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# Potential SVHCs in environment and products: Measurements of the presence of potential substances of very high concern in the environment and in products

von

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## Abstract

The identification and assessment of substances of very high concern (SVHCs) is an integral element in the context of REACH ((EG) 1907/2006). The German Environment Agency prepares SVHC dossiers in due consideration of environmental hazard criteria (REACH Art 57, d) to f)). The SVHC candidate list comprises several chemicals that are categorized as representatives of perfluoroalkyl and polyfluoroalkyl substances (PFASs) or para substituted alkylphenols (APs). The objective of the present study was the identification and analysis of PFASs and APs in industrial goods and the study of the aquatic distribution and fate of AP representatives.

Sample selection was based on an extended literature search focusing on building materials and industrial textiles. In total, 23 building materials and 28 industrial textiles were collected and analyzed on 29 selected PFASs. Furthermore, the concentration of four APs was analyzed in 18 building material samples. To complement the investigation of APs, 53 surface waters and 4 wastewater treatment plants were also analyzed on their AP concentration and additional transformation studies were performed for 4-tert.-butylphenol (4tBP) and 4-tert.-pentylphenol (4tPP).

PFASs were detected in 53% of investigated samples with vastly different results for building materials and industrial textiles and their subcategories. The chain lengths of detected ionic PFASs ranged from C4-C14 with concentrations from 2.4-430 µg/kg. Nonionic precursors (fluorotelomer alcohols) were detected in concentrations that were several magnitudes higher compared to other PFASs (40 µg/kg up to 4.3 g/L), with 8:2 FTOH being the dominant precursor in most samples. Marquee and coating samples have been identified as potential sources of PFASs in the environment, showing the highest concentrations (sum of ionic species up to 287 µg/kg and 885 µg/kg, respectively).

APs were detected in a majority of investigated building materials with 4tBP being the dominant AP. Concentrations of APs in building material samples were as high as up to 320 g/kg, clearly indicating use of APs as a main ingredient in tested formulations. Detected concentrations and concentration pattern indicated different application areas for short chain alkylphenols compared to longer chain derivatives. Relevance of short chain APs in the aquatic environment was found to be lower compared to nonylphenol or octylphenol and transformation experiments of 4tBP and 4tPP indicated complete mineralization of 4tBP and complete primary degradation of 4tPP in 50% of tests.

## Kurzbeschreibung

Für die Identifizierung besonders besorgniserregender Stoffe (Engl.: substances of very high concern (SVHCs)) erstellt das Umweltbundesamt im Rahmen von REACH ((EG) 1907/2006) Dossiers, auf Grundlage von ökologisch besonders besorgniserregenden Eigenschaften (REACH Art 57 d) to f)). Vertreter der Stoffklassen per- und polyfluorierte Alkylsubstanzen (Engl.: perfluoroalkyl and polyfluoroalkyl substances (PFASs)) sowie para substituierten Alkylphenolen (APs) befinden sich bereits auf der SVHC Kandidatenliste. Im Zuge dieses Projektes wurden einerseits Baumaterialien und industriell genutzte Textilien auf deren Gehalt an PFASs und andererseits der Gehalt an APs in Baumaterialien untersucht. Des Weiteren wurde der Verbleib von APs in der aquatischen Umwelt und die Biotransformation von kurzkettigen Alkylphenolen (Engl.: short chain alkylphenols (SCAPs)) untersucht.

Im Anschluss an eine ausführliche Literaturrecherche wurden 23 Baumaterialien und 28 industriell genutzte Textilien für die Untersuchung auf PFASs ausgewählt. In Summe wurden diese Proben auf eine Auswahl von 29 PFASs analysiert. Zudem wurden 18 weitere Baumaterialien auf deren Gehalt an vier APs untersucht. Die Messungen zu den APs wurden durch die Beprobung von 53 Fließgewässern sowie vier Kläranlagen ergänzt. Zuletzt wurde die Biotransformation von 4-tert.-Butylphenol (4tBP) und 4-tert.-Pentylphenol (4tPP) in Laborexperimenten untersucht.

PFASs wurden in 53% der untersuchten Proben detektiert, wobei sich deren Konzentrationen und Art der detektierten Spezies für Baumaterialien, industriell genutzte Textilien und deren Untergruppen wesentlich unterschieden. Die in den Proben detektierten PFASs wiesen Kettenlängen von $C_4$-$C_{14}$ in

Konzentrationen von 2,4-430 µg/kg auf. Im Vergleich zu allen anderen Analyten, wurden flüchtige Vorläuferverbindungen (FTOHs) in signifikant höheren Konzentrationen detektiert (von 40 µg /kg bis zu 4,3 g/L), wobei 8:2 FTOH die vorherrschende Spezies war. Mit einer Summe an nichtflüchtigen Analyten von bis zu 287 bzw. 885 µg/kg, wiesen Proben aus den Kategorien Markisen und Beschichtungen die höchsten Konzentrationen auf und stellen somit eine relevante Quelle für PFASs in der Umwelt dar.

APs wurden in der Mehrheit der untersuchten Baumaterialproben detektiert, wobei 4tBP die höchste Detektionsfrequenz aufwies. Mit Konzentrationen von bis zu 320 g/kg (32% w/w) stellen APs einen der Hauptbestandteile der untersuchten Formulierungen dar. Eine vergleichende Betrachtung der Umweltkonzentrationen von kurzkettigen APs mit langkettigen Derivaten zeigt, dass kurzkettige APs vermehrt durch Punktquellen eingetragen werden, während langkettige APs eher diffuse Eintragsmuster aufweisen, was auf grundsätzlich andere Verwendungsarten schließen lässt. Biotransformationsexperimente zeigten eine komplette Mineralisierung von 4tBP und vollständigen Primärabbau von 4tPP. Aufgrund von Umweltkonzentrationen und durchgeführten Biotransformationsstudien ist die generelle Relevanz von SCAPs für die aquatische Umwelt vermutlich geringer, als jene von langkettigen Derivaten wie Nonylphenol.

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| Peer reviewed Publication | 2019 | Combined study of source, environmental monitoring and fate of branched alkylphenols: The chain length matters.; Raphael M. Janousek, Jutta Müller, Thomas P. Knepper; Chemosphere, 2019 |
| Doctoral thesis | 2019 | Raphael Janousek; in preparation |

## List of Abbreviations

| | |
|---|---|
| **4:2-FTS** | 1H, 1H, 2H, 2H-Perfluorohexane sulfonic acid |
| **6:2-PAP** | 1H, 1H, 2H, 2H-perfluorooctylphosphate |
| **8:2-diPAP** | bis(1H, 1H, 2H, 2H-Perfluorodecyl) phosphate |
| **8:2-PAP** | 1H, 1h, 2H, 2H-Perfluoroddecylphosphate |
| **AOF** | Adsorbable organic fluorine |
| **AP** | Alkylphenol |
| **APEO** | Alkylphenol ethoxylate |
| **BPA-d16** | Bisphenol A-d16 |
| **DF** | Detection frequency |
| **EPDM** | Ethylene propylene dien methylene |
| **ESI** | Electrospray ionisation |
| **ETFE** | Ethylen tetrafluoroethylene |
| **FA** | Formic acid |
| **FS** | Fluorosurfactant |
| **FTOH** | Fluorotelomer alcohol |
| **HDF** | High density fibre |
| **HLNUG** | Hessisches landesamt für Naturschatz, Umwelt und Geologie |
| **HPLC** | High performance liquid chromatography |
| **HPLC-MS/MS** | High performance liquid chromatography-tandem mass spectrometry |
| **HRMS** | High resolution mass spectrometry |
| **IS** | Internal standard |
| **LOD** | Limit of detection |
| **LOQ** | Limit of quantification |
| **LSE** | Liquid-solid extraction |
| **MDF** | Middle density fibre |
| **max** | Maximum |
| **min** | Minimum |
| **MSDS** | Material safety data sheet |
| **n.a.** | Not analysed |
| **N/A** | Not applicable |
| **n.d.** | Not detected |
| **N-MeFOSE** | N-Methyl perfluorooctanoic sulfonamidoethanol |
| **NP** | Nonylphenol |
| **OECD** | Organisation for Economic Cooperation and Development |

| | |
|---|---|
| **OEM** | Original equipment manufacturer |
| **OP** | Octylphenol |
| **OSB** | Oriented strand board |
| **PE** | Polyethylene |
| **PEG** | Polyethylene glycol |
| **PFAA** | Perfluoroalkyl acid |
| **PFASs** | Perfluoroalkyl and polyfluoroalkyl substances |
| **PFBA** | Perfluorobutanoic acid |
| **PFBS** | Perfluorobutane sulfonic acid |
| **PFC** | Perfluorinated compounds |
| **PFCA** | Perfluoroalkyl carboxylic acid |
| **PFDA** | Perfluorodecanoic acid |
| **PFDoA** | Perfluorododecanoic acid |
| **PFHpA** | Perfluoroheptanoic acid |
| **PFHxA** | Perfluorohexanoic acid |
| **PFNA** | Perfluorononanoic acid |
| **PFOA** | Perfluorooctanoic acid |
| **PFOS** | Perfluorooctane sulfonic acid |
| **PFOSA** | Perfluorooctane sulfonamide |
| **PFPeA** | Perfluoropentanoic acid |
| **PFSA** | Perfluoroalkane sulfonic acid |
| **PFTeA** | Perfluorotetradecanoic acid |
| **PFTrA** | Perfluorotridecanoic acid |
| **PFUnA** | Perfluoroundecanoic acid |
| **PP** | Polypropylene |
| **PTFE** | Polytetrafluoroethylen |
| **PVC** | Polyvinyl chloride |
| **PVDF** | Polyvinylidene fluoride |
| **4tBP** | para-tert.-Butylphenol |
| **4tPP** | para-tert.-Pentylphenol |
| **QqQ MS** | Triple quadrupole mass spectrometer |
| **RC** | Regenerated cellulose |
| **RP** | Reversed phase |
| **RT** | Room temperature |
| **SFVE** | Sulfonyl fluoride vinyl ether |

| | |
|---|---|
| **SPE** | Solid phase extraction |
| **TOP** | Total oxidizable precursor |
| **UBA** | German environmental protection agency (translation: Umweltbundesamt) |
| **WW** | Wastewater |
| **WWTP** | Wastewater treatment plant |

## Summary

Detailed understanding of the sources, release, environmental concentrations and fate of chemicals is required to elaborate the assessment of substances of very high concern (SVHCs) in the context of REACH ((EG) 1907/2006) for both, already listed substances and potential new candidates. As several representatives of perfuoroalkyl and polyfluoroalkyl substances (PFASs) and para substituted alkylphenols (APs) are already listed on the SVHC candidate list, in depth understanding of the occurrence in goods and their environmental behavior is vital. While some PFASs and APs are already listed, a large number of other homologues exist that are expected to exhibit comparable environmental hazards, which must be evaluated prior to any suggestions for listing.

While environmental concentrations and fate of various PFAS homologues are studied to a high extent, their properties render them suitable for manifold applications and previously unknown sources must be investigated in order to identify them. Similar, the source, environmental concentrations and fate of nonylphenol (NP) are also heavily investigated. Short chain alkylphenols (SCAPs) on the other hand are hardly analyzed.

The present study focused on the occurrence of PFASs and APs in industrial goods and environmental AP concentrations in surface water and wastewater treatment plant (WWTP) influent and effluent samples. Additional laboratory transformation studies of SCAPs were performed to elucidate their fate. Sample selection was based on a detailed literature search in order to identify relevant sample categories. A total of 23 building material samples from three categories ((A) coatings, lacquers, stains and paints, (B) foils and composite materials and (C) sealants and adhesives and 28 industrial textile samples from four categories ((A) seat covers, (B) covers for truck trailers, (C) covers for maritime applications and (D) awnings and tarpaulins were collected and analyzed on a selected set of 29 PFASs. Analyzed PFASs comprised perfluoro carboxylic acids ($C_4$-$C_{14}$), perfluoro sulfonic acids ($C_4$-$C_8$, $C_{10}$ and $C_{12}$), n:2 fluorotelomer sulfonates (n=4, 6 and 8), n:2 FTOHs (n=6, 8 and 10), 2H,2H-perfluorodecanoic acid (8:2 FTCA), 2H,2H,3H,3H-perfluoroundecanoic acid (8:3 FTCA), 7H-perfluoroheptanoic acid (7HPFHpA), perfluoro-3,7-dimethyloctanoic acid (PF37DMOA) and perfluorooctane sulfonamide. Samples were extracted via liquid solid extraction using methanol and water or solid phase extraction. Samples were analyzed using high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) and ionization was achieved using electro spray ionization (ESI) in negative mode.

PFASs were detected in 39% of investigated building material samples and 60% of industrial textile samples yielding in an overall detection frequency of 53%. Concentrations of detected non-volatile PFASs ranged from 2.4-430 µg/kg and volatile precursors were detected with concentrations from 40 µg/kg up to 4.3 g/L. Samples from the categories coatings and awnings revealed the highest chain length diversity and sum of non-volatile PFASs (up to 885 µg/kg).

Eighteen building material samples were collected and analyzed on AP concentrations. Sample selection was conducted to fit in one of three categories, namely (A) paints, (B) coatings and (C) glues/adhesives. A set of five surface waters was sampled three times in 2017. In addition, 24 surface waters were monthly sampled in 2017, 24 different surface waters were monthly sampled in 2018 and further two surface waters were monthly sampled over the course of 2017 and 2018. Influent and effluent samples of three WWTPs and effluent samples of an additional WWTP were also collected and analyzed on AP concentrations.

Building material samples were dissolved in acetone and diluted prior to analysis, while surface water and WWTP samples were enriched using solid phase extraction. Samples that were withdrawn from biotransformation experiments and diluted prior to analysis. Analysis was carried out with HPLC-MS/MS and ionization was achieved using ESI in negative mode.

APs were detected in 59% of investigated building materials with 4tBP being the dominant AP, which was detected in 56% of samples, while NP was only detected in 22% of samples and 4-tert.-pentylphenol (4tPP) and octylphenol (OP) were only detected in 6% of samples, respectively. AP concentrations ranged from 1.9 g/kg (OP) to 320 g/kg (4tBP), clearly indicating use of APs as a main ingredient in tested formulations. Nonylphenol was found to be the dominant AP in surface water and wastewater treatment plant samples. Concentrations of NP and 4tBP decreased from WWTP influent to effluent samples, while no OP or 4tPP were detected. Detected 4tBP concentrations in surface water samples indicated point source release thereof into aquatic environments. Contrary, concentrations of longer chain derivatives indicated diffuse entrance. Relevance for short chain APs in the aquatic environment was found to be lower compared to nonylphenol or octylphenol. While biotransformation tests indicated complete mineralization of 4tBP, only complete primary degradation of 4tPP could be shown in 50% of tests, however, complete mineralization cannot be ruled out.

## Zusammenfassung

Für die Bewertung und Regulierung von besonders besorgniserregende Stoffen (Engl.: substances of very high concern (SVHCs)) im Kontext von REACH ((EG) 1907/2006), ist ein gutes Verständnis der Quellen und Eintragswege, sowie Umweltkonzentrationen und deren Verbleib in der Umwelt nötig. Einige Vertreter von per- und polyfluorierten Alkylsubstanzen (Engl.: perfluoroalkyl and polyfluoroalkyl substances (PFASs)) und para substituierten Alkylphenolen (APs) befinden sich bereits auf der Liste der SVHC Kandidaten. Da weitere Homologe der bereits aufgelisteten Derivate mitunter ebenfalls ein ähnliches Potenzial für ökologischen Gefährdungen besitzen können, müssen detaillierte Untersuchungen dieser Derivate durchgeführt werden, um Bewertungen abgeben zu können.

Sowohl Umweltkonzentrationen als auch der Verbleib von PFASs in der Umwelt wurden bereits gut untersucht. Aufgrund der Stoffeigenschaften dieser Substanzen ergeben sich eine Fülle an verschiedenen Anwendungsgebieten, weshalb Verwendungsgebiete an sich und dessen Ausmaß vermutlich noch nicht vollständig aufgeklärt sind. Betrachtet man die Situation bezüglich APs, so zeigt sich, dass Verwendung, Eintrag, Umweltkonzentration und Verbleib von Nonylphenol (NP) weitestgehend aufgeklärt sind, während kurzkettige Alkylphenole (Engl.: short chain alkylphenols (SCAPs)) bisher eher selten untersucht worden sind.

Die vorliegende Studie beschäftigte sich mit den Vorkommen von PFASs und APs in industriell genutzten Erzeugnissen (Baumaterialien und industriell genutzte Textilien), sowie AP Konzentrationen in Fließgewässern und Kläranlagenzulauf und -ablauf. Zusätzlich wurden Biotransformationsstudien von SCAPs im Labormaßstab durchgeführt, um deren Verbleib in der Umwelt besser zu verstehen. Die Auswahl der Proben basierte auf einer zuvor durchgeführten Literaturrecherche um relevante Produktkategorien zu identifizieren. Es wurden 23 Baumaterialien und 28 industriell genutzte Textilien ausgewählt und auf deren Gehalt an PFASs untersucht. Die ausgewählten Produktkategorien an Baumaterialien setzen sich aus (A) Beschichtungen, Lacken, Lasuren und Farben, (B) Folien und Verbundwerkstoffen und (C) Dichtstoffen und Klebstoffen zusammen. Industriell genutzten Textilien wurden aus den Kategorien (A) Sitzbezügen, (B) LKW Planen, (C) Abdeckungen für Anwendungen im maritimen Bereich und (D) Markisen und Planen ausgewählt. Insgesamt wurden 29 PFASs, bestehend aus perfluorierten Carbonsäuren ($C_4$-$C_{14}$), perfluorierten Sulfonsäuren (C4-C8, C10 und C12), n:2 fluorotelomer Sulfonsäuren (n=4, 6 und 8), n:2 fluorotelomer Alkohole (n=6, 8 und 10), 2H,2H-Perfluordecansäure (8:2 FTCA), 2H,2H,3H,3H-Perfluordecansäure (8:3 FTCA), 7H-Perfluorheptansäure (7HPFHpA), Perfluor-3,7-dimethylocansäure (PF37DMOA) und Perfluoroctansulfonamid, analysiert. Die Extraktion der Proben wurde mittels fest/flüssig Extraktion unter der Verwendung von Methanol sowie Wasser oder mittels Festphasenextraktion durchgeführt. Die anschließende Analyse wurde mit Hochleistungsflüssigchromatographie und Kopplung zu einem Tandem-Massenspektrometer (HPLC-MS/MS) durchgeführt und die Ionisation der Analyten erfolgte mittels Elektrospray Ionisation (ESI).

In 39% der Baumaterialien sowie 60% der industriell genutzten Textilien wurden PFASs detektiert, was zu einer gesamten Detektionsfrequenz von 53% führt. Die Konzentrationen der nichtflüchtigen Einzelsubstanzen reichten von 2,4-430 µg/kg, während flüchtige Vorläufersubstanzen mit Konzentrationen von 40 µg/kg bis zu 4,3 g/L detektiert wurden. Die größte Vielfalt an verschiedenen Kettenlängen sowie die höchsten Summenkonzentrationen an nichtflüchtigen Analyten (bis zu 885 µg/kg) wurden in Proben der Kategorien Beschichtungen und Markisen detektiert.

Es wurden 18 Baumaterialproben der Kategorien (A) Farben, (B) Beschichtungen und (C) Klebstoffe ausgewählt und auf ihren Gehalt an APs analysiert. Des Weiteren wurden fünf Fließgewässer je dreimal im Jahr 2017 beprobt und analysiert. Zusätzlich wurden 24 weitere Fließgewässer im Jahr 2017, 24 Fließgewässer im Jahr 2018 und zwei zusätzliche Fließgewässer in beiden Jahren in circa monatlichem Abstand beprobt und analysiert. Ergänzend wurden Zulauf und Ablauf von drei Kläranlagen und Ablauf einer weiteren Kläranlage beprobt.

Für die Probenvorbereitung der Baumaterialien wurden Aliquote in Aceton gelöst und verdünnt. Sämtliche Proben von Fließgewässern und Kläranlagen wurden mittels Festphasenextraktion angereichert, während Biotransformationsproben passend verdünnt wurden. Die Analyse der Proben erfolgte mittels HPLC-MS/MS und die Ionisation wurde mittels ESI erzielt.

In 59% der Baumaterialproben wurden APs detektiert, wobei 4tBP in den höchsten Konzentrationen und in den meisten Proben detektiert wurde (Detektionsfrequenz: 56%). Im Gegensatz dazu wurde Nonylphenol (NP), Octylphenol (OP) und 4tBP in absteigender Reihenfolge lediglich in 22%, 6% und 6% der Baumaterialien detektiert. Die Konzentrationen der APs lagen mit 1,9-320 g/kg meist im Prozentbereich, wodurch hervorgeht, dass APs vermutlich als eine der Hauptkomponenten in den untersuchten Formulierungen verwendet wurden. Hingegen wurde in den untersuchten Fließ- und Kläranlagenwässern NP in den höchsten Konzentrationen der untersuchten APs detektiert. Weder OP noch 4tPP wurden in den untersuchten Kläranlagenproben detektiert. Die NP und 4tBP Konzentrationen nahmen in allen Kläranlagen von Zulauf zu Ablauf hin ab. Die Umweltkonzentrationen der Alkylphenole lassen auf diffusen Eintrag von NP und OP schließen, während 4tBP vermutlich aus Punktquellen stammt und 4tPP wohl eine geringe Relevanz in der aquatischen Umwelt hat. In den durchgeführten Biotransformationsstudien zeigte sich eine komplette Mineralisierung von 4tBP in allen Experimenten und vollständiger Primärabbau von 4tPP in 50% der durchgeführten Ansätze, wobei zu erwähnen ist, dass eine komplette Mineralisierung nicht ausgeschlossen werden konnte.

## Application of perfluoroalkyl and polyfluoroalkyl substances in non-consumer products with a focus on building materials and industrial textiles

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) comprise a diverse class of chemicals with properties that are suitable for manifold applications. They are in use in various consumer as well as non-consumer products since the 1950s, such as aqueous film forming foams, food contact paper or in impregnations for durable and water repellent apparel. As a consequence of numerous monitoring, fate and toxicity studies performed in humans, wildlife and the environment, partial use restrictions of some PFASs representatives such as e.g. listing of PFOS and its salts in Annex B of the Stockholm convention 2009 have been initiated. In correlation to environmental concerns regarding PFASs, two main substance classes are in the focus: perfluoroalkane sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs). [1] Residues of PFSAs or PFCAs and their precursors can for example result from not reacted raw material such as polyfluorinated telomer alcohols or salts of PFCAs, which are used in production of fluorinated polymers. [2], [3] J.W. Martin et al. (2003) showed that C8 PFASs exhibit longer half-life compared to shorter alkyl chains and that PFSAs derivatives are more prone to be bioaccumulated than corresponding derivatives of PFCAs. [4] Perfluorooctane sulphonic acid (PFOS) and its salts have been rated by the Organisation for Economic Co-operation and Development (OECD) to be highly bioaccumulative and H.J. Hansen et al. detected perfluorooctane sulphonamide (PFOSA) and perfluorooctanoic acid (PFOA) in serum samples of 65 individuals with higher concentrations of PFOS. [5]

In order to estimate the impact of PFASs and possible release into the environment through generally termed “non-consumer products”, two categories were investigated, whereby “non-consumer” products are such goods that are not directly applied by a single individual but rather a company or a certain industry. The following summary gives an overview on the application of PFASs in (A) building materials such as e.g. surface treatment agents (coatings, dyes, roughcast), derived timber products, insulating material, glass, roofing material or the like and (B) textiles for technical utilisations such as e.g. fabrication of car seats, seats in public transportation, filtration or membrane materials and alike as well as the use of PFASs containing processing aids. Although PFASs are likely to be applied in building materials and industrial used textiles, only few studies have been published to monitor PFAS concentrations and possible release into the environment.

## 1.1 Application of PFASs containing components, additives or processing aids in building materials

Various construction projects and finished roofing or facades of buildings are exposed to all weather conditions. As a consequence, water or dirt repellent properties of deployed materials are advantageous. To achieve water, oil or dirt repellent properties and protect building materials from weather influence, PFASs can be applied. Besides repellent functions of PFAS containing coatings for applications in construction industry, use of fluorosurfactants (FSs) can yield in higher stability or resilience of foams for the formation of low-density concrete building blocks or adjustment of surface tension for better wetting behaviour of paints [6], [7]. In this context FSs refers to surfactants that exhibit a hydrophobic portion with F bound to C or often perfluoroalkyl moieties and represent a subcategory of PFASs. Direct influence of weather conditions holds a potential entry pathway for PFASs into the environment. Table 1 gives an overview of materials and additives that can be applied in building industry. Most dominant representative of coating additives are FSs, which are used in cleaning and impregnating products as well as in paints and lacquers. As a result of higher increasing bioaccumulation of PFCAs or PFSAs with increasing chain length, general trends for their structure head towards application of shorter derivatives. For example, 3MTM voluntarily phased-out any C8 chemistry regarding PFASs [8]. Other companies follow similar plans, hence, most material safety data sheets (MSDSs) or brochures indicate C2, C4 or C6 based PFASs. [9]–[12]

**Table 1: PFASs containing additives that can applied in products of the building industry, corresponding CAS numbers with content of PFASs in per cent, anonymised producers and product designation**

| Application field | Compound class | CAS | Producer/product acronym | Content range [wt%] |
|---|---|---|---|---|
| Paint/coating additive | 4:2-FTS ethyl ester acrylate | 1017237-78- 3 | C01-0101 | 75-100 |
| | | | C01-0102 | 75-100 |
| | | | C01-0103 | < 1-49 |
| | PFBS | 34454-97-2 | C01-0101 | < 1-24 |
| | | | C01-0102 | < 1-24 |
| | | 68298-12-4 | C01-0102 | < 1-24 |
| | PFBS ethyl ester acrylate | 67584-55-8 | C01-0103 | < 1-24 |
| | Mixture including 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl methacrylate (CAS 2144-53-8) with unknown percentage | 1793072-86-2 | C02-0101 | 25-74 |
| | Polyfluoroalkyl betaine | 34455-29-3 | C02-0102 | 25-49 |

| | | | | |
|---|---|---|---|---|
| | 8:2-PAP | 01-2119436357-36 | C02-0103 | 25-49 |
| | 8:2-PAP/8:2-diPAP | 01-2120049762-53 | C02-0104 | < 1-49 |
| | Reaction product of partially fluorinated alkyl with $P_2O_5$ (ammonium salt) | N/A | C02-0105 | 25-49 |
| | Reaction product of 3,3,4,4,5,5,6,6,7,7,8,8,8 – tridecafluorooctan-1-ol and polysubstituted alkane with $P_2O_5$ (diammonium salt) | 01-2119860935-26 | C02-0106 | < 1-24 |
| | Ammonium salts of mono- and bis[3,3,4,4,5,5,6,6,7,7,8,8, 8-tridecafluorooctyl and/or poly (substituted alkene)] phosphate | 01-2119463279-29-0000 | C02-0107 | < 1-49 |
| | PFSA | N/A | C02-0108 | 25-49 |
| | FS ($(CF_2)_2$) | N/A | C03-0101 | N/A |
| | FS $(CF_2)_n$; n < 3) | N/A | C03-0102 | N/A |
| Roof or wall coating | PFC; no further specification | N/A | C04-0201 | < 1-49 |
| | | N/A | C04-0202 | 25-49 |
| | | N/A | C04-0203 | 25-49 |
| | | N/A | C04-0104 | 25-49 |
| | | N/A | C04-0105 | 25-49 |
| | | N/A | C04-0306 | 25-49 |
| | | N/A | C04-0307 | 25-49 |
| | | N/A | C04-0308 | 25-49 |
| Sealer additives for stone, tile or concrete | Mixture including 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl methacrylate (CAS 2144-53-8) with unknown percentage | 1793072-86-2 | C02-0301 | 25-74 |
| | 6:2-PAP (ammonium salt) | 01-2119436357-36 | C02-0302 | < 1-24 |
| Sealants, Glue, Adhesives additives | PFASs | N/A | C02-0401 | 25-49 |
| | FS $(CF_2)_n$; n < 3) | N/A | C03-0401 | N/A |
| Floor coating | FS ($(CF_2)_2$) | N/A | C03-0501 | N/A |

[10], [13]–[28]

1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (4:2 FTS), perfluorobutane sulphonic acid (PFBS), 1H, 1H, 2H, 2H-perfluorodecylphosphate (8:2-PAP), bis(1H, 1H, 2H, 2H-perfluorodecyl) phosphate (8:2-diPAP), perfluorinated compounds (PFC), 1H, 1H, 2H, 2H-perfluorooctylphosphate (6:2-PAP)

N/A not applicable

Besides application of FSs as additives, some sectors of building industry directly incorporate fluoropolymers as a construction material. Non-polymeric PFASs can be applied during the production of fluoropolymers or to modify the properties of the polymer.[29] Application of polymers in building industry often involves ethylene tetrafluoroethylene (ETFE), which can be adopted for lightweight building shells (ETFE cushions), transparent roofing systems, greenhouses, covering of photovoltaic panels, or simply facade materials [30]. Polytetrafluorethylen (PTFE; also referred to Teflon®) is by far the most used fluoropolymer with numerous applications and can also be applied in stadium roofing or as a facade for other building projects when low friction, fire resistance, UV resistance or water repellent properties are required. [31] Table 2 lists producers of such polymers for building industry.

**Table 2: Fluoropolymers that can applied in products of the building industry, corresponding CAS numbers with content of PFASs in percent, anonymised producers and product designation**

| Application field | Compound class | CAS | Producer/Product acronym | Content range [wt%] |
|---|---|---|---|---|
| Paint/coating additive | Partially fluorinated PEG | N/A | C02-0109 | < 1-49 |
| | | N/A | C02-0110 | < 1-49 |
| | | N/A | C02-0111 | < 1-49 |
| | | N/A | C02-0112 | 75-100 |
| | Partially fluorinated acrylic polymer | N/A | C02-0113 | 25-49 |
| | | N/A | C02-014 | 25-49 |
| Roof or wall material | Fluoro-polymer blend; no further specification | N/A | C05-0201 | 50-74 |
| | ETFE | 25038-71-5 | C06-0201 | N/A |
| | | | C07-0201 | N/A |
| | Fluoropolymer blend | 65530-63-4 | C02-0201 | N/A |
| Sealer additives for stone, tile or concrete | Fluorinated acrylic copolymer | N/A | C02-0303 | < 1-49 |
| | | N/A | C02-0304 | < 1-49 |
| | Fluorinated acrylic alkylamino copolymer | N/A | C02-0305 | < 1-49 |
| Sealants, Glue, Adhesives additives | Partially fluorinated PEG | N/A | C02-0402 | < 1-49 |
| | | N/A | C02-0403 | < 1-49 |
| | | N/A | C02-0404 | < 1-49 |
| | | N/A | C02-0405 | 75-100 |
| Photovoltaic module coating | PTFE | 25038-71-5 | C08-0601 | N/A |
| Window coating | PTFE | 25038-71-5 | C46-0701 | N/A |

[32]–[45]
Polyethylene glycol (PEG)
N/A not applicable

### 1.1.1 PFASs for surface improvement in construction industry

#### 1.1.1.1 Fluorosurfactant additives for paints and coatings

Surface treatment in general comprises all processes that are applied to a surface in order to enhance its properties [46]. In correlation to construction industry or building materials, surface treatment refers to coatings, paints or equivalent. PFASs containing additives can be added to formulations to reach desired surface properties [7]. During the last decades, producers of surface treatment agents avoided the use of PFOA, PFOS and their precursors and replaced them by shorter alkyl chain derivatives [47].

FSs mode of action when used as surface treatment additives was explained by 3MTM (Deutschland GmbH). They yield in a lower surface tension and therefore improved wetting behaviour, which enables even distribution of paints or coatings when using FSs containing additives. Further improvements for paints and coatings using FSs are lower surface contamination, effectiveness in aqueous and solvent-borne systems, dirt pick up resistance, easy oil stain removal, open time improvement (container), low foam formation, anti-blocking properties and deployment as wetting and levelling agent. 3MTM explained common problems for poor surface wetting due to surface tension gradients as a result of coating components with different surface tensions, causing an a so called “orange peel” effect. Further problems that might occur result from contaminants. Contaminants (e.g. solid particles) lead to surface tension gradients and result in crater formation or so called “fish eye” effects. Lowering of surface tension is crucial to prevent these defects.

Studies of Dinglasan-Panlilio et al., showed contents of 6:2, 8:2 and 10:2 fluorotelomer alcohol (FTOH) (with decreasing percentages) in Zynol® FSN-100 and FSE [2], [48].

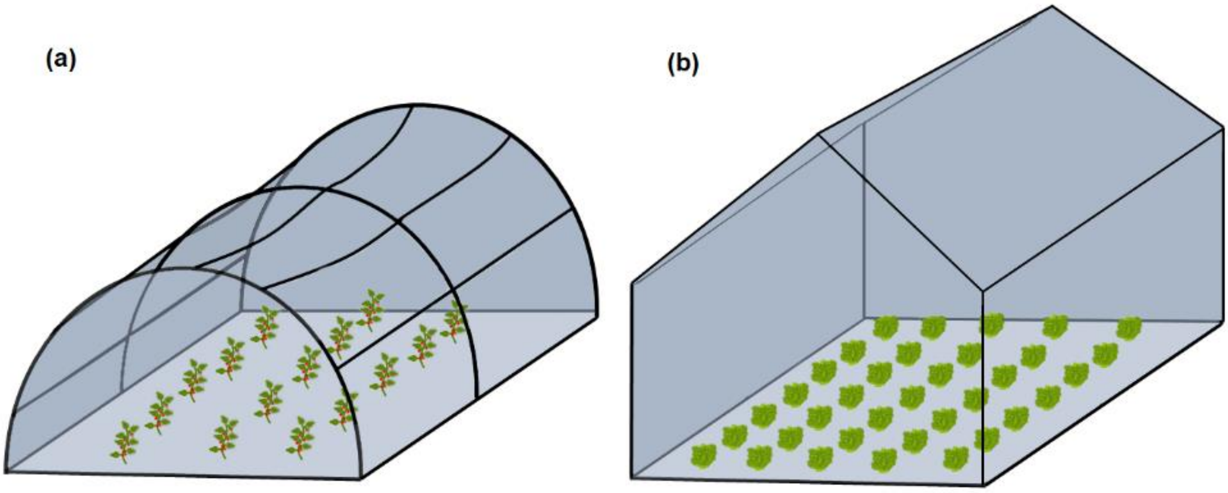
#### 1.1.1.2 Fluorinated polymer foils for walls, roofing and building facades

Polymeric building materials offer several advantages like good durability or weight saving. ETFE was originally invented by DuPont in the middle of the 20th century for the use in aerospace industry, but found its way into building industry with the application in the course of the Eden Project (Cornwall, UK) in the 1990s [49], [50]. Further prominent examples for the implementation of ETFE foils in building industry are the Burj Al Arab tower (Dubai, UAE) or the Allianz Arena football stadium (Munich, GER) [45]. Main superior properties of ETFE over glass or other conventional building materials are low dirt pick-up (leading to easy cleanability), corrosion protection, UV-light transparency, anti-fouling properties and long lasting colour retention. Besides that, ETFE has a superior weight to surface ratio to glass builds, which enables low transport costs, while providing similar stability for the use as facades of roofs [30], [51]. The application of ETFE films is differentiated in single and double or triple layer foils. In order to maintain desired shape and provide stability, single layered films are reinforced with wire cable, lightweight steel or aluminium constructions. Double or triple layer ETFE film is further processed to form cushions, which are filled with air to provide stability. Small cables can provide further stabilisation if necessary. In addition to stabilisation of constructions, the air inside the cushion offers thermal insulation [52]. During polymerisation of ETFE, FSs or other PFASs (e.g. FTOHs) might be applied and unreacted portions could partially remain in the polymer [53], [54]. Even tough incorporation of PFASs into fluorinated membranes is well-known [29], [55] and producers of such polymers try to minimize contaminations or entrance into the environment [56], to our knowledge there are no analytical investigations of these materials or water drainage from these materials regarding PFASs leaching or total content.

#### 1.1.1.3 Fluoropolymer foils for applications with requirements for good UV-transparency

For coating applications in photovoltaic technology, a high UV-transparency is required. Even though fluoropolymer foils (e.g. ETFE) can provide sufficient UV-transparency to enable glazing of solar panels, they are more often used in backing layers of the photovoltaic modules. These coverings of solar modules can contain up to 50% fluorinated polymer [58], [59]. Similar requirements are of importance in utilization of greenhouse coverings (walls and roofing). Depending on the building technique of a greenhouse, fluoropolymer films can be applied for glazing. One way of employing fluoropolymers for greenhouse applications is the use of EFTE cushions like explained in chapter 1.1.1.2. Another utilization for greenhouse glazing using fluoropolymers is the application of ETFE foils (e.g. F-CLEAN®), which can be used to cover a greenhouse framework (for example tunnel shaped greenhouses or any gable roof types (see Figure 1)) [60], [61].

Figure 1: Schematic drawings of tunnel (a), gable roof (b) shaped greenhouse constructions; own representation, Hochschule Fresenius



Producers of ETFE films claim that UV-transmittance is higher compared to glass for similar applications (with more than 90% UV-transmittance). AGC Chemicals Americas, Inc. is a company producing ETFE resins and other fluoropolymers, which explicitly states to not use PFOA in any of their products [64], [65]. In conclusion, ETFE's good UV-transparency offers specific potential for the use as greenhouse walls and roofing as well as covering of photovoltaic panels, where they are exposed to all weather conditions, enabling a possible entry for PFASs into the environment. Analytic data for the content of PFASs in polymer materials used for these applications is so far not available.

### 1.1.2 PFASs in glues, adhesives and sealers in construction industry

#### 1.1.2.1 PFASs as additives in adhesives and glues

The main purpose of adhesives is the linkage of substrates to each other. In order to form a connection and optimal adhesion of glue, the contact surface is of high importance. To enable good distribution of adhesives and glues over the substrate surfaces, a low surface tension is required to enhance wetting and therefore even distribution of adhesives. Better wetting can be achieved by addition of FSs. In addition to improved wetting, fluorochemical additives enable better penetration of the adhesive into the substrate and lead to defoaming [67]–[69].

**Adhesives and glues used for the production of derived timber products**

Derived timber products is an umbrella term for wooden sheets (e.g. chipboards, oriented strand boards (OSB), middle density fibre (MDF), high density fibre (HDF), fibre slabs, plywood and panel boards, etc.), construction framework or likewise, which are generated from wooden pieces that are glued together [70], [71]. In order to produce derived timber products, wood chips, wood particles, wood dust or alike are covered with adhesive and dried in one or more layers. Therefore, good covering of woodchips with adhesive is important, which can be improved by good wetting and substrate penetration of the used adhesive [67], [72]–[74]. In 2016, Běcanová et al. investigated 46 samples from diverse building materials (e.g. OSB, wood, insulating material or facade materials) for perfluoroalkyl acids (PFAAs) and detected the highest average concentration (4.87 µg/kg) in the 14 OSB and wood products [75].

#### 1.1.2.2 PFASs as additives in sealers

Sealers in general need to provide three basic functions. They have to fill a gap between two or even more substrates, formation of a barrier and maintenance of its sealing properties. In order to form a barrier, a sealant must be connected to the substrate and exhibit physical properties to act as a barrier.

As a result, many sealers are derived from adhesives. The main differences to adhesives are lower strength and higher elongation, which is necessary to expand and fill the gap between substrates. FS additives can be added to sealers to provide properties such as moisture resistance [76], [77]. Liu et al. investigated stone and wood sealants and Běcanová et al. three other types of insulating materials (results are listed in Table 3)[75], [78].

**Table 3: Monitoring data for PFASs investigated in sealers; showing type of PFASs and the concentration rage for investigated samples**

| Samples | Detected PFASs | | |
|---|---|---|---|
| Floor waxes and stone or wood sealants (n = 5)[78] | 6:2 FTOH [mg/kg]<br>1.6-331 | 8:2 FTOH [mg/kg]<br>0.4-92.4 | 10:2 FTOH [mg/kg]<br>< LOQ |
| Insulating material (n = 16; 2016)[75] | $\Sigma_{15}$PFAA [µg/kg]<br>< LOQ-0.384 | | |
| Mounting and sealing foam (n = 6; 2016)[75] | $\Sigma_{15}$PFAA [µg/kg]<br>0-24.5 | | |
| Polystyrene (n = 5; 2016)[75] | $\Sigma_{15}$PFAA [µg/kg]<br>< LOQ-0.18 | | |

<LOQ Below limit of quantification

## 1.2 Application of PFASs containing components, additives or processing aids in industrial textile applications

The main purpose of PFASs in textile industry is the achievement of water, oil and dirt repellent properties to enable easy cleanability or water resistance. In order to reach desired properties, FTOHs can be embedded into natural or synthetic fabrics [7]. This application is used for consumer products such as so called durable and water resistant apparel [79]. Similar products can also be applied for textiles in non-consumer products. In general, textiles can be obtained as woven or nonwoven materials, whereby woven materials are most probably treated with PFASs as fibres or finished textile sheets, unlike implementation of PFASs into nonwovens during production of the polymer. However, nonwovens could also be impregnated as finished sheets [80]–[83]. Polyvinylidene fluoride (PVDF), as an example for nonwoven materials, can be used as a filter membrane and during production of such a material PFASs may be applied in order to reach better wetting behaviour [84].

### 1.2.1 PFASs for surface improvement in industrial textiles

#### 1.2.1.1 PFASs as impregnation for carpets

Sampling and analysis regarding PFAS concentrations of indoor environments was performed in various studies. Thus, PFASs were detected in indoor dust and air samples [85], [86]. Since results of studies from Schlummer et al. showed PFASs in offices with no other textiles than the ones used for flooring, the results indicate PFAS contamination through applied carpet materials. They compared two carpet samples of different age and showed higher PFASs concentration in recently applied carpets compared with a 10-year-old carpet [87]. In addition, studies of Gremmel et al., which are published in the course of a study from the UBA, showed high concentrations of PFASs in an office environment with new carpets.

Table 4 shows detected concentrations in office or household air and dust as well as in carpet samples.

PFAS treatment of carpets can be implemented for both, the carpet yarn or finished carpets, whereby carpet yarn can be derived from extruded synthetic polymers or natural fibres [83].

**Table 4: Monitoring data for PFASs investigated in carpets or bath mats as well as air from rooms with carpets; showing type of PFASs and the concentration rage for investigated samples**

| Samples | Detected PFASs | | | | | |
|---|---|---|---|---|---|---|
| Carpet, bath mat (n = 3, 2; 2012-2013) [88] | PFHxA [ng/m$^2$] | PFHpA [ng/m$^2$] | PFOA | PFNA | PFDA | |
| | < 5 - 39 | < 5 - 7 | < 5 - 87 | < 5 - 6 | < 5 - 14 | |
| Office air (n = 2; 2011, 2003) [87] | 6:2 FTOH [ng/m$^3$] | 8:2 FTOH [ng/m$^3$] | 10:2 FTOH [ng/m$^3$] | | | |
| | < 0.2 - < 0.8 | ≈0.2 - ≈ 0.8 | < 0.1 - < 0.4 | | | |
| Carpet shop air (n = 1; 2013) [87] | 6:2 FTOH [ng/m$^3$] | 8:2 FTOH [ng/m$^3$] | 10:2 FTOH [ng/m$^3$] | | | |
| | ≈ 37 | ≈ 30 | ≈ 8 | | | |
| Carpet (n = 5; 2x2011, 3x2013) [78] | 6:2 FTOH [ng/g] | | 8:2 FTOH [ng/g] | | 10:2 FTOH [ng/g] | |
| | 1300 | | 352 - 502 | | 1210 | |
| Office air (n = 10; 2010) [85] | PFOS [ng/m$^3$] | | | PFOA [ng/m$^3$] | | |
| | 0.029 - 0.49 | | | 0.013 - 0.51 | | |
| Office air (n = 1; 2013) [89] | PFOA [ng/m$^3$] | 6:2 FTOH [ng/m$^3$] | 8:2 FTOH [ng/m$^3$] | 10:2 FTOH [ng/m$^3$] | N-Methyl perfluorooctane sulfonamido-ethanol (N-MeFOSE) [ng/m$^3$] | N-Ethyl perfluorooctane sulfonamido-ethanol (N-EtFOSE) [ng/m$^3$] |
| | 0.025* | 1.14* | 1.33* | 0.27 | 0.09 | 0.04 |
| Carpet (n = 14; 2010) [90] | PFBA [µg/m$^2$] | PFOA [µg/m$^2$] | PFBS [µg/m$^2$] | 6:2 FTOH [µg/m$^2$] | 8:2 FTOH [µg/m$^2$] | 10:2 FTOH [µg/m$^2$] |
| | < LOQ-14.7 | < LOQ-1.1 | < LOQ-26.8 | 11.0-21.2 | 17.2-32.8 | 6.8-19.5 |

*medium concentrations calculated from two of three samplings
Perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutanoic acid (PFBA), potassium perfluoro-1-butanesulfonate (PFBS)

### PFASs as impregnation of other household textiles

In addition to investigations of PFASs in carpets, there is some data available for further textiles used in household environment. Examples for investigated textiles are curtains, towels, upholstering (including pillows or alike), sofa covers, mattress pads or equivalent. Vestergren et al. (results listed in Table 5 “furniture textiles”) detected the highest PFAS concentrations within their furniture textile samples in one curtain sample. Table 5 shows detected concentrations in household textile samples.

**Table 5: Monitoring data for PFASs investigated in household textiles other than carpets; showing type of PFASs and the concentration rage for investigated samples**

| Samples | Detected PFASs | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Furniture textiles (n = 27; 2012-2013) [88] | PFPeA [ng/m$^2$] | PFHxA [ng/m$^2$] | PFHpA [ng/m$^2$] | PFOA [ng/m$^2$] | PFNA [ng/m$^2$] | PFDA [ng/m$^2$] | PFUnDA [ng/m$^2$] | PFDoA [ng/m$^2$] | PFTrA [ng/m$^2$] |
| | < 5 - 246 | < 5 - 812 | < 5 - 1022 | < 5 - 914 | < 5 - 97 | < 5 - 425 | < 5 - 51 | < 5 - 247 | < 5 - 8 |
| Treated home textiles and upholstering (n = 5; 2x2011, 3x2013) [78] | 6:2 FTOH [µg/g] | | | 8:2 FTOH [µg/g] | | | 10:2 FTOH [µg/g] | | |
| | 1.430 – 40.900 | | | 0.377 – 2.950 | | | 1.950 – 12.100 | | |

Perfluoropentanoic acid (PFPeA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrA)

### 1.2.1.2 PFASs used in impregnations for car interior

During the life cycle of industrial textiles from automobile industry like car seats, carpets or soft tops, these products are exposed to a lot of stress (e.g. rain/snow, sweat, dirt). Like described for office and other indoor contaminations of carpets, textiles that are implemented in cars can also be treated with PFASs to enable repellent properties. However, direct indications for the general treatment with water repellent agents of textiles used in automotive industry are hardly available. There are some applications of car textile-care in correlation with “consumer product” applications that can also be linked to the use of fluorochemicals (e.g. ScotchgardTM Auto Fabric & Carpet Protector [91]). Available results of car air analysis, however, indicate the presence of PFASs in automotive textiles. Table 6 shows detected concentrations of PFASs in car air samples.

**Table 6: Monitoring data for PFASs investigated in car air; showing type of PFASs and the concentration range for investigated samples**

| Samples | Detected PFASs | | | | |
|---|---|---|---|---|---|
| Car interior (n = 10; 2016) [75] | $\Sigma_{15}$PFAA [µg/kg] | | | | |
| | 0.033-35.5 | | | | |
| Car air (n = 1; 2013) [89] | PFOA [ng/m$^3$] | 6:2 FTOH [ng/m$^3$] | 8:2 FTOH [ng/m$^3$] | 10:2 FTOH [ng/m$^3$] | N-MeFOSE [ng/m$^3$] |
| | < LOQ | 0.42 | 2.04 | 0.61 | 0.08 |
| Car air (9 months old car; n = 1; 2012) [87] | 6:2 FTOH [ng/m$^3$] | 8:2 FTOH [ng/m$^3$] | 10:2 FTOH [ng/m$^3$] | | |
| | ≈ 0.5 | ≈ 8.4 | ≈ 3.5 | | |

N-methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)

### 1.2.1.3 PFASs used in impregnations of textiles used for public transport seats

Similar to research regarding car seats or textile interior, information regarding used impregnation techniques or products of seats, textile wall coverings or curtains in public transport are hardly available. However, a German company, which produces upholstering for public transport seats advertises their special treatment, which is applied on all of their wool moquettes and produces anti stain properties for water and oil stains [92], [93]. This company produces upholstering for public transport seats in London’s Underground, railway seats in the USA as well as in France, Hungary, or Czech Republic. There is no information available regarding fabrics for German train or bus seats and their water repellent properties.

Other than fabrics for train or bus seats, PFASs could also be used in airplane seats. Coatings for the surface of products with an open cell structure to provide hydrophobic or oleophobic properties may be used for the production of foam that is implemented in airplane seats. Saturated or unsaturated fluorocarbons are possible monomers that can be used for this process [96].

### 1.2.1.4 PFASs in fluoropolymer membranes

**Fluoropolymer filter membranes**

Flouropolymers (e.g. PTFE or polyvinylidene fluoride (PVDF)) can be utilized for the production of filter membranes, which belong to products for the category “nonwoven” textiles. These hydrophobic membranes possess good chemical and temperature resistant properties and can be employed for the filtration of aqueous liquids. In order to reach desired wettability, surfactants could be applied [84]. There are various additives that can be used to reach desired wettability. Some applications include production of e.g. sulfonyl fluoride vinyl ether(SFVE) copolymers [97]. Furthermore, PFOA can be used as a processing aid for the production of PTFE [98]. The application of PFASs for the production of fluoropolymers is also explained in a patent of 3MTM Innovative Properties Company [99]´. PTFE membrane filters are for example used in mineral production, coal fired power generation, chemical or pharmaceutical processing, food manufacturing, metal processing and production of semiconductors [100]–[102]. In 2014 Feng et al. investigated the thermolysis products of a membrane exhibiting a PTFE backbone (Nafion®). They detected different PFCA analogues of various chain lengths [103]. Furthermore, membranes like Nafion® might be applied in environmental friendly fuel cells [104], [105].

**Other areas for the use of fluoropolymer membranes**

In addition to fluoropolymer applications for filter membranes, they are also used for a variety of other applications. Possible fields of application are tent or truck canvas. Furthermore, the same product (Durascin® (PFTE) can be used for roofing or facades like explained for ETFE in Subchapter 1.1.1.2) [106].

#### 1.2.1.5 PFASs in maritime applied textiles

Textiles for maritime applications (e.g. sailcloth or boat covers) are directly exposed to rain and waters, whereby they exhibit a peculiar need for water repellent properties and offer an easy entry pathway for applied additives into the environment. To the best of our knowledge there are no analytical investigations of PFASs in maritime textiles, however, vendors and producers of sailcloth and boat covers advertise their products either with implementation of fluorocarbon coatings or Teflon® [107]–[109] or with water and dirt repellent properties [110].

#### 1.2.1.6 PFASs in awning clothing textiles

Textiles that can be used in awnings require similar properties as textiles for maritime applications. Some producers of textiles like boat covers or sailcloth also produce awnings for e.g. sunscreens. Kothoff et al. analysed the PFASs content in textile awning cloth (results of highest concentrations detected listed in Table 7) [90].

Table 7: Monitoring data for PFASs investigated in awning clothing; showing type of PFASs and the concentration rage for investigated samples

| Samples | Detected PFASs [µg/m²] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | PFBA | PFPA | PFHxA | PFOA | PFNA | PFDoA | PFTrA | PFTeA | PFOS |
| Textile awning clothing (n = 1; 2010) [90] | 0.5 | 8.5 | 1.0 | 10.9 | 3.9 | 1.4 | 0.8 | 0.9 | 2.3 |

Perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrA), perfluorotetradecanoic acid (PFTeA)

#### 1.2.1.7 PFASs in workwear textiles

Similar to consumer outdoor clothing, work-wear requires functional properties like water or dirt repellence. Engelbert Strauss GmbH & Co KG, as one of the leading producers of workwear, published a statement that they are trying to stop the implementation of per and polyfluorinated chemicals in their products as a part of their social report 2015. In this report they also mention that from 2015 they only use C6 PFAS derivatives [111]. In addition, fluorocarbon coatings maybe also applied on uniforms (e.g. fire brigade, police, ambulance, military). However, there is no literature available for analytical investigations of PFASs in work-wear. German police uniforms are for example impregnated with a water and dirt repellent layer [112]–[114].

# 2 Application of alkylphenols in non-consumer products with a focus on building material

## 2.1 Alkylphenols in building materials

### 2.1.1 Application fields of alkylphenols in building materials

Alkylphenols (APs) are a class of substances that are generally used as raw material for polymers (phenolic and epoxy resins), and intermediates for the production of AP ethoxylates (APEOs), whereby most references for industrial applications are linked to nonylphenol (NP) and octylphenol (OP) derivatives[115]. Risk assessment and hazards due to environmental exposure to APs are most times related to NP and its derivatives, which are considered to have estrogenic effects [116], [117]. As a consequence, NP and nonylphenol ethoxylates are listed in Annex XVII to REACH, and hence, they shall not be placed on the marked or used as substances or in mixtures in concntrations equal or greater than

0.1% by weight for industrial and institutional cleaning, domestic cleaning, textiles and leather processing, emulsifiers in agricultural teat dips, metal working, manufacturing of pulp and paper, cosmetic products, other personal care products and co-formulations in pesticides and biocides (European Chemicals Agency, REACH, Annex XVII – conditions of restriction). The estrogenic effect of NP and its precursors has been discussed in detail [117]–[119]. As a result, there are numerous studies available on NP concentration in the environment[120]–[123]. The present summary furthermore focuses on 4-tert.-butylphenol (4tBP), 4-tert.-pentylphenol (4tPP), 4-tert.-octylphenol (OP) and the use of APs in industrial applications for (1) paints and lacquers, (2) coatings and (3) glues and adhesives. As a part of the European Union Risk Assessment Report, the European Union stated that direct entrance of 4tBP into the environment is unlikely, but rather as an unreacted portion that is part of products made from/with APs [124]. One example for products that contain APs are phenolic resins. Phenolic resins are discriminated in novolac and resole resins [125]. These resins can be used for a variety of applications such as the pure resign, or in multi-resin systems as cross-linkers for epoxide resins or epoxide lacquers [126], [127]. In order to increase the filler loading for epoxy adhesives, APs (NP) can be used as non-reactive diluents [128]. APs furthermore possibly result as degradation product of APEOs via biotransformation processes [119]. APEOs can be added to paint formulations as non-ionic detergents to provide stability though electrostatic processes and steric hindrance or in order to act as wetting and dispersing agents, allowing pigment agglomerates to break apart [129], [130]. A main application field of phenolic resins is the production of adhesives; however, similar requirements for resins in coatings, base coatings sealers and also paints and lacquers are responsible for the use of APs in these areas. Table 8 shows products for the sector of paint coatings and glues that include APs in their composition. As pictured in Table 8 the majority of products for all application field categories contain 4tBP or 4tBP as a reaction educt for the production of resins, e.g. a formaldehyde reaction product with 1,3-benzenedimethanamine and 4tBP. Safety data sheets of 14 exemplary products also show the implementation of NP.

**Table 8: APs containing products or additives (n = 68) that can be applied in products categories paints, lacquers, coatings, base coatings, glues, adhesives, sealants and resins, corresponding CAS number of used APs, their content in per cent, anonymised producers and product designation**

| Application field | Compound class | CAS | Producer/product acronym | Content range [wt%] |
|---|---|---|---|---|
| Paints and lacquers | 4tBP | 98-54-4 | C09-0801 | < 1-24 |
| | | | C09-0802 | < 1-24 |
| | | | C10-0801 | < 1-24 |
| | | | C11-0801 | < 1-24 |
| | | | C12-0801 | < 1-24 |
| | OP | 1440-66-9 | C11-0801 | < 1-24 |
| | 4tPP | 80-46-6 | C44-0801 | < 1-24 |
| | | | C44-0802 | < 1-24 |
| Coatings and base coatings | 4tBP | 98-54-4 | C13-0901 | < 1-49 |
| | | | C13-0902 | < 1-49 |
| | | | C14-0901 | 25-74 |
| | | | C15-0901 | < 1-24 |
| | | | C10-0901 | < 1-24 |
| | | | C16-0901 | < 1-24 |
| | | | C17-0901 | < 1-24 |
| | | | C18-0901 | < 1-49 |
| | | | C19-0901 | 25-74 |
| | | | C13-0903 | < 1-49 |

| | | | | |
|---|---|---|---|---|
| | | | C01-0901 | < 1-24 |
| | | | C01-0902 | < 1-24 |
| | | | C20-0901 | < 1-24 |
| | | | C21-0901 | < 1-24 |
| | | | C21-0902 | < 1-24 |
| | | | C21-0903 | < 1-49 |
| | | | C21-0904 | < 1-24 |
| | | | C22-0901 | < 1-49 |
| | | | C23-0901 | < 1-24 |
| | | | C45-0901 | < 1-24 |
| | NP | 25154-52-3 | C15-0901 | < 1-24 |
| | | | C10-0901 | < 1-24 |
| | | | C16-0901 | < 1-24 |
| | | | C19-0901 | < 1-24 |
| | | | C01-0901 | < 1-24 |
| | | | C23-0901 | < 1-24 |
| | | | C24-0901 | < 1-49 |
| | | | C24-0902 | 25-74 |
| | OP | | C45-0901 | < 1-24 |
| | Formaldehyde reaction product with 1,3-benzendimethanamine and 4tBP | 158800-93-2 | C21-0901 | < 1-24 |
| | | | C21-0903 | < 1-24 |
| | | | C24-0901 | < 1-24 |
| | Formaldehyde, polymer with 4-(1,1- dimethylethyl)phenol, magnesium oxide complex | 68037-42-3 | C01-0903 | < 1-24 |
| Glues, adhesives, sealants and resins | 4tBP | 98-54-4 | C01-1001 | < 1-24 |
| | | | C16-1001 | < 1-24 |
| | | | C25-1001 | < 1-24 |
| | | | C16-1002 | < 1-24 |
| | | | C21-1001 | < 1-24 |
| | | | C13-1001 | < 1-24 |
| | | | C26-1001 | < 1-24 |
| | | | C27-1001 | < 1-24 |
| | | | C28-1001 | < 1-49 |
| | | | C29-1001 | < 1-49 |
| | | | C30-1001 | < 1-49 |
| | | | C27-1002 | < 1-24 |
| | | | C13-1002 | < 1-24 |
| | | | C31-1001 | < 1-24 |
| | | | C32-1001 | < 1-24 |

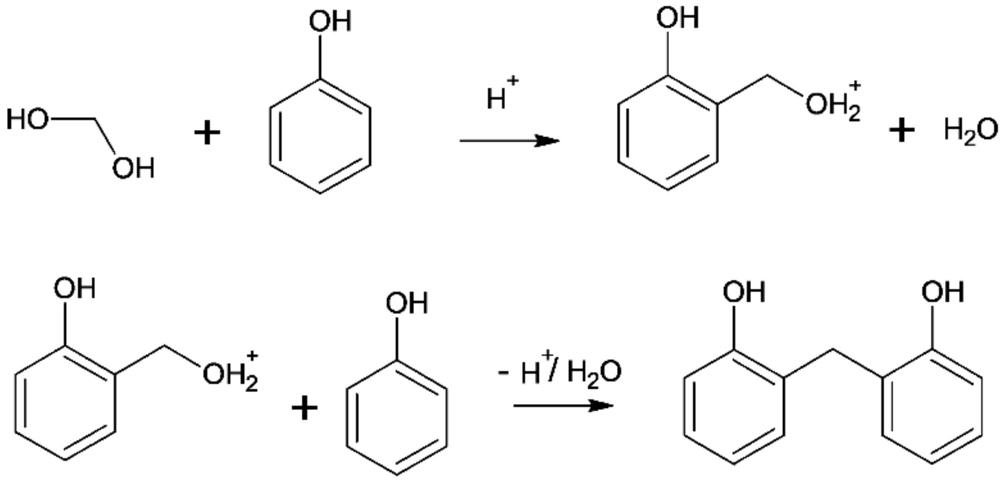
| | | | | |
|---|---|---|---|---|
| | | | C33-1001 | < 1-24 |
| | | | C34-1001 | < 1-24 |
| | | | C35-1001 | 25-74 |
| | | | C16-1003 | < 1-24 |
| | | | C16-1004 | < 1-24 |
| | | | C32-1002 | < 1-24 |
| | | | C36-1001 | < 1-24 |
| | | | C36-1002 | < 1-24 |
| | | | C37-1001 | < 1-24 |
| | | | C16-1005 | < 1-24 |
| | | | C38-1001 | < 1-24 |
| | | | C39-1001 | < 1-24 |
| | | | C21-1002 | < 1-24 |
| | | | C21-1003 | < 1-24 |
| | | | C40-1001 | < 1-24 |
| | | | C21-1004 | < 1-24 |
| | | | C41-1001 | < 1-24 |
| | | | C42-1001 | < 1-24 |
| | | | C43-1001 | 25-74 |
| | NP | 25154-52-3 | C01-1001 | < 1-24 |
| | | | C25-1001 | < 1-24 |
| | | | C16-1005 | < 1-24 |
| | | | C39-1001 | < 1-24 |
| | | | C40-1001 | < 1-24 |
| | | | C43-1001 | < 1-24 |
| | Formaldehyde reaction product with 1,3-benzendimethanamine and 4tBP | 158800-93-2 | C28-1001 | 25-74 |
| | | | C30-1001 | 25-74 |
| | oligomeric reaction products with 4-tert-butylphenol, 4-nonylphenol, m-phenylenebis (methylamine) and trimethylhexane-1,6-diamine | 161278-27-9 | C43-1001 | < 1-49 |

[131]–[198]

### 2.1.2 Production of phenolic resins

Phenolic resins exist since the 1900s and they are typically obtained by a condensation reaction of phenols with formaldehyde, whereby the type of used phenol depends on the desired backbone (e.g. phenol for novolac resin). Figure 2 shows the general reaction scheme for the condensation of phenolic resins. Depending on the planned application and thus, required characteristic of the polymer, the ratio of formaldehyde to phenolic monomers can vary. APs with C4-C6 chains are generally chosen in order to obtain oil-soluble phenolic resins [199].

Figure 2: General reaction scheme of phenolic resins; adopted from [200]



### 2.1.3 Classification of phenolic resins

As mentioned in chapter 2.1.1 phenolic resins are discriminated as novolac or resole resins, which generally refers to a different substitution of the phenolic monomers.

#### 2.1.3.1 Novolac resins

Novolac resins are obtained by the reaction of a phenol with formaldehyde under acid catalysis. Substitution can occur in ortho or para position and formation of cross linkage occurs if one phenol gets substituted twice. Since production of novolac resins are typically performed with excess of phenol, which cannot further react if formaldehyde cross linkers are consumed, this may leads to unreacted phenol within the resin. These resins are so called “two-stage” resins, which means they need an additional curing agent (e.g. hexamethylenetetramine) [199], [200].

#### 2.1.3.2 Resole resins

Resole resins are obtained under basic catalysis of phenols and formaldehyde, whereby the phenolic educt might be phenolic or a hydroxymethyl phenol. This leads to the formation of ortho-ortho phenol oligomers, a dibenzyl ether (formation of ethylene bridge) or an oligomer exhibiting a longer chain methylol phenolic compound. Resol resins are produced with an excess of formaldehyde, which leads to a sufficient number of methylol and dibenzyl ethers reaming reactive to cure the resin. Therefore, resol resins do not need additional curing agents and are referred to as so-called “single-stage” products [199], [200].

### 2.1.4 Production of epoxy resins under the application of alkylphenols

Alkylphenols can be used for the production of epoxy resins. Literature indicates use of alkyphenols as reactive dillutants for the production of epoxy resins [201]-[203], which can be used in order to enhance processing properties of the resin.

### 2.1.5 Analytic investigation of alkylphenols

Investigation of APs in environment, wastewater (WW) and sewage sludge has been performed to a high extend. Table 9 gives an overview of some analytical results for AP residues in environment [204]–[207]. To the best of our knowledge analytic investigations of free phenolic compounds in resins used for paints, adhesives or coatings have not been performed. Furthermore, only few studies dealt with environmental levels of 4tBP or 4tPP.

**Table 9: Monitoring data for APs investigated in sediment, water, wastewater treatment plants (WWTPs) and sewage sludge; showing type of AP and the concentration rage for investigated samples**

| Samples | Detected AP | | | |
|---|---|---|---|---|
| [204] | NP | | OP | |
| Sediment | 0.63-1.70 mg/g | | - | |
| Maritime sediments | 0.0001-0.017 µg/g | | <LOD-0.002 µg/g | |
| Municipal WW influent | <LOD-23 µg/L | | <LOD-0.1 µg/L | |
| Municipal WW effluent | <LOD-1.0 µg/L | | <LOD-0.2 µg/L | |
| Municipal Sewage sludge | <LOD-125 mg/g | | <LOD-2 mg/g | |
| Industrial WW influent | <LOD-400 µg/L | | <LOD-100 µg/L | |
| Industrial WW effluent | <LOD-1.2 µg/L | | <LOD-0.13 µg/L | |
| Industrial WW sewage sludge | <LOD-2500 mg/g | | <LOD-24 mg/g | |
| [205] | NP | | OP | |
| Water from a sewage-impacted urban estuary | 201 ng/L | | 3.27 ng/L | |
| Sediment | 846 ng/g | | 8.11 ng/g | |
| Untreated wastewater [209] | NP | OP | 4tBP | 4tPP |
| | 25-33 µg/L | 0.20-0.74 µg/L | 0.042-0.1 µg/L | 0.029-0.19 µg/L |
| WWTP Effluent (n = 4) [122] | NP | | OP | |
| | 0.37-2.5 µg/L | | <LOD-0.014 µg/L | |

# 3 Deviations from original sampling plan

Deviation of sampling procedures and amount of samples was coordinated with UBA. As stated throughout the document, number of samples and sampling mode were altered due to different factors. This chapter summarizes all alternations.

## 3.1 Deviations regarding sampling for PFAS analysis

Originally, analysis of 20 samples for building materials and 20 samples for industrial textiles was planned. In order to better illustrate entrance pathways through different product categories and draw a more complete picture of occurrence and use of PFASs in those categories, a total of 23 building material and 28 industrial fabric samples was analyzed. We believe that the extension of 15% for building materials and 40% for industrial textiles was necessary to (1) enable investigation of more products of one category and (2) provide a broader overview of different sample categories and thus, benefit the elucidation of entrance pathways.

## 3.2 Deviation regarding sampling for alkylphenol analysis

Instead of 45 stream samples (five samplings of nine streams over the course of one year) that were included in the original sampling plan, only three samples of each stream were collected in 2017. Since few to no SCAPs were detected in those samples, the sampling plan was increased by 50 additional streams, whereby 24 of them were sampled in 2017, 24 in 2018 and 2 in both years (leading to a total of 766 samples). Also, sampling of WWTPs was altered. Instead of only sampling WWTP effluents, influent and effluent of three WWTPs were sampled. Furthermore, biotransformation experiments of 4tBP and 4tPP were additionally performed. Both, sampling of WWTP influent and effluent, as well as biotransformation experiments, were carried out in order to investigate biodegradation of these substances. Furthermore, the corresponding stream of one of the WWTPs that was investigated was sampled at three different sites in order to complete this data, which proved to provide valuable information. Last but not least, the number of analyzed building materials was reduced to 18 instead of originally planned 24 samples, since the obtained results of investigated samples already demonstrated extensive use of APs in these materials.

# 4 Materials and methods

## 4.1 PFASs in building materials and industrial used fabrics

Analytical methods were based on DIN CEN/TS 15968:2010-11.

### 4.1.1 Samples

Samples were collected in the time between October 2016 and August 2017 and analyzed as soon as possible. Upon analyses, samples were stored as indicated by the supplier. Table 10 and Table 11 show collected samples, sample category and subcategory, sample-IDs, application field and additional remarks for building materials and industrial textiles, respectively.

Table 10: List of investigated building materials; showing individual categories, subcategories, sample IDs, application field and additional remarks

| Category | Subcategory | Sample-ID | Application | Remarks |
|---|---|---|---|---|
| Coatings, lacquers, stains and paints | Coating | PFAS-BM01 | Stone, walls, shoos, apparel, etc. | Consists of top (PFAS-BM01 A) and bottom (PFAS-BM01 B) coat |
| | Coating | PFAS-BM02 | Metal, concrete, wood, plastic, awnings, etc. | Consists of top (PFAS-BM02 A) and bottom (PFAS-BM02 B) coat |
| | Coating | PFAS-BM03 | Stone and concrete | - |
| | Coating | PFAS-BM04 | Stone, concrete and cobblestone | - |
| | Paint | PFAS-BM05 | Facade | - |
| | Paint | PFAS-BM06 | Facade | - |
| | Paint | PFAS-BM07 | Facade | - |
| | Lacquer | PFAS-BM08 | Wood | - |
| | Lacquer | PFAS-BM09 | Metal | - |
| | Stain | PFAS-BM10 | Wood | - |
| Foils and composite materials | Foil | PFAS-BM11 | Front siding for solar panels | ETFE |
| | Roofing | PFAS-BM12 | Roofing material for flat roofs | Ethylene propylene diene monomer (EPDM) rubber |
| | Roofing | PFAS-BM13 | Roofing material for flat roofs | Ethylene propylene diene monomer (EPDM) rubber |
| | OSB wood | PFAS-BM14 | Sheeting, sidings and other applications | - |
| | Foil | PFAS-BM15 | Façade material/glass substitute | ETFE |
| | Foil | PFAS-BM16 | Façade material/glass substitute | ETFE |
| | Foil | PFAS-BM17 | Fiber glass material for façade or textile constructions | PTFE |
| | Foil | PFAS-BM18 | Fiber glass material for façade or textile constructions | PTFE |
| | Foil | PFAS-BM19 | Packaging of e.g. building materials | PE |
| | Foil | PFAS-BM20 | Packaging of e.g. building materials | PE |
| Sealants and glues | Sealant | PFAS-BM22 | Universal sealant | - |
| | Sealant | PFAS-BM23 | Sealant for outdoor applications | - |
| | Glue | PFAS-BM24 | Wood | - |

Table 11: List of investigated industrial textiles; showing individual categories, subcategories, sample IDs, application field and additional remarks

| Category | Subcategory | Sample-ID | Application | Remarks |
|---|---|---|---|---|
| Seat covers | furniture | PFAS-IT01 | Furniture upholstering | - |
| | Public transport | PFAS-IT02 | Train seat upholstering | - |
| | Car | PFAS-IT03 | Car seat upholstering | - |
| | Car | PFAS-IT04 | Car seat upholstering | - |
| | Car | PFAS-IT05 | Car seat upholstering | - |
| | Public transport | PFAS-IT23 | Bus/train seat upholstering | - |
| | Public transport | PFAS-IT24 | Bus/train seat upholstering | - |
| | Public transport | PFAS-IT25 | Bus/train seat upholstering | - |
| | Public transport | PFAS-IT26 | Bus/train seat upholstering | - |
| | Public transport | PFAS-IT27 | Bus/train seat upholstering | - |
| | Public transport | PFAS-IT28 | Bus/train seat upholstering | - |
| Covers for truck trailers | Tarpaulin | PFAS-IT06 | Tarpaulin for truck trailers | Polyvinyl chloride (PVC) |
| | Tarpaulin | PFAS-IT07 | Tarpaulin for truck trailers | PVC |
| | Tarpaulin | PFAS-IT08 | Tarpaulin for truck trailers | PVC |
| Covers for maritime applications | Maritime covers | PFAS-IT09 | Boat covers, seats, canopies and other applications | Acrylic material; polyurethane coated |
| | Maritime covers | PFAS-IT10 | Seat cover, console cover or bimini top | Polyester; polyurethane coated |
| | Maritime covers | PFAS-IT11 | Seat cover, console cover or bimini top | Polyester; polyurethane coated |
| | Maritime covers | PFAS-IT12 | Boat covers, bimini top, awning and other applications | Polyester fabric |
| | Maritime covers | PFAS-IT13 | Boat covers, bimini top, awning and other applications | Polyester fabric |
| Awnings and tarpaulins | Tarpaulin | PFAS-IT14 | Carnival marquee, party tent | PVC |

| | | | |
|---|---|---|---|
| Tarpaulin | PFAS-IT15 | Carnival marquee, party tent | PVC |
| Tarpaulin | PFAS-IT16 | Carnival marquee, party tent | Polyvinyliden fluoride |
| Tarpaulin | PFAS-IT17 | Carnival marquee, party tent | PVC; coated |
| Awning | PFAS-IT18 | Marquee awning | Acryl; waterproof finish |
| Awning | PFAS-IT19 | Marquee awning | Acryl; waterproof finish |
| Awning | PFAS-IT20 | Marquee awning | Acrylic fiebre |
| Awning | PFAS-IT21 | Marquee awning | Acryl |
| Awning | PFAS-IT22 | Marquee awning | Acrylic fiber; coating for better cleaning behavior |

### 4.1.2 Standards and materials

Table 12 shows an overview of monitored PFASs and quantification limits. Depending on sample matrices, LOQs were adjusted (see appendix Table 68). Standards of volatile PFASs and isotopically labeled standards were purchased from Wellington Laboratories INC (Canada), whereas standards of FTOHs were purchased from Neochema GmbH (Germany). All standards were purchased as certificated solutions of single compounds (50 µg mL$^{-1}$) or as mixtures (2 µg L$^{-1}$). Working solutions of all compounds were prepared at 500 ng mL$^{-1}$ and stored at 4 °C

**Table 12: List of investigated PFASs, their abbreviations and quantification limits**

| Substance | Abbreviation | LOQ |
|---|---|---|
| Perfluorobutanoic acid | PFBA | < 2 µg/kg |
| Perfluorobutane sulfonic acid | PFBS | < 2 µg/kg |
| Perfluoropentanoic acid | PFPeA | < 2 µg/kg |
| Perfluoropentane sulfonic acid | PFPeS | < 2 µg/kg |
| Perfluorohexanoic acid | PFHxA | < 2 µg/kg |
| Perfluorohexane sulfonic acid | PFHxS | < 2 µg/kg |
| Perfluoroheptanoic acid | PFHpA | < 2 µg/kg |
| Perfluorohaptane sulfonic acid | PFHpS | < 2 µg/kg |
| Perfluorooctanoic acid | PFOA | < 2 µg/kg |
| Perfluorooctane sulfonic acid | PFOS | < 2 µg/kg |
| Perfluorooctanesulfonamide | PFOSA | < 2 µg/kg |
| Perfluorononanoic acid | PFNA | < 2 µg/kg |
| Perfluorodecanoic acid | PFDA | < 2 µg/kg |
| Perfluorodecane sulfonic acid | PFDS | < 2 µg/kg |
| Perfluoroundecanoic acid | PFUnDA | < 2 µg/kg |
| Perfluorododecanoic acid | PFDoDA | < 2 µg/kg |
| Perfluorododecane sulfonic acid | PFDoDS | < 2 µg/kg |
| Perfluorotridecanoic acid | PFTrDA | < 2 µg/kg |
| Perfluorotetradecanoic acid | PFTeDA | < 2 µg/kg |
| 7H-Perfluoro heptanoic acid | 7HPFHpA | < 2 µg/kg |
| 1H,1H,2H,2H-Perfluorhexane sulfonic acid | 4:2 FTS | < 2 µg/kg |
| 1H,1H,2H,2H-Perfluoroctane sulfonic acid | 6:2 FTS | < 2 µg/kg |
| 1H,1H,2H,2H-Perfluorodecane sulfonic acid | 8:2 FTS | < 2 µg/kg |
| 1H,1H,2H,2H-Perfluorodecanoic acid | 8:2 FTCA | < 2 µg/kg |
| 1H,1H,2H,2H,3H,3H-Perfluoroundecanoic acid | 8:3 FTCA | < 2 µg/kg |
| 1H,1H,2H,2H-Perfluoroctanol | 6:2 FTOH | < 0.04 µg/g |
| 1H,1H,2H,2H-Perfluorodecanol | 8:2 FTOH | < 0.04 µg/g |
| 1H,1H,2H,2H-Perfluorododecanol | 10:2 FTOH | < 0.04 µg/g |

Table 13 shows a list of of used reference materials, retention times, transitions and corresponding internal standards. Standard mixtures were used for calibrations and recovery experiments.

**Table 13: List of investigated analytes and corresponding internal standards, showing their transitions and $t_R$**

| Analyte Abbr. | MRM | | $t_R$ [min] | IS Abbr. | $MRM_{IS}$ | | $t_R$ [min] |
|---|---|---|---|---|---|---|---|
| | Q1 | Q3 | | | Q1 | Q3 | |
| PFBA | 213 | 169 | 1.6 | $^{13}C_4$ PFBA | 217 | 172 | 1.6 |
| PFBS | 299 | 80<br>99 | 3.5 | $^{13}C_3$ PFBS | 302 | 80 | 3.5 |
| PFPeA | 263 | 219 | 3.2 | $^{13}C_5$ PFPeA | 268 | 223 | 3.2 |
| PFPeS | 349 | 80<br>99 | 4.4 | $^{18}O_2$ PFHxS | 403 | 84 | 5.1 |
| PFHxA | 313 | 269<br>119 | 4.3 | $^{13}C_2$PFHxA | 315 | 270 | 4.3 |
| PFHxS | 399 | 80<br>99 | 5.1 | $^{18}O_2$ PFHxS | 403 | 84 | 5.1 |
| PFHpA | 363 | 319<br>169 | 5.1 | $^{12}C_4$PFHpA | 367 | 322 | 5.1 |
| PFHpS | 449 | 80<br>99 | 5.7 | $^{18}O_2$ PFHxS | 403 | 84 | 5.1 |
| PFOA | 413 | 369<br>169 | 5.6 | $^{13}C_4$PFOA | 417 | 372 | 5.6 |
| PFOS | 499 | 80<br>99 | 6.1 | $^{13}C_4$PFOS | 503 | 80 | 6.1 |
| PFOSA | 498 | 87<br>169 | 6.9 | $^{13}C_8$ PFOSA | 506 | 78 | 6.9 |
| PFNA | 463 | 419<br>219 | 6.1 | $^{13}C_5$ PFNA | 468 | 423 | 6.1 |
| PFDA | 513 | 469<br>219 | 6.5 | $^{13}C_2$ MPFDA | 515 | 470 | 6.5 |
| PFDS | 599 | 80<br>99 | 6.9 | $^{13}C_2$ MPFDA | 515 | 470 | 6.5 |
| PFUnDA | 563 | 519<br>219 | 6.9 | $^{13}C_2$ PFUnDA | 565 | 520 | 6.9 |
| PFDoDA | 613 | 569<br>319 | 7.3 | $^{13}C_2$ PFDoDA | 615 | 570 | 7.3 |
| PFDoDS | 699 | 80<br>99 | 7.8 | $^{13}C_2$ PFDoDA | 615 | 570 | 7.3 |
| PFTrDA | 663 | 619<br>319 | 7.9 | $^{13}C_2$ PFDoDA | 615 | 570 | 7.3 |
| PFTeDA | 713 | 669<br>319 | 8.5 | $^{13}C_2$ PFTeDA | 715 | 670 | 8.5 |
| 7HPFHpA | 345 | 281 | 3.9 | $^{13}C_5$ PFPeA | 268 | 223 | 3.2 |
| PF37DMOA | 469 | 269<br>219 | 6.3 | $^{13}C_2$ MPFDA | 515 | 470 | 6.5 |
| 4:2 FTS | 327 | 307<br>81 | 4.2 | $^{13}C_2$ H4PFHxS | 329 | 81 | 4.2 |
| 6:2 FTS | 427 | 407<br>81 | 5.6 | $^{13}C_2$ H4PFOS | 529 | 81 | 5.6 |
| 8:2 FTS | 527 | 507<br>81 | 6.5 | $^{13}C_2$ H4PFDS | 459 | 81 | 6.5 |
| 8:2 FTCA | 457 | 393 | 6.3 | $^{13}C_2$ H2PFDA | 459 | 394 | 6.3 |
| 8:3 FTCA | 491 | 387 | 6.7 | $^{13}C_2$ H2PFDA | 615 | 570 | 6.3 |
| 6:2 FTOH | 423 | 59 | 4.4 | - | - | - | - |
| 8:2 FTOH | 523 | 59 | 4.9 | - | - | - | - |
| 10:2 FTOH | 623 | 59 | 5.2 | - | - | - | - |

### 4.1.3 Sample preparation

Two different sample preparation techniques were used for most samples. Depending on the sample, either liquid-solid extraction (LSE) or solid phase extraction (SPE) were performed. In order to gather more information about different extract-profiles and thus, derive possible entry pathways, LSE was performed with water as well as methanol. FTOHs were directly measured in resulting methanol extracts, whereas further enrichment was performed for non-volatile components. Prior to extraction, solid samples were cut into small pieces and weight. If samples were only available as liquids, they were either dried prior to weighing (e.g. paints, adhesives, etc.) or enriched via SPE. In order to do so, samples were applied on aluminum weighing pans, dried at room temperature, scraped of and further treated similar to solid samples. Samples that were only available in pressurized containers were frozen with liquid nitrogen, center-drilled so that the fuel gas could evaporate during thawing and further treated similar to liquids.

### 4.1.4 Extraction

Solid samples were extracted via LSE using water as well as methanol. Samples were weight (1 g) into a 50 mL polypropylene (PP) tube, 20 mL water or methanol were added and extraction was performed for two hours under constant sonication at 60 °C. Prior to extraction with methanol, internal standard (IS) was added (50 µL of 100 ng mL$^{-1}$). After cooling to room temperature (RT), samples were further processed. Methanol extracts were filtered using a syringe filter (PTFE, 0.2 µm, 13 mm and 25 mm, respectively) and separated into 3 fractions à 15 mL for PFAA determination. Two fractions were spared for quality assurance, whereas the third fraction was evaporated to dryness (under a stream of $N_2$ at 40 °C). Afterwards, dry residues were reconstituted with 250 mL of a methanol-water mixture (1/1; v/v), vortexed and analyzed via HPLC-MS/MS.

Extractions for FTOH determination were performed in the same manner as previously described, however, two aliquots à 500 µL were directly withdrawn after extraction without further enrichment and analyzed using HPLC-MS/MS.

Aqueous extracts as well as liquid samples were enriched using SPE cartridges (Phenomenex Strata-X-AW, 60 mg, 3 mL) were conditioned using 2 mL 0.1% NH3 in MeOH, 2 mL MeOH and 2 ml ultrapure water. The pH values of all samples were adjusted to 6-8. Samples were spiked with internal standard (IS) at 0.25 ng L-1 (50 µL of 100 ng ml-1 in MeOH). Cartridges were loaded with 60 ml of aqueous products and complete water extracts, respectively. Samples were eluted into 15 ml PP centrifuge tubes using 0.1% $NH_3$ in MeOH (2x1 ml), evaporated to dryness under a constant stream of nitrogen gas at 40 °C and reconstituted in 200 µL water/MeOH (1/1; v/v), vortexed and analyzed using HPLC-MS/MS.

### 4.1.5 Quality assurance

Samples were spiked at known concentrations of PFASs and analyzed for quality assurance. Prior to SPE, aqueous samples were spiked at 0.01 µg L-1 (60 µL of 10 ng ml-1 in MeOH) and 0.1 ng L-1 (60 µL of 100 ng ml-1 in MeOH). Water extracts were spiked at 0.03 µg L-1 (60 µL of 10 ng ml-1 in MeOH) and 0.3 µg L-1 (60 µL of 100 ng ml-1 in MeOH), respectively. Spiked water extracts and aqueous samples were proceeded as stated in section 4.1.4. One of the three fractions from MeOH extracts was spiked with PFAAs at 2 ng g-1 dry sample (50 µL of 10 ng ml-1 in MeOH) and one fraction was spiked at 8 ng g-1 dry sample (200 µL of 10 ng ml-1 in MeOH). Afterwards, these fractions were proceeded as stated in section 4.1.4. Finally, another 500 µL aliquot of MeOH extracts for the FTOH determination was partitioned and spiked at 2 ng mL-1 (10 µL, 100 ng mL-1 FTOH solution in MeOH) and 10 ng mL-1 (10 µL, 500 ng mL-1), respectively. All non-volatile PFASs were calculated against isotopically labeled internal standards. Extra care was used for the analysis of FTOHs, in order to avoid false positive results thereof, since there is only one MRM transition available and they are detection as [M+Ac]-, whereby all ions having the same nominal mass that form acetate adducts will generate a signal. Thus, FTOH data was only reported when baseline separation was observed and good recovery rates were obtained. Chromatograms with examples for FTOHs that were not reported are appended to this report. Further explanations are available in their captions.

### 4.1.6 HPLC-MS/MS method for the analysis of PFASs in building materials and industrial used textiles

Quantitative data was recorded with three different UPLC-MS/MS systems. All used mass analyzers were triple quadrupole mass spectrometer (QqQ-MS). Two UPLC-MS/MS systems consisted of an Agilent 1290 infinity HPLC (CTC PAL autosampler) either coupled with a Triple Quad 5500 or Triple Quad 6500 (AB Sciex LLC, Framingham, MA, USA, software MultiQuant version 3.0.3, AB SCIEX). The third UPLC-MS/MS system was a Waters Acquity UPLC with a Acquity UPLC Autosampler and a Aquity UPLC Binary Solvent Pump, coupled to a QqQ-MS (Waters Xevo TQ MS, software MassLynx version 4.1, Waters). Ionization was performed with an electrospray ionization (ESI) source in negative mode (-4.5 kV). Separation was carried out on a Waters AQUITY UPLC BEH T3 reversed phase (RP) column with 1.7 µm particle size and dimensions of 2.1x100 mm at 25 °C column oven temperature and a flow rate of 300 µL/min. Used instruments, HPLC settings and gradient are shown in Table 14 to

Table 16.

**Table 14: List of used instruments for analysis of PFASs in building materials and industrially used textiles; showing autosampler, UPLC and mass spectrometer**

| Autosampler | Chromatographic system | Mass analyzer |
|---|---|---|
| CTC PAL | Agilent 1290 Infinity | AB Sciex Triple Quad 5500 |
| CTC PAL | Agilent 1290 Infinity | AB Sciex Triple Quad 6500 |
| Acquity UPLC | Acquity UPLC Binary Solve | Waters Xevo TQ MS |

**Table 15: List of method settings, used separation column and mobile phases for analysis of PFASs in building materials and industrial used textiles**

| HPLC setting | Value |
|---|---|
| Injection volume [µL] | 10 |
| Column oven temperature [°C] | 25 |
| Column | Waters AQUITY UPLC BEH T3 1.7 µm, 2.1x100 mm |
| Mobile phase A | $H_2O$ LC-MS grade + 20 mMol Ammonium acetate |
| Mobile phase B | MeOH LC-MS grade + 20 mMol Ammonium acetate |

**Table 16: Used gradient program for analysis of PFAS in building materials and industrial used textiles**

| Step | Time [min] | Flow rate [µL/min] | Mobile phase A [%] | Mobile phase B [%] |
|---:|---:|---:|---:|---:|
| 0 | 0.0 | 300 | 90 | 10 |
| 1 | 1.5 | 300 | 90 | 10 |
| 2 | 2.1 | 300 | 35 | 65 |
| 3 | 4.6 | 300 | 27 | 73 |
| 4 | 6.5 | 300 | 27 | 73 |
| 5 | 8.2 | 300 | 0 | 100 |
| 6 | 10.7 | 300 | 0 | 100 |
| 7 | 10.9 | 300 | 90 | 10 |
| 8 | 12.9 | 300 | 90 | 10 |

## 4.2 Alkylphenols

### 4.2.1 Samples

Stream water and WWTP influent/effluent samples were collected in 2017 and 2018 (sampling date see Table 50,

Table 55-Table 58 and Table 59-Table 61) and analyzed as soon as possible. Stream samples of originally planned sampling as well as WW effluent samples of WWTP 4 were collected as grab samples. Other stream and WWTP samples (additionally sampled streams) were collected as 24 h composite samples. Upon analysis, samples were stored in the dark at 4 °C. Table 17 and Table 18 show sampling dates of WWTPs.

**Table 17: Sampling dates for WWTPs 1-3; influent and effluent were sampled**

| WWTP | Sampling 1 | Sampling 2 | Sampling 3 | Sampling 4 | Sampling 5 |
|---|---|---|---|---|---|
| 1 | 18.12.17 | 04.01.18 | 25.01.18 | 22.02.18 | 01.03.18 |
| 2 | 18.12.17 | 08.01.18 | 26.01.18 | 09.02.18 | 23.03.18 |
| 3 | 12.06.17 | n.s. | n.s. | n.s. | n.s. |

**Table 18: Sampling dates for WWTP 4; only effluent was sampled**

| WWTP | Sampling 1 | Sampling 2 | Sampling 3 | Sampling 4 | Sampling 5 |
|---|---|---|---|---|---|
| 4 | 14.03.17 | 08.09.17 | 28.09.17 | 17.12.17 | 02.02.18 |

Building material samples were collected between July 2017 and July 2018 and analyzed in July/August 2018. Upon analysis, samples were stored as indicated by the producer. Table 19 shows a list of collected building material samples for the analysis of APs.

**Table 19: List of investigated building materials for the analysis of APs; showing category, sample-ID and remarks/application field**

| Category | Sample-ID | Remarks/application field. |
|---|---|---|
| Paint and lacquer | AP-PL01 | Lacquer for boats |
| | AP-PL02 | Wood primer |
| Coating | AP-C01 | Multipurpose epoxy resin |
| | AP-C02 | Bonding course for floor finish |
| | AP-C03 | General building coating/plastic; component B |
| | AP-C04 | Removable coating for soldering |
| | AP-C05 | Multipurpose epoxide resin; component B |
| | AP-C06 | Multipurpose epoxide resin; component B |
| | AP-C07 | General primer, bonding course for floor finish, flaw repair resin; component B |
| | AP-C08 | Coating for filling flaws in concrete; component B |
| | AP-C09 | Bonding course for concreate repair; component B |
| | AP-C10 | General coating, bonding course or sealing for floors; component B |
| Glue and adhesives | AP-GA01 | Hardener for epoxy resin |
| | AP-GA02 | - |
| | AP-GA03 | Hardener for epoxy resin |
| | AP-GA04 | - |
| | AP-GA05 | General epoxy resin/glue; component B |
| | AP-GA06 | General epoxy resin/glue; component B |

### 4.2.2 Standard and materials for the analysis of water samples

Table 20 shows an overview of monitored APs and quantification limits in stream water and WWTP influent/effluent samples. Depending on sample matrices and sample preparation, LOQs were adjusted. Standards of NP, OP and isotopically labeled IS (bisphenol A-d16 (BPA-d16)) were purchased from Neochema GmbH (Germany), whereas standards of 4tBP and 4tPP were purchased from Sigma Aldrich (Germany) in a purity of 99%. NP and OP were purchased as certificated solutions of mixed standards (10 µg/mL) and IS was purchased as a certificated solution of the single compound (100 µg/mL). 4tBP and 4tPP were purchased as solid standard materials and stock solutions were prepared. Working solutions of all compounds were prepared at 1 or 10 ng/µL in MeOH and stored at -30°C. Table 21 shows used transitions and assignment of IS. Used solvents were purchased from Carl Roth GmbH & Co KG (Germany) and HPLC-MS grade. Ultrapure water was obtained from a Merck Millipore Simplicity UV water purification system (Merck KGaA, Germany). Na-benzoate and Na-azide were purchased from Carl Roth GmbH & CO KG (Germany) or Sigma Aldrich (Germany), respectively, with a purity of ≥99% or 99.5% respectively.

**Table 20: Quantification limits of APs in different aqueous matrices**

| | | Quantification limit [µg/L] | | | |
|---|---|---|---|---|---|
| Compound | CAS-Nr. | Originally planned sampling of streams | Sampling of 50 additional streams | WWTP influent | WWTP effluent |
| 4tBP | 98-54-4 | 0.005 | 0.03 | 0.03 | 0.06 |
| 4tPP | 80-46-6 | 0.01 | 0.03 | 0.06 | 0.10 |
| OP | 140-66-9 | 0.005 | 0.03 | 0.03 | 0.06 |
| NP | 104-40-5 | n.a. | 0.03 | 0.03 | 0.06 |

n.a. not analyzed

**Table 21: Monitored APs with corresponding IS; showing m/z of precursor ion, m/z of product ion and $t_R$**

| Compound | m/z precursor ion | m/z product ion | $t_R$ [min] | IS | IS m/z precursor ion | IS m/z product ion | IS $t_R$ [min] |
|---|---|---|---|---|---|---|---|
| 4tBP | 149 | 133 | 3.5 | BPA-d16 | 241 | 223<br>142 | 2.86 |
| 4tPP | 163 | 147 | 4.1 | BPA-d16 | 241 | 223<br>142 | 2.86 |
| OP | 205 | 133<br>134 | 5.3 | BPA-d16 | 241 | 223<br>142 | 2.86 |
| NP | 219 | 133<br>117 | 5.9 | BPA-d16 | 241 | 223<br>142 | 2.86 |

### 4.2.3 Standards and materials for the analysis of building material samples

Table 22 shows an overview of monitored APs and quantification limits. Solid standard materials were purchased from Sigma Aldrich (Germany) or Dr. Ehrenstorfer (Germany). Stock solutions were prepared in methanol and stored at -18 °C. Working solutions of all compounds were prepared at 10 µg/mL in mixture of methanol:water (1:1; v:v) and stored at -18 °C.

**Table 22: List of used standard materials, their suppliers, concentration of stock solutions as well as method quantification limits (LOQ) and method detection limits (LOD) for the analysis of APs in building materials**

| Substance | CAS-Nr. | Supplier | Stock solution [mg/ml] | LOQ | LOQ | LOD | LOD |
|---|---|---|---|---|---|---|---|
| 4-tert-Butylphenol | 98-54-4 | Sigma Aldrich (Germany) | 0.9997 | 1 µg/ml | 1 g/kg | 0.25 µg/mL | 0.25 µg/kg |
| 4-tert-Amylphenol | 80-46-6 | Sigma Aldrich (Germany) | 1.0002 | 1 µg/ml | 1 g/kg | 0.25 µg/mL | 0.25 µg/kg |
| 4-tert-Octylphenol | 140-66-9 | Dr. Ehrenstorfer (Germany) | 4.9861 | 1 µg/ml | 1 g/kg | 0.25 µg/mL | 0.25 µg/kg |
| 4-Nonylphenol | 104-40-5 | Dr. Ehrenstorfer (Germany) | 1.8476 | 1 µg/ml | 1 g/kg | 0.25 µg/mL | 0.25 µg/kg |
| Nonylphenol | 25154-52-3 | Dr. Ehrenstorfer (Germany) | 4.86 | 1 µg/ml | 1 g/kg | 0.25 µg/mL | 0.25 µg/kg |

A technical nonylphenol standard (CAS-Nr. 25154-52-3) was used in addition to the 4-nonylphenol standard (CAS-Nr. 104-40-5). This was done in order to test if different structural isomers can be observed with baseline separation. However, since observed signals did not match the standard of pure 4-nonylphenol, quantification was performed against the technical mixture (CAS-Nr. 25154-52-3).

## 4.2.4 Sample preparation of stream water and WWTP samples

Samples were stored at 4 °C upon analysis. Prior to sample enrichment, all stream water samples and WWTP influent/effluent samples were filtered through a vacuum-aided glass fiber filters (0.45 µm 55 mm diameter). Samples were further proceeded as stated in chapter 4.2.4.1.

### 4.2.4.1 Sample enrichment

Surface water, as well as WWTP influent and effluent were enriched using SPE. Cartridges (Oasis HLB, 3cc, 60 mg) were conditioned using 3x2 mL MeOH, followed by 5x2 mL ultrapure water. 200 mL WWTP effluent/stream water or 100 mL WWTP influent were spiked with 5 ng internal standard, homogenized and loaded on the cartridge. Cartridges were dried for 40 min under a constant stream of nitrogen and eluted using 4x1.5 mL acetone/ethyl acetate mixture (1/1, v/v).

2 mL eluate of stream samples that were analyzed with a multi-analyte method (chapter 5.4.2) were evaporated under a constant stream of nitrogen and reconstituted in 1 mL of an ultrapure water/MeOH mixture (1/1, v/v). Samples were vortexed, filtered through a syringe filter (regenerated cellulose (RC), 0.2 µm pore size, 13 mm diameter) and directly analyzed using ultra high performance liquid chromatography (UPLC)-MS/MS.

Complete eluates (6 mL) of all WWTP samples and stream samples according to chapter 5.4.1 were evaporated and treated in the same manner.

## 4.2.5 Sample preparation of building material samples

Samples were extracted via liquid solid extraction (LSE) using acetone. In order to do so, samples were weight (2 g) into a 50 mL screw cap vial (glass) and 20 mL acetone were added. Extraction was performed for two hours under constant shaking at room temperature (25 °C). Next, 1 mL of acetone extracts was diluted with a methanol/water mixture (50/50; v/v) by a factor 10. Extracts were filtered using a syringe filter (PTFE, 0.2 µm, 13 mm and 25 mm, respectively). Afterwards, extracts were diluted with methanol/water (50/50; v/v) by a factor 10 and submitted to LC-MS/MS measurements. Depending on the AP concentration, samples were further diluted and again submitted to LC-MS/MS measurements.

Table 23 shows final dilution factors of building material samples.

**Table 23: List of dilution factors for the analysis of APs in building materials**

| Sample | Dilution factor | Sample | Dilution factor |
|---|---|---|---|
| AP-PL1 | 100 | AP-C8 | 10000 |
| AP-PL2 | 100 | AP-C9 | 1000 |
| AP-C1 | 100 | AP-C10 | 1000 |
| AP-C2 | 100 | AP-GA1 | 100 |
| AP-C3 | 10000 | AP-GA2 | 100 |
| AP-C4 | 100 | AP-GA3 | 100 |
| AP-C5 | 10000 | AP-GA4 | 100 |
| AP-C6 | 1000 | AP-GA5 | 1000 |
| AP-C7 | 10000 | AP-GA6 | 1000 |

Recovery experiments were performed at the method quantification limit (450 µl of extract + 50 µl of 10 µg/mL AP working solution). Recovery rates were between 60% and 135% and were taken into account for calculation of reported concentrations.

## 4.3 HPLC-MS/MS method for the analysis of alkylphenols in environmental samples and transformation experiments

Quantitative data of APs in environmental samples was recorded on a triple quadrupole MS (QqQ MS) (5500, AB Sciex LLC, Framingham, MA, USA, software MultiQuant version 3.0.3, AB SCIEX). Separation was performed on a Waters ACQITY UPLC HSS T3 c18 column (1.8 µm pore size, 2.1x50 mm) at a column over temperature of 30 °C and flow rate of 500 mL/min. Used chromatograph was an Shimadzu Nexar X2 (consisting of a DGU 203R and DGU 20A5R degaser, Nexar X2 LC-30AD Pump, Nexar X2 SIL-30AC autosampler, CBM-20A Communication Bus System and a LTO-20 AC column oven) that was coupled with the QqQ-MS. Ionization was performed with an electrospray ionization (ESI) source in negative mode (-4.5 kV). Used HPLC settings and gradient are shown in Table 24 and Table 25.

**Table 24: List of method settings, used separation column and mobile phases for analysis of APs in stream water and WWTP samples**

| Type of feature | Feature description |
|---|---|
| Injection volume [µL] | 5 |
| Column oven temperature [°C] | 30 |
| Column | Waters AQUITY UPLC BEH T3 1.7 µm, 2.1x50 mm |
| Mobile phase A | Ultrapure water |
| Mobile phase B | Acetonitrile |

**Table 25: Used gradient program for analysis of APs in stream water and WWTP samples**

| Step | Time [min] | Flow rate [µL/min] | Mobile phase A [%] | Mobile phase B [%] |
|---|---|---|---|---|
| 0 | 0.00 | 500 | 70 | 30 |
| 1 | 1.00 | 500 | 70 | 30 |
| 2 | 7.00 | 500 | 5 | 95 |
| 3 | 9.00 | 500 | 5 | 95 |
| 4 | 9.10 | 500 | 70 | 30 |
| 5 | 11.0 | 500 | 70 | 30 |

## 4.4 HPLC-MS/MS method for the analysis of alkylphenols in building materials

Quantitative data of APs in building materials was recorded on an AB Sciex 5500 triple quadrupole instrument (Framingham, MA, USA) coupled to an Agilent 1290 infinity LC system with a CTC Pal. Ionization was performed with an ESI source in negative mode (-4.5 kV). Used HPLC settings and gradient are shown in Table 26 and Table 27.

**Table 26: List of method settings, used separation column and mobile phases for analysis of APs in building material samples**

| Type of feature | Feature description |
|---|---|
| Injection volume [µL] | 96 |
| Column oven temperature [°C] | 25 |
| Column | Waters AQUITY UPLC BEH T3 1.7 µm, 2.1x100 mm |
| Mobile phase A | $H_2O$ LC-MS grade + 2 mMol ammonium acetate + 0.1% acetic acid |
| Mobile phase B | Acetonitril LC-MS grade + 0.1% formic acid |

**Table 27: Used gradient program for analysis of APs in building material samples**

| Step | Time [min] | Flow rate [µL/min] | Mobile phase A [%] | Mobile phase B [%] |
|---|---|---|---|---|
| 0 | 0.00 | 300 | 82 | 18 |
| 1 | 0.40 | 300 | 82 | 18 |
| 2 | 4.00 | 300 | 11 | 89 |
| 3 | 4.20 | 300 | 0 | 100 |
| 4 | 7.00 | 300 | 0 | 100 |
| 5 | 7.20 | 300 | 82 | 18 |
| 6 | 8.20 | 300 | 82 | 18 |

Table 28 shows a list of observed retention times and used transitions for the analysis of APs in building materials.

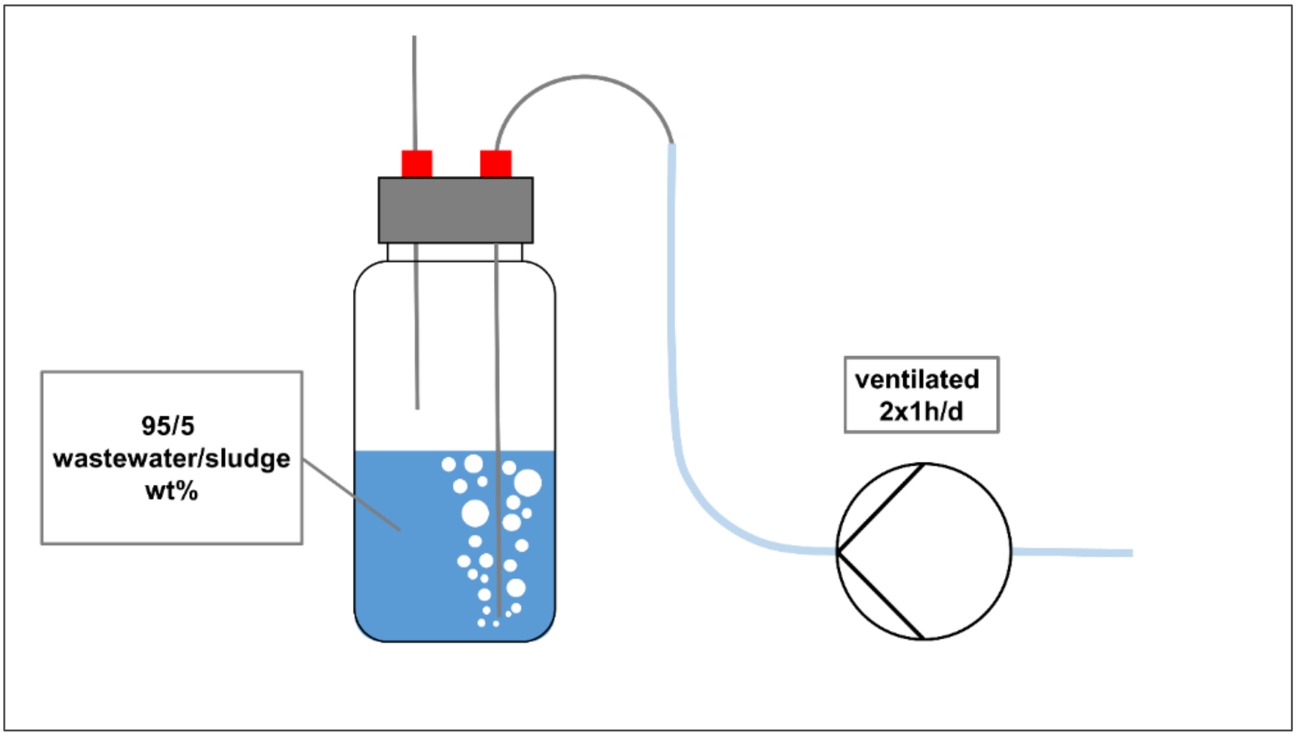
**Table 28: Retention times and used transitions for the analysis of APs in building material samples**

| Compound | Q1 | Q3 | $t_R$ [min] |
|---|---|---|---|
| 4tBB | 149 | 117<br>133<br>134 | 4.04 |
| 4tPP | 163 | 117<br>133<br>134 | 4.26 |
| OP | 205 | 117<br>133<br>148 | 4.74 |
| NP | 219 | 119<br>133<br>147 | 5.10 |

## 4.5 Biotransformation experiments of short chain alkylphenols

Biotransformation was performed via incubation of the test substance in 1 L inoculum and tests were based on OECD 301 (A). However, if not stated otherwise, solely primary degradation was monitored. Experiments were conducted for 28 days. 1 L of a 95/5 (w/w-%) mixture WWTP effluent/sludge were filled into 2 L screw top glass bottles (see Figure 3).

Figure 3: General setup of performed biotransformation experiments in 2 L glass bottles; own representation, Hochschule Fresenius



Two assays were treated with 1 g Na-azide in order to sterilize the microorganisms. For both, 4tBP and 4tPP one sterile assay and one active assay were spiked at 10 mg/L. A Na-benzoate control assay was spiked at 100 mg/L Na-benzoate. Furthermore, one bottle was not spiked at all (reffered to as a blank assay). All assays were incubated in the dark and aerated two times a day for a time of 1 h. Samples were withdrawn on day 0, 1, 2, 3, 4, 5, 6, 7, 8, 11, 12, 14, 18, 21 and 28 (10 mL each assay and sampling time point). After 28 days of incubation, sterile assays were again treated with 1 g Na-azide, sterile and active assays were spiked at 10 mg/L 4tBP or 4tPP, respectively. Also, benzoate control assays were again spiked at 100 mg/L Na-benzoate and further incubated for 9 days. Samples were withdrawn on day 0, 1, 2, 3, 4, 7, 8 and 9 (10 mL each assay and sampling time point).

Directly after withdrawing samples, 0.5 mL of each were diluted with 0.5 mL MeOH. Diluted samples and originally withdrawn samples were stored at -30°C upon analysis. AP samples were diluted to a final concentration of 100 ng/L (in ultrapure water/MeOH (80/20, v/v)), spiked with 5 ng IS, filtered through a syringe filter (regenerated cellulose (RC), 0.2 µm pore size, 13 mm diameter)

Sodium benzoate controls were diluted using a syringe filter (RC, 0.2 µm pore size, 13 mm diameter) and directly analyzed using HPLC-UV/VIS at 210 and 266 nm. Separation was performed using a MZ-Aqua Perfect column (C18, 5 µm, 2.1x50 mm) and gradient elution (Eluent A: $H_2O$ + 0.1% formic acid (FA); eluent B: MeOH + 0.1% FA). The used instrument was an Agilent 1100 series chromatograph (Agilent Technologies, Santa Clara, CA, USA; comprised of a G1312A binary-pump, WPALS G1367A autosampler, G1316A column oven and a G1315A DAD detector). The used injection volume was 5 µL.

Table 29 shows the applied gradient elution program.

Calibration was performed with five standards in the range of 5 to 150 mg/L that were prepared in a methanol-water mixture (1/1).

**Table 29: Used gradient program for the determination of Na-benzoate concentration in degradation controls**

| Time [min] | Eluent A [%] | Eluent B [%] | Flow rate [ml/min] |
|---:|---:|---:|---:|
| 0 | 95 | 5 | 400 |
| 8 | 45 | 55 | 400 |
| 9 | 0 | 100 | 400 |
| 12 | 0 | 100 | 400 |
| 13 | 95 | 5 | 400 |
| 18 | 95 | 5 | 400 |

### 4.5.1 Biotransformation experiments for testing of total mineralization of alkylphenols

In order to test total mineralization of SCAPs, biotransformation experiments were conducted with a similar setup as described in chapter 4.5 (adapted from OECD 301 A). A total of eight batches was prepared and filled with 1 L each of a WWTP effluent:sludge mixture (95/5; w/w-%). One assay was used as a blank sample and one was spiked with Na-benzoate in order to test general activity and biotransformation capability of used inoculum. Both, 4tBP and 4tPP were prepared in an active and a sterile assay, with a concentration of 100 mg/L each, which corresponds to 80 and 80.5% TOC respectively. Simultaneously, active and sterile assays of both APs were also prepared at a concentration of 10 mg/L in order to correct for the influence of the inoculum respiration and to check physical/chemical processes of elimination. Biotransformation experiments were conducted over a period of 28 days and 15 ml samples were withdrawn twice to three times a week. The concentration of APs due to primary degradation was measured as stated in chapter 4.3 and concentration of Na-benzoate was measured as stated in chapter 4.5. Complete mineralization of 4tBP was monitored as TOC and tested using a multi N/C® 3100 analyzer (Analytik Jena AG, Jena, Germany). Calibration was performed using Na-benzoate standards from 0.5-50 mg/L TOC. Standards were prepared in ultrapure water. 10 mL of each sample from active and sterile assays (with a starting concentration of 100 mg/L 4tBP) as well as the blank sample were filtered using 0.45 µm cellulose acetate syringe filters, diluted with 10 mL ultrapure water acidified using 500 µL HCl (2N) and directly analyzed.

# 5 Results

## 5.1 PFASs in non-consumer products

In total, 51 samples were investigated regarding their PFASs content, in order to determine possible entry pathways of PFASs into the environment.

Sample selection was performed under consideration of prior literature search and in agreement with UBA. If samples could not be purchased, sample selection was mainly restricted to availability and accessibility, thus depended on the willingness of manufactures/vendors to provide them. If a proposed sample could not be substituted with different products for the same application, sample collection was performed in regard of literature search (see chapter 1.1 and 1.2) in order to substitute unavailable items with products used for a different application (e.g. coating instead of paint). The investigated products for building materials can be summarized in three categories: (1) coatings/impregnations, lacquers, stains and paints, (2) foils or composite materials and (3) sealants and glues. Four categories of products that are referred to as industrial textiles were investigated: (1) seat covers, (2) covers for truck trailers (3) covers for maritime applications and (4) awnings and tarpaulins. Detailed results of individual products for building materials and industrial textiles are listed in subchapters 5.2 and 5.3.

All samples were investigated as aqueous and methanol extracts. Aqueous extracts deliver a better impression regarding the short-term impact and environmental fate resulting from precipitation, e.g. through urban runoff. Although, extraction with methanol is rather harsh and methanol extracts should be generally considered as a worst case scenario, they do give an impression regarding the total potential of investigated samples to leach PFASs. Thus, weather influence, shear forces or aging might reveal the possibility of further environmental entry pathways and higher concentrations in aqueous runoff samples. Samples are not shown if no PFASs were detected in investigated samples (all PFASs <LOD).

## 5.2 Building materials

### 5.2.1 Coatings, lacquers, stains and paints

Overall, four samples of coatings/impregnations, three samples of paints, two samples of lacquers and one sample of a wood stain were investigated. No PFASs were detected in paint and lacquer samples. Individual results are listed in chapter 5.2.1.1 and 5.2.1.2.

#### 5.2.1.1 Coatings

The products PFAS-BM01 and PFAS-BM02 consist of a top coat (reffered to as PFAS-BMxx A) and a bottom coat (reffered to as PFAS-BMxx B). No methanol extracts were prepared for PFAS-BM02 A + B, PFAS-BM03 and PFAS-BM04.

PFAS-BM02 A, PFAS-BM 02 B, PFAS-BM03 and PFAS-BM04 were directly enriched via SPE. Sample PFAS-BM03 was diluted with MeOH and directly analyzed (see methanol extract

Table 30).

Within the category coatings, PFASs were detected in all samples but PFAS-BM02 A and B (see

Table 30). Concentrations of PFAAs ranged from 1 to 29 µg/kg and < LOQ to 430 µg/kg in aqueous or methanol extracts, respectively. PFBA, PFPeA, PFHxA, PFHpA and PFOA were detected in aqueous extracts, whereas up to 11 PFAAs per sample were detected in methanol extracts. Comparison of water and methanol extracts showed higher concentrations, in methanol extracts for all samples. Also, more individual PFAAs were detected in methanol extracts of all samples compared with corresponding water extracts (e.g. no PFASs were detected in aqueous extracts of PFAS-BM01 B, however, PFASs were detected in corresponding methanol extracts).

No FTOHs were detected in samples PFAS-BM01 B, PFAS-BM02 A and PFAS-BM02 B. 6:2 FTOH was detected in sample PFAS-BM01 A with a concentration of 1700 µg/kg (see Table 31). This matches positive findings of PFAAs in sample PFAS-BM01 A, since mostly PFHxA and PFHpA were detected. Furthermore, FTOHs were detected in sample PFAS-BM03 and PFAS-BM04. Sample PFAS-BM03 and PFAS-BM04 had to be diluted (1:1,000, 1:10,000 and 1:100,000). Observed FTOH concentrations in these samples ranged from 94 to 4300000 µg/mL. Due to high dilution factors, concentrations should be considered as approximate values. However, both, peak shape and retention time that were observed in dilutions matched standards.

### Table 30: Concentrations of detected PFSAs and PFCAs for the samples PFAS-BM01 (A + B), PFAS-BM2 (A + B), PFAS-BM03 and PFAS-BM04, resulting from aqueous and methanol extracts

| | Aqueous extracts [µg/kg] | | | | | | MeOH Extracts [µg/kg] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | PFAS-BM01 | | PFAS-BM02* | | *PFAS-BM03 | *PFAS-BM04 | PFAS-BM01 | | PFAS-BM02 | | **PFAS-BM03 | PFAS-BM04 |
| - | A | B | A | B | - | - | - | B | A | B | - | - |
| PFBA | 6.3 | n.d. | n.d. | n.d. | 4.7 | n.d. | 39 | 4.0 | N/A | N/A | 4.7 | N/A |
| PFPeA | 7.7 | n.d. | n.d. | n.d. | n.d. | 3.2 | 53 | 4.1 | N/A | N/A | 1.0 | N/A |
| PFHxA | 36 | n.d. | n.d. | n.d. | 25.0 | 13 | 360 | 3.6 | N/A | N/A | 2.5 | N/A |
| PFHpA | 28.7 | n.d. | n.d. | n.d. | n.d. | n.d. | 430 | 5.1 | N/A | N/A | 0.05 | N/A |
| PFOA | n.d. | n.d. | n.d. | n.d. | n.d. | 1.8 | < LOQ | 6.3 | N/A | N/A | 0.09 | N/A |
| PFOS | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | < LOQ | n.d. | N/A | N/A | 0.01 | N/A |
| PFNA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | < LOQ | 9.2 | N/A | N/A | 0.01 | N/A |
| PFDA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | < LOQ | 9.9 | N/A | N/A | 0.05 | N/A |
| PFUnDA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 8.9 | N/A | N/A | n.d. | N/A |
| PFDoDA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | < LOQ | 9.2 | N/A | N/A | 0.01 | N/A |
| PFTrDA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 3.8 | N/A | N/A | n.d. | N/A |
| PFTeDA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | < LOQ | 9.2 | N/A | N/A | 0.01 | N/A |
| 6:2 FTS | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.9 | n.d. | N/A | N/A | 0.03 | N/A |

*sample preparation similar to water (enrichment); conc. in µg/L

**sample diluted and measured directly; conc. in µg/L

| | |
|---|---|
| N/A | not applicable |
| n.d. | not detected |
| < LOQ | below limit of quantification |

### Table 31: Concentrations of detected FTOHs for the samples PFAS-BM01 (A + B), PFAS-BM2 (A + B), PFAS-BM03 and PFAS-BM04

| | FTOHs [µg/kg] | | | | | |
|---|---|---|---|---|---|---|
| Compound | PFAS-BM01 | | PFAS-BM02 | | PFAS-BM03* | PFAS-BM04* |
| - | A | B | A | B | - | - |
| 6:2-FTOH | 1700 | n.d. | n.d. | n.d. | 4300000 | 520000 |
| 8:2-FTOH | n.d. | n.d. | n.d. | n.d. | 161 | 28000 |
| 10:2-FTOH | n.d. | n.d. | n.d. | n.d. | 94 | 48000 |

*Concentration in µg/L

| | |
|---|---|
| n.d. | not detected |

The potential impact, which is represented by methanol extracts, showed more findings and higher concentrations in comparison to aqueous extracts. Overall, the possible environmental impact of investigated coating samples should be considered as high. However, PFOS was only detected once (< LOQ) and PFOA was detected in aqueous extracts of one sample (PFAS-BM04, 1.8 µg/L) and two times in methanol extracts with rather low concentrations (PFAS-BM01 A, < LOQ; PFAS-BM01 B, 6.3 µg/kg). Homologues with a carbon chain length of > C8 were only detected in methanol extracts, exhibiting relatively low concentrations. Besides one positive finding for PFOS and two positive findings for 6:2 FTS, only PFCAs were detected in investigated extracts. Furthermore, evaporation and atmospheric degradation of FTOHs from samples with high concentrations thereof could lead to entrance of PFCAs into the environment.

#### 5.2.1.2 Stains

Only PFBA was detected in the investigated stain sample (see Table 32). An interview with one chemical company confirmed the possible use of PFASs for wood stains or related products. However, due to the overall restricted amount of investigated samples, only one sample for wood stains was investigated. Further investigations of similar products or non-target analysis in order to detect novel PFASs might lead to more positive findings.

Table 32: Concentrations of detected PFSAs and PFCAs for the sample PFAS-BM10 resulting from methanol extract

| | Methanol extract [µg/kg] |
|---|---|
| Compound | PFAS-BM10 |
| PFBA | 5.9 |

### 5.2.2 Foils or composite materials

In total, nine different foil samples with applications like sidings, facades, roofing or packaging of building materials were investigated. Foil samples consisted either of ETFE or PTFE, Ethylene propylene diene monomer (EPDM) rubber or polyethylene (PE). In addition, one OSB wood sample was investigated. Individual results are listed in chapter 5.2.2.1 and 5.2.2.2.

#### 5.2.2.1 Foils

PFASs were detected in nine foil samples. Most PFASs were detected in fluoropolymer foil samples (see

Table 33). In general, methanol extracts exhibited slightly higher concentrations, except for PFAS-BM16 with no positive finding in methanol extracts. Relatively high concentrations of PFBA were detected in PFAS-BM15. PFOA was detected in sample PFAS-BM18, and PFOS was detected in sample PFAS-BM16, both with rather low concentrations. Concentrations ranged from 2.5 to 30.0 µg/kg for PFAAs. No FTOHs were detected in any foil sample.

No PFASs were detected in the investigated samples of roofing materials. EPDM rubbers can be considered robust and quite stable to weathering conditions. Thus, EPDM materials for roofing are probably not treated with coatings or other upgrades containing PFASs.

In addition, no PFASs were detected in PE foils for packaging purposes.

Table 33: Concentrations of detected PFSAs and PFCAs for the samples PFAS-BM15, PFAS-BM16, and PFAS-BM18, resulting from aqueous and methanol extracts

| | Aqueous extracts [µg/kg] | | | MeOH Extracts [µg/kg] | | |
|---|---|---|---|---|---|---|
| Compound | PFAS-BM15 | PFAS-BM16 | PFAS-BM18 | PFAS-BM15 | PFAS-BM16 | PFAS-BM18 |
| PFBA | 23.5 | n.d. | n.d. | 30 | n.d. | n.d. |
| PFPeA | 2.8 | n.d. | n.d. | 2.5 | n.d. | n.d. |
| PFOA | n.d. | n.d. | 2.5 | n.d. | n.d. | 3.9 |
| PFOS | n.d. | 3 | n.d. | n.d. | n.d. | n.d. |

n.d. not detected

Although, foil samples showed only few positive findings, the results raise some concerns. Samples PFAS-BM15, PFAS-BM16 and PFAS-BM18 are materials that can be used for e.g. light weight facade applications in skyscrapers or football stadiums, glass substitutes (e.g. for greenhouses) textile constructions in architecture and further applications. It can be assumed that such materials are used to relatively high extends and for rather large buildings, which would result in a higher relase of PFASs. Furthermore, it is not clear how old the investigated samples were upon receipt. If possible, further investigations regarding such materials should be carried out with fresh samples. Also, runoff samples could be collected to estimate the real environmental impact.

#### 5.2.2.2 Wood

Only PFBA was detected in the aqueous extract of the investigated OSB wood sample (PFAS-BM14; see

Table 34) with a concentration of 2.5 µg/kg. Although, same or higher concentrations are generally expected in methanol extracts, no PFASs were detected in the methanol extract. Furthermore, the IS areas of the water extract were very low, which could indicate problems due to high matrix influences (e.g. ion suppression during ionization). Considering that PFAS have already been detected in OSB samples [75], we think that the general potential for such products should be considered relatively high. Since only one sample was investigated for this category, further studies regarding such products should be considered.

Table 34: Concentration of detected PFBA for the sample PFAS-BM14, resulting from the aqueous extract

| | Aqueous extract [µg/kg] |
|---|---|
| Compound | PFAS-BM14 |
| PFBA | 2.5 |

### 5.2.3 Sealants and glues

Two products of the category sealants and one product of the category glues were investigated.

No PFAAs could be detected for the investigated products of the category sealants and glues. 8:2 FTOH and 10: FTOH were detected in sample PFAS-BM21 (see

Table 35). Concentrations ranged from 230 to 310 µg/kg for FTOHs.

Table 35: Concentrations of detected FTOHs for the sample PFAS-BM21

| | FTOHs [µg/kg] |
|---|---|
| Compound | PFAS-BM21 |
| 8:2-FTOH | 230 |
| 10:2-FTOH | 310 |

### 5.2.4 Summarized results for PFASs in building materials

PFASs were detected in each of the three investigated categories within the category building materials, but not for all samples or subcategories. In total, PFASs were detected in 39% of investigated samples. Figure 4 shows detection frequencies of investigated building materials with positive findings for PFAAs (A) and FTOHs (B). Detection frequency of PFCAs with chain lengths <C8 increased with decreasing chain length. This observation could be a consequence of production/formulation dates. However, individual formulation dates and storage times before sample collection are unknown; thus, no general conclusion can be drawn. Detection frequencies of investigated FTOHs were lower compared to some PFAAs.

Figure 4: Detection frequencies of PFAAs (A) and FTOHs (B) in investigated building materials with positive findings in percent. Sorted by substance class and chain length (top: longest chain length; bottom: shortest chain length)

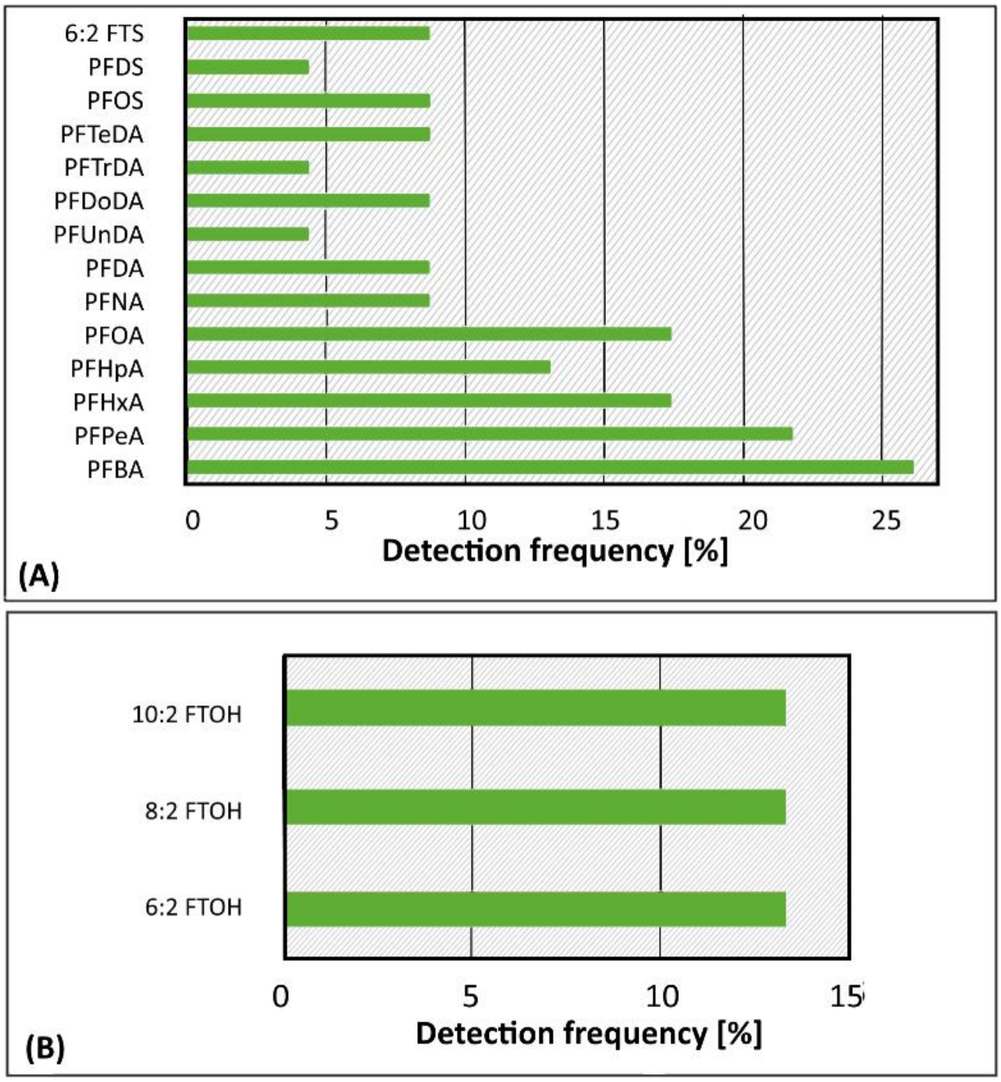


Table 36 shows the number of detections as well as the minimum (min), maximum (max) and average concentration of PFAAs in building materials for both, aqueous and methanol extracts. In total, 13 PFAAs were detected for investigated building material samples. Only PFAAs with a chain length ≤ C8 were detected in aqueous extracts, whereas PFAAs with a chain length > C8 were only detected in methanol extracts. That agrees with previous findings regarding increasing KOC with additional CF2 moieties. [208] Although, sample preparation and the total number of measurements approximately doubled due to the investigation of water extracts and additional methanol extracts, long chain derivatives could not have been detected without the additional extractions with methanol. However, environmental impact of these PFAS classes due to higher bioaccumulation is an important aspect, whereas additional conducted measurements proved to be of high importance. Also, only a comparison of water and methanol extracts displays the different behavior of direct entrance via aqueous run-off versus total potential. Furthermore, average and maximum concentrations of ≤ C8 PFAAs drastically increased from water to methanol extracts. The detection frequency of PFAAs in methanol extracts indicates the predominant application of short chain PFAAs in investigated samples. Likewise, average and max concentration of PFAAs with a chain length ≤ C7 were significant higher. Highest concentrations were detected for C6 and C7 PFCAs. Furthermore, PFOS and 6:2 FTS are the only sulfonic acid derivatives that were detected (with detection frequencies of 1, respectively 2), thus, mainly PFCAs were detected in building materials.

**Table 36: Summary of detection frequency as well as minimum concentration, maximum concentration and average concentration for aqueous and methanol extracts of detected PFAAs in investigated building materials**

| | Aqueous extracts | | | | Methanol extracts | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | Number or detections | Min [µg/kg] | Max [µg/kg] | Average [µg/kg] | Number or detections | Min [µg/kg] | Max [µg/kg] | Average [µg/kg] |
| PFBA | 4 | 2.50 | 23.5 | 9.25 | 4 | 4 | 39 | 19.8 |
| PFPeA | 4 | 1.00 | 7.70 | 3.68 | 3 | 2.5 | 53 | 19.9 |
| PFHxA | 3 | 13.0 | 36.0 | 24.7 | 2 | 3.6 | 360 | 181.8 |
| PFHpA | 1 | 28.7 | 28.7 | 28.7 | 2 | 5.1 | 430 | 217.6 |
| PFOA | 2 | 1.80 | 2.50 | 2.15 | 3 | < LOQ | 6.3 | 5.1 |
| PFOS | 1 | 3.00 | 3.00 | 3.00 | 1 | < LOQ | N/A | N/A |
| PFNA | 0 | N/A | N/A | N/A | 2 | < LOQ | 9.2 | 9.2 |
| PFDA | 0 | N/A | N/A | N/A | 2 | < LOQ | 9.9 | 9.9 |
| PFUnDA | 0 | N/A | N/A | N/A | 1 | 8.9 | 8.9 | 8.9 |
| PFDoDA | 0 | N/A | N/A | N/A | 2 | < LOQ | 9.2 | 9.2 |
| PFTrDA | 0 | N/A | N/A | N/A | 1 | 3.8 | 3.8 | 3.8 |
| PFTeDA | 0 | N/A | N/A | N/A | 2 | < LOQ | 9.2 | 9.2 |
| 6:2 FTS | 0 | N/A | N/A | N/A | 1 | 2.9 | 2.9 | 2.9 |

N/A not applicable

Table 37 shows detected FTOHs in building material samples with number of detections as well as min, max and average concentrations in µg/kg. Highest max concentration was detected for 6:2 FTOH. All FTOHs were detected in the same frequency. Furthermore, highest concentrations of FTOHs were approximately 10,000-fold higher than highest PFAAs concentrations in building materials. This was strongly bias by one sample. However, in general, FTOH concentrations were about 10 to100-fold higher than PFAA concentrations. Since the used sample preparation technique was disadvantageous for volatile compounds, real FTOHs concentrations in investigated samples might be higher than concentrations stated in

Table 37, which was also displayed by the high FTOH concentrations in sample PFAS-BM03 and PFAS-BM04.

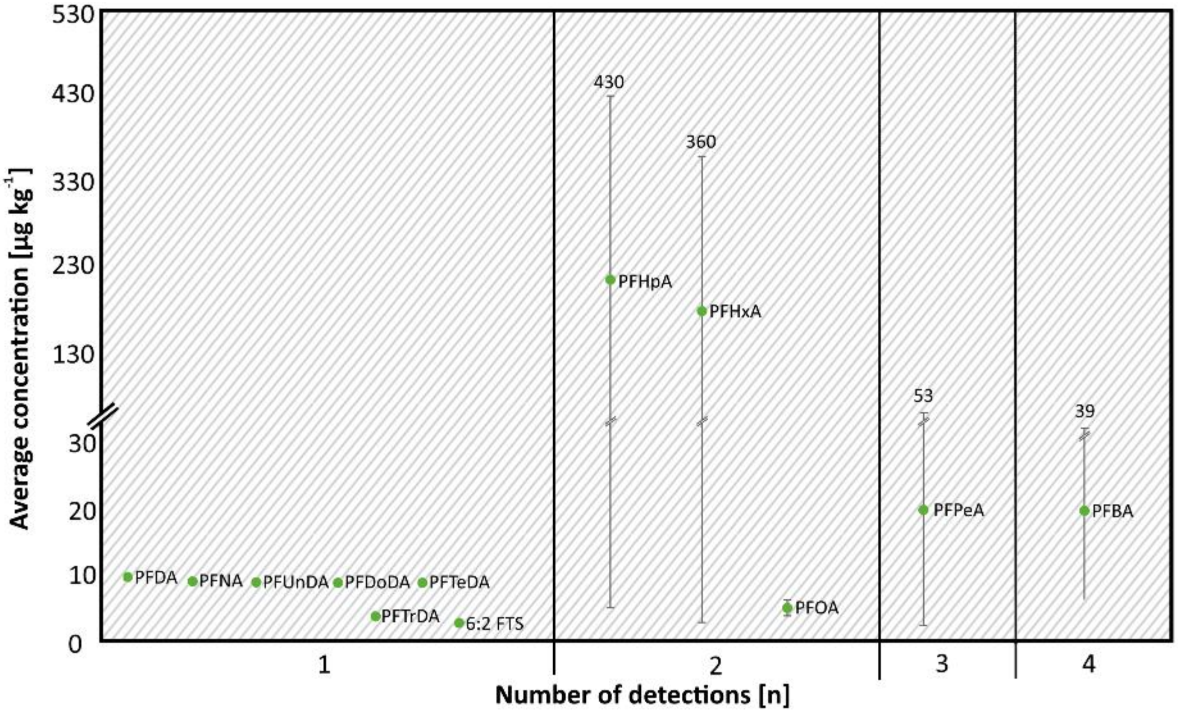
**Table 37: Summary of detection frequency as well as minimum concentration, maximum concentration and average concentration for FTOHs in investigated building materials**

| | Number or detections | Min [µg/kg] | Max [µg/L] |
|---|---|---|---|
| 6:2 FTOH | 3 | 1700 | 4300000 |
| 8:2 FTOH | 3 | 230 | 28000 |
| 10:2 FTOH | 3 | 310 | 48000 |

N/A not applicable

Figure 5 displays the average concentrations of detected PFASs as well as the highest and lowest concentrations that were detected, sorted by number of detections in building material samples (only methanol extracts and samples with concentrations >LOQ). Obviously, the average concentrations of PFHpA and PFHxA were bias by PFAS-BM01 A (PFHpA and PFHxA concentration of 430 and 360 µg/kg, respectively).

Figure 5: Average concentration and number of detection for all PFASs in building material samples that were detected ≥LOQ in methanol extracts; error bars indicate highest and lowest concentration, which was detected



In category 1 (Coatings, lacquers, stains and paints) 40% of investigated samples exhibited positive findings (from subcategories coatings, paints and stain). Most PFASs were detected coating samples (positive findings in 75% of investigated samples) and satins (n=1). Also, only PFBA was detected in the investigated stain sample. Furthermore, greatest varieties of PFASs were detected in coating samples, whereby PFASs were detected in 75% of investigated coating samples. No PFASs were detected in investigated paint sample, however, use of novel PFASs or other PFASs that were not included into the monitoring cannot be ruled out. Since the used sample preparation technique is not favorable for FTHOs, further investigations of paints, coatings, etc. should only be performed in closed systems (e.g. drying of samples in screw top flasks) with the possibility to enrich the gas phase (e.g. via SPE cartridges), which would enable trapping of evaporating FTOHs, which could also be suitable to overcome detection of interfering matrix components. However, detected FTOHs in coating samples showed the highest concentrations in all building material samples. PFAS-BM10 exhibited concentration of PFBA below the average concentration. Although the use of PFASs for wood stains was confirmed by industrial representatives of the chemical industry (anonymous personal communication), no PFASs were detected in samples for lacquer applications. Few or no findings in subcategories paints, lacquers and stains could be due to high costs of PFASs for such applications or their use for special applications only. This was also stated by representatives of the paint industry. Furthermore, the amount of investigated samples only allowed a general conspectus and selected samples might be misfortune picks.

Within category 2 (Foils or composite materials), 40% of the investigated samples showed positive findings. This being said, PFASs were detected in 75% of the investigated foil samples for façade covering or glass substituents and no positive findings were made in foils used for packaging of building materials or roofing material. PFBA, PFPeA, PFOA and PFOS were detected in the category foils. Only PFBA was detected in the investigated OSB sample. Unfortunately, the internal standards in extracts of the OSB sample showed very low intensities, which points towards disruptive effects (e.g. matrix problems).

For the last category of investigated building materials (Sealants and glues), only few PFASs were detected. 8:2 and 10:2 FTOH were detected in one of the two investigated sealants and no PFASs were detected in both, the second sealant sample and the investigated wood glue. One industrial representative that was interviewed, stated that PFASs are in general no longer used by German glue producers but rather applied in countries with less regulated environments. However, such samples were rather hard to obtain, whereas the investigated sample was one of a German company.

Figure 6 shows the sum of PFAAs and Figure 7 the sum of FTOHs for all building materials with positive findings. Since ∑(PFAAs) for PFAS-BM01 A is tenfold higher than for other samples, the results for PFAS-BM01 A are illustrated with a different axis. Same accounts for ∑(FTOHs) of sample PFAS-BM02 and PFAS-BM03. If not indicated otherwise, concentrations of PFASs are shown in µg/kg. ∑(PFAAs) of samples PFAS-BM01 B, PFAS-BM03 and PFAS-BM04, as well as ∑(FTOHs) of sample PFAS-BM03 and PFAS-BM04 are shown in µg/L or g/L, because corresponding samples were directly enriched vie SPE or diluted, respectively. If not indicated otherwise, only ∑(PFAAs) of methanol extracts are shown. ∑(PFAAs) for PFAS-BM01 A and B (top and bottom coat) showed the highest concentrations. However, it is not clear how the leaching of PFASs for PFAS-BM01 B behaves, if both, the top and the bottom coat are applied in layers. Although, shear forces or aging might reveal the bottom coating, enableing leaching of PFASs from it. Most positive findings and highest concentrations of PFAAs were detected in the two subcategories coatings and foils. Also, the highest concentrations of FTOHs were detected in coating samples. However, it should be stated that less samples were investigated in other subcategories, which questions the statistic relevance of findings per category if no or few PFASs were detected. After all, no positive or only few findings as well as low concentrations could also result from a misfortunate sample selection.

Figure 6: Sum of PFASs for building material samples with positive findings; concentration showed in µg/kg or µg/L

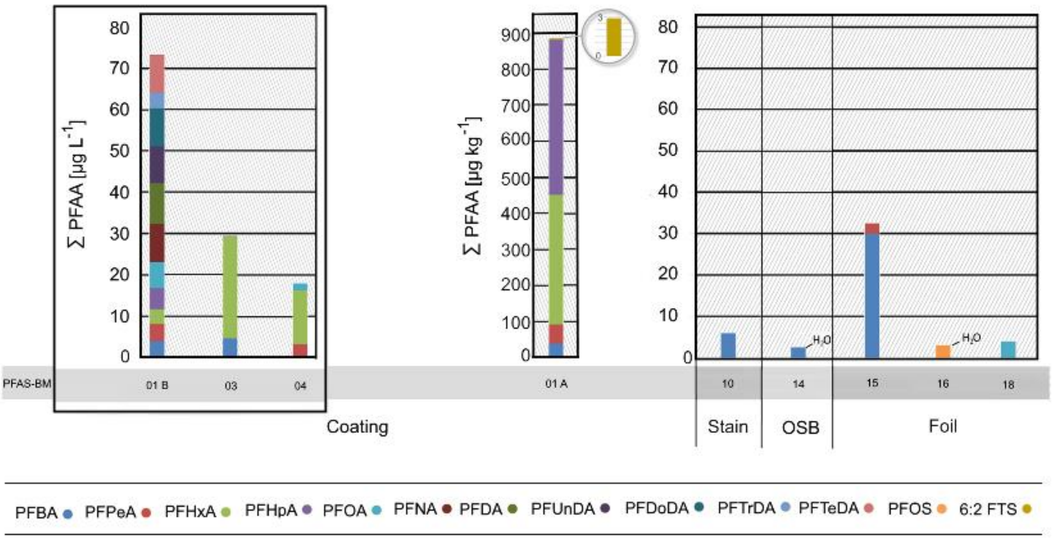
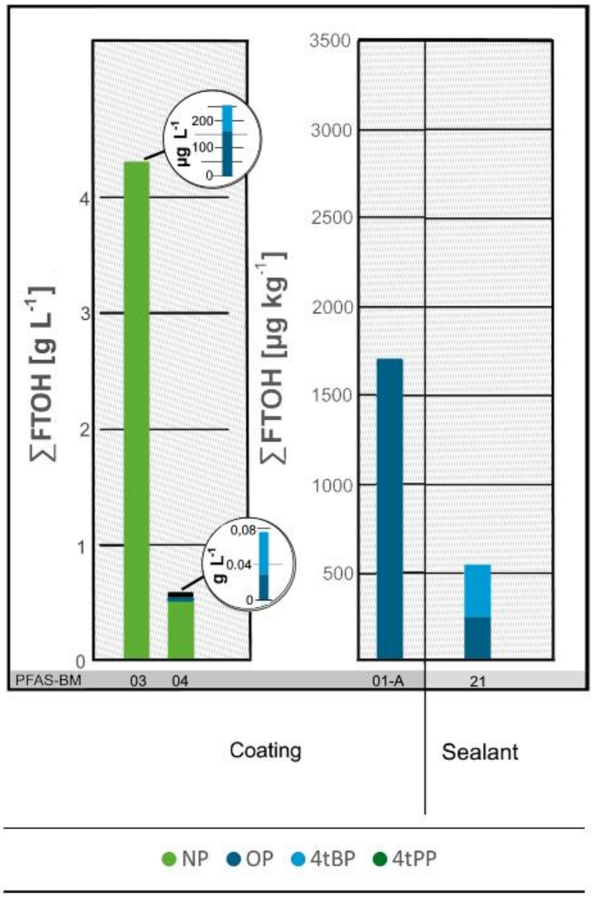
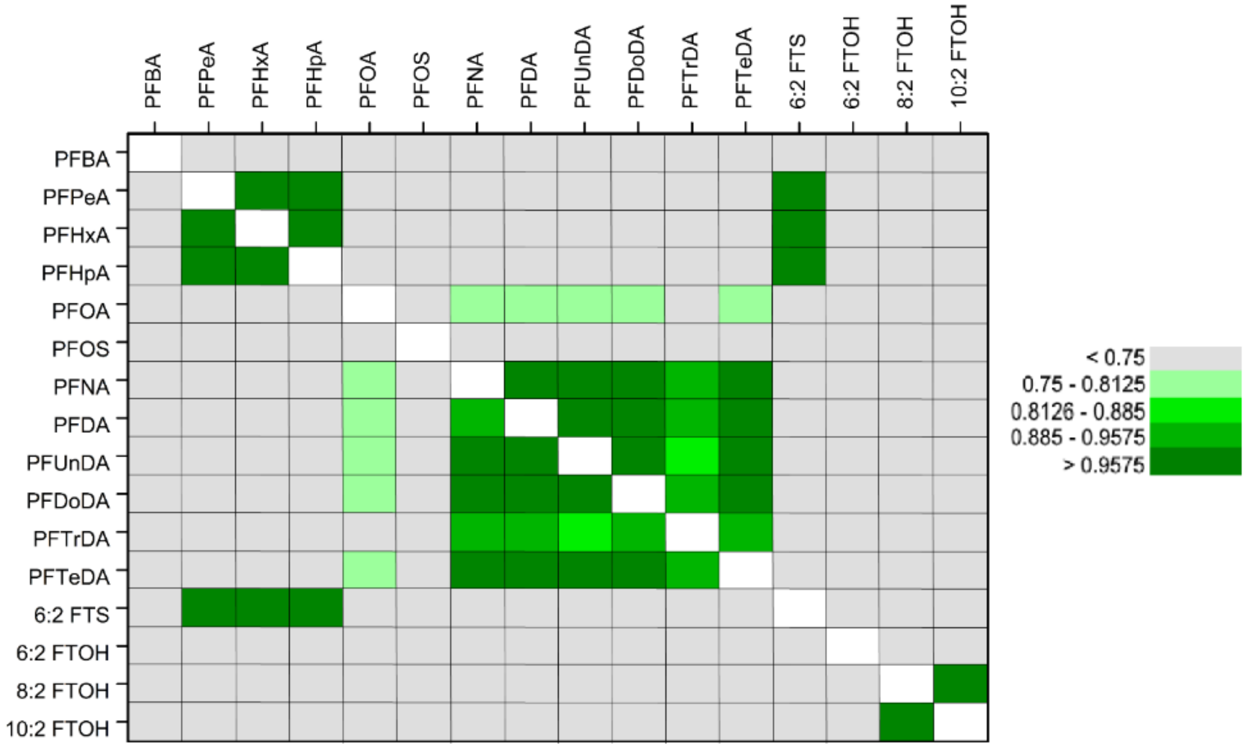


Figure 7: Sum of FTOHs for building material samples with positive findings; concentration showed in µg/kg or g/L



In addition, obtained data were statistically investigated. Pairing of PFASs concentrations was investigated using a scatterplot. Samples without positive findings as well as PFASs that were not detected in any sample were prior excluded. Obtained R2 values were than plotted in a heat map (see Figure 8). Correlations did not reveal significant or unusual correlations of PFASs.

Figure 8: Heat map of PFAS pairing derived from $R^2$ values of scatterplots for building material samples



#### 5.2.4.1 Environmental impact

Since most of the investigated building materials with positive findings are implemented for outdoor applications (e.g. façade paint, coatings, ETFE/PTFE foils), a direct entry pathway into the environment can result as a consequence of evaporation (FTOHs) or as a result of urban runoff after precipitation. Although, water extracts showed lower concentrations for most samples, the total potential of most samples is significantly higher if methanol extracts are considered. Furthermore, especially samples from the subcategory coatings showed high concentrations of FTOHs. Their outdoor application can lead to evaporation, atmospheric transformation and finally formation of PFCAs [209]. Thus, considering the amount of findings as well as the detected concentrations, the overall potential of entrance pathways into the environment and possible environmental pollution are concerning.

### 5.2.5 Conclusion

Although, the investigated subsets of samples with a relatively limited number of total samples does not allow a complete statistic conclusion, trends for the application of PFASs in various subcategories for the category building materials could be described very well. Since, only one sample was investigated for some subcategories, a misfortunate sample selection could also play a major role if no PFASs were detected. Nevertheless, it can be assumed that some subcategories hold a high potential for further investigations. We suggest investigation of bigger subsets for the subcategories coatings and foils for applications in buildings. Furthermore, different sample preparation techniques should be considered in order to better encompass volatile precursors. Since industrial representatives stated possible use of PFASs in products for wood, also, derived timber products and wood treatment products (e.g. stain) should be considered for further investigations. Lastly, it is not certain if all samples with no positive findings did not contain any PFASs, since only a certain subset of PFASs was investigated with targeted methods only and furthermore interfering matrix components hampered FTOH analysis in some samples. Thus, non-target approaches or methologies for sum parameters (e.g. absorbable organic fluorine (AOF) or total oxidizable precursor (TOP) assays) should be considered for further investigations.

## 5.3 Industrial textiles

### 5.3.1 Seat covers

A total of three textiles used for upholstering of car seats, seven textiles used for upholstering of public transport seats (e.g. train or bus seats) and one for upholstering of indoor furniture were investigated.

PFASs were detected in six of seven seat covers for upholstering of public transport seats. PFAA concentrations in public transport seat upholstering ranged from 2 to 26 µg/kg, whereby only PFASs with a chain length ≥C8 were detected (PFOA, PFDA, PFDoA, PFOS and 8:2 FTS, see Table 38). Furthermore, 8:2 FTOH was the only FTOH that was detected in one of the samples, ranging from (40 µg/kg; see Table 39). PFBA, PFPeA and PFHxA could be detected in the sample PFAS-IT01, which represents the textile used for upholstering of indoor furniture (see Table 40). Furthermore, 6:2 FTOH could be detected in this sample (see Table 41). Concentrations ranged from 2.5 to 5.0 µg/kg for PFAAs. No PFASs were detected in passenger car seat upholstering samples. Considering that PFAS-IT01 is supposed to be only used for indoor applications, investigation of textiles used for outdoor furniture could also be interesting and might exhibit positive findings. Unfortunately, no such samples could be obtained. Besides that, some of the textiles for maritime applications can be used for upholstering of seats on boats (see chapter 5.3.3).

**Table 38: Concentrations of detected PFSAs and PFCAs for the sample PFAS-IT23, PFAS-IT24, PFAS-IT25, PFAS-IT26, PFAS-IT27 and PFAS-IT28, resulting from aqueous and methanol extracts**

| | Aqueous extracts [µg/kg] | | | | | | Methanol extracts [µg/kg] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | PFAS-IT23 | PFAS-IT24 | PFAS-IT25 | PFAS-IT26 | PFAS-IT27 | PFAS-IT28 | PFAS-IT23 | PFAS-IT24 | PFAS-IT25 | PFAS-IT26 | PFAS-IT27 | PFAS-IT28 |
| PFOA | 5.8 | n.d. | n.d. | n.d. | 16 | 2.4 | 6 | 2 | 2 | 10.5 | 19 | 2.4 |
| PFDA | n.d. | n.d. | n.d. | n.d. | 8.6 | 5.7 | n.d. | n.d. | n.d. | 6.0 | 15 | n.d. |
| PFDoDA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 3 | n.d. |
| PFOS | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2.3 | n.d. | n.d. |
| 8:2 FTS | 6.7 | 5.0 | n.d. | n.d. | 7.4 | n.d. | 15 | 9.5 | n.d. | 26 | 12 | n.d. |

n.d. not detected

**Table 39: Concentrations of detected FTOHs for the sample PFAS-IT28**

| | FTOHs [µg/kg] |
|---|---|
| Compound | PFAS-IT28 |
| 8:2-FTOH | 40 |

**Table 40: Concentrations of detected PFSAs and PFCAs for the sample PFAS-IT05, resulting from aqueous and methanol extracts**

| | Aqueous extracts [µg/kg] | MeOH Extracts [µg/kg] |
|---|---|---|
| Compound | PFAS-IT01 | PFAS-IT01 |
| PFBA | 2.4 | 2.7 |
| PFPeA | 2.4 | 2.5 |
| PFHxA | 5.0 | 4.9 |

**Table 41: Concentrations of detected FTOHs for the sample PFAS-IT05**

| | FTOHs [µg/kg] |
|---|---|
| Compound | PFAS-IT01 |
| 6:2-FTOH | 690 |
| 8:2-FTOH | n.d. |
| 10:2-FTOH | n.d. |

n.d. not detected

### 5.3.2 Covers for truck trailers

Three different covers for truck trailers from two individual vendors (PFAS-IT06 and PFAS-IT07 from one company and PFAS-IT08 from another company) were investigated. All samples of truck trailer covers were made from PVC.

260 µg/kg 6:2 FTOH were detected in sample PFAS-IT12 (see Table 42). No other PFASs were detected in any sample of this category. From this data, we assume that PVC covers for truck trailers are generally not treated or upgraded with PFAS containing coatings.

Table 42: Concentrations of 6:2 FTOH detected for the sample PFAS-IT08

| | FTOHs [µg/kg] |
|---|---|
| Compound | PFAS-IT08 |
| 6:2-FTOH | 260 |

### 5.3.3 Covers for maritime applications

Five different covers for a variety of maritime applications were investigated. One was made from acrylic materials and the others were made from polyester. Three of them were treated with a polyurethane coat.

PFASs were detected in all investigated materials of this category (seeTable 43 Table 43 and Table 44). Concentrations ranged from 2.4 to 4.8 µg/kg for PFAAs and 40 to 790 µg/kg for FTOHs. PFHxA and PFOA were detected in the samples PFAS-IT10 and PFAS-IT11. FTOHs were detected in samples PFAS-IT09, PFAS-IT10, PFAS-IT12 and PFAS-IT13 (see Table 44).

Table 43: Concentrations of detected PFSAs and PFCAs for the samples PFAS-IT10 and PFAS-IT11, resulting from aqueous and methanol extracts

| | Aqueous extracts [µg/kg] | | MeOH Extracts [µg/kg] | |
|---|---|---|---|---|
| Compound | PFAS-IT10 | PFAS-IT11 | PFAS-IT10 | PFAS-IT11 |
| PFHxA | 2.4 | 2.6 | n.d. | 2.6 |
| PFOA | n.d. | 4.8 | n.d. | 4.4 |

n.d. not detected

Table 44: Concentrations of detected FTOHs for the samples PFAS-IT09, PFAS-IT10, PFAS-IT12 and PFAS-IT13

| | FTOHs [µg/kg] | | | |
|---|---|---|---|---|
| Compound | PFAS-IT09 | PFAS-IT10 | PFAS-IT12 | PFAS-IT13 |
| 6:2 FTOH | n.d. | 40 | n.d. | 790 |
| 8:2 FTOH | 90 | n.d. | 80 | 70 |
| 10:2 FTOH | 70 | n.d. | 40 | 50 |

n.d. not detected

The advantages of using materials with water repelling coatings for maritime applications is obvious. Concentrations of PFASs in these materials were rather low for most samples, nevertheless, the use of such substances for maritime applications presents a direct entry pathway into the aquatic environment, which should be of high concern.

### 5.3.4 Awnings and tarpaulins

A total of three tent tarpaulin samples and six textiles used for awnings were investigated. Most of the awning materials exhibited some kind of coating.

PFASs were not detected in any of the tarpaulin samples. As most of the investigated tarpaulin materials were made from PVC, this aligns with the results, which were obtained for covers for truck trailers (see chapter 5.3.2). On the contrary, PFASs were detected in all marquee samples except PFAS-IT20. (see .

Table 45). Between one and nine PFASs were detected in the samples PFAS-IT18, PFAS-IT19, PFAS-IT21 and PFAS-IT22. Concentrations for PFCAs in methanol extracts ranged from 2 to 130 µg/kg. In general, more PFASs were detected in methanol extracts, also exhibiting higher concentrations in most cases. FTOHs were also only detected in the samples PFAS-IT18, PFAS-IT19, PFAS-IT21 and PFAS-IT22 (see Table 46).

Table 45: Concentrations of detected PFSAs and PFCAs for the samples PFAS-IT18, PFAS-IT19, PFAS-IT21 and PFAS-IT22, resulting from aqueous and methanol extracts

| | Aqueous extracts [µg/kg] | | | | MeOH Extracts [µg/kg] | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | PFAS-IT18 | PFAS-IT19 | PFAS-IT21 | PFAS-IT22 | PFAS-IT18 | PFAS-IT19 | PFAS-IT21 | PFAS-IT22 |
| PFBA | 2.4 | 2.3 | 4.2 | n.d. | 2.8 | 2.7 | 4.3 | 2.4 |
| PFPeA | 2.5 | 2.4 | 3.7 | n.d. | 2.4 | 2.4 | 3.0 | n.d. |
| PFHxA | 15 | 11 | 15 | 2.6 | 16 | 12 | 18 | 5.7 |
| PFHpA | 4.1 | 4.2 | n.d. | n.d. | 5.1 | 5.0 | 2.6 | n.d. |
| PFOA | 78 | 36 | n.d. | n.d. | 130 | 62 | 4.0 | 3.8 |
| PFNA | n.d. | n.d. | n.d. | n.d. | 4.1 | 3.1 | n.d. | n.d. |
| PFDA | 7.0 | 3.2 | n.d. | n.d. | 71 | 35 | n.d. | n.d. |
| PFDoDA | n.d. | n.d. | n.d. | n.d. | 35 | 17 | n.d. | n.d. |
| PFTeDA | n.d. | n.d. | n.d. | n.d. | 21 | 7.8 | n.d. | n.d. |

n.d. not detected

Table 46: Concentrations of detected FTOHs for the samples PFAS-IT18, PFAS-IT19, PFAS-IT21 and PFAS-IT22

| | FTOHs [µg/kg] | | | |
|---|---|---|---|---|
| Compound | PFAS-IT18 | PFAS-IT19 | PFAS-IT21 | PFAS-IT22 |
| 6:2 FTOH | 220 | 220 | 200 | n.d. |
| 8:2 FTOH | 2300 | 2200 | 510 | 140 |
| 10:2 FTOH | 1600 | 1600 | 720 | 140 |

n.d. not detected

The results of these investigations are alarming. Not only that the high concentrations of PFOA (up to 130 µg/kg) and other PFASs offer a high hazard potential for the environment, also an estimation of possible application fields for such materials point towards manifold entry pathways into the environment. Awning materials like the once investigated can be used in private homes, markets, in front of businesses and many other fields like general sun protection in pedestrian zones or equivalents.

### 5.3.5 Summarized results for PFASs in industrial textiles

PFASs were detected in all categories of industrial textile samples. Most findings for industrial textiles were made in category 3 and 4 (Covers for maritime applications and Awnings and tarpaulin). Nine samples of these subcategories showed positive findings. PFASs were detected in 61% of all investigated textile samples. Figure 9 shows detection frequencies of PFAAs (A) and FTOHs (B). PFOA was the most frequently detected PFAA over all textile samples. Furthermore, PFAAs with chain lengths of C4 to C14 were detected with no real trends in detection frequencies. 8:2 FTOH was the most frequently detected FTOH.

Figure 9: Detection frequencies of PFAAs (A) and FTOHs (B) in investigated industrial textile samples with positive findings in percent. Sorted by substance class and chain length (top: long-est chain length; bottom: shortest chain length)

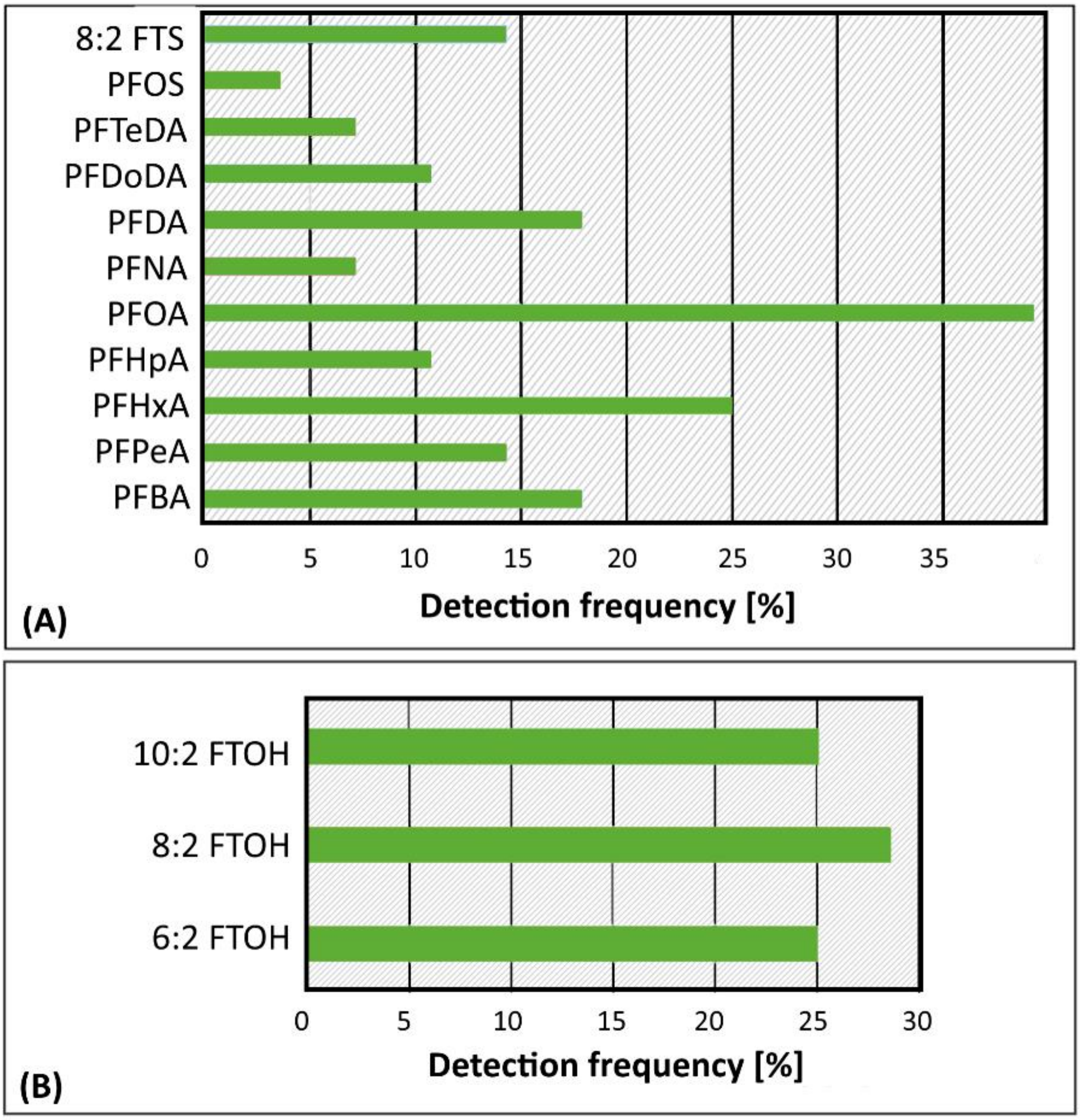


Table 47 shows the number or detections as well as the min, max and average concentrations of PFAAs in industrial textile samples for both, aqueous and methanol extracts. In total, nine PFAAs were detected in industrial textile samples. Comparison of the results for aqueous and methanol extracts shows that average concentrations of PFAAs with a chain length ≤ C8 are approximately the same for both extraction methods, thus, full potential is almost illustrated with aqueous extracts. However, consideration of max concentrations shows more than a doubling of the max PFOA concentration. PFDA is the only PFAA with a chain length > C8 that was detected in aqueous extracts, whereas max and average concentrations were tenfold higher in methanol extracts. This agrees with previous findings regarding increasing KOC with additional CF2 moieties. [208] The detection frequency of PFAAs in methanol extracts of industrial textile samples indicates a predominant application of ≥ C8 derivatives. Unlike detection frequencies of PFAAs in building material samples, no drastic shift towards short chain PFASs is indicated by these results, which reinforces the importance of all additional methanol extract to complement the results that can be obtained by aqueous extracts only. Number of detections for

PFAAs with a chain length of > C8 is comparable low but if long chain derivatives were detected, concentrations were relatively high. Furthermore, no PFSAs except PFOS were detected in industrial textile samples and 8:2 FTS was the only other sulfonic acid derivative that was detected.

**Table 47: Summary of detection frequency as well as minimum concentration, maximum concentration and average concentration for aqueous and methanol extracts of detected PFAAs in investigated industrial textiles**

| | Aqueous extracts | | | | Methanol extracts | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | Number or detections | Min [µg/kg] | Max [µg/kg] | Average [µg/kg] | Number or detections | Min [µg/kg] | Max [µg/kg] | Average [µg/kg] |
| PFBA | 4 | 2.3 | 4.2 | 2.8 | 5 | 2.4 | 4.3 | 3.0 |
| PFPeA | 4 | 2.4 | 3.7 | 2.8 | 4 | 2.2 | 3.0 | 2.5 |
| PFHxA | 7 | 2.4 | 15 | 7.7 | 6 | 2.6 | 18 | 9.9 |
| PFHpA | 2 | 4.1 | 4.2 | 4.2 | 3 | 2.6 | 5.1 | 4.2 |
| PFOA | 6 | 2.4 | 52.0 | 19.5 | 11 | 2 | 130 | 22.4 |
| PFNA | 0 | N/A | N/A | N/A | 2 | 3.1 | 4.1 | 3.6 |
| PFDA | 3 | 3.2 | 8.6 | 6.3 | 5 | 5.7 | 71 | 26.5 |
| PFDoDA | 0 | N/A | N/A | N/A | 3 | 3 | 35 | 18.3 |
| PFTeDA | 0 | N/A | N/A | N/A | 2 | 7.8 | 21 | 14 |
| PFOS | 0 | N/A | N/A | N/A | 1 | 2.3 | 2.3 | 2.3 |
| 8:2 FTS | 3 | 5 | 7.4 | 6.4 | 4 | 9.5 | 26 | 15.6 |

N/A not applicable

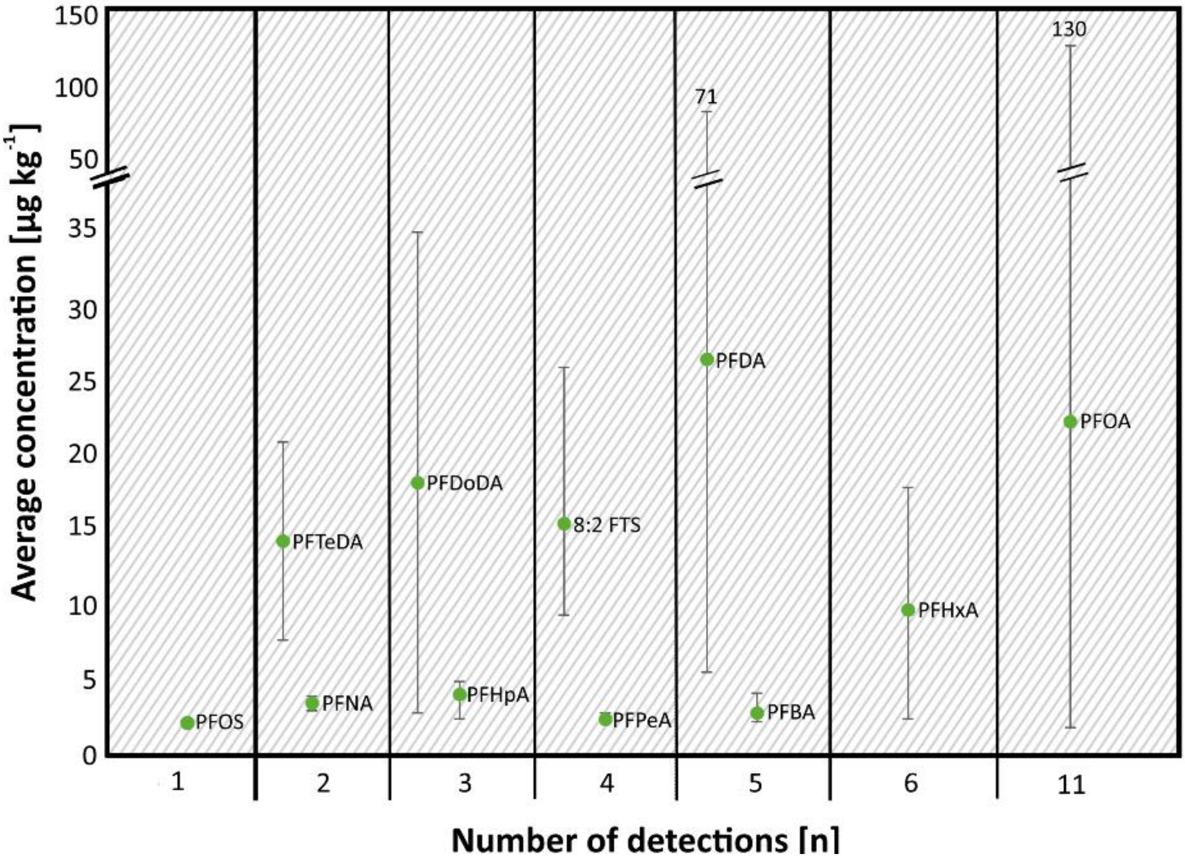
Table 48 shows detected FTOHs in industrial textile samples with number of detections as well as min, max and average concentration in µg/kg. Detection frequency of FTOHs in industrial textiles was higher than the FTOH detection frequencies for building material samples. This might be due to the advantageous sample preparation of textiles, since no drying is required prior to extraction. However, age and storage conditions prior to receipt of the samples is not known. Nevertheless, concentrations of FTOHs in industrial textile samples were up to tenfold higher than concentrations of PFAAs.

**Table 48: Summary of detection frequency as well as minimum concentration, maximum concentration and average concentration for FTOHs in investigated industrial textiles**

| | Number or detections | Min [µg/kg] | Max [µg/kg] | Average [µg/kg] |
|---|---|---|---|---|
| 6:2 FTOH | 7 | 40 | 790 | 350 |
| 8:2 FTOH | 7 | 40 | 2300 | 680 |
| 10:2 FTOH | 7 | 40 | 1600 | 600 |

Figure 10 displays the average concentrations of detected PFASs as well as the highest and lowest concentrations that were detected, sorted by number of detections in industrial textile samples (only methanol extracts and samples with concentrations >LOQ). As already explained for Figure 9, PFOA was most frequently detected. Furthermore, PFOA was the most frequently detected PFAA over all samples (building materials and industrial textiles). Although the max concentration of PFOA was the highest PFAA concentration in textile samples, PFDA had the highest average concentration. Furthermore, PFDA was detected five times in industrial textile samples. High number of detections and concentrations of long chain PFASs (PFOA, PFDA, PFDoDA, PFTeDA and 8:2 FTS) is alarming. However, as already stated numerous times, production date of samples is unknown and high findings for long chain derivatives could be attributed to old batches.

Figure 10: Average concentration and number of detection for all PFASs in industrial fabric samples that were detected ≥LOQ in methanol extracts; error bars indicate highest and lowest concentration, which was detected



PFASs were detected in seven samples of subcategory 1 of industrial textiles (seat covers; 64% positive findings). Besides detection of PFASs in multiple samples of this subcategory, concentrations were amongst the highest for PFAAs in textile samples. Furthermore, 33% of samples from category 2 showed positive findings. As already stated in chapter 5.3.2 this could result from the nature of the material. All samples of this category were made from PVC and no further coating is mentioned by producers, thus, PVC might not be treated with PFASs containing coatings.

PFASs were detected in 100% of samples in Category 3 (Covers for maritime applications). FTOHs were detected in 4 of the investigated samples with medium concentrations, however, 6:2 FTOH concentration in PFAS-IT13 was relatively high (790 µg/kg). Since products of category 3 are used for maritime applications, impregnation or coating with PFASs to obtain water repelling properties is not surprising. Also, some producers directly advertised their product with fluorocarbon or Teflon® coating (as already stated in chapter 1.2.1.5).

The fourth category of industrial textiles (Awnings and tarpaulin) exhibited positive findings in 44% of investigated samples. However, category 4 can be divided in two subcategories: (1) Marquees and (2) tarpaulins for party or carnival tents. No PFASs were detected in subcategory 2. Three of the four investigated tarpaulin samples were made from PVC, thus, as stated before it could be possible that PFAS containing coatings are rarely used for PVC materials. However, 80% of the investigated samples in subcategory 1 (marquees/awnings) showed positive findings. Among all samples, ∑(PFAAs) and ∑(FTOHs) in this subcategory were the highest once detected for industrial used textiles. Furthermore, PFAS-IT18 and PFAS-IT19 exhibited the highest concentrations of PFOA in methanol extracts with 130 and 62 µg/kg, respectively. Also, PFAS-IT18 and PFAS-IT19 are two different samples of the same producer and PFASs that were detected in these two samples exhibited similar ratios. PFAS-IT21 and PFAS-IT22 showed the highest concentrations of PFHxA.

Figure 11 shows the sum of PFAAs for industrial textile samples with positive findings (results of methanol extracts are shown if not indicated otherwise). All concentrations are displayer in µg/kg. The concentrations of sample PFAS-IT18 and PFAS-IT19 were approximately four to tenfold higher than the ∑(PFAAs) of other samples, thus, are displayed with a different axis. As already mentioned before, the same PFAAs were detected in samples PFAS-IT18 and PFAS-IT19, showing similar ratios of detected PFASs. Thus, showing similar patterns, which probably resulted due to the use of same formulations that were used by this producer. Another striking feature of the displayed data is that manly C8-based chemistry (PFOA and 8:2 FTS) was used for the impregnation of investigated public transport seat cover. These samples were received from one manufacturer, whereas no PFAAs were detected in other covers for public transport applications as well as passenger cars seats.

Figure 12 shows the sum of FTOHs for investigated industrial textile samples with positive findings. All concentrations are displayed in µg/kg, whereas the ∑(FTOHs) of samples PFAS-IT18 and PFAS-IT19 is represented with a different axis. FTOHs were detected in almost every investigated textile for maritime applications and marquee samples.

Figure 11: Sum of PFASs for industrial textile samples with positive findings; concentration showed in µg/kg

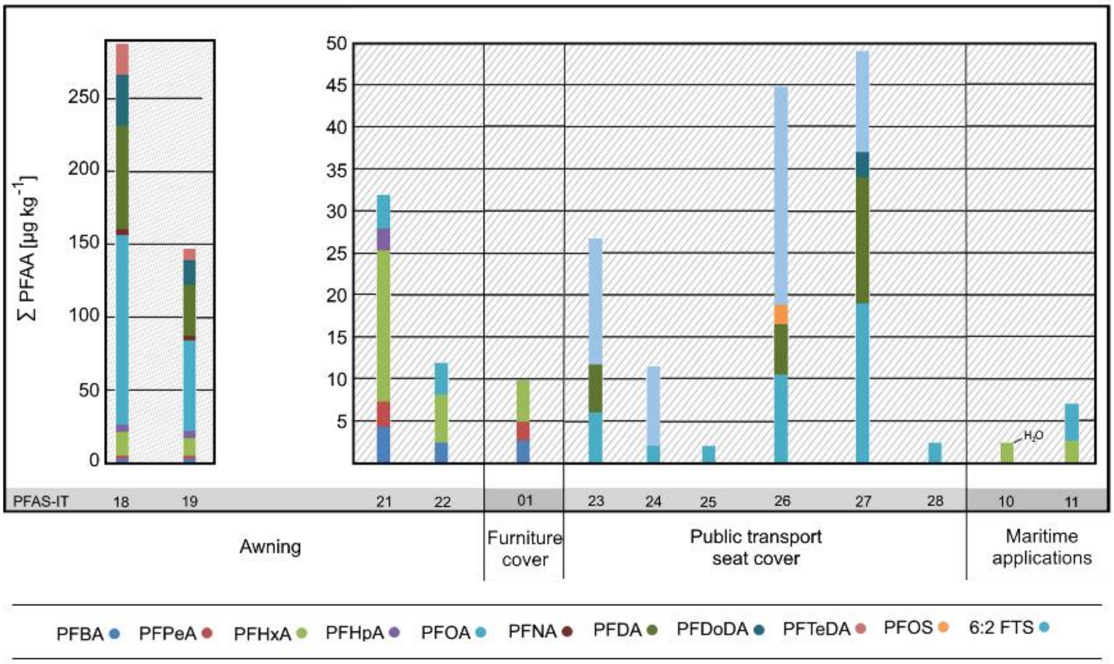
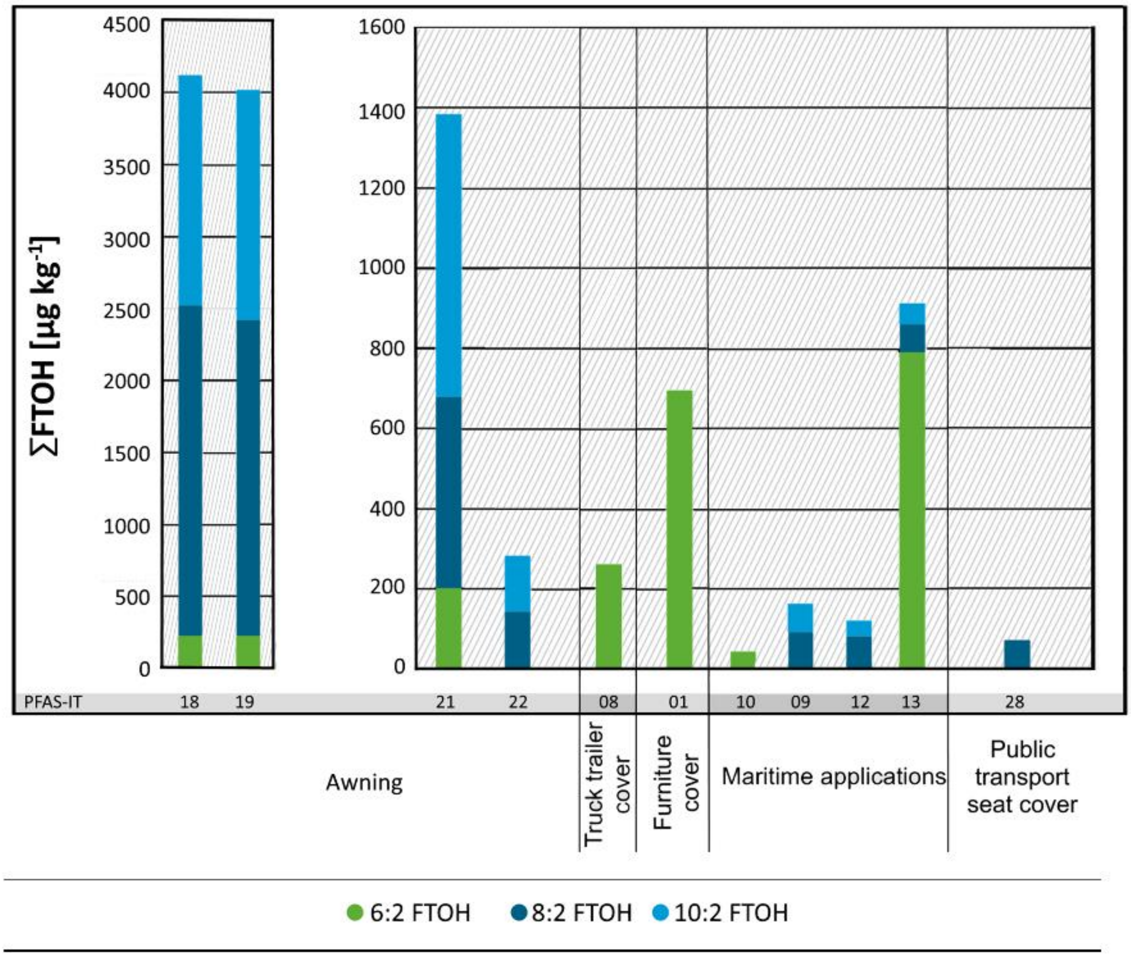
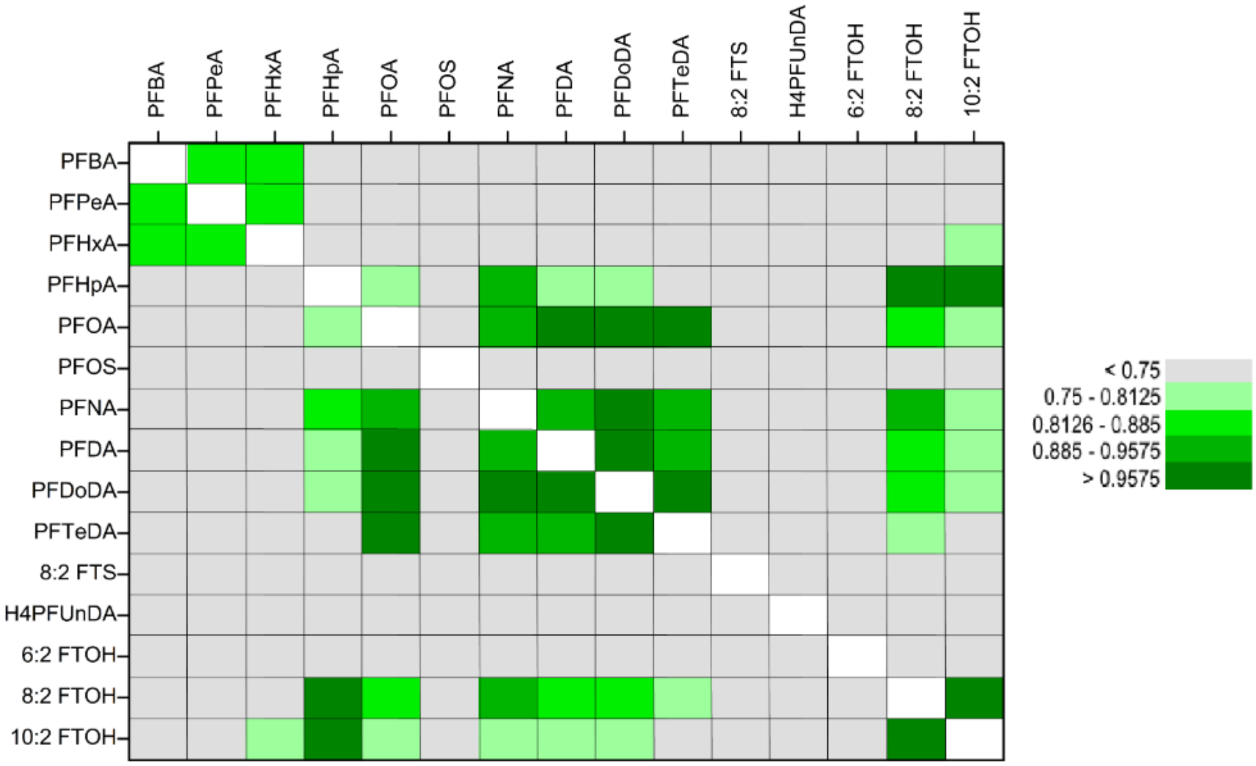


Figure 12: Sum of FTOHs for industrial textile samples with positive findings; concentration showed in µg/kg



Similar to building material product samples, statistic evaluation of industrial used textile samples was performed. Figure 13 show the heat map of R2 values, resulting from paring of detected PFASs. Statistic evaluation of detected PFASs did not show any abnormal trends.

Figure 13: Heat map of PFAS pairing derived from R² values of scatterplots for industrial textile samples



### 5.3.5.1 Environmental impact

Entrance pathways for PFASs into the environment can be partially derived from obtained data. Textiles for maritime applications serve the purpose of protection from sun or precipitation and lake or seawater, which directly results in runoff that might contain these substances. Similar, awning materials are generally used for protection from sun or precipitation, whereas rain can also directly cause an entrance of PFASs into the environment. Furthermore, evaporation of FTOHs can also lead to atmospheric degradation and formation of PFCAs. Seat covers for furniture do not provide a direct entrance pathway of PFAAs into the environment, however, they could allow for direct uptake by humans (dermal uptake). Furthermore, FTOHs might evaporate and leaching of PFAAs into the environment can occur after waste disposal of such products. Concluding, most of the investigated materials are applied outdoors and thus, enable entrance of PFASs trough run-off after precipitation as well as evaporation of volatile compounds. Therefore, entrance pathways of PFASs into the environment from investigated products are plausible, hence, obtained results are concerning.

### 5.3.6 Conclusion

As already stated for the results of PFASs in building materials, the limited number of samples does not allow a statistic relevant conclusion, however, most results are rather distinct. It seems that tarpaulins for carnival or party tents do contain PFASs. However, small party tents (e.g. for backyard application) were not investigated during this study and might exhibit PFASs. Furthermore, PFASs could not be detected in passenger car seat covers. Samples of passenger car seat covers were collected from original equipment manufacturers (OEMs). Considering that we do not know if the actual car companies further treat the material, the samples could originate from an unfortunate step of the supply chain. This could be circumvented if pieces of real car seats are investigated. Taking into account that PFASs were detected in seat covers for public transport applications, they seem to have applications for such seats in general. However, misfortune sample selection could also be a possible reason for these observations. Since PFASs were detected in the analyzed seat cover sample for indoor furniture, investigation of covers for indoor and outdoor applications might be of interest and should be considered for further studies. Only few PFASs were detected in covers for truck trailers and only special applications with direct indication of coatings should be considered for new samplings. However, PFASs were detected in textiles for maritime applications and especially in textiles for awning materials with partially very high concentrations. Thus, these categories should also be considered for further studies.

## 5.4 Alkylphenols in surface water

### 5.4.1 Short chain alkylphenols in surface waters according to considered scenarios

Nine streams were investigated regarding their 4tBP, 4tPP and OP concentration in order to determine the contribution of short chain APs on the pollution of aquatic systems. Sampling sites were chosen to fulfill one of three scenarios: (1) Surface water downstream WWTPs in catchment area of municipalities without relevant industrial direct dischargers (2) surface water downstream WWTPs in catchment area of municipalities with relevant industrial direct dischargers of industries known to apply APs during their production and (3) Surface water downstream WWTPs in catchment area of rural municipalities without any industrial direct dischargers. Table 49 shows selected surface waters.

**Table 49: List of Streams for the sampling of AP measurements in surface water; showing number of the streams, corresponding scenario, name, share of municipal wastewater and if what kind of manufacturer is situated near by or directly at the stream**

| Stream | Scenario | Share of municipal wastewater | Manufacturer situated near by or directly at the stream |
|---|---|---|---|
| 1 | 1 | <10% | Several chemical industries and urban environment |
| 2 | 1 | Unknown | N/A |
| 3 | 1 | Unknown | N/A |
| 4 | 2 | Unknown | Paper manufacture |
| 5 | 2 | Up to 100% | Chemical industry |
| 6 | 2 | <20% | Several chemical industries and urban environment |
| 7 | 3 | Unknown | N/A |
| 8 | 3 | Unknown | N/A |
| 9 | 3 | Unknown | N/A |

N/A not applicable

Sampling started in February 2017 and samples were collected in intervals of two to three months (see Table 50).

**Table 50: Sampling date of streams; showing number of the stream and sampling dates**

| Streams | Sampling 1 | Sampling 2 | Sampling 3 |
|---|---|---|---|
| 1 | Mar 2017 | May 2017 | Sep 2017 |
| 2 | Mar 2017 | Jun 2017 | Sep 2017 |
| 3 | Mar 2017 | Jun 2017 | No sample |
| 4 | Feb 2017 | May 2017 | No sample |
| 5 | Mar 2017 | Jun 2017 | Sep 2017 |
| 6 | Mar 2017 | Jun 2017 | Sep 2017 |
| 7 | Mar 2017 | Jun 2017 | Sep 2017 |
| 8 | Mar 2017 | Jun 2017 | Sep 2017 |
| 9 | Mar 2017 | Jun 2017 | Sep 2017 |

Table 51 shows a summary of the results that were generated under consideration of the originally proposed sampling scheme over three months of observation. Table 52, Table 53 and Table 54 show results of individual samplings. No SCAPs were detected in corresponding samples of streams 1-7. Stream 8 and 9 showed up to 100% detection frequency of 4tBP and OP, with concentrations all below 0.05 µg/L. 4tPP was not detected in any of the investigated samples. The results that were obtained in accordance to this sampling procedure indicated that the overall abundance of investigated SCAPs is restricted to some streams. In order to obtain more information of AP concentrations in a broader spectrum over different streams, HSF and UBA agreed on a deviation of the originally proposed sampling.

**Table 51: Summary of the results from the first screening of alkylphenols that corresponded to originally proposed sampling scheme; showing min, average (Ø) and max concentration in µg/L as well as number of detections (#) für 4tPP, 4tBP and OP in stream 1-9**

| Stream | PP | | | | BP | | | | OP | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | min | Ø | max | # | min | Ø | max | # | min | Ø | max | # |
| 1 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 |
| 2 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 |
| 3 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 |
| 4 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 |
| 5 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 |
| 6 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 |
| 7 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 | N/A | N/A | N/A | 0 |
| 8 | N/A | N/A | N/A | 0 | **n.d.** | **0.02** | **0.03** | **2** | **n.d.** | **0.01** | **0.02** | **1** |
| 9 | N/A | N/A | N/A | 0 | **0.03** | **0.04** | **0.07** | **3** | **0.02** | **0.04** | **0.07** | **3** |

N/A not applicable
n.d. not detected

**Table 52: Concentrations of detected 4tBP in surface water samples in µg/L**

| Stream | Sampling 1 | Sampling 2 | Sampling 3 |
|---|---|---|---|
| 1 | n.d. | n.d. | n.d. |
| 2 | n.d. | n.d. | n.d. |
| 3 | n.d. | n.d. | n.d. |
| 4 | n.d. | n.d. | n.s. |
| 5 | n.d. | n.d. | n.d. |
| 6 | n.d. | n.d. | n.d. |
| 7 | n.d. | n.d. | n.d. |
| 8 | n.d. | **0.02** | **0.03** |
| 9 | **0.03** | **0.07** | **0.03** |

n.d. not detected
n.s. no sample

**Table 53: Concentrations of detected 4tPP in surface water samples in µg/L**

| Stream | Sampling 1 | Sampling 2 | Sampling 3 |
|---|---|---|---|
| 1 | n.d. | n.d. | n.d. |
| 2 | n.d. | n.d. | n.d. |
| 3 | n.d. | n.d. | n.d. |
| 4 | n.d. | n.d. | n.s. |
| 5 | n.d. | n.d. | n.d. |
| 6 | n.d. | n.d. | n.d. |
| 7 | n.d. | n.d. | n.d. |
| 8 | n.d. | n.d. | n.d. |
| 9 | n.d. | n.d. | n.d. |

n.d. not detected
n.s. no sample

Table 54: Concentrations of detected OP in surface water samples in µg/L

| Stream | Sampling 1 | Sampling 2 | Sampling 3 |
|---|---|---|---|
| 1 | n.d. | n.d. | n.d. |
| 2 | n.d. | n.d. | n.d. |
| 3 | n.d. | n.d. | n.d. |
| 4 | n.d. | n.d. | n.s. |
| 5 | **<LOQ** | n.d. | n.d. |
| 6 | n.d. | n.d. | **<LOQ** |
| 7 | n.d. | n.d. | n.d. |
| 8 | n.d. | **0.02** | n.d. |
| 9 | **0.03** | **0.07** | **0.02** |

| | |
|---|---|
| n.d. | not detected |
| n.s. | no sample |

Other than 4tBP, 4tPP and 4tOC, NP concentration was also determined for some samples. Since NPs tend to adsorb easily, sample workup requires additional steps in order to achieve reliable data. These steps were not performed for investigated sample-sets. Thus, reliability of results can be questioned and results are not shown. Furthermore, NPs in surface water were investigated to a high extent in other studies (see Table 9), whereas this project rather focuses on short chain APs. However, NP was analyzed in all further samples.

### 5.4.2 Aalkylphenols in additional surface waters

In addition to considered scenarios for sampling of surface waters, 26 surface waters were sampled in 2017 and 26 additional surface waters in 2018. Two of the sampled surface waters were sampled in both years, whereas remaining 48 surface waters were only sampled over the course of one year each. These samples were than analyzed on their AP concentrations. Thankfully, samples were provided by the "Hessisches Landesamt für Naturschutz, Umwelt und Geologie (HLNUG)". If not indicated otherwise, sampling was performed monthly over the time course of 2017 (24h composite samples). Analysis of these samples was not executed via a tailored method for APs but in the course of a multi-component analysis. Thus, LOD and LOQ levels vary from the ones in the previous screening. Obtained data is presented individually for each year.

### 5.4.2.1 Alkylphenols in additional surface waters in 2017

Table 55 shows the concentrations of 4tBP for the 26 investigated streams. 4tBP was detected in 11 out of the 26 investigated streams in 2017. However, over the course of one year, the maximal number of 4tBP detections did not exceed three for all streams but two (detection frequency over all samples: 9%). Detection frequency of 4tBP in those two streams (12 and 23) was 71% and 82%, respectively. Furthermore, reported concentrations were below or close to the method LOQ for most streams. Thus, environmental concentrations are rather low. This could for example be attributed to (1) low environmental levels that might be the result of the use of neglectable quantities or (2) environmental transformation of 4tBP.

**Table 55: Detected concentrations of 4tBP in 26 streams over the course of 2017; concentration in in µg/L**

| Stream number | Jan | Feb | Mar | Apr | Apr | May | May | Jun | Jun | Jul | Aug | Sep | Oct | Oct | Nov | Nov | Dec |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | n.s. | n.d. | n.d. | n.d. | n.d. | **0.05** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 11 | n.s. | n.d. | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. |
| 12 | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | n.s. | **<LOQ** | n.s. | **<LOQ** | n.s. | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | n.s. | **<LOQ** | n.s. | **<LOQ** |
| 13 | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | **<LOQ** | n.s. | n.d. | **0.05** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 14 | n.d. | n.d. | n.d. | n.s. | n.s. | n.d. | n.s. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d.* | n.d. |
| 15 | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 16 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 17 | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 18 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 19 | n.d. | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | n.s. | **<LOQ** | n.d. | n.d. | n.s. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 20 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 21 | n.s. | n.d. | n.d. | **0.07** | n.d. | n.d. | n.d. | **0.03** | n.d. | n.d. | n.s. | **0.02** | **0.03** | n.d. | n.s. | n.d. | n.s. |
| 22 | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.d. | **0.04** | **0.04** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 23 | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | **0.05** | **0.08** | **0.09** | **0.03** | **0.05** | n.d. | **0.04** | **0.07** | **0.04** | **0.05** | n.d. | **<LOQ** | **<LOQ** |
| 24 | **<LOQ** | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 25 | n.d. | n.s. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | **<LOQ** |
| 26 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 27 | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.s. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 28 | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.s. | n.d. | n.s. | n.s. |
| 29 | 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.d. | n.d. | n.d. | n.d. | n.d. |
| 30 | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 31 | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 32 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 33 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 34 | 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.d. | n.s. | n.d. | n.s. | n.d. |
| 35 | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

*Sampling performed in December

| | |
|---|---|
| <LOQ | below limit of quantification |
| n.d. | not detected |
| n.s. | no sample |

Table 56 shows the concentrations of 4tPP for the 26 investigated streams in 2017. Over all samples (354), 4tPP was only detected three times, never exceeding LOQ (detection frequency: 1%). The overall picture that was obtained from these results is similar to the impression that was obtained during the first screening. Thus, 4tPP can hardly be detected in investigated compartments of the aquatic environment. As stated before for 4tBP, this could be attributed to (1) general low environmental levels or (2) environmental transformation of 4tPP.

**Table 56: Detected concentrations of 4tPP in 26 streams over the course of 2017; concentration in in µg/L**

| Stream number | Jan | Feb | Mar | Apr | Apr | May | May | Jun | Jun | Jul | Aug | Sep | Oct | Oct | Nov | Nov | Dec |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | n.s. | 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.d. | n.d. | n.d. | n.d. |
| 11 | n.s. | n.d. | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. |
| 12 | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 13 | n.d. | n.d. | n.d. | **<LOQ** | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 14 | n.d. | n.d. | n.d. | n.s. | n.s. | n.d. | n.s. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | *n.d. | n.d. |
| 15 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 16 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 17 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 18 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 19 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 20 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 21 | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. |
| 22 | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 23 | 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.d. | n.d. | n.d. | n.d. | n.d. |
| 24 | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 25 | n.d. | n.s. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 26 | 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.d. | n.s. | n.d. | n.s. | n.d. |
| 27 | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.s. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 28 | n.d. | **<LOQ** | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.s. | n.d. | n.s. | n.s. |
| 29 | 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.d. | n.d. | n.d. | n.d. | n.d. |
| 30 | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 31 | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 32 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 33 | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. |
| 34 | 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.d. | n.s. | n.d. | n.s. | n.d. |
| 35 | n.s. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

*Sampling performed in December

| | |
|---|---|
| <LOQ | below limit of quantification |
| n.d. | not detected |
| n.s. | no sample |

Table 57 shows the concentrations of OP for the 26 investigated streams. Unlike 4tBP and 4tPP, OP was detected in each investigated stream. Although the concentrations rarely exceeded LOQ, OP was detected in 53% of investigated samples. This clearly legitimizes the change in sampling procedure, since the first sampling series indicated a low detection frequency of OP. The OP concentration only exceeded the LOQ in 27 samples, with concentrations that were only slightly above LOQ.

**Table 57: Detected concentrations of OP in 26 streams over the course of 2017; concentration in in µg/L**

| Stream number | Jan | Feb | Mar | Apr | Apr | May | May | Jun | Jun | Jul | Aug | Sep | Oct | Oct | Nov | Nov | Dec |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | n.s. | **<LOQ** | **<LOQ** | **<LOQ** | n.d. | n.d. | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | n.d. | n.d. | n.d. | **<LOQ** | **<LOQ** | **<LOQ** |
| 11 | n.s. | **0.03** | **0.04** | n.d. | n.s. | n.s. | n.s. | n.d. | **<LOQ** | n.s. | n.d. | **<LOQ** | n.d. | n.s. | **<LOQ** | **<LOQ** | **<LOQ** |
| 12 | **0.05** | **<LOQ** | **<LOQ** | **<LOQ** | n.s. | **<LOQ** | n.s. | n.d. | n.s. | **<LOQ** | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | **0.03** |
| 13 | n.d. | n.d. | **<LOQ** | n.d. | n.s. | **<LOQ** | **<LOQ** | n.d. | n.s. | **0.03** | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | **0.03** |
| 14 | **<LOQ** | **<LOQ** | n.d. | n.s. | n.s. | **<LOQ** | n.s. | n.s. | n.s. | **0.04** | **<LOQ** | **<LOQ** | **<LOQ** | n.s. | **<LOQ** | ***0.03** | **0.04** |
| 15 | n.d. | n.d. | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | n.s. | n.s. | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | **0.03** |
| 16 | n.d. | n.d. | **<LOQ** | n.d. | **0.04** | **<LOQ** | n.s. | **<LOQ** | **<LOQ** | n.s. | n.s. | n.d. | n.d. | n.d. | **<LOQ** | **<LOQ** | **<LOQ** |
| 17 | n.d. | n.d. | **<LOQ** | **<LOQ** | **0.03** | **<LOQ** | n.s. | n.d. | **<LOQ** | n.s. | n.s. | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | *<LOQ* |
| 18 | n.d. | **<LOQ** | **0.03** | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | n.s. | n.d. | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** |
| 19 | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | n.s. | n.d. | **<LOQ** | n.s. | n.d. | **<LOQ** | **<LOQ** |
| 20 | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | n.s. | **<LOQ** | n.d. | n.d. | n.s. | n.s. | **<LOQ** | n.s. | n.d. | n.s. | **<LOQ** |
| 21 | n.s. | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. |
| 22 | n.s. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | **<LOQ** | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.d. | **<LOQ** |
| 23 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | n.d. | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** |
| 24 | **0.05** | n.d. | **<LOQ** | n.s. | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | **<LOQ** |
| 25 | n.d. | n.s. | **<LOQ** | **<LOQ** | n.s. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | n.d. | n.d. | **<LOQ** | n.s. | **<LOQ** | n.s. | **<LOQ** |
| 26 | n.d. | **<LOQ** | **0.04** | **<LOQ** | n.d. | **0.03** | n.d. | **0.04** | **<LOQ** | **0.03** | **0.04** | **<LOQ** | **<LOQ** | n.s. | **<LOQ** | n.s. | **0.03** |
| 27 | n.s. | **<LOQ** | n.s. | **<LOQ** | n.d. | **<LOQ** | n.s. | n.s. | n.s. | **<LOQ** | n.s. | n.d. | n.d. | n.s. | n.d. | n.s. | **<LOQ** |
| 28 | n.d. | n.d. | n.d. | n.d. | n.s. | **0.04** | n.d. | **0.03** | **<LOQ** | n.d. | **<LOQ** | n.d. | n.s. | n.s. | **<LOQ** | n.s. | n.s. |
| 29 | n.d. | **<LOQ** | **<LOQ** | n.d. | **0.03** | **<LOQ** | n.d. | **<LOQ** | **0.03** | n.d. | **0.03** | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** |
| 30 | n.d. | **0.04** | n.s. | **<LOQ** | n.d. | **0.03** | n.d. | **<LOQ** | **<LOQ** | n.s. | n.s. | n.s. | n.d. | n.s. | **<LOQ** | n.s. | **<LOQ** |
| 31 | n.d. | n.d. | n.d. | n.d. | n.s. | **0.03** | **<LOQ** | **<LOQ** | **<LOQ** | **0.03** | **0.04** | n.s. | **0.04** | n.s. | **<LOQ** | n.s. | **0.03** |
| 32 | n.d. | n.d. | **0.03** | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | n.s. | n.s. | n.s. | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | **<LOQ** |
| 33 | n.d. | n.d. | **0.04** | n.d. | n.d. | **0.04** | n.s. | **<LOQ** | **<LOQ** | **<LOQ** | n.d. | n.d. | **<LOQ** | n.s. | **<LOQ** | n.s. | **0.03** |
| 34 | n.d. | n.d. | **<LOQ** | n.d. | n.d. | **0.04** | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | n.s. | n.d. | n.s. | **0.03** |
| 35 | n.s. | n.s. | n.d. | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | n.s. | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | **0.03** |

*Sampling performed in December

| | |
|---|---|
| <LOQ | below limit of quantification |
| n.d. | not detected |
| n.s. | no sample |

Table 58 shows the concentrations of NP for the 26 investigated streams in 2017. NP was detected in each of the 26 streams. Similar results were also reported in numerous other studies. NP was detected in 80% of investigated samples. Concentrations ranged from <LOQ to 0.42 µg/L. As a consequence of restriction in the use of NP in 2002, environmental concentrations decreased. Thus, observed results are as expected.

**Table 58: Detected concentrations of NP in 26 streams over the course of 2017; concentration in in µg/L**

| Stream number | Jan | Feb | Mar | Apr | Apr | May | May | Jun | Jun | Jul | Aug | Sep | Oct | Oct | Nov | Nov | Dec |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | n.s. | **0.04** | **0.06** | **<LOQ** | **0.04** | **0.06** | **<LOQ** | **0.06** | n.d. | **<LOQ** | **<LOQ** | **0.2** | **0.03** | **<LOQ** | **<LOQ** | **<LOQ** | **0.03** |
| 11 | n.s. | **0.07** | **0.34** | **0.04** | n.s. | n.s. | n.s. | **<LOQ** | **0.08** | n.s. | **0.06** | n.d. | **0.15** | **0.19** | **<LOQ** | **0.15** | **0.14** |
| 12 | **0.05** | **0.05** | **0.05** | n.d. | n.s. | n.d. | n.s. | **<LOQ** | n.s. | **<LOQ** | **<LOQ** | **0.06** | **0.09** | n.s. | **0.18** | n.s. | **0.16** |
| 13 | **<LOQ** | **0.09** | **0.03** | n.d. | n.s. | **<LOQ** | **0.07** | n.d. | n.s. | n.d. | **0.09** | **0.06** | n.d. | **<LOQ** | **0.03** | **0.16** | **0.05** |
| 14 | **0.03** | **0.06** | **0.14** | n.s. | n.s. | **<LOQ** | n.s. | n.s. | n.s. | **0.12** | **0.06** | **0.08** | n.d. | n.s. | n.d. | *n.d. | **0.05** |
| 15 | **<LOQ** | **0.13** | **0.09** | **0.06** | **0.03** | n.d. | **0.03** | **0.05** | n.s. | n.s. | **0.15** | n.d. | n.d. | **0.11** | n.d. | **0.18** | **0.17** |
| 16 | **0.08** | **0.12** | **0.05** | **0.05** | **0.04** | **0.03** | n.s. | n.d. | n.d. | n.s. | n.s. | **0.06** | **0.03** | **0.05** | **0.04** | **0.03** | **0.10** |
| 17 | **<LOQ** | **0.05** | **0.04** | **0.06** | n.d. | **0.03** | n.s. | **0.04** | n.d. | n.s. | n.s. | **<LOQ** | **0.25** | **0.16** | **0.19** | **0.24** | **0.15** |
| 18 | **<LOQ** | **0.06** | **0.11** | **<LOQ** | **0.05** | **<LOQ** | **0.08** | **<LOQ** | **0.26** | n.s. | **0.03** | **0.02** | **0.03** | **0.11** | **0.06** | **0.08** | **0.10** |
| 19 | n.d. | **0.07** | **0.05** | **0.04** | n.d. | n.d. | n.s. | n.d. | n.d. | **0.16** | n.s. | **0.05** | **0.08** | n.s. | **0.05** | n.s. | **0.08** |
| 20 | **<LOQ** | **0.08** | **0.08** | **0.12** | n.d. | n.d. | n.s. | **0.03** | **<LOQ** | **0.30** | n.s. | n.s. | **0.07** | **n.s.** | **0.04** | n.s. | **0.07** |
| 21 | n.s. | **0.06** | **0.09** | **0.13** | **0.10** | **<LOQ** | **<LOQ** | n.d. | **0.03** | **0.03** | n.s. | n.d. | n.d. | **0.07** | n.s. | **<LOQ** | n.s. |
| 22 | n.s. | **0.05** | **0.08** | **0.04** | n.s. | **0.03** | n.s. | **<LOQ** | **0.11** | n.d. | **0.12** | **<LOQ** | n.d. | **0.03** | **<LOQ** | **0.03** | n.d. |
| 23 | **0.03** | **0.04** | **0.07** | **0.19** | n.d. | n.d. | **0.05** | **0.04** | **0.09** | n.d. | n.d. | n.d. | n.d. | **0.07** | **0.05** | **0.03** | **<LOQ** |
| 24 | **0.15** | **0.04** | **0.07** | **0.08** | n.d. | n.d. | **0.04** | n.d. | n.d. | n.s. | **0.18** | n.s. | **0.34** | **0.11** | **0.12** | **0.13** | n.d. |
| 25 | **0.06** | n.s. | **<LOQ** | **0.18** | n.s. | n.d. | **<LOQ** | **0.03** | **0.03** | n.d. | **0.03** | **0.07** | **0.04** | n.s. | **0.24** | n.s. | **0.05** |
| 26 | **<LOQ** | **0.08** | **0.13** | **0.08** | **0.07** | n.d. | **0.06** | **0.10** | **0.03** | n.d. | **0.11** | n.d. | **0.03** | n.s. | **<LOQ** | n.s. | **<LOQ** |
| 27 | n.s. | **0.05** | n.s. | **0.08** | **<LOQ** | **<LOQ** | n.s. | n.s. | n.s. | **<LOQ** | n.s. | **0.04** | **0.14** | n.s. | **0.13** | n.s. | n.d. |
| 28 | **<LOQ** | **0.11** | **0.05** | **<LOQ** | n.s. | **0.06** | **<LOQ** | **0.04** | **0.18** | **0.12** | **0.07** | **0.05** | n.s. | n.s. | **0.04** | n.s. | n.s. |
| 29 | **0.10** | **0.05** | **0.08** | **0.20** | **0.19** | **<LOQ** | **0.04** | **<LOQ** | **0.07** | **0.06** | **0.18** | **0.03** | **0.10** | **0.17** | n.d. | **0.18** | n.d. |
| 30 | **0.14** | **0.05** | n.s. | n.d. | **0.06** | **0.05** | **<LOQ** | n.d. | n.d. | n.s. | n.s. | n.s. | n.d. | n.s. | **0.16** | n.s. | **0.07** |
| 31 | **0.42** | **0.05** | **0.07** | **0.05** | n.s. | **0.03** | **0.09** | **0.11** | **0.05** | **0.06** | **0.11** | n.s. | **<LOQ** | n.s. | **<LOQ** | n.s. | **0.06** |
| 32 | **0.07** | **0.06** | **0.07** | **0.14** | **0.12** | **0.08** | **0.04** | n.d. | n.s. | n.s. | n.s. | **0.11** | **0.10** | **0.09** | **<LOQ** | **0.17** | **0.03** |
| 33 | **0.15** | **0.05** | **0.12** | **0.13** | **<LOQ** | **0.11** | n.s. | **0.03** | n.d. | n.d. | **0.04** | n.d. | **0.06** | n.s. | **<LOQ** | n.s. | **0.18** |
| 34 | **0.03** | **0.05** | **0.11** | **0.03** | **<LOQ** | **0.04** | **<LOQ** | **0.03** | **0.14** | n.d. | **0.04** | n.d. | n.d. | n.s. | **0.05** | n.s. | **0.10** |
| 35 | n.s. | n.s. | **0.06** | **0.03** | **0.05** | n.d. | **0.13** | **0.11** | **<LOQ** | n.s. | **0.11** | **0.04** | **0.33** | **0.12** | **0.04** | **0.03** | **0.05** |

*Sampling performed in December

| | |
|---|---|
| <LOQ | below limit of quantification |
| n.d. | not detected |
| n.s. | no sample |

Figure 14 shows the sum of APs (4tBP, 4tPP, OP and NP) of the 26 investigated streams over the course of 2017. Samples with a concentration <LOQ are shown as ½ LOQ (0.015 µg/L). The error bars indicate the highest and lowest sum that was detected in corresponding streams. As already discussed, NP and OP were detected in each stream. While average concentrations of OP and NP remained relatively steady over most streams, the highest ∑(APS) were strongly bias by high NP concentrations. In contrast, 4tPP was only detected in streams 13, 28 and 33. Although, 4tBP was detected in 11 investigated streams, the average concentration in stream 21 and 23 was significantly higher.

Figure 14: Average sum of 4tBP, 4tPP, OP and NP in 26 investigated stream samples over the course of 2017; black bars indicate highest and lo west sum of APs that was detected in corresponding streams (2017).

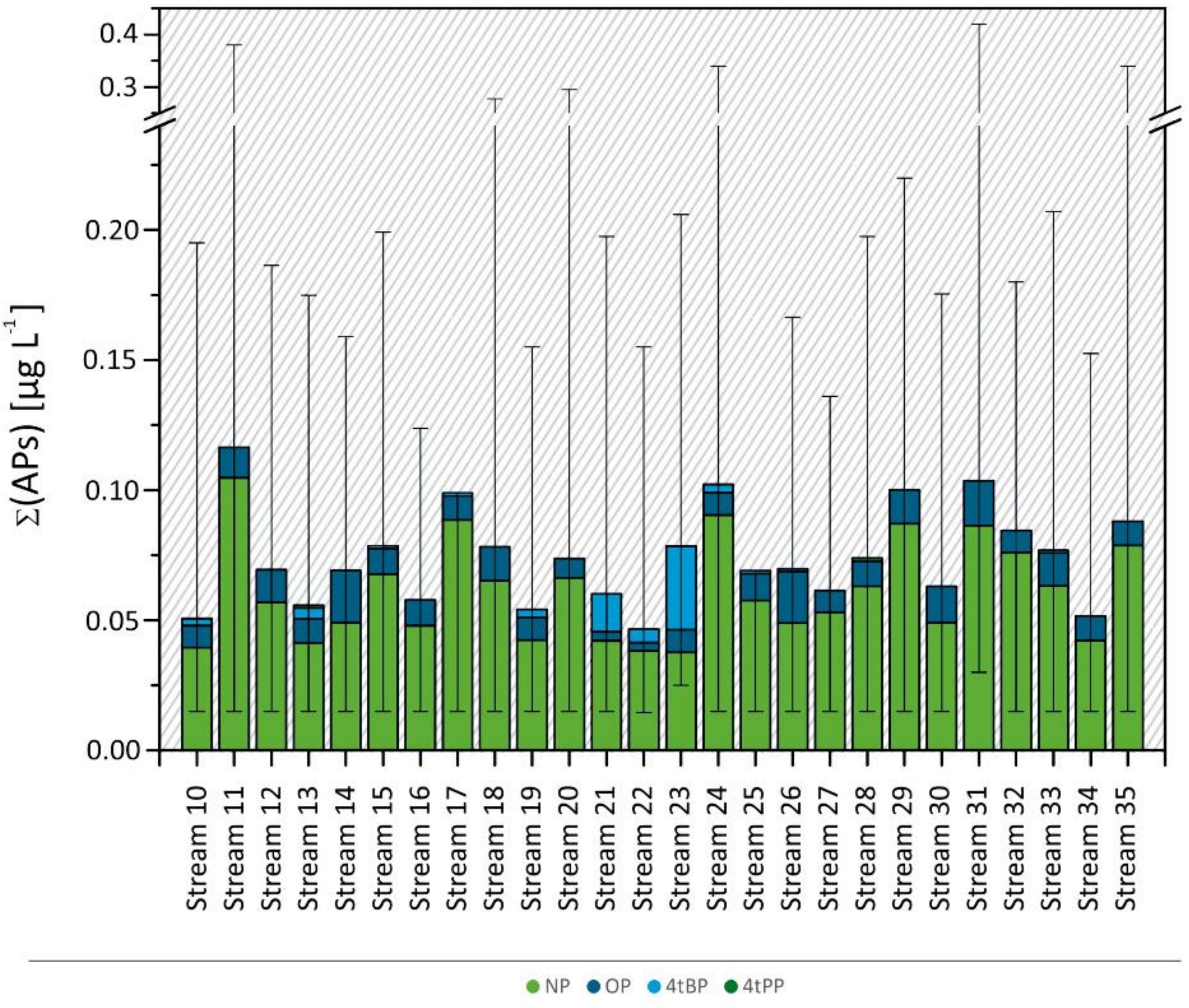
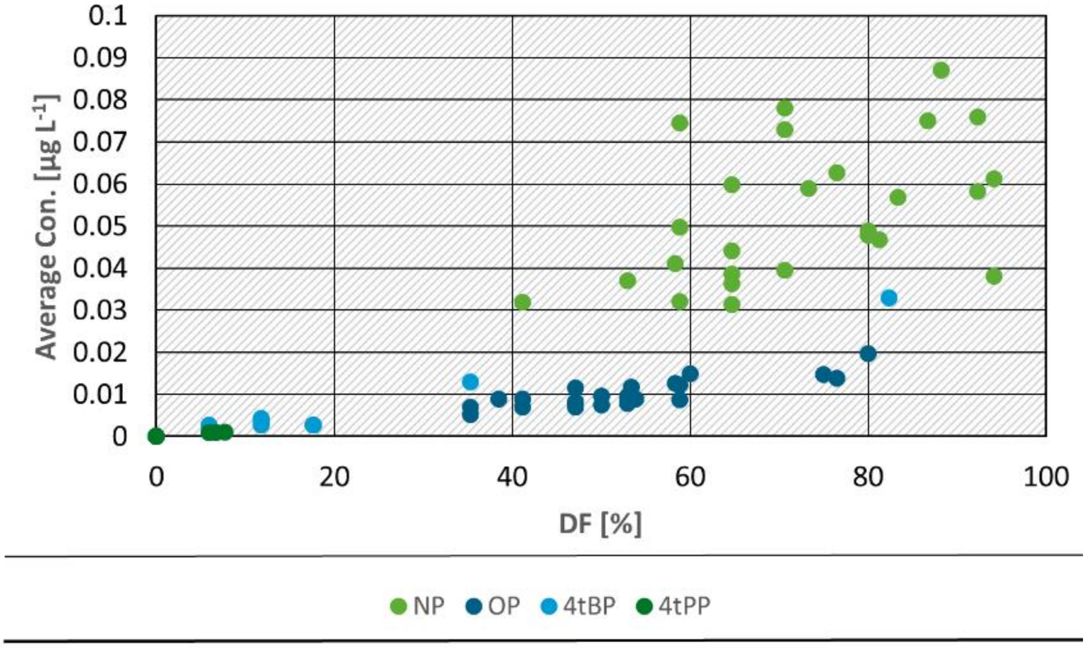


Figure 15 shows the average concentration of 4tBP, 4tPP, OP and NP in streams over the course of 2017, sorted by detection frequency (DF) in this particular year, thus, each dot represents one stream. Samples with a concentration <LOQ are shown as ½ LOQ (0.015 µg/L). As already stated, 4tPP was rarely detected and did not exceed LOQ. NP was detected in the highest concentrations over all samples and analytes. While OP was most times detected in more than 30% of samples per stream, average concentrations showed a narrow distribution. The number of detections for OP were ≤ 60% for all streams but three, which exhibited OP in 75% (stream 5), 80% (stream 17) and 76% (stream 23) of collected samples. A comparable pattern was observed for 4tBP, whereas only one sample showed a particular high DF (82%, stream 14) and 4tBP was detected in <30% samples of another stream (stream 21). Since concentrations and number of detections of SCAPs were very low for all streams but stream 23, special sampling of this stream and the corresponding WWTP were performed (see chapter 5.5).

Figure 15: Average concentration and detection frequency for 4tPP (dark green), 4tBP (light blue), OP (dark blue) and NP (light green) in 26 investigated stream samples over the course of 2017 (n = 369)



### 5.4.2.2 Alkylphenols in additional surface waters in 2018

No 4tPP was detected in investigated surface water samples of 2018, thus, data will not be shown. However, this fortifies the assumption that environmental relevance of 4tPP in the catchment area of investigated streams can be considered to be very low.

Table 59 shows detected concentrations of 4tBP in 2018. In total 4tBP was detected in 11% of investigated samples. Similar to 2017, 4tBP was only detected in 20 out of 26 streams of 2018. Furthermore, DFs in individual streams were very low except for one stream (stream 48), also showing the highest concentrations. This could possibly point towards point source emission, which is a phenomenon that was also observed in 2017.

**Table 59: Detected concentrations of 4tBP in 26 streams over the course of 2018; concentration in in µg/L**

| Stream number | Jan | Feb | Mar | Apr | Apr | May | May | Jun | Jun | Jul | Aug | Sep | Oct | Oct | Nov |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 0.05 | <LOQ | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. |
| 36 | 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.d. | n.d. | n.d. |
| 14 | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. |
| 37 | 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.d. | n.d. | n.d. |
| 38 | 0.08 | 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.d. | n.d. |
| 39 | n.d. | **<LOQ** | 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.d. |
| 40 | n.d. | **<LOQ** | 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.d. |
| 41 | n.d. | **0.03** | 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.d. |
| 42 | n.d. | **<LOQ** | 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.d. |
| 43 | **0.07** | **0.04** | 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.d. |
| 44 | n.d. | **<LOQ** | 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.d. |
| 45 | **0.07** | **<LOQ** | n.d. | n.d. | n.d. | **0.04** | **0.14** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 46 | n.d. | **<LOQ** | 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.d. |
| 47 | n.d. | **0.03** | 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.d. |
| 48 | n.d. | **0.05** | **0.21** | **0.06** | **0.09** | **0.04** | **<LOQ** | **<LOQ** | **0.03** | **<LOQ** | **0.05** | **0.06** | **0.10** | **0.09** | **0.09** |
| 49 | **0.06** | **<LOQ** | 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.d. |
| 50 | n.d. | **0.03** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. |
| 51 | n.d. | **<LOQ** | 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.d. |
| 52 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. |
| 53 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. |
| 54 | 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.d. | n.d. | n.d. |
| 55 | **0.08** | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. |
| 56 | **0.03** | **n.d.** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.s. | n.d. | n.d. | n.d. | n.d. |
| 57 | **0.05** | **<LOQ** | 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.d. |
| 58 | **0.03** | **<LOQ** | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 59 | **0.03** | 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.d. | n.d. |

| | |
|---|---|
| <LOQ | below limit of quantification |
| n.d. | not detected |
| n.s. | no sample |

Table 60 shows concentrations of OP in investigated streams of 2018. OP was detected in all streams with an overall DF of 49%, however, strongly bias by samples with a concentration <LOQ (DF of OP for samples <LOD: 35%).

**Table 60: Detected concentrations of OP in 26 streams over the course of 2018; concentration in in µg/L**

| Stream number | Jan | Feb | Mar | Apr | Apr | May | May | Jun | Jun | Jul | Aug | Sep | Oct | Oct | Nov |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | n.d. | n.d. | **0.03** | **<LOQ** | n.s. | n.d. | n.s. | **<LOQ** | n.s. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | n.s. | **0.07** |
| 36 | n.d. | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. | **0.05** |
| 14 | n.d. | **<LOQ** | n.d. | **0.02** | n.s. | n.d. | n.s. | n.d. | n.s. | n.d. | n.d. | **<LOQ** | **<LOQ** | n.s. | n.d. |
| 37 | n.d. | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | **0.04** |
| 38 | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | n.d. | n.d. | n.d. | **0.03** |
| 39 | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.d. | **<LOQ** | **<LOQ** |
| 40 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.d. | **0.03** | **<LOQ** | n.d. | n.d. | **<LOQ** |
| 41 | **<LOQ** | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | n.d. | n.d. | n.d. |
| 42 | **<LOQ** | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. |
| 43 | n.d. | **<LOQ** | n.d. | n.d. | n.d. | **<LOQ** | **0.03** | **<LOQ** | **0.03** | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. |
| 44 | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 45 | **<LOQ** | **<LOQ** | **<LOQ** | **0.03** | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 46 | **<LOQ** | **<LOQ** | **n.d.** | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | n.d. |
| 47 | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | **0.04** | **<LOQ** | **0.04** | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | n.d. |
| 48 | n.d. | **<LOQ** | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 49 | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 50 | **<LOQ** | **0.04** | **0.03** | n.d. | **0.04** | n.d. | **0.03** | n.d. | n.d. | **<LOQ** | n.s. | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** |
| 51 | **<LOQ** | n.d. | **0.03** | n.d. | **<LOQ** | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. |
| 52 | **<LOQ** | **<LOQ** | n.d. | n.d. | **0.03** | n.d. | **0.04** | n.d. | n.d. | **<LOQ** | n.s. | **<LOQ** | **<LOQ** | **<LOQ** | n.d. |
| 53 | **<LOQ** | **<LOQ** | **0.03** | n.d. | **<LOQ** | **<LOQ** | **0.03** | **<LOQ** | **<LOQ** | **<LOQ** | n.s. | n.d. | **<LOQ** | n.d. | n.d. |
| 54 | **<LOQ** | **<LOQ** | **0.03** | n.d. | **0.03** | **0.03** | **0.03** | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | n.d. | n.d. | n.d. |
| 55 | **<LOQ** | **0.03** | **0.03** | **0.03** | **0.04** | n.d. | **0.03** | n.d. | **<LOQ** | n.d. | n.s. | **<LOQ** | **<LOQ** | **<LOQ** | n.d. |
| 56 | n.d. | **<LOQ** | **<LOQ** | n.d. | **0.03** | n.d. | **0.03** | n.d. | **<LOQ** | n.d. | n.s. | n.d. | **<LOQ** | **<LOQ** | n.d. |
| 57 | **<LOQ** | **<LOQ** | **<LOQ** | **<LOQ** | n.d. | n.d. | **0.03** | n.d. | **<LOQ** | n.d. | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. |
| 58 | n.d. | **<LOQ** | **0.03** | **<LOQ** | **<LOQ** | **<LOQ** | **0.03** | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | **<LOQ** | n.d. | n.d. |
| 59 | n.d. | **<LOQ** | **0.03** | n.d. | **<LOQ** | n.d. | **<LOQ** | n.d. | **<LOQ** | **<LOQ** | **0.04** | n.d. | **<LOQ** | n.d. | **<LOQ** |

| | |
|---|---|
| <LOQ | below limit of quantification |
| n.d. | not detected |
| n.s. | no sample |

Table 61 shows concentrations of NP in streams that were sampled in 2018. Similar to streams that were sampled in 2017, NP was detected in every stream with an overall DF of 64%, which is slightly lower than the DF in 2017. Concentrations of NP ranged from <LOQ to 0.5 µg/L, which is also comparable to results that were obtained in 2017.

**Table 61: Detected concentrations of NP in 26 streams over the course of 2018; concentration in in µg/L**

| Stream number | Jan | Feb | Mar | Apr | Apr | May | May | Jun | Jun | Jul | Aug | Sep | Oct | Oct | Nov |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | **<LOQ** | **<LOQ** | **0.13** | **0.13** | n.s. | **<LOQ** | n.s. | **<LOQ** | n.s. | **0.11** | **<LOQ** | **0.08** | **0.10** | n.s. | **0.07** |
| 36 | n.d. | n.d. | **0.05** | **0.10** | **0.12** | n.d. | **0.06** | **0.06** | **0.06** | **0.05** | **0.09** | n.d. | **0.11** | **0.07** | **0.03** |
| 14 | n.d. | n.d. | n.d. | **0.05** | n.s. | **<LOQ** | n.d. | **0.09** | n.d. | n.d. | n.d. | **0.08** | **0.03** | n.s. | n.d. |
| 37 | **0.05** | **0.17** | **0.03** | **0.14** | **0.05** | **0.14** | **0.07** | **<LOQ** | **0.04** | n.d. | **0.03** | n.d. | **0.15** | n.d. | **0.09** |
| 38 | **0.26** | n.d. | n.d. | **<LOQ** | **0.08** | **0.05** | n.d. | **0.04** | **0.05** | n.d. | n.d. | **0.10** | n.d. | **<LOQ** | n.d. |
| 39 | n.d. | **0.04** | **0.09** | **0.17** | **<LOQ** | n.d. | **0.15** | n.d. | **0.07** | **0.15** | n.d. | **0.08** | **0.15** | **0.04** | **0.12** |
| 40 | **0.10** | **0.19** | **<LOQ** | **0.016** | **0.05** | **<LOQ** | **0.09** | **0.12** | **0.11** | **0.15** | n.d. | **<LOQ** | **0.09** | **<LOQ** | n.d. |
| 41 | n.d. | **0.08** | n.d. | n.d. | **0.08** | **0.10** | **<LOQ** | **0.14** | **0.03** | n.d. | n.d. | **<LOQ** | n.d. | n.d. | n.d. |
| 42 | n.d. | **0.10** | **0.10** | **0.03** | **0.18** | **0.04** | **0.11** | n.d. | n.d. | **0.06** | n.d. | **0.06** | n.d. | n.d. | **0.07** |
| 43 | n.d. | **0.15** | **0.05** | **0.20** | **0.05** | **0.06** | **0.14** | **0.04** | **0.17** | **0.03** | **0.13** | **0.12** | **0.09** | **<LOQ** | n.d. |
| 44 | **<LOQ** | **0.31** | **0.05** | n.d. | **0.05** | **0.18** | **0.11** | **0.04** | n.d. | n.d. | n.d. | **0.09** | **n.d.** | **0.05** | **<LOQ** |
| 45 | n.d. | **<LOQ** | **0.08** | **0.07** | **0.19** | **0.11** | **0.06** | **0.06** | n.d. | n.d. | n.d. | **<LOQ** | **n.d.** | **<LOQ** | **0.11** |
| 46 | **<LOQ** | **0.06** | **0.10** | **0.30** | **0.05** | **0.09** | **0.10** | n.d. | n.d. | **0.03** | n.d. | **0.07** | **n.d.** | **0.04** | **0.05** |
| 47 | **0.06** | **0.08** | n.d. | **0.03** | **0.09** | n.d. | **0.16** | n.d. | n.d. | n.d. | n.d. | **0.03** | n.d. | n.d. | n.d. |
| 48 | n.d. | **0.07** | **0.20** | **0.04** | n.d. | **0.09** | **0.05** | n.d. | **0.04** | n.d. | **0.03** | n.d. | n.d. | **<LOQ** | n.d. |
| 49 | n.d. | n.d. | **0.21** | n.d. | **0.10** | **0.14** | **0.10** | **0.07** | n.d. | n.d. | **0.06** | **0.09** | n.d. | n.d. | **0.06** |
| 50 | n.d. | **0.04** | **0.06** | n.d. | **0.08** | **0.05** | **0.12** | n.d. | n.d. | n.d. | **n.s.** | **0.07** | **0.14** | n.d. | n.d. |
| 51 | **0.05** | **0.08** | **0.06** | **0.14** | n.d. | n.d. | **0.11** | **0.05** | n.d. | n.d. | n.d. | **0.06** | n.d. | **0.07** | **0.04** |
| 52 | n.d. | **0.10** | **0.08** | n.d. | **0.15** | **0.09** | **0.15** | **0.06** | n.d. | n.d. | n.s. | **0.10** | n.d. | **0.05** | n.d. |
| 53 | n.d. | **0.14** | n.d. | n.d. | **0.04** | n.d. | n.d. | n.d. | **<LOQ** | **0.10** | n.s. | **0.06** | n.d. | n.d. | n.d. |
| 54 | n.d. | **0.10** | **0.11** | **0.14** | **0.19** | n.d. | **0.11** | n.d. | n.d. | **<LOQ** | **<LOQ** | n.d. | n.d. | **<LOQ** | **0.05** |
| 55 | **0.13** | **0.05** | **0.07** | **0.02** | **0.09** | **<LOQ** | **0.13** | n.d. | **0.09** | n.d. | n.s. | n.d. | **0.15** | **0.09** | **0.07** |
| 56 | **0.08** | **0.07** | **0.12** | **0.09** | **0.30** | **0.16** | **0.24** | **0.05** | n.d. | **0.03** | n.s. | **0.06** | **0.09** | **<LOQ** | n.d. |
| 57 | **0.11** | **0.10** | **0.50** | n.d. | n.d. | **0.04** | **0.15** | **0.12** | n.d. | n.d. | n.d. | **<LOQ** | n.d. | **0.03** | **0.03** |
| 58 | **0.07** | n.d. | **0.13** | **0.08** | **0.06** | **0.03** | **0.13** | n.d. | **0.03** | n.d. | **0.04** | n.d. | n.d. | n.d. | **0.08** |
| 59 | **0.03** | **0.08** | **0.09** | n.d. | **0.09** | n.d. | **0.05** | **<LOQ** | **0.07** | **0.07** | **0.05** | **0.18** | n.d. | **0.08** | n.d. |

| | |
|---|---|
| <LOQ | below limit of quantification |
| n.d. | not detected |
| n.s. | no sample |

Figure 16 shows the sum of APs of the 26 investigated streams in 2018. Samples with a concentration <LOQ are shown as ½ LOQ (0.015 µg/L). Similar to the streams that were investigated in 2017, both, NP and OP were detected in each stream. 4tPP was not detected in any of the samples that were collected in 2018. However, contrary to 2017, 4tBP was detected in 20 out of 26 streams. Furthermore, average concentrations of 4tBP were slightly higher in 2018. While NP was the dominant AP in most streams, stream 48 was dominated by 4tBP. As already mentioned, this could indicate a point source in the catchment area of stream 48.

Figure 16: Average sum of 4tBP, 4tPP, OP and NP in 26 investigated stream samples over the course of 2017; black bars indicate highest and lowest sum of APs that was detected in corresponding streams (2018).

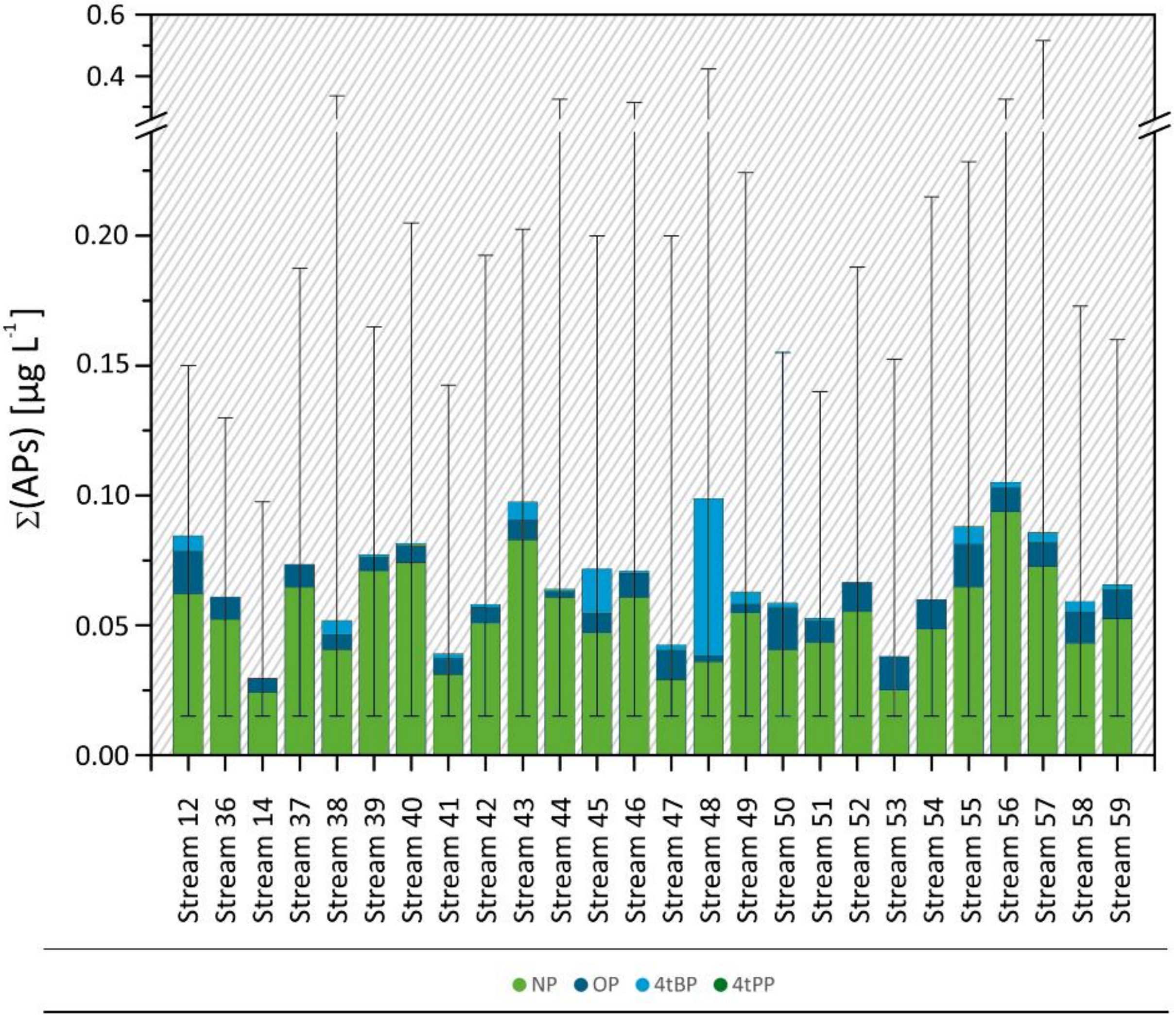
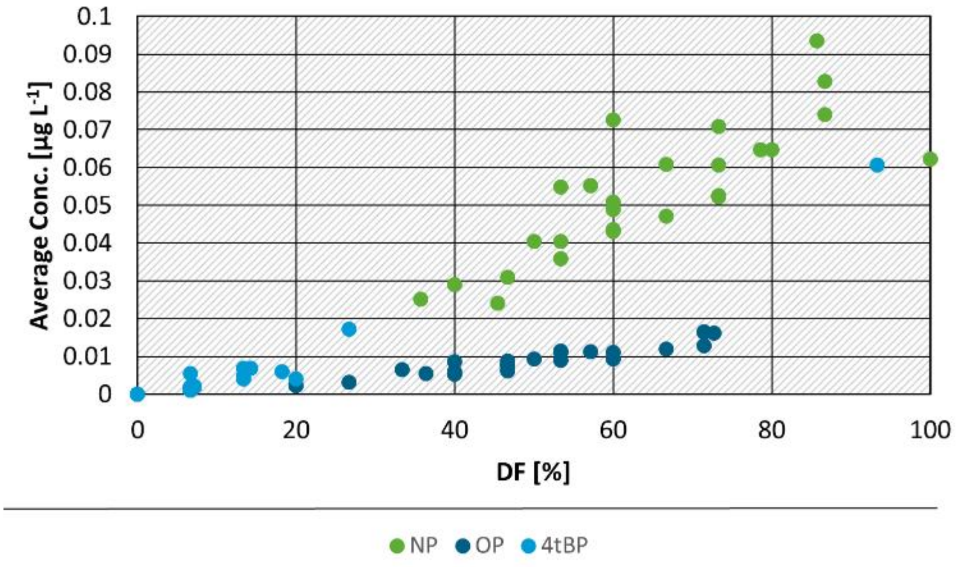


Figure 17 show the average concentration of APs in streams that were sampled over the course of 2018, sorted by DF in this year. Samples with a concentration <LOQ are shown as ½ LOQ (0.015 µg/L).

The graph that is represented in Figure 17 shows a similar course as the same graph for 2017 (see Figure 15). NP was detected in <36% of sample per stream, all showing a mostly linear correlation with average concentrations, thus, indicating comparable concentration for all samples. Same coherence can be observed for OP, however, revealing a shallower slope. In the case of 4tBP one stream exhibited a DF of 93%, which is dramatically higher than the average concentration of other streams. This observation was also made for one stream in 2017 and as already mentioned several times, could possible point towards point source emission. However, it should be considered that application fields of 4tPP and 4tBP strongly vary from the ones of longer chain derivatives (also see chapter 5.7).

Figure 17: Average concentration and detection frequency for 4tBP (light blue), OP (dark blue) and NP (green) in 26 investigated stream samples over the course of 2018 (n = 377)



## 5.5 Alkylphenols in WWTPs

As already stated in chapter 5.4.1, deviations from sampling scenarios that were originally planned were made in agreement with UBA. In total, four WWTPs were sampled and analyzed regarding their AP concentration. Since low environmental concentrations for SCAPs were observed previously, biotransformation studies of these substances were discussed with UBA. It was concluded, that fast biotransformation of SCAPs could also be observed inside of WWTPs and thus, effluent concentration should be lower than influent concentration. As a consequence, influent and effluent of three WWTPS were sampled instead of only sampling WWTP effluents. samples.

Table 62, Table 63 and Table 64 show AP concentrations of influent and effluent samples of WWTP 1-3, whereas Table 65 shows effluent concentrations of WWTP 4. WWTP 2 possesses two individual influents that are channeled to one effluent. OP, and 4tPP were not detected in any sample. 4tBP was detected in WWTP 1, 2 and 4. NP was detected in every WWTP. Whenever influent and effluent were sampled, both, concentration of NP and 4tBP decreased from influent/influents to effluent. This might be explained due to transformation. However, it should be stated that NP is very prone to adsorption processes, whereas balances should be treated with care and decreasing concentrations thereof could also result due to sorption (e.g. to sludge). Furthermore, concentration of NP could also increase due to transformation of NP ethoxylates. Concentration of NP in influents ranged from 0.53 to 2.34 µg/L (average concentration 1.19 µg/L) and NP was detected in every influent sample but one of WWTP 1. Effluent concentrations of NP ranged from 0.07 to 0.86 µg/L (average concentration 0.19 µg/L). The concentration of 4tBP ranged from 0.06 to 056 (average concentration 0.06 µg/L) and 0.1 to 0.04 (average concentration 0.01 µg/L) in influents or effluents, respectively. Furthermore, 4tBP was detected in 80% of investigated influent samples of WWTP 1 and 60% effluent samples. WWTP 1 is the corresponding WWTP to stream 23, thus, matches high detection frequency of 4tBP in stream 23. Detection frequencies and concentration range in effluent samples of WWTP1 showed comparable results to data that was recorded for stream samples.

**Table 62: AP concentrations for influent and effluent samples of WWTP 1; concentration in µg/L**

| WWTP 1 | Sampling 1 | Sampling 2 | Sampling 3 | Sampling 4 | Sampling 5 |
|---|---|---|---|---|---|
| 4tBP Influent | **0.13** | **0.08** | n.d. | **0.56** | **0.19** |
| 4tBP Effluent | **0.04** | n.d. | n.d. | **0.05** | **0.10** |
| 4tPP Influent | n.d. | n.d. | n.d. | n.d. | n.d. |
| 4tPP Effluent | n.d. | n.d. | n.d. | n.d. | n.d. |
| OP Influent | n.d. | n.d. | n.d. | n.d. | n.d. |
| OP Effluent | n.d. | n.d. | n.d. | n.d. | n.d. |
| NP Influent | **0.59** | **2.34** | n.d. | **0.77** | **2.34** |
| NP Effluent | **0.86** | **0.57** | n.d. | n.d. | **0.66** |

n.d. not detected

### Table 63: AP concentrations for influent and effluent samples of WWTP 2; concentration in µg/L

| WWTP 2 | Sampling 1 | Sampling 2 | Sampling 3 | Sampling 4 | Sampling 5 |
|---|---|---|---|---|---|
| 4tBP Influent 1 | n.d. | n.d. | **0.06** | n.d. | n.d. |
| 4tBP Influent 2 | n.d. | n.d. | n.d. | n.d. | n.d. |
| 4tBP Effluent | n.d. | n.d. | n.d. | n.d. | n.d. |
| 4tPP Influent 1 | n.d. | n.d. | n.d. | n.d. | n.d. |
| 4tPP Influent 2 | n.d. | n.d. | n.d. | n.d. | n.d. |
| 4tPP Effluent | n.d. | n.d. | n.d. | n.d. | n.d. |
| OP Influent 1 | n.d. | n.d. | n.d. | n.d. | n.d. |
| OP Influent 2 | n.d. | n.d. | n.d. | n.d. | n.d. |
| OP Effluent | n.d. | n.d. | n.d. | n.d. | n.d. |
| NP Influent 1 | **0.71** | **1.90** | **1.55** | **1.24** | **1.34** |
| NP Influent 2 | **0.88** | **0.93** | **0.53** | **1.19** | **1.01** |
| NP Effluent | **0.26** | **0.07** | **0.30** | n.d. | **0.85** |

n.d. not detected

### Table 64: AP concentrations for influent and effluent sample of WWTP 3; concentration in µg/L

| WWTP 3 | Sampling 1 |
|---|---|
| 4tBP Influent | n.d. |
| 4tBP Effluent | n.d. |
| 4tPP Influent | n.d. |
| 4tPP Effluent | n.d. |
| OP Influent | n.d. |
| OP Effluent | n.d. |
| NP Influent | **1.69** |
| NP Effluent | **0.51** |

n.d. not detected

### Table 65: AP concentrations for effluent samples of WWTP 1; concentration in µg/L

| WWTP 4 | Sampling 1 | Sampling 2 | Sampling 3 | Sampling 4 | Sampling 5 |
|---|---|---|---|---|---|
| 4tBP effluent | **0.04** | **0.07** | n.d. | n.d. | n.d. |
| 4tPP effluent | n.d. | n.d. | n.d. | n.d. | n.d. |
| OP effluent | n.d. | n.d. | n.d. | n.d. | n.d. |
| NP effluent | **0.14** | **0.24** | **0.55** | **0.45** | **0.19** |

n.d. not detected

While environmental behavior and release pathways of NP have been studied to a high extend, only few studies dealt with 4tBP. Since stream 23 revealed most findings of 4tBP, further sampling of this stream was performed. In order to better understand release pathways into the environment, stream 23 was sampled after the spring and upstream as well as downstream the WWTP effluent (see Figure 18). Sampling was performed in the form of grab samples on the same days as sampling of WWTP 1. No 4tBP was detected in any sample upstream WWTP effluent, whereas 4tBP was detected in samples that were withdrawn after the WWTP effluent (see Table 66). Data suggests entrance of 4tBP into stream 23 through WWTP 1. Furthermore, decreasing concentration from influent to effluent and stream water suggest primary degradation of 4tBP. However, decreasing concentrations from WWTP effluent to stream water most probably result due to dilution effects.

Figure 18: Sampling scheme of WWTP 1 and stream 23; own representation, Hochschule Fresenius

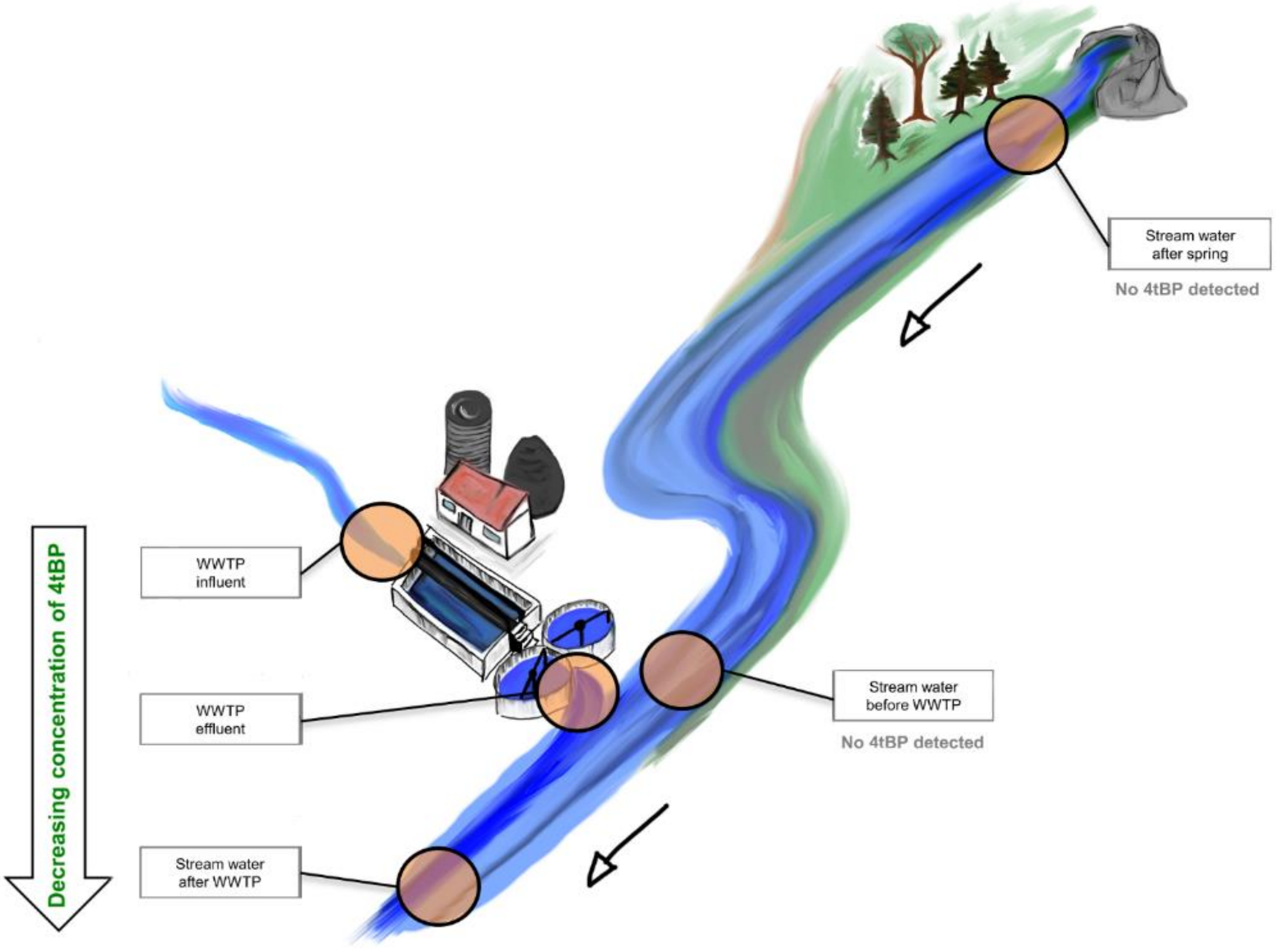


**Table 66: Concentations of 4tBP in stream 23 after the spring and upstream as well as downstrem the WWTP effluent on sampling days of the WWTP; concentration in µg/L**

| | Sampling 1 | Sampling 2 | Sampling 3 | Sampling 4 | Sampling 5 |
|---|---|---|---|---|---|
| Stream water after spring | n.d. | n.d. | n.d. | n.d. | n.d. |
| Stream water before WWTP | n.d. | n.d. | n.d. | n.d. | n.d. |
| Stream water after WWTP | **0.02** | n.d. | n.d. | **0.02** | n.d. |

n.d. not detected

## 5.6 Biotransformation of short chain alkylphenols

### 5.6.1 Biotransformation of short chain alkylphenols for the testing of primary degradation

Since 4tBP and 4tPP were detected in few of the investigated stream and WWTP samples, further studies were performed. Data that was generated during monitoring of 4tBP in WWTP samples suggested the possibility of biotransformation of 4tBP. Thus, lab scale transformation experiments were performed in order to test this hypothesis. Blank samples as well as Na-benzoate control samples were prepared in addition to active and sterile assays that were spiked with 4tBP and 4tPP, respectively. Na-benzoate underwent complete primary degradation within 10 days, which showed a general activity of used microorganisms. Figure 19 and Figure 20 show that both, 4tBP and 4tPP underwent complete primary degradation within 21 days during the first experiments. In order to test a possible adaptation of microorganisms, same assays were spiked again. The second incubation was performed over a period of 9 days and complete primary degradation of 4tBP and 4tPP was observed after 7 days. Thus, indicating adaptation of microorganisms.

Figure 19: Observed results from transformation experiments for primary degradation of 4tBP after 28 days of incubation (first incubation; light green active assay and dark blue sterile assay) and (2) 9 days incubation (second incubation; light blue active assay and dark green sterile assay) in the same assay; time in days plotted against concentration divided by concentration at t=0d ($c/c_0$)

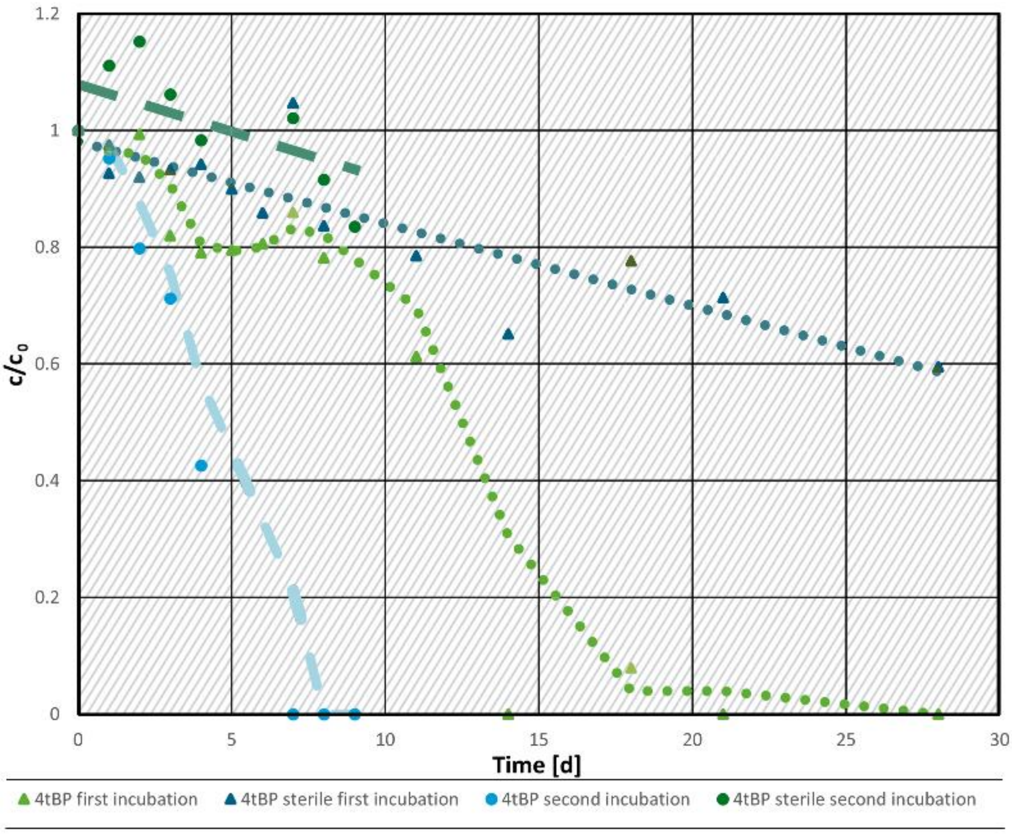
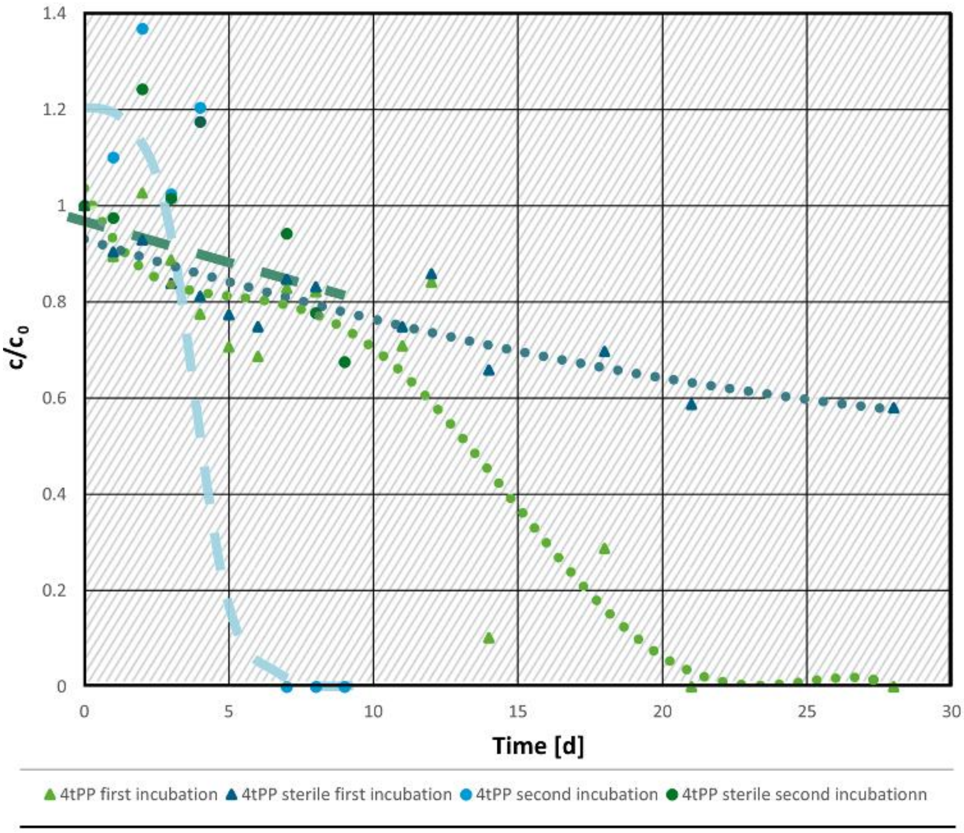


Figure 20: Observed results from transformation experiments for primary degradation of 4tPP after 28 days of incubation (first incubation; light green active assay and dark blue sterile assay) and (2) 9 days incubation (second incubation; light blue active assay and dark green sterile assay) in the same assay; time in days plotted against concentration divided by concentration at t=0d ($c/c_0$)



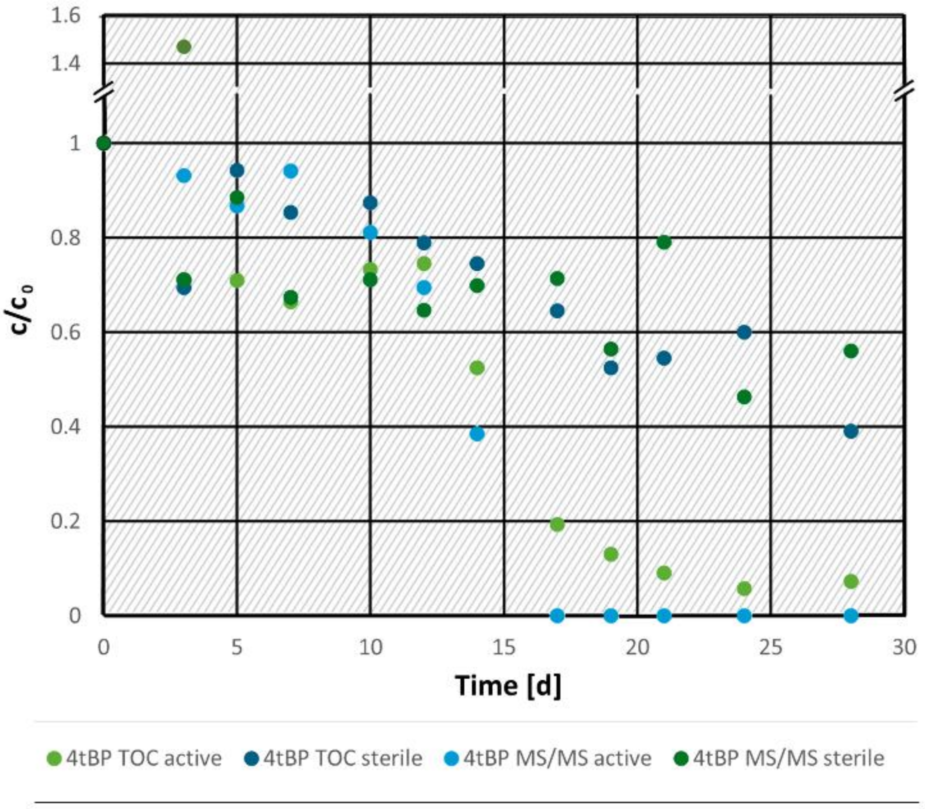
Performed degradation tests indicate that 4tBP and 4tPP are biotransformed in a 10-day period within 28 days of testing and thus, another transformation experiment with factor 10 higher starting concentrations was performed in order to test ready biodegradability (see chapter 5.6.2).

### 5.6.2 Biotransformation of short chain alkylphenols for the testing of total mineralization

Experiments were conducted with a starting concentration of 10 as well as 100 mg/L and were performed over a period of 28 days. Analysis was performed via HPLC-MS/MS in order to quantify APs as well as TOC. Figure 21 shows a rapid primary degradation of 4tBP (within 5 days (from day 12 to day 17)). Simultaneously, TOC also drastically decreased after day 12. In contrast to observed primary degradation, TOC levels decrease slightly shifted, but finally reached a value of approximately 10% starting concentration. Unfortunately, 4tPP did not undergo primary degradation within the test period (neither in the assay with 10 mg/L nor 100 mg/L starting concentration). Transformation experiments of 4tPP were conducted for additional 21 days, however, still not showing primary degradation. Hence, experiments were repeated. New incubation of 4tPP at 10 mg/L with fresh inoculum led to primary degradation of 4tPP (data not shown), however, no primary transformation was observed for experiments at 100 mg/L. This observation may could have been caused by toxicity of the test substance at a higher concentration, however, toxicity tests were not performed, hence, it has not been proven. Furthermore, 4tPP was spiked to the same assays that were used for 4tBP, in order to test biotransformation in inoculum that was already able to biotransform SCAPs. No primary degradation of 4tPP was observed either.

Based on observed results, no high resolution mass spectrometry (HRMS) will be performed, since data does not indicate the formation of stable transformation products. However, primary transformation of 4tBP and 4tPP could explain low environmental levels. Furthermore, performed test show adaption of microorganisms to 4tBP. Thus, microorganisms that are regularly exposed to SCAPs, should be capable to convert 4tBP. As a result, samples should always be analyzed within a few days after sample collection. Unfortunately, transformation experiments with 4tPP showed mixed results, hence, it cannot be clearly stated that 4tPP is stable in the environment. Further studies need to be conducted in order to verify one hypothesis or the other.

Figure 21: Observed results from transformation experiments of 4tBP after 28 days of incubation from a starting concentration of 100 mg/L showing results obtained from quantification using HPLC-MS/MS (light blue active assay and dark green sterile assay) and TOC (light green active assay and dark blue sterile assay); time in days plotted against concentration divided by concentration at t=0d ($c/c_0$)



## 5.7 Alkylphenols in building materials

Table 67shows a List of investigated building material samples, with indication of detected APs and observed concentrations. Quantification of NP was performed using two different standards (4-nonylphenol and a technical mixture containing different isomers).

APs were detected in each of the three investigated categories. 4tBP was detected the most samples (n=10; detection frequency=56%) with concentrations ranging from 2.5 to 320 g/kg (Ø=52.8 g/kg), followed by NP (n=4; detection frequency=22%) with concentrations from 3.4 to 11 g/kg (Ø=1.6 g/kg) and 4tPP and OP (n=1, detection frequency=6%), with concentrations of 3.6 and 1.9 g/kg, respectively.

**Table 67: List of building material samples that were investigated on their AP content and observed concentrations in g/kg**

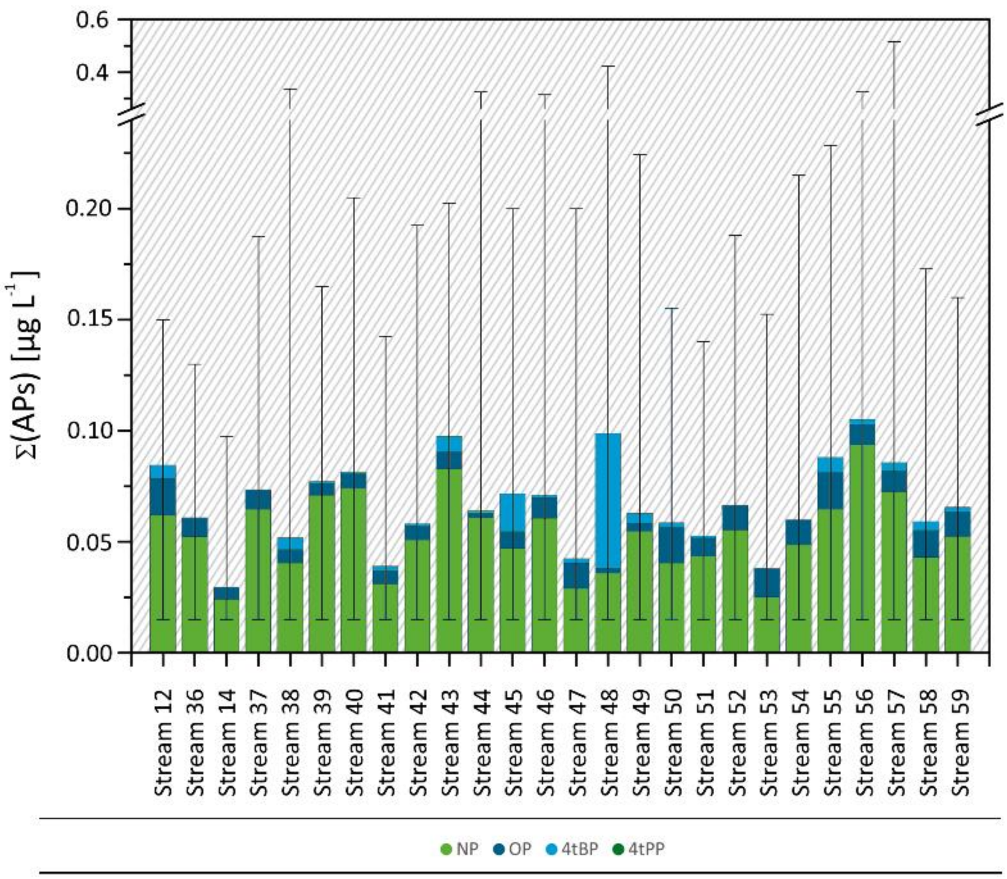
| Sample Category | Sample-ID | 4tBP | 4tPP | OP | NP |
|---|---|---|---|---|---|
| Paints and lacquers | AP-PL01 | **7.3** | **3.6** | **1.9** | n.d. |
| | AP-PL02 | **2.5** | n.d. | n.d. | n.d. |
| Coatings | AP-C01 | n.d. | n.d. | n.d. | n.d. |
| | AP-C02 | n.d. | n.d. | n.d. | n.d. |
| | AP-C03 | **320** | n.d. | n.d. | n.d. |
| | AP-C04 | n.d. | n.d. | n.d. | **3.4** |
| | AP-C05 | **120** | n.d. | n.d. | n.d. |
| | AP-C06 | **41** | n.d. | n.d. | **9.6** |
| | AP-C07 | **150** | n.d. | n.d. | n.d. |
| | AP-C08 | **140** | n.d. | n.d. | n.d. |
| | AP-C09 | n.d. | n.d. | n.d. | n.d. |
| | AP-C10 | **38** | n.d. | n.d. | **11** |
| Glues and adhesives | AP-GA01 | n.d. | n.d. | n.d. | n.d. |
| | AP-GA02 | n.d. | n.d. | n.d. | **5.5** |
| | AP-GA03 | n.d. | n.d. | n.d. | n.d. |
| | AP-GA04 | n.d. | n.d. | n.d. | n.d. |
| | AP-GA05 | **72** | n.d. | n.d. | n.d. |
| | AP-GA06 | **60** | n.d. | n.d. | n.d. |

*data not fully evaluated

n.d. not detected

Figure 22 shows the sum of APs for all samples with positive findings. APs were detected in 100% of investigated paint and lacquer samples, 70% of investigated coating samples and 50% of investigated glue and adhesive samples. Concentrations of APs in coating samples were among the highest, with a maximum concentration of 320 g/kg (AP-C3; sum of APs). Whenever available, concentrations were compared to MSDSs of investigated products, whereby observed concentrations matched indicated percentages. Overall, observed concentrations indicate that detected APs are main components of investigated formulations. Furthermore, only 4tBP and NP were detected in coating as well as glue and adhesive samples. 4tPP was only detected in one of the two investigated paint and lacquer samples.

Figure 22: Building material samples with positive findings of APs, showing the sum of APs in g/kg



Obtained results suggest that 4tPP, OP and NP play a minor role in the investigated type of building materials. However, 4tBP was detected in most samples in the procent range (up to 32%). Both paint formulations are single component systems. We assume that APs in paint formulations are added as additives (e.g. as surfactants for wetting behavior). Furthermore, all coating and glued/adhesive samples with detection of APs were two component systems, mostly epoxy based. However, sample AP-C3 was most likely a phenolic resin. Thus, high amounts of APs in these samples is mandatory for the functionality of the compositions. It should be stated that all herein mentioned building materials were investigated as single components and thus, not in their cured state. Thus, high concentrations cannot be directly linked to high release to the environment. However, application as well as production of these products could lead to high increased release into the environment. Furthermore, small portions of unreacted APs could also enter the environment after curing of the products during service life.

## 5.8 Environmental impact

In order to fully understand the possible environmental impact of APs and especially SCAPs on the environment, further tests are necessary. Transformation experiments of SCAPs suggest complete mineralization of 4tBP. Contrary, transformation experiments of 4tPP yielded ambiguous results, since primary degradation was observed for some experiments only. It could be possible that biotransformation of 4tPP strongly depends on available microorganisms (e.g. metabolization by specialized microorganisms only), as suggested by Toyama et al. [210]. Thus, further experiments are necessary to fully understand biotransformation of SCAPs and differences in the transformation of 4tPP and 4tBP. However, low 4tBP concentrations in investigated building materials in combination with the observed mineralization should therefore lead to a low release into the aquatic environment. Furthermore, detection frequency and detected concentrations of 4tPP in investigated products were negligible. In view of the results of this study, the environmental releases of SCAPs appear to be low compared to the findings of OP and NP. In addition, observed concentrations of OP and NP in investigated products were low and therefore, environmental levels cannot be assigned to these building materials. From the obtained data, we suppose that OP and NP pollutions in the aquatic environment are mainly driven by use of other products (e.g. use of ethoxylates).

## 5.9 Summary of results for Alkylphenols

In total, 766 stream samples, 32 WWTP samples and 18 building materials were tested on their 4tBP, 4tPP and OP concentration. Furthermore, the NP concentration of 639 of those stream samples, as well as the 32 WWTP samples and 18 building materials was analyzed. Analysis of stream samples by far exceeds the originally planned number of samples (originally planned: 45) and WWTP samples exceed the planed number by one sample (originally planned: 31). Investigated building materials revealed positive findings of APs in a majority of the samples. In compliance with UBA, no further building materials were investigated on their AP content. Extended environmental screening showed high detection frequencies of NP and OP. Furthermore, 4tPP was hardly detected at all. Interestingly, high detection frequency of 4tBP was mostly limited to few streams and WWTPs. No OP or 4tPP were detected in WWTP samples. In addition, concentration of NP and 4tBP decreased in all WWTPs from influent to effluent. In order to better understand pathways of 4tBP, additional sampling of the stream next to one of the WWTPs was performed, showing point source release of 4tBP via the WWTP into this stream. However, decreasing concentration from influent to effluent suggested a biotransformation of 4tBP. Thus, lab-scale biotransformation tests were performed for 4tBP as well as 4tPP. 4tBP underwent biotransformation within the test period (28 days). Biotransformation tests of 4tPP led to mixed results. While primary degradation of 4tPP was observed in two out of three WWTP effluent:sludge mixtures when spiked at starting concentrations of 10 mg/L, no primary degradation was observed in tests with starting concentrations of 100 mg/L. Adaption of microorganisms was tested via additional spiking with test substances into assays after complete primary degradation of 4tBP and 4tPP, respectively, showing complete primary degradation after seven days. Further experiments regarding the biotransformation of 4tBP showed a decrease in total organic carbon to approximately 10% starting concentration. Higher concentration and detection frequency of 4tBP for few streams only suggest point source release thereof. Furthermore, investigated building materials contained high portions of 4tBP (up to 32%), whereby they depict possible emission sources during their manufacture and use. However, we assume that the release of 4tBP from cured products does not play an important role.

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# 8 Appendix

## Table 68: Altered quantification limits for PFASs in building materials and industrial used textiles

| Sample-ID | Substance class and unit | PFAAs | | | | | | | | | | | | | | | | | | | | | | | | | | FTOHs | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | PFBA | PFPeA | PFHxA | PFHpA | PFOA | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA | PFTeDA | PFBS | PFPeS | PFHxS | PFHpS | PFOS | PFDS | PFDoDS | 6:2 FTS | 8:2 FTS | 10:2 FTS | PFOSA | 8:2 FTCA | 8:3 FTCA | 7HPFHpA | PF37DMOA | 6:2 FTOH | 8:2 FTOH | 10:2 FTOH |
| PFAS-BM01 | [µg kg$^{-1}$] | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | 5 | 2 | 2 | 2 | 5 | 2 | 2 | 2 | 2 | 40 | 180 | 40 |
| PFAS-BM06 | [µg kg$^{-1}$] | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 10 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | 2 | 2 | 2 | 5 | 2 | 2 | 2 | 2 | 40 | 40 | 40 |
| PFAS-BM09 | [µg kg$^{-1}$] | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 40 | 40 | 40 |
| PFAS-BM14 | [µg kg$^{-1}$] | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 40 | 40 | 40 |
| PFAS-BM03 | PFAAs [µg L$^{-1}$]; FTOHs [µg kg$^{-1}$] | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 01. | 0.5 | 0.5 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.5 | 0.5 | 0.1 | 0.1 | 0.1 | 1 | 1 | 0.5 | 0.1 | 0.1 | N/A | N/A | N/A |
| PFASN/ABM04 | PFAAs [µg L$^{N/A1}$]; FTOHs [µg kg$^{N/A1}$] | 10 | 1 | 10 | 1 | 1 | 10 | 10 | 50 | 50 | 50 | 50 | 10 | 1 | 10 | 10 | 20 | 50 | 50 | 10 | 10 | 10 | 1 | 100 | 50 | 10 | 10 | N/A | N/A | N/A |
| PFASN/ABM02 A and PFASN/ABM02 B | PFAAs [µg L$^{N/A1}$]; FTOHs [µg kg$^{N/A1}$] | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 10 | 10 | 10 | 10 | 1 | 1 | 1 | 1 | 1 | 1 | 10 | 10 | 1 | 1 | 10 | 10 | 50 | 10 | 1 | N/A | N/A | N/A |
| PFASN/AIT14, PFASN/AIT15, PFASN/AIT21 and PFASN/AIT22 | [µg kg$^{N/A1}$] | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | 2 | 8 | 8 | 2 | 2 | 2 | 2 | 2 | 5 | 8 | 2 | 2 | 8 | 2 | 8 | 8 | 8 | 2 | 40 | 40 | 40 |
| PFASN/AIT07, PFASN/AIT16 and PFASN/AIT17 | [µg kg$^{N/A1}$] | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | 2 | 8 | 8 | 2 | 2 | 2 | 2 | 2 | 5 | 2 | 2 | 2 | 8 | 8 | 8 | 8 | 8 | 2 | 40 | 40 | 40 |
| PFASN/AIT23 | [µg kg$^{N/A1}$] | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | 8 | 8 | 8 | 2 | 2 | 2 | 8 | 2 | 5 | 8 | 2 | 5 | 8 | 2 | 8 | 8 | 8 | 2 | 160 | 40 | 40 |
| PFASN/AIT24 | [µg kg$^{N/A1}$] | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 2 | 2 | 2 | 2 | 8 | 8 | 8 | 2 | 40 | 40 | 40 |
| PFASN/AIT25 | [µg kg$^{N/A1}$] | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 2 | 2 | 8 | 2 | 8 | 8 | 8 | 2 | 40 | 40 | 40 |
| **PFASN/AIT26** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 2 | 2 | 8 | 2 | 8 | 8 | 8 | 2 | 160 | 40 | 40 |
| **PFASN/AIT27** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 2 | 8 | 8 | 2 | 2 | 40 | 40 | 40 |
| **PFASN/AIT28** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 8 | 8 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | 8 | 2 | 8 | 8 | 8 | 2 | 40 | 40 | 40 |
| **PFASN/AIT02** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | 8 | 2 | 8 | 2 | 2 | 2 | 40 | 40 | 40 |
| **PFASN/AIT08** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | 8 | 8 | 8 | 2 | 2 | 2 | 2 | 2 | 5 | 8 | 2 | 2 | 8 | 8 | 8 | 8 | 8 | 2 | 40 | 40 | 40 |
| **PFASN/AIT21** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | N/A | N/A | N/A |
| **PFASN/AIT22** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 8 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | N/A | N/A | N/A |
| **PFASN/AIT23** | **[µg kg$^{N/A1}$]** | 8 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 2 | 2 | N/A | N/A | N/A |
| **PFASN/AIT03, PFASIT24 and PFASN/AIT26** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | N/A | N/A | N/A |
| **PFASN/AIT27** | **[µg kg$^{N/A1}$]** | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 8 | 8 | 2 | 2 | N/A | N/A | N/A |

N/A not applicable

Figure 23: Chromatograms of 6:2 FTOH (A-1 and B-1), 8:2 FTOH (A-2 and B-2) and 10:2 FTOH (A-3 and B-3) *of an awning sample*; top (A): sample; bottom (B): sample + 10 ng/mL spike; A signal for 10:2 FTOH was observed and spiked analyte at 10 ng/mL was detected (107% recovery), however, 10:2 FTOH was detected below the method quantification limit. Furthermore, no 6:2 FTOH was detected and spiked analyte was detected (88% recovery). While, the observed signal for 8:2 FTOH suggests a detection thereof, recovery experiments reveal insufficient chromatographic separation as a consequence of interfering matrix components and thus, 8:2 FTOH was rated “not evaluable” for this sample.

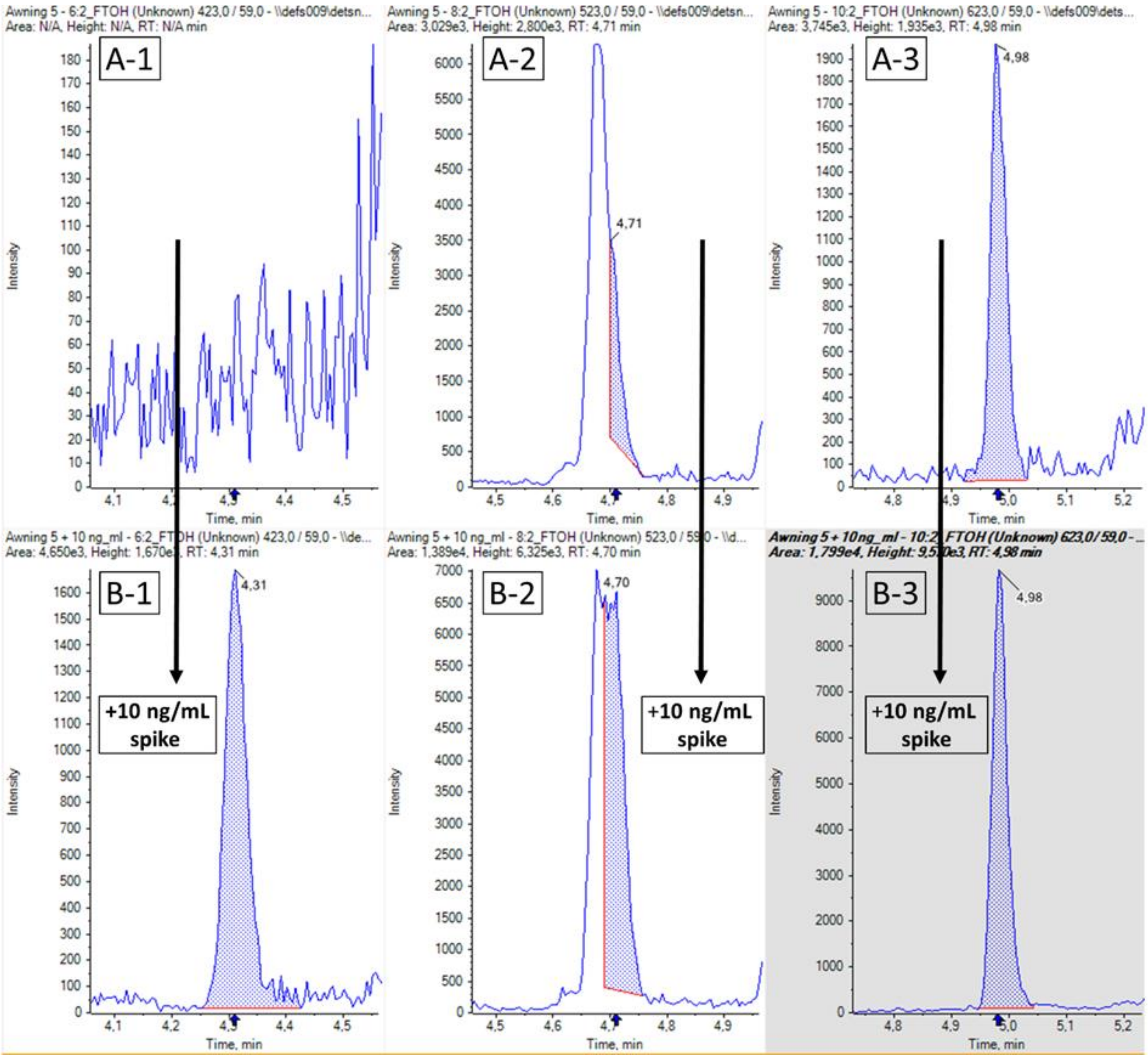

Figure 24: Chromatograms of 6:2 FTOH (A-1 and B-1), 8:2 FTOH (A-2 and B-2) and 10:2 FTOH (A-3 and B-3) *of analyzed OSB material*; top (A): sample; bottom (B): sample + 10 ng/mL spike; High matrix pollution leads to a higher baseline, which complicates flawless interpretation. However, spiking experiments provided clarification. Considering the high matrix load, excellent recoveries were observed for 6:2 (111%) and 10:2 FTOH (102%) and good recovery for 8:2 FTOH (65%).

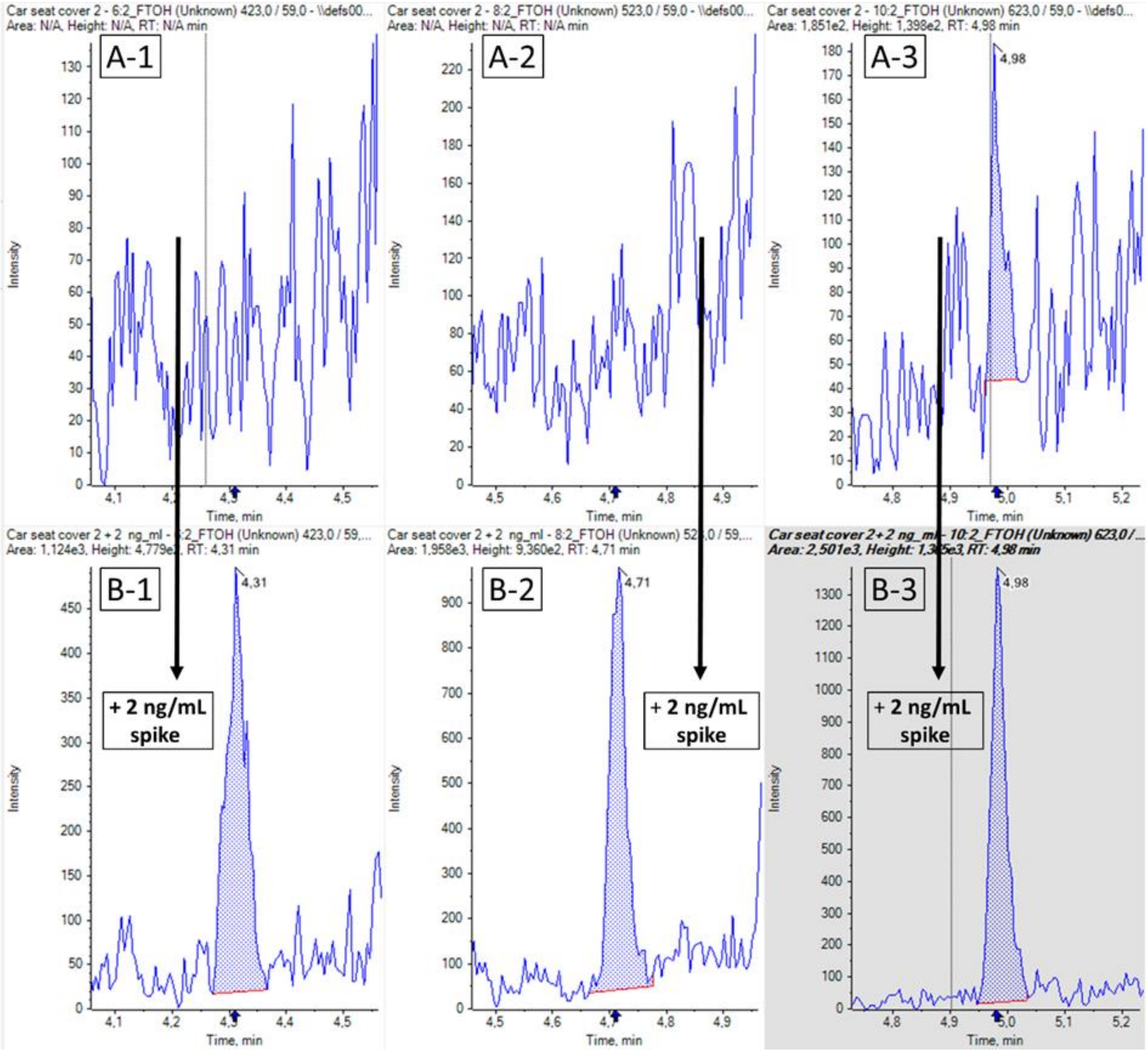

Figure 25: Chromatograms of 6:2 FTOH (A-1 and B-1), 8:2 FTOH (A-2 and B-2) and 10:2 FTOH (A-3 and B-3) *of a car seat cover sample;* top (A): sample; bottom (B): sample + 2 ng/mL spike; Neither 6:2, 8:2 nor 10:2 FTOH were detected above the method quantification limit. Spiked analyte at the method LOQ (2 ng/mL) was observed with a sufficient recovery for 6:2 FTOH (160%), good recovery for 10:2 FTOH (120%) and excellent recovery for 8:2 FTOH (100%).

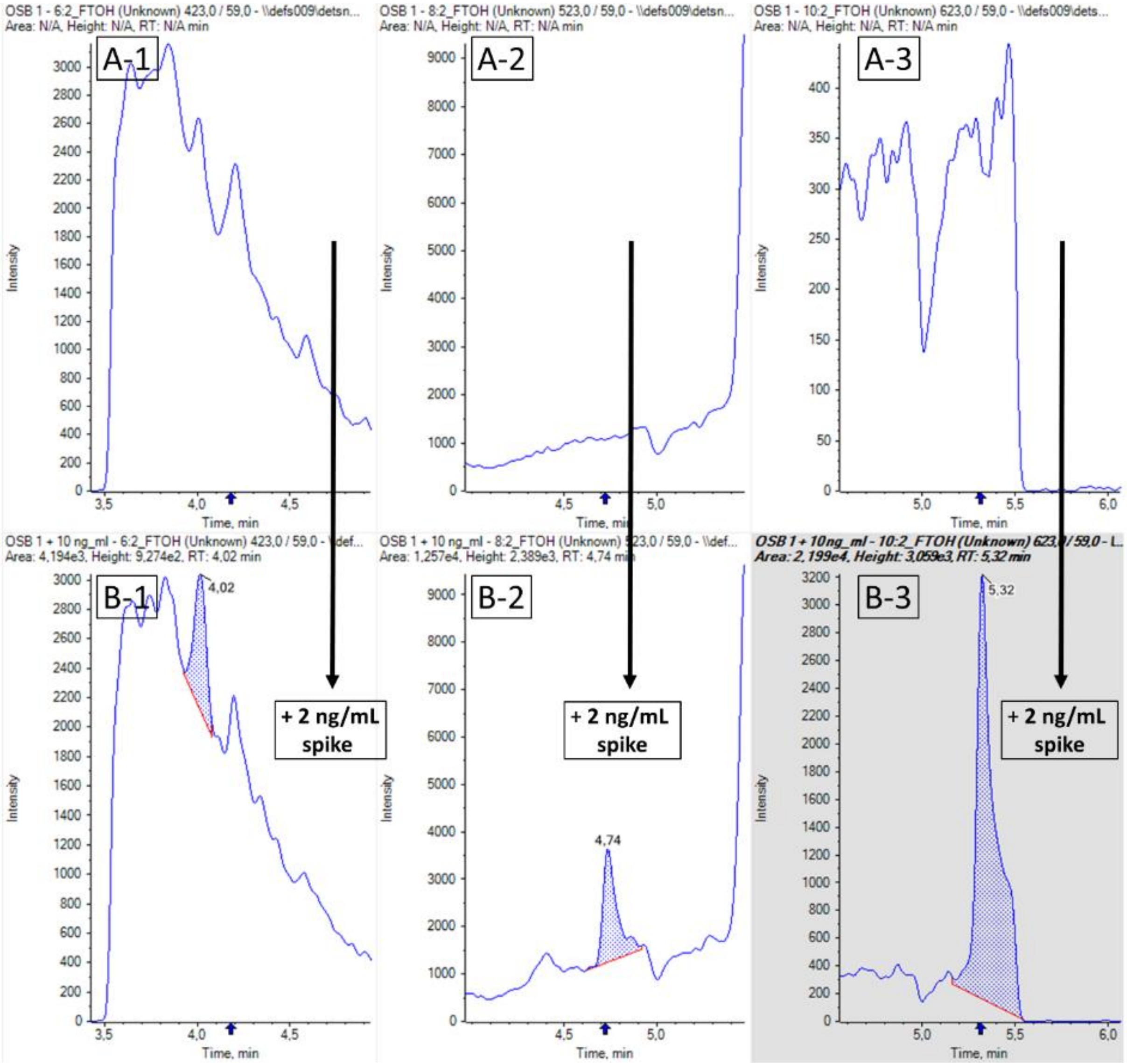

Figure 26: Chromatograms of 6:2 FTOH (A-1 and B-1), 8:2 FTOH (A-2 and B-2) and 10:2 FTOH (A-3 and B-3) *of a coating sample*; top (A): sample; bottom (B): sample + 2 ng/mL spike*;* No FTOHs were detected above the method quantification limit. Spiking experiments at the method LOQ (2 ng/mL) led to a sufficient recovery for 6:2 FTOH (75%) and good recoveries for 8:2 FTOH (80%) and 10:2 FTOH (80%).