via pump 2. The air and the volatile compounds evolved during bubbling were forced through cartridge 2. The PFASs eluted out of cartridges 1 and 2 represent the PFASs distribution in air and water respectively.

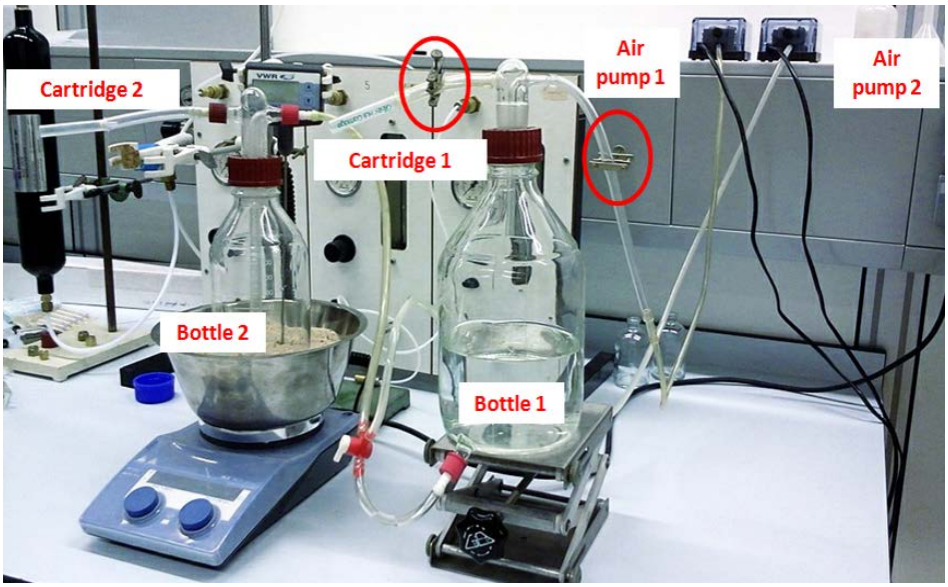


Figure 8. Set-up of the pseudo-partitioning experiment.

2.7 Sample campaigns

2.7.1 General

Six WWTPs were chosen, among which three are supplied with industrial wastewater from PFAS-using industry, such as textile or paper industry, or fluorochemical manufacturing plants. The list of WWTPs under investigation is presented in Table 17.

Table 17: Overview and characteristics of selected WWTPs.

WWTP	Type of WWTP	Share of municipal wastewater	Amount of wastewater [$10^6 m^3/a$]	Population	Population equivalents
I1	Industrial	-	-	-	-
I2	Municipal/industrial	-	-	-	-
I3	Municipal/industrial	50%	20-22	150,000	300,000
M1	Municipal/industrial	> 90%	50	200,000	300,000
M2	Municipal/industrial	50%	90	800,000	1,300,000
M3	Municipal/industrial	>90%	73	900,000	-

- no statement can be made due to confidentiality reasons

Even though most of the WWTPs are fed by both municipal and industrial wastewater, classification of the WWTPs was done by dividing them into 'industrial' (abbreviated -I) and 'municipal' (abbreviated -M). This classification is based on the fact that those WWTPs with discharges from PFAS-using or producing industries will be called 'industrial', whereas those without known discharges from aforementioned industries will be referred to as 'municipal' although these WWTPs may also receive wastewater from other industrial branches. The choice of municipal WWTPs was based on their population equivalents allowing the generation of representative data for Germany and Europe.

Figure 9 shows a simplified general scheme of a WWTP and the sampling points. At least eight influent samples were taken within a period of four weeks as well as corresponding air samples above the influent. In dependence of the WWTP, the exact position of air sampling varied as the first point of contact between air and influent differed between the WWTPs under investigation. Furthermore, four corresponding effluent samples and sludge samples were taken.

For WWTP-I2 and I3 as well as M1-M3, the aqueous samples were analyzed using SPE-1/HPLC-a/n methods as well as SPE-2/GC-MS. For WWTP-I1, the samples were measured directly with by HPLC-MS. Air samples were collected above the influent during the same time as the influent water samples using a time switch and the two sampling techniques AIR-2 (measured by GC-MS) and AIR-3 (measured by HPLC-MS).

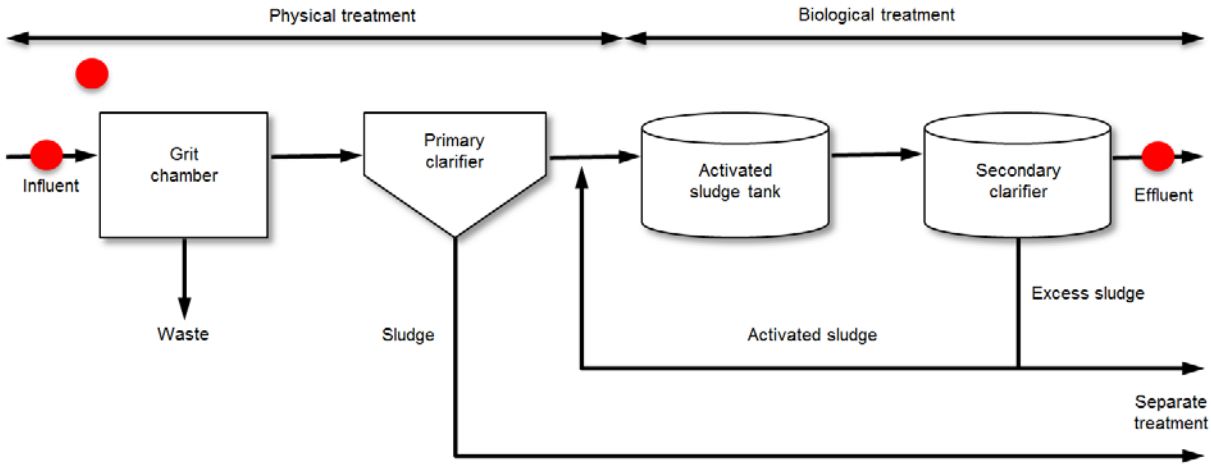


Figure 9: Simplified general scheme of a WWTP. Red dots mark sampling points of influent, air above influent and effluent. Sampling point for sludge is not depicted as it changed between WWTPs investigated.

2.7.2 Industrial wastewater treatment plant WWTP-I1

Samples from WWTP-I1 were collected in the period between May 13th and June 5th 2013. Aqueous samples were measured by GC-MS after SPE-2 (see 2.4.2.4) and by direct HPLC-MS (see chapter 2.4.2.2). Eight air samples were collected corresponding to the time of influent sampling. Due to the expected high concentration of PFASs, a low-volume air sampler was used. The samples were collected above the ship lift (first place where influent is in contact with ambient air). The samples were treated by the protocol AIR-1, as explained in chapter 2.4.2.5. Four grab sludge samples were taken from the secondary clarifier.

2.7.3 Industrial wastewater treatment plant WWTP-I2

A total of 12 influent samples, eleven effluent samples, nine air samples, and three sludge samples (grab sludge samples from the secondary clarifier) were taken between January 20th and February 15th 2015. Two additional samples were taken and measured, that is the return flow from nitrification to denitrification tank and the centrate. The latter one represents the water centrifuged from the digested activated sludge and primary sludge Figure 38.

2.7.4 Industrial wastewater treatment plant WWTP-I3

Seven influent samples including corresponding air samples as well as four effluent samples were drawn in the period between April 15th and May 12th 2015. Aqueous samples were taken using a time-proportional sampler. Additionally, three grab sludge samples were taken from the secondary clarifier.

2.7.5 Municipal wastewater treatment plant WWTP-M1

For the influents and effluents, the 24-hour composite samples were collected using time-proportional sampler. Eight influent samples (INF) and eight air samples above the influent

were collected between October 28th and November 22nd of 2014. Eight influent samples were taken on Tuesdays and Thursdays, and the effluent samples were taken on Wednesdays/Thursdays and Fridays/Saturdays, respectively. Depending on the daily influent volume, the residence time varies between 24 and 48 h and therefore, the more appropriate corresponding effluent sample was chosen afterwards. Four activated sludge grab samples were taken correspondingly to the effluent samples.

2.7.6 Municipal wastewater treatment plant WWTP-M2

The sampling period for WWTP-M2 was from February 26th to March 12th 2015. WWTP-M2 is fed by two individual influents which were sampled separately and will be named 'A' and 'B', where flow rates of A and B are in the ratio 3:2. Eight influent samples were taken for each influent, as well as four corresponding effluent samples and eight air samples above influent B. The WWTP is equipped with air suction above the indoor physical treatment in order clean the air prior to emission into the environment. Air sampling was performed by connecting the air samplers to the air suction pipes. Four grab sludge samples were taken which was composed of different kinds of sludge (primary, secondary, activated).

2.7.7 Municipal wastewater treatment plant WWTP-M3

Influent and effluent samples were collected as 24-hour composite samples using a time proportional sampler between December 2nd and December 18th of 2014. Effluent samples corresponding to influent samples were taken for influent samples 1, 2, 4 and 7. Eight air samples were taken correspondingly to influent samples as well as four sludge samples. Additional data for WWTP-M3 samples are shown in the annex in Table 76.

2.7.8 Indoor air samples

24 h indoor air samples were drawn using the methods AIR-2 (see 2.4.2.6) and AIR-3 (see 2.4.2.7) in parallel. The two air samplers were placed on the ground and in the center of the room sampled. Indoor Air 1 was taken in a building of approximately 150 y age, made of wood, clay and slate, having one room with a 2x2 m carper of approximately 20 y age. Only wooden furniture is present. This sample was supposed to serve as an indoor air sample with low background contamination. Indoor Air 2 was collected in a new office of approximately 35 m^2 with six workstations, where new carpet was laid only few years ago. Indoor Air 3 was sampled in a small outdoor clothing storage room. This sampling point could only be sampled once due to the following reasons: failure of sampling number 2 due to brown out caused by thunderstorm and failure of sampling number 3 due to failure of one of the air sampling systems. Since these samplings could not be performed again because of annoyance of the customers, an additional sampling in the fond of a three year old car has been added. All samples were collected in triplicates and over 24 h.

2.7.9 Indoor dust samples

Corresponding dust samples were collected for Indoor Air 1 (DUST-1) and Indoor Air 2 (DUST-2). Additional dust samples (DUST-3) were collected in another office without carpet in the same building as for DUST-2. The two offices for the samples DUST-2 and DUST-3 had approximately the same size of 35 m^2 and six workstations. These two rooms were used for typical office operation. Three dust samples were collected in each room on different places (on top of shelves) and days.

2.7.10 Statistical evaluation

The free software R (The R Project for Statistical Computing by the Free Software Foundation) was used in the visual representation of selected results and in the chemometric analysis of the dataset.

To obtain a general overview and to compare the different WWTPs, the data for selected PFASs are presented using boxplots. Prior to the generation of the boxplots, the data for selected PFASs were pre-treated as follows: 1. Non-detected analytes were given a concentration value of zero; and 2. Analytes with concentrations below the LOQ were assigned with values equal to (LOD+LOQ)/2. Extreme values were excluded from the calculation of statistical parameters but were shown in the boxplot graphs as separate points. Extreme values were selected based on the bounds set by the outlier rule, Q3 + 1.5*IQR and Q1 - 1.5* IQR, where Q1, Q3 and IQR are the first quartile, third quartile and the interquartile range, respectively. The boxplot's scales were adjusted accordingly. The R package 'ggplot2' was used to generate the boxplots.

Multivariate analysis was done to examine a dataset (WWTP-I2 Data). Canonical Correlations Analysis (CCA) was found to be the most appropriate statistical method for the multidimensional exploration of the WWTP dataset. In CCA, two sets of variables are compared to reduce their dimensionalities. In this analysis, the different PFASs in the influents and the different PFASs in the effluents were taken as the two sets of variables. In the end, the aim of the analysis was to find which variables in the influent set and effluent set are strongly correlated to each other.

The R package 'CCA' was found to be most suitable (Gonzalez et al., 2008) to establish correlations between concentrations of PFASs in the influent and in the effluent. The function Regularized CCA (rcc) enabled the analysis of the influent set in comparison to the effluent set. These sets were matrices containing more variables than the samples making them unfit for the classical CCA analysis (Gonzalez et al., 2008). Data pre-treatment included the substitution of zero to the non-detected analytes and substituting the value of the LOD for the analytes below the LOQ. The analytes that are not detected in all of the samples were taken out of the dataset and were not included in the modeling. As mentioned earlier, in CCA, the dataset is divided into two sets. In this analysis, the most convenient way of division was to separate the influent variables (composed of analytes measured in the influent and was designated by X) and the effluent variables (composed of analytes measured in the

effluent and was designated as Y). Prior to the CCA, matrix correlation survey was performed to get a glimpse of the fitness of the data and to evaluate whether there was enough logical evidence to proceed. The rcc was then done after the demonstration of fitness of the dataset. In rcc, the initial step was to estimate λ1 and λ2 to optimize (the cross validation correlation score) by leave-one-out method (Gonzalez et al., 2008). This step differentiates rcc to the classical CCA and is done to compensate for the fewer sample size compared to the variable sizes of both X and Y. The optimized λ1 and λ2 were the main output that was of interest in this study was the plot of the variables in any two of the reduced dimensions to find for their correlations.

3 Results and discussion: Method development

3.1 Method development of the HPLC-MS-a method

3.1.1 Development of HPLC-MS-a method

The HPLC-MS-a method was developed to determine the C_4-C_{14} PFCAs, 6:2, 8:2- and 10:2-FTCAs and FTUCAs, C_6, C_8, C_{10} PFPAs, 3:3-7:3-acids , C_4, C_6-C_8,C_{10} PFSAs, 4:2, 6:2, 8:2-FTSs, 6:2- and 8:2-FTEO$_1$Cs, 6:2- and 8:2-PAPs, 6:2-, 8:2- and mixed 6:2/8:2- and 8:2/10:2-diPAPs, FOSAA, N-MeFOSAA, N-EtFOSAA, FOSA, N-MeFOSA and N-EtFOSA. In total 22 ^{2}H, ^{13}C and ^{18}O labelled internal standards were used to compensate matrix effects and minor retention time shifts.

The gradient of an existing HPLC method, which had been developed and validated during a previous project in the host laboratory (Knepper et al., 2014), was optimized regarding method runtime and peak shape of the short-chain PFCAs PFBA and PFPeA. The method runtime was reduced by about 8 min compared to the previous gradient profile. The two gradient profiles are shown in Figure 10.

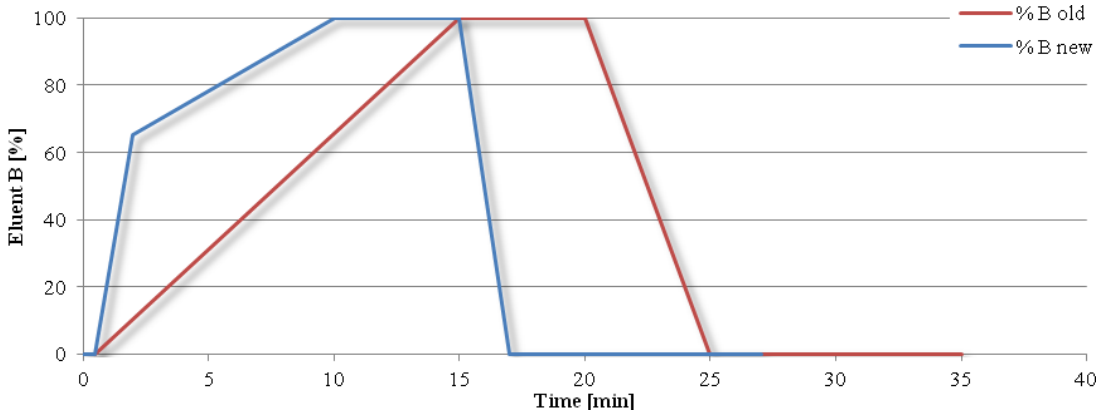


Figure 10: Gradient profile of the optimized HPLC eluent compared to a previously established HPLC method.

With the optimized gradient profile, the peak shape of for the short-chain PFCAs (C_4-C_6) could be improved significantly. The comparison of the chromatograms of selected PFCAs (C_4 – C_{10}) by using the previous gradient profile is shown in Figure 11A and by using the

optimized gradient profile is shown in Figure 11B. The chromatograms represent the measurement of a standard with the concentration of 12 ng/mL for the previous gradient profile (A) and the measurement of a standard with the concentration of 10 ng/mL for the new gradient profile.

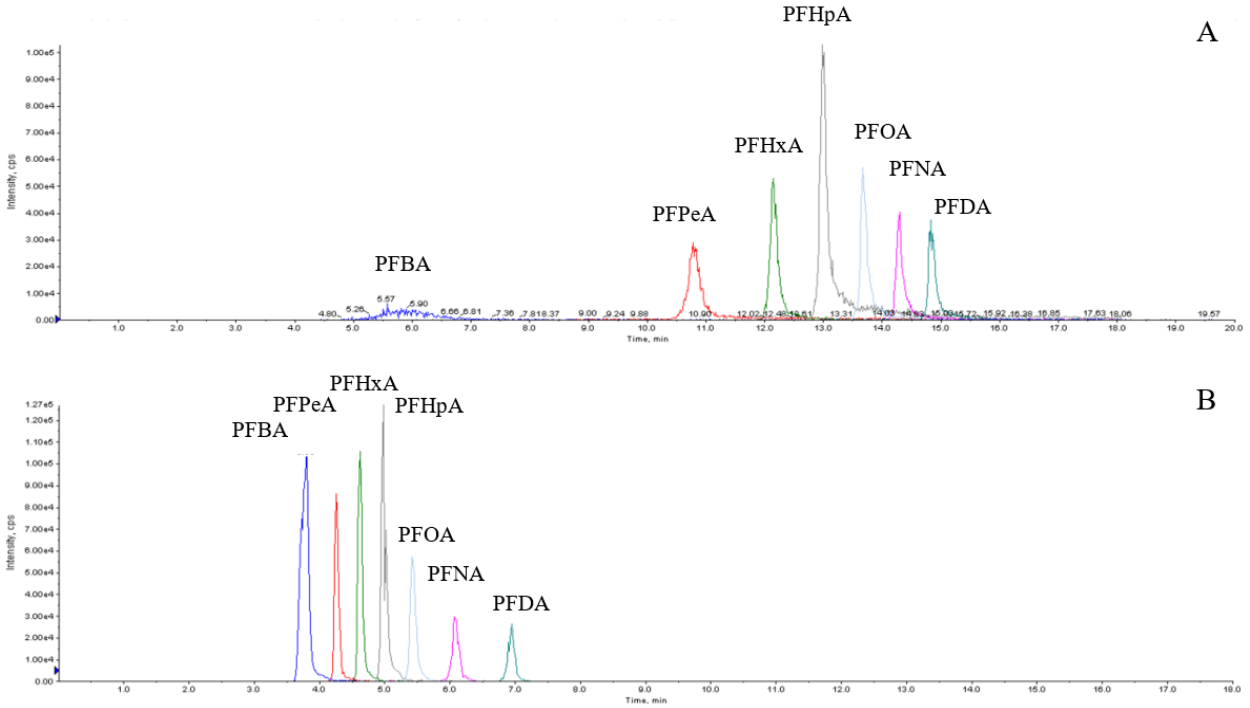


Figure 11: Comparison of the HPLC-ESI-MS/MS extracted ion chromatograms of selected PFCAs (C_4 – C_{10}) by using the previous gradient profile (A) and by using the optimized gradient profile (B).

3.1.2 Assessment of method development of the HPLC-MS-a method

The developed HPLC-MS-a method provided a promising method for determination and quantification of 44 different analytes of the substance classes PFCA, FTCA, FTUCA, PFPA, X:3-acid, PFSA, FTS, $FTEO_1C$, PAP, diPAP, FOSAA and FOSA. The compounds 6:2/8:2-diPAP and 8:2/10:2-diPAP could only be determined qualitatively due to non-available authentic standards. The peak shapes of the PFCAs were significantly improved compared to previously used methods by the optimization of the gradient profile of the HPLC method. Through successful calibration the LOD and LOQ could be determined for each investigated analyte. Furthermore, it was observed that the preparation with $MeOH/H_2O$ leads to adsorption of the internal standard M-MeFOSA, which resulted in a decrease of the detected peak area. However, it was possible to create a calibration curve for each individual analyte.

3.2 Validation of the HPLC-MS-a method

For validation of the HPLC-MS-a method, the reproducibility, robustness and precision were tested by different standards. Using effluent and influent samples from the industrial WWTP-I1, the trueness of the method was tested.

3.2.1 Calibration and determination of LOD and LOQ of the HPLC-MS-a method

Two series of standards in a range of 0.05 ng/mL to 48 ng/mL with ten concentration levels were prepared in MeOH/H_2O (1:1, V:V). The first series of standards was measured three times and the second prepared series two times. Only the results with accuracy between 70% and 130% to the set point and at least three of five measurements for each concentration level with a signal to noise ratio > 9 were quantified and implied in the calibration curve. These parameters were also used to determine the limit of quantification (LOQ). The ratio of response (area) of mass transitions (M_2:M_1) with an acceptance criterion of ± 30% was the third controlled parameter to imply the results in the calibration curve. A higher priority was acquired to the lower concentration levels by the application of this weighting. The method LOD and LOQ to analyze the water samples from the industrial WWTP without enrichment are shown in Table 18. Due to a lack of reference material, no LOD and LOQ could be calculated for mixed diPAPs, i.e. 6:2/8:2-diPAP and 8:2-10:2-diPAP, even though these substances were integrated into the MRM method for real samples.

The calibration curves showed a coefficient of determination (r^2) of 0.97 for 8:2-FTCA, 0.97 for 10:2-FTCA and 0.98 for 8.2-$FTEO_1C$ and 3:3-acid. All other calibration curves showed an r^2 of ≥ 0.99. The calibration of 6:2/8:2-diPAP and 8:2/10:2-diPAP was not possible, because no reference substances were available. These substances were only qualified. Only one measurement of series of standards was used for the calibration curve of FOSA. The peak area of the used internal standard (M-MeFOSA) decreased over time. The detected peak area of M-MeFOSA of selected standards is shown in Figure 12. The x-axis indicates the time interval between the preparation and the measurement. All standards were prepared simultaneously and analyzed successively in order of low concentration to high concentration levels. The concentration of internal standards was equal in all standards and in the case of M-MeFOSA the concentration was 10 ng/mL.

Table 18: Method LOD and LOQ of the developed HPLC-MS-a method to determine the amount of PFASs in the water samples of the industrial WWTP-I1 without enrichment. Instrumental LODs and LOQs can be calculated from the method LODs and LOQs by division by 2.

Analyte	LOD [ng/mL]	LOQ [ng/mL]	Analyte	LOD [ng/mL]	LOQ [ng/mL]
PFBA	0.1	0.2	6:3-acid	1.0	10.0
PFPeA	0.2	1	7:3-acid	1.0	10.0
PFHxA	0.1	0.2	PFBS	0.1	0.2
PFOA	0.1	0.2	PFHxS	0.1	0.5
PFNA	1.0	2	PFHpS	0.1	1.0
PFDA	0.5	1	PFOS	0.1	1.0
PFUnA	0.5	2	PFDS	0.5	1.0
PFDoA	1.0	2	4:2-FTS	0.5	2.0
PFTrA	0.5	1	6:2-FTS	0.2	1.0
PFTeA	0.5	1	8:2-FTS	0.5	1.0
6:2-FTCA	2.0	10	FOSA	0.1	0.2
8:2-FTCA	10.0	20	N-MeFOSA	1.0	10
10:2-FTCA	10.0	20	N-EtFOSA	0.5	2.0
6:2-FTUCA	0.1	0.5	FOSAA	0.5	2.0
8:2-FTUCA	0.1	2	N-MeFOSAA	2.0	10.0
10:2-FTUCA	1.0	10	N-EtFOSAA	1.0	10.0
PFHxPA	0.5	2	6:2-FTEO$_1$C	0.5	10.0
PFOPA	2.0	10	8:2-FTEO$_1$C	10.0	20.0
PFDPA	10.0	20	6:2-PAP	2.0	10.0
3:3-acid	10.0	20	8:2-PAP	2.0	10.0
4:3-acid	0.5	2	6:2-diPAP	0.5	10.0
5:3-acid	0.2	1	8:2-diPAP	0.1	1.0

Due to the preparation in MeOH/H_2O (1:1, V:V), M-MeFOSA might be adsorbed to the HPLC vial over time and leading to the decrease of the detected peak area. The standards were prepared simultaneously and the time interval between the measurements of the standards was 30 min. A reduction of 78% of the peak area of M-MeFOSA after 3.5 hours was observed compared to the peak area of the standard, which was analyzed one hour after the preparation. The concentration was determined by the ratio of peak area of the internal standard to the peak area of the analyte. FOSA did not adsorb to the HPLC vial. This resulted in the determination of higher concentration over time. Only the first measurements of the two series of standards could be used for the calibration of FOSA to reduce the influence by adsorption of the internal standard over time. When SPE was performed prior to HPLC-MS measurement (see 2.4.2.3), the methanolic eluate was used for analysis FOSA and its derivatives. When injecting from methanolic solution, no such sorption effects were observed thereby circumventing this problem.

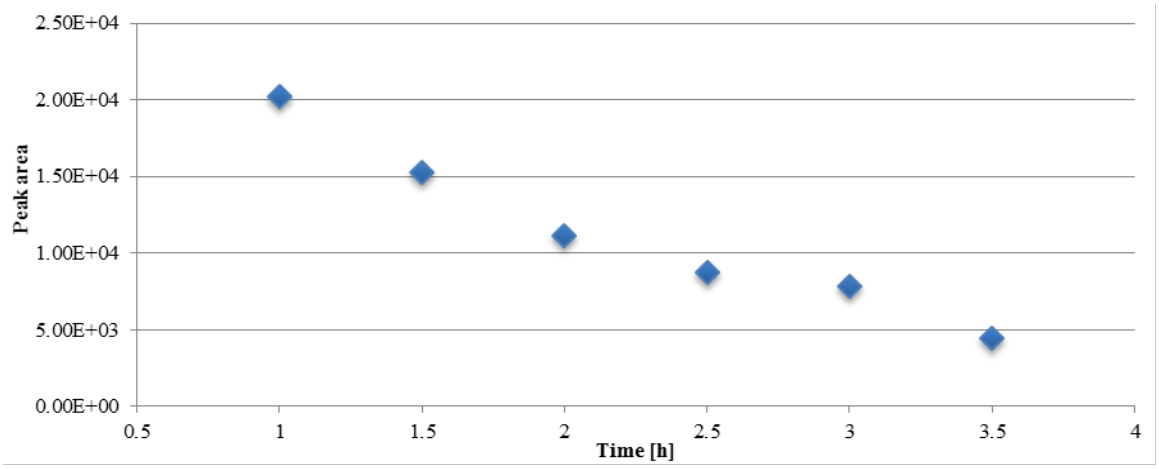


Figure 12: Peak area of M-MeFOSA (10 ng/mL) over time injected from the same HPLC vial.

3.2.2 Repeatability of the HPLC-MS-a method

For the determination of the repeatability and precision of the HPLC-MS-a method six individual standards with a concentration of 3 ng/mL were prepared in MeOH:H_2O (1:1; V:V) and analyzed. The standard deviation (SD) and the accuracy of the six analyzed standards are shown in Table 19. The LOQ for the FTCAs, FTEO1Cs, 10:2-FTUCA, PFOPA, PFDPA, 3:3-acid, 6:3-acid, 7:3-acid, N-MeFOSA, N-MeFOSAA, N-EtFOSAA, 8:2-PAP and 6:2-diPAP was above 3 ng/mL. Therefore, only the compounds, which are listed in Table 19 were used to evaluate the repeatability and precision of the HPLC-MS-a method.

Table 19: SD and accuracy of individual standards (3 ng/mL) analyzed for the determination of repeatability and precision of the HPLC-MS-a method; n=6

Analyte	SD	Accuracy	Analyte	SD	Accuracy
PFBA	0.06	88%	5:3-acid	0.22	83%
PFPeA	0.05	77%	PFBS	0.23	120%
PFHxA	0.20	102%	PFHxS	0.13	90%
PFOA	0.12	87%	PFHpS	0.26	109%
PFNA	0.11	94%	PFOS	0.09	85%
PFDA	0.24	100%	PFDS	0.16	83%
PFUnA	0.20	89%	4:2-FTS	0.26	101%
PFDoA	0.09	107%	6:2-FTS	0.07	99%
PFTrA	0.06	103%	8:2-FTS	0.15	90%
PFTeA	0.17	108%	FOSA	0.28	111%
6:2-FTUCA	0.16	82%	N-EtFOSA	0.51	84%
8:2-FTUCA	0.19	103%	FOSAA	0.20	83%
PFHxPA	0.16	94%	8:2-diPAP	0.11	73%
4:3-acid	0.16	84%			

All standards showed accuracy between 73% and 120% and a SD in a range of 0.06 to 0.51. Only eleven compounds have a LOQ ≥ 0.5 ng/mL and were used for the evaluation of repeatability and precision. The results of the six individual standards with a concentration of 0.5 ng/mL are shown in Table 20.

Table 20: SD and accuracy of six standards (0.5 ng/mL) analyzed for the determination of repeatability and precision of the developed HPLC-MS-a method.

Analyte	SD	Accuracy	Analyte	SD	Accuracy
PFBA	0.01	72%	PFHxS	0.04	66%
PFOA	0.05	67%	PFHpS	0.04	122%
PFTrA	0.04	98%	PFOS	0.02	102%
PFTeA	0.04	94%	PFDS	0.05	96%
6:2-FTUCA	0.05	66%	8:2-FTS	0.05	105%
5:3-acid	0.04	97%			

The eleven compounds showed accuracy in a range from 66% to 122% and a SD in a range from 0.01 to 0.05.

3.2.3 Robustness of the HPLC-MS-a method

Six individual standards with a concentration of 3 ng/mL were prepared in effluent water from a municipal WWTP instead of milli-Q-water to test the developed HPLC-MS-a method for robustness. The SD and accuracy of the analyzed samples are shown in Table 21.

Table 21: SD and accuracy of six standards (3 ng/mL) prepared with effluent water (Beuerbach, Germany) and analyzed for the determination of robustness of the developed HPLC-MS-a method.

Analyte	SD	Accuracy	Analyte	SD	Accuracy
PFBA	0.08	95%	5:3-acid	0.21	70%
PFPeA	0.10	87%	PFBS	0.20	104%
PFHxA	0.17	96%	PFHxS	0.22	89%
PFOA	0.09	89%	PFHpS	0.21	96%
PFNA	0.25	91%	PFOS	0.10	83%
PFDA	0.26	95%	PFDS	0.18	70%
PFUnA	0.39	94%	4:2-FTS	0.10	87%
PFDoA	0.38	93%	6:2-FTS	0.07	88%
PFTrA	0.25	69%	8:2-FTS	0.05	74%
PFTeA	0.17	55%	FOSA	0.36	118%
6:2-FTUCA	0.16	86%	N-EtFOSA	0.40	103%
8:2-FTUCA	0.12	105%	FOSAA	0.32	69%
PFHxPA	0.32	97%	8:2-diPAP	0.26	75%
4:3-acid	0.20	70%			

The results shown in Table 21 are similar to those of the repeatability and precision determination. Most samples showed accuracy of ± 30%. The accuracy of PFTrA (69%), PFTeA (55%) and FOSAA (69%) exceeded these boundaries. For these substances, the matrix effects cannot be entirely compensated by the internal standards used. No labelled internal standard was available for these three substances and this might be a reason for this phenomenon. The SD ranged from 0.07 to 0.40 and displayed the similar SD such as the SD in the determination of repeatability and precision.

3.2.4 Trueness of the HPLC-MS-a method

Two influent samples and the two corresponding effluent samples were spiked with a spiking solution that contains all standards. The concentration of each compound in the spike was 3 ng/mL and was determined by using the HPLC-MS-a. The concentration in the spiked samples was compared to the unspiked samples to calculate the recovery after correction for internal standards. The recovery results sorted by retention time (t_R) are shown in Table 22.

Table 22: Recovery results of spiked influent and effluent samples (WWTP-I1) sorted by retention time; concentration of the spike was 3 ng/mL.

Analyte	Recovery rate [%]				t_R [min]
	INF 1	INF 5	EFF 1	EFF 5	
PFBA	52	50	138	105	3.86
PFPeA	20	27	117	65	4.30
PFHxPA	109	125	111	102	4.33
PFBS	161	156	147	156	4.33

Analyte	Recovery rate [%]				t_R [min]
	INF 1	INF 5	EFF 1	EFF 5	
4:2-FTS	70	69	60	52	4.59
PFHxA	87	71	90	163	4.63
4:3-acid	87	71	103	n.c.	4.71
PFHxS	116	131	94	100	5.00
5:3-acid	110	58	236	82	5.07
6:2-FTUCA	74	89	324	50	5.12
6:2-FTS	94	96	115	98	5.37
PFHpS	174	191	175	189	5.39
PFOA	76	95	144	86	5.41
PFOS	89	86	96	92	5.96
PFNA	104	104	111	137	6.01
8:2-FTUCA	165	158	163	119	6.25
8:2-FTS	85	93	99	111	6.81
PFDA	88	92	70	111	6.85
FOSA	114	98	127	116	7.26
PFDS	74	88	95	94	7.61
PFUnA	76	90	89	104	7.68
PFDoA	99	91	103	114	8.48
N-EtFOSA	95	96	117	111	8.67
PFTrA	82	89	90	96	9.14
FOSAA	90	95	92	77	9.24
PFTeA	99	87	99	106	9.79

n.c.: not calculated, calculated concentration < LOQ

For the analytes, which are not listed in Table 22 the concentration of the spike was below the determined LOQ. These substances were those with the lowest response factors in HPLC-MS and using higher concentrations to enable detection would have caused memory effects for other analytes. In the spiked influent samples the recovery of PFBA (50% and 52%) and PFPeA (20% and 27%) was very low. Additionally, the retention times of PFBA and PFPeA in the HPLC-MS-a method were very close to each other (3.9 min to 4.3 min). This may indicate matrix effects, which could be traced back to high salt concentration in the influent (2500 mg/L Cl^-). Despite the application of ^{13}C labelled internal standard not all matrix effects might be compensated in the influent samples. Comparing to the INF sample, this low recovery rate was not detected in the corresponding effluent samples with a recovery in the rage of 65% to 138%. The recovery rate for 8:2-FTUCA, PFBS, and PFHpS was mainly higher than 150%. Yet, concentrations given in the results part were not corrected for recovery, as it would have to be assessed separately for each sample. Thus, for WWTP-I1 samples, concentrations of PFBS should be interpreted carefully. For enriched samples however, PFBS recovery is not of concern as shown in chapter 3.7.2.

One explanation might be the unavailable labelled substances for PFHpS. MPFHxS was assigned as internal standard for these two compounds. The different properties between PFHxS, PFBS and PFHpS might be a reason for this high recovery rate. Due to the LOQ of 1 ng/mL for 8:2-FTUCA, the lower concentration could not be used to calculate the recovery rate. This led to the high recovery rate for 8:2-FTUCA whereas almost all other recovery rates ranged from 71% to 127%.

One influent sample (INF) and the corresponding effluent sample (EFF) were prepared and measured in duplicates during the analysis of the sample campaign to determine the trueness of the HPLC-MS-a method. The results of the duplicates, the average and the coefficient of variation by using the developed HPLC-MS-a method are shown in Table 23.

The coefficients of variation ≤ 17% underline the repeatability of the developed HPLC-MS-a method.

Table 23: Results of the duplicate determination of PFASs, the average (AVG) and the coefficient of variation (CV) of one influent sample and the corresponding effluent sample by using the developed HPLC-MS-a method.

Analyte	INF 5/1 [µg/L]	INF 5/2 [µg/L]	AVG	CV	EFF 5/1 [µg/L]	EFF 5/2 [µg/L]	AVG	CV
PFBA	22.9	22.0	22.5	3%	11.8	11.4	11.6	2%
PFPeA	20.4	18.7	19.6	6%	11.3	11.0	11.1	2%
PFHxA	5.96	5.5	5.73	6%	51.5	47.1	49.3	6%
PFOA	3.00	3.20	3.10	5%	3.27	3.08	3.18	4%
PFNA	<LOQ	<LOQ	-	-	<LOQ	<LOQ	-	-
PFDA	1.06	1.06	1.06	0%	0.55	<LOQ	0.4[1]	53%[1]
PFUnA	1.86	2.34	2.1	16%	n.d.	n.d.	-	-
PFTrA	1.32	1.58	1.45	13%	n.d.	n.d.	-	-
6:2-FTCA	<LOQ	<LOQ	-	-	8.62	6.78	7.7	17%
6:2-FTUCA	0.94	1.02	0.98	6%	8.91	8.92	8.92	0%
8:2-FTUCA	<LOQ	<LOQ	-	-	1.40	1.33	1.37	4%
4:3-acid	n.d.	<LOQ	-	-	<LOQ	<LOQ	-	-
5:3-acid	4.48	4.88	4.68	6%	7.27	7.43	7.35	2%
6:3-acid	<LOQ	<LOQ	-	-	n.d.	<LOQ	-	-
7:3-acid	<LOQ	<LOQ	-	-	<LOQ	<LOQ	-	-
PFBS	0.54	0.64	0.59	12%	n.d.	n.d.	-	-
6:2-FTS	n.d.	n.d.	-	-	<LOQ	<LOQ	-	-
6:2-FTE01C	n.d.	<LOQ	-	-	n.d.	<LOQ	-	-

[1]: The AVG and CV were calculated by using 1/2 LOQ (0.5 ng/mL) of PFDA.

3.2.5 Conclusion on the validation of the developed HPLC-MS-a method

The repeatability of the validated HPLC-MS-a method resulted in accuracy < 30% and a SD in a range of 0.06 to 0.51 by analyzing a standard with a concentration of 3 ng/mL. Due to the LOQ, only 27 substances could be controlled in case of repeatability. The substances FTCAs, $FTEO_1Cs$, 10:2-FTUCA, PFOPA, PFDPA, 3:3-acid, 6:3-acid, 7:3-acid, N-MeFOSA, N-MeFOSAA, N-EtFOSAA, 8:2-PAP and 6:2-diPAP had a LOQ higher than 3 ng/mL. Nevertheless, the HPLC-MS-a method indicated repeatability at the concentration of 3 ng/mL as well as for the concentration of 0.5 ng/mL. The robustness of the developed HPLC-MS-a method could be demonstrated by the determination of PFASs in the effluent samples. The accuracy of only three substances was not in the rage of ± 30%, because no isotopically labelled compounds were available for these substances and the assigned internal standard compensated not all matrix effects. This phenomenon could also be observed during the trueness experiment. Furthermore, the complex composition of the influent of the industrial WWTP might disturb chromatographic separation for the substances, which have the smallest retention time. However, the duplicates of the influent and effluent sample underline the trueness and repeatability of the developed method with a coefficient of variation ≤ 17%.

3.3 Method development of the HPLC-MS-n method

The peak shape of the analytes determined with the HPLC-MS-n method could be significantly improved compared to the previous method (Knepper et al., 2014). The disadvantage of the preparation method by using MeOH/H_2O (50:50; V:V) is the decrease of the peak area of FTOHs after a time, probably due to adsorption to the HPLC vial walls. The peak area of a quality control standard with a concentration of 100 ng/mL, which was measured directly after preparation, after 5.5 hours, after 22.5 hours and after 31.5 hours, is shown in Figure 13.

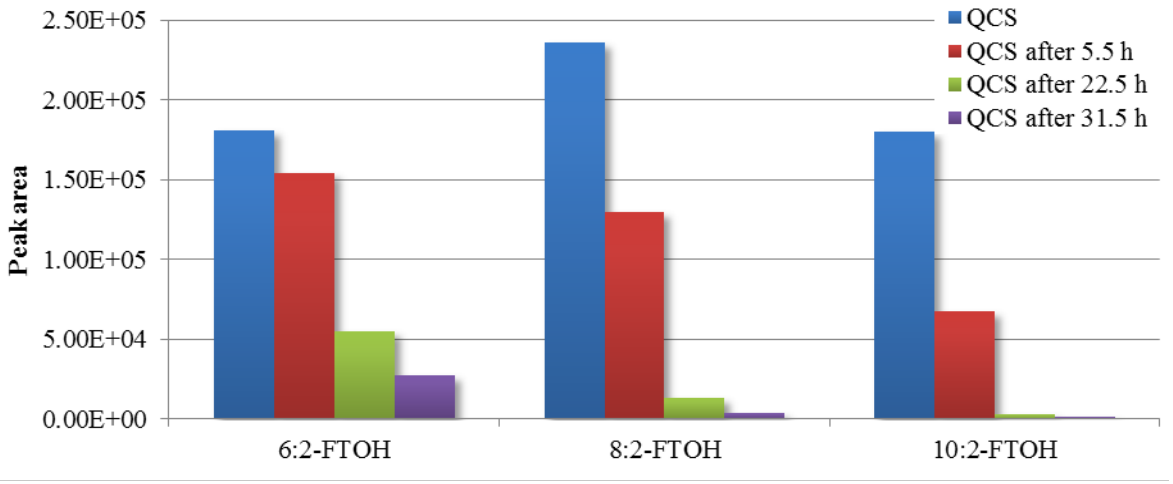


Figure 13: Peak area of a fourfold measurement of a quality control standard (QCS) with a concentration of 100 ng/mL; measured directly after the preparation, after 5.5 hours, after 22.5 hours and after 31.5 hours

The FOSEs were excluded from this diagram to clarify the reduction of the peak area of FTOHs over time. The FOSEs exhibited a decrease of the peak area as well as the FTOHs. The range of decrease was only 16% for N-MeFOSE and 17% for N-EtFOSE after 31.5 hours. Absorption of FTOHs from to vials or volatilization of FTOHs might be the reason for the decrease of the peak area over time. Due to these results, all further prepared samples, which were directly analyzed by the HPLC-MS-n method were measured directly after the preparation. For enriched samples, this problem was circumvented by injecting from methanolic eluate directly, where no adsorption occurs.

3.4 Validation of the developed HPLC-MS-n method

For validation of the enhanced HPLC-MS-n method the reproducibility, robustness and precision was tested by different standards. Using effluent and influent samples from the industrial WWTP the trueness of the method was tested.

3.4.1 Calibration of the HPLC-MS-n method

Three series of standards in a range of 0.1 ng/mL to 500 ng/mL with eight concentration levels were prepared in MeOH/H_2O (1:1, V:V). Each standard was directly measured with the developed HPLC-MS-n method after the preparation. Only the results with accuracy of ± 30% and with a signal to noise ratio > 9 were quantified and implied in the calibration curve. These parameters were also used to determine the limit of quantification (LOQ). The software Analyst® 1.5.1 (AB Sciex) was used for the determination of the signal to noise ratio of the LOQ as well as for the limit of detection (LOD) with a signal to noise ratio of > 3. The software MultiQuant® 2.1 (AB Sciex) was used for the determination of accuracy as well as the calibration with a weighting of 1/x. A higher priority was acquired to the lower concentration levels by the application of this weighting. The method LOD and LOQ to analyze the water samples from the industrial WWTP are shown in Table 24.

Table 24: Method LOD and LOQ of the developed HPLC-MS-n method to determine the amount of PFASs in the water samples of the WWTP-I1.

Analyte	LOD [ng/mL]	LOQ [ng/mL]	Analyte	LOD [ng/mL]	LOQ [ng/mL]
6:2-FTOH	5	10	N-MeFOSE	< 2	10
8:2-FTOH	2	10	N-EtFOSE	< 2	10
10:2-FTOH	2	10			

The calibration curve of 10:2-FTOH showed a R^2 > 0.97 and the R^2 of 6:2-FTOH, 8:2-FTOH, N-MeFOSE and N-EtFOSE was > 0.99.

3.4.2 Repeatability and precision of the HPLC-MS-n method

A method for the determination of FTOHs and N-Me/Et-FOSE was already available from previous PFAS projects (Knepper et al., 2014) and thus did not have to be developed. Except for the addition of a mass-labeled 6:2-FTOH internal standard, previous parameters were maintained.

For the determination of the repeatability and precision of the HPLC-MS-n method six individual standards with a concentration of 100 ng/mL were prepared in MeOH:H_2O (1:1; V:V) and analyzed directly after the preparation, respectively. The standard deviation (SD) and the accuracy of the six standards analyzed are shown in Table 25.

Table 25: SD and accuracy of six standards (100 ng/mL) analyzed for the determination of repeatability and precision of the developed HPLC-MS-n method; n=6.

Analyte	SD	Accuracy
6:2-FTOH	10.5	105%
8:2-FTOH	8.36	104%
10:2-FTOH	16.4	127%
N-MeFOSE	14.2	149%

N-EtFOSE	13.5	149%

The replicate determinations of FTOHs showed accuracy between 70% and 130%. No labelled compound was available for FOSEs and therefore M-8:2-FTOH was used as internal standard. Responsible for the accuracy of 149% of FOSEs might be the different properties compared to the used internal standard. Due to this accuracy FOSEs will be only qualified and not quantified.

3.4.3 Robustness of the HPLC-MS-n method

Three individual standards with a concentration of 100 ng/mL were prepared with effluent water from a municipal WWTP (Beuerbach, Germany) instead of milli-Q-H_2O to verify the capability of the HPLC-MS-n method. The SD and accuracy of the analyzed samples are shown in Table 26.

Table 26: SD and accuracy of three standards (100 ng/mL) prepared with effluent water and analyzed for the determination of robustness of the developed HPLC-MS-n method; n=3.

Analyte	SD	Accuracy
6:2-FTOH	7.07	114%
8:2-FTOH	3.83	112%
10:2-FTOH	23.3	205%
N-MeFOSE	3.94	84%
N-EtFOSE	8.62	106%

Besides for 10:2-FTOH the accuracy was 70-130% for all other analytes. Matrix effects might influence the determination of 10:2-FTOH and were not compensated by the internal standard M-8:2-FTOH due to the different retention time. This possible matrix effects might be compensated for the FOSEs due to their retention time, which was closer to the used internal standard than the retention time of 10:2-FTOH.

3.4.4 Trueness of the HPLC-MS-n method

Two influent samples and the two corresponding effluent samples were spiked with a spiking solution that contains all standards. The concentration of the spike was 100 ng/mL for each compound and was determined by using the HPLC-MS-n method. The concentration in the spiked samples was compared to the unspiked samples to calculate the recovery after correction for internal standards. The recovery results of the experiment are shown in Table 27.

Table 27: Recovery results of spiked influent and effluent samples of WWTP-I1 sorted by retention time; concentration of the spike was 100 ng/mL.

Analyte	Recovery rate			
	INF 1	INF 5	EFF 1	EFF 5
6:2-FTOH	168%	98%	109%	110%

8:2-FTOH	108%	99%	115%	112%
10:2-FTOH	229%	186%	188%	181%
N-MeFOSE	80%	76%	82%	81%
N-EtFOSE	102%	91%	103%	102%

The recovery rate of 10:2-FTOH in all samples was determined in a range from 180% to 229%. This substance showed significant differences in the recovery rate compared to the other substances in the group of FTOHs. The complex ionization process leading to ammonium adducts seems to be hampered significantly even for substances whose retention times differ only slightly. This phenomenon was also observed in the robustness experiment where effluent water was used instead of milli-Q-H_2O. Except for the recovery rate for 6:2-FTOH in the sample INF 1, all others were in a range of 76% to 115%. For WWTP samples directly measured by HPLC-MS-n method, concentrations for 10:2-FTOH should be interpreted carefully, as the values determined may be overestimated.

One influent sample and the corresponding effluent sample were prepared and measured in triplicates during the analysis of the sample campaign to determine the trueness of the HPLC-MS-a method. No FTOHs and no FOSEs were detected in the effluent samples. The results of the triplicates of the influent, the AVG and the CV by using the HPLC-MS-n method are shown in Table 28.

Table 28: Results of the triple determination of PFASs, the average (AVG) and the coefficient of variation (CV) of one influent sample by using the HPLC-MS-n method.

Analyte	INF 5/1 [µg/L]	INF 5/2 [µg/L]	INF 5/3 [µg/L]	AVG	CV
6:2-FTOH	458	489	514	487	6%
8:2-FTOH	85.9	79.4	88.1	84.4	5%
10:2-FTOH	48	37.5	46.0	43.8	13%
N-MeFOSE	n.d.	n.d.	n.d.	-	-
N-EtFOSE	n.d.	n.d.	n.d.	-	-

No FOSEs were detected in the influent samples. The CV ≤ 13% shows the repeatability of the HPLC-MS-n method.

3.4.5 Conclusion on the validation of the HPLC-MS-n method

The repeatability of the developed HPLC-MS-n method showed accuracy < 30% for the FTOHs. Due to the missing internal standard the accuracy for the FOSEs was with a value of 149% too high. The SD of all compounds analyzed during the repeatability experiment ranged from 8.4 to 16.4 by the measurement of a 100 ng/mL standard. By using effluent water from a municipal WWTP instead of milli-Q-H_2O the robustness of the HPLC-MS-n method was tested. Beside for 10:2-FTOH the accuracy was < 30% for all analytes. The SD of 10:2-FTOH was 23.3 and ranged from 3.9 to 8.6 for all other analytes during the investigation of a 100 ng/mL standard. Apart from 10:2-FTOH, the recovery rate of the spiked influent and

effluent samples ranged from 76% to 115%. The recovery rate of 10:2-FTOH in all samples analyzed was between 180% and 229% and therefore too high, compared to 6:2-FTOH and 8:2-FTOH. However, the triplicate measurements of three influent samples underline the trueness and repeatability of the developed method with a coefficient of variation ≤ 13%.

3.5 Development of an analytical method for selected GC-compatible volatile PFASs in water and air samples

3.5.1 Development of a GC-MS method

A GC-MS method was developed apart from the LC-MS/MS method for the determination of the volatile PFASs with the exception of FTOHs. These compounds were found to be non-ionizable using ESI. Aside from this main reason, GC is a well suited method to separate these highly volatile PFASs. Three ionization techniques were explored: electron ionization (EI), positive chemical ionization (PCI) and electron capture negative ionization (ECNI).

Initially, the separation of the different analytes was optimized by developing a column oven temperature program. Two types of injection system were tested: on-column injection (at an initial temperature of 35 ^{o}C) and splitless injection (injector system temperature was set at 180 ^{o}C). Because of the high influence of the system leak on the injection repeatability (high standard deviation of the areas) of the most volatile analytes, the splitless injection was eventually chosen as the final method of sample introduction. The splitless injection system produced a broader peak shape for the most volatile compounds particularly 6:2-FTO and PFHxI. This resulted in slightly lower sensitivity of the method towards the mentioned PFASs. Figure 14 shows the resulting chromatogram generated with the +EI detection. Some peaks were assigned based on the match of the generated mass spectrum to that in the NIST library. Other analytes that are not in the NIST library were assigned based on the observed spectral pattern. The retention times of the injected single analyte standard solution provided additional confirmation of the identity of the compounds represented at each peak. PFBI co-eluted with pentane due to its very high vapor pressure and no modification of the method resulted in an improvement regarding this issue. Thus, it was no longer analyzed in this study. 6:2-FTO (t_R = 2.88 min) co-eluted with a pentane impurity. Separation was done by selection of unique masses for quantification and qualification.

EI is the most common mode of ionization after GC separation. In this method, the analyte molecules in the gas phase and eluting out of a GC column are passed through the ion source, where a current of electrons in a vacuum are accelerated from a heated filament. A radical cation is normally produced when an electron is knocked-out from the molecule, from a region with high electron density. The radical cation fragments to smaller ions and neutral species depending on its stability. During the method development, two electron energies were tested: 70 and 45 eV. Not much difference was observed in terms of the fragmentation patterns and the resulting ion intensities. The electron energy of 70 eV was eventually selected because it is the normal setting.

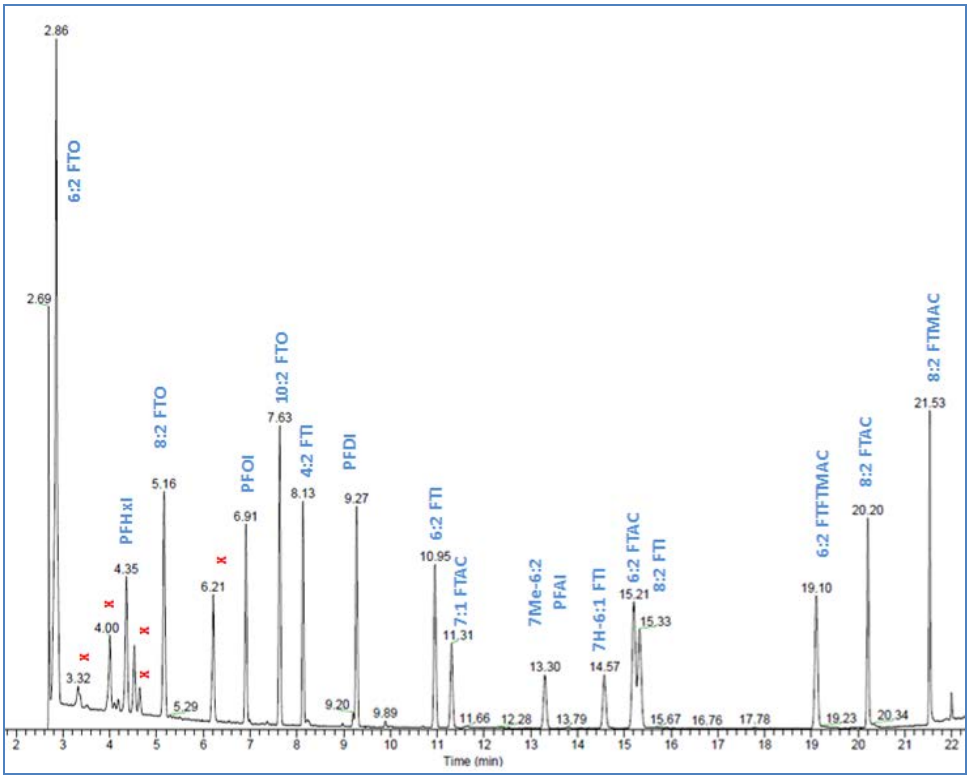


Figure 14. Total Ion Chromatogram generated in the +EIMS detection (10 μg/mL solution). Peaks labeled with 'x' represent n-pentane impurities.

In PCI, a reagent gas (in this case, methane) is first ionized via EI (usually also set at 70 eV) in the ion source. The resulting reagent ions CH_5^+ and $C_2H_5^+$ are made to react with the analyte molecules forming $[M+H]^+$ and $[M+C_2H_5]^+$ ions. In the method development, the flow rate of methane and the ion energy are the most important parameters to optimize. Air leak has greater effect on this ionization mode than in other modes.

In ECNI, the methane reagent gas slows down some electrons making it possible for these electrons to be captured by the highly electronegative atoms in the analyte molecules. This mode is sensitive to molecules with halogens, nitrogen and oxygen but is not useful to molecules without heteroatoms and without double bonds. In the method development, the flow rate of methane and the ion energy are the most important parameters to optimize.

To illustrate the differences in the ionization, Figure 15A to C show the mass spectra generated for PFHxI using the different ionization techniques. The generated mass spectra are very different from each other. The ions produced and detected by the EI shows cleavage of C-C bonds with the terminal C-C bond the easiest to be cleaved generating a fragment with *m/z* of 69. It can be emphasized that the fragment with *m/z* of 69 is in fact, produced in all the compounds being analyzed in this study although at varying extent from one compound class to another.

In PCI, as mentioned above, the prominent ions are the $[M+H]^+$ and $[M+C_2H_5]^+$. The adduct $[M+H]^+$ can fragment by cleaving off HI and HF resulting to $[M-I]^+$ and $[M-F]^+$ ions, respectively. Chemical ionization is a softer ionization technique compared to EI, thus the ions produced in this mode have higher *m/z* values.

In ECNI, the iodide ion (*m/z* 127) creates a very high baseline and affects the chromatographic peak shape of all analytes. In the TIC chromatogram generated by ECNI MS detection there is an observed tailing of the peaks. The observed tailing of peaks is solely due to the iodide ion. The ion signals (with the exception from that of I^-) in ECNI are low compared to that in EI and PCI. This can be the due to two reasons: 1. Ionization efficiency is low and 2. Many different kinds of ions are generated. Given this, ECNI will not be an ideal method for the trace level determination of the precursor compounds.

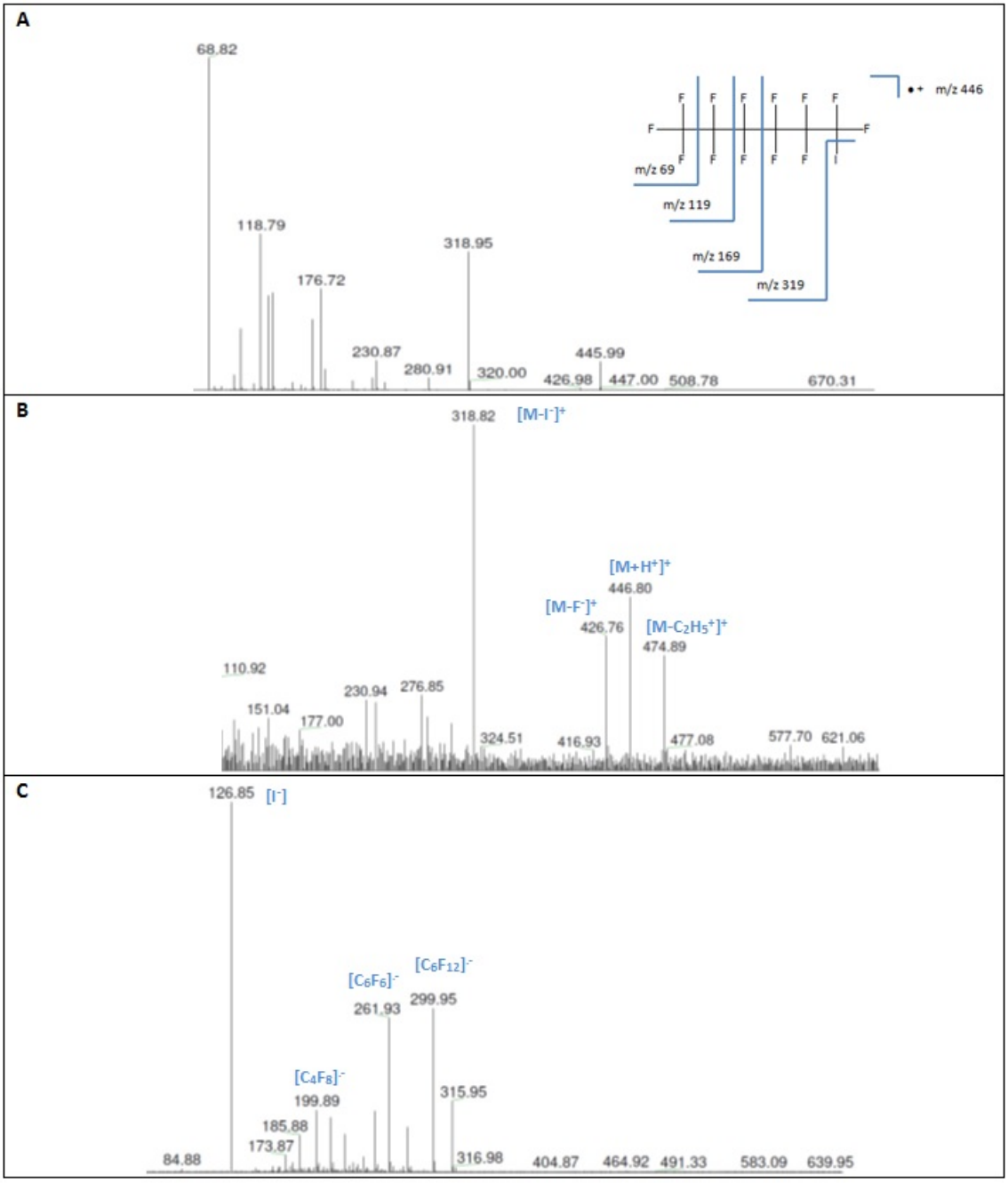


Figure 15. Mass spectra of perfluorohexyl iodide generated using three ionization modes: A. EI; B. PCI; and C. ECNI. Also shown are the most likely identities of the ions.

3.5.2 Performance characteristics of EI and PCI

The performance characteristics of both EI MS and PCI MS were determined to evaluate which ionization technique will be better suited in the trace level analysis of volatile PFASs. Selected ion monitoring (SIM) mode was used to increase the sensitivity of detection. Table 29 shows the ions initially chosen to quantify and qualify the analytes. The ions with the

highest intensity (base ions) were chosen as the quantification ions. If the base ion produces a very high and noisy baseline (usually becomes the case for smaller ions), then another ion is selected for quantification.

Table 29. Quantification and qualification ions used in the SIM analysis with EI and PCI MS detection.

	EI		PCI	
	Quantification [*m/z*]	Qualification [*m/z*]	Quantification [*m/z*]	Qualification [*m/z*]
6:2-FTO	77	131	327	347
8:2-FTO	77	131	427	447
10:2-FTO	77	131	527	547
PFHxI	319	69	319	447
PFOI	69[a]	419[a]	419	527
PFDI	69[a]	519[a]	519	627
4:2-FTI	374	227	355	403
6:2-FTI	474	327	455	503
8:2-FTI	574	427	555	427
7H-6:1-FTI*	191	442	423	277
7Me-6:2-FTI*	524	377	505	553
6:2-FTAC	55	99	419	447
7:1-FTAC*	55	85	455	503
8:2-FTAC	55	99	519	547
6:2-FTMAC	432	69	433	461
8:2-FTMAC	532	69	533	561

Substances labeled with * were used either as internal standard or control standards.

[a]The ion with *m/z* 69 is not unique and can be present in the matrix. The quantification ions were changed to *m/z* 419 and 519 for PFOI and PFDI respectively in the later stages of method development.

Table 30 and Table 14 show the instrumental figures of merit determined for the PCI and EI respectively. It can be observed that the sensitivity of EI is two orders of magnitude greater than PCI. It is primarily because of this (although not entirely) that the EI can achieve a subpicogram LOD for most of the analytes. The calibration curve was linear for both the EI and PCI within the bounds specified. Therefore, EI is a better suited ionization mode in the determination of volatile PFAS.

The % residuals were also calculated to have a thorough evaluation of the linearity of the calibration curve. Relying on the coefficients of determination alone will not be sufficient to evaluate linearity. The % residuals represent the deviation of the calculated concentrations using the equation of the calibration curve from the actual concentrations as prepared. The larger the % residual, the higher is the estimation error. Table 16 and Table 75 show the average % residuals of the prepared calibration curves using external standard and internal

standard methods respectively. As expected, the external calibration curve has higher average % residuals than the corresponding calibration curve with internal standard correction. Moreover, it can be observed in Table 16 that the calculated concentration of the standard solution with 2 pg/µL has a large positive % residual of up to nearly 65%. This can be interpreted as a bias of ± 1.3 pg/µL. The individual % residuals were randomly distributed across the whole concentration range and between trials. With $R^2 > 0.99$ and with a random distribution of % residuals, it can be concluded that the calibration method was linear.

Table 30. Summary of the GC with PCI MS instrumental figures of merit.

Compound	Selectivity Area Ratio Criterion		Absolute LOQ[d] (pg)	R^2 (LOQ-8000 pg) with IS	R^2 (LOQ-8000 pg) without IS	Sensitivity (slope of calibration curve without IS, pg^{-1})
	Area Ratio	RSD (%)				
6:2-FTO	88.6	9.0	<100[b]	0.9974[e]	0.9904[e]	1.3E+02
8:2-FTO	90.3	4.6	<100[b]	0.9955[e]	0.9992	1.9E+02
10:2-FTO	83.5	5.1	<100[b]	0.9991	0.9985[e]	1.6E+02
PFHxI	2.0	1.7	400	0.9904	0.9863	3.4E+01
PFOI	1.9	1.3	400	0.9935	0.9934	2.6E+01
PFDI	1.3	2.0	400	0.9813	0.9907	1.9E+01
4:2-FTI	2.6	0.9	100	0.9984	0.9992	1.2E+02
6:2-FTI	2.6	2.5	100	0.996	0.9988	1.0E+02
8:2-FTI	5.5	4.9	100	0.9848[e]	0.9931[e]	7.6E+01
6:2-FTAC	5.7	3.4	<100[b]	0.9964[e]	0.9985	1.8E+02
8:2-FTAC	5.5	2.2	100	0.9849[e]	0.9986	9.2E+01
6:2-FTMAC	5.4	1.6	<100[b]	0.9991	0.9990	1.6E+02
8:2-FTMAC	5.3	1.7	100	0.9799[e]	0.9846[e]	1.3E+02

[a]The molecular ion is not fragmented, so that the qualifier *m/z* has a very low intensity.

[b]LOQ can be lowered to less than 0.1 μg/mL.

[c]Limit represents the minimum concentration at which the qualifier ion can be integrated with reasonable precision area>5000).

[d]LOQ is only a simple estimation based on the minimum concentration in which the quantifier ion can be integrated with reasonable precision (area>5000).

[e] The coefficient of determination can be improved further if the range is limited to 6 μg/mL.

3.6 Water-air partitioning of PFASs

The results of the pseudo-partition experiment for a 20 ng volatile PFASs spiked into the 2 L water are summarized in Table 31. It can be seen from the table that a significant portion (up to more than half for some compounds) of the 20 ng compounds was lost into the air. The results for the FTACs were not included because of cross contamination of the set-up from the adsorbed FTACs in the glass bottles giving unusually high amounts of FTACs. The total absolute amounts in water and in air roughly sum up to 20-30 ng. The results confirmed that indeed, there is partitioning of the volatile PFASs favoring the air.

The partitioning behavior of volatile PFASs including FTOs, PFAIs, FTIs and even FTACs and FTMACs are expected because of their high volatility and high hydrophobicity. Currently, there are no experimental data on the Henry's law coefficient (or partition coefficient) of these compounds. An estimation of the Henry's law coefficient was attempted using the computational approach with the EPISUITE™ software of the United States Environmental Protection Agency (US EPA). Caution must be taken however in interpreting data generated by software. The lack of representation in the model of PFASs is enough reason to doubt the fitness of the calculated values to the experimental ones. Here, the theoretical data is used to get a glimpse of the general partitioning behavior of the volatile PFASs being analyzed.

The results of the theoretical calculations are shown in Figure 16. The water solubility versus vapor pressure plot enables the comparison of the Henry's law constants (H, diagonal lines) of the volatile PFASs and the common volatile compounds. Three diagonal lines were labeled in the plot namely H = 10^3, 100 and 10^{-3} atm m^3/mol. The H increases logarithmically from right to left. For example, ethyl acetate and 2-pentanone have H between 10^{-4} and 10^{-3} atm m^3/mol while toluene and p-xylene have H between 10^{-3} and 10^{-2} atm m^3/mol. Compounds with high Henry's law constant are easily released into the air from water. Thus, greater fractions of ethyl acetate and 2-pentanone can remain in the water compared to toluene and p-xylene. The H value of 10^{-3} atm m^3/mol (dotted red line) can be taken as a rule of thumb to distinguish between compounds that will most likely partition into the water and those that will mostly be in the air. The 6:2-FTOH and 8:2-FTOH have comparable H values to that of the linear alkanes. However, the volatile PFASs are situated at the far left of the graph with H > 10^1 atm m^3/mol. In terms of theoretical vapor pressures (y-axis), the volatile PFASs are not significantly different from the other volatile organic compounds. However, based on theoretical solubilities (x-axis), the volatile PFASs are far more insoluble than the organic compounds. These observations can be translated into a generalization that the very high tendency of the volatile PFASs to partition into the air is mainly due to their very low solubilities in water rather than their vapor pressures. The general trends in the graph agree very well with the results of the pseudo-partitioning experiment.

Table 31. Distribution of volatile PFASs (20 ng each) spiked into a 2 L water with 2 L air above it after 24 h equilibration (n=2).

Compound	Absolute Amount (ng)			Distribution (%)	
	air	water	total	air	water
6:2-FTO	15	8	23	66	34

Compound	Absolute Amount (ng)			Distribution (%)	
	air	water	total	air	water
8:2-FTO	13	16	30	46	54
10:2-FTO	11	13	24	44	56
PFHxI	17	10	27	63	37
PFOI	11	14	25	45	55
PFDI	10	12	22	47	53
4:2 FTI	12	8	21	60	40
6:2-FTI	8	12	20	41	59
8:2-FTI	7	14	20	33	67
6:2-FTAC	-	-	-	-	-
8:2-FTAC	-	-	-	-	-
6:2-FTMAC	5	11	16	31	69
8:2-FTMAC	8	15	23	33	67

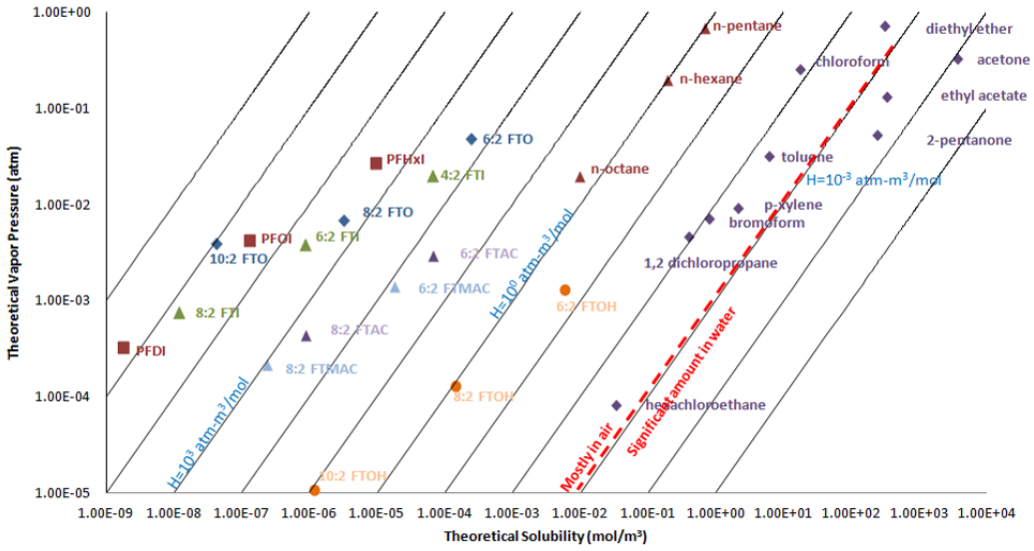


Figure 16. EPISUITE™-generated water solubilities and vapor pressures of the volatile PFASs compared to other volatile compounds (the diagonal lines are the Henry's law constant lines).

The results of the water-air partitioning experiment have major implications on the development of the method to determine these compounds in water. First, spiking of the water with the analytes to determine method trueness would not be possible due to the near-instantaneous partitioning of the compounds to air resulting in low recoveries. The calculated % recovery would be only up to 70%. Second, the enrichment control standard added into the water prior to sample preparation cannot be used as an internal standard. The determination of volatile PFASs in water with enrichment using HLB SPE was still possible. However, the direct assessment of method accuracy by spiking would not be possible due to the near-instantaneous partitioning of the compounds to air resulting to low recoveries. A unique quality control and quality assurance procedure was developed for this analysis. The method is discussed in details in section 3.7.3.

3.7 Development of SPE methods for aqueous samples

3.7.1 Recovery of the analytes determined using the SPE-1 and HPLC-MS-n method

In the first step the loaded SPS columns were eluted with MeOH. This first eluate contained the FTOHs and the FOSEs and was measured by using the HPLC-MS-n method. The peak areas of the analytes after SPE were compared to the peak areas of a 50 ng/mL standard. The standard had the same concentration as the spiked sample (see 2.4.1.1) and was measured simultaneously. The recovery rate of the peak areas after SPE is shown in Figure 17.

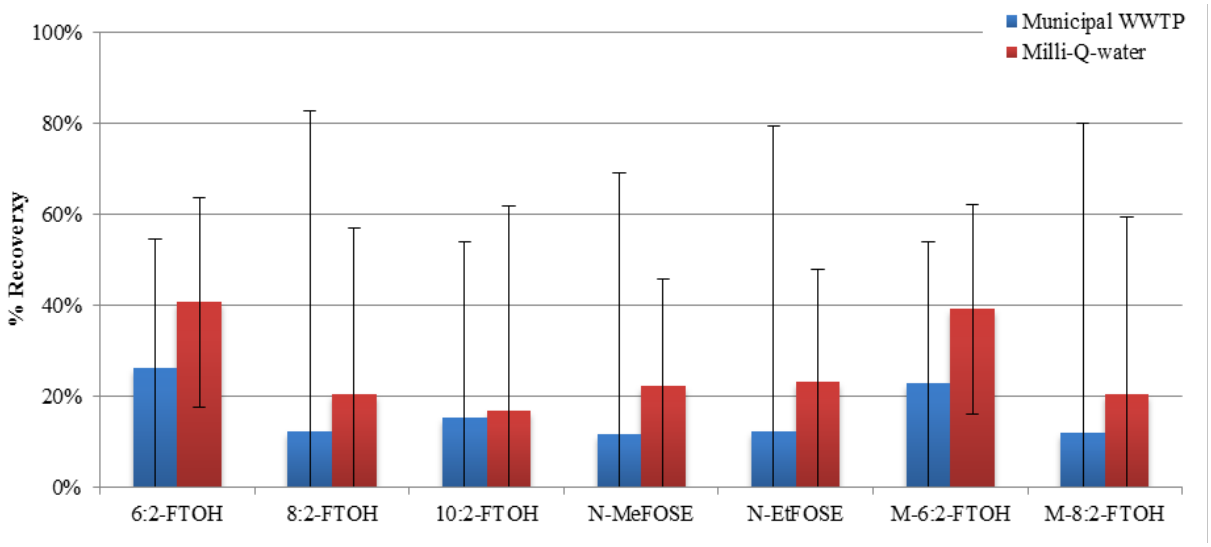


Figure 17: Recovery rates of the spike after SPE; comparison of the peak areas for enriched municipal WWTP (Beuerbach) to the peak areas of a prepared standard (50 ng/mL). Error bars represents standard deviation (n=3).

The recovery rate of all analytes was < 40% by the comparison of the peak area, as peak areas are based on acetate adduct formation in ESI-MS, which may not be as reproducible as deprotonation for the HPLC-MS-a method. The recovery rate after correction for the used internal standard is displayed in Figure 18 and shows that inclusion of an internal standard can overcome this issue.

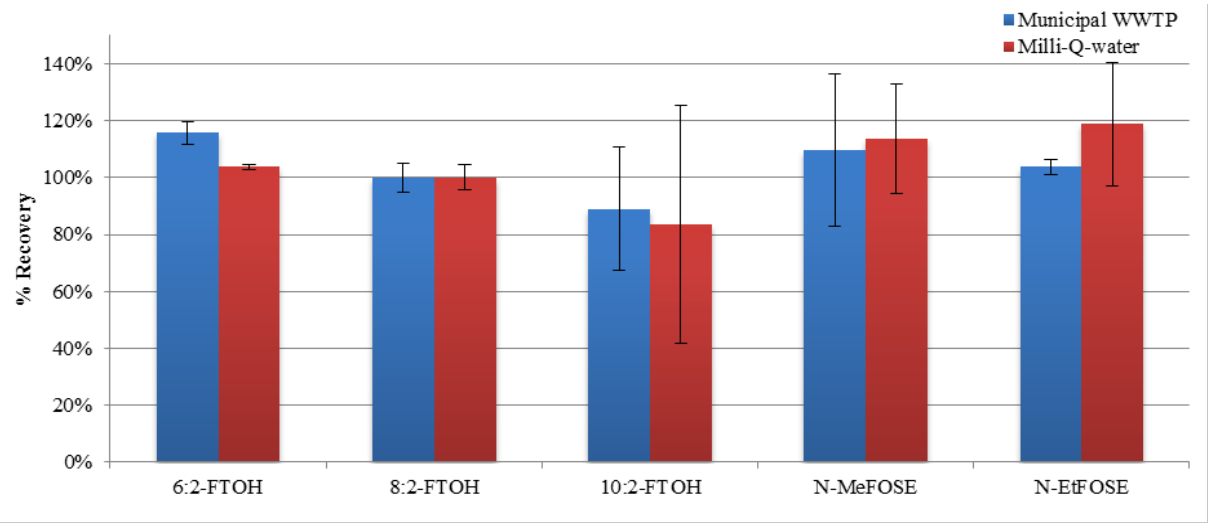


Figure 18: Recovery rates of the spike after SPE of effluent of a municipal WWTP (Beuerbach) and Milli-Q water after correction for the used internal standards; compared to a prepared standard (50 ng/mL). Error bars represent standard deviation (n=3).

The recovery rate of all analytes ranged from 84% to 119%. Due to the used internal standards, the results of 6:2-FTOH and 8:2-FTOH exhibited a very good recovery rate. The retention time of 10:2-FTOH showed the highest variance compared to the retention time of the used internal standard (M-8:2-FTOH). This might be the reason for the lower recovery rate and high SD. No significant difference could be detected by the comparison of effluent water to milli-Q-H_2O as matrix. It was shown, that the developed SPE is well suited for the determination of FTOHs and FOSEs in aqueous samples.

3.7.2 Recovery of the analytes determined by using the SPE-1 method in combination with HPLC-MS-a

In the second step of the developed SPE-1 method, the loaded column was eluted with MeOH containing 1% NH_3. This second eluate contained all analytes of the HPLC-MS-a method except for FOSA, N-MeFOSA and N-EtFOSA. The peak areas of the analytes after the three experiments (enrichment of Milli-Q-water, municipal WWTP effluent and municipal WWTP effluent with subsequent cleanup via EnviCarb, see chapter 2.4.1.1) were compared to the peak areas of a 10 ng/mL standard. The standard was prepared with the same concentration as the spiked sample and was measured simultaneously. The recovery rate of the peak areas after SPE is shown in Figure 19, Figure 20, Figure 21 and Figure 22.

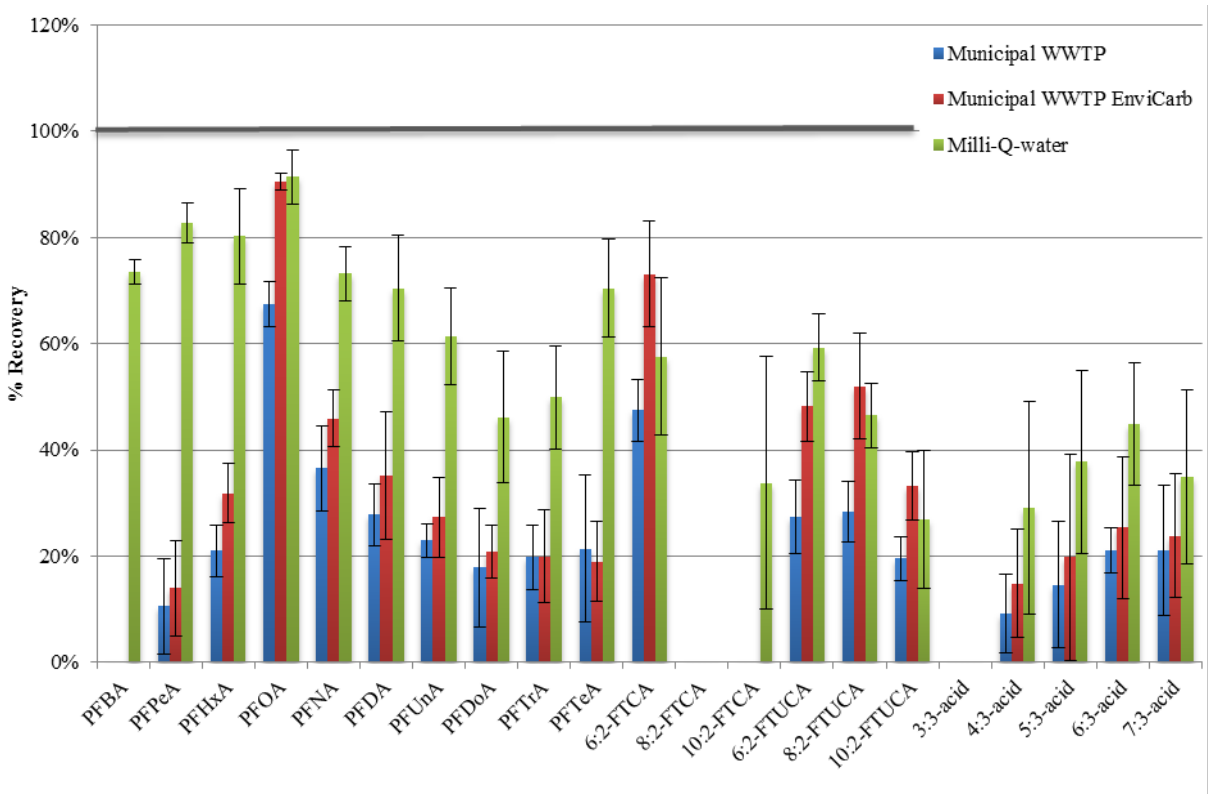


Figure 19: Recovery rates of the spiked PFCAs, FTCA, FTUCAs, PFPAs and X:3-acids after SPE (10 ng/mL); comparison of the peak areas determined to the peak areas of standard at the same concentration level. Municipal WWTP=Beuerbach. Error bars represent standard deviation (n=3).

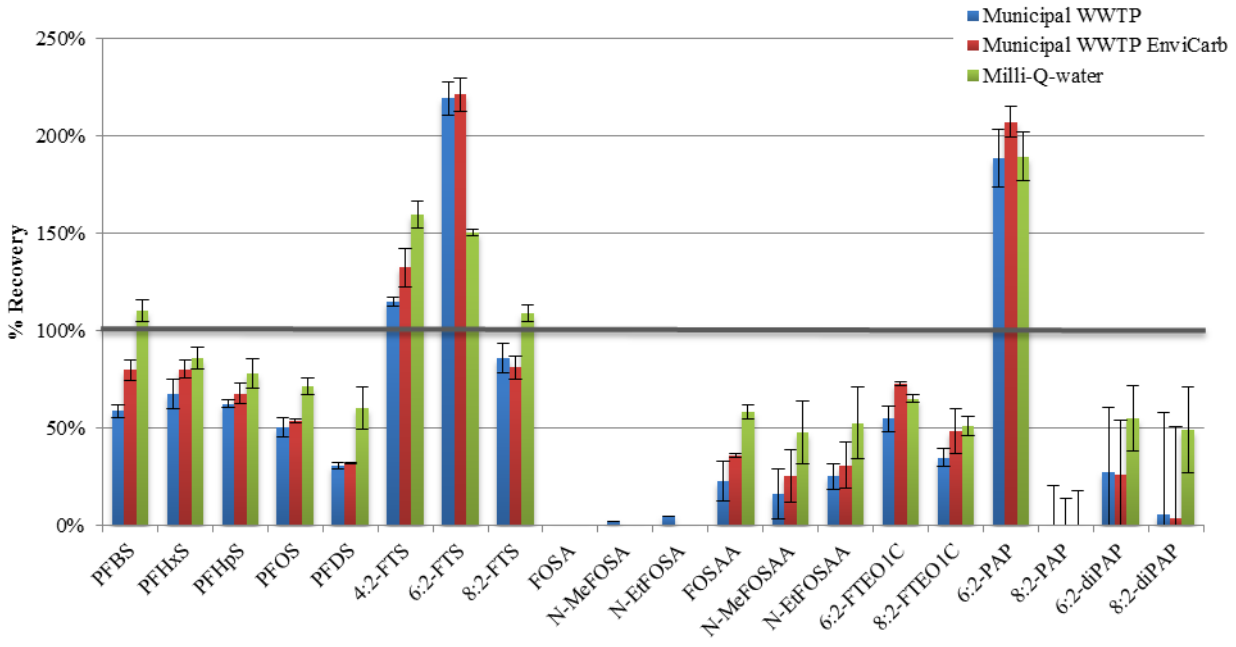


Figure 20: Recovery rates of the spiked PFSAs, FTS, FOSAs, FTEOCs, PAPs and diPAPs after SPE (10 ng/mL); comparison of the peak areas determined to the peak areas of standard. Municipal WWTP=Beuerbach. Error bars represent standard deviation (n=3).

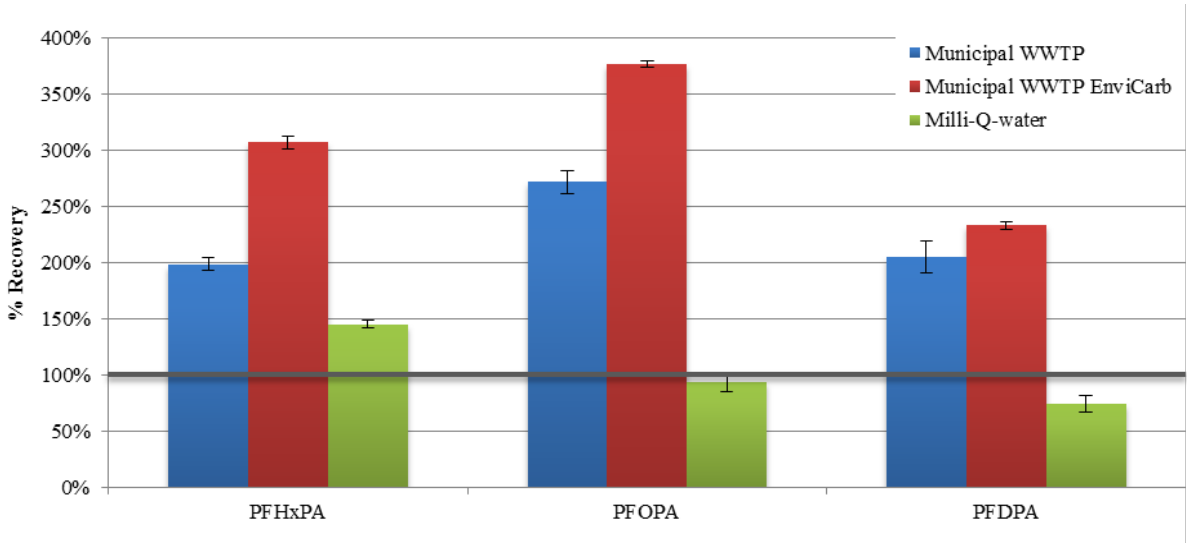


Figure 21: Recovery rate of the spiked PFPAs after SPE (10 ng/mL); comparison of the peak areas determined to the peak areas of standard. Municipal WWTP=Beuerbach. Error bars represent standard deviation (n=3).

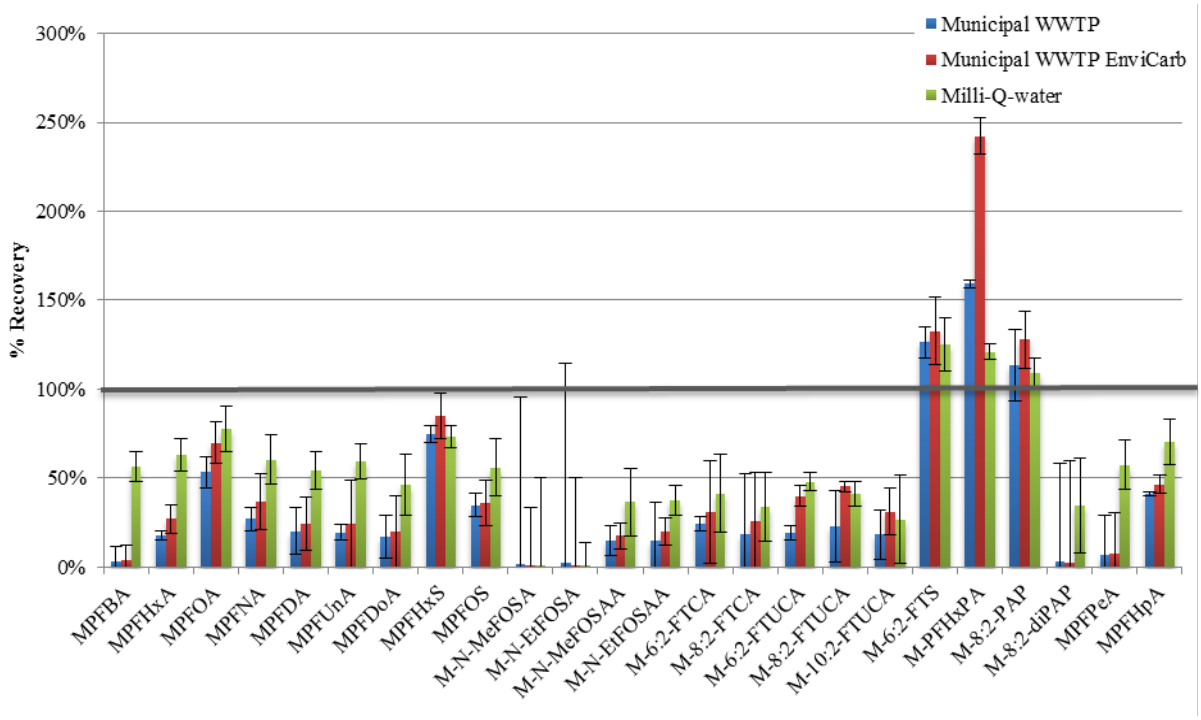


Figure 22: Recovery rate of the spiked internal standards after SPE (10 ng/mL); comparison of the peak areas determined to the peak areas of standard. Municipal WWTP=Beuerbach. Error bars represent standard deviation (n=3)

Apart from PFOA, all PFCAs as well as 10:2-FTCA, X:3-acids and diPAPs were suppressed in the WWTP samples compared to the samples, which were prepared with milli-Q-H_2O. The PFSAs showed a similar suppression but less pronounced. 8:2-FTCA, 3:3-acid and FOSA were not detected during the investigation of the recovery. The 8:2-PAP could not be quantified in all three arrangements and N-MeFOSA and N-EtFOSA were only detected in the WWTP sample without clean up.

The PFPA, as well as 6:2-FTS showed a significant increase of the peak areas in the WWTP samples. In all analyzed samples, the peak areas of 6:2-PAP were twice as high as the peak area of the compared standard. A similarity could be observed by the recovery rate of the internal standards.

The recovery rate after correction for the internal standards is shown in Figure 23 and Figure 24. 8:2-FTCA, 3:3-acid, FOSA and 8:2-PAP were excluded from the shown diagrams because they were not detected or quantified during the investigation of recovery. The results of recovery for 6:2-diPAP was excluded from Figure 24 due to an extraordinarily high recovery rate of ca. 1000%. The reason for this high recovery rate was the significant decrease in the peak area of M-8:2-diPAP, which was also used as internal standard for 6:2-diPAP.

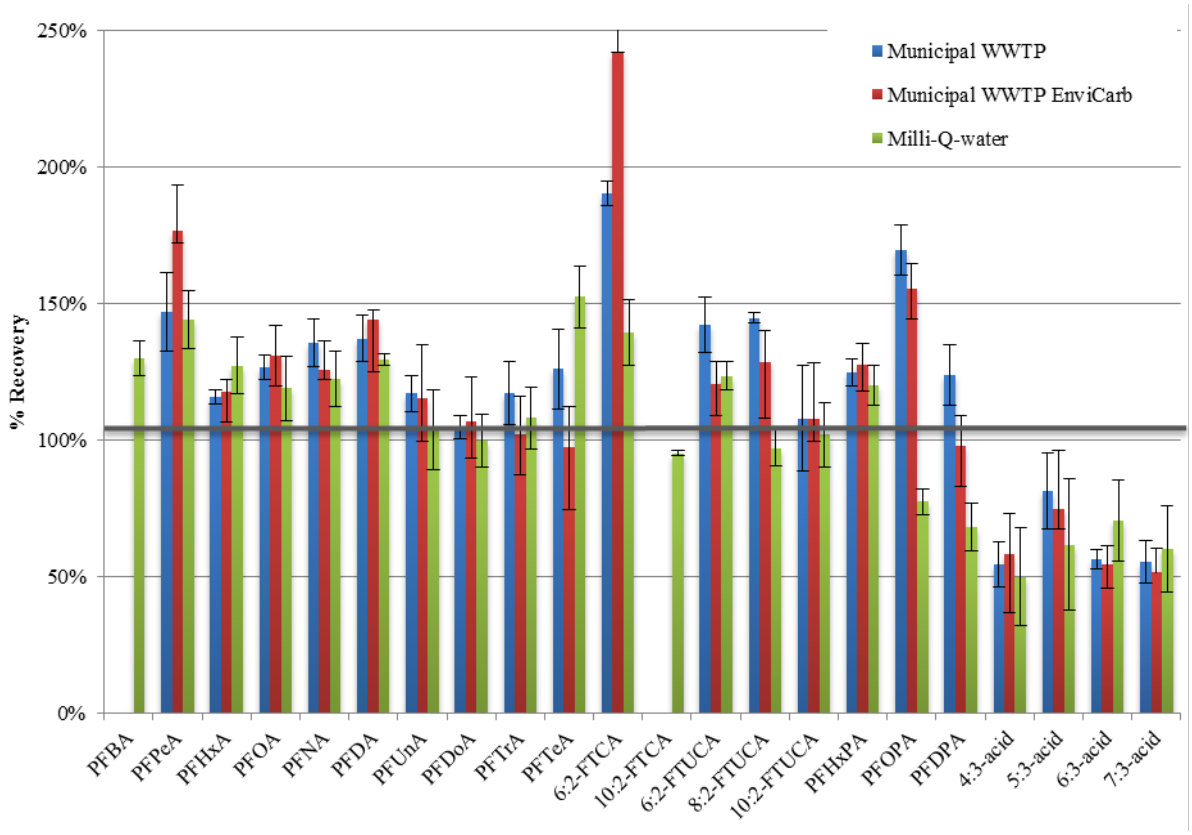


Figure 23: Recovery rate of the spiked PFCAs, FTCA, FTUCAs, PFPAs and X:3-acids after SPE (10 ng/mL) after correction for internal standards; peak area ratios compared with a simultaneously measured standard (10 ng/mL). Error bars represent standard deviation (n=3).

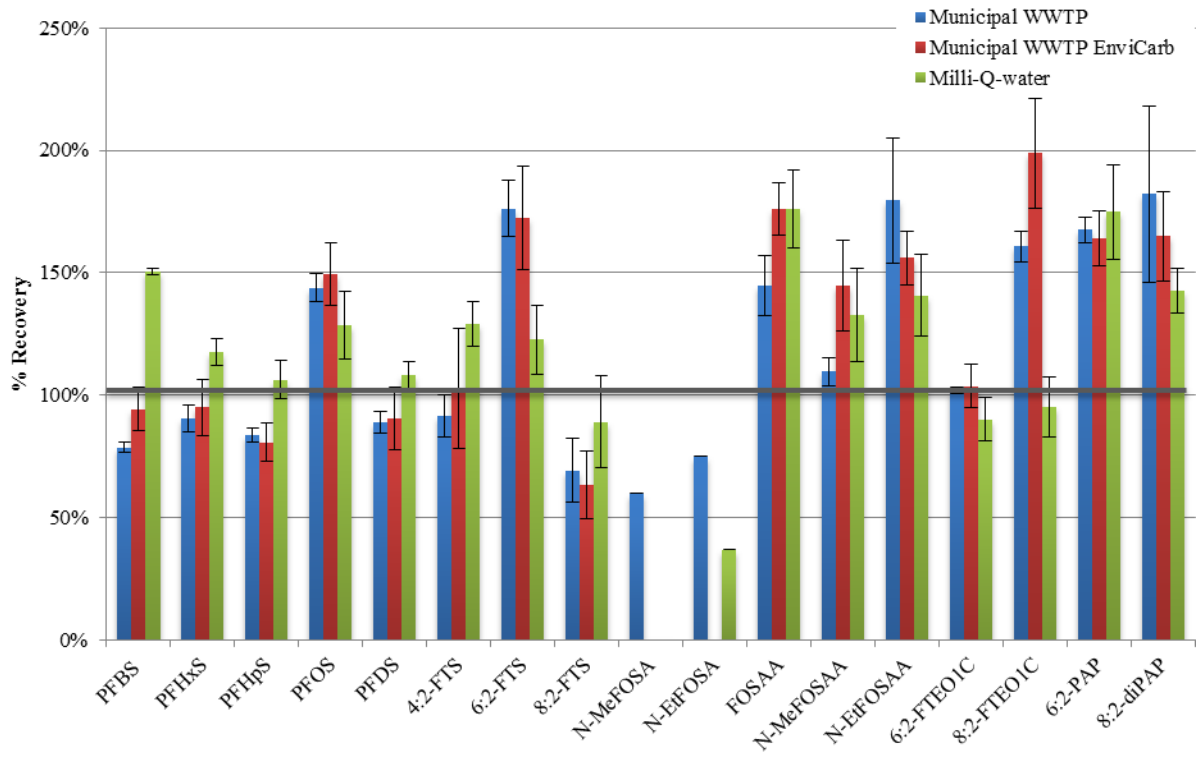


Figure 24: Recovery rate of the spiked PFSAs, FTS, FOSAs, FTEOCs, PAPs and diPAPs after SPE (10 ng/mL) after correction for internal standards; compared with a simultaneously measured standard (10 ng/mL). Error bars represent standard deviation (n=3).

The recovery rate for the PFCAs ranged from 105% to 177%. PFBA as well as 10:2-FTCA could only be quantified in the spiked milli-Q-Water. The recovery rate of 6:2-FTCA ranged from 139% to 242%. The recovery rate of FTUCAs, PFPAs and PFSAs ranged from 68% to 156%. The recovery rate for FTSs, FTEO1Cs, PAPs and diPAPs ranged from 63% to 199%. The MRM transition *m/z* 299 > 80 of PFBS was disturbed by several matrix compounds. Therefore, the MRM transition *m/z* 299 > 99 was used for the recovery rate evaluation of PFBS. The used internal standard compensated most of the detected suppressions. However, the recovery rates for the X:3-acids ranged from 50% to 81%. The assigned internal standards for these substances have different properties compared to the X:3-acids and cannot compensate all matrix effects. As EnviCarb clean-up is time-consuming and did not yield significantly higher recoveries, it was excluded from the final methods.

To ascertain that no breakthrough of acidic substances occurs during the first elution with MeOH, the first SPE eluate (MeOH elution) of a spiked sample for the determination of FTOHs and FOSEs, which is usually foreseen to be analyzed with HPLC-MS-n, was analyzed by the developed HPLC-MS-a method. Eleven compounds of the HPLC-MS-a method were detected in in the first eluate. The three first eluates of the spiked WWTP samples were measured to quantify the concentration of those substances. The peak areas were compared to the peak areas of a standard with the same concentration to evaluate the recovery rate in the first eluate. The results are shown in Figure 25.

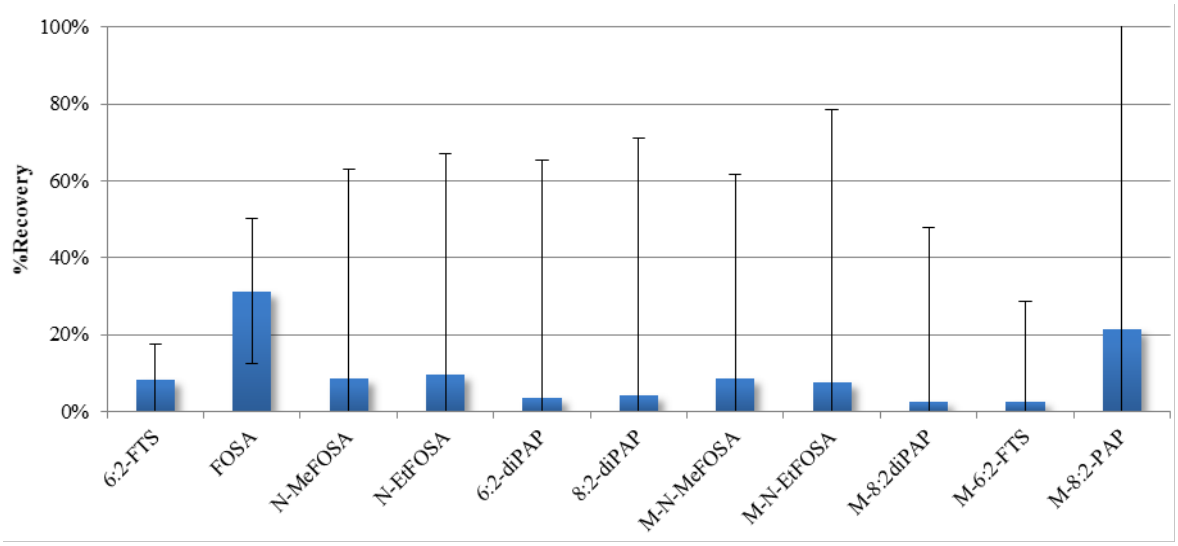


Figure 25: Recovery rate of the detected compounds in the first eluate (MeOH elution) of a spiked WWTP sample after SPE (10 ng/mL); comparison of the peak areas determined to the peak areas of standard. Error bars represent standard deviation (n=3).

The SD was very high for all detected compounds. The internal standards for 6:2-FTS, FOSAs and diPAPs were also detected in the first eluate of the SPE method. The recovery rate after correction for the used internal standard is shown in Figure 26.

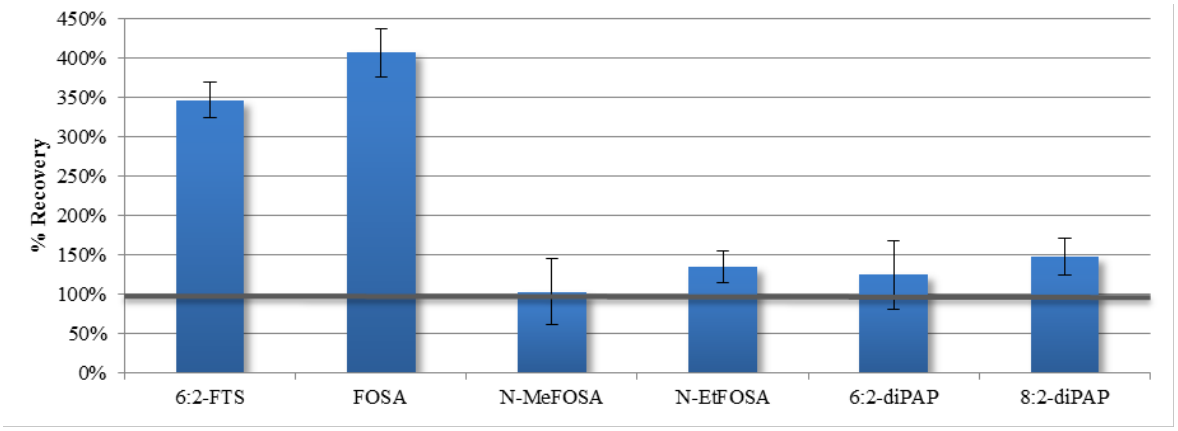


Figure 26: Recovery rate of the detected compounds in the first eluate (MeOH elution) of a spiked WWTP sample after SPE (10 ng/mL) after correction for internal standards; compared with a simultaneously measured standard (10 ng/mL). Error bars represent standard deviation (n=3).

The recovery rate of 6:2-FTS was determined in the first eluate (Figure 24) as well as in the second eluate (Figure 25). Analysis of the second eluate should be done for quantification due to the higher recovery rate by the comparison of the peak area. The reason for the high recovery rate of FOSA was the internal standard M-MeFOSA, which has different properties compared to FOSA. The recovery rate of N-MeFOSA, N-EtFOSA and the diPAP could be determined by analyzing the first eluate with the developed HPLC-MS-a method. Thus, FOSA and derivatives were finally measured by enrichment with SPE, elution with MeOH and measurement via the HPLC-MS-a method.

3.7.3 Development of an extraction method for selected volatile PFASs from aqueous samples

A liquid-liquid extraction set-up was initially tested for enrichment purposes. Absolute recovery of each analyte and the IS were calculated by comparing the areas of the peaks of the extract to that of the standards. Table 32 shows the average absolute recoveries based on peak areas and the RSD of three trials. 7H-6:1-FTI and 7:1-FTAC were planned to be used as extraction or enrichment control standards. 7H-6:1 FTI was used for control of FTO, PFAI and FTI while 7:1 FTAc was used for FTAC and FTMAC. It can be observed that the absolute recoveries for each compound are relatively low and vary greatly. The control standards have the lowest recoveries.

Table 32. Absolute recovery (n=3) based on peak areas of the LLE extract of the spiked milli Q water sample with n-pentane.

Compound	Average Absolute Recovery %	RSD %
6:2-FTO	56	14
8:2-FTO	59	6
10:2-FTO	48	13
PFHxI	55	14
PFOI	55	10
PFDI	41	19
4:2-FTI	47	10
6:2-FTI	58	10
8:2-FTI	60	5
6:2-FTAC	98	20
8:2-FTAC	89	2
6:2-FTMAC	99	17
8:2-FTMAC	64	12
7:1-FTAC*	42	12
7H-6:1-FTI*	44	6

Substances labeled with * were used as enrichment control standards.

Table 33 shows the initial results of the experiment to evaluate the efficiency of the SPE enrichment using two different cartridges: HLB and WAX. The recovery of the analytes and control standards were significantly low. There are two possible explanations: 1) the HLB and WAX cartridges were not efficient enough to trap the dissolved volatile PFASs in water; or 2) the volatile PFASs were lost and readily partitioned into the air during spiking. There is no way of confirming reason number 1 unless reason number 2 is investigated.

Table 33. Percent recoveries of the SPE enrichment of 100 mL milli Q water spiked with 100 ng of the volatile PFASs (n=1). Substances labeled with * were used as control standards.

Compounds	HLB	WAX
6:2-FTO	26	30
8:2-FTO	15	20
10:2-FTO	9	5
PFHxI	29	32

Compounds	HLB	WAX
PFOI	18	20
PFDI	9	5
4:2-FTI	52	45
6:2-FTI	40	37
8:2-FTI	18	21
6:2-FTAC	68	29
8:2-FTAC	32	18
6:2-FTMAC	56	45
8:2-FTMAC	21	22
7:1-FTAC*	39	6
7H-6:1-FTI*	72	61

Substances labeled with * were used as enrichment control standards.

To validate the results obtained for milli-Q water, 150 mL aliquots of an influent and an effluent sample (both from WWTP-M3) were spiked with 20 ng of the volatile PFASs from a working solution with methanol as solvent. The calculated % recoveries after SPE (after correction with elution IS) of the analytes are summarized in Table 34. The % recoveries ranged from 9 to 60% for those detected in the GC-MS. These recoveries were consistent with earlier findings and with the pseudo-partitioning experiment results (see chapter 2.5). A considerable amount of analyte is lost instantly as soon as the analyte solution is spiked into the water sample and partitions into the air. The high Henry's Law constant of these compounds are mainly due to their exceptionally low solubilities in water. Each analyte had comparable % recoveries in influent and effluent samples indicating that the matrix effects from both the influents and effluents were similar.

Table 34. % Recoveries of the volatile PFASs spiked in influent and effluent samples (n=2).

	Influent		Effluent	
Compound	**Average Recovery (%)**	**% RSD**	**Average Recovery (%)**	**% RSD**
6:2-FTO	25	13	35	1
8:2-FTO	39	9	39	7
10:2-FTO	9	3	13	2
PFHxI	41	2	44	9
PFOI	21	4	30	5
PFDI	0	-	0	-
4:2-FTI	53	10	53	5
6:2-FTI	58	9	56	5
8:2-FTI	25	5	33	5
6:2-FTAC	0	-	0	-
8:2-FTAC	0	-	0	-
6:2-FTMAC	0	-	62	7
8:2-FTMAC	34	1	43	1

The spiked PFDI was not recovered in both the influent and effluent samples. This can be due to the combination of high Henry's law constant of PFDI (see chapter 2.5) and the low sensitivity of the method to this analyte. On the other hand, the non-detection of the spiked FTACs on both the influent and effluent, and the 6:2-FTMAC in influent is due to matrix interferences. In the case of FTACs, the *m/z* used for both their quantification and identification are small (*m/z* 55 and *m/z* 99, respectively) and can be classified as common fragments. It was decided to use these *m/z* even with greater risk of matrix effect because the other fragment ions and even the molecular ions have significantly low intensities. As an illustration, the EI mass spectrum of 8:2-FTAC is shown in Figure 27. The non-detection of 6:2-FTMAC is also due to a nearby unresolved matrix peak. It can be noted that for FTMAC, the *m/z* used are large and there is less chance for matrix interferences. However for this sample, these interferences were actually present.

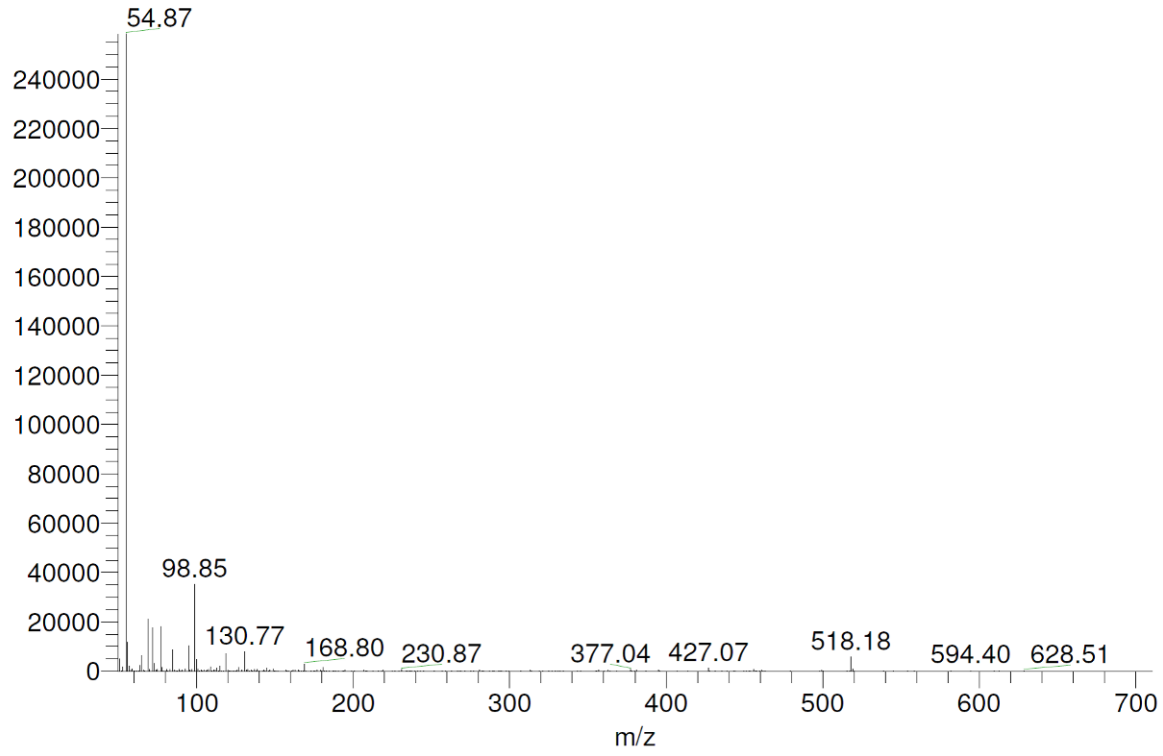


Figure 27. EI Mass Spectrum of 8:2-FTAC at 70 eV ion source voltage.

It was initially planned to use 7:1-FTAC and 7H-6:1-FTI as internal standards added prior to enrichment. However, due to partitioning losses during spiking, 7:1 FTAC and 7H-6:1 FTI cannot be used as internal standards to correct enrichment biases and random errors. Instead, these compounds were used as enrichment control standards. The enrichment control standard was still spiked into all water samples prior to enrichment. Its signal in each sample can be used to gauge how repeatable the enrichment step is. The ratio of the enrichment control standard to the GC injection IS was plotted in a control chart (Figure 28). The GC injection IS (7Me-6:2-FTI) was added prior to the injection of the sample or standard into the GC-MS. Compared to the average control standard ratio from standard solutions, the average control standard ratio from enriched samples is only half (approx. 50% recovery). The within-samples and the between-samples variability are relatively high but they are within the expected precision. The imprecision also comes from the variations in the spiking of the elution IS and even the injection itself. These low recoveries can be reasoned by the very high air-water partitioning coefficients which cause rapid volatilization of these substances after spiking into the aqueous samples. These substances are therefore expected not to be detected in the aqueous compartments within WWTPs. The quantitative data generated by this method can therefore be regarded as ‘current concentrations’, but for a comprehensive screening of these substances, the air above the sampling site should always be sampled simultaneously, which was also the strategy followed in this project.

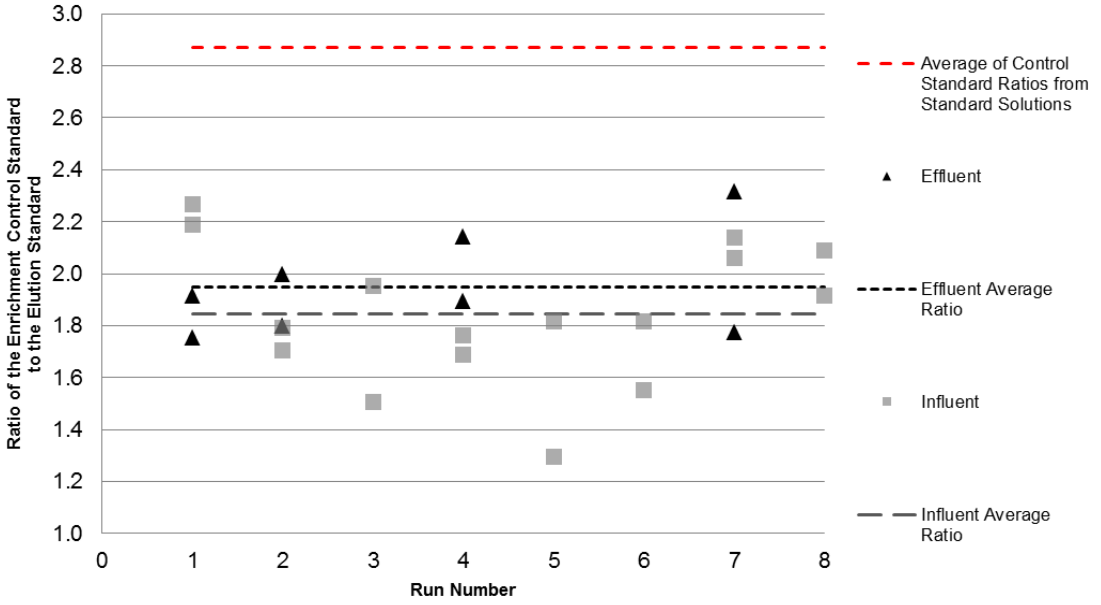


Figure 28. Control chart showing the variations of the ratio of the enrichment control standard spiked directly into the influent and effluent, and the elution IS.

Given the information above, the method detection limit of the volatile PFASs with the exception of the PFDI, FTACs and 6:2-FTMAC can still safely be stated to be 0.01 µg/L.

3.8 Development of air sampling methods to enrich volatile PFASs

3.8.1 Sampling and enrichment of GC-compatible substances from air

The efficiency of the HLB SPE cartridges to trap the volatile PFASs was studied. Two spiking techniques were investigated. The volatilization method made use of the set-up shown in Figure 4B. The analyte and control standard solutions were spiked into a cooled Erlenmeyer flask. The Erlenmeyer flask was then closed and was connected to an air source at one end and to an SPE trap on the other end. The volatile PFASs were then volatilized in a stream of air towards the cartridge at 60 °C. The second method involved direct spiking of the methanolic solution into the HLB material. The injection internal standard solution was spiked prior to elution with n-pentane. The % recoveries of the two techniques are summarized in Table 35. The FTOs, PFAIs and FTIs have recoveries greater than 80%. The FTACs and FTMACs initially had low recoveries. These compounds can be adsorbed in the glass surfaces and the 30 min of sampling time might not be enough to desorb and volatilize them into the SPE cartridges. When the sampling time was increased to 6 h, the percent recoveries of the compounds have greatly improved. The use of the lower amount of spike has also greater percent recovery. Direct spiking of the methanolic stock solution into the SPE cartridges yielded lower recoveries for FTOs, PFAIs and FTIs, especially for the most volatile analytes.

Table 35. Percent recoveries of the HLB enrichment using the volatilization and direct spiking methods.

	Volatilization Method			Direct Spiking	
Compound	200 ng; 30 min (n=2)	200 ng; 6 h (n=1)	20 ng; 30 min (n=4)	200 ng (n=1)	20 ng (n=1)

Compound	Volatilization Method			Direct Spiking	
	200 ng; 30 min (n=2)	200 ng; 6 h (n=1)	20 ng; 30 min (n=4)	200 ng (n=1)	20 ng (n=1)
6:2-FTO	87	91	90	35	62
8:2-FTO	90	97	97	55	87
10:2-FTO	89	100	90	68	82
PFHxI	91	91	105	51	95
PFOI	92	96	98	69	86
PFDI	97	114	90	81	79
4:2-FTI	92	98	88	69	118
6:2-FTI	89	97	91	77	92
8:2-FTI	82	109	89	86	88
6:2-FTAC	77	109	86	91	68
8:2-FTAC	46	106	73	79	84
6:2-FTMAC	53	114	84	90	90
8:2-FTMAC	24	130	61	70	84
7:1-FTAC*	86	94	130	86	100
7H-6:1-FTI*	86	93	74	61	96

The volatilization method gave better recovery of the volatile PFASs than the direct spiking method. This method was further evaluated. Using the spiking set-up, the SPE tubes were spiked with the analytes by volatilization at 80 °C for 30-45 min; and the % recoveries were determined. Table 36 shows the % recoveries from air. Most of the analytes were recovered with the exception again of the FTAC whose signal was interfered by matrix compounds.

Prior to sampling, all the HLB cartridges that will be used will be spiked with the control standards. The % recovery of the control standard can be used to evaluate the efficiency of the sample enrichment.

Table 36: % Recoveries of the volatile PFASs spiked by volatilization (n=2).

Compound	Average Recovery (%)	% RSD
6:2-FTO	83	12
8:2-FTO	88	9
10:2-FTO	83	4
PFHxI	83	4
PFOI	85	11
PFDI	96	11
4:2-FTI	90	9
6:2-FTI	91	7
8:2-FTI	100	6
6:2-FTAC	-	-
8:2-FTAC	-	-
6:2-FTMAC	85	5
8:2-FTMAC	86	24

The reproducibility of the spiking in real samples was compared using the control chart in Figure 29. The control standard ratio was monitored for all the spiked samples and standards.

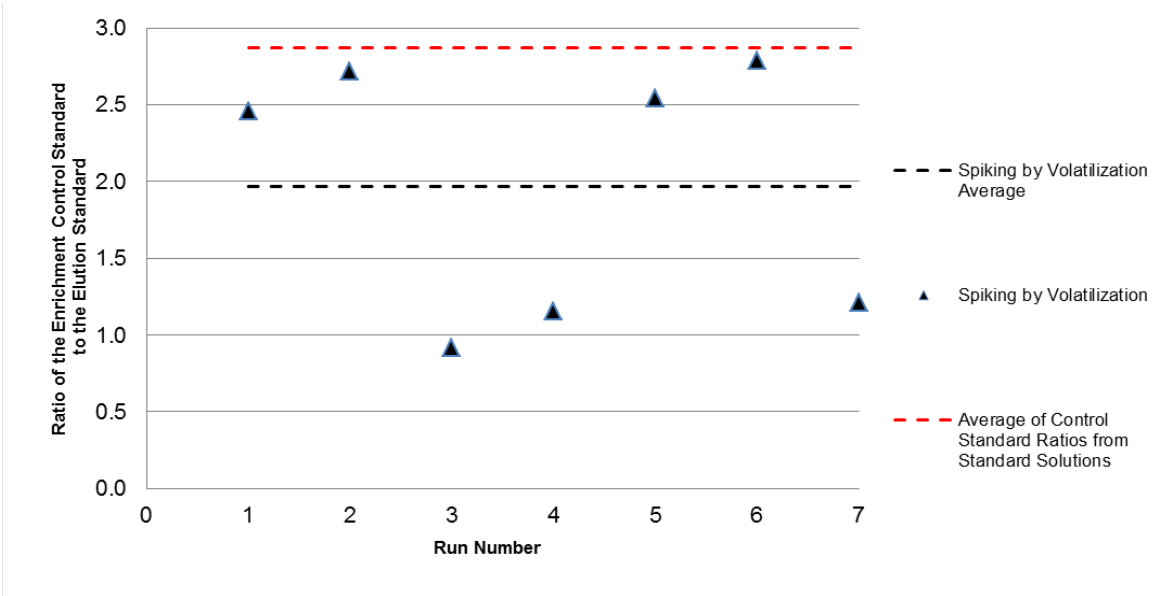


Figure 29: Control chart showing the variations of the ratio of the enrichment control standard spiked by volatilization, and the elution IS. Data shown for WWTP-M1.

For four of the samples, the peak area ratios of enrichment control standard and elution internal standard nearly reached the average of solvent standard solutions. The remaining three samples showed ratios < 50% indicating problems during sampling, such as volatilization of the enrichment control standards. A possible reason for this could be displacement of enrichment control standard by compounds contained in the sample.

3.8.2 Method validation for air sampling of HPLC-MS compatible PFASs (method AIR-3)

To validate the high-volume air sampling (AIR-3), 1 mL of a spiking solution was pipetted on the ground of a 1 L glass bottle. The methanolic spiking solution contained FTOHs in a concentration of 100 ng/mL. The glass bottle was closed with a cap, which has two metal capillaries represents the air inlet and the air outlet. The high-volume air setup (see 2.4.2.7) was connected to the air outlet and enriched the air for 24 h. The SPE columns were stored in 50 mL centrifugation tubes to protect them from potential contamination, which were stored at -20 °C prior to elution. For the elution of FTOHs from the SPE cartridges, 8 mL MeOH was passed through the column by gravitational flow. The eluates were spiked with the internal standards of the HPLC-MS-n methods and evaporated to 500 µL using a gentle stream of nitrogen. The eluates were filtrated through a syringe filter (regenerated cellulose, 0.45 µm) and analyzed using the HPLC-MS-n method. The recoveries of four enrichments are shown in Figure 30.

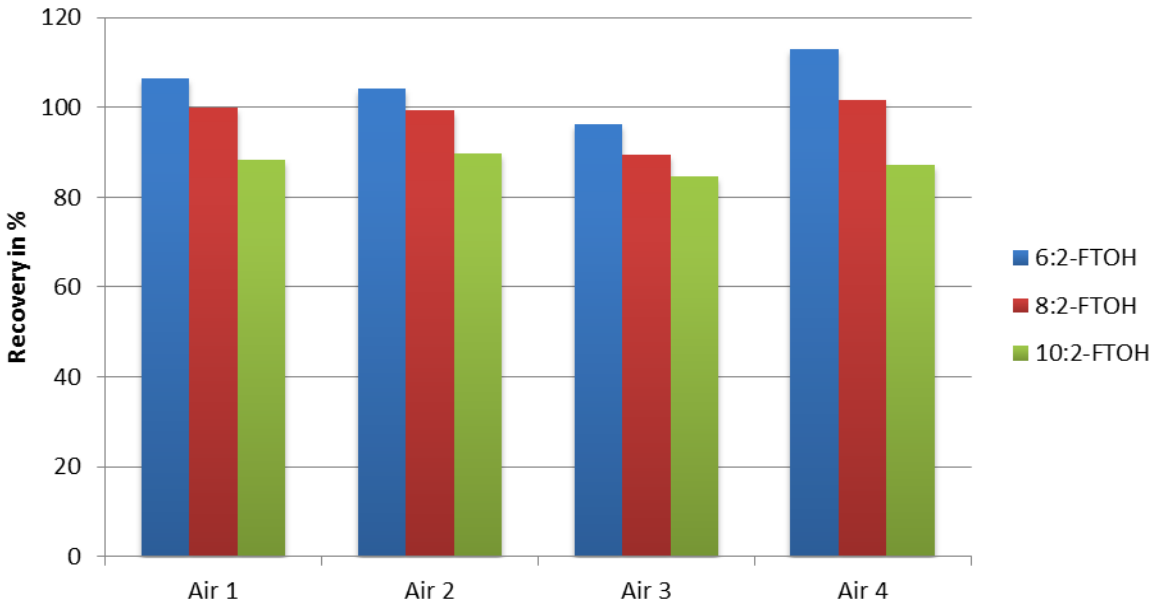


Figure 30: Recoveries of FTOHs from bottles using Isolute ENV+ cartridges and the setup explained in chapter 2.4.2.7. 100 ng of each compound were spiked and recovery was calculated as the amount determined in the sample divided by the theoretically spiked amount.

The recoveries of the FTOHs were in the range of 88% to 112% in all four experiments indicating suitability of the method used for the purpose of enriching these substances. Other substances were not involved in this spiking experiment as the remaining volatile PFASs are covered by method AIR-2 and no recovery can be stated for non-volatile PFASs.

3.9 Analysis of the particulate phase of influent and effluent samples

Samples from both, WWTP influent and effluent were filtered over a 0.45 µm filter for two purposes: i) as clean-up step and ii) to collect the particulate phase for further analyses on PFASs.

However, in WWTP effluent samples, there was never enough particulate phase to be analyzed. In influent samples, the particulate phase was either not present in considerable amounts or not analyzable due to clogging of the filters. This method

suffered from poor reproducibility and internal standards could not be added in a reproducible manner. Thus, following method development, analysis of sludge from WWTPs instead was favorized.

A draft procedure published by EPA in 2011 (USEPA, 2011) could not be used since this procedure has been developed for PFCAs, PFSAs, N-Me/EtFOSA, and N-Me/EtFOSE. Unfortunately, it is not suitable for the determination of FTOHs and related precursor compounds, which can degrade to form PFCAs and PFSAs.

4 Results and discussion: Determination of PFASs in the WWTP samples

In the following sections, results of PFASs determination in WWTPs will be presented. The following abbreviations will be used to denote the sample type:

Influent: INF

Effluent: EFF

Air above influent: AIR

Sludge: SLU

Corresponding samples will carry the same number, e.g. INF 1, EFF 1, AIR 1 and S 1 are corresponding samples.

The sample preparation of the WWTP samples is described in chapter 2.4.2.2. If not explicitly stated otherwise, all samples were measured with the PFCA-a method and the HPLC-MS-n method as well as the GC-MS method.

In this chapter, results will only be shown for substances that were detected at least once in any of the sample types. The complete result tables are shown in the annex in order to show the respective LODs and LOQs per sample.

If not stated otherwise, questionnaire data (see chapter 8.1) returned by the WWTP operators was insufficient to be included in the report.

4.1 Industrial wastewater treatment plant WWTP-I1

Due to the comparably high concentrations of several compounds in the samples from WWTP-I1, no enrichment by SPE was necessary for LC-MS measurements of aqueous samples.

4.1.1 Influent samples

The PFASs detected in the influent samples of WWTP-I1 are shown in Table 37 (complete results shown in Table 77 in the annex). Concentrations are given in µg/L and are thus very high compared to literature data published so far (see discussion in chapter 4.11). Out of the 64 PFASs analyzed, almost 50% (30 analytes) could be detected in the various influent samples. The dominant compounds in the influent samples were 6:2-FTOH with a maximum concentration of almost 1 mg/L, 6:2-FTMAC and their longer-chained homologs, albeit at much lower concentrations. Other synthetic intermediates of fluorotelomer chemicals, such as FTOs, PFAIs and FTIs, were measured, but at inferior concentrations than FTOHs and FTMACs.

PFCAs, especially PFBA and PFPeA were quantified in concentrations up to 93.5 µg/L. Additionally, the C_6-C_{14}-PFCAs were detected, with exception of PFDoA and PFTeA.

Interestingly, several substances that are thought to be formed only by biotransformation processes, such as x:3-acids, FTCAs and FTUCAs, were measured in influent samples. This might have been caused by low extent of biotransformation of FTOHs and FTMACs in sewage pipes.

No extreme variations within the different influent samples taken were observed.

Table 37: PFAS concentrations in µg/L in the influent samples of WWTP-I1. Only substances with at least one detection are shown. Concentrations for PFBS and 10:2-FTOH should be interpreted semiquantitatively due to high recoveries. PFHpA was excluded from the analyte list for this set of results due to abnormally high instrumental background levels.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	[µg/L]									
PFBA	0.1	0.2	22.5	46.7	13.4	23.8	22.9	9.3	17.3	11.7
PFPeA	0.2	1	21.3	93.5	17.4	20.2	20.4	14.8	20.5	17.7
PFHxA	0.1	0.2	4.8	6.6	3.4	5.1	6.0	4.8	6.2	4.5
PFOA	0.1	0.2	3.4	4.2	2.0	2.1	3.0	3.3	4.8	3.8
PFNA	1.0	2	< LOQ	n.d.	n.d.	n.d.	< LOQ	< LOQ	< LOQ	2.3
PFDA	0.5	1	1.0	< LOQ	n.d.	n.d.	1.1	1.1	<L OQ	< LOQ
PFUnA	0.5	2	2.5	1.5	1.9	1.7	1.9	n.d.	1.9	2.3
PFTrA	0.5	1	1.5	n.d.	n.d.	1.4	1.3	< LOQ	1.5	1.6
6:2-FTCA	2.0	10	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
6:2-FTUCA	0.1	0.5	2.2	1.7	3.2	0.7	0.9	0.7	1.0	2.1
8:2-FTUCA	0.1	2	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
4:3-acid	0.5	2	n.d.	n.d.	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.
5:3-acid	0.2	1	2	1.9	1.9	2.3	4.5	8.6	7.3	6.3
6:3-acid	1.0	10.0	n.d.	n.d.	< LOQ	n.d.	< LOQ	< LOQ	n.d.	< LOQ
7:3-acid	1.0	10.0	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
PFBS	0.1	0.2	n.d.	5.7	n.d.	4.1	0.5	n.d.	n.d.	n.d.
6:2-FTS	0.2	1.0	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.
6:2-FTOH	5	10	986	413	441	691	489	136	71.7	78.9
8:2-FTOH	2	10	76.5	42.9	42.6	95.1	79.4	49.3	31.2	80.3
10:2-FTOH	2	10	32.5	13.3	11.9	42.3	37.5	35.0	10.4	38.5
6:2-FTO	0.01	0.03	0.043	0.106	0.018	0.033	0.068	0.041	0.037	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	[µg/L]									
8:2-FTO	0.01	0.03	0.40	0.15	0.13	0.20	0.70	0.17	0.28	0.06
10:2-FTO	0.01	0.03	0.069	0.077	0.036	0.112	0.584	0.042	0.057	0.058
PFHxI	0.01	0.03	0.22	0.36	<LOQ	0.11	0.20	<LOQ	<LOQ	n.d.
PFOI	0.01	0.03	0.56	0.52	0.076	0.18	0.55	<LOQ	<LOQ	0.072
PFDI	0.01	0.03	<LOQ	<LOQ	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
6:2-FTI	0.01	0.03	2.3	0.89	0.83	1.7	1.81	0.57	0.68	0.78
8:2-FTI	0.01	0.03	0.087	n.d.	0.022	0.070	0.099	0.024	0.018	0.030
6:2-FTMAC	0.01	0.03	80	31	22	90	59	5.7	5.3	5.5
8:2-FTMAC	0.01	0.03	0.32	0.058	0.14	0.26	0.13	0.038	n.d.	0.019

n.d.: not detected; <LOQ: lower than limit of detection

4.1.2 Effluent samples

The number of PFASs detected at least once in the effluent samples decreased to a number of 17. The concentrations of the detected compounds in the effluents samples are listed in Table 38 (complete results shown in Table 78 in the annex).

The volatile substances were not detected in the effluent samples, with exception of 6:2-FTMAC, 6:2-FTO and 8:2-FTO. However, concentrations were up to four orders of magnitude lower compared with influent samples.

Apart from that, C_4-C_{11}-PFCAs dominated the spectrum of substances detected as well a fluorotelomer-based biotransformation products, such as 4:3-acid, 5:3-acid and 7:3-acid as well as 6:2-FTCA, 6:2-FTUCA and 8:2-FTUCA.

Table 38: PFAS concentrations in µg/L measured in effluent samples of WWTP-I1. Only substances with at least one detection are shown. PFHpA was excluded from the analyte list for this set of results due to abnormally high instrumental background levels.

Analyte	LOD	LOQ	EFF 1	EFF 3	EFF 5	EFF 7
			[µg/L]			
PFBA	0.1	0.2	21.7	13.9	23.6	15.4
PFPeA	0.2	1	23.8	23.2	22.7	18.5
PFHxA	0.1	0.2	22.1	59.9	80.0	11.1
PFOA	0.1	0.2	3.8	4.3	6.5	7.1
PFNA	1.0	2	< LOQ	< LOQ	< LOQ	< LOQ
PFDA	0.5	1	2.6	1.2	1.1	< LOQ
PFUnA	0.5	2	0.9	n.d.	n.d.	0.6
6:2-FTCA	2.0	10	< LOQ	< LOQ	17.2	< LOQ
6:2-FTUCA	0.1	0.5	2.0	6.1	17.8	1.2
8:2-FTUCA	0.1	2	< LOQ	< LOQ	2.8	3.5
4:3-acid	0.5	2	n.d.	n.d.	< LOQ	n.d.
5:3-acid	0.2	1	7.0	10.0	14.5	5.0
7:3-acid	1.0	10.0	< LOQ	< LOQ	< LOQ	< LOQ
6:2-FTS	0.2	1.0	n.d.	< LOQ	< LOQ	< LOQ
6:2-FTO	0.01	0.03	<LOQ	<LOQ	0.033	<LOQ
8:2-FTO	0.01	0.03	<LOQ	<LOQ	0.030	<LOQ
6:2-FTMAC	0.01	0.03	<LOQ	0.032	<LOQ	0.052

n.d.: not detected; <LOQ: lower than limit of detection

4.1.3 Air samples

Altogether, eight air samples were taken corresponding to the influent samples. However, due to technical errors during, sampling of AIR 3, AIR 6 and AIR 8 over night at the WWTP-I1, only five of the eight air samples could be analyzed. All obtained results for air sample measurements are summarized in Table 39 (complete results shown in Table 79 in the annex).

Except for 4:2-FTI, 6:2-FTAC and 8:2-FTAC, all volatile substances were detected and quantified in all air samples. 6:2-FTMAC and 6:2-FTOH were the dominating compounds with concentrations of up to 4.4 µg/L for 6-2-FTMAC. These values are considered to be extraordinarily high air concentrations.

A series of non-volatile PFASs including C_4-C_{14}-PFCAs, 6:2-FTS and 8:2-FTS as well as the fluorotelomer-based biotransformation products 6:2-FTCA, 6:2-FTUCA and 8:2-FTUCA as well as 5:3-7:3-acid were measured in the low ng/m^3 range. These substances are thought to be expelled from the influent in form of aerosols which have not been separated from air during sampling.

Table 39: PFAS concentrations in air samples of WWTP-I1. Only substances with at least one detection are shown. Concentrations for volatile PFASs (FTOHs, FOSE derivatives, FTOs, PFAIs, FTIs and FT(M)ACs are given in mg/m³ due to high concentrations, the results of remaining substances are given in ng/m³).

Analytes	LOD	LOQ	AIR 1	AIR 2	AIR 4	AIR 5	AIR 7
				ng/m³			
PFBA	0.002	0.004	0.9	1.6	1.4	0.9	0.6
PFPeA	0.002	0.004	1.8	1.7	1.4	1.2	1.7
PFHxA	0.004	0.021	10.4	13.8	11.7	8.3	9.8
PFHpA	0.004	0.021	2.2	1.2	0.6	0.7	0.7
PFOA	0.002	0.021	11.0	0.7	4.2	0.4	4.1
PFNA	0.002	0.022	1.3	1.8	0.5	0.5	1.0
PFDA	0.004	0.021	4.4	2.7	0.8	1.1	1.6
PFUnA	0.021	0.042	0.9	1.7	0.5	0.8	0.8
PFDoA	0.021	0.042	1.9	1.8	0.4	1.1	0.6
PFTrA	0.021	0.042	n.d.	0.9	n.d.	0.7	0.3
PFTeA	0.021	0.042	0.6	0.5	n.d.	n.d.	n.d.
6:2-FTCA	0.042	0.208	2.8	3.7	4.5	1.4	0.8
6:2-FTUCA	0.004	0.021	2.9	4.0	2.7	1.3	0.6
8:2-FTUCA	0.004	0.021	0.4	0.3	0.3	0.2	0.3
5:3-acid	0.021	0.042	1.0	2.1	0.9	0.8	2.1
6:3-acid	0.021	0.042	0.4	0.5	0.3	0.2	0.4
7:3-acid	0.021	0.042	0.4	0.5	0.3	0.3	0.4
6:2-FTS	0.002	0.004	13.8	20.7	37.9	1.7	18.1
8:2-FTS	0.021	0.042	0.4	0.4	1.0	0.4	0.3
				mg/m³			
6:2-FTOH	0.335	1.00	3.29	4.20	1.73	1.87	0.411
8:2-FTOH	0.165	0.335	0.186	0.283	0.107	0.180	0.158
10:2-FTOH	0.165	0.335	0.078	0.101	0.022	0.037	0.035
6:2-FTO	0.0004	0.0012	0.12	0.12	0.074	0.042	0.20
8:2-FTO	0.0004	0.0012	0.41	0.13	0.19	0.16	0.48
10:2-FTO	0.0004	0.0012	0.15	0.11	0.059	0.074	0.11
PFHxI	0.0004	0.0012	0.078	0.076	0.12	0.046	0.10
PFOI	0.0004	0.0012	0.14	0.10	0.044	0.021	0.032
PFDI	0.0004	0.0012	0.044	0.033	0.003	0.004	0.005
6:2-FTI	0.0004	0.0012	0.56	0.46	0.22	0.23	0.36
8:2-FTI	0.0004	0.0012	0.011	0.014	0.004	0.006	0.006
6:2-FTMAC	0.0004	0.0012	4.40	2.31	0.70	0.87	0.08
8:2-FTMAC	0.0004	0.0012	0.005	0.008	0.002	0.002	0.002

n.d.: not detected; <LOQ: lower than limit of detection

4.1.4 Discussion

A comparison of changes in the individual concentrations of PFASs entering and leaving the WWTP (see chapters 4.1.1-4.1.3) should give insight into transformation processes occurring during the waste water treatment process. Focus should be led solely on concentration differences leaving out the WWTP-specific parameters, such as e.g. adaptation processes, sorption phenomena and hydraulic retention time.

For a better comparison, concentrations were calculated in μmol/L. Results from air sample analyses were not included in these balance calculations. Firstly, the exact air volume at the sampling point is unknown, secondly the air sampler can only manage to sample an unknown fraction of the substances emitted from the influent and thirdly, the potential influence of aerosols cannot be controlled. Thus, the air data enhances the comprehensiveness of the monitoring and it can be used to pinpoint precursors to PFCAs and PFSAs in a qualitative manner, but it cannot be used to close the mass balance. The difference of the determined concentrations between the effluent and the influent is shown in Figure 31. The total concentration of PFASs in the effluent was significantly lower than in the influent. The area under the x-axis in Figure 31 illustrates the sum of decrease of determined PFASs in the effluent compared to the influent. The area above the x-axis shows the increase of determined PFASs in the effluent.

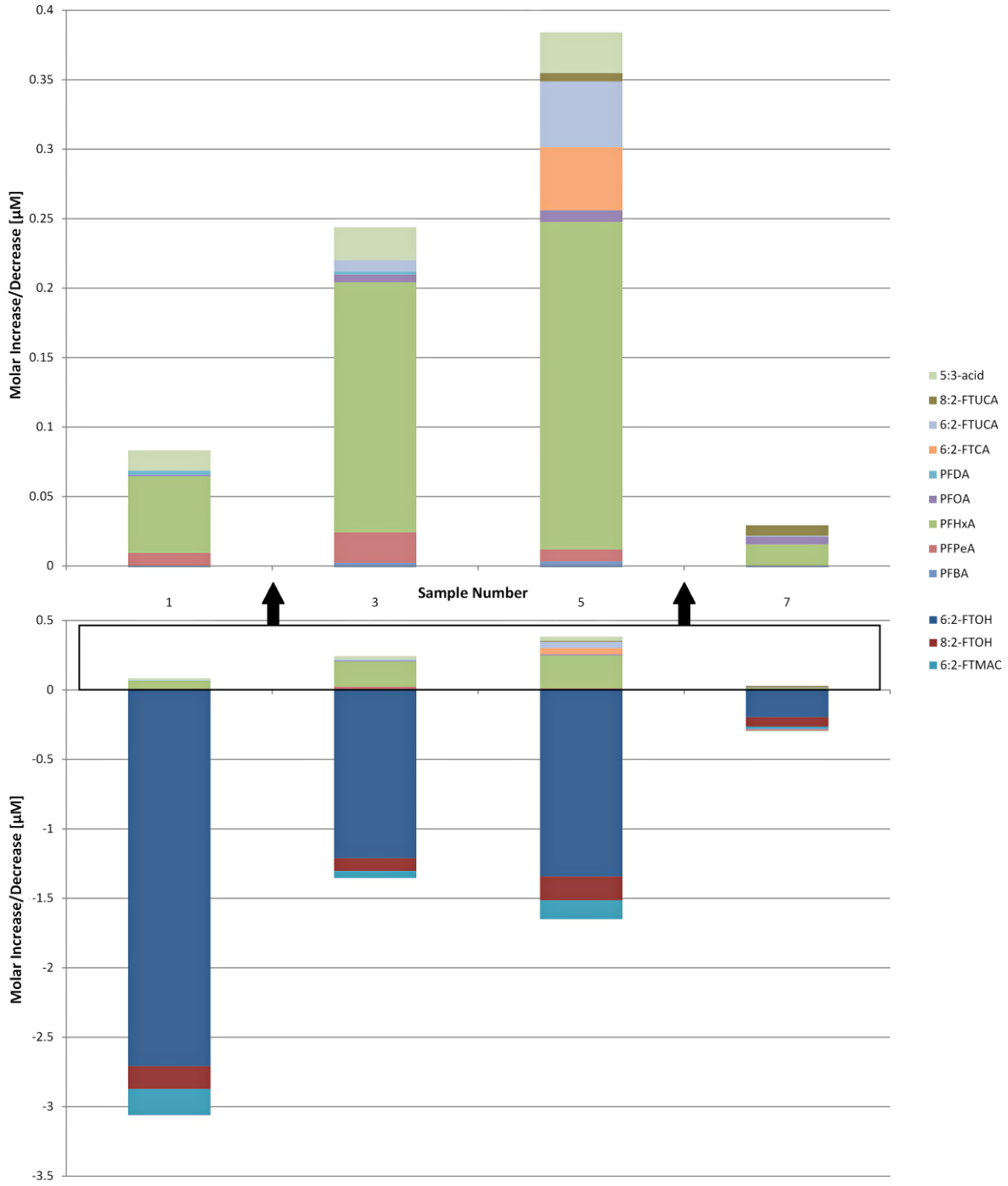


Figure 31: Difference in molar PFAS concentrations between effluents and corresponding influents in WWTP-I1. The upper plot shows a magnified view of the substances with increases in concentration. Only substances with significant decreases and increases in at least one case are shown.

The significant increase of the persistent acids PFHxA, PFPeA and PFOA most likely results from the biodegradation of 6:2-FTOH, 8:2-FTOH and 6:2-FTMAC. This is confirmed by the increased concentrations of the known biodegradation intermediates of 6:2-FTOH, such as 6:2-FTUCA, 6:2-FTUCA and 5:3-acid in the effluent. The oxidation of the hydroxyl group during the biodegradation leads to the corresponding aldehyde (6:2-FTAL), which can be transformed into 6:2-FTCA and afterwards into the unsaturated 6:2-FTUCA by the cleavage of hydrogen fluoride. The 6:2-FTUCA can be transformed into PFHxA and PFPeA

by different pathways as well as into the unsaturated carboxylic acid 5:3-FTUCA. This 5:3-FTUCA can be metabolized to 4:3-acid, 5:3-acid as well as into PFBA by different transformation pathways (Wang et al., 2012). The concentration of 6:2-FTOH in the influent and the concentration of possible biodegradation products in the corresponding effluent, calculated in mol% is shown in Table 40. PFHxA could also result from the biodegradation of 8:2-FTOH. Therefore, the determined concentration of PFHxA was calculated by using the ratio between 6:2-FTOH and 8:2-FTOH in the corresponding influent. Only analytes with increasing molar concentrations in the effluent compared to the influent are listed in Table 40.

Table 40: 6:2-FTOH concentrations in the different investigated influents of WWTP-I1 and calculated increase of possible biodegradation products in the corresponding effluents.

INF [µmol/L] 6:2-FTOH		Increase observed in the corresponding EFF [µmol/L]							
		6:2-FTCA	6:2-FTUCA	5:3-acid	PFHxA	PFPeA	PFBA	Sum	mol%
1	2,707	0.0	0.0	14.7	51.7	9.5	0.0	75.9	3%
3	1,212	0.0	8.2	23.9	165	22.0	2.4	222	18%
5	1,343	43.6	47.2	29.4	205	8.7	3.1	337	25%
7	197	0.0	0.8	0.0	10.4	0.0	0.0	11.1	6%

The concentration of potential biodegradation products of 6:2-FTOH, that showed an increase in the effluent, ranged from 3% to 25% compared to the concentration of 6:2-FTOH in the influent. Despite the highest concentration of 6:2-FTOH in INF 1, the sum of all determined degradation products was only 3% in the corresponding effluent. Despite that the concentrations of 6:2-FTOH in INF 3 and INF 5 were in a similar range, the concentration of the transition products such as e.g. 6:2-FTCA and 6:2-FTUCA were different in the corresponding effluents. However, it is known from various studies published so far, that a balance of transformation processes including both, sorptive and volatile micropollutants, is often not even achieved under controlled lab conditions (Dinglasan et al., 2004).

The concentrations of 6:2-FTCA in INF 1 and INF 7 were higher compared to the corresponding effluents. This has also been the case for 6:2-FTUCA in INF 1. 6:2-FTCA and 6:2-FTUCA might have been further degraded during the wastewater treatment. The concentration of PFBA in the EFF 1and EFF 7 was < 10% higher than the concentration in the corresponding influent samples. (The decreases of the compounds in the effluent were not used for the calculation of mass balance.)

The increase of 8:2-FTUCA, PFOA and PFHxA in the effluents could be attributed to the transformation of 8:2-FTOH. The oxidation of the hydroxyl group of 8:2-FTOH leads to 8:2-FTAL, which can be transformed into 8:2-FTCA and afterwards into 8:2-FTUCA. The 8:2-FTUCA can be transformed into PFOA, PFHpA and 7:3-FTUCA, which can be further transformed into 6:3-acid, 7:3-acid as well as into PFHxA (see chapter 1.2). The concentration of 8:2-FTOH in the influent and the concentration of possible biodegradation products in the corresponding effluent is shown in Table 41. PFHxA could also be the result of the biodegradation of 6:2-FTOH. Therefore, the determined concentration of PFHxA was set in relation of the ratio between 6:2-FTOH and 8:2-FTOH in

the corresponding influent. PFOA could also be the result of the biodegradation of 10:2-FTOH. The ratio between the concentration of 8:2-FTOH and the concentration of 10:2-FTOH was used to calculate the concentration of PFOA in the corresponding effluents. Only the increase of the biodegradation products 8:2-FTUCA, PFHxA and PFOA could be determined.

Table 41: Concentration of 8:2-FTOH in the different investigated influents of WWTP-I1 and the increase of possible biodegradation products in the corresponding effluents.

INF [µmol/L]		Increase in the corresponding EFF [µmol/L]				
	8:2-FTOH	8:2-FTUCA	PFHxA	PFOA	Sum	mol%
1	165	0.0	3.3	0.6	4.0	2%
3	91.8	0.0	14.4	4.2	18.6	20%
5	171	6.1	30.6	5.2	42.0	25%
7	67.3	7.7	1.9	4.0	13.6	20%

The concentration of the degradation products of 8:2-FTOH, which increased in the effluent compared to the concentration of 8:2-FTOH in the influent ranged from 2% to 25%. The ratio between PFHxA and PFOA in the effluent compared to the concentration of 8:2-FTOH in the corresponding influent showed a similarity between INF/EFF 3 and INF/EFF 5. The sum of the determined degradation products as well as the mol% compared to the concentration of 8:2-FTOH in the influent showed a similarity between INF/EFF 3 and INF/EFF 5 as well. The only difference in these two samples was the concentration of 8:2-FTUCA and that resulted in a higher sum of biodegradation products in the INF/EFF 5.

The biodegradation of 10:2-FTOH resulted in the homologs transformation products as mentioned before. PFOA and PFDA were the only biodegradation products of 10:2-FTOH. 10:2-FTCA and 10:2-FTUCA could not be detected in the analyzed samples. The possible degradation products 8:3-acid and 9:3-acid were not determined. PFOA could also be the result of the biodegradation of 10:2-FTOH. The ratio between the concentration of 8:2-FTOH and the concentration of 10:2-FTOH was used to calculate the expected concentration of PFOA in the corresponding effluents. The concentration of 10:2-FTOH in the influent and the concentration of the possible biodegradation products PFOA and PFDA in the corresponding effluent is shown in Table 42.

Table 42: Concentration of 10:2-FTOH in the different investigated influents of WWTP-I1, the increase of possible biodegradation products in the corresponding effluents.

INF [µmol/L]		Increase in the corresponding EFF [µmol/L]			
	10:2-FTOH	PFOA	PFDA	Sum	mol%
1	57.6	0.3	3.2	3.5	6%
3	21.1	1.3	2.3	3.6	17%
5	66.4	3.3	0.1	3.4	5%
7	18.4	1.5	0.0	1.5	8%

The increase in concentration of the degradation products of 10:2-FTOH accounted for 5 mol% to 17 mol% of the 10:2-FTOH determined in the influent.

One reason for the high decrease in FTOHs concentration might be the volatile properties of FTOHs. The FTOHs might be vaporized during the wastewater treatment. Especially in the biological treatment, stripping with air in the activated sludge tank might cause the evaporation. Adsorption of FTOHs and their biotransformation products to sludge is another reason for the significant decrease of the total concentration of PFASs in the effluent.

In the samples of WWTP-I1, EFF 1, EFF 3, EFF 5 and EFF 7 only 10%, 27%, 34 and 44% respectively of the total PFASs concentration compared to the corresponding influent concentrations could be determined. A correlation between the concentration in the effluent and the volume of water, which passed the WWTP on the day of sampling (Figure 32) is given.

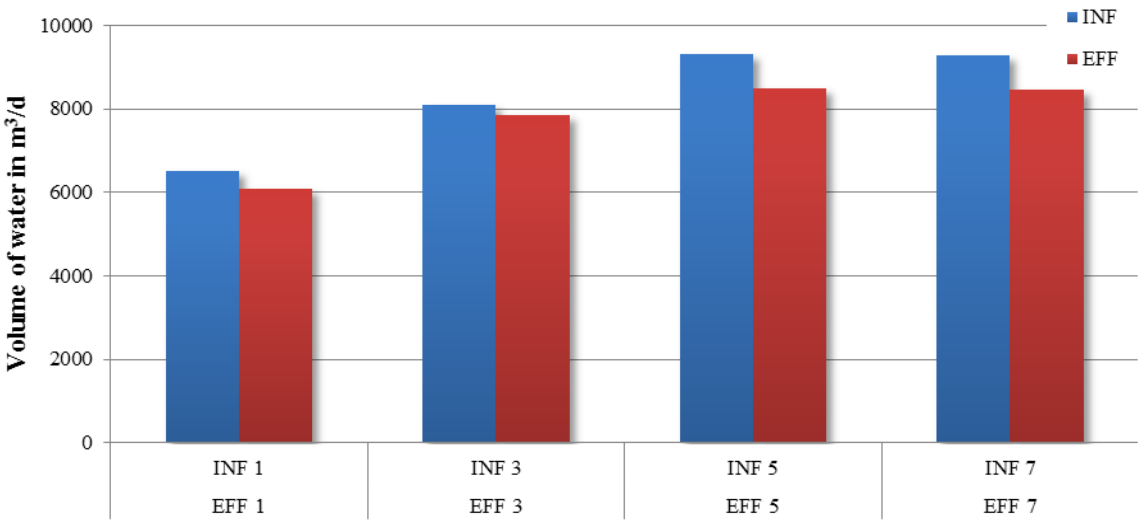


Figure 32: Volume of water passing the WWTP-I1 on the day of sampling.

The volume of water was between 23% and 43% higher in INF 3, INF 5 and INF 7 compared to INF 1. The lower hydraulic retention time and lower sludge contact time will most likely result in the observed lower removal rate. The concentration of PFUnA was higher in all and the concentration of PFTrA in INF 1, INF 5 and in the INF 7 higher than in the corresponding effluent samples. The adsorptive properties of long-chain PFASs to the sludge might be the reason for the observed decrease of these compounds (see chapter 4.7). In summary, the overall increase of PFASs monitored in the effluent of WWTP-I1 most likely results from the biodegradation of the individual FTOHs and FTMAC. However, with the results obtained from the non-target analysis and (chapter 4.10) a valid “total bound organic fluorine” method, one could get a further insight into the individual processes occurring during the waste water treatment process of PFASs-precursors.

4.2 Industrial wastewater treatment plant WWTP-I2

4.2.1 Influent samples

In this industrial WWTP, a total of 12 influents (WWTP-I2 INF 1 to INF 12) were sampled as indicated in chapter 2.7.3. Out of the 65 PFASs analyzed, approximately a third (20 analytes) could be detected in the influent samples (see Table 43, complete results table see Table 80 in the annex).

The dominant compounds in the influent samples were 6:2-FTOH with a maximum concentration of approximately 18.5 µg/L, 6:2-FTMAC with concentrations between 0.33 µg/L and 4.6 µg/L. However, the frequency of the quantified precursors of PFCAs and PFSAs clearly indicates the influence of at least one industrial point source as concentrations differed significantly. For example, the concentration of 6:2-FTOH was extremely high in INF 1, INF 2 and INF 4 whereas it was not detected in any other influent. In contrast, 8:2-FTOH occurred with the highest concentration in INF 4. This pattern could only be interpreted in such a way that there might be different sources or batch processes.

Additionally, N-MeFOSE was measured in all influent samples except for one at relatively constant concentrations around 50 ng/L.

From the analyzed PFCAs, only PFOA could be quantified above the LOQ. No extreme variations within the different influent samples taken were observed for PFOA, whereas the concentrations of PFBS varied in the range between above 1 µg/L and not detected. A more detailed statistical approach for data evaluation is given in chapter 4.2.5.

Table 43: PFAS concentrations in influent samples of WWTP-I2 in ng/L. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8	INF 9	INF 10	INF 11	INF 12
	ng/L													
PFHxA	7.3	36.3	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	2.3	11.6	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d.	n.d.	< LOQ	< LOQ	< LOQ	< LOQ
PFOA	0.8	7.7	12.5	10.9	12.8	11.3	7.7	12.9	7.8	< LOQ	8.3	10.4	< LOQ	8.3
PFDA	2.9	14.6	n.d.	n.d.	n.d.	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	26.5	133	< LOQ	n.d.	< LOQ	n.d.	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	7.7	15.3	n.d.	n.d.	n.d.	n.d.	18.4	26.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	3.6	7.3	569[a]	n.d.	1089[a]	n.d.	97.0	n.d.	n.d.	n.d.	381	91.3	n.d.	n.d.
PFHxS	0.3	3.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	55.6	17.0	51.6	53.7	50.7	51.1
PFOS	0.7	3.7	440[a]	96.9	537[a]	58.2	74.0	46.3	14.4	n.d.	121	61.0	31.1	21.2
6:2-FTS	0.4	0.7	5.0	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	20.7	62.1	5,727[b]	1,360	18,519[b]	n.d.	2,886[b]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	11.9	22.9	451	n.d.	n.d.	456	n.d.	n.d.	n.d.	n.d.	1,064	539	n.d.	n.d.
10:2-FTOH	11.9	22.9	n.d.	n.d.	n.d.	44.2	n.d.	n.d.	n.d.	n.d.	63.2	61.6	n.d.	n.d.
N-MeFOSE	2.4	4.6	46.6	48.2	65.6	53.0	40.6	56.7	47.1	50.8	44.2	50.1	n.d.	86.6
8:2-FTO	10.0	30.0	n.a.	n.a.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
10:2-FTO	10.0	30.0	n.a.	n.a.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10.0	30.0	n.a.	n.a.	2,710	300	4,610	960	410	230	890	330	n.d.	n.d.

[a] Concentration exceeding the highest calibration point of 240 ng/L. Concentrations estimated by assumption of linear correlation.

[b] Concentration exceeding the highest calibration point of 2500 ng/L. Concentrations estimated by assumption of linear correlation.

n.a.: not analyzed; n.d.: not detected; <LOQ: lower than limit of detection

4.2.2 Effluent samples

A total of 17 PFASs could be detected in the effluent samples of WWTP-I2 (see Table 44, complete data shown in Table 81 in the annex). The total concentration of PFASs in the effluents was significantly lower than in the influents. All PFCAs from C_5 (PFPeA) to C_{10} (PFDA) could be quantified in all samples reaching high concentrations of up to 512 ng/L for PFHxA.

Both, 6:2-FTUCA and 8:2-FTUCA were present in low concentrations (n.d. to 51.2 ng/L), but no clear tendency is given. 6:2-FTCA was detected in four of the eleven samples with concentrations between <LOQ and 88.3 ng/L. From the x:3 acids, only 5:3 acid and 7:3 acid were detected, whereas 6:3-acid did not occur. In addition, the sulfonates PFBS, PFOS and 6:2-FTS were detected in the effluent samples.

Table 44: PFAS concentrations in ng/L in the effluent samples of WWTP-I2. Effluent sample corresponding to INF 3 was not taken. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 4	EFF 5	EFF 6	EFF 7	EFF 8	EFF 9	EFF 10	EFF 11	EFF 12
							ng/L						
PFPeA	2.3	4.5	254[a]	166[a]	97.2	78.1	108	79.3	78.2	86.7	83.3	78.0	51.4
PFHxA	1.4	7.0	512[a]	436[a]	220[a]	211[a]	200[a]	211[a]	235[a]	196[a]	161[a]	143[a]	103
PFHpA	0.7	3.5	145[a]	104	39.6	36.8	38.5	42.4	39.2	44.2	36.3	29.7	21.9
PFOA	0.2	1.8	176[a]	127[a]	70.5	59.8	66.0	79.5	97.0	122[a]	132[a]	113	92.8
PFNA	0.2	2.0	12.8	9.0	5.2	5.4	5.2	5.5	6.9	7.3	6.5	5.8	4.7
PFDA	0.4	2.0	102	65.3	37.7	35.7	33.1	36.3	39.4	39.4	34.0	34.8	27.2
PFUnA	2.8	5.7	< LOQ	< LOQ	n.d.	n.d.	< LOQ	< LOQ	n.d.	n.d.	< LOQ	< LOQ	n.d.
6:2-FTCA	10.0	50.1	178[a]	< LOQ	88.3	< LOQ	n.d.	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	33.8	67.5	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	1.2	6.2	33.3	25.0	51.2	20.2	< LOQ	6.7	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
8:2-FTUCA	0.8	3.8	n.d.	n.d.	1.1	0.6	n.d.	3.8	3.5	2.2	1.9	1.1	0.9
5:3-acid	7.0	13.9	133[a]	79.0	42.7	37.4	37.8	49.1	55.3	49.1	48.4	47.3	32.1
7:3-acid	1.8	3.6	14.3	9.0	4.4	4.5	3.9	5.5	5.5	6.1	7.4	5.6	5.2
PFBS	0.7	1.4	351[a]	194[a]	53.3	44.4	38.9	85.8	108.1	77.8	53.1	51.5	30.4
PFHxS	0.1	1.3	n.d.	n.d.	< LOQ	n.d.	< LOQ	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.
PFOS	0.3	1.4	118	102	57.0	49.6	42.6	55.7	56.0	48.1	40.9	39.1	33.4
6:2-FTS	0.1	0.3	2.2	2.1	0.47	0.5	0.5	n.d.	0.8	0.5	0.3	< LOQ	< LOQ

[a] Concentration exceeding the highest calibration point of 120 ng/L. Concentrations estimated by assumption of linear correlation; n.a.: not analyzed; n.d.: not detected; <LOQ: lower than limit of detection; n.d.: not detected; <LOQ: lower than limit of detection.

4.2.3 Air samples

Altogether, nine air samples were taken corresponding to the influent samples. Positive results obtained for air sample measurements are summarized in Table 45 (complete results table shown in Table 82 in the annex).

17 substances were detected in the air samples, among which 6:2-FTMAC (up to 33 µg/m^3) and 6:2-FTOH (up to 1.3 µg/m^3) were the substances with highest concentrations. These values are considered to be extraordinarily high air concentrations. Among the detected synthetic intermediates of 6:2- and 8:2-fluorotelomer chemistry, such as FTOs, FTACs and FTMACs, 6:2-congeners generally showed higher concentrations than their 8:2-homologs. Beside these analytes, again some of the PFCAs, such as PFPeA, PFHxA and PFOA were frequently detected with the highest concentration of 0.167 ng/m^3 for PFHxA. Additionally, 6:2- and 8:2-FTUCA and 5:3- and 7:3 acid were detected with highest concentration for 6:2-FTUCA of 0.03 ng/m^3.

Table 45: PFAS concentrations measured in air samples of WWTP-I2 in ng/m³. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	AIR 4	AIR 5	AIR 6*	AIR 7*	AIR 8	AIR 9	AIR 10	AIR 11	AIR 12
						ng/m³					
PFPeA	0.002	0.004	0.004	0.004	< LOQ	< LOQ	0.004	n.d.	0.004	n.a.	n.a.
PFHxA	0.004	0.021	0.083	0.167	0.042	0.025	< LOQ	< LOQ	0.046	n.a.	n.a.
PFOA	0.002	0.021	0.023	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.043	n.a.	n.a.
6:2-FTUCA	0.004	0.021	< LOQ	0.030	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.a.	n.a.
8:2-FTUCA	0.004	0.021	< LOQ	n.d.	n.d.	< LOQ	< LOQ	< LOQ	< LOQ	n.a.	n.a.
5:3-acid	0.021	0.042	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.a.	n.a.
7:3-acid	0.021	0.042	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTOH	0.067	0.200	360	1349	247	52.5	55.7	139	210	n.a.	n.a.
8:2-FTOH	0.033	0.067	173	91.6	52.8	25.3	28.8	172	414	n.a.	n.a.
10:2-FTOH	0.033	0.067	13.2	11.1	8.3	5.7	6.8	10.1	40.4	n.a.	n.a.
6:2-FTO	1.0	3.0	n.d.	n.d.	115		9.5	6.7	14.6	6.1	2.7
8:2-FTO	1.0	3.0	n.d.	n.d.	7.4		2.9	<LOQ	6.6	6.5	<LOQ
10:2-FTO	1.0	3.0	n.d.	215	31.6		6.4	12.3	56.7	37.8	10.7
6:2-FTAC	40.0	120	<LOQ	n.d.	n.d.		n.d.	<LOQ	<LOQ	<LOQ	<LOQ
8:2-FTAC	40.0	120	n.d.	n.d.	n.d.		n.d.	645	1,603	329	163
6:2-FTMAC	1.0	3.0	1,370	33,101	2,342		369	471	1,871	1,196	854
8:2-FTMAC	1.0	3.0	n.d.	22.3	n.d.		n.d.	n.d.	7.2	n.d.	n.d.

* due to an instrumental error for sampling method AIR-2, merged concentration for AIR 6 and AIR 7 are given. n.a.: not analyzed; n.d.: not detected; <LOQ: lower than limit of detection

4.2.4 Discussion

Comparison between molar concentrations of the most frequently detected substances in influents and effluents of WWTP-I2 is shown in Figure 33 in such a way that molar concentration differences between the influent and corresponding effluent are plotted. Only fluorotelomer-based compounds and their transformation products are shown. The presence of fluorotelomer compounds with different perfluoroalkyl chain length complicates the establishment of a mass balance, or at least a causal link between the presence of substances in the influent and in the effluent. This is due to the fact that several biotransformation products, e.g. PFHxA can be formed by biotransformation of several homologs of a substance class. For instance, both 8:2-FTOH and 6:2-FTOH generate PFHxA as a biotransformation product (Wang et al., 2009) and it is assumed that other 6:2-and 8:2-fluorotelomer compounds will also form PFHxA. Thus, the 6:2-and 8:2-precursors and biotransformation products are shown in one figure.

It is evident that in many of the samples, only a small fraction of the precursors in the influent is biotransformed and detected in the corresponding effluent, especially in samples 1, 3, and 5. It should be pointed out that 6:2-FTMAC, which was detected in several samples, was not analyzed in INF 1 and INF 2, thus the mass balance might even be less complete. This suggests volatilization of these substances once outdoor water-air contact is provided. This is substantiated by the water-air partitioning behavior shown in chapter 3.6.

Contrarily, for samples 4, 6, 8, 11, and 12, no fluorotelomer-based precursors were detected in the influents, but related transformation products were detected in the effluent. As the substances were detected in corresponding air samples above the influent, it is assumed that the precursors might be present in the aqueous phase at concentrations <LOD and thus reach the biological treatment where they are biotransformed. However, given the LOD for precursors and other volatile precursors, which is in the range of 10 ng/L-20 ng/L, only a small fraction of the biotransformation products formed can be substantiated by this explanation. Even for sample 12, which exhibits the lowest total molar increase of substances in the influent (+0.88 nM), only approximately 10% of the transformation products could be formed from present, but non-detected 6:2- and 8:2-fluorotelomer compounds when assuming that all of these substances are present at concentrations equaling the LODs (-0.082 µM). Thus, other precursors must be present in these samples which are not on the list of target analytes. Non-target screening, as shown in 4.10, was performed for WWTP-I2, but no substances could be identified.

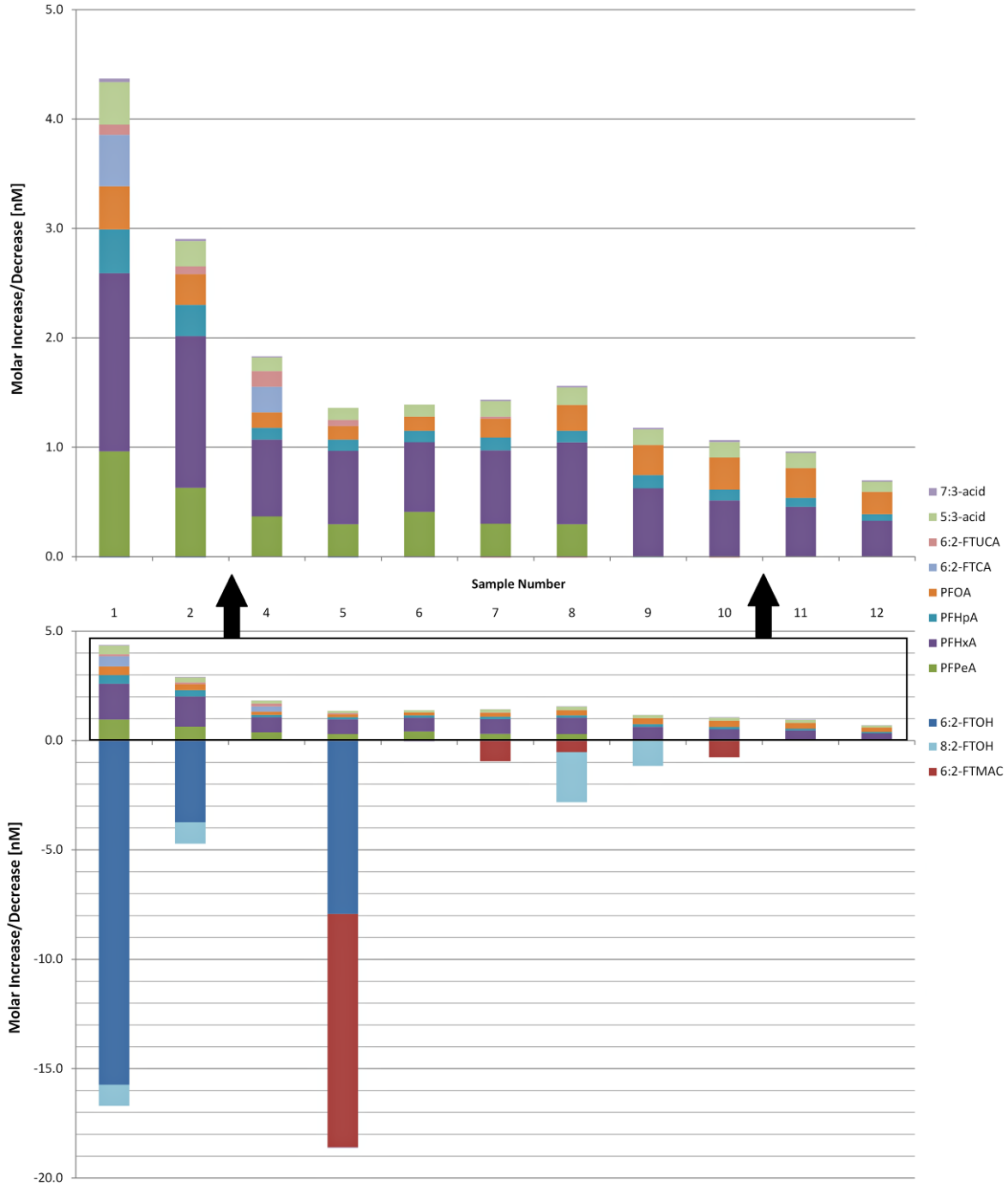


Figure 33: Molar increase and decrease in concentration of 6:2-FTOH, 6:2-FTMAC and their transformation products between influent and effluent samples of WWTP-I2. 6:2-FTMAC was not measured in influent samples 1 and 2 as well as effluent samples 1, 4, 6, 9 and 12.

Interestingly, the molar increase of several PFCAs from influent to effluent remains relatively constant despite very different concentrations of precursors. For instance, PFOA increase ranges from 0.13 nM to 0.39 nM whereas the sum of the precursor decrease ranges from n.d. to 18.6 nM. No quantitative correlation between concentrations of precursors in influents and formation of biotransformation products could be established even by application of sophisticated statistical tools (see chapter 4.2.5).

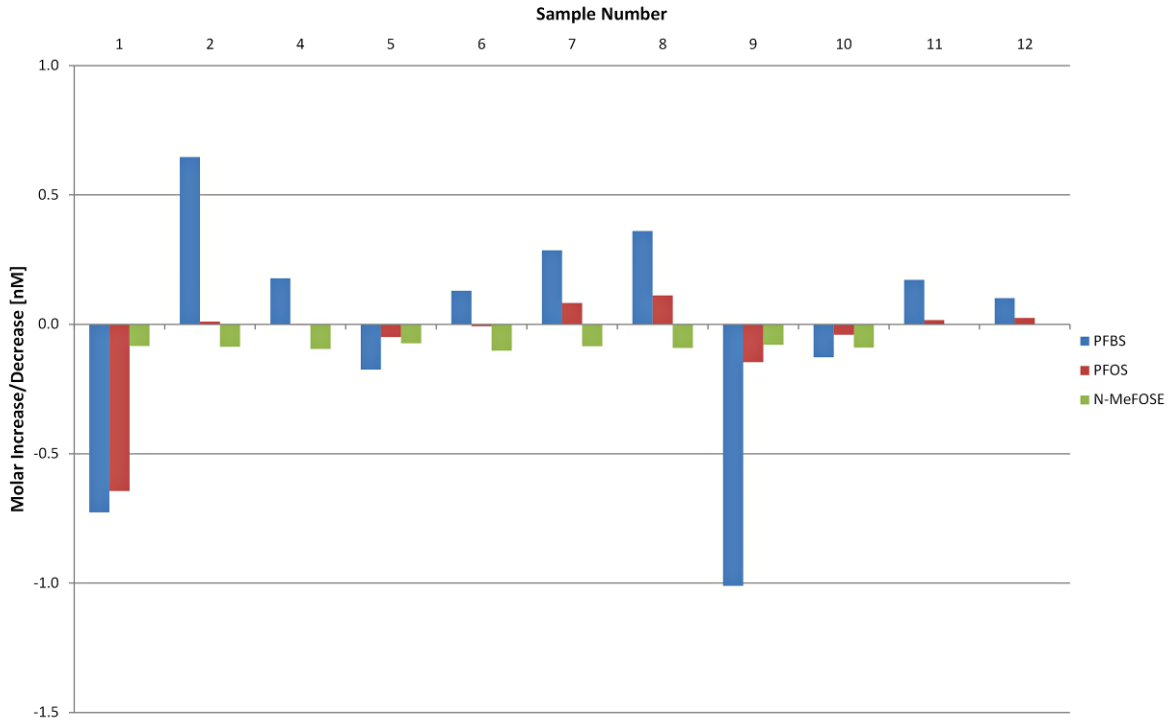


Figure 34: Molar increase and decrease in concentration PFBS and PFOS corresponding samples from influent and effluent samples of WWTP-I2.

As shown in Figure 34, the behavior of the two frequently detected PFBS and PFOS is different from that of fluorotelomer-based substances and their transformation products. Both PFSAs showed higher concentrations in effluent samples than in influent samples for some corresponding samples, but the opposite behavior in other corresponding samples. Thus, these substances can either be eliminated during wastewater treatment or be generated. Formation of these substances can be explained by biotransformation processes of precursors, e.g. FASAs, FASEs and their N-alkylated derivatives. However, no precursor of PFBS was on the list of target analytes in this study. Although N-MeFOSE was detected in influent samples of WWTP-I2 (see Figure 37 and Table 44), there is no logical link between the concentrations of precursors and the increase or decrease of PFOS. Indeed, in samples with large concentration increases in PFOS, N-MeFOSE was not even detected and in samples with strongest concentration decreases in PFOS concentration from influent to effluent, high concentrations of N-MeFOSE were detected. So far, there is no explanation for this behavior.

Decrease of concentration from influent to effluent cannot be readily explained, at least for PFBS. While PFOS can be sorbed onto sludge, PFBS is regarded a mobile chemical in

aqueous compartments, i.e. it is considered not to be adsorbed. However, this fate was already observed by Huset et al. (2008).

4.2.5 Multivariate statistical analysis of WWTP-I2 data

In dealing with large datasets, that is having large sample size with many variables, chemometrics is usually used to find the not-so-obvious factors that characterize a group of samples. In this regard, principal component analysis (PCA) is often employed to find similarities and differences in the samples and the variables that are responsible in the groupings. However, for large datasets and more complex analytical problems, PCA often has become less suitable in extracting relevant information. Nowadays, there are many other specific techniques that can be used for a wide variety of problems. Most of these techniques are either extensions or modifications of PCA.

In this study, CCA was chosen to analyze the data from WWTP I2. The WWTP-I2 dataset was specifically selected because it had the greatest sample size (n = 9) and had more of the target analytes detected than any other WWTP. Combination of data from different WWTP was deliberately avoided to factor out the effect of the origin of the sample. Unlike in PCA that treats the whole dataset together (only X variables), the dataset is divided into X and Y subgroups in CCA. This division was useful in the WWTP dataset that has the influent and effluent subgroups. One requirement needed for performing the classical CCA is that the number of samples (n) must be higher than the number of variables (x and y). This requirement was not met by the WWTP dataset. Therefore, regularized canonical correlation (RCC), a variant of CCA, was used.

To perform RCC, the dataset was divided into X and Y matrices. The X matrix was the matrix showing the PFASs in the influents while Y was the matrix with PFASs in the effluents. The first step done was to run a matrix correlation function to survey the correlation of each variable within X and within Y, and between X and Y. Figure 35 summarizes the result of the matrix correlation survey. The more the color becomes dark brown, the nearer is the correlation coefficient to 1 while the more the color becomes dark blue, the correlation coefficient approaches -1. The green color represents the variables with very low correlation against each other. In the wastewater influent (X), PFHxA (variable 1) is negatively correlated to PFHxS (variable 8). Within X and within Y, the variables do not have strong correlations with each other (there are many green-shaded regions). The Y variables are more correlated to each other than the X variables to each other. The cross-correlation between the variables in X and Y is also shown in Figure 35. This is more interesting due to the blue block that indicates strong negative correlation between variables. It must be noted that matrix correlations do not correct for covariance with other variables. This also implies that the result of this initial step is only to test whether there is enough reason to do RCC analysis.

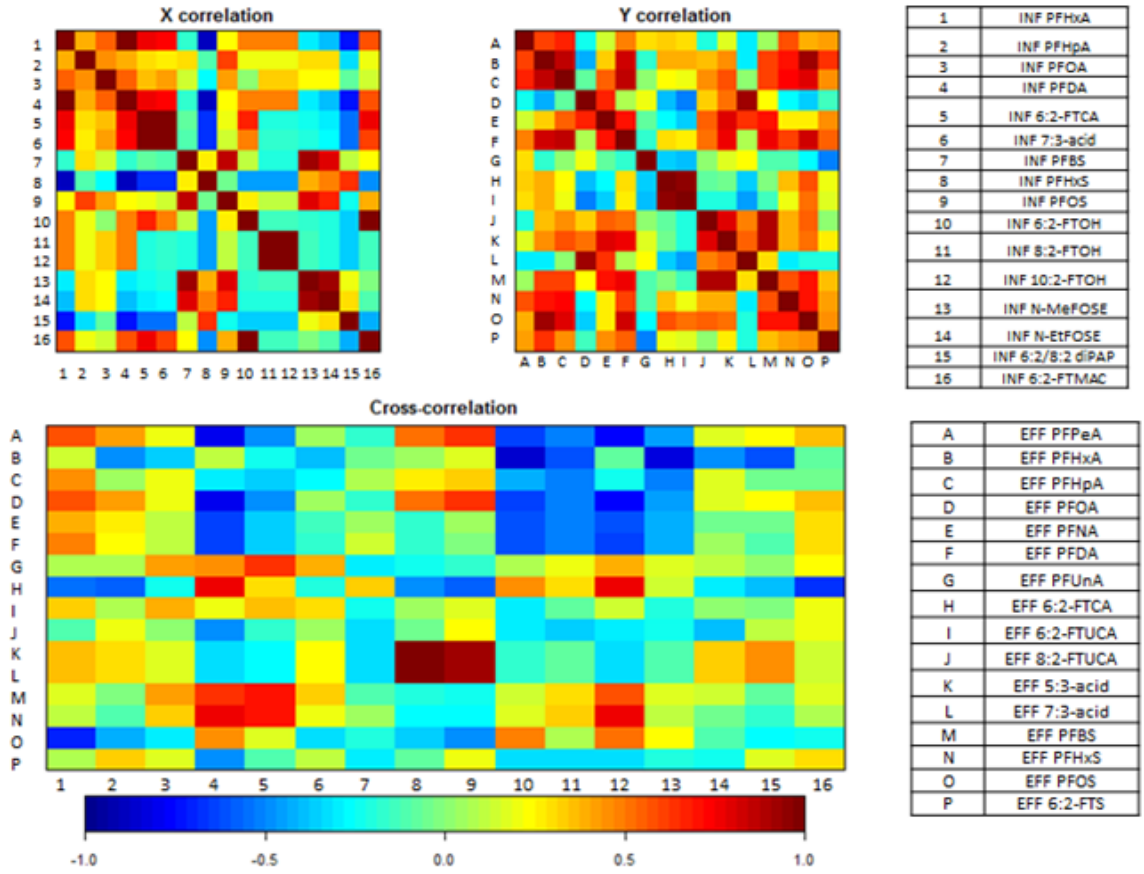


Figure 35: Matrix Correlation Survey of the variable set X (influent) and variable set Y (effluent) of WWTP-I2.

The plot of the variables in the canonical dimension 1 versus canonical dimension 2 is shown in Figure 36. The variables that are on the same direction from the origin are strongly correlated. The colors distinguish the X and the Y variables.

It can be observed that the concentrations of PFOA, 8:2 FTOH and 10:2 FTOH in the influent are correlated to the concentrations of PFOA, PFPeA, PFPeA, PFNA, 7:3-acid and PFUnA in the effluent. Some of these compounds are related to each other in degradation pathway. It can be suggested that if 8:2 FTOH are present in the influent, then these were transformed into PFOA during the treatment of the wastewater. This led to the higher level of the latter compounds in the corresponding effluent. Aside from this, the high amount of PFOA initially in the influent will also contribute to the high amount of PFOA in the effluent as this is not degraded during the treatment process.

There are also several variables that are grouped together but whose correlation either has no chemical basis or just not yet been investigated scientifically. For example, the concentration of PFHxS in the influent has high correlation with the concentration of 7:3-acid and PFOA in the effluent, but PFHxS cannot be transformed to either of the substances.

Chemometric graphs such as in Figure 36 are based only on the empirical correlations and are not conclusive as to the causal relationships of the variables being studied. Especially in complex systems where not all variables are measurable, high correlations can exist between variables that are not, at first glance, causally related. In this case, chemometrics can be a good start in finding the still missing (latent) variables. The method can be improved by increasing the sample size.

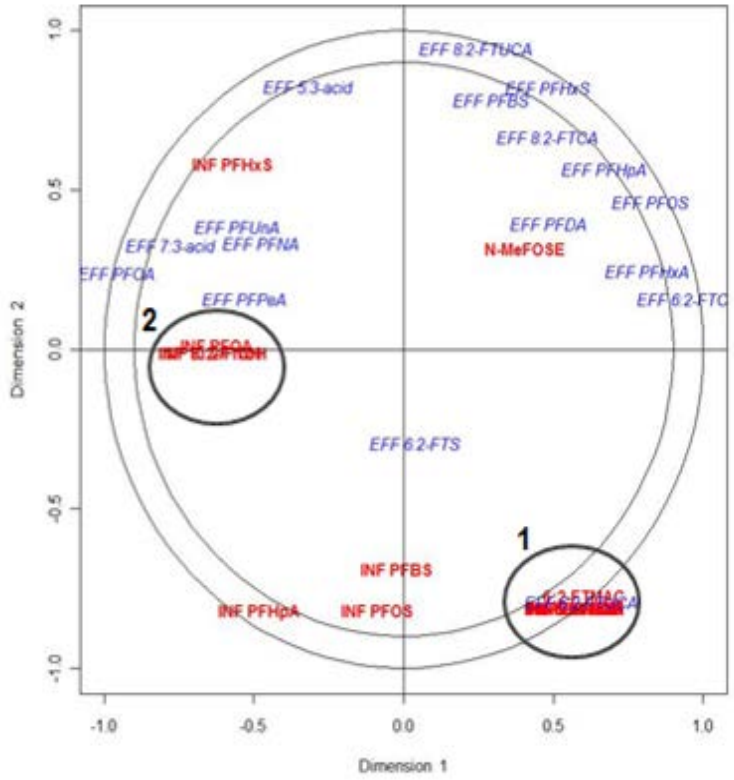


Figure 36: X and Y variables in the first two canonical dimensions generated using the regularized CCA of WWTP-I2 data. The variables in the circled cluster 1 include: EFF 6:2-FTUCA; INF PFHxA, PFDA, 6:2-FTCA, 7:3-acid, 6:2-FTOH, 8:2-FTO, 10:2-FTO and 6:2-FTMAC while in the circled cluster 2 are: INF PFOA, 6:2-FTOH, 8:2-FTOH and 10:2-FTOH.

However, even for this WWTP with different kinds of precursors and transformation products detected, CCA did not yield any further information regarding causalities between compounds detected. Therefore, no such multivariate statistics was carried out for other WWTPs where the spectrum of analytes detected was not as broad as for WWTP-I2.

4.3 Industrial wastewater treatment plant WWTP-I3

This WWTP has been chosen due to known potential industrial emitters, which most likely apply PFASs during the finishing process of textile manufacturing. Despite low effluent concentrations of PFCAs being analyzed a few years ago, there had been a tendency of exhibiting higher PFASs concentrations in the effluent compared to the influent (personal communication with WWTP operator). For example, PFOA concentrations in the influents varied between 27 and 29 ng/L and in the corresponding effluents between 56 and 320 ng/L (data not shown). Similar ratios had been observed for PFBA, PFPeA, PFHxA, PFHpA, PFNA and PFDA. However, the data analyzed within the present project do not confirm this tendency anymore and are in line with previous PFASs concentration data of WWTP-I3 (confidential data).

4.3.1 Influent samples

Concentrations of PFASs measured in seven influent samples of WWTP-I3 are shown in Table 46 (complete results table see Table 83 in the annex). From the 65 analytes measured, only PFOA and 6:2-FTS could be quantified in all influent samples with concentrations varying for PFOA between 14.4 ng/L and 24.4 ng/L and for 6:2-FTS between 2.7 ng/L and 8.45 ng/L. Additionally, some PFASs, such as PFHxA, PFHpA, 8:2-FTS, PFDPA, 8:2-diPAP could be detected in some of the influents with maximum concentration for 8:2-FTS in INF 1 with a concentration of 15.4 ng/L.

Table 46: PFAS concentrations in ng/m³ in the influent samples of WWTP-I3. Air samples corresponding to INF 1-3 were not taken. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7
					ng/L				
PFHxA	3.5	17.5	n.d.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHpA	2.3	11.5	n.d.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	0.7	7.1	24.4	26.4	21.2	14.4	15.4	17.2	13.0
PFDPA	3.4	6.8	11.9	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.3	0.7	6.5	5.7	5.1	4.4	8.45	2.7	3.2
8:2-FTS	3.3	6.6	15.4	8.2	n.d.	7.6	n.d.	n.d.	n.d.
6:2-diPAP	19.2	95.8	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	19.2	95.8	<LOQ	<LOQ	<LOQ	<LOQ	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

4.3.2 Effluent samples

Concentrations of PFASs determined in effluent samples of WWTP-I3 are summarized in Table 47 (complete results table see Table 84). Compared to the corresponding influents, the spectrum of detected PFASs was slightly higher, especially in case of the PFCAs, where C_5-C_{10}-PFCAs were detected in all of the samples. PFOA could be quantified in all effluent samples with concentrations between 17.7 ng/L and 30.8 ng/L. Additionally, PFSAs, such as PFHxS, PFOS, and the potential precursor 6:2-FTS could be detected in all of the effluents, although at very low concentrations. Only PFBS showed higher concentrations between 44.5 ng/L and 110 ng/L.

Table 47: Concentrations of PFASs determined in effluent samples of WWTP-I3. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	EFF 1	EFF 3	EFF 5	EFF 6
				ng/L		
PFPeA	2.9	5.8	12.2	14.3	14.7	11.0
PFHxA	1.7	8.7	14.6	24.9	23.0	16.6
PFHpA	1.1	5.7	15.6	7.7	<LOQ	<LOQ
PFOA	0.4	3.5	30.8	21.6	20.2	17.7
PFNA	0.4	3.8	<LOQ	4.1	<LOQ	4.2
PFDA	0.7	3.3	<LOQ	<LOQ	<LOQ	<LOQ

Analyte	LOD	LOQ	EFF 1	EFF 3	EFF 5	EFF 6
	ng/L					
PFBS	0.9	1.7	110	48.2	44.5	53.7
PFHxS	0.1	1.0	1.5	1.7	1.4	1.1
PFOS	0.3	1.3	5.0	4.2	4.1	3.3
6:2-FTS	0.2	0.3	11.7	3.2	1.8	2.3

<LOQ: lower than limit of detection

4.3.3 Air samples

Concentrations of PFASs in air samples drawn above the influent of WWTP-I3 are shown in Table 48 (complete results table see Table 85 in the annex). All investigated FTOHs were quantified in all of the samples at high concentrations of up to several hundred ng/m^3. No constant ratio of concentrations between FTOH congeners was observed, but 6:2-FTOH and 8:2-FTOH were the dominating FTOH homologs, whereas 10:2-FTOH always showed the lowest concentrations. Apart from FTOHs, no other volatile PFASs were detected in any of the samples.

However, several PFAAs were detected, with PFOA being quantified in all of the samples at varying concentrations. Air sample AIR 4 exhibited further PFAAs, such as C_4-C_6-PFCAs and 6:2-FTS. Furthermore, PFNA, PFDA, 6:2-FTCA, 6:2-FTUCA, PFOS and even 5:3-acid were detected below the LOQ.

Table 48: PFAS concentrations in ng/m³ in air samples above influent of WWTP-I3. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7
					ng/m³				
PFBA	0.002	0.004	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.
PFPeA	0.002	0.004	n.d.	n.d.	0.047	0.004	0.45	n.d.	n.d.
PFHxA	0.004	0.021	n.d.	n.d.	n.d.	0.028	1.57	n.d.	n.d.
PFOA	0.002	0.021	4.86	6.54	0.48	0.038	3.90	0.34	0.47
PFNA	0.002	0.022	n.d.	0.19	n.d.	<LOQ	n.d.	n.d.	n.d.
PFDA	0.004	0.021	n.d.	0.39	n.d.	<LOQ	n.d.	n.d.	n.d.
6:2-FTCA	0.042	0.208	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
6:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	<LOQ	0.18	n.d.	n.d.
5:3-acid	0.021	0.042	5.43	6.64	0.31	<LOQ	0.05	0.17	n.d.
PFOS	0.004	0.021	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
6:2-FTS	0.002	0.004	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.
6:2-FTOH	0.067	0.200	665	883	34.5	32.8	528	8.7	44.8
8:2-FTOH	0.033	0.067	480	746	49.8	8.2	674	6.4	33.8
10:2-FTOH	0.033	0.067	39.4	45.2	12.3	1.8	165	2.3	9.4

n.d.: not detected; <LOQ: lower than limit of detection

4.3.4 Discussion

Comparing the analytes detected in both, the influents and corresponding effluents, no direct industrial source seems to play a role for this WWTP as concentrations of detected PFASs were lower than in other industrial WWTPs and no compounds related to production processes (FTOs, FTIs, PFAIs, etc.) were detected. Concentrations were much lower compared to historical data (see Table 49) where large increases in concentrations from influent to effluent were observed. These data were the reasons why this WWTP was considered 'industrial' as defined in chapter 2.7.1. This might result from changing the product spectrum of potential imitters or changes within the production processes. The only interesting hint for an industrial influence can be retrieved from the high FTOH concentrations detected in the air samples. Based on this, especially the air samples one and two indicates an industrial influence. In contrast to the water samples, the air samples were enriched continuously over 24 hours. This might be the reason why the FTOHs were not detected in the influent samples. PFPeA was only detected in the effluent samples. PFOA increased in all effluent samples analyzed compared to the corresponding influent samples. This increase might be an indicator of the transformation of FTOHs, which were quantified in all air samples. PFPeA was detected and quantified only in the effluent and indicates the transformation of precursors.

Table 49: Concentrations of PFASs in corresponding influent (INF) and effluent (EFF) samples from WWTP-I3 from 2010. The data was handed out by the WWTP operator and was not measured with the methods explained in this study.

	1	2	3	4	5

Analyte	INF	EFF	INF	EFF	INF	EFF	INF	EFF	INF	EFF
PFBA	31	49	14	34	23	64	30	45	32	440
PFPeA	11	87	15	40	7	73	15	48	28	340
PFHxA	46	122	41	76	27	102	24	72	29	230
PFHpA	8	14	9	7	4	13	9	10	42	350
PFOA	27	92	29	57	19	76	25	56	28	320
PFNA	9	20	11	33	7	16	6	13	38	410
PFDA	4	36	8	31	4	16	4	14	23	260
PFOS	6	12	8	11	8	11	6	11	n.a.	n.a.
6:2-FTS	47	6	47	5	21	6	136	1	n.a.	n.a.

n.a.: not analyzed

4.4 Municipal wastewater treatment plant WWTP-M1

4.4.1 Influent samples

PFASs concentrations determined in the influent samples of WWTP-M1 are summarized in Table 50 (complete results table see Table 86). Most of the substances under investigation were not detected, only seven substances were detected. PFOA (5.0-7.6 ng/L) and PFOS (4.6-12.3 ng/L) were detected in all samples, even if the PFOA concentration was only slightly above the LOQ for this particular WWTP.

Most of the precursor substances were not detected, except for 6:2-FTS (mostly <LOQ), 6:2-FTUCA (only <LOQ) and 8:2-diPAP, which was quantified in one sample at 109 ng/L and <LOQ in three out of eight samples.

Table 50: PFAS concentrations in ng/L in the influent samples of WWTP-M1. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	ng/L									
PFHpA	1.7	8.4	<LOQ	<LOQ	<LOQ	n.d.	n.d.	n.d.	<LOQ	n.d.
PFOA	0.5	4.7	6.0	5.4	7.6	5.5	5.5	5.0	5.5	5.9
6:2-FTUCA	2.6	13.0	n.d.	n.d.	<LOQ	<LOQ	n.d.	n.d.	n.d.	n.d.
PFDPA	5.9	11.7	31.9	17.3	n.d.	<LOQ	<LOQ	n.d.	n.d.	n.d.
PFOS	0.6	2.8	7.2	12.3	5.4	6.5	4.6	6.5	4.8	5.6
6:2-FTS	0.3	0.5	n.d.	2.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
8:2-diPAP	15.7	78.3	n.d.	109	<LOQ	<LOQ	<LOQ	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

4.4.2 Effluent samples

Concentrations of investigated PFASs in the five corresponding effluents of WWTP-M1 are summarized in Table 51 (complete results table see Table 87 in the annex). In total, eleven compounds were detected, among these C_5-C_{10}-PFCAs, PFBS, PFHxS, PFOS and 6:2-FTS were detected in effluent samples. The dominating substance was PFPeA with low fluctuations between 8.6 ng/L and 16.9 ng/L. PFOS and 6:2-FTS showed highest concentrations in samples EFF 1 with 18.7 ng/L and 14.6 ng/L, respectively.

Table 51: PFAS concentrations in ng/L in the effluent samples of WWTP-M1. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 5	EFF 7	EFF 8
				ng/L			
PFPeA	2.2	4.5	16.9	13.1	16.8	12.8	8.6
PFHxA	1.4	7.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHpA	1.0	5.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	0.3	2.8	7.3	8.1	5.8	6.3	6.3
PFNA	0.3	3.2	<LOQ	<LOQ	n.d.	<LOQ	<LOQ
PFDA	0.7	3.7	<LOQ	n.d.	<LOQ	n.d.	n.d.
6:2-FTUCA	1.5	7.4	<LOQ	n.d.	n.d.	n.d.	n.d.
PFBS	0.7	1.4	7.5	12.5	14.8	9.9	10.3
PFHxS	0.1	1.3	<LOQ	1.4	<LOQ	1.5	1.7
PFOS	0.4	2.1	18.7	7.2	6.9	4.2	5.1
6:2-FTS	0.1	0.3	14.6	1.4	1.7	1.8	1.6

n.d.: not detected; <LOQ: lower than limit of detection

4.4.3 Air samples

PFAS concentrations determined in air above the influent of WWTP-M1 are shown in Table 52 (complete results shown in Table 87 in the annex). Seven substances were detected in the samples among which FTOHs, notably 6:2-FTOH dominated with concentrations of up to 15.3 ng/m^3, but also 8:2-FTOH and 10:2-FTOH could be quantified in all samples. Again PFOA was present in all air samples, but not above the LOQ of 0.021 ng/m^3. Additionally, 6:2-FTS could be detected in some of the investigated samples.

Table 52: PFAS concentrations in ng/m³ in WWTP-M1 air samples taken above the influent.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
PFOA	0.002	0.021	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFDA	0.004	0.021	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.004	0.021	n.d.	n.d.	0.026	n.d.	n.d.	n.d.	<LOQ	<LOQ
6:2-FTS	0.002	0.004	n.d.	0.005	<LOQ	<LOQ	n.d.	0.005	n.d.	n.d.
6:2-FTOH	0.07	0.2	5.4	12.5	15.3	4.0	10.7	9.0	10.6	5.6
8:2-FTOH	0.04	0.07	1.6	4.3	4.4	1.7	3.8	4.2	4.0	2.3
10:2-FTOH	0.04	0.07	0.1	0.2	0.2	0.1	0.3	0.5	0.5	0.2

n.d.: not detected; <LOQ: lower than limit of detection

4.4.4 Discussion

As expected, the diversity of PFASs detected in the municipal WWTP was not as wide as that of the industrial WWTP and the concentrations of target substances was in the lower ng/L range. For PFOA, similar concentrations in corresponding influent and effluent samples were detected with slight increases in the effluent which are in the range of method uncertainty. For sample 2, the largest increase was observed with 5.4 ng/L in the influent and 8.1 ng/L in the effluent sample. This might be an indication for formation of PFOA from precursors. In this sample, 8:2-diPAP was detected in the corresponding influent at 109 ng/L, which might be the cause for the increase. Furthermore, the presence of 8:2-FTOH in all air samples shows that this substance is present even though it could not be detected in aqueous samples, probably due to the high vapor pressure and thus too low concentrations below the LOD.

For PFOS, increases, decreases and constant concentrations from influent to effluent were observed. In sample 1, an increase from 7.2 ng/L to 18.7 ng/L indicates formation of PFOS by transformation of precursors. Increases in the effluent could not be substantiated by transformation of target PFOS precursors since none of them were detected in any of the samples, thus, other PFOS precursors must be present that have not been included in the screening. In sample 2, the opposite was observed which suggests sorption of PFOS to sludge, which will still be examined.

PFBS was quantified in all effluent samples, but it was not detected in a single influent sample which indicates formation of PFBS during biological treatment. Since none of the potential PFBS precursors, such as perfluorobutane sulfonamidoethanol (FBSE) derivatives, were included in this study, the origin of PFBS could not be pinpointed.

6:2-FTS concentrations showed a similar pattern as PFOS with one decrease and several increases of up to 14.6 ng/L where no 6:2-FTS had been detected in the influent. While 6:2-FTS is considered a precursor of several PFCAs, such as PFPeA and PFHxA, as well as x:3-acids (Wang et al., 2011), it is apparently also formed from precursor substances in this case. Scientific literature indicates several FTS derivatives, e.g. betaine surfactants or cationic surfactants (Place and Field, 2012). These surfactants contain a non-fluorinated moiety attached to the FTS basic structure and these are used in aqueous film-forming foams. Even though there is no information about biotransformation of such substances,

it can be assumed that they might be degraded to FTS as an intermediate transformation product. The increase for PFPeA for all effluents might be correlated to the frequent detection of 6:2-FTS.

4.5 Municipal wastewater treatment plant WWTP-M2

4.5.1 Influent samples

WWTP-M2 is fed by two different influents which were sampled and analyzed separately. Results for the first influent are marked by the suffix ‘A’ and are summarized in Table 53 (complete results shown in Table 89 in the annex) and those for the second influent are marked with the suffix ‘B’ and are shown in Table 54 (complete results shown in Table 90). In total, 16 influent samples have been taken and analyzed.

Influent A only exhibited three detected substances (PFHpA, PFOA and 6:2-FTS) among which PFOA showed the highest concentrations with up to 5 ng/L. Most other detected analytes showed concentrations <LOQ.

Influent B featured the same substances as influent A, but additionally PFOS was detected in 5 of 8 samples. PFOS showed the highest concentrations in effluent B with up to 6.4 ng/L.

Table 53: PFAS concentrations in ng/L in the influent samples of influent A of WWTP-M2. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	INF 1A	INF 2A	INF 3A	INF 4A	INF 5A	INF 6A	INF 7A	INF 8A
	ng/L									
PFHpA	1.7	8.4	n.d.	<LOQ	n.d.	n.d.	<LOQ	<LOQ	n.d.	<LOQ
PFOA	0.5	4.6	<LOQ	5.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4.7
6:2-FTS	0.3	0.5	n.d.	0.62	n.d.	n.d.	<LOQ	0.8	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 54: PFAS concentrations in ng/L in the influent samples of influent B of WWTP-M2. Only substances with at least one detection are show

Analyte	LOD	LOQ	INF 1B	INF 2B	INF 3B	INF 4B	INF 5B	INF 6B	INF 7B	INF 8B
	ng/L									
PFHpA	1.9	9.4	<LOQ	n.d.	<LOQ	<LOQ	n.d.	<LOQ	n.d.	<LOQ
PFOA	0.5	4.9	<LOQ	<LOQ	5.8	5.4	<LOQ	5.1	<LOQ	n.d.
PFOS	0.5	2.4	n.d.	n.d.	4.6	3.9	4.2	6.1	6.4	n.d.
4:2-FTS	0.5	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.7
6:2-FTS	0.3	0.5	n.d.	n.d.	n.d.	2.5	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

4.5.2 Effluent samples

Concentrations of investigated PFASs in the four corresponding effluents, namely EFF 1, EFF 2, EFF 5, and EFF 6 of WWTP-M2 are summarized in Table 55 (complete results shown in Table 91 in the annex). In total, ten analytes were detected, notably C_4-C_{10}-PFCAs. PFOA occurred at levels of up to 6.1 ng/L. PFHxS, PFOS and 6:2-FTS were additionally detected in effluent samples at concentrations of up to 5.6 ng/L for PFOS.

Table 55: PFAS concentrations in ng/L in the effluent samples of WWTP-M2. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 5	EFF 6
	ng/L					
PFBA	2.7	5.3	n.d.	n.d.	n.d.	4.2
PFPeA	1.7	3.4	6.4	4.9	n.d.	4.9
PFHxA	1.1	5.4	5.0	4.9	2.2	7.2
PFHpA	0.8	4.0	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	0.2	2.3	6.1	5.3	2.8	6.2
PFNA	0.3	2.7	<LOQ	<LOQ	n.d.	<LOQ
PFDA	0.7	3.7	<LOQ	<LOQ	<LOQ	<LOQ
PFHxS	0.1	1.3	2.4	1.9	n.d.	2.6
PFOS	0.3	1.4	5.0	5.6	4.6	5.5
6:2-FTS	0.1	0.3	0.6	0.5	1.7	<LOQ

n.d.: not detected; <LOQ: lower than limit of detection

4.5.3 Air samples

PFAS concentrations determined in air above influent B of WWTP-M2 are shown in Table 56 (complete results shown in Table 92 in the annex). Air above influent A was not sampled. Six substances were detected, of which all investigated FTOHs were detected in all investigated samples. 6:2-FTOH dominated with concentrations of up to 98.5 ng/m^3 in the sample AIR 8, but particularly in this sample, also 8:2-FTOH and 10:2-FTOH could be quantified with maximum concentrations. In this particular sample, also 6:2-FTS could be detected at a concentration of 0.107 ng/m^3. The concentrations of the further air samples analyzed were significantly lower and at a comparable level. Thus, a direct PFASs source for AIR sample 8 can be considered. Of the investigated PFCAs only PFOA could be detected.

Table 56: PFAS concentrations in ng/m³ in air samples of WWTP-M2. Samples were taken above influent B. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
PFHxA	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.240
PFOA	0.002	0.021	n.a.	<LOQ	<LOQ	<LOQ	0.035	0.023	0.045	0.039
6:2-FTS	0.002	0.004	n.a.	0.005	0.005	n.d.	n.d.	0.004	0.008	0.107
6:2-FTOH	0.067	0.200	n.a.	3.4	3.3	2.3	3.3	24.5	4.7	98.5
8:2-FTOH	0.033	0.067	n.a.	1.0	0.8	0.7	1.0	1.0	1.3	16.6
10:2-FTOH	0.033	0.067	n.a.	0.1	0.1	0.1	0.1	0.1	0.2	0.2

n.a.: not analyzed; n.d.: not detected; <LOQ: lower than limit of detection

4.5.4 Discussion

Closing the mass balance for PFASs, especially when involving strongly adsorbable or volatile substances, is generally hard to achieve, as stated in chapter 4.2.4, but in the case of WWTP-M2, it is further impeded by the fact that the WWTP is fed by two influents. As a consequence and considering that only few PFASs were detected in influent samples and air samples – most of which do not even undergo biotransformation - attempts to establish links between precursors and biotransformation products have failed.

In the air samples above influent B, the three investigated FTOHs were measured in low concentrations between 0.1 ng/m^3 (10:2-FTOH) and 98.5 ng/m^3 (6:2-FTOH). The latter one was detected in sample AIR 8 and is an outlier as most of the concentrations in other samples were in the low ng/m^3 range. Interestingly, also 8:2-FTOH showed a peak in concentration in this sample suggesting a point source of a product containing mixed 6:2/8:2-fluorotelomer chemistry. Contrarily, the other air sample with pronounced 6:2-FTOH concentration (24.5 ng/m^3, AIR 6), does not contain increased levels of 8:2-FTOH compared to the average background concentration in this specific WWTP. While INF 6 indeed shows highest concentration of PFHxA, a known biotransformation product of 6:2-FTOH, the concentration is not significantly higher compared to the remaining effluent samples (7.4 ng/L compared to 5.0 ng/L, 4.9 ng/L and 2.2 ng/L. Another precursor that can be responsible for PFHxA formation is 6:2-FTS, which was only detected in very low concentrations in some of the influents (0.62 ng/L in INF 2A, 0.8 ng/L in INF 6A and 2.5 ng/L in INF 4B.

4.6 Municipal wastewater treatment plant WWTP-M3

4.6.1 Influent samples

PFASs concentrations determined in the influent samples of WWTP-M3 are summarized in Table 57 (complete results shown in Table 93 in the annex). Eight analytes were detected with PFOA (4.4-9.1 ng/L) quantified in all samples. PFOS was determined in all but one sample (7.1-42.1 ng/L). Additionally, 6:2-FTS was quantified in all samples (2.6-120 ng/L) and showed the highest concentrations. Interestingly, PFBA was determined at very high concentrations in three samples (142-179 ng/L), but it was not detected in the remaining five samples.

Table 57: PFAS concentrations in ng/L in the influent samples of WWTP-M3. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	ng/L									
PFBA	5.8	11.7	153	142	179	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	2.1	10.7	<LOQ	n.d.	n.d.	<LOQ	<LOQ	n.d.	n.d.	n.d.
PFOA	0.6	5.7	4.8	4.4	4.7	9.1	5.7	5.8	5.0	5.6
PFDPA	6.7	13.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16.9	n.d.
PFOS	0.6	2.8	16.9	13.8	n.d.	7.1	7.8	6.9	22.9	42.1
6:2-FTS	0.3	0.6	5.2	6.3	120	19.9	21.9	2.6	32.0	13.3
6:2-diPAP	22.7	113	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.
8:2-diPAP	22.7	113	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

4.6.2 Effluent samples

Concentrations of PFASs determined in the effluent of WWTP-M3 are summarized in Table 58 (complete results shown in Table 94 in the annex). Eleven substances were detected, especially PFPeA (9.9-21.4 ng/L), PFOA (7.4-10.3 ng/L), PFBS (12.2-13.0 ng/L), 6:2-FTS (20.1-56.9 ng/L) were quantified in all samples. Furthermore, PFHxA, PFHpA and PFHxS were detected in all samples, but below the LOQ.

Table 58: PFAS concentrations in ng/L in the effluent samples of WWTP-M3. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 4	EFF 6
			ng/L			
PFPeA	2.5	5.1	14.0	9.9	21.4	14.3
PFHxA	1.3	6.6	<LOQ	<LOQ	<LOQ	<LOQ
PFHpA	1.0	4.8	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	0.2	2.3	10.2	9.7	10.3	7.4
PFNA	0.3	3.1	<LOQ	n.d.	<LOQ	n.d.
PFDA	0.7	3.3	<LOQ	n.d.	n.d.	n.d.
PFBS	0.7	1.3	13.0	12.5	12.2	12.9
PFHxS	0.1	1.3	<LOQ	<LOQ	<LOQ	<LOQ
PFOS	0.4	1.8	22.8	20.4	13.5	12.8
6:2-FTS	0.1	0.3	20.1	56.9	33.3	23.8
8:2-FTS	1.3	2.5	n.d.	<LOQ	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

4.6.3 Air samples

A summary of the PFAS concentrations detected in air samples of WWTP-M3 is shown in Table 59 (complete results shown in Table 95 in the annex). None of the volatile substances was quantified in any of the samples, only 6:2-FTOH and 8:2-FTOH were detected, but below the LOQ. Additionally, PFOA and 6:2-FTS were measured in the low ng/m^3 range (up to 0.211 ng/m^3 for 6:2-FTS in AIR 1).

Table 59: PFAS concentrations in ng/m³ in the air samples of WWTP-M3. Only substances with at least one detection are shown.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
PFOA	0.002	0.021	0.037	0.046	0.060	0.068	0.030	n.d.	0.030	0.041
6:2-FTS	0.002	0.004	0.050	0.211	n.d.	n.d.	n.d.	n.d.	0.048	n.d.
6:2-FTOH	0.07	0.2	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	0.04	0.07	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

n.d.: not detected; <LOQ: lower than limit of detection

4.6.4 Discussion

For WWTP-M3, very few precursors were detected in the samples and even fewer could be quantified. Considering 6:2-FTS a precursor for PFCAs and 3:3-acids, it was the only PFAS precursor quantified in the samples reaching up to 120 ng/L in INF 3 sample. However, in most of the corresponding samples, 6:2-FTS concentrations were higher in the effluent samples. The difference was up to 50 ng/L which suggests formation of 6:2-FTS as an intermediate biotransformation product of FTS derivatives (see chapter 4.4.4).

Similarly to WWTP-M1, PFBS was quantified in all effluent samples at very similar levels (12.2-13.0 ng/L), but again, no precursors of PFBS were investigated. The same holds for PFPeA, which was not detected in any influent sample, and quantified in all effluent samples at concentrations between 9.9 ng/L and 21.4 ng/L. PFPeA could be formed by partial biotransformation of 6:2-FTS.

As far as PFOA concentrations are concerned, samples 1 and 2 show an increase from ca. 5 ng/L to ca. 10 ng/L, the remaining two sets of samples show similar concentrations in influents and effluents. However, none of the investigated PFOA precursors were detected in the influent and air samples.

The PFBA concentrations in the first three influent samples were exceptionally high and interestingly, PFBA was not even detected in any further influent sample. Furthermore, PFBA was not detected in the corresponding effluent samples. This behavior cannot be reasoned since PFBA does not readily sorb to sludge nor is it biodegradable (Gellrich et al., 2012). As a result, one would expect PFBA, when present in influent, to be present in corresponding effluents too, as can be seen, for example, in WWTP-I1. From an analytical point of view, PFBA shows several difficulties: It is very polar and thus elutes early from the chromatographic column, it is not quantitatively sorbed to the SPE material and – most importantly – it yields only one intense product ion by collision-induced dissociation in MS, that is the product ion at *m/z* 169, which is formed by loss of CO_2 from the deprotonated molecule. This cleavage, however, is not very selective, since there will be numerous carboxylic acids in environmental samples, most of which will also show such a loss of CO_2 upon fragmentation. Therefore, the method is not highly selective for PFBA and the observed high concentrations could be due to a chemical interference. These concentrations were attempted to be verified by high-resolution MS, which offers improved selectivity due to the negative mass defect of fluorine. However, the sensitivity of the instrument was inferior to that of the triple quadrupole system. Therefore, verification of the PFBA levels failed.

4.7 Particulate phase of WWTP-I2 influent samples

For the two investigated samples of the particulate phase of the influents of WWTP-I2, very few precursors were detected in the samples and even fewer could be quantified (see Table 60, complete results table see Table 103 in the annex). Considering 6:2-FTS a precursor for PFCAs and 3:3-acids, and 8:2-diPAP, these were the only PFAS precursors quantified in the samples reaching up for the latter to 7.6 ng/g wet weight in INF 8 sample. Besides these precursors, only PFOS with values of 0.8 and 1.1 ng/g could be quantified. The C_6 to C_{10}-PFCAs were present in concentrations below 2 ng/g.

Table 60: Results of analysis of particulate phase of influent of WWTP-I1. Only substances with at least one detection are shown.

Analyte	LOD [ng/g]	LOQ [ng/g]	INF 7	INF 8
			ng/g wet weight	
PFHxA	0.4	1.9	<LOQ	<LOQ
PFHpA	0.4	2.0	<LOQ	<LOQ
PFOA	0.1	0.9	<LOQ	<LOQ
PFNA	0.2	1.9	<LOQ	<LOQ
PFDA	0.4	1.9	<LOQ	<LOQ
PFOS	0.1	0.7	1.1	0.8
6:2-FTS	0.1	0.1	0.2	n.d.
8:2-diPAP	0.7	3.5	<LOQ	7.6
6:2/8:2-diPAP	-	-	detected	detected
8:2/10:2-diPAP	-	-	detected	detected

n.d.: not detected; <LOQ: lower than limit of detection

However, despite the gentle sample preparation technique used, no volatile precursors such as e.g. 6:2-FTOH and 6:2-FTMAC, which were detected in high concentrations in the corresponding water phase were detectable.

Due to the lack of further material from the other WWTPs being investigated and the obtained results described above, additional analyses of the particulate phases were disregarded. More promising results were anticipated through the analyses of the additional sludge samples taken from all WWTPs.

4.8 WWTP sludge samples

Sludge samples of municipal and industrial WWTPs were analyzed with the method described in chapter 2.4.2.8. The results for two sludge samples from municipal WWTP (M1 and M3) and three sludge samples from industrial WWTP-I2 are shown in Table 61(complete results table see Table 101 in the annex). The recoveries of the internal standards in the sludge samples analyzed are shown in Table 62.

Table 61: LODs, LOQs and concentrations of analytes in HPLC-MS-a method in sludge samples from WWTP-M1, M3 and I2. Only substances with at least one detection are shown.

Analyte	LOD [ng/g]	LOQ [ng/g]	WWTP-M1	WWTP-M3	WWTP-I2		
					ng/g		
			SLU 8	SLU 1	SLU 6	SLU 9	SLU 11
PFPeA	7.4	14.7	n.d.	n.d.	60	68	71
PFHxA	6.0	29.8	n.d.	n.d.	301*	278*	248*
PFHpA	4.9	24.6	n.d.	n.d.	16.9	16.3	24.3
PFOA	1.9	19.3	n.d.	n.d.	185*	173*	256*
PFNA	2.3	24.1	n.d.	n.d.	11	9	11

			WWTP-M1	WWTP-M3	WWTP-I2		
					ng/g		
Analyte	LOD [ng/g]	LOQ [ng/g]	SLU 8	SLU 1	SLU 6	SLU 9	SLU 11
PFDA	6.0	30.0	n.d.	n.d.	201*	191*	146*
PFUnA	33.9	67.8	n.d.	n.d.	920*	568*	807*
5:3-acid	29.8	59.6	n.d.	n.d.	660*	655*	688*
7:3-acid	19.3	38.5	n.d.	n.d.	311*	352*	433*
PFOS	1.3	6.7	n.d.	13.1	109*	152*	98*

* > highest calibration point and thus only an estimated value; n.d.: not detected

The recoveries of the largest share of the internal standards were low with values of only 43% for M-PFHxS in the sludge sample of WWTP-M3. Thus, the calculated LODs and LOQs were too high to detect the analytes in the sludge samples of the municipal WWTPs, except for PFOS which was determined at a concentration of 13.1 ng/g in the WWTP-M3 samples. Due to the high peak areas of detected analytes in the sludge samples of WWTP-I2 the calculated concentrations of PFHxA, PFOA, PFDA, PFUnA, 5:3-acid, 7:3-acid and PFOS were out of the highest calibration level. Thus, the concentration in Table 61, labeled with * can be only an estimation.

When applying this method to sludge samples from industrial WWTP I-1, the situation deteriorated even further, as shown in Table 63. Isotopically labeled standards were only detected in few cases, thereby disallowing quantification of PFASs in the samples. Sludge as one of the most challenging cases obviously led to very pronounced ion suppression during HPLC-ESI-MS.

Table 62: Recoveries of isotopically labelled internal standards from sludge samples of WWTP-M1, M3 and I2

	WWTP-M1	WWTP-M3		WWTP-I2	
			Recovery		
Analyte	SLU 8	SLU 1	SLU 6	SLU 9	SLU 11
MPFBA	3%	4%	1%	2%	2%
MPFPeA	3%	3%	2%	1%	2%
MPFHxA	7%	10%	5%	5%	6%
MPFHpA	9%	9%	10%	10%	8%
MPFOA	9%	14%	14%	12%	10%
MPFNA	10%	11%	18%	16%	15%
MPFDA	6%	10%	18%	16%	21%
MPFUnA	6%	9%	1%	1%	1%
MPFDoA	6%	5%	2%	2%	1%
M-6:2-FTCA	4%	4%	6%	6%	9%
M-8:2-FTCA	2%	3%	17%	13%	11%
M-10:2-FTCA	0%	0%	32%	16%	5%
M-6:2-FTUCA	4%	6%	8%	7%	8%
M-8:2-FTUCA	3%	7%	14%	12%	13%
M-10:2-FTUCA	0%	0%	17%	6%	1%
MPFHxS	32%	43%	24%	20%	23%
MPFOS	29%	30%	31%	15%	24%
M-6:2-FTS	23%	29%	19%	28%	16%
M-N-MeFOSAA	1%	5%	16%	16%	20%
M-N-EtFOSAA	0%	2%	14%	11%	7%
M-N-MeFOSA	2%	2%	6%	3%	4%
M-N-EtFOSA	8%	6%	0%	0%	0%
M-Cl(35)-PFHxPA	3%	3%	14%	11%	9%
M-8:2-PAP	16%	7%	0%	0%	0%
M-8:2-diPAP	2%	1%	0%	0%	0%

Corresponding to the influent samples, C_4-C_8-PFCAs as well as PFTrA were detected in the sludge samples. This is striking as PFBA is considered a very mobile chemical that should not have great tendency to sorb onto sludge as it also does not sorb onto soil during soil passage (Gellrich et al., 2012). Apart from PFCAs, transformation products of fluorotelomer compounds, namely 6:2-FTA, 3:3- to 7:3-acid, 8:2-FTUCA and 6:2-FTUCA were detected. The latter one represents the substance with the highest peak area of all substances under investigation. Since only peak areas are stated, this does not automatically imply the highest concentration for this substance due to very differing response factors in HPLC-ESI-MS/MS for the group of PFASs. Thus, this should be interpreted as a qualitative statement only.

Table 63: Recoveries of isotopically labelled internal standards from sludge samples of WWTP-I1.

Analyte	Recovery

	SLU 1	SLU 3	SLU 5	SLU 7
MPFBA	5%	5%	5%	5%
MPFPeA	3%	3%	6%	5%
MPFHxA	10%	5%	17%	11%
MPFHpA	9%	0%	17%	8%
MPFOA	12%	4%	21%	9%
MPFNA	0%	0%	0%	0%
MPFDA	0%	0%	0%	0%
MPFUnA	0%	0%	0%	0%
MPFDoA	0%	0%	0%	0%
M-6:2-FTA	0%	0%	0%	0%
M-8:2-FTA	0%	0%	0%	0%
M-6:2-FTUA	25%	0%	90%	23%
M-8:2-FTUA	33%	0%	0%	0%
M-10:2-FTUA	0%	0%	0%	0%
MPFHxS	0%	0%	23%	6%
MPFOS	0%	0%	0%	0%
M-6:2-FTS	0%	0%	0%	0%
M-N-MeFOSAA	0%	0%	0%	0%
M-N-EtFOSAA	0%	0%	0%	0%
M-N-MeFOSA	0%	0%	0%	0%
M-N-EtFOSA	0%	0%	0%	0%
M-Cl(35)-PFHxPA	0%	0%	0%	0%
M-8:2-PAP	0%	0%	0%	0%
M-8:2-diPAP	0%	0%	68%	0%

As the results for these three WWTPs indicated poor analytical validity due to low recoveries for internal standards and no additional substances were detected in sludge samples corresponding to influent, effluent and air samples, no further sludge samples were analyzed within the scope of this study. Further tailor-made pretreatment methods need to be established allowing clean-up of sludge extracts thereby circumventing ion suppression in ESI-MS.

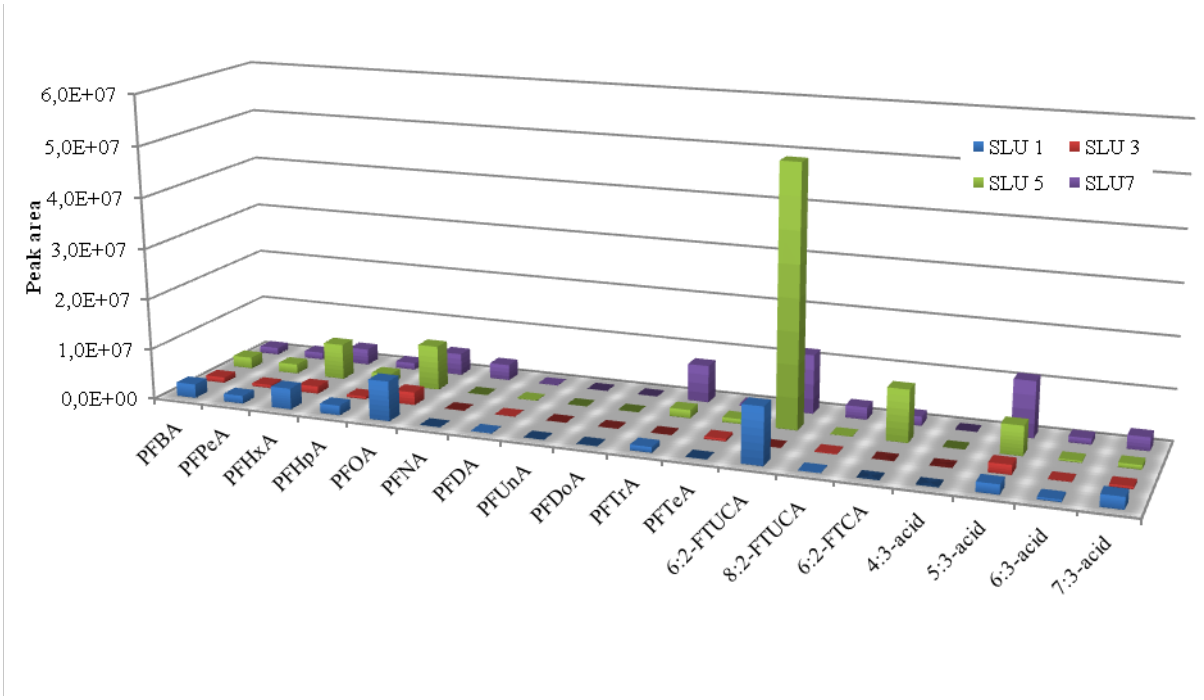


Figure 37: Peak areas of analytes in sludge samples corresponding to influents and effluents 1, 3, 5, and 7 of WWTP-I1.

4.9 Additional WWTP samples of WWTP-I2 and M2

In WWTP-I2, sampling points were amended by return flow from the nitrification tank to the denitrification tank (see Figure 38) as well as the centrate, which is the water separated from digested sludge by centrifugation. This centrate is led back into the primary clarifier.

The results obtained for these two further samples are summarized in Table 96.

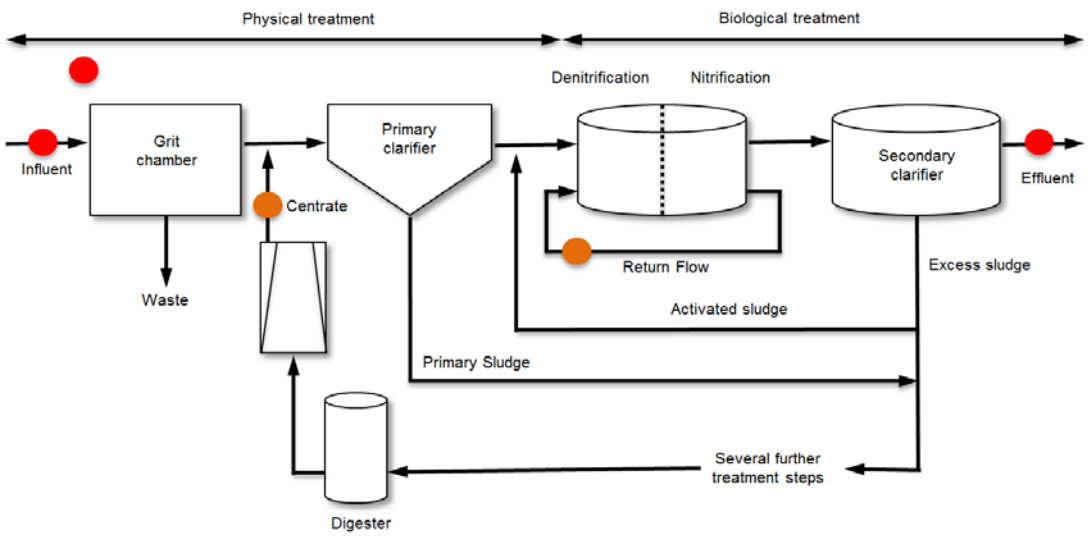


Figure 38: Simplified scheme of WWTP-I2. The red dots mark the regular sampling sites, orange dots indicate further sampling sites.

The results show several very high concentrations. In the return flow, mainly PFCAs as well as PFBS and PFOS were detected in the range of up to 149 ng/L for PFHxA. Interestingly, also 5:3-acid and 7:3-acid were determined, which had probably been formed from 8:2-fluorotelomer-based precursors and may have sorbed onto the sludge.

Table 64: PFAS concentrations in ng/L in the additional samples (return flow and centrate) of WWTP-I2. Only substances with at least one detection are shown.

Analyte	LOD Return Flow	LOQ Return Flow	Return Flow	LOD Centrate	LOQ Centrate	Centrate
	ng/L					
PFPeA	3.9	7.7	60.2	9.0	18.0	177[a]
PFHxA	2.5	12.7	149	5.0	25.1	488[a]
PFHpA	1.3	6.4	34.5	2.8	13.9	64.4
PFOA	0.4	3.6	113	1.2	12.1	228[a]
PFNA	0.4	4.2	7.9	0.6	6.3	8.4
PFDA	0.8	3.8	43.3	1.2	6.2	100
PFUnA	5.1	10.2	2.5	9.8	19.6	n.d.
PFDoA	6.2	12.4	n.d.	12.8	25.6	< LOQ
6:2-FTCA	17.2	86.1	< LOQ	29.3	146	1,208[a]
8:2-FTCA	72.5	145	< LOQ	182	363	601[a]
6:2-FTUCA	2.3	11.3	< LOQ	4.8	24.2	153[a]
8:2-FTUCA	1.5	7.6	< LOQ	3.5	17.5	5.1
4:3-acid	12.7	25.4	n.d.	25.1	50.2	439[a]
5:3-acid	12.7	25.4	60.2	25.1	50.2	23,991[a]
6:3-acid	3.6	7.1	n.d.	12.1	24.3	53.0
7:3-acid	3.6	7.1	9.9	12.1	24.3	778[a]
PFBS	1.3	2.5	53.0	2.5	5.0	22.5
PFOS	0.5	2.4	57.8	0.7	3.7	32.9
6:2-FTS	0.3	0.5	< LOQ	0.4	0.8	n.d.

[a] Concentration exceeding the highest calibration point of 120 ng/L. Concentrations estimated by assumption of linear correlation.

n.d.: not detected; <LOQ: lower than limit of detection

More strikingly, the centrate contained many PFASs at extremely high levels actually exceeding the calibration used by far. Apart from more frequently detected substances, such as PFCAs and PFOS, which also reached relatively high levels (488 ng/L for PFHxA), several biotransformation intermediates were determined in extraordinarily high concentrations, namely 4:3-acid to 7:3-acid as well as 6:2- and 8:2-FTCA and –FTUCA. An extrapolated estimation of 5:3-acid concentration yielded approximately 24 µg/L. These findings corroborate the high levels of 6:2-FTOH and 8:2-FTOH detected in air samples (see Table 45) and partially also in influent samples (see Table 80).

Table 65: PFAS concentrations in ng/L in stack gas water (SGW) samples of WWTP-M2.

Analyte	LOD	LOQ	SGW 1	SGW 2
	ng/L			
PFPeA	1.1	2.2	5.1	6.9
PFHxA	1.1	5.5	<LOQ	6.2
PFHpA	1.2	6.0	<LOQ	<LOQ
PFOA	0.3	3.0	9.7	8.4
PFNA	0.4	4.0	<LOQ	<LOQ
PFDA	0.8	4.0	<LOQ	<LOQ
PFOS	0.7	3.5	15.1	n.d.
6:2-FTS	0.3	0.5	7.4	2.3

<LOQ: lower than limit of detection

The stack gas of WWTP-M2, resulting from the combustion of the thickened sludge was cleaned by using a gas purification before the release into the atmosphere. The water, which was used during this treatment was sampled on two days and analyzed (see Table 65). PFCAs from C_5 to C_{10} were determined in a range up to approximately 21 ng/L stack gas water. PFOA showed the highest concentration of the PFCAs analyzed. PFOS was determined in one sample with a concentration of 15 ng/L and the 6:2-FTS showed a concentration range of 2 to 7 ng/L in both samples analyzed. These results indicate that the stack gas might be a source for the release of PFASs into the environment.

4.10 Screening for non-target PFASs in wastewater treatment plant samples

Non-target screening of samples with high concentration of target PFASs was performed by HPLC-ESI-HRMS (Orbitrap-MS). Application of peak picking using the 'Compound Discoverer' initially led to up to a total of 6,837 peaks in all sample in total (Figure 39). Since fluorine exhibits a significant negative mass defect (monoisotopic mass=18.9984 → mass defect=-0.0016), highly fluorinated substances have a negative total mass defect. For instance, the perfluorooctanoate anion has an exact mass of 413.9664, thus a mass defect of -0.0336. Unknown highly fluorinated substances therefore also exhibit an overall negative mass defect.

Peaks detected were thus filtered by a mass defect filter in the software allowing absolute mass defects from -0.06 to 0. This tremendously decreased the number of peaks to identify.

Identification of homolog series was carried out by applying so-called Kendrick plots (Kendrick, 1963), which are frequently used in HRMS in order to facilitate identification of homolog series in 'petroleomics' (Marshall and Rodgers, 2004). Instead of using the traditionally applied CH_2 repeating unit, CF_2 was assumed a repeating unit; therefore exact masses of ions were transformed to the CF_2 mass scale by multiplying the exact masses of all ions by 49.9968 and dividing by 50. Kendrick mass defects were calculated by subtraction of the nominal mass from the exact Kendrick mass.

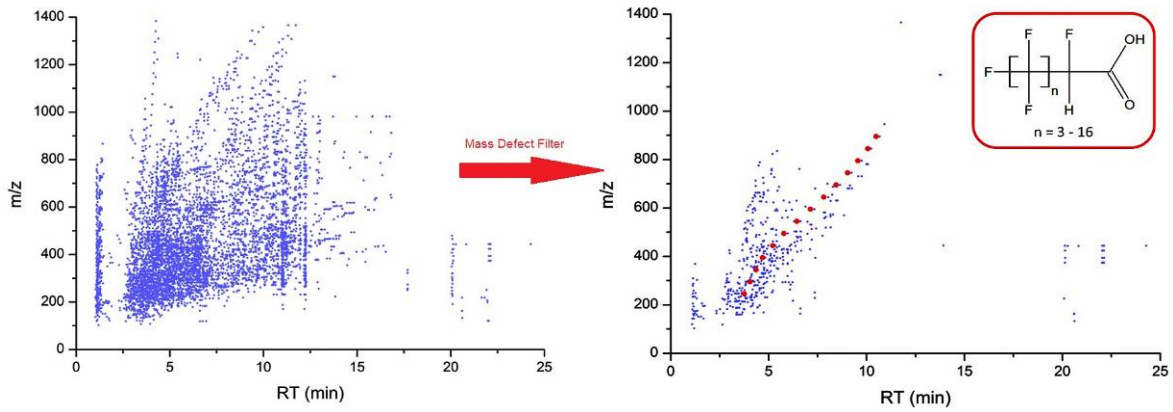


Figure 39: Scatter plot of peaks detected by peak picking (left, 6837 peaks) in all investigated samples and after application of a mass defect filter from -0.3 to 0 (absolute) (right, 475 peaks). Dots representing tentatively assigned 2H-PFCAs are marked in red. RT: retention time.

Several homolog series were detected in the Kendrick plot, however only few of them were assigned tentative structures. The series labeled 'A' in Figure 40 (right) was calculated to comprise peaks that have the composition $C_nHO_2F_{2n-2}^-$ with absolute mass deviation less than 2 ppm. These substances uniformly yielded $[M\text{-}H\text{-}CO_2\text{-}HF]^-$ as the only CID fragment of considerable intensity. Comparison to literature suggests that these substances represent 2H-PFCAs (see Figure 39), which also showed these fragments in a study by Wang et al. (2009), at least the detected 2H-PFOA. It should be pointed out that this structure cannot be proven with the methods applied, thus this is a tentative assignment. Other peaks in the range labeled 'A' in Figure 40 were found have the elemental composition $C_nH_{2n-1}^-$.

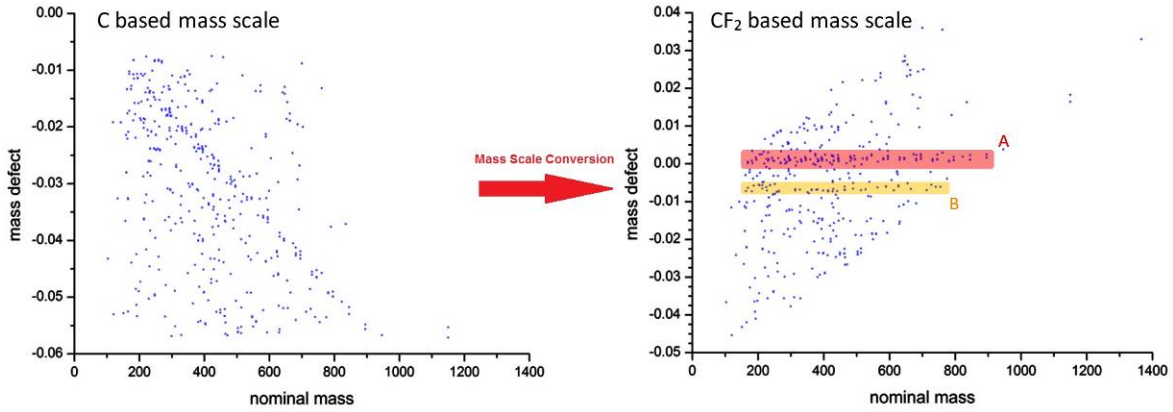


Figure 40: Mass defect plot of peaks detected after mass defect filtering from all samples analyzed by HPLC-ESI-HRMS. Left: C-based mass scale; Right: Kendrick plot using CF_2 as repeating unit. Dots in areas labeled A and B are mainly deprotonated 2H-PFCAs and their in-source CID fragmentation products (see 'major fragments' in Table 66).

However, these are no deprotonated molecules of another set of substances, but in-source fragments of the abovementioned 2H-PFCAs, as was proven by the fact that retention times of the $[M\text{-}H]^-$ ions of 2H-PFCAs and the $C_nH_{2n-1}^-$ ions were always identical for a respective pair of peaks. Apparently, loss of CO_2 and HF from the deprotonated molecule seems to be so energetically favorable that the 2H-PFCAs readily yield this fragment.

The majority of peaks in the range labeled ‘B’ were PFCAs and their in-source fragments $[M\text{-}H\text{-}CO_2]^-$, similarly to the 2H-PFCAs. Additionally to the target PFCAs, perfluoropropionic acid PFPrA was identified by its accurate mass (measured *m/z*: 162.9824, theoretical *m/z*: 162.9824, Δ=-0.07 ppm), its in-source fragment $C_2F_5^-$ (measured *m/z*: 118.9925, theoretical *m/z*: 118.9926, Δ=-0.20 ppm) and its retention behavior. PFPrA was detected in INF 1, EFF1 and EFF 3 of WWTP-I1.

Thus, non-target screening can provide valuable additional information about the spectrum of PFASs in the environment. However, it should be addressed that such analyses are very time-consuming and identification of true unknown substances can be very challenging if no MS/MS data is available. In the case of 2H-PFCAs, comparison to literature helped to confirm the presence of these substances, but otherwise, further techniques, such as preparative chromatography and nuclear magnetic resonance spectroscopy might be necessary for unequivocal identification.

Table 66: Overview of HPLC-HRMS data for substances tentatively assigned as 2H-PFCAs in INF 1, INF 2, INF 3, EFF 1, EFF 3 of WWTP-I1. Measured values are shown for the samples with highest intensity of the individual substance.

Measured *m/z*	Elemental composition	Theoretical *m/z*	← ppm	Major Fragment (deviation)	Suggested compound
244.9853	$C_5HO_2F_8^-$	244.9854	-0.68	180.9896 ($C_4F_7^-$) 1.27 ppm	2H-PFPeA
294.9824	$C_6HO_2F_{10}^-$	298.9822	0.53	230.9862 ($C_5F_9^-$) 0.10 ppm	2H-PFHxA
344.9791	$C_7HO_2F_{12}^-$	344.9790	0.21	280.9826 ($C_6F_{11}^-$) -1.36 ppm	2H-PFHpA
394.9759	$C_8HO_2F_{14}^-$	394.9758	0.03	330.9800 ($C_7F_{13}^-$) 0.64 ppm	2H-PFOA
444.9728	$C_9HO_2F_{16}^-$	444.9727	0.34	380.9768 ($C_8F_{15}^-$) 0.54 ppm	2H-PFNA
494.9693	$C_{10}HO_2F_{18}^-$	494.9695	-0.27	430.9731 ($C_9F_{17}^-$) -0.70 ppm	2H-PFDA
544.9669	$C_{11}HO_2F_{20}^-$	544.9663	1.20	480.9712 ($C_{10}F_{19}^-$) 2.06 ppm	2H-PFUnA
594.9634	$C_{12}HO_2F_{22}^-$	594.9631	0.48	530.9673 ($C_{11}F_{21}^-$) 0.54 ppm	2H-PFDoA
644.9605	$C_{13}HO_2F_{24}^-$	644.9599	0.97	580.9615 ($C_{12}F_{23}^-$) -3.99 ppm	2H-PFTrA
694.9570	$C_{14}HO_2F_{26}^-$	694.9567	0.49	630.9626 ($C_{13}F_{25}^-$) 3.13 ppm	2H-PFTeA
744.9543	$C_{15}FO_2F_{28}^-$	744.9535	1.12	680.9572 ($C_{14}F_{27}^-$) 0.34 ppm	2H-C_{15}-PFCA
794.9509	$C_{16}HO_2F_{30}^-$	794.9503	0.73	730.9556 ($C_{15}F_{29}^-$) 1.86 ppm	2H-C_{16}-PFCA
844.9470	$C_{17}HO_2F_{32}^-$	844.9471	-0.15	low intensity	2H-C_{17}-PFCA
894.9443	$C_{18}HO_2F_{34}^-$	894.9439	0.46	low intensity	2H-C_{18}-PFCA

4.11 Discussion and comparison of WWTP data

As an overview of all analyses performed within the current project, Figure 41 and Figure 42 summarize the analytes detected in different WWTPs sorted by compartment. The results are presented in form of a heatmap visualizing the order of magnitude of the maximum concentration measured in these samples. A quantitative summary of the data is presented in the annex in form of maximum concentrations Table 100.

The concentrations of detected PFCAs in WWTPs varied within five orders of magnitude, where industrial WWTP-I1 should be regarded separately due to extremely high concentrations. Samples of this WWTP featured C_4-C_{13}-PFCAs (with exception of PFHpA, which was not measured in WWTP-I1 as a result of high instrumental blanks as well as PFDoA, which was not detected) were measured in the µg/L range, up to 93 g/L for PFPeA. It should be highlighted that LC-MS analyses in samples from this WWTP were carried out by direct injection as concentrations of many of the substances were so high that no SPE was necessary. Consequently, LODs and LOQs are about two orders of magnitude higher than for other WWTP samples. Thus, substances that were not detected in WWTP-I1 samples may be present at similar concentrations as in other WWTPs, but could not be detected with the method applied.

PFBA was detected only in effluent samples of WWTP-M2 and in influents of WWTP-M3. The latter case is rather hard to explain as PFBA is considered a very mobile chemical that has a high water solubility and virtually no tendency to adsorbed onto particles (Gellrich et al., 2012). Adding to that, concentration in this case was even relatively high at 180 ng/L. The maximum concentration in effluent of WWTP-M2 was 4.2 ng/L. Literature data for the presence of PFBA in European WWTPs is so far scarce. It was measured in two studies, where concentrations up to 15 ng/L (Llorca et al., 2012) and 60 ng/L (Campo et al., 2014) were detected.

PFPeA was one of the most frequently detected substances in this study. It was detected in effluents of all WWTPs, mostly in the range of approximately 10 ng/L, but peaks in WWTP-I2 were up to 254 ng/L. When comparing influent and effluent concentrations (see Figure 43 and Figure 44), it became evident that PFPeA concentrations in effluents were generally higher than in influent samples thus suggesting biotransformation processes of precursors along the wastewater treatment process. The levels measured in most of the samples exhibit similar concentrations as in the literature where typically, concentrations in the range of 10 ng/L are measured (Ahrens et al., 2009) with peak concentrations up to 40 ng/L. Such high levels as in WWTP-I2 have not been measured in European WWTPs. These high concentrations are probably caused by high amounts of 6:2-fluorotelomer based precursors (see Figure 33 as well as Table 43 and Table 45).

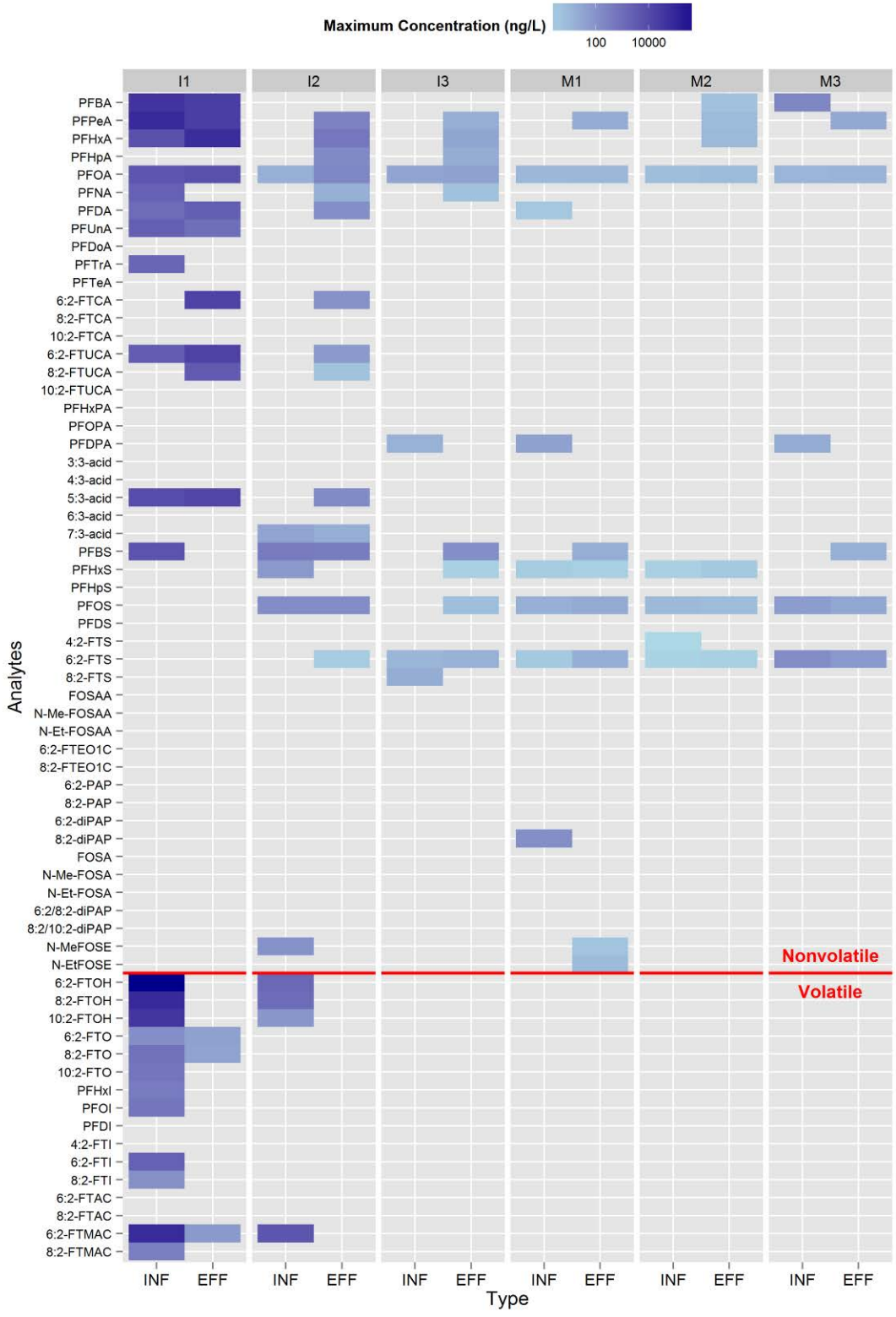


Figure 41: Heatmap of PFAS concentrations in aqueous WWTP samples. Please notice that PFHpA was not measured in WWTP-I1.

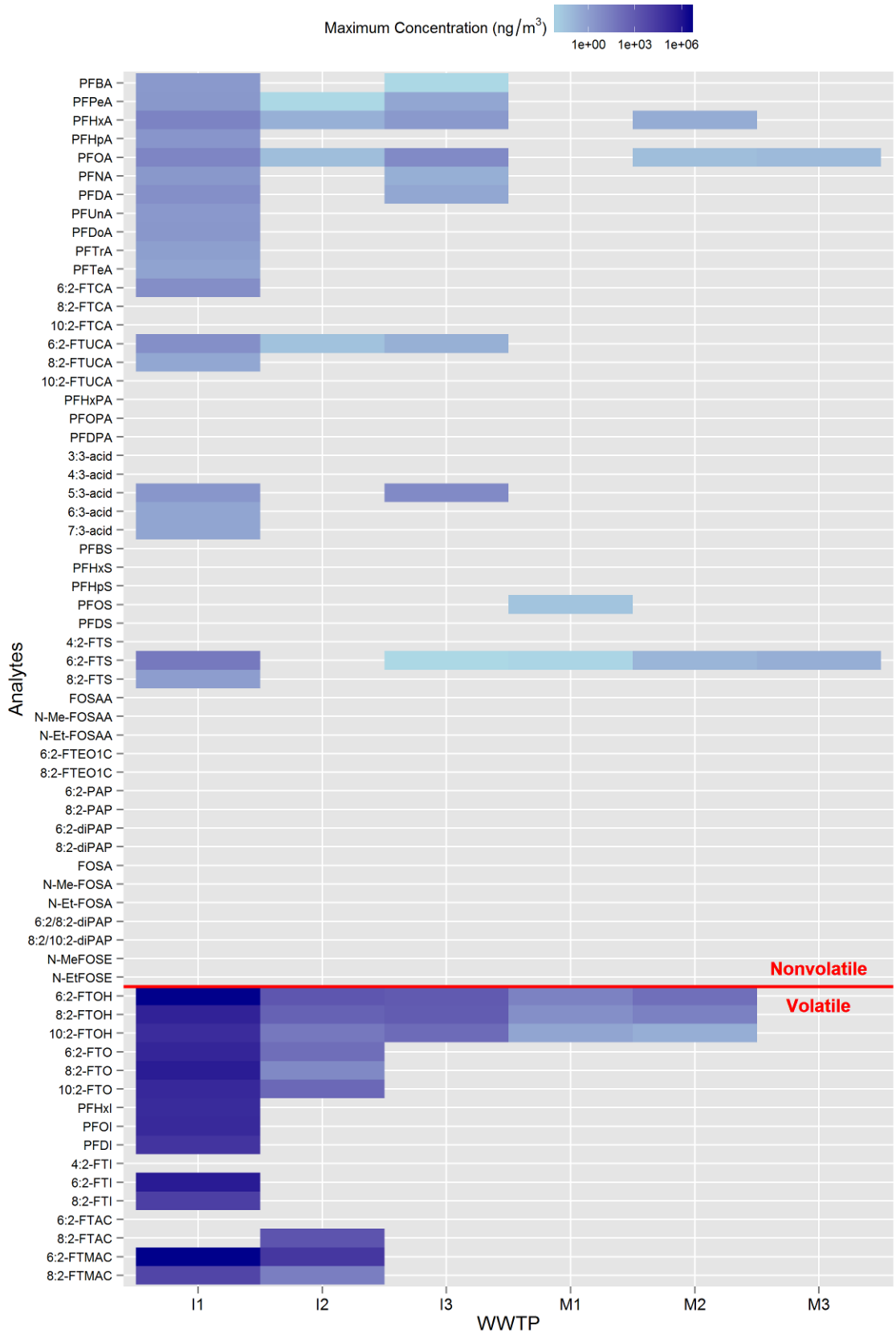


Figure 42: Heatmap of PFAS concentrations in WWTP air samples above the influent.

PFHxA was detected in influent samples of WWTP-I2, but at concentrations <LOQ, as well as in effluent samples of WWTP-I2, I3 and M3. Effluent samples of WWTP-I2 exhibited very high concentrations in the range of several hundred ng/L (up to 512 ng/L), which, again, is caused by high levels of precursors in the influent and air (see Figure 33 as well as Table 43 and Table 45). Concentrations in effluents of WWTP-I3 and M2 were much lower, the highest levels were found in WWTP-I3, where up to 24.9 ng/L were measured. These levels are comparable to literature data, where typically, concentrations <10 ng/L are measured (Huset et al., 2008, Ahrens et al., 2009, Arvaniti et al., 2012). Only in WWTPs outside of Europe, extreme concentrations up to 1.3 µg/L were measured (Kim et al., 2012), which is comparable to concentrations measured for WWTP-I1 herein thus implying strong industrial activities.

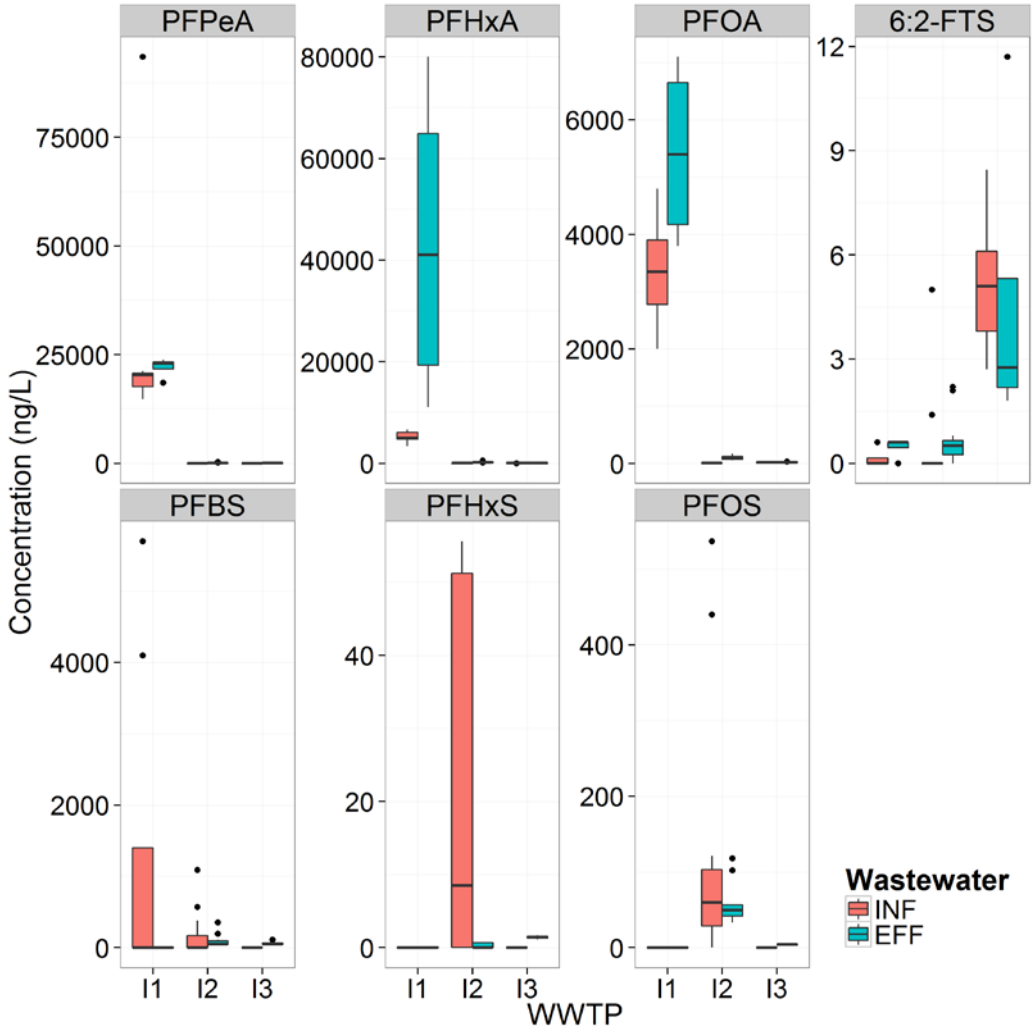


Figure 43: Box plots of influent and effluent concentrations of PFBA, PFPeA, PFHxA and PFBS, PFHxS and PFOS in industrial WWTPs I1-I3.

PFHpA was only detected in effluent samples of WWTP-I2 (several 10 ng/L to 145 ng/L) and I3 (<LOQ-15.6 ng/L). The high levels in WWTP-I2 can be attributed to high levels of precursors measured in influent and air samples (see Table 43 and Table 45). Again, these levels are similar to literature data for European WWTPs, where typically, around 5 ng/L are measured (Huset et al., 2008, Ahrens et al., 2009) with a maximum of 16 ng/L (Arvaniti et al., 2012).

PFOA was the most frequently detected PFAS throughout this study, which confirms literature data stating that it can be detected ubiquitously (Prevedouros et al., 2006, Buck et al., 2011). Concentrations in WWTP-I2 were generally higher than in other WWTPs (except for WWTP-I1) with up to 12.9 ng/L in the influent and up to 176 ng/L in the effluent. Municipal WWTPs showed lower concentrations in the range of 3-10 ng/L (see Figure 44). These observations are comparable to literature data, where generally concentrations up to 20 ng/L are detected (Becker et al., 2008, Ahrens et al., 2009, Arvaniti et al., 2012), but high concentrations up to 500 ng/L may occur in European WWTPs (Stasinakis et al., 2013). All of the WWTPs investigated in this study exhibited higher concentrations in effluents compared with influents which confirming the observations explained in chapter 1.4, where also PFOA concentrations in WWTP effluents were higher than in influents (Sinclair and Kannan, 2006, Kunacheva et al., 2011, Pan et al., 2011, Chen et al., 2012). As already explained above for PFPeA and PFHxA, biotransformation processes are suspected to account for this phenomenon. Except for WWTP-I2, where the concentrations between influent and effluent differ by a factor of about 10, other WWTPs show approximately doubling of the concentration from influent to effluent (see Figure 43 and Figure 44), suggesting that indirect sources of PFOA – as delineated by Prevedouros et al. (2006)– have a significant impact on environmental concentrations of PFOA. The data on precursors generated in this study corroborate this hypothesis as will be shown later in this chapter.

PFNA was detected only sporadically in effluent samples of WWTP-I2 and I3, but always at low concentrations (maximum 12.8 ng/L in WWTP-I2), which is comparable to previous studies, where concentrations were also in this range, if detected at all (Huset et al., 2008, Ahrens et al., 2009). It seems to be formed from precursor substances as well since an increase from influent to effluent was observed for both WWTP-I2 and I3. Possible precursors detected in these WWTPs are 10:2-FTOH which is suspected to yield PFNA as a biotransformation product if the biotransformation pathway is similar to that of 8:2-FTOH (Wang et al., 2009, Frömel and Knepper, 2010a, Liu and Mejia Avendano, 2013).

Longer-chained PFCAs did not occur frequently in the WWTP samples investigated. Except for WWTP-I1, PFDA was only detected in effluent of WWTP-I2 (27.2 ng/L to 102 ng/L and in influent samples of WWTP-M1, but only once and <LOQ (< 3.3 ng/L). In previous studies, PFDA was detected more frequently, but mostly in the low concentration range around 2 ng/L (Huset et al., 2008, Ahrens et al., 2009, Arvaniti et al., 2012).

Beyond PFDA, PFUnA was detected in influent and effluent samples of WWTP-I1 and PFTrA was detected in influent samples of WWTP-I1.

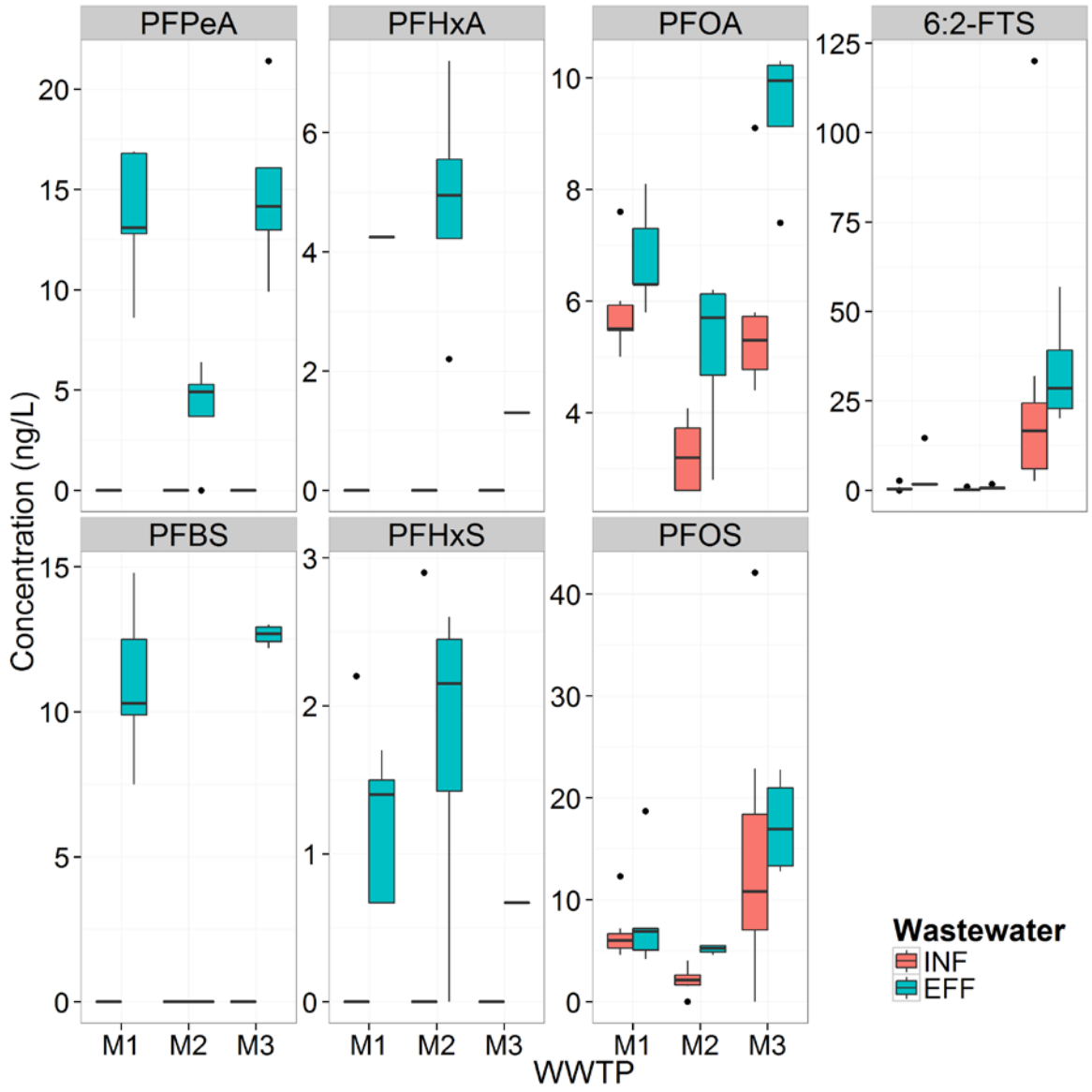


Figure 44: Box plots of influent and effluent concentrations of PFBA, PFPeA, PFHxA and PFBS, PFHxS and PFOS in municipal WWTPs M1-M3. Concentrations of influent of WWTP-M2 were calculated as weighted average of influents A and B (see chapter 2.7.6).

As for PFSAs, PFBS was detected very frequently in this study indicating the shift to short-chained sulfonate chemistry. It was detected in all effluents except for WWTP-I1 and WWTP-M2 and additionally in influent samples of WWTP-I1 and I2. In WWTP-I2, up to 351 ng/L were detected in the effluent; concentrations in municipal WWTPs were significantly lower with concentrations up to 14.8 ng/L. The concentrations detected in this study were similar to levels reported in literature, where concentrations in the range < 10 ng/L were measured (Huset et al., 2008, Ahrens et al., 2009) with peak concentrations of up to 60 ng/L (Campo et al., 2014).

For municipal WWTPs, PFBS levels were higher in effluent samples compared to influent samples of WWTP suggesting formation of PFBS by C_4 sulfonamide-based precursors. However, none of such precursors, e.g. FBSA or N-alkylated FBSA as well as FBSE and its N-alkylated derivatives, were part of the target analyte list of this study. Based on the

results, inclusion of these analytes into further WWTP monitoring campaigns is suggested to investigate whether these substances are responsible for formation of PFBS.

PFHxS was detected in influent samples of WWTP-I2 at concentrations of about 50 ng/L, but not in corresponding effluent samples. Beyond that, PFHxS was detected in effluent samples of WWTP-I3 and in influent and effluent samples of WWTP-M1 and M2, all of which are in the very low ng/L range with maximum concentration of 2.9 ng/L and 2.6 ng/L in influent samples and effluent samples, respectively. However, frequency of detection in influent samples was rare, whereas it was frequently detected in the effluent samples of WWTP-M1 and M2. Thus, formation of PFHxS by biotransformation of perfluorohexane sulfonyl compounds is assumed, but like for C_4-sulfonate chemistry, none of these precursors was investigated in this study.

PFOS is considered ubiquitous in the environment (Buck et al., 2011) and in WWTP samples (Arvaniti and Stasinakis, 2015). In this study, PFOS was not detected in all samples, which can be attributed to the complex matrices under investigation, especially WWTP sludge and influent. It was detected in most of the WWTP samples with exception of WWTP-I1 and in influent samples of WWTP-I3. It should be emphasized that PFOS was measured by direct injection LC-MS/MS in samples from WWTP-I1 due to very high concentrations of other PFASs. Thus, LODs and LOQs for WWTP-I1 were about two orders of magnitude higher than for other WWTPs and one can expect PFOS to be present in these samples as well, although this was not proven. In WWTP-I2, strong fluctuations in concentrations in influent and effluent samples were observed (n.d.-440 ng/L) suggesting point sources by industrial activities, where batch processes are involved. Apart from WWTP-I2, concentrations in other WWTPs were generally in the range of 4-10 ng/L regardless of the compartment. Outliers were measured with 42.1 ng/L (influent of WWTP-M3) and 22.8 ng/L (effluent of WWTP-M3). These concentrations are comparable to literature data where a wide range was observed from the low ng/L range up to several hundred ng/L (Huset et al., 2008). Often, concentrations were in the range of concentrations as found in this study (Ahrens et al., 2009).

As shown in Figure 43 and Figure 44, concentrations in effluent samples were generally higher than in influent samples, except for WWTP-I2 and M1. Thus, PFOS is obviously formed regularly by biotransformation of precursors although this could not be proven for WWTPs other than WWTP-I2 which might be explained by too high LODs and LOQs for FOSEs and FASEs.

6:2-FTS was one of the most frequently detected compounds in WWTPs in this study. It was detected in all WWTPs, although in WWTP-I1, it was only detected in air samples above the influent. Again, this can be reasoned by the analytical method for aqueous samples of this specific WWTP and the resulting high LODs and LOQs. Most of the concentrations measured were in the low ng/L range, both in influents (where it was often not detected) and in effluents. Maximum concentration was observed in sample INF3 of WWTP-M3 with 120 ng/L. This is in accordance with literature data, where it was likewise frequently detected at concentrations in the low ng/L range (Schultz et al., 2006, Huset et al., 2008, Ahrens et al., 2009). Concerning the comparison of corresponding influent and effluent samples, the effluent samples normally contained higher concentrations of 6:2-FTS thus suggesting formation by biotransformation processes. There are several FTS-based precursors, as shown by Place and Field (2012) which might theoretically form 6:2-FTS as an (intermediate) biotransformation product. 6:2-FTS itself

can be further transformed generating PFCAs and the typical fluorotelomer-based biotransformation products (Wang et al., 2011), which might explain the slight decrease in concentration from influent to effluent of WWTP-I3.

The homologs of 6:2-FTS, however, were much less frequently detected. 4:2-FTS was detected once in influent of WWTP-M2 at low concentration (2.7 ng/L) and 8:2-FTS was detected in three of seven influent samples of WWTP-I2 (7.6-15.4 ng/L).

Concentrations of precursors differed significantly between industrial and municipal WWTPs (compare Figure 45 and Figure 46). Again, WWTP-I1 showed abnormally high concentrations, especially of FTOHs and FTMACs, which were present up to the µg/L range in air. Beyond that, very high concentrations of fluorotelomer-based biotransformation products, such as FTCAs, FTUCAs, 5:3-acid and 7:2-acid were detected (µg/L range) Thus, this WWTP should be regarded as a special case.

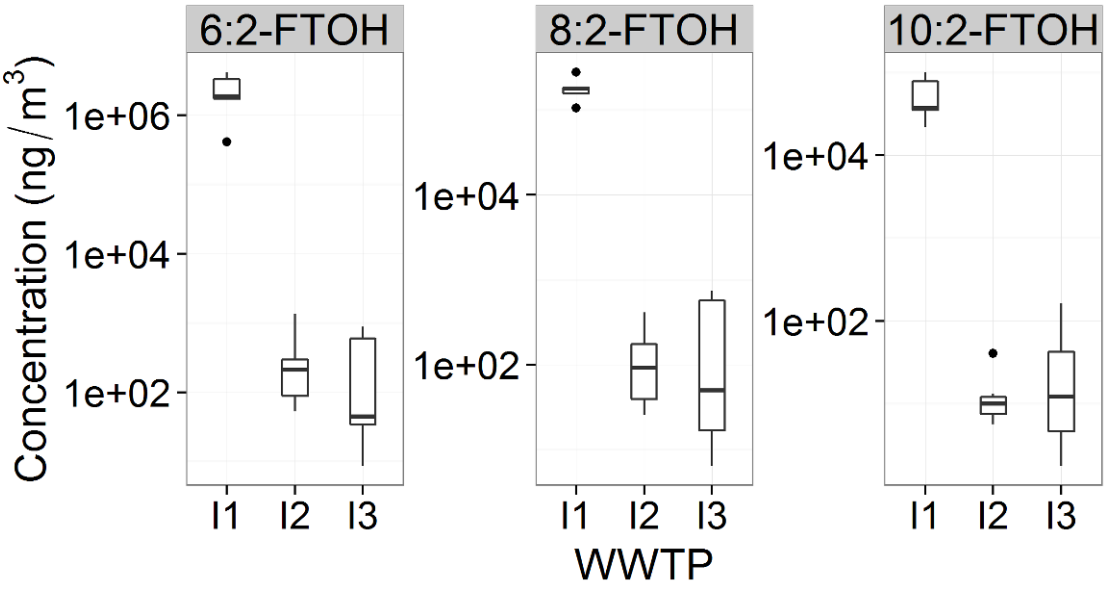


Figure 45: Box plots of air concentrations of 6:2-FTOH, 8:2-FTOH and 10:2-FTOH in municipal WWTPs I1-I3. Please notice the logarithmic scales.

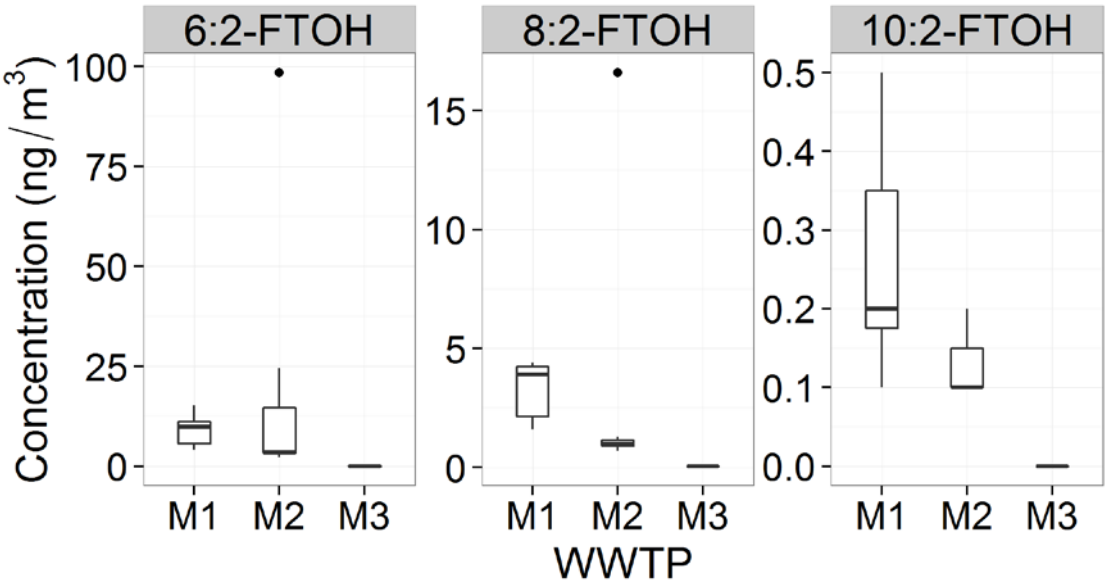


Figure 46: Box plots of air concentrations of 6:2-FTOH, 8:2-FTOH and 10:2-FTOH in municipal WWTPs M1-M3.

All other WWTPs, regardless of the presence of PFAS-using industry, showed FTOH concentrations that were at least three orders of magnitude lower than in air of WWTP-I1. WWTP-I2 also exhibited relatively high concentrations of FTOHs, up to 1.3 µg/m^3 of 6:2-FTOH. Municipal WWTPs showed maximum concentrations of up to 98.5 ng/m^3 (6:2-FTOH), 16.6 ng/m^3 (8:2-FTOH) and 0.5 ng/m^3 (10:2-FTOH) and were thus much lower compared to concentrations in industrial WWTPs, except for WWTP-I3 which exhibited intermediate concentrations between industrial and municipal WWTPs. As to aqueous samples, FTOHs were only detected in WWTP-I1 and I2, which are the WWTPs with air concentrations greater than 1 µg/m^3. It can be concluded that FTOHs can only be detected if very high amounts are present, which is due to their pronounced partitioning from aqueous to air phase (see chapter 3.6).

Furthermore, the data generated in this study showed that volatile substances other than FTOHs were only detected if high concentrations of FTOHs (> 1 µg/m^3) were detected. These were FTMACs (I1/I2), FTACs (I2), FTIs (I1), PFAIs (I1) and FTOs (I1/I2). Throughout this study, 6:2-fluorotelomer compounds were the dominant homologs. It seems that 8:2-homologs and 10:2-homologs were only accompanying compounds to the 6:2-homologs, i.e. synthesis was intended to form 6:2-fluorotelomer compounds and other homologs are synthetic byproducts as the telomerization process cannot yield only one homolog (Lehmler, 2005, Buck et al., 2011). This is in accordance to the shift from 8:2-fluorotelomer chemistry to 6:2-fluorotelomer chemistry.

Coherently to concentrations of fluorotelomer-based precursors, biotransformation products, namely FTCAs, FTUCAs and x:3-acids, were found in samples with high FTOH or FT(M)AC burden. Thus, WWTP-I1 exhibited very high concentrations of these compounds, whereas in WWTP-I2, the concentrations of the detected 6:2-FTCA, 6:2-FTUA, 8:2-FTUCA, 5:3-acid and 7:3-acid were lower with highest concentration occurring for 6:2-FTCA at 178 ng/L. Thus, these biotransformation products can give valuable additional information regarding the presence of fluorotelomer-based precursors, especially in monitoring campaigns which do not involve air sampling.

Table 67 gives the number of PFASs detected in total in the samples taken at the municipal and industrial WWTP. From a total of 65 compounds analyzed, approximately 50% could be quantified in both, the water phase of and the air above the industrial influent, whereas in the corresponding effluents approximately one third could be quantified. The amount of analytes detected in sludge was also about 50%. In municipal WWTP, the amount of quantified PFASs was significantly lower, despite a less complex matrix. Here, between 50 and 57 analytes out of 65 were not detected in any sample, whereas almost no analytes were detected in sludge.

Table 67: Total number of PFAS detected and not detected in WWTP water and air.

	Industrial			Municipal		
	Influent	Effluent	Air	Influent	Effluent	Air
Total number of PFASs detected in at least one sample	32	20	34	9	10	7
Total number of PFASs detected in at least one sample but with concentrations below LOQ	8	2	2	3	5	1
Total number of PFASs that were not detected in any of the sample	25	43	29	53	50	57
Total Compounds Analyzed	65	65	65	65	65	65

Taking into account the spectrum of analytes detected as well as their concentrations, distinct differences between the WWTPs can be observed. Whereas WWTP-I1 is a special case regarding the concentrations of the analytes detected (up to higher µg/L range), WWTP-I2 also exhibits differences to all other investigated WWTPs. The impact of PFAS-using industry is obvious by the spectrum of analytes, such as 6:2-FTMAC, 6:2-FTO and 8:2-FTO, N-MeFOSE and N-EtFOSE, the pronounced fluctuations of PFOS in influent samples (n.d. to 537 ng/L) as well as the high concentrations of biotransformation products, such as FTCAs, FTUCAs and X:3-acids. WWTP-I3, however, does not show such a pattern implying either other PFASs being used or much lower amounts of PFASs used in these industries. The municipal WWTPs investigated in this study show rather uniform patterns and concentrations which are comparable to previous studies. Precursors were detected much less frequently and at very low concentrations. The relevance of different precursor classes and substances will be addressed in chapter 6.

The samples measured additionally to influent, effluent, air and sludge samples gave valuable insight in the fate of several PFASs in WWTPs. These samples were return flow and centrate of WWTP-I2 and stack gas water from WWTP-M2. While the return flow showed the several transformation intermediates such as FTCAs and FTUCAs in concentrations up to 145 ng/L, the concentrations of these substances were even more elevated in the centrate, where up to 24 µg/L were observed for 5:3-acid, and also 8:2-FTCA (363 ng/L) and 7:3-acid (778 ng/L) showed elevated concentrations. These levels can be explained by the biotransformation processes of fluorotelomer-based compounds, which were detected in influent (Table 43) and air (Table 45) samples and their sorption tendency which is very pronounced for x:3-acids (Ning Wang, Dupont, personal communication). Contrarily, the stack gas water of WWTP-M2 exhibited a less broad spectrum of PFASs and low concentrations, thus it did not help to unveil the fate of PFASs in that WWTP.

5 Results and discussion: Determination of PFASs in indoor air and dust samples

5.1 Indoor air

Indoor air samples were taken at four different locations and analyzed for the whole set of PFASs investigated in this study. The results concerning substances that were detected at least once are summarized in Table 68 (complete results shown in Table 98 in the annex).

Indoor Air 1 was collected in a regular household without known sources for PFASs, whereas Indoor Air 2 was taken in an office with carpet laid only a few years ago. Indoor Air 3 was collected in an outdoor clothing storage room. Indoor air 4 was taken in interior of a car. Due to technical failures of the pump system, the Indoor Air 3 as well as the Indoor Air 4 could only be sampled once.

PFOA, 6:2-FTOH and 8:2-FTOH were detected in all samples taken, although PFOA was detected <LOQ in most of the samples. 10:2-FTOH and N-MeFOSE were detected at all locations, but not for every replicate. 6:2-FTS was detected at all locations except for Indoor Air 4.

Highest concentrations were generally observed for 8:2-FTOH (maximum 5.44 ng/m^3 in Indoor Air 4), followed by 6:2-FTOH (2.43 ng/m^3 in Indoor Air 4). Concentrations of 8:2-FTOH were generally higher than for 6:2-FTOH, which suggests that the consumer products used or stored in these rooms were treated with older fluorochemical impregnation, where 8:2-fluorotelomer chemistry was still used.

As mentioned above, also sulfonamide-based chemicals were detected, i.e. both N-MeFOSE and N-EtFOSE. There was no constant ratio between the concentrations of these substances and also no clear tendency that one of the homologs was more prevalent than the other one.

PFASs could be detected in all indoor samples taken, even in rooms of an approximately 150-year-old house with an expected low background concentration. In particular the following analytes were present at low concentrations (< 1 ng/m^3): PFPeA, PFHxA, PFOA, 5:3 acid and 6:2-FTS. Slightly higher concentrations were monitored for the individual FTOH homologs, with 8:2-FTOH exhibiting a maximum concentration of 2.01 ng/m^3. This might result from older furniture or carpets being treated with PFASs-mixtures. Compared to other air samples taken, the findings of N-EtFOSE and N-MeFOSE are to be highlighted. However, these concentrations were a factor of about 100 lower than other data reported in the literature for PFASs exposed rooms, as well as own unpublished data (Table 69).

The rooms were sampled over a period of time of three weeks. The different conditions, like temperature or ventilation of the room on the certain sample days might be a reason for the deviation within the triplicates of Indoor Air 1 and Indoor Air 2.

Table 68: PFASs concentrations in ng/m³ in indoor air samples. Only substances with at least one detection are shown.

Analyte			Indoor Air 1			Indoor Air 2			Indoor Air 3	Indoor Air 4
			Household			Office			Outdoor clothing storage room	Car
	LOD	LOQ	1	2	3	1	2	3		
			ng/m³							
PFPeA	0.002	0.004	0.008	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	0.004	0.021	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	0.002	0.021	<LOQ	<LOQ	<LOQ	<LOQ	0.027	0.023	<LOQ	<LOQ
5:3-acid	0.021	0.042	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.002	0.004	0.007	n.d.	n.d.	<LOQ	n.d.	n.d.	<LOQ	n.d.
6:2-FTOH	0.067	0.200	1.17	0.95	0.48	0.50	1.39	1.53	2.43	0.42
8:2-FTOH	0.033	0.067	2.01	2.27	1.41	0.86	1.94	1.19	5.44	2.04
10:2-FTOH	0.033	0.067	0.58	n.d.	n.d.	0.27	n.d.	n.d.	2.21	0.61
N-MeFOSE	0.007	0.013	n.d.	0.09	0.20	0.09	n.d.	n.d.	0.40	0.08
N-EtFOSE	0.007	0.013	n.d.	0.69	0.27	0.04	n.d.	n.d.	0.05	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

The FTOH concentrations measured in the outdoor clothing stores (Indoor Air 3) prior to the change from C_8 to C_6 chemistry clearly show an almost factor ten higher concentration of the C_8 precursors (see Table 66). During two sample campaigns in an outdoor store in the year 2013 and 2014, the shift from the C_8 to C_6 chemistry was significant (data not shown due to confidentiality).

However, the data from this study also show higher concentrations of 8:2-FTOH compared to the 6:2-FTOH concentrations determined. The production date of the potential sources for FTOH in the ambient air probably influences the ratio of 6:2-FTOH and 8:2-FTOH. If these sources were produced before the industry switched to the C_6 chemistry, the concentration of 8:2-FTOH should be higher compared to the 6:2-FTOH.

Table 69: Comparison of concentrations in Indoor air samples between results from this study and literature data. Concentrations are given in ng/m³.

Location	6:2-FTOH	8:2-FTOH	10:2-FTOH	Reference
	ng/m³			
Indoor air	2.4	3.8	1.4	(Shoeib et al., 2011)
Outdoor clothing store	13-37	79-209	28-54	(Langer et al., 2010)
Outdoor clothing store	n.d.	17-21	7.8-9.4	(Knepper et al., 2014)
Indoor laboratory air	n.d.	1.9	1.2	(Knepper et al., 2014)
Residential indoor air (Indoor Air 1)	0.48-1.17	1.41-2.27	n.d-0.58	This study
Office indoor air (Indoor Air 2)	0.50-1.53	0.86-1.94	n.d.	This study
Outdoor clothing storage room (Indoor Air 3)	2.43	5.44	2.21	This study

n.d.: not detected

5.2 Dust samples

The results of indoor dust analysis are summarized in Table 70 (complete results shown in Table 99 in the annex).

Samples DUST-2 and DUST-3 contained C_5-C_{10}-PFCAs (DUST-3) and C_7-C_{10} (DUST-2), respectively, partially in relatively high concentrations (261 ng/g for sample 3 of DUST-3). Adding to that, PFOS was detected in samples of DUST-2 and DUST-3 as well as 6:2-FTS and 8:2-FTS.

Regarding precursors, the most frequently detected compound was N-EtFOSAA, which was present in all dust samples and in high concentrations of up to 813 ng/g in DUST-1. The detection of this substance is linked to N-EtFOSE detected in indoor air samples

corresponding to DUST-1 and 2. Interestingly, no N-MeFOSAA was detected in any of the sludge samples although its precursor N-MeFOSE was detected in Indoor Air-1 and -2. Also the non-alkylated FOSAA was detected in one sample of DUST-2.

Apart from that, only 6:2-diPAP, 8:2-diPAP and the mixed 6:2/8:2-diPAP and 8:2/10:2-diPAP were detected in one sample of DUST-2 as well as in the three DUST-3 samples.

Comparing to literature, the concentrations measured herein can be considered rather low, especially for DUST-1. Only the high concentrations for N-EtFOSAA are relatively high, but not an exception to concentrations reported in literature where a median of 243.5 ng/g was reported (Kato et al., 2009).

Table 70: PFAS concentrations in ng/g measured in indoor dust samples. Samples for each sampling location were taken at different days within a three weeks period. Only substances with at least one detection are shown.

Analyte			DUST-1			DUST-2			DUST-3		
			Household			Office			Office		
	LOD	LOQ	1	2	3	1	2	3	1	2	3
						ng/g					
PFPeA	2.3	4.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.7	n.d.	n.d.
PFHxA	2.7	13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	22.8	<LOQ	<LOQ
PFHpA	2.2	11	n.d.	n.d.	n.d.	11.2	172	261	51.0	207	225
PFOA	0.9	8.9	n.d.	n.d.	n.d.	58.2	47.4	53.8	190	19.2	18.7
PFNA	0.9	9.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	<LOQ	<LOQ
PFDA	1.7	8.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.6	<LOQ	<LOQ
PFOS	1.0	5.0	n.d.	n.d.	n.d.	57.4	35.2	34.2	44.3	n.d.	n.d.
6:2-FTS	0.7	1.4	n.d.	n.d.	n.d.	27.4	15.1	8.2	15.7	4.0	3.5
8:2-FTS	6.9	14	n.d.	n.d.	n.d.	15.0	15.4	13.6	24.7	<LOQ	<LOQ
FOSAA	59	118	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	18	36	<LOQ	49.5	<LOQ	813	490	765	507	91.7	110
6:2-diPAP	0.7	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.0	8.7
8:2-diPAP	0.7	3.6	n.d.	n.d.	n.d.	7.9	n.d.	n.d.	19.8	11.3	9.9
6:2/8:2-diPAP	-	-	n.d.	detected	detected	detected	detected	detected	detected	detected	detected
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	detected	detected	detected	detected	detected	detected

Detected: detected in the sample, but not quantified due to a lack of authentic standards; n.d.: not detected; <LOQ: lower than limit of detection

6 Conclusion

Several classes of PFASs have been shown to be transformed to PFCAs and PFSAs, as explained in chapter 1.2. These can be divided into fluorotelomer-based PFASs, which yield different transformation products, such as x:3-acids, FTCAs, FTUCAs and, most importantly, PFCAs. The fluorotelomer-based precursors targeted at in this study were FTOHs, FTOs, FTIs, PFAIs, FTOs, FTACs and FTMACs as well as the biotransformation intermediates FTCAs, FTUCAs and x:3-acids. Furthermore, the non-volatile FTSs can be amended to this category.

On the other hand, there are several precursors of PFSAs, all of which share the perfluoroalkane sulfonyl moiety. The target analytes of this group investigated in this study are FOSA and its N-methylated and ethylated derivatives as well as N-Me/EtFOSE and the biotransformation intermediates N-Me/EtFOSAA.

Based on frequency of detection and concentrations, fluorotelomer-based precursors were identified as the more relevant precursor substances compared with PFSA precursors (see Figure 47 and Figure 48). This is mainly due to FTOHs, which were detected in samples from all WWTPs except WWTP-M2 as well as in indoor air samples. In industrial WWTPs (I1 and I2), concentrations > 1 µg/m^3 (WWTP-I2) and even > 1 mg/m^3 (WWTP-I1) were detected in air samples above the influent, allowing even the detection of them in influent samples, which has not been observed to the best of our knowledge. In municipal WWTPs, concentrations were much lower, thus FTOHs were only detected in air samples above the influent and not in the aqueous phase. The concentration in corresponding influent samples was probably below the LODs. In most of the samples, levels of 6:2-FTOH were highest, followed by 8:2-FTOH and 10:2-FTOH. It is recommended to include 4:2-FTOH to monitor shorter chain-length homologs.

The data generated in this study suggests that FTOHs might be accompanying precursors of other precursors as in several cases, concentrations of transformation products such as PFCAs increased from influent to effluent without any of the target precursors detected, at least in the aqueous phase. However, in these cases, FTOHs were detected in air above the influent suggesting that other water-soluble fluorotelomer-based precursors were present in the influent actually causing the increase of concentrations of transformation products. Such precursors might be fluorotelomer-based polymers or oligomers (Russell et al., 2008, Washington et al., 2009, Rankin and Mabury, 2015), but this remains to be proven.

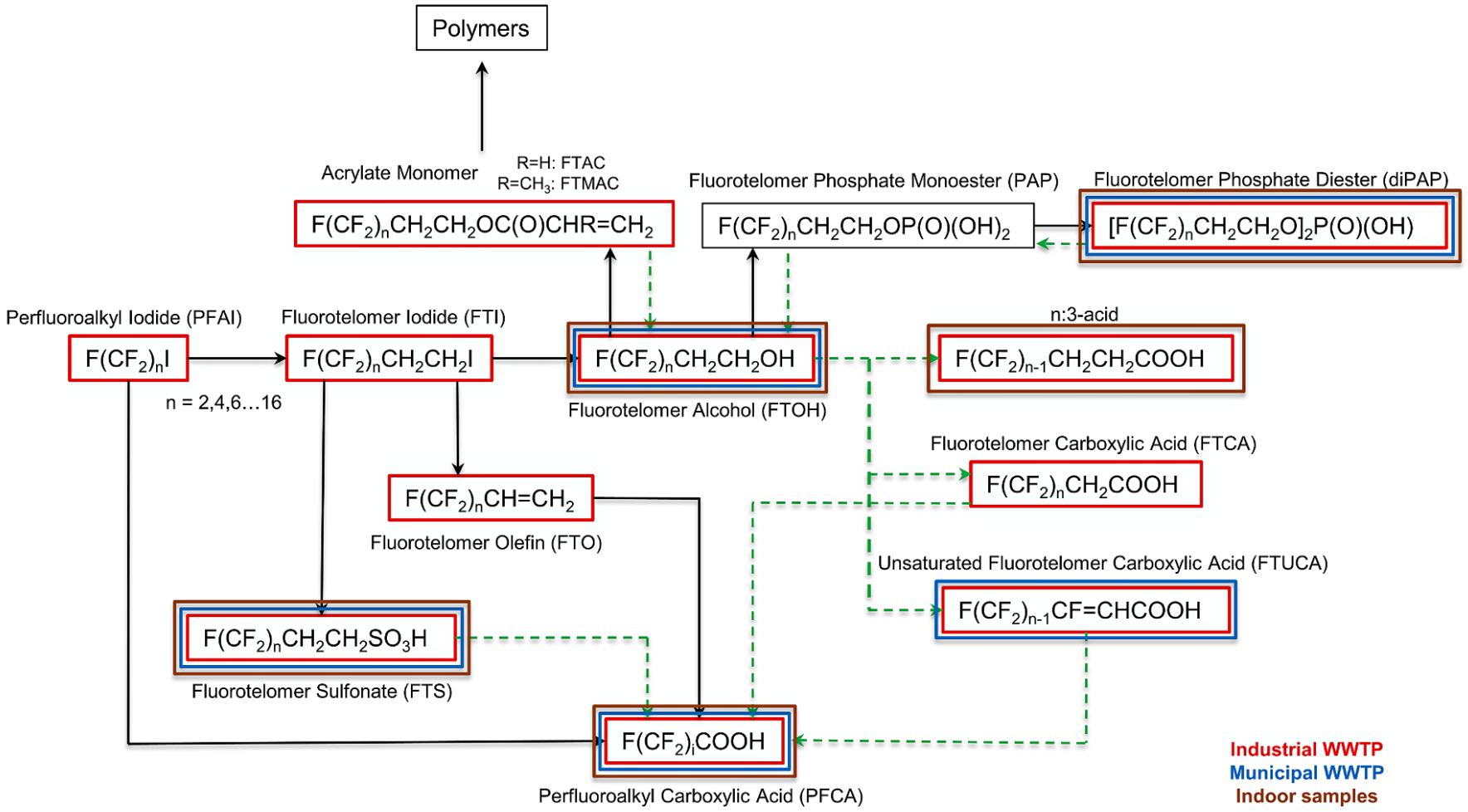


Figure 47: Overview of detected fluorotelomer-based PFASs, including synthetic intermediates and transformation products by sample type (red: industrial WWTP, blue: municipal WWTP, brown: indoor air/dust). Black solid arrows indicate synthetic pathways, green dashed arrows indicate biotransformation processes. Polymers were not measured.

FTMACs were observed in industrial WWTPs-I1 and I2. As explained for FTOHs in WWTP-I1, concentrations of 6:2-FTMAC and 8:2-FTMAC above the influent of WWTP-I1 were so high that they could even be detected in the aqueous phase, unlike for WWTP-I2.

Although mostly detected at low concentrations, 6:2-FTS was detected very frequently, unlike its homologs 8:2-FTS and 4:2-FTOH. 6:2-FTS was shown to occur in both municipal and industrial WWTPs and it is not only a precursor, but also a biotransformation intermediate of FTS derivatives (Backe et al., 2013, Harding-Marjanovic et al., 2015).

Although no marketed products, several of the biotransformation intermediates investigated in this study are considered helpful for the detection of fluorotelomer-based compounds. As explained above, FTOHs are usually only detected in air samples above the influent or in indoor rooms. When sampling of WWTPs is carried out, air sampling is often not performed due to the complexity of the sampling system. In such cases, analysis of the biotransformation intermediates, FTCAs, FTUCAs and x:3-acids, is recommended.

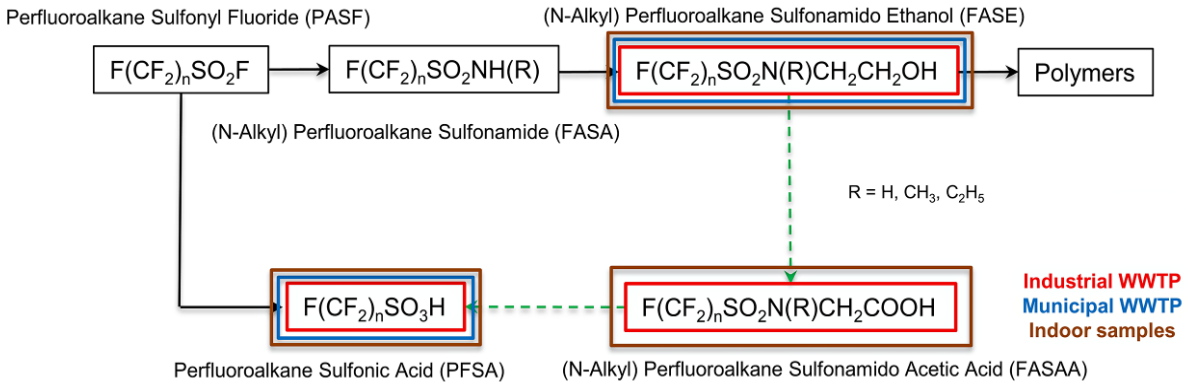


Figure 48: Overview of detected sulfonamide-based PFASs, including synthetic intermediates and transformation products by sample type (red: industrial WWTP, blue: municipal WWTP, brown: indoor air/dust). Black solid arrows indicate synthetic pathways, green dashed arrows indicate biotransformation processes. Perfluoroalkane sulfonyl fluorides and polymers were not measured.

Precursors of PFSAs were detected much less frequently throughout this study. N-MeFOSE and N-EtFOSE were detected at all locations of indoor air sampling as well as in one WWTP fed by PFAS-using industry (WWTP-I2). Similarly to FTOHs, it is recommended to extend the target analyte list by shorter-chained homologs of FASAs and FASEs and their N-Me/Et derivatives in future studies.

Two of the three indoor dust samples contained diPAPs, as well as the effluent of WWTP-M1, thus this compound class seems to be of inferior relevance compared to the abovementioned precursors.

Other precursors were either not detected, detected very sporadically (PFDPA) or only in cases where other precursors showed extremely high concentrations, as was the case for FTOs, PFAIs and FTIs for WWTP-I1, where all other structurally related compound classes (FTOHs, FTMACs) were also detected.

Based on the abovementioned discussion, the precursors measured in this study can be prioritized in the following way:

Priority 1: FTOHs (6:2-FTOH, 8:2-FTOH, 10:2-FTOH); 6:2-FTS

Priority 2: FTMACs (6:2-FTMAC), N-MeFOSE, N-EtFOSE, diPAPs

Priority 3: FTOs, FTIs, PFAIs

where priority 1 substances were detected very frequently and nearly regardless of the sample type, priority 2 substances could be detected frequently, but not in all sample types (e.g. 6:2-FTMAC only detected in industrial WWTPs) and priority 3 substances could be detected only in very special cases, e.g. industrial WWTPs, but if so, these could even be found in very high concentrations.

Interestingly, the set of samples investigated in this study showed trends regarding the perfluoroalkyl chain length depending on the sample type: In WWTP samples, C_6-based precursors were dominating, mainly 6:2-FTOH, but also FTMAC, when detected, whereas in indoor samples, C_8-based precursors were more abundant; at least this holds for FTOHs. Unfortunately, no such statement can be drawn for sulfonamide-based precursors, as no C_6 or C_4-based precursors were included in the target analyses.

As shown in chapter 4.10, further relevant PFASs can be identified by non-target screening using HRMS and MS/MS. Herein, 2H-PFCAs, were identified by sum formula generation via HRMS and confirmation of the MS/MS pattern by comparison to literature data. In case entirely unknown PFASs are detected, identification up to the level of molecular structure may be hard to achieve by MS-based techniques only, mainly because CID fragmentation of PFASs often yields limited number of fragments and thus limited structural information. Therefore, non-target screening can only be used complementarily to target analysis but it can help to bring light into the entirety of PFASs in the water cycle.

7 Acknowledgement

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Last but not least, Robert Buck and Ning Wang from Dupont are acknowledged for providing isotopically labeled 6:2-FTOH and 8:2-FTOH standard as well as the x:3-acid reference materials.

8 Annex

8.1 Questionnaire

1 Questionnaire / Hochschule Fresenius

Questionnaire

General information:

Name of the Waste Water Treatment Plant (WWTP)	
City / country	
Capacity /Layout of population equivalents (EW)	
Actual population equivalents	
Average percentage of municipal and industrial wastewater in the influent a. Specified as proportion of waste load (EW-connected to inhabitants) or b. Based on volume of water	
If possible provide a digital scheme of the WWTP setup.	

Flow rate information:

Provide an estimate of the flow in a typical dry weather day:	
a) Total flow rate [m^3/d]	
b) Minimum flow rate	
c) Maximum flow rate	
Maximum flow on a wet day	
Fraction of external water	

Wastewater sampling device (influent):

Where exactly is the raw influent taken?	
Before fine screen	
After fine screen	
After primary clarifier	
Manufacturer and type of the sampling device	
Are the sampling bottles in the sampler cooled?	
Composite sample extends over how many hours?	
Provide sampling mode:	
Time proportional	
Volume proportional	
Flow proportional	
Manual sampling	

Wastewater sampling device (effluent):

Manufacturer and type of the sampling device	
Are the sampling bottles in the device cooled?	
Composite sample extends over how many hours?	
Provide sampling mode:	
Time proportional	
Volume proportional	
Flow proportional	
Manual sampling	

3 Questionnaire / Hochschule Fresenius

Air sampling, to be filled in by Hochschule Fresenius

Samples should be taken as close as possible to the primary clarifier

Samples were taken…	
…around primary clarifier	
…inside covered primary clarifier	
What is the flow rate of the sampling device? (m^3/h)	
What was the duration of air sampling [h]	

Chemical parameters measured:

What are the standard parameters measured online? E.g. pH, O_2, COD, BOD, temperature, etc.

Please fill in the sheet “Sampling” (next page) for every sample taken.

Have poly- and perfluorinated compounds been determined during sampling campaigns as main goal? If yes, is there any data available?

4 Questionnaire / Hochschule Fresenius

Sampling protocol

WWPT: _____

Date: _____

Further parameters, please complete

Parameter	Flow rate	pH	O_2	TKN	P	COD	BOD	Temp.			
Measured online?											
Units (e.g. mg/L)								°C			
Influent 1											
Influent 2											

pH, Oxygen Content (O_2),Total Kjeldahl Nitrogen (TKN), Total Phosphor (P), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and temperature

8.2 Letter - To whom it may concern

Hochschule Fresenius · Limburger Straße 2 · D-65510 Idstein

HOCHSCHULE FRESENIUS
UNIVERSITY OF APPLIED SCIENCES

To whom it may concern

Prof. Dr. Thomas Knepper
Dean, Department Chemistry & Biology
Director, Institute for Analytical Research

Fon +49 (0)61 26. 93 52 - 68
Fax +49 (0)61 26. 93 52 - 173
weil@hs-fresenius.de

Idstein, 26.09.2012

Cooperation with Hochschule Fresenius, Wastewater sampling

Dear Sir or Madam,

I'm writing you to introduce our sampling campaign, protocol and questionnaire.

The purpose of the sampling campaign carried out among different WWTPs in Germany and the Netherlands is to identify the presence of Perfluorinated compounds and their possible precursors in wastewater. It has been shown that PFOA and PFOS can potentially increase during WWTP passage, and this has often been attributed to precursor compounds. In this project we aim at identifying these compounds in the wastewater.

The protocol will enable you to take the samples in a way that the samples are conserved properly and taken in a homogeneous way across the different WWTPs which are sampled. In order to obtain high quality data and to be able to assess the presence of the organic chemicals of interest in a scientifically valid and robust way, we encourage you to follow the protocol.

The questionnaire will give us valuable information about your WWTP and enables a precise interpretation of the monitoring data. The obtained data from the WWTP and the analysis of the samples will be treated as confidential and published only after acceptance by the WWTP managers.

Could you possibly read carefully the protocol and fill in the questionnaire. Thank you for your help.

Again, we want to thank you for your kind cooperation and allowing the access to the WWTP to the sample and analyse.

Please call if you have any questions.

Best regards,

Thomas Knepper
Prof. Dr., Dean Department Chemistry & Biology

Schulträger: Hochschule Fresenius gemeinnützige GmbH · Limburger Straße 2 · D-65510 Idstein
Geschäftsführer: Dipl.-Kfm. Hermann Kögler · Amtsgericht Wiesbaden · HRB 19044
Nassauische Sparkasse KTO-Nr. 104 000 363 · BLZ 510 500 15
Frankfurter Sparkasse KTO-Nr. 200 386 654 · BLZ 500 502 01
vr Bank Untertaunus eG KTO-Nr. 12 587 708 · BLZ 510 917 00
Finanzamt-Nr. 2222 · Steuer-Nr. 22/870/01919 · USt.-Identifikations-Nr. DE196697659

Qualitätsmanagement ISO 9001:2008

8.3 Sampling protocol

WWTP sampling protocol

Wastewater is collected at the influent and effluent of the wastewater treatment plant. Additionally one air sample is taken in the vicinity of the influent wastewater location.

The actual sampling is performed using the operational equipment of the individual WWTP. Regarding the air sampling, automated samplers can be provided upon request.

Preferentially 24-h composite wastewater samples are automatically collected on each day, and the mode of sampling is **flow proportional**. This allows for a proper overview of the concentrations taking the variability of concentrations into account.

All wastewater samples are taken and stored in **high-density polyethylene (HDPE) containers (supplied by HSF)**. The HDPE bottles will be provided to you in the weeks prior the sampling dates. Containers will have been pre-washed three times with the wastewater itself before sampling (to do by WWTP) and filled to five centimeter below the cap (expansion of the water upon freezing).

After the wastewater samples have been collected from the sampling device, samples have to be frozen immediately at −20°C or spiked with Sodium azide (NaN_3) and refrigerated in a fridge at 4°C to prevent degradation of target compounds.

Depending on the location of the WWTP, samples will be picked up by the Hochschule Fresenius (within 12h after taken out of the freezer) or sent to the Hochschule Fresenius by express delivery. You will be contacted by us to discuss the details.

Please write on the sample bottle the start and stop time when the water was sampled. For example, when a 24 h influent composite sample is taken on the Tuesday the 24th of August from 12h in the afternoon to 24 h in the evening, write down Influent Tuesday (date) 12h to 24h. Appropriate labeling material will be provided.

Please fill in the form "sampling protocol" for every sample to document the flow rate (m3/d) and standard parameters like pH, Oxygen Content (O_2),Total Kjeldahl Nitrogen (TKN), Total Phosphor (P), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and temperature.

8.4 MS/MS methods

Table 71: Compound-independent MS parameters for the AB Sciex 3200 Q Trap HPLC-MS-a method.

Parameter	Value
Curtain Gas (CUR)	25 psi
IonSpray Voltage (IS)	- 4500 V
Temperature (TEM)	600°C
Ion Source Gas (GS1)	35 psi
Ion Source Gas (GS2)	65 psi

Table 72: sMRM instrumental parameters of the developed HPLC-MS-a method; The numbers included in the Analyte ID state the *m/z* of the corresponding product ion.

Analyte ID	Q1 (*m/z*)	Q3 (*m/z*)	t_R [min]	DP [V]	EP [V]	CE [V]	CXP [V]
PFBA 213	213	169	3.9	-13	-5	-16	-4
PFPeA 219	263	219	4.3	-10	-8	-10	-6
PFHxA 269	313	269	4.6	-15	-5	-10	-4
PFHxA 119	313	119	4.6	-15	-5	-28	0
PFHpA 319	363	319	5	-15	-4	-12	-4
PFHpA 169	363	169	5	-15	-4	-22	-4
PFOA 369	413	369	5.4	-15	-5.5	-12	-4
PFOA 169	413	169	5.4	-15	-5.5	-24	-2
PFNA 419	463	419	6	-15	-7.5	-14	-14
PFNA 169	463	169	6	-15	-7.5	-26	-2
PFDA 469	513	469	6.9	-10	-5	-14	-16
PFDA 269	513	269	6.9	-10	-5	-24	-4
PFUnA 519	563	519	7.7	-15	-5.5	-16	-20
PFUnA 319	563	319	7.7	-15	-5.5	-24	-4
PFDoA 569	613	569	8.5	-15	-7	-18	-24
PFDoA 219	613	219	8.5	-15	-7	-26	-6
PFTrA 619	663	619	9.1	-20	-5	-18	-6
PFTrA 169	663	169	9.1	-20	-5	-36	-2
PFTeA 669	713	669	9.8	-15	-8	-18	-10
PFTeA 169	713	169	9.8	-15	-8	-36	0
PFBS 80	299	80	4.3	-55	-5	-48	-2
PFBS 99	299	99	4.3	-55	-5	-38	0
PFHxS 80	399	80	5	-45	-8.5	-70	-2
PFHxS 99	399	99	5	-45	-8.5	-60	-2
PFHpS 80	449	80	5.4	-60	-10.5	-72	-4
PFHpS 99	449	99	5.4	-60	-10.5	-70	0
PFOS 80	499	80	6	-50	-10	-72	-2
PFOS 99	499	99	6	-50	-10	-70	-2

Analyte ID	Q1 (*m/z*)	Q3 (*m/z*)	t_R [min]	DP [V]	EP [V]	CE [V]	CXP [V]
PFDS 80	599	80	7.6	-75	-7	-98	0
PFDS 99	599	99	7.6	-75	-7	-82	0
FOSA 78	498	78	7.3	-45	-10	-58	0
N-Me-FOSA 169	512	169	8.7	-50	-7.5	-34	0
N-Me-FOSA 219	512	219	8.7	-50	-7.5	-32	-4
N-Et-FOSA 169	526	169	9.2	-45	-8.5	-36	-4
N-Et-FOSA 219	526	219	9.2	-45	-8.5	-32	0
MPFBA 172	217	172	3.9	-10	-3	-10	-2
MPFHxA 270	315	270	4.6	-10	-5	-10	-4
MPFHxA 119	315	119	4.6	-10	-5	-26	0
MPFOA 372	417	372	5.4	-15	-6	-12	-4
MPFOA 169	417	169	5.4	-15	-6	-26	0
MPFNA 423	468	423	6	-10	-5.5	-12	-6
MPFNA 219	468	219	6	-10	-5.5	-22	0
MPFDA 470	515	470	6.9	-5	-5	-16	-2
MPFDA 270	515	270	6.9	-5	-5	-24	-4
MPFUnA 520	565	520	7.7	-20	-4	-16	-2
MPFUnA 219	565	219	7.7	-20	-4	-24	-4
MPFDoA 570	615	570	8.5	-15	-6	-14	-6
MPFDoA 169	615	169	8.5	-15	-6	-36	-2
MPFHxS 84	403	84	5	-50	-10.5	-62	0
MPFHxS 103	403	103	5	-50	-10.5	-50	0
MPFOS 80	503	80	6	-55	-7.5	-68	0
MPFOS 99	503	99	6	-55	-7.5	-70	0
M-N-Me-FOSA 169	515	169	8.7	-59	-6	-37	-5
M-N-Me-FOSA 219	515	219	8.7	-59	-6	-37	-3
M-N-Et-FOSA 169	531	169	9.2	-59	-8	-37	-4
M-N-Et-FOSA 219	531	219	9.2	-59	-8	-36	-4
FOSAA 498	556	498	6.7	-56	-6	-40	-6
N-Me-FOSAA 169	570	169	7.3	-47	-7	-40	-1
N-Et-FOSAA 419	584	419	7.8	-35	-9	-26	-10
N-Et-FOSAA 169	584	169	7.8	-35	-9	-42	0
M-N-Me-FOSAA 419	573	419	7.3	-33	-8	-28	-5
M-N-Me-FOSAA 169	573	169	7.3	-33	-8	-41	-1
M-N-Et-FOSAA 419	589	419	7.8	-42	-5	-29	-6
M-N-Et-FOSAA 169	589	169	7.8	-42	-5	-42	-2
8:2-FTCA 393	477	393	6.4	-5	-3	-18	-4
8:2-FTCA 63	477	63	6.4	-5	-3	-22	-8
10:2-FTCA 493	577	493	8.1	-15	-5	-20	-4
10:2-FTCA 63	577	63	8.1	-15	-5	-22	-2
M-6:2-FTCA 294	379	294	5.1	-9	-6	-20	-9
M-6:2-FTCA 64	379	64	5.1	-9	-6	-23	-1
M-8:2-FTCA 394	479	394	6.4	-14	-5	-21	-6
M-8:2-FTCA 64	479	64	6.4	-14	-5	-24	-1
6:2-FTUCA 293	357	293	5.1	-18	-6	-18	-5
8:2-FTUCA 393	457	393	6.3	-24	-5	-17	-4

Analyte ID	Q1 (*m/z*)	Q3 (*m/z*)	t_R [min]	DP [V]	EP [V]	CE [V]	CXP [V]
10:2-FTUCA 493	557	493	8	-22	-7	-21	-11
M-6:2-FTUCA 294	359	294	5.1	-20	-6	-17	-6
M-8:2-FTUCA 394	459	394	6.3	-20	-6	-18	-6
M-10:2-FTUCA 494	559	494	8	-20	-7	-20	-6
4:2 FTS 81	327	81	4.6	-25	-9	-50	-2
4:2 FTS 307	327	307	4.6	-25	-9	-22	-4
6:2-FTS 81	427	81	5.4	-60	-5	-54	-4
M-6:2-FTS 81	429	81	5.4	-55	-4	-56	-2
8:2-FTS 81	527	81	6.8	-50	-9	-66	0
M-Cl(35)-PFHxPA 79	415	79	4.4	-55	-7	-70	-2
M-Cl(37)-PFHxPA 79	417	79	4.4	-55	-7	-70	-2
PFOPA 79	499	79	5	-50	-6	-68	0
PFDPA 79	599	79	6.2	-80	-10	-68	-2
PFHxPA 79	399	79	4.3	-50	-7	-52	-2
6:2-PAP 97	443	97	-	-20	-8	-36	0
6:2-PAP 79	443	79	-	-20	-8	-70	0
8:2-PAP 97	543	97	-	-35	-7	-35	0
8:2-PAP 79	543	79	-	-35	-7	-80	-2
M-8:2-PAP 97	545	97	-	-20	-7	-35	0
M-8:2-PAP 79	545	79	-	-20	-7	-80	-2
6:2-diPAP 97	789	97	9.4	-35	-11	-66	0
6:2-diPAP 79	789	79	9.4	-35	-11	-122	-2
8:2-diPAP 97	989	97	11	-55	-8	-60	0
8:2-diPAP 79	989	79	11	-55	-8	-128	0
M-8:2-diPAP 97	993	97	11	-55	-9	-62	0
M-8:2-diPAP 79	993	79	11	-55	-9	-126	-2
6:2/8:2-diPAP 97	889	97	-	-35	-11	-66	0
6:2/8:2-diPAP 79	889	79	-	-35	-11	-122	-2
8:2/10:2-diPAP 97	1089	97	-	-55	-9	-62	0
8:2/10:2-diPAP 79	1089	79	-	-55	-9	-126	-2
3:3-acid 177	241	177	4.3	-35	-9	-10	-4
3:3-acid 117	241	117	4.3	-35	-9	-46	0
4:3-acid 187	291	187	4.7	-15	-10.5	-22	-2
4:3-acid 167	291	167	4.7	-15	-10.5	-28	-2
5:3-acid 237	341	237	5.1	-20	-7.5	-14	-6
5:3-acid 217	341	217	5.1	-20	-7.5	-26	-4
6:3-acid 287	391	287	5.6	-10	-5.5	-18	-4
6:3-acid 267	391	267	5.6	-10	-5.5	-26	-6
7:3-acid 337	441	337	6.2	-15	-5	-16	-10
7:3-acid 317	441	317	6.2	-15	-5	-32	-10
6:2-FTE01C 75	421	75	5.6	-25	-9	-30	0
6:2-FTE01C 255	421	255	5.6	-25	-9	-44	-4
8:2-FTE01C 75	521	75	7.2	-25	-9	-30	0
8:2-FTE01C 355	521	355	7.2	-25	-9	-44	-4
FOSAA 78	556	78	6.7	-40	-8.5	-76	0
N-Me-FOSAA 219	570	219	7.3	-35	-9	-32	-4

Analyte ID	Q1 (*m/z*)	Q3 (*m/z*)	t_R [min]	DP [V]	EP [V]	CE [V]	CXP [V]
MPFPeA 223	268	223	4.3	-5	-3	-10	-6
MPFHpA 322	367	322	5	-15	-4	-14	-10
MPFHpA 169	367	169	5	-15	-4	-24	0
6:2-FTCA 293	377	293	5.1	-14	-5	-16	-9
6:2-FTCA 243	293	243	5.1	-60	-12	-33	-9

Table 73: Compound-independent MS parameters for the AB Sciex 3200 Q Trap HPLC-MS-n method.

Parameter	Value
Curtain Gas (CUR)	25 psi
IonSpray Voltage (IS)	- 4500 V
Temperature (TEM)	150°C
Ion Source Gas (GS1)	55 psi
Ion Source Gas (GS2)	65psi

Table 74: MRM parameters of the developed HPLC-MS-n method.

Analyte ID	Q1	Q3	DP	EP	CE	CXP
6:2-FTOH	423	59	-2	-3.5	-29	-1
8:2-FTOH	523	59	-2	-3.5	-33	-1
10:2-FTOH	623	59	-2	-3.5	-38	-1
N-MeFOSE	616	59	-10	-6	-42	-1
N-EtFOSE	630	59	-10	-6	-42	-1
M-8:2-FTOH	527	59	-30	-10	-50	-1
M-6:2-FTOH	428	59	-2	-3.5	-29	-1

8.5 GC-MS method

Table 75. Average % residuals in the estimation of concentration using internal standard method (n=5).

Compound	2 pg/μL	5 pg/μL	10 pg/μL	20 pg/μL	40 pg/μL	60 pg/μL
6:2-FTO	-4.6	-4.2	-2.3	1.0	2.5	-1.1
8:2-FTO	-15.1	-4.1	-0.7	2.1	1.9	-1.0
10:2-FTO	-16.4	-3.3	0.7	2.2	0.8	-0.6
PFHxI	17.7	-6.2	-4.1	0.9	1.2	-0.5
PFOI	26.3	16.4	-5.4	-5.8	-0.3	0.8
PFDI	-55.5	2.4	9.2	1.4	0.1	-0.4
4:2 FTI	-15.2	-5.2	2.5	1.6	0.8	-0.5
6:2-FTI	-6.8	-8.7	2.3	2.3	0.2	-0.4
8:2-FTI	8.1	-11.2	1.8	1.3	0.3	-0.3
6:2-FTAC	-20.6	-3.6	0.0	3.0	1.3	-0.8
8:2-FTAC	-10.2	-2.5	-0.1	1.5	0.9	-0.5
6:2-FTMAC	32.2	23.3	-11.0	-6.2	0.3	0.6
8:2-FTMAC	-10.2	-4.8	-1.0	2.5	1.3	-0.8

Table 76: Detailed information for samples from WWTP-M3.

Sample No.	Air											Influent					Effluent					Sludge
	Sampling			AIR-3 (FTOHs)				Air-2 (Other Volatile PFASs)														
	Start	End	Total Time	Flow Controller % (start)	Flow Controller % (end)	Average Flow (L/hr)	V (L) (integration)	Flow Controller % (start)	Flow Controller % (end)	Average Flow (L/hr)	V (L) (integration)	Sampling Start	Sampling End	Time of Collection	T during collection (℃)	pH	Sampling Start	Sampling End	Time of Collection	T during collection (℃)	pH	Time of Collection
1	02.12.2014 13:15	03.12.2014 13:00	23.75	19.8	16.8	55	1304	17.3	-	NA	NA	02.12.2014 08:00	03.12.2014 08:00	03.12.2014 13:00	-	7.51	03.12.2014 08:00	04.12.2014 08:00	04.12.2014 08:15	4.4	7.31	04.12.2014 08:20
2	03.12.2014 13:00	04.12.2014 08:00	19.00	19.0	19.3	57	1092	18.7	18.4	111	2115	03.12.2014 08:00	04.12.2014 08:00	04.12.2014 08:00	2.6	7.56	04.12.2014 08:00	05.12.2014 08:00	05.12.2014 08:15		7.18	05.12.2014 08:30
3	04.12.2014 08:00	05.12.2014 08:20	24.33	19.3	19.3	58	1409	19.0	19.0	114	2774	04.12.2014 08:00	05.12.2014 08:00	05.12.2014 08:20	5.6	7.40	NA	NA	NA	NA	NA	NA
4	10.12.2014 10:30	11.12.2014 08:30	22.00	19.3	19.3	58	1274	19.0	19.0	114	2508	10.12.2014 08:00	11.12.2014 08:00	11.12.2014 08:30	5.0	7.23	11.12.2014 08:00	12.12.2014 08:00	11.12.2014 08:15	4.8	7.20	12.12.2014 08:45
5	11.12.2014 08:30	12.12.2014 08:30	24.00	19.3	19.3	57.9	1390	19.0	19.0	114	2736	11.12.2014 08:00	12.12.2014 08:00	12.12.2014 08:30	4.9	7.49	NA	NA	NA	NA	NA	NA
6	15.12.2014 08:30	16.12.2014 08:30	24.00	19.3	19.3	57.9	1390	19.4	19.0	115	2765	15.12.2014 08:00	16.12.2014 08:00	16.12.2014 08:30	3.8		NA	NA	NA	NA	NA	NA
7	16.12.2014 08:30	17.12.2014 11:00	26.50	19.3	19.3	57.9	1534	19.1	19.1	115	3037	17.12.2014 08:00	17.12.2014 11:00	17.12.2014 11:00	6.3		17.12.2014 08:00	18.12.2014 08:00	18.12.2014 08:30	4.4		18.12.2014 08:30
8	17.12.2014 11:00	18.12.2014 08:00	21.00	19.3	19.3	57.9	1216	19.1	19.0	114	2400	17.12.2014 08:00	18.12.2014 08:00	18.12.2014 08:00	3.6		NA	NA	NA	NA	NA	NA

8.6 Complete result tables

8.6.1 WWTP-I1

Table 77: PFAS concentrations in µg/L in the influent samples of WWTP-I1. Concentrations for PFBS and 10:2-FTOH should be interpreted semiquantitatively due to high recoveries. PFHpA was excluded from the analyte list for this set of results due to abnormally high instrumental background levels.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
						[µg/L]				
PFBA	0.1	0.2	22.5	46.7	13.4	23.8	22.9	9.3	17.3	11.7
PFPeA	0.2	1	21.3	93.5	17.4	20.2	20.4	14.8	20.5	17.7
PFHxA	0.1	0.2	4.8	6.6	3.4	5.1	6.0	4.8	6.2	4.5
PFOA	0.1	0.2	3.4	4.2	2.0	2.1	3.0	3.3	4.8	3.8
PFNA	1.0	2	< LOQ	n.d.	n.d.	n.d.	< LOQ	< LOQ	< LOQ	2.3
PFDA	0.5	1	1.0	< LOQ	n.d.	n.d.	1.1	1.1	<L OQ	< LOQ
PFUnA	0.5	2	2.5	1.5	1.9	1.7	1.9	n.d.	1.9	2.3
PFDoA	1.0	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	0.5	1	1.5	n.d.	n.d.	1.4	1.3	< LOQ	1.5	1.6
PFTeA	0.5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	2.0	10	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
8:2-FTCA	10.0	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	10.0	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	0.1	0.5	2.2	1.7	3.2	0.7	0.9	0.7	1.0	2.1
8:2-FTUCA	0.1	2	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
10:2-FTUCA	1.0	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.5	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	2.0	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	[µg/L]									
PFDPA	10.0	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	10.0	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	0.5	2	n.d.	n.d.	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.
5:3-acid	0.2	1	2	1.9	1.9	2.3	4.5	8.6	7.3	6.3
6:3-acid	1.0	10.0	n.d.	n.d.	< LOQ	n.d.	< LOQ	< LOQ	n.d.	< LOQ
7:3-acid	1.0	10.0	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
PFBS	0.1	0.2	n.d.	5.7	n.d.	4.1	0.5	n.d.	n.d.	n.d.
PFHxS	0.1	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	0.1	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.1	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDS	0.5	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.5	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.2	1.0	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.
8:2-FTS	0.5	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	0.5	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	2.0	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	1.0	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTEO1C	0.5	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTEO1C	10.0	20.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	2.0	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	2.0	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	0.5	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	0.1	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.1	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	[µg/L]									
N-MeFOSA	1.0	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	0.5	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	5	10	986	413	441	691	489	136	71.7	78.9
8:2-FTOH	2	10	76.5	42.9	42.6	95.1	79.4	49.3	31.2	80.3
10:2-FTOH	2	10	32.5	13.3	11.9	42.3	37.5	35.0	10.4	38.5
N-MeFOSE	0.1	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.1	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	0.01	0.03	0.043	0.106	0.018	0.033	0.068	0.041	0.037	n.d.
8:2-FTO	0.01	0.03	0.40	0.15	0.13	0.20	0.70	0.17	0.28	0.06
10:2-FTO	0.01	0.03	0.069	0.077	0.036	0.112	0.584	0.042	0.057	0.058
PFHxI	0.01	0.03	0.22	0.36	<LOQ	0.11	0.20	<LOQ	<LOQ	n.d.
PFOI	0.01	0.03	0.56	0.52	0.076	0.18	0.55	<LOQ	<LOQ	0.072
PFDI	0.01	0.03	<LOQ	<LOQ	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
4:2-FTI	0.01	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	0.01	0.03	2.3	0.89	0.83	1.7	1.81	0.57	0.68	0.78
8:2-FTI	0.01	0.03	0.087	n.d.	0.022	0.070	0.099	0.024	0.018	0.030
6:2-FTAC	0.4	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	0.4	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	0.01	0.03	80	31	22	90	59	5.7	5.3	5.5
8:2-FTMAC	0.01	0.03	0.32	0.058	0.14	0.26	0.13	0.038	n.d.	0.019

n.d.: not detected; <LOQ: lower than limit of detection

Table 78: PFAS concentrations in μg/L in effluent samples of WWTP-I1. PFHpA was excluded from the analyte list for this set of results due to abnormally high instrumental background levels.

Analyte	LOD	LOQ	EFF 1	EFF 3	EFF 5	EFF 7
			[μg/L]			
PFBA	0.1	0.2	21.7	13.9	23.6	15.4
PFPeA	0.2	1	23.8	23.2	22.7	18.5
PFHxA	0.1	0.2	22.1	59.9	80.0	11.1
PFOA	0.1	0.2	3.8	4.3	6.5	7.1
PFNA	1.0	2	< LOQ	< LOQ	< LOQ	< LOQ
PFDA	0.5	1	2.6	1.2	1.1	< LOQ
PFUnA	0.5	2	0.9	n.d.	n.d.	0.6
PFDoA	1.0	2	n.d.	n.d.	n.d.	n.d.
PFTrA	0.5	1	n.d.	n.d.	n.d.	n.d.
PFTeA	0.5	1	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	2.0	10	< LOQ	< LOQ	17.2	< LOQ
8:2-FTCA	10.0	20	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	10.0	20	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	0.1	0.5	2.0	6.1	17.8	1.2
8:2-FTUCA	0.1	2	< LOQ	< LOQ	2.8	3.5
10:2-FTUCA	1.0	10	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.5	2	n.d.	n.d.	n.d.	n.d.
PFOPA	2.0	10	n.d.	n.d.	n.d.	n.d.
PFDPA	10.0	20	n.d.	n.d.	n.d.	n.d.
3:3-acid	10.0	20	n.d.	n.d.	n.d.	n.d.
4:3-acid	0.5	2	n.d.	n.d.	< LOQ	n.d.
5:3-acid	0.2	1	7.0	10.0	14.5	5.0
6:3-acid	1.0	10.0	n.d.	n.d.	n.d.	n.d.
7:3-acid	1.0	10.0	< LOQ	< LOQ	< LOQ	< LOQ
PFBS	0.1	0.2	n.d.	n.d.	n.d.	n.d.
PFHxS	0.1	0.5	n.d.	n.d.	n.d.	n.d.
PFHpS	0.1	1.0	n.d.	n.d.	n.d.	n.d.
PFOS	0.1	1.0	n.d.	n.d.	n.d.	n.d.
PFDS	0.5	1.0	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.5	2.0	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.2	1.0	n.d.	< LOQ	< LOQ	< LOQ
8:2-FTS	0.5	1.0	n.d.	n.d.	n.d.	n.d.
FOSAA	0.5	2.0	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	2.0	10.0	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	1.0	10.0	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	0.5	10.0	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	EFF 1	EFF 3	EFF 5	EFF 7
			[µg/L]			
8:2-FTEO1C	10.0	20.0	n.d.	n.d.	n.d.	n.d.
6:2-PAP	2.0	10.0	n.d.	n.d.	n.d.	n.d.
8:2-PAP	2.0	10.0	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	0.5	10.0	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	0.1	1.0	n.d.	n.d.	n.d.	n.d.
FOSA	0.1	0.2	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	1.0	10	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	0.5	2.0	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	5	10	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	2	10	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	2	10	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	0.1	0.3	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.1	0.3	n.d.	n.d.	n.d.	n.d.
6:2-FTO	0.01	0.03	<LOQ	<LOQ	0.033	<LOQ
8:2-FTO	0.01	0.03	<LOQ	<LOQ	0.030	<LOQ
10:2-FTO	0.01	0.03	n.d.	n.d.	n.d.	n.d.
PFHxI	0.01	0.03	n.d.	n.d.	n.d.	n.d.
PFOI	0.01	0.03	n.d.	n.d.	n.d.	n.d.
PFDI	0.01	0.03	n.d.	n.d.	n.d.	n.d.
4:2-FTI	0.01	0.03	n.d.	n.d.	n.d.	n.d.
6:2-FTI	0.01	0.03	n.d.	n.d.	n.d.	n.d.
8:2-FTI	0.01	0.03	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	0.4	1.2	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	0.4	1.2	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	0.01	0.03	<LOQ	0.032	<LOQ	0.052
8:2-FTMAC	0.01	0.03	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 79: PFASs concentrations in air samples of WWTP-I1. Concentrations for volatile PFASs (FTOHs, FOSE derivatives, FTOs, PFAIs, FTIs and FT(M)ACs are given in mg/m3 due to high conentrations, the results of remaining substances are given in ng/m³.

Analytes	LOD	LOQ	AIR 1	AIR 2	AIR 4	AIR 5	AIR 7
				ng/m³			
PFBA	0.002	0.004	0.9	1.6	1.4	0.9	0.6
PFPeA	0.002	0.004	1.8	1.7	1.4	1.2	1.7
PFHxA	0.004	0.021	10.4	13.8	11.7	8.3	9.8
PFHpA	0.004	0.021	2.2	1.2	0.6	0.7	0.7
PFOA	0.002	0.021	11.0	0.7	4.2	0.4	4.1
PFNA	0.002	0.022	1.3	1.8	0.5	0.5	1.0
PFDA	0.004	0.021	4.4	2.7	0.8	1.1	1.6
PFUnA	0.021	0.042	0.9	1.7	0.5	0.8	0.8
PFDoA	0.021	0.042	1.9	1.8	0.4	1.1	0.6
PFTrA	0.021	0.042	n.d.	0.9	n.d.	0.7	0.3
PFTeA	0.021	0.042	0.6	0.5	n.d.	n.d.	n.d.
6:2-FTCA	0.042	0.208	2.8	3.7	4.5	1.4	0.8
8:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	0.004	0.021	2.9	4.0	2.7	1.3	0.6
8:2-FTUCA	0.004	0.021	0.4	0.3	0.3	0.2	0.3
10:2-FTUCA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	0.021	0.042	1.0	2.1	0.9	0.8	2.1
6:3-acid	0.021	0.042	0.4	0.5	0.3	0.2	0.4
7:3-acid	0.021	0.042	0.4	0.5	0.3	0.3	0.4
PFBS	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.002	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
PFDS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.002	0.004	13.8	20.7	37.9	1.7	18.1
8:2-FTS	0.021	0.042	0.4	0.4	1.0	0.4	0.3
FOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.

Analytes	LOD	LOQ	AIR 1	AIR 2	AIR 4	AIR 5	AIR 7
				ng/m³			
N-EtFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTEO1C	0.104	0.208	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTEO1C	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.
				mg/m³			
6:2-FTOH	0.335	1.00	3.29	4.20	1.73	1.87	0.411
8:2-FTOH	0.165	0.335	0.186	0.283	0.107	0.180	0.158
10:2-FTOH	0.165	0.335	0.078	0.101	0.022	0.037	0.035
N-MeFOSE	0.035	0.065	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.035	0.065	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	0.0004	0.0012	0.12	0.12	0.074	0.042	0.20
8:2-FTO	0.0004	0.0012	0.41	0.13	0.19	0.16	0.48
10:2-FTO	0.0004	0.0012	0.15	0.11	0.059	0.074	0.11
PFHxI	0.0004	0.0012	0.078	0.076	0.12	0.046	0.10
PFOI	0.0004	0.0012	0.14	0.10	0.044	0.021	0.032
PFDI	0.0004	0.0012	0.044	0.033	0.003	0.004	0.005
4:2-FTI	0.0004	0.0012	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	0.0004	0.0012	0.56	0.46	0.22	0.23	0.36
8:2-FTI	0.0004	0.0012	0.011	0.014	0.004	0.006	0.006
6:2-FTAC	0.0004	0.0012	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	0.0004	0.0012	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	0.0004	0.0012	4.40	2.31	0.70	0.87	0.08
8:2-FTMAC	0.0004	0.0012	0.005	0.008	0.002	0.002	0.002

n.d.: not detected; <LOQ: lower than limit of detection

8.6.2 WWTP-I2

Table 80: PFAS concentrations in influent samples of WWTP-I2 in ng/L.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8	INF 9	INF 10	INF 11	INF 12
	ng/L													
PFBA	22.8	45.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	7.0	13.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	7.3	36.3	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	2.3	11.6	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d.	n.d.	< LOQ	< LOQ	< LOQ	< LOQ
PFOA	0.8	7.7	12.5	10.9	12.8	11.3	7.7	12.9	7.8	< LOQ	8.3	10.4	< LOQ	8.3
PFNA	0.8	8.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	2.9	14.6	n.d.	n.d.	n.d.	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	45.2	90.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	83.5	167	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	83.5	167	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	83.5	167	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	26.5	133	< LOQ	n.d.	< LOQ	n.d.	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	157	315	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	315	631	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	4.1	20.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	3.4	16.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	103	206	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.6	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	1.1	5.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	5.7	11.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8	INF 9	INF 10	INF 11	INF 12
	ng/L													
3:3-acid	363	725	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	36.3	72.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	36.3	72.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	7.7	15.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	7.7	15.3	n.d.	n.d.	n.d.	n.d.	18.4	26.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	3.6	7.3	569[a]	n.d.	1089[a]	n.d.	97.0	n.d.	n.d.	n.d.	381	91.3	n.d.	n.d.
PFHxS	0.3	3.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	55.6	17.0	51.6	53.7	50.7	51.1
PFHpS	1.5	7.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.7	3.7	440[a]	96.9	537[a]	58.2	74.0	46.3	14.4	n.d.	121	61.0	31.1	21.2
PFDS	9.0	45.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.7	3.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.4	0.7	5.0	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTS	3.7	7.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	56.8	114	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	56.8	114	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	91.2	182	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTEO1C	38.4	76.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTEO1C	29.3	146	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	13.4	66.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	13.4	66.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	14.2	70.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	14.2	70.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	3.9	19.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	19.4	38.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8	INF 9	INF 10	INF 11	INF 12
	ng/L													
N-EtFOSA	17.7	35.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	20.7	62.1	5,727[b]	1,360	18,519[b]	n.d.	2,886[b]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	11.9	22.9	451	n.d.	n.d.	456	n.d.	n.d.	n.d.	n.d.	1,064	539	n.d.	n.d.
10:2-FTOH	11.9	22.9	n.d.	n.d.	n.d.	44.2	n.d.	n.d.	n.d.	n.d.	63.2	61.6	n.d.	n.d.
N-MeFOSE	2.4	4.6	46.6	48.2	65.6	53.0	40.6	56.7	47.1	50.8	44.2	50.1	n.d.	86.6
N-EtFOSE	2.4	4.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10.0	30.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	10.0	30.0	n.a.	n.a.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
10:2-FTO	10.0	30.0	n.a.	n.a.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	10.0	30.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	10.0	30.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	10.0	30.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	10.0	30.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	10.0	30.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	10.0	30.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10.0	30.0	n.a.	n.a.	2,710	300	4,610	960	410	230	890	330	n.d.	n.d.
8:2-FTMAC	10.0	30.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Concentration exceeding the highest calibration point of 240 ng/L. Concentrations estimated by assumption of linear correlation.

[b] Concentration exceeding the highest calibration point of 2500 ng/L. Concentrations estimated by assumption of linear correlation.

n.a.: not analyzed; n.d.: not detected; <LOQ: lower than limit of detection

Table 81: PFAS concentrations in ng/L in the effluent samples of WWTP-I2. Effluent sample corresponding to INF 3 was not taken.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 4	EFF 5	EFF 6	EFF 7	EFF 8	EFF 9	EFF 10	EFF 11	EFF 12
							ng/L						
PFBA	4.3	8.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	2.3	4.5	254[a]	166[a]	97.2	78.1	108	79.3	78.2	86.7	83.3	78.0	51.4
PFHxA	1.4	7.0	512[a]	436[a]	220[a]	211[a]	200[a]	211[a]	235[a]	196[a]	161[a]	143[a]	103
PFHpA	0.7	3.5	145[a]	104	39.6	36.8	38.5	42.4	39.2	44.2	36.3	29.7	21.9
PFOA	0.2	1.8	176[a]	127[a]	70.5	59.8	66.0	79.5	97.0	122[a]	132[a]	113	92.8
PFNA	0.2	2.0	12.8	9.0	5.2	5.4	5.2	5.5	6.9	7.3	6.5	5.8	4.7
PFDA	0.4	2.0	102	65.3	37.7	35.7	33.1	36.3	39.4	39.4	34.0	34.8	27.2
PFUnA	2.8	5.7	< LOQ	< LOQ	n.d.	n.d.	< LOQ	< LOQ	n.d.	n.d.	< LOQ	< LOQ	n.d.
PFDoA	3.4	6.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	3.4	6.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	3.4	6.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	10.0	50.1	178[a]	< LOQ	88.3	< LOQ	n.d.	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	33.8	67.5	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	41.1	82.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	1.2	6.2	33.3	25.0	51.2	20.2	< LOQ	6.7	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
8:2-FTUCA	0.8	3.8	n.d.	n.d.	1.1	0.6	n.d.	3.8	3.5	2.2	1.9	1.1	0.9
10:2-FTUCA	4.3	8.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.1	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	0.3	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	1.3	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	69.6	139	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	7.0	13.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	7.0	13.9	133[a]	79.0	42.7	37.4	37.8	49.1	55.3	49.1	48.4	47.3	32.1

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 4	EFF 5	EFF 6	EFF 7	EFF 8	EFF 9	EFF 10	EFF 11	EFF 12
							ng/L						
6:3-acid	1.8	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	1.8	3.6	14.3	9.0	4.4	4.5	3.9	5.5	5.5	6.1	7.4	5.6	5.2
PFBS	0.7	1.4	351[a]	194[a]	53.3	44.4	38.9	85.8	108.1	77.8	53.1	51.5	30.4
PFHxS	0.1	1.3	n.d.	n.d.	< LOQ	n.d.	< LOQ	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.
PFHpS	0.4	1.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.3	1.4	118	102	57.0	49.6	42.6	55.7	56.0	48.1	40.9	39.1	33.4
PFDS	0.6	2.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.3	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.1	0.3	2.2	2.1	0.47	0.5	0.5	n.d.	0.8	0.5	0.3	< LOQ	< LOQ
8:2-FTS	1.3	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	129	258	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	4.9	9.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	4.9	9.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	9.1	18.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	4.0	20.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	2.5	12.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	2.5	12.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	12.5	62.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	12.5	62.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.6	2.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-Me-FOSA	14.1	70.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-Et-FOSA	70.4	141	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 4	EFF 5	EFF 6	EFF 7	EFF 8	EFF 9	EFF 10	EFF 11	EFF 12
							ng/L						
6:2-FTOH	6.4	19.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	4.1	7.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	4.1	7.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	0.8	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.8	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
8:2-FTO	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
10:2-FTO	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
PFHxI	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
PFOI	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
PFDI	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
4:2-FTI	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
6:2-FTI	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
8:2-FTI	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
6:2-FTAC	400	1,200	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
8:2-FTAC	400	1,200	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
6:2-FTMAC	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.
8:2-FTMAC	10.0	30.0	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	n.d.	n.d.	n.a.

[a] Concentration exceeding the highest calibration point of 120 ng/L. Concentrations estimated by assumption of linear correlation. n.a.: not analyzed; n.d.: not detected; <LOQ: lower than limit of detection

Table 82: PFAS concentrations in ng/m³ in the air samples of the influent of WWTP-I2.

Analyte	LOD	LOQ	AIR 4	AIR 5	AIR 6*	AIR 7*	AIR 8	AIR 9	AIR 10	AIR 11	AIR 12
						ng/m³					
PFBA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFPeA	0.002	0.004	0.004	0.004	< LOQ	< LOQ	0.004	n.d.	0.004	n.a.	n.a.
PFHxA	0.004	0.021	0.083	0.167	0.042	0.025	< LOQ	< LOQ	0.046	n.a.	n.a.
PFHpA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFOA	0.002	0.021	0.023	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.043	n.a.	n.a.
PFNA	0.002	0.022	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFDA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFUnA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFDoA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFTrA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFTeA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTCA	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
10:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTUCA	0.004	0.021	< LOQ	0.030	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.a.	n.a.
8:2-FTUCA	0.004	0.021	< LOQ	n.d.	n.d.	< LOQ	< LOQ	< LOQ	< LOQ	n.a.	n.a.
10:2-FTUCA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFHxPA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFOPA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFDPA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
3:3-acid	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
4:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
5:3-acid	0.021	0.042	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.a.	n.a.

Analyte	LOD	LOQ	AIR 4	AIR 5	AIR 6*	AIR 7*	AIR 8	AIR 9	AIR 10	AIR 11	AIR 12
						ng/m³					
6:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
7:3-acid	0.021	0.042	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFBS	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFHxS	0.002	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFHpS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFOS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFDS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
4:2-FTS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTS	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-FTS	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
FOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
N-Me-FOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
N-Et-FOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTE01C	0.104	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-FTE01C	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
FOSA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
N-Me-FOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
N-Et-FOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.

Analyte	LOD	LOQ	AIR 4	AIR 5	AIR 6*	AIR 7*	AIR 8	AIR 9	AIR 10	AIR 11	AIR 12
						ng/m³					
6:2-FTOH	0.067	0.200	360	1349	247	52.5	55.7	139	210	n.a.	n.a.
8:2-FTOH	0.033	0.067	173	91.6	52.8	25.3	28.8	172	414	n.a.	n.a.
10:2-FTOH	0.033	0.067	13.2	11.1	8.3	5.7	6.8	10.1	40.4	n.a.	n.a.
N-MeFOSE	0.007	0.013	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
N-EtFOSE	0.007	0.013	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTO	1.0	3.0	n.d.	n.d.	115		9.5	6.7	14.6	6.1	2.7
8:2-FTO	1.0	3.0	n.d.	n.d.	7.4		2.9	<LOQ	6.6	6.5	<LOQ
10:2-FTO	1.0	3.0	n.d.	215	31.6		6.4	12.3	56.7	37.8	10.7
PFHxI	1.0	3.0	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	1.0	3.0	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	1.0	3.0	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	1.0	3.0	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	1.0	3.0	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	1.0	3.0	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	40.0	120	<LOQ	n.d.	n.d.		n.d.	<LOQ	<LOQ	<LOQ	<LOQ
8:2-FTAC	40.0	120	n.d.	n.d.	n.d.		n.d.	645	1,603	329	163
6:2-FTMAC	1.0	3.0	1,370	33,101	2,342		369	471	1,871	1,196	854
8:2-FTMAC	1.0	3.0	n.d.	22.3	n.d.		n.d.	n.d.	7.2	n.d.	n.d.

*Cartridges for Air-2 sampling method were not changed, therefore combined concentration for AIR 6 and AIR 7 are provided

n.a.: not analyzed; n.d.: not detected; <LOQ: lower than limit of detection

8.6.3 WWTP-I3

Table 83: PFAS concentrations in ng/L in influent samples of WWTP-I3.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7
					ng/L				
PFBA	10.8	21.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	5.8	11.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	3.5	17.5	n.d.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHpA	2.3	11.5	n.d.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	0.7	7.1	24.4	26.4	21.2	14.4	15.4	17.2	13.0
PFNA	0.7	7.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	1.3	6.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	6.4	12.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	8.4	16.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	8.4	16.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	8.4	16.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	48.1	240	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	134	268	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	215	429	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	4.6	23.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	2.9	14.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	12.2	24.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.3	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	0.7	3.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	3.4	6.8	11.9	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	175	350	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	17.5	35.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	17.5	35.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	7.1	14.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	7.1	14.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	1.7	3.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.2	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	1.4	7.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.5	2.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDS	1.3	6.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.7	3.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.3	0.7	6.5	5.7	5.1	4.4	8.45	2.7	3.2
8:2-FTS	3.3	6.6	15.4	8.2	n.d.	7.6	n.d.	n.d.	n.d.
FOSAA	6.5	13.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	6.5	13.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7
					ng/L				
N-EtFOSAA	6.4	12.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTEO1C	35.4	70.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTEO1C	13.2	65.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	1.8	9.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	1.8	9.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	19.2	95.8	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	19.2	95.8	<LOQ	<LOQ	<LOQ	<LOQ	n.d.	n.d.	n.d.
FOSA	4.7	23.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	23.3	46.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	18.9	37.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	11.2	33.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	20.9	40.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	20.9	40.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	2.1	8.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	2.1	8.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	10	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 84: Concentrations of PFASs determined in effluent samples of WWTP-I3.

Analyte	LOD	LOQ	EFF 1	EFF 3	EFF 5	EFF 6
			ng/L			
PFBA	5.4	10.8	n.d.	n.d.	n.d.	n.d.
PFPeA	2.9	5.8	12.2	14.3	14.7	11.0
PFHxA	1.7	8.7	14.6	24.9	23.0	16.6
PFHpA	1.1	5.7	15.6	7.7	<LOQ	<LOQ
PFOA	0.4	3.5	30.8	21.6	20.2	17.7
PFNA	0.4	3.8	<LOQ	4.1	<LOQ	4.2
PFDA	0.7	3.3	<LOQ	<LOQ	<LOQ	<LOQ
PFUnA	3.2	6.4	n.d.	n.d.	n.d.	n.d.
PFDoA	4.2	8.4	n.d.	n.d.	n.d.	n.d.
PFTrA	4.2	8.4	n.d.	n.d.	n.d.	n.d.
PFTeA	4.2	8.4	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	24.0	120	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	67.0	134	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	107	215	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	2.3	11.5	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	1.5	7.3	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	6.1	12.2	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.2	0.3	n.d.	n.d.	n.d.	n.d.
PFOPA	0.3	1.7	n.d.	n.d.	n.d.	n.d.
PFDPA	1.7	3.4	n.d.	n.d.	n.d.	n.d.
3:3-acid	87.4	175	n.d.	n.d.	n.d.	n.d.
4:3-acid	8.7	17.5	n.d.	n.d.	n.d.	n.d.
5:3-acid	8.7	17.5	n.d.	n.d.	n.d.	n.d.
6:3-acid	3.5	7.1	n.d.	n.d.	n.d.	n.d.
7:3-acid	3.5	7.1	n.d.	n.d.	n.d.	n.d.
PFBS	0.9	1.7	110	48.2	44.5	53.7
PFHxS	0.1	1.0	1.5	1.7	1.4	1.1
PFHpS	0.7	3.5	n.d.	n.d.	n.d.	n.d.
PFOS	0.3	1.3	5.0	4.2	4.1	3.3
PFDS	0.6	3.2	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.3	1.6	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.2	0.3	11.7	3.2	1.8	2.3
8:2-FTS	1.6	3.3	n.d.	n.d.	n.d.	n.d.
FOSAA	3.3	6.5	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	3.3	6.5	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	3.2	6.4	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	17.7	35.4	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	EFF 1	EFF 3	EFF 5	EFF 6
	ng/L					
8:2-FTEO1C	6.6	33.0	n.d.	n.d.	n.d.	n.d.
6:2-PAP	0.9	4.6	n.d.	n.d.	n.d.	n.d.
8:2-PAP	0.9	4.6	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	9.6	47.9	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	9.6	47.9	n.d.	n.d.	n.d.	n.d.
FOSA	1.2	6.1	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	6.1	12.1	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	7.8	15.7	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	3.0	9.0	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	2.8	5.4	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	2.8	5.4	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	0.3	1.1	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.3	1.1	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10	30	n.d.	n.d.	n.d.	n.d.
8:2-FTO	10	30	n.d.	n.d.	n.d.	n.d.
10:2-FTO	10	30	n.d.	n.d.	n.d.	n.d.
PFHxI	10	30	n.d.	n.d.	n.d.	n.d.
PFOI	10	30	n.d.	n.d.	n.d.	n.d.
PFDI	10	30	n.d.	n.d.	n.d.	n.d.
4:2-FTI	10	30	n.d.	n.d.	n.d.	n.d.
6:2-FTI	10	30	n.d.	n.d.	n.d.	n.d.
8:2-FTI	10	30	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10	30	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	10	30	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 85: PFAS concentrations in ng/m³ in air samples above influent of WWTP-I3.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7
					ng/m³				
PFBA	0.002	0.004	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.
PFPeA	0.002	0.004	n.d.	n.d.	0.047	0.004	0.45	n.d.	n.d.
PFHxA	0.004	0.021	n.d.	n.d.	n.d.	0.028	1.57	n.d.	n.d.
PFHpA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	0.002	0.021	4.86	6.54	0.48	0.038	3.90	0.34	0.47
PFNA	0.002	0.022	n.d.	0.19	n.d.	<LOQ	n.d.	n.d.	n.d.
PFDA	0.004	0.021	n.d.	0.39	n.d.	<LOQ	n.d.	n.d.	n.d.
PFUnA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	0.042	0.208	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
8:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	<LOQ	0.18	n.d.	n.d.
8:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7
					ng/m³				
5:3-acid	0.021	0.042	5.43	6.64	0.31	<LOQ	0.05	0.17	n.d.
6:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.002	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.004	0.021	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
PFDS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.002	0.004	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.
8:2-FTS	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTEO1C	0.104	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTEO1C	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7
					ng/m³				
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	0.067	0.200	665	883	34.5	32.8	528	8.7	44.8
8:2-FTOH	0.033	0.067	480	746	49.8	8.2	674	6.4	33.8
10:2-FTOH	0.033	0.067	39.4	45.2	12.3	1.8	165	2.3	9.4
N-MeFOSE	0.007	0.013	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.007	0.013	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	40	120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	40	120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

8.6.4 WWTP-M1

Table 86: PFAS concentrations in ng/L in the influent samples of WWTP-M1.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
						ng/L				
PFBA	4.6	9.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	3.8	7.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	2.8	13.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	1.7	8.4	<LOQ	<LOQ	<LOQ	n.d.	n.d.	n.d.	<LOQ	n.d.
PFOA	0.5	4.7	6.0	5.4	7.6	5.5	5.5	5.0	5.5	5.9
PFNA	0.6	5.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	1.6	8.0	n.d.	n.d.	2.8	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	22.9	45.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	24.2	48.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	24.2	48.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	24.2	48.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	24.4	122	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	88.1	176	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	436	873	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	2.6	13.0	n.d.	n.d.	<LOQ	<LOQ	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	2.1	10.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	50.5	101	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.6	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	1.2	5.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	5.9	11.7	31.9	17.3	n.d.	<LOQ	<LOQ	n.d.	n.d.	n.d.
3:3-acid	139	277	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	ng/L									
4:3-acid	13.9	27.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	13.9	27.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	4.7	9.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	4.7	9.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	1.4	2.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.3	2.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.2
PFHpS	0.9	4.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.6	2.8	7.2	12.3	5.4	6.5	4.6	6.5	4.8	5.6
PFDS	4.6	22.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.5	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.3	0.5	n.d.	2.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
8:2-FTS	2.5	5.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	26.9	53.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	26.9	53.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	33.4	66.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	23.6	47.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	15.9	79.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	7.6	37.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	7.6	37.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	15.7	78.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	15.7	78.3	n.d.	109	<LOQ	<LOQ	<LOQ	n.d.	n.d.	n.d.
FOSA	2.5	12.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	12.5	25.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	12.5	25.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	ng/L									
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	12.3	36.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	10.4	20.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	10.4	20.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	2.1	4.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	2.1	4.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 87: PFAS concentrations in ng/L in the effluent samples of WWTP-M1.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 5	EFF 7	EFF 8
				ng/L			
PFBA	3.0	6.0	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	2.2	4.5	16.9	13.1	16.8	12.8	8.6
PFHxA	1.4	7.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHpA	1.0	5.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	0.3	2.8	7.3	8.1	5.8	6.3	6.3
PFNA	0.3	3.2	<LOQ	<LOQ	n.d.	<LOQ	<LOQ
PFDA	0.7	3.7	<LOQ	n.d.	<LOQ	n.d.	n.d.
PFUnA	5.4	10.8	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	5.2	10.4	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	5.2	10.4	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	5.2	10.4	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	13.9	69.6	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	46.8	93.7	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	97.9	196	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	1.5	7.4	<LOQ	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	0.9	4.7	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	6.1	12.2	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.1	0.3	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	0.3	1.4	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	1.4	2.8	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	71.2	142	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	7.1	14.2	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	7.1	14.2	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	2.8	5.6	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	2.8	5.6	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	0.7	1.4	7.5	12.5	14.8	9.9	10.3
PFHxS	0.1	1.3	<LOQ	1.4	<LOQ	1.5	1.7
PFHpS	0.6	2.8	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.4	2.1	18.7	7.2	6.9	4.2	5.1
PFDS	1.1	5.4	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.3	1.3	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.1	0.3	14.6	1.4	1.7	1.8	1.6
8:2-FTS	1.3	2.6	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	4.8	9.6	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	4.8	9.6	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	4.2	8.3	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	13.9	27.8	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 5	EFF 7	EFF 8
				ng/L			
8:2-FTEO1C	7.4	37.1	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	3.2	15.8	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	3.2	15.8	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	5.1	25.5	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	5.1	25.5	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	1.2	6.0	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	6.0	11.9	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	6.3	12.5	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	4.9	14.6	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	4.3	8.3	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	4.3	8.3	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	0.4	1.7	n.d.	n.d.	3.7	n.d.	n.d.
N-EtFOSE	0.4	1.7	n.d.	n.d.	6.3	n.d.	n.d.
6:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 88: PFAS concentrations in ng/m³ in WWTP-M1 air samples taken above the influent.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
PFBA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	0.002	0.021	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFNA	0.002	0.022	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	0.004	0.021	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
6:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.002	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.004	0.021	n.d.	n.d.	0.026	n.d.	n.d.	n.d.	<LOQ	<LOQ
PFDS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.002	0.004	n.d.	0.005	<LOQ	<LOQ	n.d.	0.005	n.d.	n.d.
8:2-FTS	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	0.104	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
6:2-FTOH	0.07	0.2	5.4	12.5	15.3	4.0	10.7	9.0	10.6	5.6
8:2-FTOH	0.04	0.07	1.6	4.3	4.4	1.7	3.8	4.2	4.0	2.3
10:2-FTOH	0.04	0.07	0.1	0.2	0.2	0.1	0.3	0.5	0.5	0.2
N-MeFOSE	0.008	0.014	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.008	0.014	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-FTO	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
10:2-FTO	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFHxI	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFOI	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
PFDI	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
4:2-FTI	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTI	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-FTI	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTAC	40.0	120	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-FTAC	40.0	120	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
6:2-FTMAC	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
8:2-FTMAC	1.0	3.0	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.

n.a.: not analyzed due to problems with air sampler, n.d.: not detected; <LOQ: lower than limit of detection

8.6.5 WWTP-M2

Table 89: PFAS concentrations in ng/L in the influent samples of influent A of WWTP-M2.

Analyte	LOD	LOQ	INF 1A	INF 2A	INF 3A	INF 4A	INF 5A	INF 6A	INF 7A	INF 8A
	ng/L									
PFBA	4.3	8.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	4.0	8.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	2.5	12.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	1.7	8.4	n.d.	<LOQ	n.d.	n.d.	<LOQ	<LOQ	n.d.	<LOQ
PFOA	0.5	4.6	<LOQ	5.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4.7
PFNA	0.5	5.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	1.5	7.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	16.3	32.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	24.5	48.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	24.5	48.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	24.5	48.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	22.4	112	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	69.2	138	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	431	863	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	2.4	11.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	1.6	7.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	52.4	105	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.5	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	1.0	5.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	5.0	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	125	251	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1A	INF 2A	INF 3A	INF 4A	INF 5A	INF 6A	INF 7A	INF 8A
	ng/L									
4:3-acid	12.5	25.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	12.5	25.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	4.6	9.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	4.6	9.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	1.3	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.3	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.9
PFHpS	0.9	4.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.5	2.5	4.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.8
PFDS	3.3	16.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.5	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.3	0.5	n.d.	0.62	n.d.	n.d.	<LOQ	0.8	n.d.	n.d.
8:2-FTS	2.5	5.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	26.7	53.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	26.7	53.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	35.6	71.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	23.0	46.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	14.9	74.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	5.0	25.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	5.0	25.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	32.6	163	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	32.6	163	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	2.1	10.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	10.3	20.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	9.8	19.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1A	INF 2A	INF 3A	INF 4A	INF 5A	INF 6A	INF 7A	INF 8A
	ng/L									
6:2/8:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	17.4	52.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	10.8	20.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	10.8	20.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	1.1	4.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	1.1	4.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	10.0	30.0	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 90: PFAS concentrations in ng/L in the influent samples of influent B of WWTP-M2.

Analyte	LOD	LOQ	INF 1B	INF 2B	INF 3B	INF 4B	INF 5B	INF 6B	INF 7B	INF 8B
	ng/L									
PFBA	5.0	10.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	4.5	9.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	2.7	13.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	1.9	9.4	<LOQ	n.d.	<LOQ	<LOQ	n.d.	<LOQ	n.d.	<LOQ
PFOA	0.5	4.9	<LOQ	<LOQ	5.8	5.4	<LOQ	5.1	<LOQ	n.d.
PFNA	0.6	5.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	1.4	7.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	14.2	28.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	23.4	46.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	23.4	46.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	23.4	46.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	21.7	109	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	67.0	134	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	447	894	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	2.5	12.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	1.6	8.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	40.1	80.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.5	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	1.1	5.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	5.3	10.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	133	267	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	13.3	26.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	13.3	26.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1B	INF 2B	INF 3B	INF 4B	INF 5B	INF 6B	INF 7B	INF 8B
	ng/L									
6:3-acid	4.9	9.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	4.9	9.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	1.3	2.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.2	2.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	1.0	4.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.5	2.4	n.d.	n.d.	4.6	3.9	4.2	6.1	6.4	n.d.
PFDS	2.8	14.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.5	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.7
6:2-FTS	0.3	0.5	n.d.	n.d.	n.d.	2.5	n.d.	n.d.	n.d.	n.d.
8:2-FTS	2.5	5.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	27.2	54.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	27.2	54.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	27.9	55.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	24.6	49.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	13.9	69.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	4.4	22.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	4.4	22.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	45.6	228	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	45.6	228	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	3.0	14.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	14.9	29.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	17.0	34.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1B	INF 2B	INF 3B	INF 4B	INF 5B	INF 6B	INF 7B	INF 8B
	ng/L									
6:2-FTOH	13.8	41.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	9.4	18.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	9.4	18.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	0.9	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.9	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
8:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
10:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
PFHxI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
PFOI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
PFDI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
4:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
6:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
8:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
6:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
8:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
6:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
8:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 91: PFAS concentrations in ng/L in the effluent samples of WWTP-M2.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 5	EFF 6
			ng/L			
PFBA	2.7	5.3	n.d.	n.d.	n.d.	4.2
PFPeA	1.7	3.4	6.4	4.9	n.d.	4.9
PFHxA	1.1	5.4	5.0	4.9	2.2	7.2
PFHpA	0.8	4.0	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	0.2	2.3	6.1	5.3	2.8	6.2
PFNA	0.3	2.7	<LOQ	<LOQ	n.d.	<LOQ
PFDA	0.7	3.7	<LOQ	<LOQ	<LOQ	<LOQ
PFUnA	5.2	10.3	n.d.	n.d.	n.d.	n.d.
PFDoA	5.2	10.5	n.d.	n.d.	n.d.	n.d.
PFTrA	5.2	10.5	n.d.	n.d.	n.d.	n.d.
PFTeA	5.2	10.5	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	11.8	58.8	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	36.8	73.7	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	66.5	133	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	1.2	5.8	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	0.8	3.9	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	6.9	13.7	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.2	0.3	n.d.	n.d.	n.d.	n.d.
PFOPA	0.3	1.7	n.d.	n.d.	n.d.	n.d.
PFDPA	1.7	3.5	n.d.	n.d.	n.d.	n.d.
3:3-acid	53.5	107	n.d.	n.d.	n.d.	n.d.
4:3-acid	5.4	10.7	n.d.	n.d.	n.d.	n.d.
5:3-acid	5.4	10.7	n.d.	n.d.	n.d.	n.d.
6:3-acid	2.3	4.5	n.d.	n.d.	n.d.	n.d.
7:3-acid	2.3	4.5	n.d.	n.d.	n.d.	n.d.
PFBS	0.5	1.1	n.d.	n.d.	n.d.	n.d.
PFHxS	0.1	1.3	2.4	1.9	n.d.	2.6
PFHpS	0.5	2.3	n.d.	n.d.	n.d.	n.d.
PFOS	0.3	1.4	5.0	5.6	4.6	5.5
PFDS	1.0	5.2	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.3	1.4	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.1	0.3	0.6	0.5	1.7	<LOQ
8:2-FTS	1.4	2.8	n.d.	n.d.	n.d.	n.d.
FOSAA	5.9	11.9	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	5.9	11.9	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	5.9	11.7	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	11.3	22.6	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 5	EFF 6
	ng/L					
8:2-FTEO1C	7.4	37.1	n.d.	n.d.	n.d.	n.d.
6:2-PAP	2.5	12.5	n.d.	n.d.	n.d.	n.d.
8:2-PAP	2.5	12.5	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	18.4	91.8	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	18.4	91.8	n.d.	n.d.	n.d.	n.d.
FOSA	2.0	10.0	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	10.0	20.0	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	12.3	24.5	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	5.8	17.5	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	4.2	8.1	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	4.2	8.1	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	0.4	1.6	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.4	1.6	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10.0	30.0	n.a.	n.d.	n.d.	n.d.
8:2-FTO	10.0	30.0	n.a.	n.d.	n.d.	n.d.
10:2-FTO	10.0	30.0	n.a.	n.d.	n.d.	n.d.
PFHxI	10.0	30.0	n.a.	n.d.	n.d.	n.d.
PFOI	10.0	30.0	n.a.	n.d.	n.d.	n.d.
PFDI	10.0	30.0	n.a.	n.d.	n.d.	n.d.
4:2-FTI	10.0	30.0	n.a.	n.d.	n.d.	n.d.
6:2-FTI	10.0	30.0	n.a.	n.d.	n.d.	n.d.
8:2-FTI	10.0	30.0	n.a.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.a.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.a.	n.d.	n.d.	n.d.
6:2-FTMAC	10.0	30.0	n.a.	n.d.	n.d.	n.d.
8:2-FTMAC	10.0	30.0	n.a.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 92: PFAS concentrations in ng/m³ in air samples of WWTP-M2. Samples were taken above influent B.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
PFBA	0.002	0.004	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	0.002	0.004	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.240
PFHpA	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	0.002	0.021	n.a.	<LOQ	<LOQ	<LOQ	0.035	0.023	0.045	0.039
PFNA	0.002	0.022	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	0.042	0.208	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	0.208	0.417	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	0.208	0.417	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.002	0.004	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	0.208	0.417	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
6:3-acid	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	0.002	0.004	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.002	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDS	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.002	0.004	n.a.	0.005	0.005	n.d.	n.d.	0.004	0.008	0.107
8:2-FTS	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	0.104	0.208	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	0.042	0.208	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	0.042	0.208	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	0.042	0.208	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.004	0.021	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	0.021	0.042	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
6:2-FTOH	0.067	0.200	n.a.	3.4	3.3	2.3	3.3	24.5	4.7	98.5
8:2-FTOH	0.033	0.067	n.a.	1.0	0.8	0.7	1.0	1.0	1.3	16.6
10:2-FTOH	0.033	0.067	n.a.	0.1	0.1	0.1	0.1	0.1	0.2	0.2
N-MeFOSE	0.007	0.013	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.007	0.013	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
8:2-FTO	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
10:2-FTO	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
PFHxI	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
PFOI	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
PFDI	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
4:2-FTI	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
6:2-FTI	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
8:2-FTI	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
6:2-FTAC	40	120	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
8:2-FTAC	40	120	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
6:2-FTMAC	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
8:2-FTMAC	1	2	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.

n.a.: not analyzed, n.d.: not detected; <LOQ: lower than limit of detection

8.6.6 WWTP-M3

Table 93: PFAS concentrations in ng/L in the influent samples of WWTP-M3.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
						ng/L				
PFBA	5.8	11.7	153	142	179	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	4.5	8.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	3.0	15.2	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	2.1	10.7	<LOQ	n.d.	n.d.	<LOQ	<LOQ	n.d.	n.d.	n.d.
PFOA	0.6	5.7	4.8	4.4	4.7	9.1	5.7	5.8	5.0	5.6
PFNA	0.7	6.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	2.4	11.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	35.9	71.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	29.0	58.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	29.0	58.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	29.0	58.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	29.7	149	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	111	222	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	523	1046	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	3.1	15.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	2.3	11.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	55.0	110	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.7	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	1.3	6.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	6.7	13.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	16.9	n.d.
3:3-acid	153	305	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	ng/L									
4:3-acid	15.2	30.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	15.2	30.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	5.7	11.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	5.7	11.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	1.5	3.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.2	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	1.1	5.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.6	2.8	16.9	13.8	n.d.	7.1	7.8	6.9	22.9	42.1
PFDS	7.2	35.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.6	2.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.3	0.6	5.2	6.3	120	19.9	21.9	2.6	32.0	13.3
8:2-FTS	2.9	5.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	35.7	71.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	35.7	71.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	45.9	91.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	28.5	57.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	23.7	119	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	13.3	66.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	13.3	66.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	22.7	113	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.
8:2-diPAP	22.7	113	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.
FOSA	6.3	31.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	31.3	62.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	35.7	71.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	INF 1	INF 2	INF 3	INF 4	INF 5	INF 6	INF 7	INF 8
	ng/L									
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	14.3	43.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	9.9	19.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	9.9	19.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	1.0	3.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	1.0	3.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 94: PFAS concentrations in ng/L in the effluent samples of WWTP-M3.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 4	EFF 6
			ng/L			
PFBA	3.6	7.3	n.d.	n.d.	n.d.	n.d.
PFPeA	2.5	5.1	14.0	9.9	21.4	14.3
PFHxA	1.3	6.6	<LOQ	<LOQ	<LOQ	<LOQ
PFHpA	1.0	4.8	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	0.2	2.3	10.2	9.7	10.3	7.4
PFNA	0.3	3.1	<LOQ	n.d.	<LOQ	n.d.
PFDA	0.7	3.3	<LOQ	n.d.	n.d.	n.d.
PFUnA	4.8	9.6	n.d.	n.d.	n.d.	n.d.
PFDoA	5.0	9.9	n.d.	n.d.	n.d.	n.d.
PFTrA	5.0	9.9	n.d.	n.d.	n.d.	n.d.
PFTeA	5.0	9.9	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	13.5	67.5	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	45.9	91.8	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	69.0	138	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	1.3	6.5	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	0.8	4.1	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	5.0	10.0	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.2	0.3	n.d.	n.d.	n.d.	n.d.
PFOPA	0.3	1.6	n.d.	n.d.	n.d.	n.d.
PFDPA	1.6	3.3	n.d.	n.d.	n.d.	n.d.
3:3-acid	66.3	133	n.d.	n.d.	n.d.	n.d.
4:3-acid	6.6	13.3	n.d.	n.d.	n.d.	n.d.
5:3-acid	6.6	13.3	n.d.	n.d.	n.d.	n.d.
6:3-acid	2.3	4.7	n.d.	n.d.	n.d.	n.d.
7:3-acid	2.3	4.7	n.d.	n.d.	n.d.	n.d.
PFBS	0.7	1.3	13.0	12.5	12.2	12.9
PFHxS	0.1	1.3	<LOQ	<LOQ	<LOQ	<LOQ
PFHpS	0.5	2.3	n.d.	n.d.	n.d.	n.d.
PFOS	0.4	1.8	22.8	20.4	13.5	12.8
PFDS	1.0	4.8	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.3	1.3	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.1	0.3	20.1	56.9	33.3	23.8
8:2-FTS	1.3	2.5	n.d.	<LOQ	n.d.	n.d.
FOSAA	4.4	8.9	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	4.4	8.9	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	3.8	7.7	n.d.	n.d.	n.d.	n.d.
6:2-FTEO1C	11.7	23.4	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	EFF 1	EFF 2	EFF 4	EFF 6
	ng/L					
8:2-FTEO1C	6.5	32.6	n.d.	n.d.	n.d.	n.d.
6:2-PAP	5.5	27.7	n.d.	n.d.	n.d.	n.d.
8:2-PAP	5.5	27.7	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	12.0	59.9	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	12.0	59.9	n.d.	n.d.	n.d.	n.d.
FOSA	2.5	12.5	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	12.5	25.0	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	20.8	41.7	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	3.6	10.9	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	3.3	6.4	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	3.3	6.4	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	0.3	1.3	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.3	1.3	n.d.	n.d.	n.d.	n.d.
6:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.
8:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.
10:2-FTO	10.0	30.0	n.d.	n.d.	n.d.	n.d.
PFHxI	10.0	30.0	n.d.	n.d.	n.d.	n.d.
PFOI	10.0	30.0	n.d.	n.d.	n.d.	n.d.
PFDI	10.0	30.0	n.d.	n.d.	n.d.	n.d.
4:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.
6:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.
8:2-FTI	10.0	30.0	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	400	1,200	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	10.0	30.0	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 95: PFAS concentrations in ng/m³ in the air samples of WWTP-M3.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
						ng/m³				
PFBA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	0.002	0.021	0.037	0.046	0.060	0.068	0.030	n.d.	0.030	0.041
PFNA	0.002	0.022	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
5:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.002	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.002	0.004	0.050	0.211	n.d.	n.d.	n.d.	n.d.	0.048	n.d.
8:2-FTS	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	0.104	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	AIR 1	AIR 2	AIR 3	AIR 4	AIR 5	AIR 6	AIR 7	AIR 8
	ng/m³									
8:2/10:2-diPAP	/	/	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	0.07	0.2	< LOQ	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	0.04	0.07	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
10:2-FTOH	0.04	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	0.007	0.013	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	0.007	0.013	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	40.0	120	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
8:2-FTAC	40.0	120	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
6:2-FTMAC	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	1.0	3.0	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.a.: not analyzed due to problems with air sampler, n.d.: not detected; <LOQ: lower than limit of detection

8.6.7 Additional WWTP samples

Table 96: PFAS concentrations in ng/L in the additional samples (return flow and centrate) of WWTP-I2.

Analyte	LOD Return Flow	LOQ Return Flow	Return Flow	LOD Centrate	LOQ Centrate	Centrate
	ng/L					
PFBA	7.8	15.7	n.d.	29.7	59.4	n.d.
PFPeA	3.9	7.7	60.2	9.0	18.0	177[a]
PFHxA	2.5	12.7	149	5.0	25.1	488[a]
PFHpA	1.3	6.4	34.5	2.8	13.9	64.4
PFOA	0.4	3.6	113	1.2	12.1	228[a]
PFNA	0.4	4.2	7.9	0.6	6.3	8.4
PFDA	0.8	3.8	43.3	1.2	6.2	100
PFUnA	5.1	10.2	2.5	9.8	19.6	n.d.
PFDoA	6.2	12.4	n.d.	12.8	25.6	< LOQ
PFTrA	6.2	12.4	n.d.	12.8	25.6	n.d.
PFTeA	6.2	12.4	n.d.	12.8	25.6	n.d.
6:2-FTCA	17.2	86.1	< LOQ	29.3	146	1,208[a]
8:2-FTCA	72.5	145	< LOQ	182	363	601[a]
10:2-FTCA	61.8	124	n.d.	74.2	148	n.d.
6:2-FTUCA	2.3	11.3	< LOQ	4.8	24.2	153[a]
8:2-FTUCA	1.5	7.6	< LOQ	3.5	17.5	5.1
10:2-FTUCA	9.1	18.1	n.d.	10.5	21.0	n.d.
PFHxPA	0.3	0.5	n.d.	0.5	1.0	n.d.
PFOPA	0.5	2.5	n.d.	1.0	5.0	n.d.
PFDPA	2.5	5.0	n.d.	5.0	10.0	n.d.
3:3-acid	127	254	n.d.	251	502	n.d.
4:3-acid	12.7	25.4	n.d.	25.1	50.2	439[a]
5:3-acid	12.7	25.4	60.2	25.1	50.2	23,991[a]
6:3-acid	3.6	7.1	n.d.	12.1	24.3	53.0
7:3-acid	3.6	7.1	9.9	12.1	24.3	778 [a]
PFBS	1.3	2.5	53.0	2.5	5.0	22.5
PFHxS	0.2	1.7	n.d.	0.3	3.5	n.d.
PFHpS	0.7	3.6	n.d.	2.4	12.1	n.d.
PFOS	0.5	2.4	57.8	0.7	3.7	32.9
PFDS	1.0	5.1	n.d.	2.0	9.8	n.d.
4:2-FTS	0.5	2.5	n.d.	0.8	3.9	n.d.
6:2-FTS	0.3	0.5	< LOQ	0.4	0.8	n.d.
8:2-FTS	2.5	5.0	n.d.	3.9	7.8	n.d.
FOSAA	10.0	19.9	n.d.	13.0	26.0	n.d.
N-MeFOSAA	10.0	19.9	n.d.	13.0	26.0	n.d.

Analyte	LOD Return Flow	LOQ Return Flow	Return Flow	LOD Centrate	LOQ Centrate	Centrate
	ng/L					
N-EtFOSAA	10.7	21.4	n.d.	13.1	26.3	n.d.
6:2-FTEO1C	17.8	35.6	n.d.	60.7	121	n.d.
8:2-FTEO1C	7.5	37.5	n.d.	12.4	62.0	n.d.
6:2-PAP	5.0	25.0	n.d.	5.0	25.0	n.d.
8:2-PAP	5.0	25.0	n.d.	5.0	25.0	n.d.
6:2-diPAP	14.7	73.3	n.d.	28.2	141	n.d.
8:2-diPAP	14.7	73.3	n.d.	28.2	141	n.d.
FOSA	3.5	17.5	n.d.	3.4	16.8	n.d.
N-MeFOSA	17.5	35.0	n.d.	16.8	33.6	n.d.
N-EtFOSA	26.7	53.4	n.d.	27.4	54.8	n.d.
6:2/8:2-diPAP	-	-	n.d.	-	-	n.d.
8:2/10:2-diPAP	-	-	n.d.	-	-	n.d.
6:2-FTOH	10.1	30.2	n.d.	27.9	83.8	n.d.
8:2-FTOH	7.5	14.5	n.d.	41.6	79.9	n.d.
10:2-FTOH	7.5	14.5	n.d.	41.6	79.9	n.d.
N-MeFOSE	1.5	2.9	n.d.	8.3	16.0	n.d.
N-EtFOSE	1.5	2.9	n.d.	8.3	16.0	n.d.
6:2-FTO	10.0	30.0	n.a.	10.0	30.0	n.a.
8:2-FTO	10.0	30.0	n.a.	10.0	30.0	n.a.
10:2-FTO	10.0	30.0	n.a.	10.0	30.0	n.a.
PFHxI	10.0	30.0	n.a.	10.0	30.0	n.a.
PFOI	10.0	30.0	n.a.	10.0	30.0	n.a.
PFDI	10.0	30.0	n.a.	10.0	30.0	n.a.
4:2-FTI	10.0	30.0	n.a.	10.0	30.0	n.a.
6:2-FTI	10.0	30.0	n.a.	10.0	30.0	n.a.
8:2-FTI	10.0	30.0	n.a.	10.0	30.0	n.a.
6:2-FTAC	400	1,200	n.a.	400	1,200	n.a.
8:2-FTAC	400	1,200	n.a.	400	1,200	n.a.
6:2-FTMAC	10.0	30.0	n.a.	10.0	30.0	n.a.
8:2-FTMAC	10.0	30.0	n.a.	10.0	30.0	n.a.

[a] Concentration exceeding the highest calibration point of 120 ng/L. Concentrations estimated by assumption of linear correlation.

n.a.: not analyzed due to problems with air sampler, n.d.: not detected; <LOQ: lower than limit of detection

Table 97: PFAS concentrations in ng/L in stack gas water (SGW) samples of WWTP-M2.

Analyte	LOD	LOQ	SGW 1	SGW 2
	ng/L			
PFBA	3.2	6.4	n.d.	n.d.
PFPeA	1.1	2.2	5.1	6.9
PFHxA	1.1	5.5	<LOQ	6.2
PFHpA	1.2	6.0	<LOQ	<LOQ
PFOA	0.3	3.0	9.7	8.4
PFNA	0.4	4.0	<LOQ	<LOQ
PFDA	0.8	4.0	<LOQ	<LOQ
PFUnA	4.7	9.5	n.d.	n.d.
PFDoA	5.2	10.4	n.d.	n.d.
PFTrA	5.2	10.4	n.d.	n.d.
PFTeA	5.2	10.4	n.d.	n.d.
6:2-FTCA	7.9	39.5	n.d.	n.d.
8:2-FTCA	25.0	50.0	n.d.	n.d.
10:2-FTCA	32.7	65.3	n.d.	n.d.
6:2-FTUCA	0.8	4.2	n.d.	n.d.
8:2-FTUCA	0.6	2.9	n.d.	n.d.
10:2-FTUCA	3.8	7.6	n.d.	n.d.
PFHxPA	0.7	3.5	n.d.	n.d.
PFOPA	3.5	7.0	n.d.	n.d.
PFDPA	0.3	0.7	n.d.	n.d.
3:3-acid	55.3	111	n.d.	n.d.
4:3-acid	5.5	11.1	n.d.	n.d.
5:3-acid	5.5	11.1	n.d.	n.d.
6:3-acid	3.0	5.9	n.d.	n.d.
7:3-acid	3.0	5.9	n.d.	n.d.
PFBS	0.6	1.1	n.d.	n.d.
PFHxS	0.3	3.1	n.d.	n.d.
PFHpS	0.6	3.0	n.d.	n.d.
PFOS	0.7	3.5	15.1	n.d.
PFDS	0.9	4.7	n.d.	n.d.
4:2-FTS	0.5	2.5	n.d.	n.d.
6:2-FTS	0.3	0.5	7.4	2.3
8:2-FTS	2.5	5.0	n.d.	n.d.
FOSAA	5.0	10.0	n.d.	n.d.
N-MeFOSAA	5.0	10.0	n.d.	n.d.
N-EtFOSAA	5.1	10.2	n.d.	n.d.
6:2-FTE01C	14.8	29.6	n.d.	n.d.
8:2-FTE01C	8.0	39.8	n.d.	n.d.
6:2-PAP	11.1	55.6	n.d.	n.d.
8:2-PAP	11.1	55.6	n.d.	n.d.
6:2-diPAP	1.7	8.3	n.d.	n.d.
8:2-diPAP	1.7	8.3	n.d.	n.d.

Analyte	LOD	LOQ	SGW 1	SGW 2
	ng/L			
FOSA	3.2	15.9	n.d.	n.d.
N-MeFOSA	15.9	31.8	n.d.	n.d.
N-EtFOSA	21.9	43.9	n.d.	n.d.
6:2/8:2-diPAP	-	-	n.d.	n.d.
8:2/10:2-diPAP	-	-	n.d.	n.d.
6:2-FTOH	8.0	24.1	n.d.	n.d.
8:2-FTOH	5.9	11.4	n.d.	n.d.
10:2-FTOH	5.9	11.4	n.d.	n.d.
N-MeFOSE	0.6	2.3	n.d.	n.d.
N-EtFOSE	0.6	2.3	n.d.	n.d.
6:2-FTO	10.0	30.0	n.a.	n.a.
8:2-FTO	10.0	30.0	n.a.	n.a.
10:2-FTO	10.0	30.0	n.a.	n.a.
PFHxI	10.0	30.0	n.a.	n.a.
PFOI	10.0	30.0	n.a.	n.a.
PFDI	10.0	30.0	n.a.	n.a.
4:2-FTI	10.0	30.0	n.a.	n.a.
6:2-FTI	10.0	30.0	n.a.	n.a.
8:2-FTI	10.0	30.0	n.a.	n.a.
6:2-FTAC	400	1,200	n.a.	n.a.
8:2-FTAC	400	1,200	n.a.	n.a.
6:2-FTMAC	10.0	30.0	n.a.	n.a.
8:2-FTMAC	10.0	30.0	n.a.	n.a.

n.a.: not analyzed, n.d.: not detected; <LOQ: lower than limit of detection

8.6.8 Indoor air

Table 98: PFASs concentrations in ng/m³ in indoor air samples.

Analyte	LOD	LOQ	Indoor Air 1			Indoor Air 2			Indoor Air-3	Indoor Air-4
			1	2	3	1	2	3		
			ng/m³							
PFBA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	0.002	0.004	0.008	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxA	0.004	0.021	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	0.002	0.021	<LOQ	<LOQ	<LOQ	<LOQ	0.027	0.023	<LOQ	<LOQ
PFNA	0.002	0.022	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	Indoor Air 1			Indoor Air 2			Indoor Air-3	Indoor Air-4
			1	2	3	1	2	3		
			ng/m^3							
PFOPA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	0.208	0.417	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	0.021	0.042	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.002	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.002	0.004	0.007	n.d.	n.d.	<LOQ	n.d.	n.d.	<LOQ	n.d.
8:2-FTS	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	0.104	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	0.042	0.208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	Indoor Air 1			Indoor Air 2			Indoor Air-3	Indoor Air-4
			1	2	3	1	2	3		
			ng/m³							
6:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.004	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	0.021	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	0.067	0.200	1.17	0.95	0.48	0.50	1.39	1.53	2.43	0.42
8:2-FTOH	0.033	0.067	2.01	2.27	1.41	0.86	1.94	1.19	5.44	2.04
10:2-FTOH	0.033	0.067	0.58	n.d.	n.d.	0.27	n.d.	n.d.	2.21	0.61
N-MeFOSE	0.007	0.013	n.d.	0.09	0.20	0.09	n.d.	n.d.	0.40	0.08
N-EtFOSE	0.007	0.013	n.d.	0.69	0.27	0.04	n.d.	n.d.	0.05	n.d.
6:2-FTO	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	40	120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Analyte	LOD	LOQ	Indoor Air 1			Indoor Air 2			Indoor Air-3	Indoor Air-4
			1	2	3	1	2	3		
			ng/m³							
8:2-FTAC	40	120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.a.: not analyzed, n.d.: not detected; <LOQ: lower than limit of detection

8.6.9 Indoor dust

Table 99: PFAS concentrations in ng/g measured in indoor dust samples.

Analyte	LOD	LOQ	DUST-1			DUST-2			DUST-3		
			1	2	3	1	2	3	1	2	3
						ng/g					
PFBA	2.2	4.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	2.3	4.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.7	n.d.	n.d.
PFHxA	2.7	13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	22.8	<LOQ	<LOQ
PFHpA	2.2	11	n.d.	n.d.	n.d.	11.2	172	261	51.0	207	225
PFOA	0.9	8.9	n.d.	n.d.	n.d.	58.2	47.4	53.8	190	19.2	18.7
PFNA	0.9	9.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	<LOQ	<LOQ
PFDA	1.7	8.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.6	<LOQ	<LOQ
PFUnA	10	21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoA	10	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	10	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	10	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	29	147	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	124	247	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	154	309	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	3.5	17.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	2.3	11.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	25	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	2.8	5.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	5.7	28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	28	57	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

3:3-acid	133	266	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	13	27	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	13	27	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:3-acid	8.9	18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	8.9	18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	1.3	2.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.6	6.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	1.8	8.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	1.0	5.0	n.d.	n.d.	n.d.	57.4	35.2	34.2	44.3	n.d.	n.d.
PFDS	2.1	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	1.4	6.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	0.7	1.4	n.d.	n.d.	n.d.	27.4	15.1	8.2	15.7	4.0	3.5
8:2-FTS	6.9	14	n.d.	n.d.	n.d.	15.0	15.4	13.6	24.7	<LOQ	<LOQ
FOSAA	59	118	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	59	118	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	18	36	<LOQ	49.5	<LOQ	813	490	765	507	91.7	110
6:2-FTE01C	44	89	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	17	84	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	11	54	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	11	54	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	0.7	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.0	8.7
8:2-diPAP	0.7	3.6	n.d.	n.d.	n.d.	7.9	n.d.	n.d.	19.8	11.3	9.9
FOSA	2.0	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	10	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	12	24	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	-	-	n.d.	detected	detected	detected	detected	detected	detected	detected	detected
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	detected	detected	detected	detected	detected	detected

6:2-FTOH	19	56	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTOH	15	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTOH	15	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSE	1.5	5.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSE	1.5	5.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTO	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTO	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTO	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxI	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOI	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDI	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTI	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTI	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTAC	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTAC	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTMAC	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTMAC	200	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Detected: detected in the sample, but not quantified due to a lack of authentic standards; n.d.: not detected; <LOQ: lower than limit of detection

8.6.10 Maximum concentrations in WWTP samples

Table 100: Maximum concentration of individual PFASs in WWTP influent (ng/L), effluent (ng/L) and air (ng/m³).

	Industrial			Municipal		
	Influent ng/L	Effluent ng/L	Air ng/m³	Influent ng/L	Effluent ng/L	Air ng/m³
PFBA	46,700	23,600	1.6	179	4.2	n.d.
PFPeA	93,520	23,760	1.8	n.d.	21.4	n.d.
PFHxA	6,580	79,960	13.8	n.d.	7.2	0.24
PFHpA	<LOQ	145	2.2	<LOQ	<LOQ	n.d.
PFOA	4,820	7,100	11	9.1	10.3	0.068
PFNA	2,340	12.8	1.8	n.d.	<LOQ	n.d.
PFDA	1,100	2,640	4.4	2.8	<LOQ	<LOQ
PFUnA	2,500	920	1.7	n.d.	n.d.	n.d.
PFDoA	n.d.	n.d.	1.9	n.d.	n.d.	n.d.
PFTrA	1,560	n.d.	0.9	n.d.	n.d.	n.d.
PFTeA	n.d.	n.d.	0.6	n.d.	n.d.	n.d.
6:2-FTCA	<LOQ	17,240	4.5	n.d.	n.d.	n.d.
8:2-FTCA	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	3,200	17,820	4	<LOQ	<LOQ	n.d.
8:2-FTUCA	<LOQ	3,520	0.4	n.d.	n.d.	n.d.
10:2-FTUCA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	11.9	n.d.	n.d.	31.9	n.d.	n.d.
3:3-acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	<LOQ	<LOQ	n.d.	n.d.	n.d.	n.d.
5:3-acid	8,580	14,540	6.64	n.d.	n.d.	n.d.
6:3-acid	<LOQ	n.d.	0.5	n.d.	n.d.	n.d.
7:3-acid	26.6	14.3	0.5	n.d.	n.d.	n.d.
PFBS	5,660	351	n.d.	n.d.	14.8	n.d.
PFHxS	55.6	1.7	n.d.	2.9	2.6	n.d.
PFHpS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	537	118	<LOQ	42.1	22.8	0.026
PFDS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	n.d.	n.d.	n.d.	2.7	n.d.	n.d.
6:2-FTS	8.45	11.7	37.9	120	56.9	0.211
8:2-FTS	15.4	n.d.	1	n.d.	<LOQ	n.d.
FOSAA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	n.d.	n.d.	0.2	n.d.	n.d.	n.d.

	Industrial			Municipal		
	Influent ng/L	Effluent ng/L	Air ng/m³	Influent ng/L	Effluent ng/L	Air ng/m³
8:2-FTEO1C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	<LOQ	n.d.	n.d.	<LOQ	n.d.	n.d.
8:2-diPAP	<LOQ	n.d.	n.d.	109	n.d.	n.d.
FOSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTOH	18,519	n.d.	n.d.	n.d.	n.d.	98.5
8:2-FTOH	456	n.d.	n.d.	n.d.	n.d.	16.6
10:2-FTOH	986	n.d.	4,200,000	n.d.	n.d.	0.5
N-MeFOSE	1,064	n.d.	283,000	n.d.	n.d.	n.d
N-EtFOSE	63.2	n.d.	101,000	n.d.	n.d.	n.d
6:2/8:2-diPAP	86.6	n.d.	n.d.	n.d.	3.7	n.d.
8:2/10:2-diPAP	n.d.	n.d.	n.d.	n.d.	6.3	n.d.
6:2-FTO	0.106	0.033	200,000	n.d.	n.d.	n.d.
8:2-FTO	0.7	0.03	480,000	n.d.	n.d.	n.d.
10:2-FTO	0.584	n.d.	150,000	n.d.	n.d.	n.d.
PFHxI	0.36	n.d.	120,000	n.d.	n.d.	n.d.
PFOI	0.56	n.d.	140,000	n.d.	n.d.	n.d.
PFDI	<LOQ	n.d.	44,000	n.d.	n.d.	n.d.
4:2-FTI	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTI	2.3	n.d.	560,000	n.d.	n.d.	n.d.
8:2-FTI	0.099	n.d.	14,000	n.d.	n.d.	n.d.
6:2-FTAC	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.
8:2-FTAC	n.d.	n.d.	1,603	n.d.	n.d.	n.d.
6:2-FTMAC	4,610	0.052	4,400,000	n.d.	n.d.	n.d.
8:2-FTMAC	0.32	n.d.	8,000	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

8.6.11 Sludge samples

Table 101: Results for sludge analysis of samples from WWTP-M1, M3 and I2.

			WWTP-M1	WWTP-M3	WWTP-I2		
					ng/g		
	LOD [ng/g]	LOQ [ng/g]	SLU 8	SLU 1	SLU 6	SLU 9	SLU 11
PFBA	6.5	13.0	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	7.4	14.7	n.d.	n.d.	60.5	68.1	71.3
PFHxA	6.0	29.8	n.d.	n.d.	301	278	248
PFHpA	4.9	24.6	n.d.	n.d.	16.9	16.3	24.3
PFOA	1.9	19.3	n.d.	n.d.	185	173	256
PFNA	2.3	24.1	n.d.	n.d.	11	9	11
PFDA	6.0	30.0	n.d.	n.d.	201	191	146
PFUnA	33.9	67.8	n.d.	n.d.	920	568	807
PFDoA	49.7	99.5	n.d.	n.d.	n.d.	n.d.	n.d.
PFTrA	49.7	99.5	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeA	49.7	99.5	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTCA	94.9	475	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTCA	702	1,404	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	2,928	5,857	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	7.7	38.3	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTUCA	8.2	41.1	n.d.	n.d.	n.d.	n.d.	n.d.
10:2-FTUCA	836	1672	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	8.1	16.2	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	16.2	81.2	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	81.2	162	n.d.	n.d.	n.d.	n.d.	n.d.
3:3-acid	298	596	n.d.	n.d.	n.d.	n.d.	n.d.
4:3-acid	29.8	59.6	n.d.	n.d.	n.d.	n.d.	n.d.
5:3-acid	29.8	59.6	n.d.	n.d.	660	655	688
6:3-acid	19.3	38.5	n.d.	n.d.	n.d.	n.d.	n.d.
7:3-acid	19.3	38.5	n.d.	n.d.	311	352	433
PFBS	3.0	6.0	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.6	6.1	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpS	3.9	19.3	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	1.3	6.7	n.d.	13.1	109	152	97.5
PFDS	6.8	33.9	n.d.	n.d.	n.d.	n.d.	n.d.
4:2-FTS	2.0	10.1	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-FTS	1.0	2.0	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTS	10.1	20.2	n.d.	n.d.	n.d.	n.d.	n.d.
FOSAA	92.6	185	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	92.6	185	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	183	366	n.d.	n.d.	n.d.	n.d.	n.d.

			WWTP-M1	WWTP-M3	WWTP-I2		
			ng/g				
	LOD [ng/g]	LOQ [ng/g]	SLU 8	SLU 1	SLU 6	SLU 9	SLU 11
6:2-FTE01C	96.4	193	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	59.9	300	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-PAP	31.3	157	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-PAP	31.3	157	n.d.	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	39.4	197	n.d.	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	39.4	197	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	33.7	169	n.d.	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	169	337	n.d.	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	40.7	81.4	n.d.	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	-	-	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

Table 102: Peak areas measured in sludge extracts from WWTP-I1.

Analyte	SLU 1	SLU 3	SLU 5	SLU 7
PFBA	2,742,000	1,080,000	2,224,000	1,368,000
PFPeA	1,545,700	626,800	1,874,000	1,399,500
PFHxA	4,135,600	1,455,000	70,59,700	3,158,400
PFHpA	1,895,400	530,500	1,976,500	1,321,200
PFOA	7,839,200	2,533,000	8,793,300	4,332,900
PFNA	50,340	33,980	39,320	3,107,010
PFDA	123,000	57,540	85,640	72,300
PFUnA	n.d.	n.d.	n.d.	40,730
PFDoA	38,370	9,459	15,500	12,120
PFTrA	1,100,820	19,490	16,09,600	7,328,490
PFTeA	33,460	484,490	943,395	424,599
6:2-FTCA	n.d.	n.d.	1,026,0000	1,800,000
8:2-FTCA	n.d.	n.d.	n.d.	n.d.
10:2-FTCA	n.d.	n.d.	n.d.	n.d.
6:2-FTUCA	11,148,659	9,372	50,963,470	11,656,080
8:2-FTUCA	130,600	170,424	103,900	2,454,000
10:2-FTUCA	n.d.	n.d.	n.d.	n.d.
PFHxPA	n.d.	n.d.	n.d.	n.d.
PFOPA	n.d.	n.d.	n.d.	n.d.
PFDPA	n.d.	n.d.	n.d.	n.d.
3:3-acid	n.d.	n.d.	n.d.	n.d.

Analyte	SLU 1	SLU 3	SLU 5	SLU 7
4:3-acid	n.d.	n.d.	n.d.	27,650
5:3-acid	1,888,400	1,875,500	5,770,600	11,042,800
6:3-acid	469,300	94,290	360,900	11,68,640
7:3-acid	2,326,000	493,660	861,100	2,662,800
PFBS	n.d.	n.d.	n.d.	n.d.
PFHxS	n.d.	n.d.	n.d.	n.d.
PFHpS	n.d.	n.d.	n.d.	n.d.
PFOS	n.d.	n.d.	n.d.	n.d.
PFDS	n.d.	n.d.	n.d.	n.d.
4:2-FTS	n.d.	n.d.	n.d.	n.d.
6:2-FTS	n.d.	n.d.	n.d.	n.d.
8:2-FTS	n.d.	n.d.	n.d.	n.d.
FOSAA	n.d.	n.d.	n.d.	n.d.
N-MeFOSAA	n.d.	n.d.	n.d.	n.d.
N-EtFOSAA	n.d.	n.d.	n.d.	n.d.
6:2-FTE01C	n.d.	n.d.	n.d.	n.d.
8:2-FTE01C	n.d.	n.d.	n.d.	n.d.
6:2-PAP	n.d.	n.d.	n.d.	n.d.
8:2-PAP	n.d.	n.d.	n.d.	n.d.
6:2-diPAP	n.d.	n.d.	n.d.	n.d.
8:2-diPAP	n.d.	n.d.	n.d.	n.d.
FOSA	n.d.	n.d.	n.d.	n.d.
N-MeFOSA	n.d.	n.d.	n.d.	n.d.
N-EtFOSA	n.d.	n.d.	n.d.	n.d.
6:2/8:2-diPAP	n.d.	n.d.	n.d.	n.d.
8:2/10:2-diPAP	n.d.	n.d.	n.d.	n.d.

n.d.: not detected

8.6.12 Particulate phase of influent of WWTP-I2

Table 103: Results of analysis of particulate phase of influent of WWTP-I1.

Analyte	LOD [ng/g]	LOQ [ng/g]	INF 7	INF 8
			ng/g wet weight	
PFBA	0.2	0.5	n.d.	n.d.
PFPeA	0.2	0.4	n.d.	n.d.
PFHxA	0.4	1.9	<LOQ	<LOQ
PFHpA	0.4	2.0	<LOQ	<LOQ
PFOA	0.1	0.9	<LOQ	<LOQ
PFNA	0.2	1.9	<LOQ	<LOQ
PFDA	0.4	1.9	<LOQ	<LOQ
PFUnA	125	249	n.d.	n.d.
PFDoA	5.4	10.8	n.d.	n.d.
PFTrA	5.4	10.8	n.d.	n.d.
PFTeA	5.4	10.8	n.d.	n.d.
6:2-FTCA	6.5	32.5	n.d.	n.d.
8:2-FTCA	43.1	86.3	n.d.	n.d.
10:2-FTCA	85.7	171	n.d.	n.d.
6:2-FTUCA	0.3	1.4	n.d.	n.d.
8:2-FTUCA	0.4	1.8	n.d.	n.d.
10:2-FTUCA	6.1	12.3	n.d.	n.d.
PFHxPA	3.1	6.3	n.d.	n.d.
PFOPA	6.3	31.4	n.d.	n.d.
PFDPA	31.4	62.9	n.d.	n.d.
3:3-acid	18.6	37.2	n.d.	n.d.
4:3-acid	1.9	3.7	n.d.	n.d.
5:3-acid	1.9	3.7	n.d.	n.d.
6:3-acid	0.9	1.8	n.d.	n.d.
7:3-acid	0.9	1.8	n.d.	n.d.
PFBS	0.2	0.4	n.d.	n.d.
PFHxS	0.1	0.7	n.d.	n.d.
PFHpS	0.2	0.9	n.d.	n.d.
PFOS	0.1	0.7	1.1	0.8
PFDS	24.9	125	n.d.	n.d.
4:2-FTS	0.1	0.7	n.d.	n.d.
6:2-FTS	0.1	0.1	0.2	n.d.
8:2-FTS	0.7	1.5	n.d.	n.d.
FOSAA	9.2	18.3	n.d.	n.d.

Analyte	LOD [ng/g]	LOQ [ng/g]	INF 7	INF 8
			ng/g wet weight	
N-MeFOSAA	9.2	18.3	n.d.	n.d.
N-EtFOSAA	17.4	34.8	n.d.	n.d.
6:2-FTE01C	4.6	9.2	n.d.	n.d.
8:2-FTE01C	3.7	18.7	n.d.	n.d.
6:2-PAP	10.1	50.6	n.d.	n.d.
8:2-PAP	10.1	50.6	n.d.	n.d.
6:2-diPAP	0.7	3.5	n.d.	n.d.
8:2-diPAP	0.7	3.5	<LOQ	7.6
FOSA	1.6	8.0	n.d.	n.d.
N-MeFOSA	8.0	16.1	n.d.	n.d.
N-EtFOSA	12.5	24.9	n.d.	n.d.
6:2/8:2-diPAP	-	-	detected	detected
8:2/10:2-diPAP	-	-	detected	detected
6:2-FTOH	-*	-*	n.d.	n.d.
8:2-FTOH	-*	-*	n.d.	n.d.
10:2-FTOH	-*	-*	n.d.	n.d.
N-MeFOSE	-*	-*	n.d.	n.d.
N-EtFOSE	-*	-*	n.d.	n.d.

n.d.: not detected; <LOQ: lower than limit of detection

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