

Literature study on PFAS precursors in sediments and surface water



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Summary

PFAS are very persistent chemicals, and therefore often referred to as 'forever chemicals'. However, the really persistent molecules, the so-called 'end products', are often perfluoroalkyl acids (PFAAs), which have a fully fluorinated carbon backbone and a carboxylic or sulphonic acid group at the end of the molecule (abbreviated to PFCA's and PFSA's, respectively). Precursors are those fluorochemicals that can be biotically and abiotically transformed into PFAAs.

This literature review is a preliminary study that will be followed by experimental work regarding precursors present in (Dutch) sediments. First the occurrence of PFAS precursors in the Dutch surface water, sediments, SPM, and wastewater was summarized. Based on this information, scientific literature was reviewed on unknown PFAS in SPM and sediment, potential transformations of relevant PFAS under specific conditions (aerobic versus anaerobic) and on potential parent compounds.

The TOP-analysis indicates that PFAS concentrations are considerably higher than PFSA's and PFCA's. Only 11 precursors were monitored regularly and the precursors that are detected in concentrations $> 1 \mu\text{g/kg}$ in SPM and sediments are N-EtFOSAA and N-MeFOSAA). The compounds belong to the group of the N-alkyl substituted perfluorooctane sulfonamides (FOSAM). Potential parent compounds of N-Et-/MeFOSAA are N-Et-/MeFOSE and SAMPAP diester, but there may be others.

The aerobic degradation of N-Et-/MeFOSAA to PFOS seems to occur in weeks at low concentrations, whereas no studies could be found on anaerobic degradation. The field data indicate that anaerobic degradation is very slow.

Based on the conclusions and other findings we recommend to:

- Monitor more substances belonging to the group of FOSAM, at least N-Et-/MeFOSE and SAMPAP diester
- Further investigate the need for monitoring fluotelomers (FT), particularly the larger molecules. They generally bind well to sediments and they bioaccumulate.
- Monitor FOSAM in wet sediments containing N-Et-/MeFOSAA during drying (aerobic degradation) to observe the change in PFAS-compounds. Variation in temperature and light may give additional insight in the behaviour of FOSAM.
- To find out whether high N-Et-/MeFOSAA concentrations in sediment are caused by historic contamination or a secondary source of degradation of precursors of N-EtFOSAA it might be useful to analyse samples from the RWS-archive. If high concentrations are measured in older SPM, the elevated concentrations in wet sediments may be the result of historic SPM that settled, but if N-Et-/MeFOSAA is not found in older SPM samples, this must be transformed in the sediment.

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List of abbreviations

AOF	adsorbable organic fluorine
BAF	bioaccumulation factor
BCF	bioconcentration factor
BMF	biomagnification factor
BSAF	Biota-Sediment Accumulation Factor
CALUX	Chemical Activated LUciferase gene eXpression (CALUX) is a ligand-dependent nuclear receptor-based bioassay
diPAP	disubstituted polyfluoroalkyl phosphate (see also PAP)
dTOP assay	direct TOP-assay
ECF	electrochemical fluorination
EOF	extractable organic fluorine
N-EtFOSE	N-ethyl perfluorooctane sulfonamido ethanol
N-EtFOSA	N-ethyl perfluorooctane sulfonamide
N-EtFOSAA	N-ethyl perfluorooctane sulfonamido acetic acid
N-MeFOSAA	N-methyl perfluorooctane sulfonamido acetic acid
FOSA	perfluorooctane sulfonamide (=PFOSA)
FOSAA	perfluorooctane sulfonamidoacetic acid
FOSAM	N-alkyl substituted perfluorooctane sulfonamides (N-EtFOSE/-FOSA/-FOSAA belong to this group)
FT	Fluorotelomer (substance)
FTA	fluorotelomer acrylate
FTAB	fluorotelomer sulfonamide alkylbetaine
FTCA	polyfluoroalkyl carboxylate
FTOH	fluorotelomer alcohol
x:x FTS	fluorotelomer sulfonate (first number is fully fluorinated carbon atoms, second number is non-fluorinated carbon atoms)
FTUCA	fluorotelomer unsaturated carboxylic acid
HFPO-DA	hexafluoropropylene oxide dimer acid
HRMS	high resolution mass spectrometry
LoQ	limit of quantification
PFAA	perfluoroalkyl acids
PFAS	per and polyfluorinated alkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonic acid
PFCA	perfluorocarboxylic acid
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFDS	perfluorodecane sulfonic acid
PFECA	per/polyfluoroether carboxylic acid
PFESA	per/polyfluoroether sulfonic acid
PFHpA	perfluoroheptanoic acid
PFHpDA	perfluoroheptadecanoic acid
PFHpS	perfluoroheptane sulfonic acid
PFHxA	perfluorohexanoic acid
PFHxDA	perfluorohexadecanoic acid
PFHxS	perfluorohexane sulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFODA	perfluorooctadecanoic acid

PFOS	perfluorooctane sulfonic acid
PFOSA	perfluorooctane sulfonamide (=FOSA)
PFPE	perfluoropolyether
PFPeA	perfluoropentanoic acid
PFPeDA	perfluoropentadecanoic acid
PFPeS	perfluoropentane sulfonic acid
PFSA	perfluoroalkyl sulfonic acid
PFTeDA	perfluorotetradecanoic acid
PFTriDA	perfluorotridecanoic acid
PFUnDA	perfluoroundecanoic acid
POP	persistent organic pollutant
SAmPAP	N-EtFOSE based phosphates
SPM	suspended particulate matter
TMF	trophic magnification factor
TOF	total organic fluorine
TOF-CIC	TOF -Combustion Ion Chromatography
TOP	total oxidisable precursors
WWTP	wastewater treatment plant

1 Introduction

1.1 Why are precursors relevant?

PFAS are very persistent chemicals, and therefore often referred to as 'forever chemicals'. (OECD, 2021) revised the definition of PFAS to: fluorinated substances that contain **at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)**, i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-\text{CF}_3$) or a perfluorinated methylene group ($-\text{CF}_2-$) is a PFAS. There are thousands of different PFAS components of which approximately 30 are detected in Dutch water.

However, the really persistent molecules, the so-called 'end products', are often perfluoroalkyl acids (PFAAs), which have a fully fluorinated carbon backbone and a carboxylic or sulphonic acid group at the end of the molecule (abbreviated to PFCAs and PFSAAs, respectively). Precursors are those fluorochemicals that can be biotically and abiotically transformed into PFAAs, but some of them can be very persistent itself (Houtz et al., 2013).

Why should we pay attention to precursors? There are two important reasons:

- 1 A few them have been detected in Dutch sediments (particularly N-EtFOSAA and N-MeFOSAA).
- 2 Precursors probably form the majority of the PFAS present in the aquatic system and can act as secondary sources for end products like PFOS (Benskin et al., 2013; Langberg et al., 2020, Derksen and Baltussen, 2021b).

Because the detected precursors in Dutch sediments belong to the C8-compounds, the focus of this report will be on C8-compounds. A second reason is that the availability of studies on other chain lengths is limited.

Several researchers have investigated the behaviour of PFAS-precursors in sediments (Benskin 2012; Langberg, 2020), but because of the large number of known and unknown precursors, the knowledge of the fate of precursors in the environment is still limited.

1.2 Detection methods of fluorine

There are various approaches to get more insight in the presence of precursors (Winchell et al., 2021):

- Target analyses: approximately 30 PFAS are analysed routinely in the Netherlands. The total number of individual PFAS components that can be analysed is higher, but probably still below 100.
- Suspect or non-target screening: Liu et al. (2019) reported that non-target HRMS-based analytical approaches have led to discovery of more than 750 PFAS in 130 diverse chemical classes and summarized strategies for nontarget PFAS discoveries. At the moment KWR leads a consortium that develops an approach to identify PFAS in the water cycle using non-target screening (<https://www.tkiwatertechnologie.nl/projecten/een-integrale-aanpak-voor-opsporing-van-ongewenste-perfluorstoffen-in-de-waterketen/>).

- Nonspecific methods:
 - TOP analysis: Houtz and Sedlak (2012) proposed the total oxidisable precursors (TOP). However, there is no standardised method (Mitchell et al., 2021) and several modifications have been presented, e.g. direct TOP (Göckener et al., 2022) and improvements by Zhang et al. (2019). KWR also tests the improved TOP method, more TOP data on water and sediment will become available in 2023.
 - Adsorbable organic fluorine (AOF): In this method, fluorine (can be more than only PFAS such as hydrofluoric acid, fluoropolymers and other synthesized organic fluorine compounds like freon) is adsorbed, most often in a cartridge containing activated carbon, and combustion is used to release the fluoride ion (F^-). Combustion Ion Chromatography (CIC) is used for detection.
 - Extractable organic fluorine (EOF): extraction can be performed using the same solvent systems used for conventional targeted LC-MS/MS methods. A lower LoQ can be obtained compared to TOF.
 - Total organic fluorine (TOF): pyrohydrolysis at 900–1000 °C in a humid, O₂-rich environment by Combustion Ion Chromatography (CIC).
- Biological measurements. Behnisch et al. (2021) developed a human cell-based CALUX bioassay which enabled comprehensive analysis of thyroid disruption potential of compounds. It is based on the mechanism that PFAS can bind to the thyroid transport protein transthyretin (TTR) thereby competing with the natural hormone thyroxine (T₄).

1.3 Structure of this report

An analysis of the PFAS precursors detected in the Dutch aquatic system (freshwater, coastal water, wastewater (sludge), sediments) is reported in Chapter 2. A broader view of precursors measured worldwide is given in Chapter 3. Specific attention is given to so-called FOSAMs, the type of substances that have been found in Dutch sediments. Conclusion and recommendations (for further research and policy) are provided in Chapter 4.

2 Precursors in the Dutch aquatic systems.

2.1 Occurrence in various compartments

Approximately 30 PFAS are measured regularly, and 21 of them are PFAAs, 11 compounds are precursors. Table 2.1 shows the frequency of measurements >LoQ of the PFAA precursors in the Dutch large waters. The numbers are based on monitoring and project data¹. The first thing to notice is the low occurrence in floodplains. Only N-EtFOSAA and PFOSA are proved sometimes, but always in less than 10% of the samples. The precursors that are most commonly present are 6:2 FTS (although not in sediments), PFOSA, N-MeFOSAA and N-EtFOSAA.

Table 2.1: Occurrence (percentage of samples >LoQ) of precursors in large National waters, monitored by Rijkswaterstaat (RWS): surface waters, suspended particulate matter (SPM), wet sediments and floodplains (n.a.=not analysed).

Precursor	Surface water RWS (total concentration)	SPM (all RWS monitoring sites)	Wet sediment RWS (large waters)	Floodplains RWS (large rivers)
4:2 FTS	n.a.	1-5%	<1%	<1%
6:2 FTS	25-50%	50-75%	1-5%	<1%
8:2 FTS	5-10%	25-50%	1-5%	<1%
10:2 FTS	n.a.	25-50%	10-25%	<1%
MeFBSAA	n.a.	1-5%	n.a.	n.a.
N-MeFOSAA	10-25%	50-75%	25-50%	1-5%
N-EtFOSAA	25-50%	50-75%	25-50%	6-10%
PFOSA or FOSA	25-50%	50-75%	10-25%	6-10%
EtFOSA	n.a.	5-10%	n.a.	n.a.
MeFOSA	n.a.	n.a.	1-5%	<1%
8:2 diPAP	n.a.	10-25%	1-5%	<1%

2.2 Concentrations in various compartments

2.2.1 Surface waters

Jonker (2021) reported the main PFAS in the Dutch surface waters (rijkswateren). If the focus is on precursors (as far as included in the regular monitoring), 6:2 FTS shows a concentration of approximately 1 ng/l at most monitoring stations, but clearly elevated levels are observed in the Scheldt region and the Lateraalkanaal Linne Buggenum (5-6 ng/l), and to a lesser extent in the rivers Maas and IJssel (2-3 ng/l). N-EtFOSAA, N-MeFOSAA and PFOSA are a little bit higher in the Scheldt region (up to 1,7 ng/l). Other precursors are not elevated at all in surface water (rijkswateren). Precursors are barely detected in coastal waters.

¹ For water: all RWS freshwater monitoring locations from 2015 to 2021. For SPM: all RWS freshwater monitoring locations from April 2018 to December 2021.

2.2.2 Suspended particulate matter (SPM)

Table 2.1 displays that 7 precursors in the routine monitoring are detected in more than 10% of the samples: 6:2 FTS, 8:2 FTS, 10:2 FTS, PFOSA, N-MeFOSAA, N-EtFOSAA, and 8:2 diPAP. However, the average concentrations of all compounds is less than 0.5 µg/kg, except for 6:2 FTS.

The concentrations of 6:2 FTS in SPM display a strong variation. The P50, P80 and P95 values are 0.4, 3.0 and 19.2 µg/kg. Both spatial and temporal patterns are observed: the monitoring sites north of the line Amsterdam-Zwolle show clearly elevated concentrations until early 2020. From March 2020, the concentrations are close to the LoQ. Although it is unclear why concentrations until spring 2020 are so high, we propose to pay no further attention to 6:2 FTS. Furthermore, concentrations in Eijsden (Maas at the Belgium border) were occasionally increased up to 5 µg/kg and two high concentrations (8 and 40 µg/kg) were found in Hagestein (Rijn near Utrecht). It seems that 6:2 FTS is related to specific discharges/spills (as an example due to run-off of AFFF after a fire), but it possibly transforms rather fast to other PFAS. That would explain why it is never found in sediments. 8:2 FTS and 10:2 FTS are observed in low concentrations without strong temporal or spatial trends.

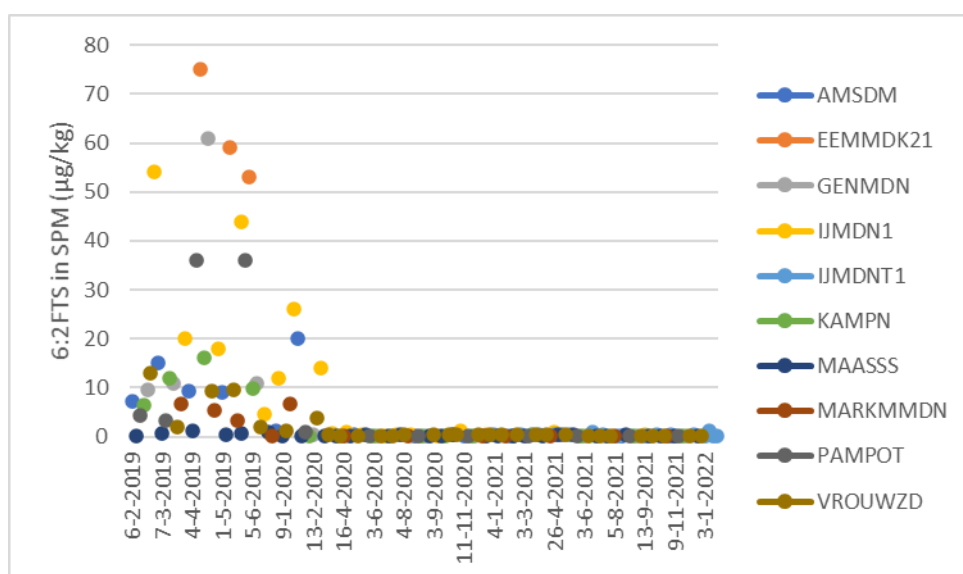


Figure 2.1: Concentration of 6:2 FTS in suspended particulate matter (SPM) in the national waters north of the line Amsterdam – Zwolle.

PFOSA (or FOSA), N-MeFOSAA and N-EtFOSAA all belong to the group of N-alkyl substituted perfluorooctane sulfonamides (or FOSAMs) as shown in Figure 2.2:

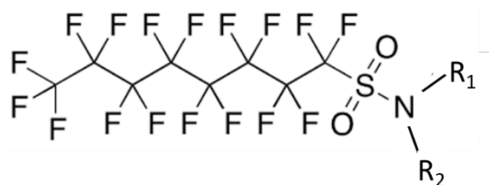


Figure 2.2: Molecular structure of N-alkyl substituted perfluorooctane sulfonamides. R_1 represents H or an alkyl group (methyl or ethyl), R_2 represents an H or a carboxylic (COOH-) group.

In case of PFOSA (or FOSA) both R_1 and R_2 are just an H-atom, so the end of the molecule is NH_2 . PFOSA has been monitored in SPM from 2018 to 2021. The highest concentrations were observed the Scheldt basin (Sas van Gent, Schaar van Ouden Doel), but they are not extremely high (all below $2 \mu\text{g/kg}$). If PFOSA is detected in sediment and water, the concentrations are relatively low. The P95 in surface water is 1.7 ng/l , and in sediments $0.5 \mu\text{g/kg}$.

N-MeFOSAA and N-EtFOSAA are very comparable molecules. They have 8 fully fluorinated C-atoms (left part of the molecule in Figure 2.3), but the sulphonic acid (SO_3)-group is replaced by a sulphonamide group. An ethyl(C_2H_5)-group is part of N-EtFOSAA (see oval in Figure 2.3) whereas a methyl(CH_3)-group is part of N-MeFOSAA.

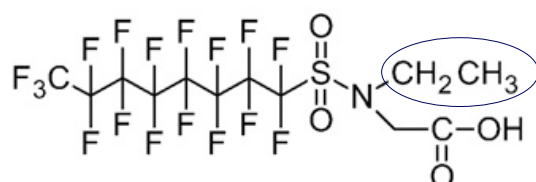


Figure 2.3: Molecular structure of N-EtFOSAA. If the CH_2-CH_3 in the oval consists of only CH_3 the molecule is called: N-MeFOSAA.

EtFOSAA-concentrations in SPM at Lobith show a decreasing trend over time (Figure 2.4). The average concentrations for the period 2018 – 2022 at each location are shown in Figure 2.5 and are clearly elevated in Kanaal Gent-Terneuzen, and to a lesser extent in the Westerscheldt and the Twentekanaal.

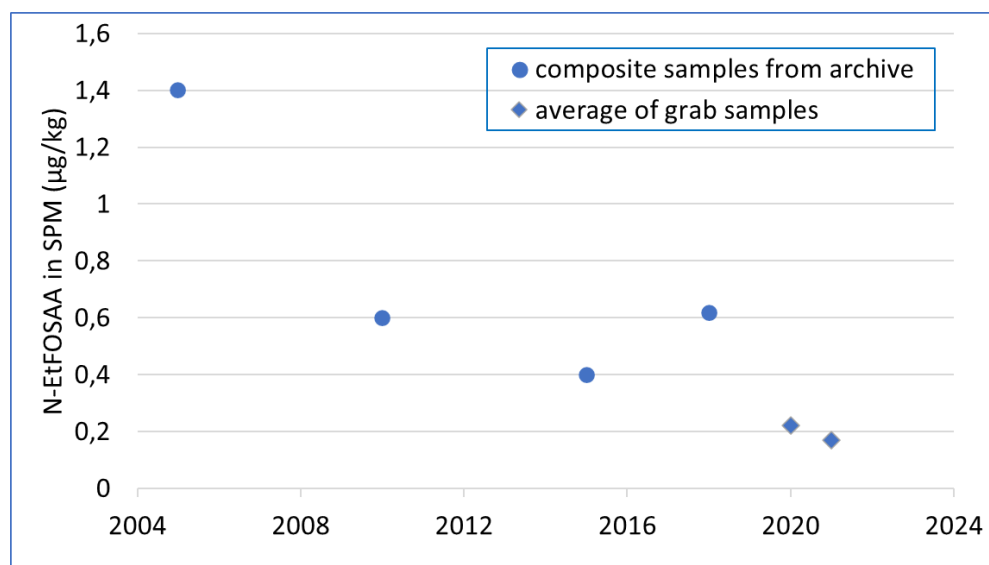


Figure 2.4: Average N-EtFOSAA concentrations in SPM sampled at Lobith over the period 2005-2020.

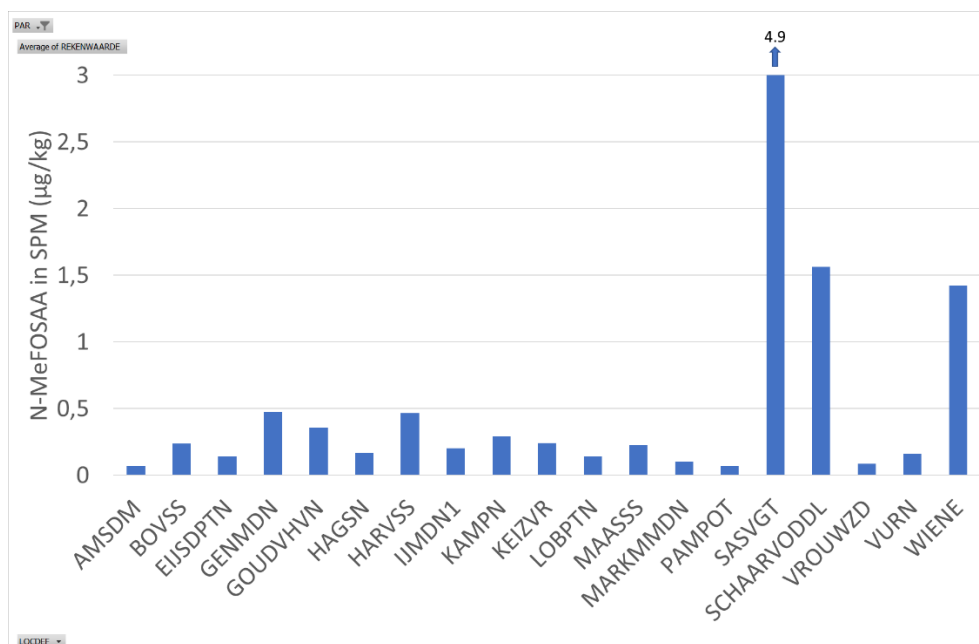


Figure 2.5: N-MeFOSAA concentrations in SPM at various location in the Netherlands.

2.2.3 PFAS in suspended matter in Bimmen (Dutch-German border in the Rhine)

Göckener et al. (2022) monitored SPM of the German rivers over the period 2005-2019 based on SPM samples from the German archive. The Bimmen station, close to Lobith, was one of the monitoring stations. They also used the so-called dTOP-assays (see textbox) to measure also (unknown) precursors.

The direct Total Oxidisable Precursors (dTOP) assay

The TOP analysis is originally published by Houtz and Sedlak (2012). Samples were exposed to hydroxyl radicals generated by thermolysis of persulfate under basic pH conditions and perfluoroalkyl acid (PFSA) precursors were transformed to PFCA's of related perfluorinated chain length. By comparing PFCA concentrations before and after oxidation, the concentrations of total PFSA precursors were inferred.

The dTOP assay is a modified procedure: a small amount of sample was directly and fully oxidised in a more concentrated oxidation solution instead of oxidizing a sample extract (Göckener et al., 2021). Although the results of the dTOP may be robust, it is not exactly known what chemical reactions are taking place. It is remarkable that precursors with a sulfonic acid group are analysed as a PFCA (carboxylic acid), whereas PFSA's are not converted in PFCA's. Another question is whether polymers, like Teflon, are partly oxidized to monomers. Göckener et al. (personal communication) motivate that analyses in biota show the same patterns, and they assume that polymers will not be taken up by biota.

It appeared that the PFCA-concentrations after a dTOP-analysis were much higher compared to the target analyses (Figure 2.7). Most of the compounds are <LoQ in the target analyses, and above 5 µg/kg in the dTOP-analysis. Göckener et al. (2022) observed a strong decrease of the total PFAS extracted with dTOP from approximately 90 µg/kg until 2008 to 45 µg/kg in 2013 (see R4 in Figure 2.6). The total PFAS concentration after 2013 mainly consists of C4-C8 chains (Figure 2.7), but the original precursors were probably a bit longer.

This is exactly the period that PFOS was regulated: PFOS was classified as a POP within the context of the Stockholm Convention in 2009, and the use is severely restricted by the European Union. PFOS has been added to Annex XVII of the Regulation on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Moermond et al., 2010).

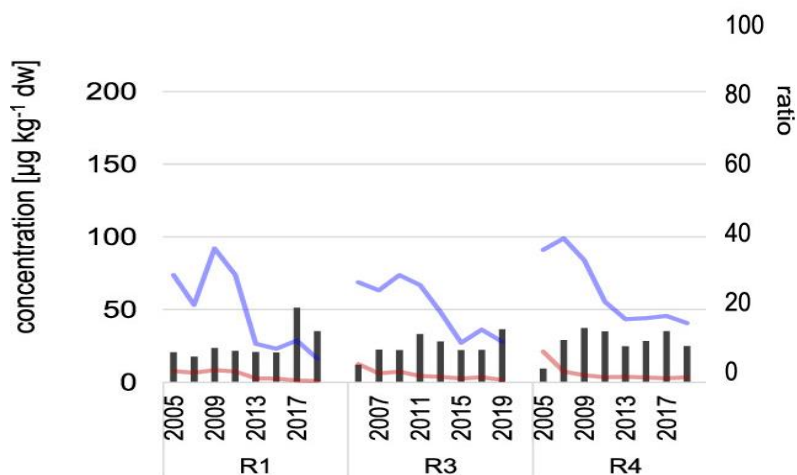


Figure 2.6 Concentrations ($\mu\text{g kg}^{-1}$ dry weight (dw)) of ΣPFAS in suspended particulate matter from rivers in Germany analyzed by target analysis (red line) and dTOP assay (blue line; both left y-axis) as well as the respective concentration ratios $\Sigma\text{PFAS}_{\text{dTOP}}/\Sigma\text{PFAS}_{\text{target}}$ (columns, right y-axis). LOQs: target analysis: $0.05\text{--}0.5 \mu\text{g kg}^{-1}$ dw, dTOP: $1.0 \mu\text{g kg}^{-1}$ dw. R1: Rhine-Weil, R3: Rhine-Koblenz; R4: Rhine-Bimmen. Figure from Göckener et al. (2022).

However, after a strong decrease, the PFAS concentrations in SPM as analysed with dTOP seem to be constant after 2013. They also observed a shift from longer chained PFCAs to shorter chained PFCAs. Despite a decrease of almost $50 \mu\text{g/kg}$, the results show that there is still $45 \mu\text{g/kg}$ of PFAS precursors present in the SPM entering the Dutch part of the Rhine. The main question is of course which PFAS are missing in a regular target analysis, and what is the behaviour of these PFAS.

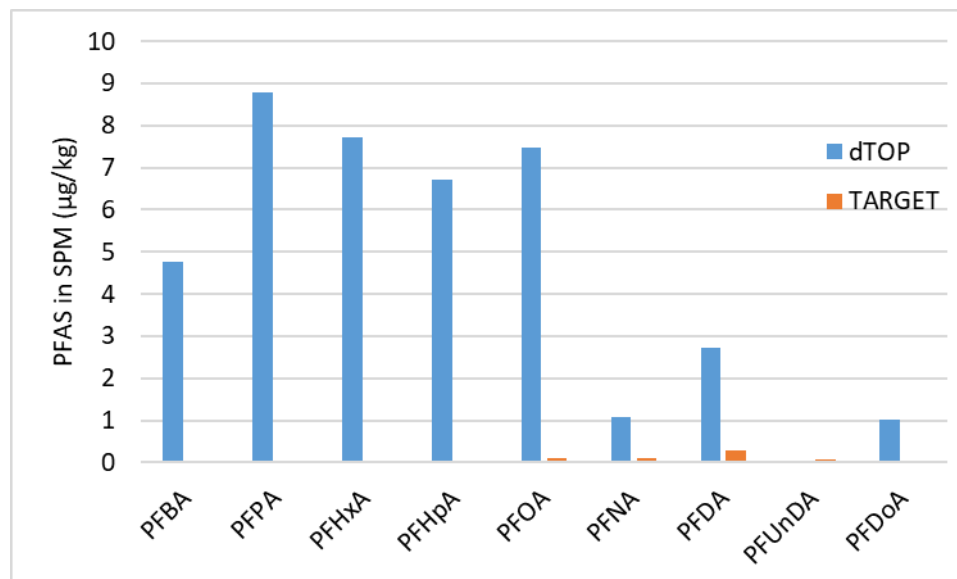


Figure 2.7: PFCAs after dTOP-analysis and target analysis in samples of 2017 (data Göckener et al., 2022).

2.2.4 Precursors in sludge of wastewater treatment plants (WWTPs)

The summed concentrations of measured PFAS in effluents are often larger than the influent concentration. This indicates that no treatment takes place in the WWTP (Derksen and Baltussen, 2021a). One reason might be that precursors are converted to end products (PFCA and PFSA) in the WWTP. A precursor that was often found in Dutch WWTP's is 6:2 FTS and also HFPO-DA (a GenX compound) was frequently detected. Van Gijn et al. (2021) referred to German WWTP's (Frömel et al., 2016) where they frequently detected fluorotelomer alcohols (FTOH), fluorotelomer phosphonic acids (6:2 and 8:2 diPAP) and fluorotelomer methyl acrylates (6:2 and 8:2 FTMAC). These fluorotelomer compounds generally decrease in the WWTP.

Also sludge had been studied by Derksen and Baltussen (2021a). A few PFAS show average concentrations above 10 µg/kg: PFOS and 10:2 FTS, but the variation is large. Several PFAS exceed 10 µg/kg in at least one WWTP: PFPeA, PFOA, 6:2 FTS and 8:2 FTS. Degradation of the sludge could also be a source of PFAS release to the effluent water.

2.3 Focus on N-EtFOSAA and N-MeFOSAA

Both N-EtFOSAA and N-MeFOSAA can be detected in water occasionally and in rather low concentrations (P95 <0.3 ng/l), but they tend to bind better to sediment than PFOS (Wintersen et al., 2020). An overview of the concentrations measured in different matrices are presented in Table 2.2.

Table 2.2: Concentrations of N-MeFOSAA and N-EtFOSAA in water, suspended matter, wet sediments in fresh and salt water and in floodplains.

	Water	SPM Rijn/ Maas	wet sediment top	wet sediment deep	floodplains top&deep	Coastal sediment
N-MeFOSAA	ng/l	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
P50	<0.05	<0.1*	<0.1	<0.1	<0.1	<0.1
P80	<0.05	0.3*	0.3	0.7	<0.1	0.1
P95	0.11	0.5*	2	2.7	<0.1	0.4
N-EtFOSAA						
P50	<0.1	0.2**	0.28	0.28	<0.1	<0.1
P80	0.17	0.6**	0.7	1.8	<0.1	0.2
P95	0.27	1.2**	3.8	13.8	0.28	0.3

*Based on measurements from January 2021 to March 2022 (n=166). Not corrected for OC.

**Based on measurements from January 2021 to March 2022 (n=414). Not corrected for OC.

The P95 of N-EtFOSAA in deeper sediment is remarkable: 13.8 µg/kg whereas it is 0.28 µg/kg in floodplain areas. This confirms the general experiences in projects that occasionally high N-EtFOSAA concentrations are found in dredged material. These high concentrations do not occur in current SPM (the P95 is 1.2 µg/kg). That raises the question how these high concentrations can occur. One reason might be that it is a heritage from earlier years. Although PFAS was never monitored before 2019, a few composite samples (from 2005, 2010, 2015 and 2018) of the RWS SPM archive were analysed for PFAS.

The results indicate indeed a decreasing trend (Figure 2.4), although the 2005 point is quite essential in the series. It might be useful to confirm the trend by analysing a few other samples from the period before 2008. Another reason might be that N-EtFOSAA is formed in the sediment as a degradation product of another precursor-PFAS or degradation of polymers.

The variation in N-EtFOSAA concentrations as a result of the emission from sediments is also seen in outdoor experiments with different sediments stored in the Dutch confined disposal facilities (CDF's). Figure 2.8 gives the concentration in the n-EtFOSAA surface water concentration in ng/l as function of contact time. Some sediments have an instant release of N-EtFOSAA, but striking is the increase in N-EtFOSAA concentrations in the surface water after 100 days.

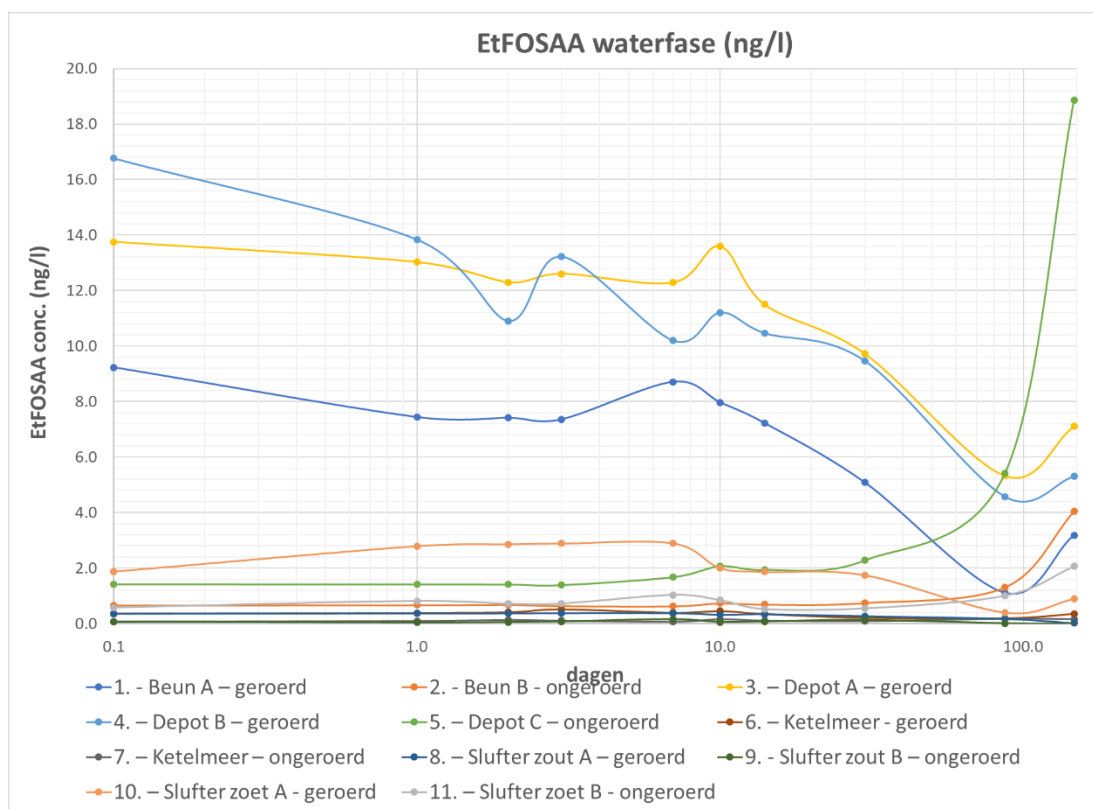


Figure 2.8 N-EtFOSAA results from report "PFAS emissie rijksbaggerdepots, de rol van baggeren op het vrijkomen van PFAS", Deltares rapport 1206062, 2021

Table 2.2 also shows the concentrations in coastal sediments. In saltwater sediments the concentrations of N-MeFOSAA are more or less equal to the N-EtFOSAA concentrations.

2.4 Questions about PFAS in aquatic systems

Based on the information shown in Chapter 2 the general questions in Chapter 1 are specified to:

- Which unknown PFAS are present in SPM, and probably also in sediment?
- What is the degradation rate of N-EtFOSAA and N-MeFOSAA in SPM and soils/floodplains? And what is the degradation rate of 6:2 FTS?
- Can the concentrations of N-EtFOSAA and N-MeFOSAA be explained by the (historic) concentrations in SPM or are these substances formed in wet sediment as a degradation product of other PFAS?
- What are the potential sources of the monitored PFAS² (PFOS, N-EtFOSAA and N-MeFOSAA)?

² The focus is on these three compounds, because other PFCA's and PFSA's have a 95-percentile <0.6 µg/kg in SPM and in sediments from freshwater systems. Precursors may be a relevant source for shorter PFAS in surface water, but this is outside the scope of this report.

3 PFAS precursors in sediment

3.1 PFAS precursors found in sediments worldwide

Most studies focus on the perfluoroalkyl acids (PFAA). However, at the same time many studies recommend focussing on potential PFAS precursors and their tendency to degrade/transform into PFAS (Benskin et al. 2012; Kurwadkar et al., 2022; Langberg et al., 2020).

sediments (Osté, 2021). These substances have also been detected in other countries. Higgins et al., (2005) detected concentrations of N-EtFOSAA and N-MeFOSAA in equal concentrations as PFOS in the sediments of the San Francisco Bay Area (concentrations ranged from <LoQ up to 4 µg/kg for individual compounds). Benskin et al. (2012) measured N-EtFOSAA concentrations up to approximately 0.5 µg/kg (Figure 3.1) They were in the same range as regular PFAS like PFOS and PFOA.

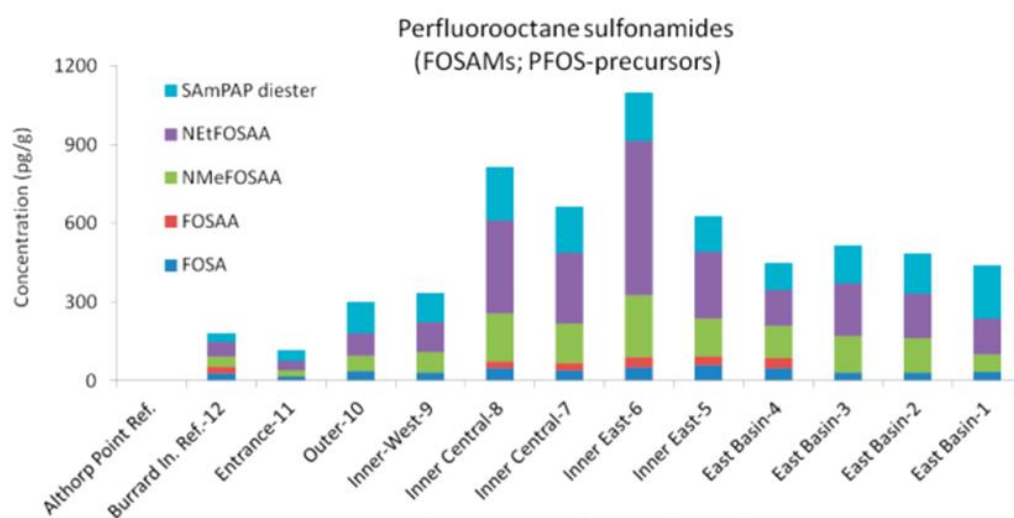


Figure 3.1: Concentrations of FOSAMs in 10 contaminated sediments in marine sediments from an urbanized marine harbor in Vancouver, Canada, as reported by Benskin et al., (2012).

Interestingly, they also measured other PFAS belonging to the group of N-alkyl substituted perfluorooctane sulfonamides (FOSAMs; Figure 3.2), like SAmPAP diester (up to 0.2 µg/kg), N-MeFOSAA, FOSAA and FOSA. A significant ($p < 0.05$) correlation was observed between SAmPAP diester and N-EtFOSAA.

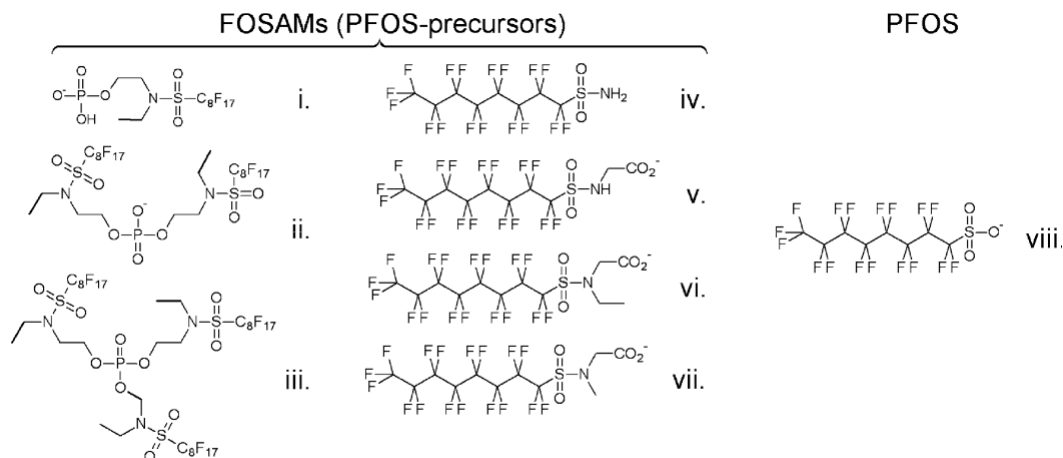


Figure 1. Structures of SAMPAP mono-, di-, and tri-esters (i–iii, respectively), FOSA, FOSAA, EtFOSAA, MeFOSAA (iv–vii, respectively), and PFOS (viii) examined in the present study. Other FOSAMs are possible.

Figure 3.2: (incomplete) overview of existing FOSAMs (from Benskin 2012).

Chen et al., (2018) measured N-EtFOSAA in Lake Taihu, but concentrations in sediment appeared to be extremely low (median is 0.007 µg/kg) whereas PFOS concentrations were 0.8 µg/kg. Langberg et al. (2020) measured N-EtFOSAA in a part of their samples near a paper products factory. Near the factory average³ N-EtFOSAA concentrations in sediment were 258±187 µg/kg, but in a lake downstream of the factory the average concentration was 9.4±2.2 µg/kg. In this lake, similar concentrations of N-EtFOSE were measured, and slightly increased concentrations of FOSAA and FOSA. SAMPAP diester was only analysed for in one sample in 2018 showing a concentration of 850 µg/kg.

Another group of compounds measured in high concentrations by Langberg et al. (2020) is the FTS's, particularly 10:2 and 12:2 FTS. However, the main source is a paper products factory, which might deviate from diffuse pollution profiles.

Macorps et al. (2021) analysed 14 precursors in the Seine River. The sum of these precursors in sediments was approximately half of the measured concentration of total PFAS (PFCA's C5–C14 and PFSA's C4, C6–C8, C10). Most frequently detected precursors were 6:2 FTAB (6:2 fluorotelomer sulfonamide alkylbetaine) and 5:3 FTCA (polyfluoroalkyl carboxylate).

Another emerging group is perfluoroether sulfonic acids (PFESAs): two chlorinated polyfluoroalkylether sulfonic acids (6:2 Cl-PFESA and 8:2 Cl-PFESA with the first as a major and the latter as a minor component) constitute the product commercially called Fe53B, which is a PFOS alternative manufactured in China (Kotthoff et al., 2020). Ali et al. (2021) could detect them in very low concentrations in fish, but not in sediments.

3.2 Bioaccumulation as an indicator for PFAS in sediments.

In general, substances that tend to accumulate biota also adsorb stronger to sediments. Although PFAS is a special chemical group – they accumulate more in proteins than in fat tissue – bioaccumulation might be an indicator for substances that can be detected in sediment. Pickard et al. (2022) studied accumulation of PFAS by fish and observed a clear pattern between chain length and bioaccumulation factor, with the highest accumulation for C11 molecules (.

³ Medians are much lower than averages indicating a number of sample containing extremely high concentrations.

Another observation was that N-EtFOSAA, N-MeFOSAA and FOSA with a certain chain length accumulate more than PFCA's/PFSA's of the same chain length.

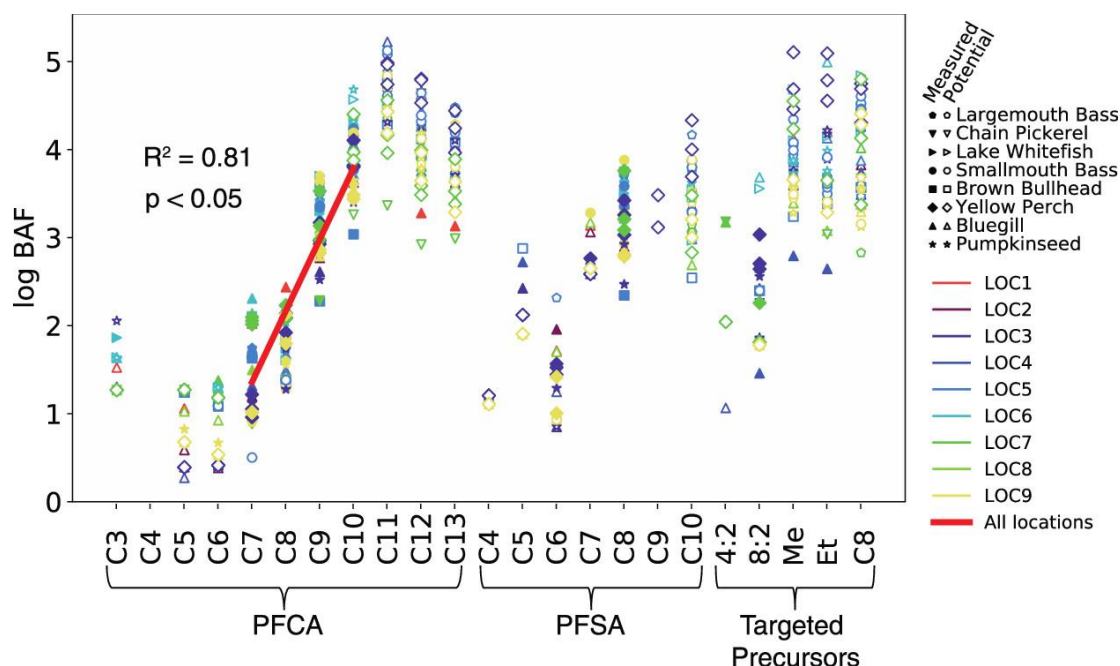


Figure 3.3: Empirically derived bioaccumulation factors (BAF, $L\ kg^{-1}$) for different PFAS, fish species, and sampling locations in New Hampshire, US. Each marker indicates an individual measurement, and each marker type denotes the fish species. Solid markers show measured BAF based on detectable water and fish concentrations, while open markers show potential BAF calculated from method detection limits for water and measured fish concentrations. Abbreviations for precursors are: perfluorooctane sulfonamide (C8), N-methyl (Me), and N-ethyl (Et) perfluorooctane sulfonamidoacetic acids, and fluorotelomer sulfonates indicated by carbon number (n:2). The red line and R^2 value are based on linear regression of the measured BAF data for the C7–C10 PFCA. Figure from Pickard et al., 2022.

Miranda et al., calculated Trophic Magnification Factors⁴ (TMF). Contrary to Pickard et al., (2022) they did not find high TMF's for N-EtFOSAA, N-MeFOSAA and FOSA (average TMF is around 1.5). Highest TMF were calculated for PFDA, PFDS and L-PFOS.

Papers that focus on Biota-Sediment Accumulation Factors report large differences, but it requires attention whether the BSAF is based on whole fish, liver/fat/muscle content or on organic carbon content of both fish and sediment. Langberg et al., (2020) report BSAF's for muscle tissue in fish (close to whole fish) of around 1-10 for PFCA's, 0.1-10 for PFOS and FOSAM, and almost zero for FTS compounds (although the larger molecules (8:2, 10:2 FT's) may require more attention in sediment, because they may bioaccumulate in the food chain). Burkhard and Votava (2022) calculated BSAF and concluded that for fish the BSAF's are much lower than 1 (0.058 for PFOS and 0.0028 for PFOA). This latter suggests that sediment does not largely contribute to the accumulation in biota. At first sight, concentrations in biota have limited value as an indicator for concentrations in sediments.

⁴ Biomagnification is suggested when the calculated TMF for the individual compound is greater than 1.0 and biodilution is suggested when less than 1.0.

3.3

The monitoring data of Dutch sediments – both sediments in large rivers and regional waters – show that, next to PFOS, N-EtFOSAA and N-MeFOSAA are found in relatively high concentrations (see section 2.3). They belong to the group of N-alkyl substituted perfluorooctane sulfonamides (FOSAMs). FOSAMs are precursors of PFOS, often called ‘preFOS’ (Martin et al., 2010; Langberg, 2020), but only a few compounds are included in the regular target analysis in the Netherlands: N-EtFOSAA, N-MeFOSAA, N-EtFOSA, N-MeFOSA, FOSA. Less than 1% of the analytical data of N-EtFOSA and N-MeFOSA is above the LoQ. FOSA is detected in 3% of the RWS sediment samples, in 8% of the regional sediment samples and in 68% of the SPM samples. Only SPM in Sas van Gent (Kanaal Gent Terneuzen) showed levels above 0.8 µg/kg. However, SAmPAP esters, N-EtFOSE and FOSAA have never been analysed. Commercial SAmPAP formulations were dominated by the disubstituted SAmPAP (SAmPAPdiester), although the ratio diester/triester in sediment was almost 1 in Lake Taihu, China (Zhang et al., 2018). It has been used in food contact paper and packaging. Benskin et al. (2013) observed no degradation of SAmPAPdiester in marine sediments, but Zhang et al. (2018) found slow ($t_{1/2} > 18$ days) biotransformation in freshwater sediments from Lake Taihu, according to the scheme in Figure 3.4. SAmPAPtriester appeared to be highly recalcitrant to microbial degradation.

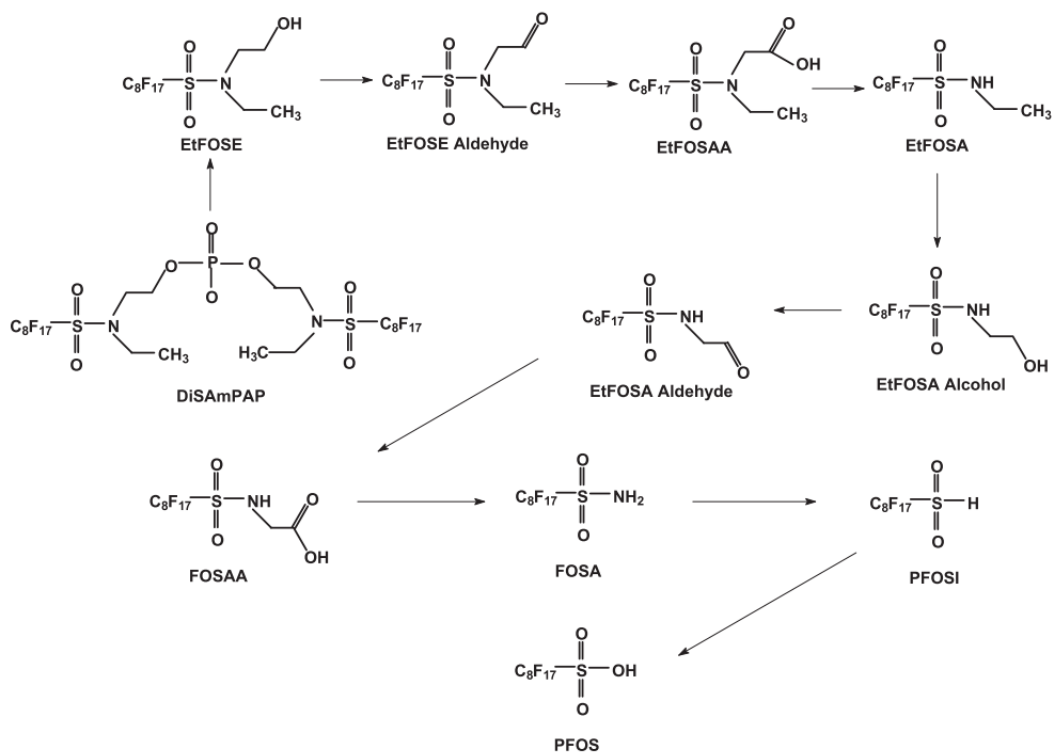


Figure 3.4: Proposed metabolic pathways for biotransformation of FOSAMs (from Zhang et al. 2021).

As already stated, the TOP-analyses by Göckener et al. (2021) show a higher total PFAS-concentration in SPM than explained by the regular target analyses. Analysing more FOSAMs, particularly SAMPAP esters and N-EtFOSE (aldehyde), would reveal whether precursors of N-EtFOSAA or N-MeFOSAA are present in SPM and sediments

Lange (2000; contract research for 3M) performed a 5-week, 8 time-point study to determine the aerobic degradability of N-EtFOSE. Municipal wastewater treatment sludge was used as microbial inoculum. N-EtFOSE completely degraded under aerobic conditions within 10 days (depending on the concentration). N-EtFOSAA was a major metabolite which disappeared in the next 25 days at low concentrations (47 ng/l), but not so fast at high concentrations (2,4 µg/l; Figure 3.5). However, degradation under anaerobic conditions has not been reported as was also concluded by Derksen and Baltussen (2021b). The concentrations in wet sediment suggest that degradation of N-EtFOSAA is at least slower.

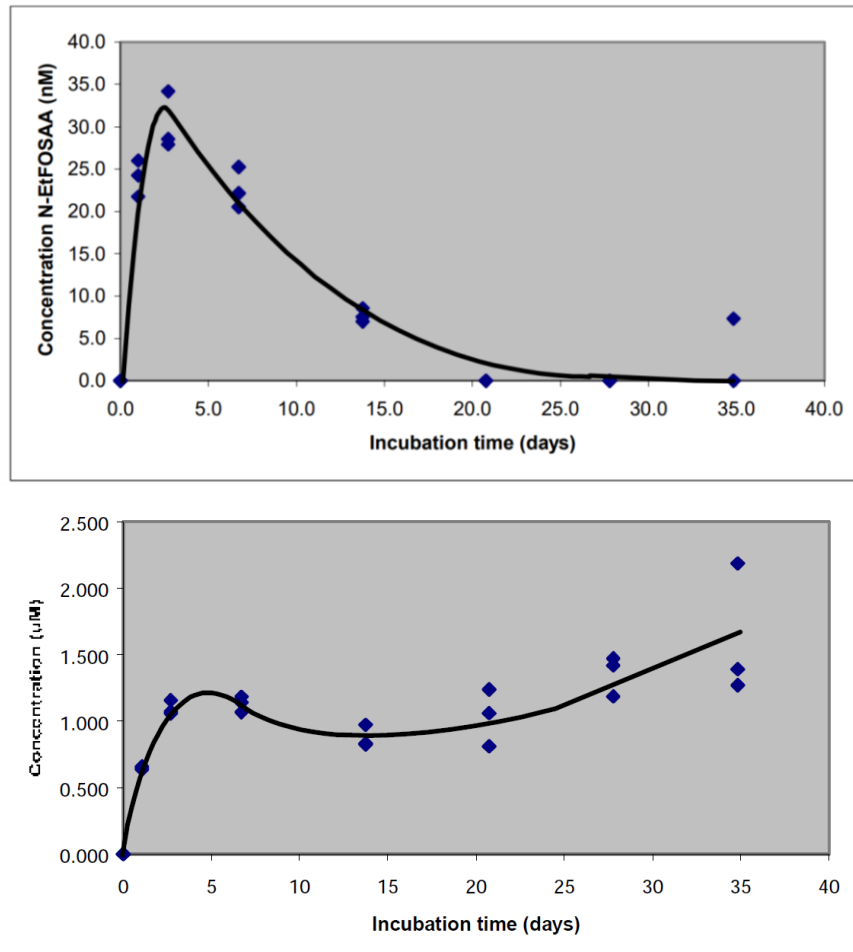


Figure 3.5: Concentrations N-EtFOSAA during an experiment studying the degradation of N-EtFOSE, top at lower concentrations (0,090 µM), bottom at higher concentrations (4.9 µM). Figure from Lange, 2000.

A few other studies pointed out other elements that might influence the fate. Plumlee, et al., (2009) showed that indirect photolysis of PFCA's is likely in sunlit environments, like the world's oceans surface. Wen et al. (2018) studied N-EtFOSAA degradation in pot experiments. They concluded that the presence of plants promoted the degradation of N-EtFOSAA in soils with maize being the most effective plant species (Figure 3.6). The dominant mechanism is the stimulation of soil microbial growth by root exudates.

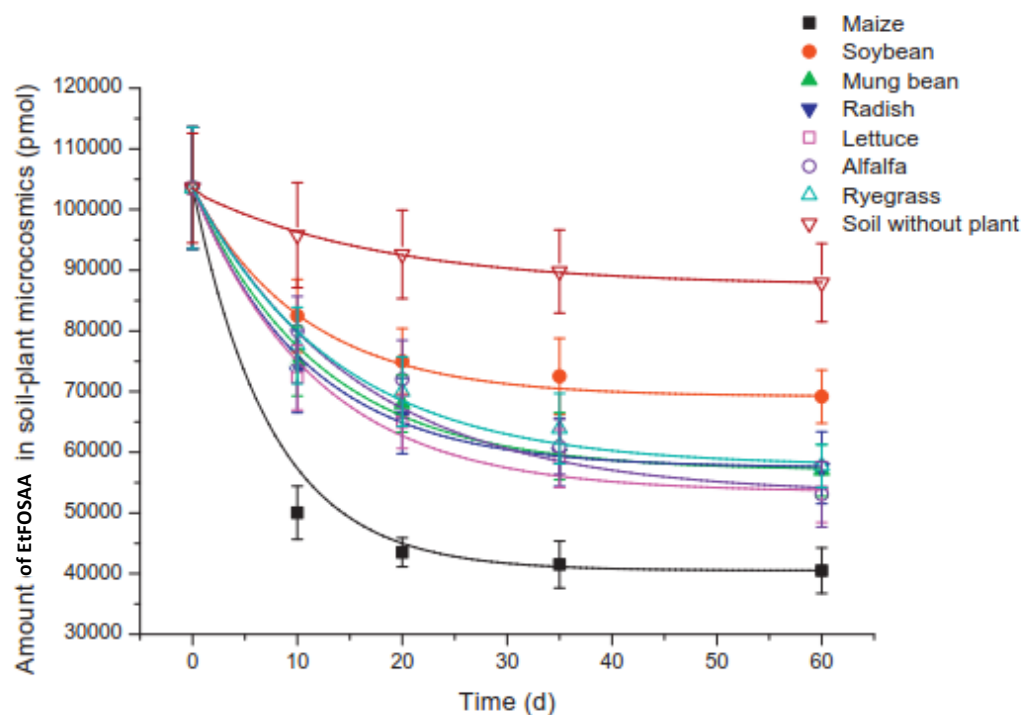


Figure 3.6: Time dependent levels of N-EtFOSAA in soil-plant microcosms (sum of N-EtFOSAA levels in soil and plants). Figure from Wen et al., 2018.

3.4 Sources of PFOS, N-EtFOSAA and N-MeFOSAA

PFAS mixtures in the environment can potentially be backtracked to production methods and possibly the application of specific products. Two methods have been used for large scale PFAS production: electrochemical fluorination (ECF) and telomerization. ECF generates a mixture of linear and branched isomers in addition to impurities of other fluorinated compounds (Prevedouros et al., 2006), while telomerization primarily produces linear isomers (Buck et al., 2011). ECF has been used to produce PFOS and perfluorooctanesulfonyl fluoride (POSF) based products (Benskin et al., 2010; Paul et al., 2009; Prevedouros et al., 2006).

ARCADIS (2021) analysed a lot of samples in different industries (dust, waste, products, cleaning agents, lubricants, etc.). Higher concentrations of PFAS were found in the carpet, leather, paper, textile, printing, paint, fluoropolymer and electronic industry. More than in products and waste, PFAS was often detected in dust; not only in industrial dust, but also in dust in households and offices. Particularly for FOSAMs (FOSA, FOSAA, N-MeFOSA, N-EtFOSA, N-MeFOSAA and N-EtFOSAA were analysed) highest concentrations were found in the carpet and leather industry, sail makers, and to a lesser extent in paper recycling. Jans and Rutten (2021) monitored PFAS and appointed paper recycling, firefighting activities, landfills, tank cleaning, textile and paint production as possible sources. Furthermore, all industrial and municipal wastewater treatment plants discharged relevant PFAS concentrations to surface waters.

On a broader scale, Salvatore et al. (2022) stated that PFAS contamination can be presumed around industrial facilities, wastewater treatment plants (WWTP's), former military sites and major airports. In the Netherlands, Rijkswaterstaat (2021) identified: industrial and communal WWTP's, paper recycling industry, fire fighting activities, disposal sites, tank cleaning companies, and possibly: the waste of reserved osmosis, textile industry, paint industry, and biodiesel production.

FOSAM-based phosphate surfactants (SAmPAPs) were first introduced in 1974 by the 3M Co. for use in food contact paper and packaging. Formulations typically consisted of 10% mono-, 85% di-, and 5% tri-substituted phosphate esters. In 1997, sales of FC-807 (a commercial SAmPAP formulation) represented the highest quantity of PFOS-equivalents sold by 3M out of all PFOS-precursor (i.e., FOSAM) or PFOS-containing commercial substances. The 3M Co. ceased production of these materials along with other perfluorooctane sulfonyl fluoride-based products in 2002, but since then a resurgence in their production has occurred in Asia (Benskin et al., 2012).

N-ethyl perfluorooctane sulfonamido ethanol (**N-EtFOSE**) is one of the important precursors of PFOS, which is attached to phosphate esters in protective paper coatings (Rhoads et al., 2008). N-EtFOSE is an important building block of SAmPAP esters. Considering that N-EtFOSE is a volatile compound, N-EtFOSE may be released into the atmosphere during its production and in applications of N-EtFOSE-containing products. Rhoads et al. (2008) modelled the fate of N-EtFOSE in a typical activated sludge aeration basin open to the atmosphere. The model predicts that 76% of the N-EtFOSE is stripped into the atmosphere, 5% sorbs to waste solids, 13% undergoes transformation to N-EtFOSAA, and 6% is discharged in the wastewater effluent.

N-ethyl perfluorooctane sulfonamide (**N-EtFOSA**), also known as sulfluramid, has been used as an insecticide to control household and agricultural insects since 1989 (Löfstedt et al. 2016), but this has not been used in Europe.

4 Conclusions and recommendations

4.1 Conclusions

The answers to the four questions defined in section 0:

- 1 Which unknown PFAS are present in SPM, and probably also in sediment?
The TOP-analysis indicates that PFAS concentrations are considerably higher than PFSA's and PFCA's. Only 11 precursors were monitored regularly and the precursors that are detected in concentrations > 1 µg/kg in SPM and sediments are N-EtFOSAA and N-MeFOSAA). The compounds belong to the group of the N-alkyl substituted perfluorooctane sulfonamides (FOSAM). Potential parent compounds of N-Et-/MeFOSAA are N-Et-/MeFOSE and SAmPAP diester, but there may be others.

6:2 FTS has not been detected in sediment, and concentrations vary strongly in SPM, suggesting that the substance is not very stable in aquatic systems. However, degradation experiments suggested a limited rate, but this might be fast enough in sediments. Other FT's, like FTOH (fluorotelomer alcohols), fluorotelomer methyl acrylates (FTMAC), and fluorotelomer sulfonamide alkylbetaine (FTAB), are found occasionally in sediments depending on the location. There is no indication that they are widely spread in sediments.
- 2 What is the degradation rate of N-EtFOSAA and N-MeFOSAA in SPM and soils/floodplains?
There are few publications quantifying the degradation rate of substances like N-EtFOSAA. The aerobic degradation of low concentrations seems to occur in weeks, whereas no studies could be found on anaerobic degradation. The field data indicate that anaerobic degradation is very slow.
- 3 Can the concentrations of N-EtFOSAA and N-MeFOSAA be explained by the (historic) concentrations in SPM or are these substances formed in wet sediment as a degradation product of other PFAS?
Both Gockener et al. (2022) and Osté et al. (2019) observed a decreasing trend of EtFOSAA between 2005 and 2015, but it is questionable whether this can explain the high concentrations of N-EtFOSAA and N-MeFOSAA in (anaerobic) sediments. The transformation of other precursors is probably responsible for the elevated concentrations of N-EtFOSAA and N-MeFOSAA in anaerobic sediment.
- 4 What are the potential mother compounds of the monitored PFAS⁵ (PFOS, N-EtFOSAA and N-MeFOSAA)?
Many substances in the group of FOSAM can be a source for PFOS, but the most probable parent compounds of N-Et-/MeFOSAA are SAmPAP-esters and Et-/MeFOSE, although FOSE's can readily degrade, so they will not be found in large concentrations.

⁵ The focus is on these three compounds, because other PFCA's and PFSA's have a 95-percentile <0.6 µg/kg in SPM and in sediments from freshwater systems. Precursors may be a relevant source for shorter PFAS in surface water, but this is outside the scope of this report.

4.2 Recommendations

Based on the conclusions and other findings we recommend to:

- Monitor more substances belonging to the group of FOSAMs, at least N-Et-/MeFOSE and SAMPAP diester
- Further investigate the need for monitoring fluortelomers (FT), particularly the larger molecules. They generally bind well to sediments and they bioaccumulate.
- Monitor FOSAM in wet sediments containing N-Et/MeFOSAA during drying (aerobic degradation) to observe the change in PFAS-compounds, using TOP to screen for shifts in total PFAA precursors. Variation in temperature and light may give additional insight in the behaviour of FOSAM.
- To find out whether high N-Et/MeFOSAA concentrations in sediment are caused by historic contamination or a secondary source of degradation of precursors of N-EtFOSAA it might be useful to analyse samples from the RWS-archive. If high concentrations are measured in older SPM, the elevated concentrations in wet sediments may be the result of historic SPM that settled, but if N-Et/MeFOSAA is not found in older SPM samples, this must be transformed in the sediment.

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