Remediation management for local and wide-spread PFAS contaminations

Umwelt Bundesamt

For our Environment

Remediation management for local and wide-spread PFAS contaminations

by

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Abstract

The group of contaminants known as PFAS is becoming an increasingly important factor to consider in the evaluation of contaminated sites. After several guidelines and methodological approaches for the investigation, assessment, and evaluation of PFAS contaminant impacts have been developed in Germany, nationwide coordinated guidelines providing management tools for the remediation of local and wide-spread PFAS contaminant impacts remain to be established, including standardized specifications for the three phases of investigation: the orienting investigation, detailed investigation, and remediation options appraisal.

This document, which has been prepared as a type of work-aid or guideline for German authorities within the context of a research project, aims to provide support to German regulative authorities in the selection, evaluation, and determination of appropriate and fitting remedial solutions for localized and wide-spread cases of PFAS contamination. While highlighting relevant boundary conditions and if necessary, any supplementary measures to consider in the analysis, this guideline shall serve as a basis for overall management of PFAS contaminant impacts.

Due to the varying properties of the individual PFAS constituent compounds, any evaluation of technical remedial options shall be based on the main PFAS constituent compound of concern. For the relevant remedial options, advantages and disadvantages, technical and German legal requirements, and the sustainability of each respective option are discussed in this guideline.

This work-aid also incorporates the results of two Germany-wide technical workshops that were held in the years 2018 and 2019.

Preface

The aim of the present English translation is to make the findings and messages from the German research project "Remediation Management for Local and Area-wide PFAS Contaminations" more visible on a European and international level and to disseminate and discuss solution approaches in terms of knowledge transfer, problem sensitization, and suitable solution concepts internationally.

With this document, it is intended to introduce into the international discussion, information on advantages and disadvantages of different approaches in Germany as well as technical and licensing requirements, including sustainability and ecological balance of methods. Especially the consideration of wide-spread contaminations appears not to play a significant role in the international discussion so far, although such contamination scenarios are known to exist. For example, in the Italian region of Vincenza, a PFAS groundwater plume with a length of more than 65 km is known to exist.

In addition to the practical remediation options, protective and restrictive measures are essential for effective regulation of PFAS impacts (local or wide-spread) in Germany. To reliably judge the suitability of classical decontamination procedures as they pertain to PFAS, determinations made with respect to type, extent, and temporal due-course of individual PFAS constituent compound properties and associated subsurface processes in soil and groundwater (accumulation, degradation, metabolism etc.) are essential.

This work-aid for German regulative authorities, presented here in English, is solely informative for non-German States and is independent of the legal requirements outside of Germany. The aim is to serve as a resource for responsible authorities in the selection, evaluation, and determination of suitable and fitting remedial solutions and management concepts, while highlighting relevant boundary conditions and, if necessary, supplementary measures.

To this end, basic requirements and key points to consider while planning and executing remedial investigations, along with the evaluation of investigation results, are detailed.

In managing PFAS contaminant impacts and in their remediation, only a narrowly limited selection of suitable and effective remedial methods and management concepts that have been tried and tested in practice is available to date. In view of the current and environmentally relevant problems caused by PFAS contamination in soil and groundwater, there is an urgent need to make available existing knowledge as well as develop new solutions and process approaches in order to promote application-oriented further developments, both nationally and internationally.

This work-aid not only contains numerous technical specifications that are not specific to any nation, but also makes reference to a number of legal constructs as they occur in Germany. Some legal aspects considered are based on European regulations, so that they are also likely to be applicable in other countries. Other aspects are exclusive to German legislation yet can be of help for non-German countries in an informative way. Specific German regulations are marked in the body of this text in that they appear in a light-blue font.

Table of contents

Appendix A   **Relevant Substance Properties**

Appendix B   **Assessment and Documents Leading to the Assessment (as of December 2019)**

Appendix C   **Remediation Technologies**

Appendix D   **Project Case Studies**

Appendix E   **Research Needs**

List of Figures

List of Tables

List of Abbreviations (General)

AA-EQS	Environmental quality standard, annual average
AbfKlärV	German sewage sludge ordinance (*Klärschlammverordnung*)
AFFF	Aqueous film forming foam
AFFF (AR)	Aqueous film forming foam (alcohol resistant)
AIX	Anion exchanger
AOF	Adsorbable organic bound fluorine
AOX	Adsorbable organic bound halogens
AP	Alkaline phosphatases
ASE	Accelerated solvent extraction
BAF	Bioaccumulation factor
BauGB	German building code (*Baugesetzbuch*)
BBodSchG	German Federal Soil Act (*Bundes-Bodenschutzgesetz*)
BBodSchV	German Federal Soil Protection and Contaminated Sites Ordinance (*Bundes-Bodenschutz und Altlastenverordnung*)
BCF	Bioconcentration factor
BfR	German federal institute for risk assessment
BImSchG	German federal immission control act (*Bundes-Immisionsschutzgesetz*)
BioAbfV	German biowaste ordinance (*Bioabfallverordnung*)
BMF	Biomagnification factor
BSAF	Biota sediment accumulation factor
BV	Bed volumes
BW	Body weight
BWaldG	German federal forest act (*Bundeswaldgesetz*)
CBA	*Cost-benefit analysis*
CIC	*Combustion ion chromatography*
CMC	Critical micelle concentration
C_{org}	Organic carbon
CSM	Conceptual site model
CVOC	Chlorinated volatile organic compounds
DCM	Dichloromethane
DIN EN	German industrial standard, European standard
dm	Dry matter
DOC	Dissolved organic carbon
DüngG	German fertilization act (*Düngegesetz*)

DüV	German fertilizer application ordinance (*Düngeverordnung*)
DW$_{GV}$	Drinking water guiding value
EBCT	Empty bed contact time
EC	European Commission
ECF	Electrochemical fluorination
ECHA	European chemicals agency
EOF	Extractable organic bound fluorine
EPA	Environmental protection agency
F&G	Funnel-and-gate
FFFP	Film forming fluoro-protein foam
FFFP (AR)	Film forming fluoro-protein foam (alcohol-resistant)
FlurbG	German land consolidation act (*Flurbereinigungsgesetz*)
FP	Fluorine protein foaming agent
FP (AR)	Fluorine protein foaming agent (alcohol-resistant)
FutMG	German Animal Feed Act (*Futtermittelgesetz*)
GAC	Granular activated carbon
GC-PCI-MS	Gas chromatography-mass spectrometry coupling with positive chem. ionization
GMW	Groundwater monitoring well
HAL	Health advisory level (*Gesundheitlicher Orientierungswert*)
HDPE	High density polyethylene
HPLC-MS/MS	High performance liquid chromatography with tandem-mass spectrometry
IA	Ion exchanger
ISCO	In-situ chemical oxidation
KrWG	German waste management act (*Kreislaufwirtschaftsgesetz*)
LD$_{50}$ / LC$_{50}$	Lethal dose / concentration for 50 % of the test organisms
LDPE	Low density polyethylene
LMBG	Food Safety and Consumer Goods Act (Lebensmittel- und Bedarfsgegenständegesetzes)
LNAPL	Light non-aqueous phase liquids
LOQ	Limit of quantitation
MTBE	Methyl tert-butyl ether
MW	Molecular weight
NF	Nanofiltration
NOAEL	No observed adverse effect level
OECD	Organization for economic cooperation and development
OGewV	German surface water ordinance (*Oberflächengewässerverordnung*)

P&T	Pump and treat
PAH	Polycyclic aromatic hydrocarbons
PBT	Persistent, bioaccumulative, toxic
PNEC	Predicted no effect concentration
POP	Persistent organic contaminants
PRB	Permeable reactive barriers
PU	Polyurethane
PVC	polyvinyl chloride
QA/QC	Quality assurance, quality control
REACH	Registration, evaluation, authorization of chemicals
RO	Reversed osmosis
RPF	Relative potency factors
RSSCT	Rapid small-scale column tests
RTF	Root transfer factor
SchALVO	German protected areas compensation ordinance (*Schutzgebiets- und Ausgleichsverordnung*)
SHMV	Maximum contaminant level ordinance (*Schadstoff-Höchstmengenverordnung*)
SPE	Solid phase extraction
TBA	tert-Butyl alcohol
TD	Thermal Desorption
TDI	Tolerable daily intake
TF	Transfer factor
TMF	Trophic magnification factor
TOC	Total organic carbon
TOP	Total oxidizable precursor
TPH	Total petroleum hydrocarbons
TrinkwV	Drinking water ordinance (Trinkwasserverordnung)
TWI	Tolerable weekly intake values
UV	Ultraviolet
vB	Very bioaccumulative
VDP	Association of German Paper Factories
VOF	*Volatile organic bound fluorine*
vPvB	very persistent, very bioaccumulative
W/S	Water-to-solid ratio
WHG	German water management act (*Wasserhaushaltsgesetz*)

List of abbreviations (fluorinated compounds)

2H-PFHxA	Perfluorohexane acid (the 2nd C-atom binds H and F)
ADONA	Ammonium 4,8-dioxa-3H-perfluoronanoate
Alkyl-PAP	Perfluoroalkyl-organic phosphates
APFO	Perfluorooctane sulfonate, ammonium salt
diPAP	Fluortelomer phosphate diesters
EtFASA	N-Ethyl perfluoroalkane sulfonamides
EtFASE	N-ethyl perfluoroalkane sulfonamide ethanols
FASA	Perfluoroalkylsulfonamides
FASE	Perfluoroalkylsulfonamidethanols
FCH	Fluorocarbon resins
FTAC	Fluortelomer acrylates
FTAL	Fluorotelomer aldehydes
FTCA	Fluorotelomer carboxylic acids
FTEO	Fluorotelomerethoxylates
FTI	Fluorotelomer iodides
FTMAC	Fluortelomer methacrylates
FTO	Fluorotelomerolefins
FTOH	Fluorotelomer alcohols
AGV	Fluorotelomer sulfonic acids
FTSaAm	Fluorotelomer sulfonamidamines
FTSaB	Fluorotelomer sulfonamide betaines
FTSAS	Fluortelomer mercaptoalkylamidosulfonate
FTUAL	Fluorotelomer unsaturated aldehydes
FTUCA	Unsaturated fluortelomer carboxylic acids
FUCA	Fluorinated unsaturated carboxylic acids
H4PFOS	H4-polyfluorooctane sulfonic acid
HFPO-DA	Hexafluoropropylene oxide dimer acid
MeFASA	N-methyl perfluoroalkanesulfonamides
MeFASE	N-methyl perfluoroalkanesulfonamide ethanols
monoPAP	Fluortelomer phosphate monoester
N,N-Me2FOSA	N,N-dimethylperfluoro-1-octane sulfonamide
N-EtFOSE	N- Ethyl perfluorooctylsulfonamidoethanol
N-MeFOSE	N-methylperfluorooctylsulfonamidoethanol
PAP	Polyalkylphosphates

PFAA	Perfluoroalkane acids
PFAI	Perfluoroalkyl iodides
PALACE	Perfluoroaldehydes
PFAS	Poly- and perfluorinated alkyl substances
PFBA	Perfluorobutane acid
PFBS	Perfluorobutanesulfonic acid
PFCA	Perfluoroalkane acids
PFDA	Perfluorodecane acid
PFDoA	Perfluorododecane acid
PFDoS	Perfluorododecanesulfonic acid
PFEA	Perfluoroalkylether acids
PFEtS	Perfluoroethane sulfonates
PFHpA	Perfluoroheptane acid
PFHpS	Perfluoroheptane sulfonic acid
PFHxA	Perfluorohexane acid
PFHxS	Perfluorohexane sulfonic acid
PFMOAA	Perfluoro-2-methoxyacetic acid
PFMOPrA	Perfluoro-2-methoxypropane acid
PFNA	Perfluorononane acid
PFO2HxA	Perfluoro-2-dioxahexane acid
PFOA	Perfluorooctane acid
PFOAF	Perfluoroalkylcarbonyl fluoride
PFOS	Perfluorooctane sulfonic acid
PFOSA	Perfluorooctane sulfonamide
PFOSF	Perfluoroalkylsulfonyl fluoride
PFPA	Perfluorinated phosphoric acids
PFPE	polyfluorinated polyethers
PFPeA	Perfluoropentane acid
PFPiA	Perfluoroalkylphosphinic acids
PFPrA	Perfluoropropane acid
PFPrS	Perfluoropropane sulfonic acid
PFSA	Perfluoroalkanesulfonic acids
PFSiA	Perfluoroalkylsulfinic acids
PTFE	Polytetrafluorethylene
SAmPAP	Sulfonamidethanol-based phosphates

sFTOH	Secondary fluorotelomer alcohols
TFA	Trifluoroacetic acid
triPAP	Fluorotelomer phosphate triesters
UAcid	Unsaturated fluorotelomer carboxylic acids

Summary

The group of contaminants known as PFAS is becoming increasingly important in the evaluation of contaminated sites. In Germany, where several guidelines and methodological approaches have been developed for the identification, investigation, and evaluation of PFAS-contaminated sites, similar guidelines for remediation management of local and wide-spread incidences of PFAS contamination have been largely missing. It is also necessary to develop specifications on PFAS-specific procedures for investigations accompanying the remediation planning process.

The aim of this guideline "Remediation management for local and wide-spread PFAS contamination", which has been developed on account of the German Federal Ministry for the Environment is intended to serve as a resource for responsible German authorities in the selection, evaluation, and determination of suitable and fitting remedial solutions and management concepts, while highlighting relevant boundary conditions and, if necessary, supplementary measures.

Due to the varying chemical properties of each specific compound belonging to the overall PFAS group of chemical compounds, any potential remedial measure shall be assessed according to the specific PFAS compound in question. For each generally applicable type of remediation technique, advantages and disadvantages, technical and permitting requirements, as well as method sustainability are addressed in the discussion. The guideline incorporates the results of two Germany-wide technical workshops that were held in the years 2018 and 2019.

The guideline is structured as follows: Chapter 2 highlights the basics that are specific to the contaminant parameter group PFAS, and which are most relevant in determining the type(s) of remedial method to pursue in the overall remediation management. These basics include most importantly, determining the relevant source-receptor-pathways, identification of the receptors themselves, the responsible governing authority, aspects of law that shall be taken into consideration in Germany, as well as specifications on sampling, key parameters, and PFAS precursors.

Chapter 3 describes remediation management of point sources. The remediation management of local PFAS point sources is not fundamentally different from the management of conventional contaminants that has been in practice for more than 30 years. However, the contaminant group PFAS has some peculiarities in its behavior, which require some changes in approach.

Chapter 4 describes the unique specifications of remediation management for cases of wide-spread PFAS contamination. At present, many cases of PFAS remediation are challenged due to a variety of aspects related to disposal regulation and the waste management act. Chapter 5 describes the current situation in Germany and provides guidance.

A fundamental challenge when dealing with PFAS-contaminated soil is that there are limited possibilities to decontaminate the soil and that only a small number of disposal sites exist (not only in Germany) that accept PFAS-containing soils. Chapter 5 describes the current situation in Germany and proposes actions on how best to deal with soils in the context of the applicable regulations on waste management.

Due to the high mobility and persistence, there is a great public interest and often a high degree of uncertainty, especially in the cases of wide-spread PFAS contamination. In Germany, there is no legal obligation, but it is recommended that the public be proactively involved, especially in the cases of known wide-spread contamination. Chapter 6 describes recommendations on public inclusion.

Appendices A to C contain detailed information on the PFAS as a group, on currently implemented methods of assessment and on remedial methods. Project examples are case-studied in Appendix D, and in Appendix E pertinent topics of further research are formulated.

The aim of the present English translation is to make the findings and messages from the German research project "Remediation Management for Local and Wide-Spread PFAS Contaminations" more visible on a European and international level and to disseminate and discuss solution approaches in terms of knowledge transfer, problem sensitization, and suitable solution concepts internationally.

1 Introduction and Objectives

The contaminant group comprising per- and polyfluorinated alkyl substances (PFAS) does not occur naturally, rather it is exclusively of anthropogenic origin. PFAS comprise more than 4,700 substances (OECD, 2018). The abbreviation "PFAS" that is used in this guidance document corresponds to the internationally uniformly used designation for the substance group. In Germany the designation "PFC" is used for the parameter group internationally referred to as "PFAS".

PFAS are persistent, very mobile, and have a high efficacy in terms of eco- and human toxicology. The partially fluorinated, so-called polyfluorinated chemicals can be degraded to persistent, fully fluorinated (perfluorinated) chemicals; these partially fluorinated chemicals are generally referred to as "precursors". An observed complete microbial degradation of PFAS has not yet been noted in the scientific literature on this topic.

An emission of PFAS into the environment is generally an ongoing process throughout the entirety of the respective product's life cycle, including all stages beginning with production of the starting chemicals, through use of such chemicals in fluoropolymer production or the use of PFAS-containing consumer products, and finally to the disposal of the products. Once PFAS have been released into the environment, they persistently remain in the environment for a very long time due to their chemical persistence (ECHA, 2018). With regard to elements of soil protection and stewardship, the source/receptor pathways "soil → groundwater" and "soil → plant" are particularly relevant.

A distinction must be made between local or point source and extensive PFAS contamination. Examples of point sources are electroplating shops and fire extinguishing stations or other specific (point) locations where PFAS haven been used. Extensive or wide-spread contaminations are determinable over a large scale. Such wide-spread contaminations are associated, for example, with the application of PFAS-contaminated fertilizers and so-called "soil improvers" or by airborne PFAS (aerosols).

So far, a fully conclusive evaluation of the existing environmental impact by PFAS has not yet been possible due to the overall lack of suitable data. The PFAS-impacts currently registered by the German federal state authorities concern mainly sites with point sources of contamination (airports including military sites, locations with major fires where PFAS-containing fire extinguishing foams were used, etc.). Much less defined are cases of extensive PFAS-contamination to soils. In the German federal state of Baden-Wuerttemberg, highly wide-spread PFAS contaminations have been found on agricultural land, which have been caused by the use of contaminated fertilizers. Also, in Gendorf (German federal state of Bavaria) and in the Dutch city of Dordrecht extensive contamination due to atmospheric deposition from fluorochemical plants has been confirmed. Such cases give strong reason to presume the presence of further wide-spread PFAS-contaminations in Germany.

In Germany, where several guidelines and methodological approaches have been developed for the identification, investigation, and evaluation of PFAS-contaminated sites, similar guidelines for remediation management of local and wide-spread incidences of PFAS contamination have been largely missing. It is also necessary to develop specifications on PFAS-specific procedures for investigations accompanying the remediation planning process.

Due to the different properties of each PFAS compound within the overall PFAS substance group (Appendix A), the range of possible technical remediation options (Appendix C) can only be assessed on the basis of the main PFAS compound in question. Each technical remediation option is therefore presented and compared with respect to respective advantages/ disadvantages, technical requirements, issues to consider with respect to approval/permitting, and the method´s sustainability as a whole.

This work-aid aims to provide support to German regulative authorities in the selection, evaluation, and determination of appropriate and fitting remediation solutions and management concepts and to identify relevant framework conditions and accompanying measures.

The level of knowledge presented in this guideline reflects the knowledge in the year 2019. It is recommended to update this guideline on a regular basis.

2   General Basics

2.1   Material Properties of PFAS Compounds Relevant to Remediation

The substance properties of PFAS are summarized in Appendix A. PFAS differ substantially from conventional "classical" contaminants. Because perfluorinated compounds are largely inert to microbial and chemical degradation and, apart from FTOH, are non-volatile, many classical remediation methods are not applicable to PFAS. The high mobility of most PFAS quickly leads to extensive groundwater plumes upon being released into the groundwater. Such extensive groundwater plumes cannot be remediated using *in-situ* processes for cost-reasons alone (Held, 2017).

Commercially available analytical detection methods exist for only a small number of the several thousand PFAS compounds used in industry and households (Appendix A, Chapter 4). At least the relevant perfluoroalkane carboxylic and sulfonic acids can be analyzed, including all 13 compounds for which current assessment values are available (Appendix B).

A large number of PFAS compounds are polyfluorinated and microbially transformable. Perfluoroalkane carboxylic and sulfonic acids are formed (often with a long-time delay) as end-products which are not further degradable. These end-products are the compounds that are mobile, toxic, and for which in-part there are already assessment values used in regulation. Due to their transformability, the starting compounds are called precursors. Disregarding the precursors can lead to incomplete evaluations in all steps of contaminated site management. Therefore, these substances should be considered while conducting remediation management, even if there are no associated regulatory values (Held and Reinhard, 2016).

As a worst-case scenario if the precursor is not considered, potential hazards may unwillingly be ignored. For example, in case of a suspected hazard investigation that is conducted immediately after the use of fire extinguishing foams containing fluorine compounds (so-called AFFF foams; aqueous foam forming films), the absence of perfluorinated PFAS may be falsely concluded. Over time, however, the analytically detectable perfluorinated PFAS are formed and released upon the completion of microbial precursor transformation. In such a case, a hazard is not able to be identified during a suspected hazard investigation, resulting in misjudgment of the situation.

Material Properties of PFAS Compounds Relevant to Remediation

PFAS do not form free-phase products (non-aqueous phase liquids or NAPLs). They accumulate mainly in the unsaturated soil zone as well as at air/water interfaces and are not microbially mineralizable. An enrichment of PFAS in dense or light NAPL or at the NAPL/water interface is possible.

PFAS that have intruded into groundwater can cause very long contaminant plumes. The biotransformation of precursors can lead to the formation of new perfluoroalkane carboxylic and sulfonic acids, depending on the redox conditions in the source and at locations far from the point of intrusion. Especially their high resistance to microbial, chemical, and thermal degradation is a decisive factor in the selection of remediation methods.

2.2   Differentiation between Local and Wide-Spread PFAS Contamination

For the following discussion, it is first necessary to adequately define terms "local" and "wide-spread" in regard to instances of PFAS contamination. This is not always easy due to the loose definition of each.

An example of a local or point case of PFAS contamination would be an intrusion of PFAS into soil and groundwater at the site of an electroplating plant. Since the PFAS can be quite mobile, they form very long contaminant plumes in groundwater, resulting at times in secondary contamination. For example, where agricultural areas are being irrigated with groundwater being extracted from such a contaminant plume, from water of sewer ditches or larger surface waters or from relocated PFAS contaminated excavated soil.

If, on the other hand, PFAS-contaminated "soil improvers" have been applied in comparatively large quantities over a large area, this is referred to as extensive PFAS contamination. Extensive PFAS contamination of soil and groundwater can also be caused by the input of airborne contaminants (e.g. from chimneys, air exhaust systems). Due to washing-out effects and particle-bound transport, PFAS are deposited into the surrounding soils and waters, mainly in the direction of dominant wind flow. With the contaminated soils as the source, such PFAS can subsequently leach through the soil into the groundwater. Due to so-called combing effects of trees, significantly higher PFAS concentrations are found in the litter layer of forest areas than on agricultural land and settlement areas (LfU Bayern, 2018). Such studies have also proven positive for other airborne contaminants. The extent of pollution around the site of emission can be considerable and can reach up to several tens of kilometers (Liu et al., 2016, Oliaei et al., 2013).

Wide-spread PFAS contamination shall be distinguished as soils generally classified as uncontaminated but which have diffuse, very low, but clearly wide-spread detectable concentrations of PFAS, that have been exclusively deposited as a result of anthropogenic factors. Cases with such characteristics are documented in the soil monitoring program of the German federal state of Baden-Wuerttemberg[1,2] (LUBW, 2016, 2017). The study of PFAS concentrations in what are referred to as "background soils", using modern instrumental analysis from aqueous soil eluates (DIN 19529; HPLC-ESI-MS/MS) has resulted in consistently determinable, albeit very low PFAS concentrations throughout. In some cases, forest soils and forest debris were found to have slightly higher PFAS concentrations than arable and grassland soils. PFAS contents in solids (DIN 38414-14) in "background soils" are usually not determinable with the mentioned analytical method. In few cases, PFOA and PFOS have been detected in the range of the analytical limit of quantification (1 µg/kg). Investigations in Bavaria (Germany) show corresponding results[3]. Ubiquitous deposition via the air path is currently presumed to be the probable cause for the background contamination in the soil eluates.

Typical cases of PFAS contamination at airports are neither fully local nor wide-spread cases of PFAS contamination, rather are somewhat in between. In addition to the known point sources, such as fire training areas, fire stations, local use of PFAS-containing fire extinguishing foams, diffuse contamination over large areas is often detected, possibly due to wind drift of fire extinguishing foams or other processes (flooding from drainage ditches, etc.).

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[1]   Germany is organized on a federal level and consists of 16 federal states. The federal states are responsible for the enforcement of soil and groundwater protection. The relevant laws are issued by the federal government.

[2]   The PFAS sum in the eluate was on average 0.2 µg/L in arable soils, 0.3 µg/L in grassland soils and 0.6 µg/L in forest soils. The carboxylic acids PFBA, PFPA, PFHxA, PFHpA and PFOA were detected in all aqueous shake eluates and with the exception of one sample which had PFNA.

[3]   https://www.lfu.bayern.de/analytik_stoffe/per_polyfluorierte_chemikalien/pfc_belastung_boeden/index.htm

For situations such as this, it must be decided on a case-by-case basis whether each area is better to be treated as a point source separately or if all areas shall be integrated and addressed as extensive contamination.

> **Differentiation Between Local and Extensive PFAS Contaminations**
>
> Local contaminations can occur especially in case of point discharges, e.g. at electroplating shops, at locations of fire damage, and when using PFAS-containing extinguishing foams. Extensive PFAS contamination is caused, for example, by the application of PFAS-contaminated fertilizers on arable land or by the deposition of PFAS-contaminated aerosols in the vicinity of production facilities. Sometimes it can be useful to treat an agglomeration of point sources on a factory site as a single extensive PFAS contamination. A black-and-white distinction between local and extensive PFAS contamination is not the goal. Rather, each case shall be assessed individually according to its relevant characteristics.

2.3 Conceptual Site Model

The aim of a Conceptual Cite Model (CSM) is to clarify and clearly present the complex interrelationships of a PFAS contamination case. Working without a conceptual site model increases the risk of misinterpretations, which can be associated with considerable cost risks during remediation.

Usually, sufficient data on a site are only available after the completion of the detailed investigation (Phase III investigation), which allows the creation of a conceptual site model. The conceptual site model combines all data (contaminant input characteristics, contaminant distribution, geology, hydrogeology, distribution of contaminants, transport pathways and processes as well as contaminant attenuation processes) of a site into an overall picture or all-encompassing model and thus allows a comprehensive understanding of a site.

For specific parts of the model, for which an analytical proof is missing, interdisciplinary expert knowledge for the formulation of a hypothesis is used. If necessary, such a hypothesis is to be verified by collecting further site data (Held, 2014). While conducting further processing of the site, additional site data will be collected until successful remediation monitoring is completed. Thus, a wide variety of data is collected at different times over very long periods of time, which must always be integrated into the conceptual site model.

The CSM allows data relevant to the location to be presented in a clear and transparent structure. This is achieved with a "format" that is easy to process, understand, and apply. The CSM can optionally include a textual description of the site, a graphical illustration of all relevant site parameters and a clustered illustration of possible exposure pathways across the different environmental compartments. Usually the construction of a conceptual site model starts with the first investigations of a site and is continuously updated. It should facilitate the formulation of the following pertinent statements:

► Identification and localization of overall contaminant potential.

► Identification and localization of the source(s) of contamination.

► Differentiation and identification of relevance for the contaminant pathways with respect to each individual environmental medium (groundwater, surface water, soil, sediments, biota, and air)

- ► Identification of anthropogenic background concentrations in each environmental medium[4]
- ► Identification and characterization of potential receptors (human and ecology).
- ► Definition and identification of system boundaries.

Due to the complex chemical behavior of PFAS, which differs in many ways from the more conventional contaminants, a conceptual site model for a worst-case scenario is presented below in form of a schematized and idealized diagram (Figure 1), which is also described in the following text. It is intended to clearly show those processes in the subsurface that are possible in the worst case. This procedure serves to facilitate subsequent planning of the site investigation.

- ► For example if AFFF foams are used to extinguish fires involving flammable liquids ①, the AFFF components including non-fluorinated organic compounds (Appendix A, Chapter 11.2) together with the liquid chemicals to be extinguished (e.g. total petroleum (TPH) from unburned fuel) reach the underground ②.
- ► It can be assumed that PFAS and TPH follow almost the same flow paths, although the extent of contamination may be significantly different. These co-contaminants, especially light non-aqueous phase liquids (LNAPL), may additionally affect the transport of PFAS (Guelfo and Higgins, 2013; Lipson et al. 2013; McKenzie et al. 2015). To what extent the mobility of the co-contaminants may be rheologically influenced by PFAS still needs to be investigated. It is possible that the PFAS can increase the mobility of the co-contaminants (as a mixture of substances).

Figure 1   Conceptual site model
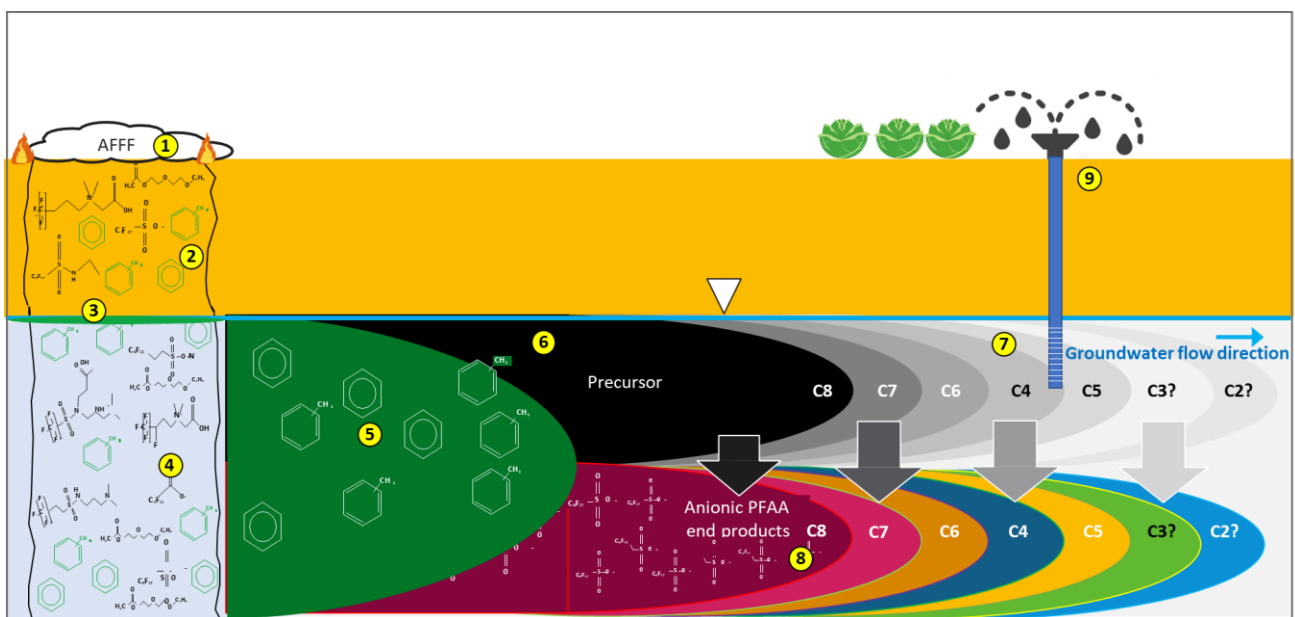
In this conceptual site model, not all possible relevant receptors are included, but this is essential for a reliable site model.
Source: Hurst, 2017

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[4]   Reason: the anthropogenic background concentrations of PFAS in soil are currently being investigated in some German states, but also internationally. Until results are available, the anthropogenic background contamination may have to be determined when investigating PFAS contaminations.

Above all, however, the PFAS including the precursors are sorbed to the unsaturated soil zone, especially in the organic-rich topsoil. This area represents the source of the contamination. Contaminant elution from the source is essentially dependent on:

- the sorption strength in the source area,
- the concentration of the co-contaminants (PFAS and accompanying substances may react as a mixture of substances; PFAS can then be released again diffusively from the mixture of substances)
- the microbial transformation processes that lead to the release of Perfluoroalkane carboxylic and sulfonic acids during the degradation of precursor and
- the release of the PFAS by degradation of TOC, i.e. as a result of a reduction in PFAS sorption.

The unsaturated zone below the source (topsoil) is initially uncontaminated. Hence, the PFAS transported across the unsaturated zone by means of seepage water are retained by sorption (with varying degrees of intensity). PFAS reach the groundwater after a retention-caused delay. The delayed PFAS-input from the unsaturated soil zone into the groundwater is mainly determined by the following parameters in addition to the above-mentioned processes:

- Seepage rate or groundwater recharge rate depending on the hydraulic permeability of the soil. These rates can be found in the publications of the individual German states, for example Armbruster (2002),
- Distance of the source from the water table.

▶ If very large quantities of co-contaminants are released as light non-aqueous phase liquid (LNAPL), such LNAPL may accumulate in the groundwater fluctuation zone ③.

▶ From the unsaturated soil zone, the PFAS are transported into the groundwater ④. Regarding the extent to which such an intrusion leads to increased concentrations of sediment-bound contaminants within the aquifer itself is not yet sufficiently examined. Considering, however, the sorption characteristics, such an enrichment is probable. Cationic PFAS are retained more strongly than anionic compounds due to the dominating negative charge of the soil surface. Also, zwitterionic PFAS are likely to show a different sorption behavior ⑧. There are not yet systematic studies available on the sorption of the precursors, this might also be difficult because the precursors are a large, very heterogeneous group. Targeted, case-specific investigations on the distribution of the precursors can likely give insight into the sorption behavior (depth-distribution of PFAS in soil, occurrence in groundwater or only in the soil, etc.).

Alongside the PFAS, transport of co-contaminants into the groundwater is ongoing. Their natural microbial degradation usually leads to an anaerobization of the aquifer and thus to a prevention of the microbial precursor transformation (Harding-Marjanovic et al. 2015; McKenzie et al. 2015; McGuire et al. 2014).

▶ The contaminant plume of the co-contaminants is usually significantly shorter than that of the PFAS ⑤. Only when the redox environment has changed again to the extent that aerobic conditions are present, is the transformation of the precursors possible ⑥.

▶ The precursors are also transported to a limited extent within the aquifer. The heterogeneous group of precursors contains molecules of different size (molecular weight). It can be assumed that hydrophobicity is positively correlated with molecular weight. Accordingly, the precursors are chromatographically separated in the aquifer according to molecular weight or (simplified) according to the length of the perfluorinated chain ⑦.

▶ If aerobic microbial transformation is possible, it is assumed that longer-chain perfluoroalkane acids are released distally (near the source) and shorter-chain perfluoroalkane acids are released longitudinally (far from the source).

▶ The perfluoroalkane acids themselves are subject to a strongly varying sorption to the soil matrix. Sulfonic acids are more strongly retarded than carboxylic acids of the same C-chain length. Furthermore, the strength of sorption increases with chain length. Accordingly, a chromatographic separation of the PFAS along the migration direction in groundwater can be expected.

The recognition of such a chromatographic separation is made more difficult by the fact that, on the one hand, in the aquifer itself perfluoroalkane acids can be formed from the precursors with a time delay and in a locally variable manner and, on the other hand, that the subsequent elution from the unsaturated soil zone can also be variable in time and place.

For example, a late release of short-chain PFAS (e.g. PFBA) from the precursors in the unsaturated topsoil can result in their detection in the groundwater within the source area long after the contamination has occurred (i.e. at a time when they should be leached out in the soil).

▶ If groundwater is taken for irrigation purposes from the typically extensive PFAS plume, a extensive secondary source can form in the topsoil. An absorption in plants is possible depending on the process parameters among other things (e.g. contaminant concentration, irrigation rate, duration) ⑨.

Conceptual Site Model (CSM)

The aim of the conceptual site model is the clear presentation and clarification of complex interrelationships of PFAS contamination. Working without the conceptual site model increases the risk of misinterpretations, which can be associated with considerable cost risks during remediation. Therefore, the conceptual site model, although not always applied in conventional contaminated site management, should be systematically integrated in the expert evaluation of PFAS contaminations.

The conceptual site model describes the contaminant transport and concentration attenuation processes taking place at the site as well as the existing redox conditions. It must consider the special behavior of the PFAS (including the transformation of the precursors only at the aerobic plume end) and it must contain all source/receptors pathways and receptors. PFAS contaminations often affect more receptors than conventional contaminated sites. The conceptual site model serves as a basis for the remediation planning and is continuously updated during the project.

2.4   Source/Receptor Pathways and Receptors

Based on the contaminant distributions described in Chapter 2.3 the individual source/receptor pathways and receptors can be identified and integrated into the conceptual site model. Figure 2 gives a schematic and exemplary overview of the possible source/receptor pathways using the example of soil contamination by contaminated soil fertilizers. Other sources of contamination can be the leakage of PFAS-containing liquids (electroplating, etc.), seepage water from deposits, firefighting-foam damage, dust- or fluid-bound damage from emissions, sludge discharge from wastewater treatment plants, etc.

If PFAS are released from point sources, the following source/receptor pathways (initially independent of the respective assessment values, see Appendix B) are often of importance and must be considered on a case-by-case basis:

(1) **Soil → Groundwater.** Soil pollution can be local or extensive. Increased soil contamination in the vicinity of production facilities due to atmospheric deposition is also possible. Soil contamination can also be a secondary source, for example after irrigation with contaminated water. From the soil the PFAS reach the groundwater by leaching through the soil with water from precipitation. The groundwater can be used in many ways. From public or private drinking water use, commercial use (e.g. for production or cooling purposes), use as drinking water for livestock, to use as irrigation water for agriculture or gardens, there are many possibilities of being affected. These must be investigated as individual cases along the spreading contaminant plume. Usually also an inspection of the areas is required.

(2) **Soil → Human (direct path).** Due to the high sorption capacity of the longer-chain PFAS in particular, the direct source/receptor pathway may be principally be relevant.

(3) **Soil → Groundwater → Surface Water → Fish → Human.** As a result of the long contaminant plumes that form, groundwater can enter surface waters and cause ecotoxicological and toxicological effects through fish consumption. The highest levels of PFAS in food have been found in fish, fish products, and seafood (Gellrich, 2014).

Figure 2   Possible exposure pathways (example of an extensive PFAS contaminated fertilizer application)
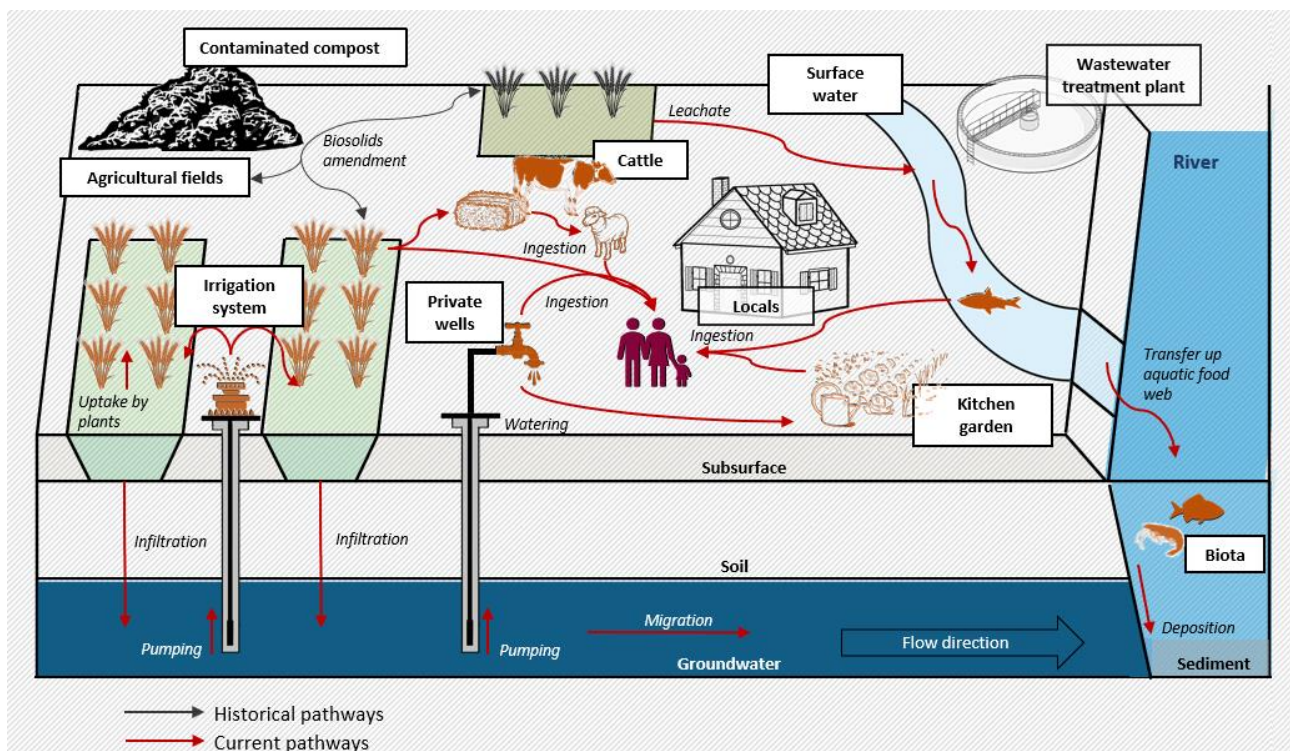
Source: Wattelle-Laslandes, 2018

(4) **Soil → Groundwater → Irrigation water → Soil.** Particularly in the case of long PFAS plumes, it is possible that the PFAS-contaminated groundwater is used for irrigation purposes for agricultural areas. As a result, the PFAS can accumulate in the topsoil and form a secondary source for further source/receptor pathways.

(5) **Soil → Crop → Human.** This source/receptor pathway plays a role above all in the contamination of agricultural land (PFAS in rooted soil). The areas themselves can be primary contaminant sources or have been secondarily contaminated by regionally increased atmospheric deposition or after irrigation of the soil with PFAS-contaminated groundwater. Plants absorb PFAS with accumulation within individual parts of the plant, sometimes with great differentiation from plant species to plant species. In addition, the uptake is subject to seasonal and weather-related fluctuations. Lastly, the type of plant species cultivated on a parcel of land changes during the year or from year to year, so that any uptake and storage of substances on a defined parcel is subject to variation.

(6) **Soil → Crop → Animal → Human.** Starting from PFAS-contaminated soil, the contaminants can reach farm animals and thus humans via feed plants and drinking water. In addition, the PFAS-contaminated soil can be directly absorbed by grazing animals (fodder accumulation). Furthermore, PFAS can be enriched in honey and wax from bees if bee colonies are kept in the immediate vicinity of contaminated areas.

Whether the source/receptor pathway

(7) **Soil → Soil air → Indoor air → Human**

is relevant, cannot yet be assessed due to lacking available data. In principle, there is the possibility that precursors could enter the unsaturated soil area below buildings (possibly also by outgassing from groundwater) and be transformed/hydrolyzed there under aerobic conditions.

It is conceivable that highly volatile fluorotelomer alcohols (FTOH) can be formed, which in principle have the potential to outgas and accumulate indoors. Due to the slow transformation rates and the fact that the FTOH themselves can be microbially transformed back to non-volatile perfluoroalkane acids, this source/receptor pathway is unlikely. Initial work on this topic seems to confirm[5] this assumption.

The source/receptor pathway

(8) **Soil → Surface water**

can be cause for effect if PFAS-containing soils or PFAS-containing liquids (industrial wastewater, fire-fighting-foam wastewater) are washed away into ditches or streams. These can lead to a secondary contamination of the waterway sediments. Starting from contaminated brooks, a delineation of contaminated catchment areas is possible.

Sometimes there are also surface waters that are embedded in the groundwater within the PFAS plumes. If the PFAS contamination in the groundwater is near the surface, a deep groundwater incision, e.g. in gravel pit excavations, can cause a vertical and horizontal widening of the plume. Responsible for this are existing currents within the surface water body, e.g. a lake. In addition to the usual convection currents, in winter the cooled water can sink into deeper areas that were heated during the summer (Figure 3).

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[5] About 10 years ago, a PFAS contamination of the topsoil used for agricultural purposes was caused at a German site. PFAS resulted presumably from paper production. A sampling of the soil air resulted in the detection of 4:2, 6:2 and 8:2 FTOH in the lower ng/m^3 range. These values are in the range of the air concentrations found, for example, at municipal wastewater treatment plants and thus at only low concentrations (Kopf, 2017). How fresh PFAS contaminations behave still needs to be investigated. Independent of the contamination, however, it can be assumed that indoor locations are contaminated by outgassing, e.g. from textiles (carpets, leather sofas, etc.) and the use of impregnation sprays and other household items. This must be considered in the assessment. The TOP assay should be included in the analysis.

Figure 3   PFAS distribution in the runoff of lakes or artificial groundwater incisions

Lake

PFAS Plume

Groundwater
flow direction

Groundwater
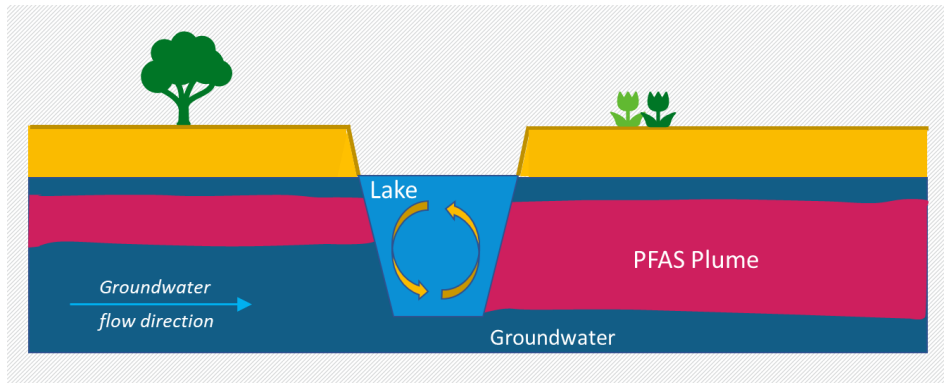
Source: Arcadis Germany GmbH, 2019

Figure 4 shows a simplified scheme, with the help of which all relevant source/receptor pathways and affected receptors can be quickly determined for a first assessment based on the respectively determined site data.

Figure 4   Simplified scheme for identification of source/receptor pathways and receptors

Potential receptors

Site residents, workers
Use of groundwater
Consumption of aquatic species
Consumption of plants, animals
Aquatic ecosystems
Terrestrial ecosystems
Leisure areas

Contaminant source

Contaminated media
Transport pathways

Source/receptor pathways

Soil

Seepage water
leads to groundwater contamination

Groundwater

Pumping

Direct contact
ingestion including inhalation of particles

Groundwater →
human Ingestion
(drinking water)

PFAS Source
Fire fighting, training areas, industry, compost, etc.

Surface-discharge
particle-bound

Input to
surface
waters

Irrigation of
agricultural
areas

Soil → Crop

Surface waters,
sediments

Surface waters →
human
Ingestion

Deposition

Air

Inhalation

Source: after NGWA, 2017, supplemented and modified

Source/Receptor Pathways and Receptors
While for conventional contaminants, the dominating source/receptor pathway is soil → groundwater, additional source/receptor pathways play a substantial role when considering PFAS in the environment. Here, in addition to migration into surface waters, the entry into human food via crops, fish, and meat must be examined in particular.
To be able to guarantee a complete evaluation, the possible source/receptor pathways must be systematically assessed at the onset of contaminated site management.

2.5 Possibly Affected Authorities and Legal Areas

Due to the special characteristics of PFAS, in which they are able to spread over very large areas without natural contaminant degradation while affecting different source/receptor pathways and several types of receptors, often a wide range of legal areas and authorities have to be considered in contaminated site management as compared to the management of conventionally contaminated sites. Especially for PFAS, the danger of ongoing expansion of contamination must also be considered, which left unhindered can cause additional receptors potentially to be affected in the future. It is advisable to conduct a scoping meeting with the potentially affected authorities while beginning to conduct contaminated site management to clarify responsibilities, tasks, and procedures for further processing. To process cases of PFAS-contamination under statutes of the German Federal Soil Act, applicable is the procedure that is described here.

The tables and explanations are intended to help in identifying the authorities and legal areas affected. The authority structures and designations may differ in the individual German Federal States. Generalizing terms were used in the tables as far as possible. The explanations are intended solely for initial orientation and do not imply any guarantee of completeness or accuracy. The legal classifications must always be checked for each individual case.

Tables 1 to 5 are structured so that first the possible primary contaminant sources (Table 1) and then the possible affected media and receptors (Table 2) can easily be identified. Both tables incorporate the same index numbers, which allow for quick identification of authorities and areas of law associated with possible primary PFAS contaminant source and media.

Table 1   Selection of possible PFAS contaminant sources and affected contaminated media

No.	Possible primary contaminant sources and affected contaminated media
	Possible primary contaminant sources
1.1	Extinguishing foams on or in soils
1.2	Seepage of PFAS-containing liquids on or in soils, handling losses (spills) at industrial plants (e.g. electroplating plants)
1.3	Air emissions via aerosols from PFAS-processing industrial plants on or in soils
1.4	Wastewater emissions to water bodies
1.5	Emissions via sludge from wastewater treatment plants on or in soils
1.6	Fertilizers

No.	Possible primary contaminant sources and affected contaminated media
	Possibly affected PFAS contaminated media
2	**Soil**
2.1	Arable land
2.2	Grassland (grazing land)
2.3	Home gardens
2.4	Erosion soils
2.5	Excavated soil in construction measures
2.6	Soils in construction areas
2.7	Soils in land consolidation areas
2.8	Forest soils
2.9	Soils on commercial and industrial properties
3	**Groundwater**
3.1	Drinking water
3.2	Garden irrigation
3.3	Cattle watering places
3.4	Irrigation on agricultural lands
3.5	Energetic use
3.6	Groundwater extraction or use in construction measures (including construction areas and traffic route construction)
3.7	Commercial use as production or cooling water
4	**Surface waters**
4.1	(Swimming) lakes
4.2	Pisciculture
4.3	Brooks, rivers
4.4	Riparian areas, -sediments
4.5	Flood plains
4.6	drinking water (see 3.1)
5	**Waste**
5.1	Landfill disposal
5.2	Recycling of production waste
5.3	Recycling of excavated soil and sewage sludge
5.4	Recycling of green waste
5.5	Recycling of building rubble
6	**Overburden from raw material mining**
6.1	Overburden from gravel mining with secondary contamination
6.2	Mining overburden with secondary contamination

Table 2   Possible affected authorities (legal areas) for different sources of pollution

Number from table 1	Short name	Authorities (legal fields)	Notes
1.1	Extinguishing foams	**Soil protection authority** (BBodSchG, BBodSchV)	Contaminated site management: BBodSchG, BBodSchV
1.2	Leakages from industrial plants	**Immission control authority** (BImSchG) **Water Authority** (WHG) **Trade Inspection** if necessary, **Soil protection authority** (BBodSchG, BBodSchV)	BImSchG-approved active plants: priority BImSchG, Contaminated sites: BBodSchG, BBodSchV If no specific rules in BImSchG: Precaution according to BBodSchG, BBodSchV, in case of harmful soil changes: BBodSchG, BBodSchV
1.3	Air	**Immission control authority** (BImSchG) if necessary, **Soil protection authority** (BBodSchG, BBodSchV)	Primarily BImSchG If no specific rules: precaution according to BBodSchG, BBodSchV. In case of harmful soil changes: BBodSchG, BBodSchV
1.4	Wastewater	**Water law authority** (WHG, AbwAG) or **Soil protection authority** (BBodSchG, BBodSchV)	For water pollution: Water law (WHG); wastewater in water bodies: AbwAG. For harmful soil changes: BBodSchG, BBodSchV
1.5	Slurries	**Waste Management Authority** (KrWG, AbfKlärV) if necessary, **Soil protection authority** (BBodSchG, BBodSchV)	Application of sludge: primarily regulations: KrWG, AbfKlärV. If no specific rules: precaution according to BBodSchG, BBodSchV. in case of harmful soil changes: BBodSchG, BBodSchV.
1.6	Fertilizers	**Agricultural authority** (DünG, DüV, BioAbfV, AbfKlärV) **Immission control law / Building law authority** (plant monitoring) if necessary, **Soil protection authority** (BBodSchG, BBodSchV	Primarily for fertilizers: DüngG, DüV, BioAbfV, AbfKlärV. Plant supervision of the manufacturer. Note: Optionally, the waste law may also be affected. If no specific rules: Precaution according to BBodSchG, BBodSchV, in case of harmful soil changes: BBodSchG, BBodSchV.

In the conversion of PFAS-contaminated sites (as point sources) and in *urban land use planning*[6] within areas of extensive PFAS-contamination, German construction law plays an essential role. According to the principle of subsidiarity, the applicable construction law is the more specific law and is initially given priority.

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[6] Urban land use planning is the most important planning tool for the urban development of a community. It is carried out in two stages in a formal procedure under building planning law. First, a land use plan for the entire municipal area is developed in the preparatory urban land use planning. In the legally binding urban land use plans, development plans are then drawn up for spatial sub-areas of the municipal territory. While the land use plan only contains legally binding statements on the basic principles of land use, the determination of the development plans regulates the structural and other use of land in detail and is legally more specific. The zoning plans thus determine essential requirements under building law under which the building supervisory authorities grant building permits for construction projects.

Table 3   Possible affected authorities (legal areas) for contaminated soils

Number from table 1	Short name	Authorities (legal fields)	Notes
2.1	Arable land	**Food Inspection Authority (LMBG)** **Feed authority**, if applicable [FutMG] **Soil protection authority (BBodSchG, BBodSchV)** **Agricultural authority**	In the production of food: Food and Consumer Goods Act (LMBG). Ordinance on Maximum Permissible Contaminant Quantities (SHmV). For production of feed: Feed Act (FutMG). In case of harmful soil changes: BBodSchG, BBodSchV. Soil application and removal to prevent erosion according to BBodSchG, BBodschV (§12 and others). Technical support for management: Agricultural authority
2.2	Grassland (grazing land	**Food Inspection Authority (LMBG)** if necessary, **feed authority (FutMG)** **Soil protection authority (BBodSchG, BBodSchV)** **Agricultural authority**	For production of food (meat industry): LMBG, SHMV (note: if necessary, the veterinary office may be involved as part of the food monitoring). For production of animal feed: FutMG. In case of harmful soil changes: BBodSchG, BBodSchV. Soil application and removal according to BBodSchG, BBodschV (§12 and others). Technical support for management: Agricultural authority.
2.3	Home gardens	**Soil protection authority (BBodSchG, BBodSchV)**	In case of harmful soil changes: BBodSchG, BBodSchV
2.4	Erosion soils	**Soil protection authority (BBodSchG, BBodSchV)** if applicable, **water rights authority (WHG)**	Soil erosion by water: BBodSchV §8 (also flood areas Soil erosion banks, water edge strips according to WHG
2.5	Relocation of excavated soil during construction work	**Building law authority, Road traffic authority, Federal railroad authority,** optionally **Soil protection authority (BBodSchG, BBodSchV)** Optionally W**aste management authority (KrWG**	Primarily: building regulation/planning law The material requirements of BBodSchG and BBodSchV are generally applicable for soil protection issues, for application to the rooting soil horizon: BBodSchV §12, for harmful soil changes: BBodSchG, BBodSchV
2.6	Soils in construction areas	**Community (BauGB)** Optionally **soil protection authority (BBodSchG, BBodSchV)** Optionally **Water rights authority (WHG)**	Preparation of land use / development plans and building permits: according to BauGB. For weighting the concerns of soil protection, material requirements of BBodSchG and BBodSchV apply, in case of harmful soil changes: BBodSchG, BBodSchV. Rainwater infiltration regulates water law (WHG)

Number from table 1	Short name	Authorities (legal fields)	Notes
2.7	Soils in land consolidation areas	**Land consolidation authority** (Flurbereinigungsbehörde (FlurbG)), Optionally, **soil protection authority** (BBodSchG, BBodSchV)	Primarily: Land Register

For concerns of soil protection, material requirements of BBodSchG and BBodSchV apply |
| 2.8 | Forest soils | **Forest Authority** (BWaldG) Optionally **Soil protection authority** (BBodSchG, BBodSchV) | Primarily BWaldG- If no specific rules: Precaution according to BBodSchG, BBodSchV, in case of harmful soil changes: BBodSchG, BBodSchV |
| 2.9 | Soils on commercial and industrial properties | **Soil protection authority** (BBodSchG, BBodSchV) | Precaution according to BBodSchG, BBodSchV, in case of harmful soil changes: BBodSchG, BBodSchV |

Table 4   Possible affected authorities (legal areas) for polluted groundwater and surface waters

Number from table 1	Short name	Authorities (legal fields)	Notes
Medium concerned: Groundwater			
3.1	Drinking water	**Water Authority** (WHG)

Public health department (TrinkwV) Optionally **Soil protection authority** (BBodSchG, BBodSchV) Health Authority | Use, management, and utilization are regulated by the Water Act (WHG). Water protection areas are regulated by WHG, prohibitions are regulated in part in SchALVO (e.g. application/depositing of soils). External monitoring of water suppliers, inspection of own water supply Soil-related water body/groundwater hazards are regulated by BBodSchG/BBodschV. Direct discharges into water bodies regulated by water law. The WHG regulates shore or watercourse margins (5 m in the interior and 10 m in the exterior from the mean water level line). Non-assignable water pollution is regulated by WHG. |
| 3.2 | Garden irrigation | **Water Authority** (WHG)

Optionally **Soil protection authority** (BBodSchG, BBodSchV) | Utilization, management, and utilization is regulated by water law (WHG). Indirect pollution of soils by polluted water: BBodSchG, BBodSchV. |
| 3.3 | Cattle watering places | **Water Authority** (WHG)

Food Inspection Authority, Veterinary Office (LMBG) | Utilization, management, and utilization is regulated by water law (WHG). For food production (meat industry): LMBG, SHMV |
| 3.4 | Irrigation Agriculture | **Water Authority** (WHG)

Food Inspection Authority (LMBG) | Utilization, management, and utilization is regulated by water law (WHG). For food production: LMBG, SHMV |

Number from table 1	Short name	Authorities (legal fields)	Notes
3.5	Energetic use	**Water Authority** (WHG)	Utilization, management, and utilization is regulated by water law (WHG).
3.6	Groundwater use in construction measures	**Water Authority** (WHG)	Utilization, management, and utilization is regulated by water law (WHG).
Medium concerned: Surface water			
4.1	(Swimming) Lakes	**Water Authority** (WHG) **Public health authority**	Utilization, management, and utilization regulates water law (WHG). Advises water authorities.
4.2	Pisciculture	**Water Authority** (WHG) **Food Inspection Authority (**LMBG)	Utilization, management, and utilization is regulated by water law (WHG). For food production: LMBG, SHMV
4.3	Brooks, Rivers	**Water Authority** (WHG)	Utilization, management, and utilization is regulated by water law (WHG).
4.4	Shore areas, sediments	**Water Authority** (WHG)	Utilization, management, and utilization is regulated by water law (WHG).
4.5	Flood plains	**Soil protection authority** (BBodSchG, BBodSchV) if applicable, **water rights authority** (WHG	Soil erosion by water: BBodSchV §8 (also flood areas. Soil erosion banks, water edge strips according to WHG.

Since the handling of soil contamination is not regulated in construction law, which is formulated according to the precautionary principle, the soil protection law or BBodSchV (e.g. the assessment values stipulated therein) is often used as an alternative in urban land use planning. Areas suspected of being contaminated, contaminated sites, areas of concern for harmful soil changes or harmful soil changes themselves are treated according to the soil protection law.

In urban land use planning, all conflicts arising from an intended use that opposes the predesignated use must be resolved. Possibilities for resolving conflicts related to contaminated excavated materials are discussed in chapter 0

The responsibility of the *agricultural authority* is, on the one hand, to surveil the use of fertilizers and, on the other, to provide advice and technical support. If the crop is contaminated, the authority can make a considerable contribution to reducing the consequences of contamination by advising farmers and making recommendations, e.g. on crop rotation.

The *Drinking Water Ordinance* (TrinkwV, 2018) stipulates, among other things, any necessary treatment of drinking water and self-monitoring by means of a suitable monitoring program (parameters, monitoring frequency). External monitoring is the responsibility of the public health department. With the update from 09.01.2018, a so-called risk-assessment-based adjustment to sampling planning was introduced. This is intended to give water suppliers more flexibility in the analysis of drinking water. In close cooperation with the responsible health authority, water suppliers can now adapt the prescribed investigations of drinking water to the individual conditions onsite to achieve maximum knowledge gain. To this end, the water supplier must prepare a risk assessment that provides a well-founded and comprehensible justification for adjusting the scope and frequency of investigations.

This also makes it necessary to include PFAS in the investigation program, if there is a suspicion that these contaminants may be involved. PFAS are not included in the standard investigation program of the Drinking Water Ordinance.

Table 5   Possible affected authorities (legal areas) for contaminated waste and overburden[7]

Number from table 1	Short name	Authorities (fields of law)	Notes
Medium concerned: Waste			
5.1	Landfill disposal	**Waste Management Authority** (KrWG)	Disposal according to waste law: KrWG
5.2	Recycling of production waste	**Waste Management Authority** (KrWG)	Waste recycling: KrWG
5.3	Recycling of sewage sludge	**Waste Management Authority** (KrWG)	Waste recycling: KrWG
5.4	Recycling of excavated soil	**Waste Management Authority** (KrWG) **Soil protection authority** (BBodSchG, BBodSchV)	Waste recycling: KrWG for application in or on a rooting layer: BBodSchV §12 Relocation within the remediation area: BodSchV §12, prohibitions to WSG partly contained in SchALVO (e.g. application/introduction of soils)
5.5	Recycling of green waste	**Waste Management Authority** (KrWG)	Waste recycling: KrWG
5.6	Recycling of building rubble	**Waste Management Authority** (KrWG)	Waste recycling: KrWG
Medium concerned: overburden from raw material mining			
6.1	Overburden gravel mining	Usually **Water authority** (WHG)	Use, management, and utilization are regulated by the Water Act (WHG). Here mostly intervention in the groundwater
6.2	Mining overburden	**Mining Authority** (BBergG)	Under mountain supervision.

The *public health department* is the professional control center for the public health service with many tasks. For example, the public health department is regularly presented with the results of the water suppliers' PFAS investigations.

Possible authorities and legal areas affected

The systematic processing of PFAS contaminations is subject to the requirements of the soil protection law. Due to the wide use and high mobility of PFAS, several further legal areas and authorities may also be affected.

At the beginning of any study, the possible source/receptor pathways, receptors and thus affected areas of law must be systematically taken into consideration.

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[7] Overburden: here: removed surface layer without use.

It is recommended to make a scoping appointment with the authorities at the beginning of the project to clarify responsibilities, tasks, and procedures for further processing. During this process, the future area of PFAS contamination in groundwater and the future receptors or influences should also be surveyed in case of an expanding area of contamination. The affected legal areas must also be considered.

2.6 Sampling, Key Parameters, Precursors, Sum Parameters and Quality Assurance

Sampling and key parameters. For all sampling, the special conditions required for PFAS (Appendix A, Chapter 4) must be considered. Since several thousand PFAS compounds may occur, the first question to be answered is to what extent the contaminants must be analyzed. It is recommended to analyze the compounds listed by the working group of the Federal/State Working Groups on Water (LAWA) and Soil Protection (LABO) in the report "*Derivation of insignificance threshold values for PFCs*" 2017. In case of updates, the list of compounds must be updated accordingly. Proposed key parameters are:

- ▶ Perfluorobutane acid   PFBA
- ▶ Perfluorobutanesulfonic acid   PFBS
- ▶ Perfluoropentane acid   PFPeA
- ▶ Perfluorohexane sulfonic acid   PFHxS
- ▶ Perfluorohexane acid   PFHxA
- ▶ Perfluoroheptane sulfonic acid   PFHpS
- ▶ Perfluoroheptane acid   PFHpA
- ▶ Perfluorooctane sulfonic acid   PFOS
- ▶ Perfluorooctane acid   PFOA
- ▶ H4-polyfluorooctane sulfonic acid   H4PFOS
- ▶ Perfluorononane acid   PFNA
- ▶ Perfluorooctane sulfonamide   PFOSA
- ▶ Perfluorodecane acid   PFDA

For perfluoropentane sulfonic acid (PFPeS) no insignificance threshold value has been derived. Irrespective of this, it is recommended that this parameter be included in the analysis to be able to completely determine the substance spectrum of the perfluorinated substances.

Foam extinguishing agents containing fluorine can lead to contamination with PFAS not included in this list. After the use of such extinguishing foams, additional analysis for such substances should therefore be carried out. In particular polyfluoroalkylbetaines may be considered, which are e.g. contained as PFOS substitutes in Capstone™ products.

Since some soils are judged PFAS-free on the basis of a solids analysis (determination limit usually 1 - 10 µg/kg) but then show PFAS concentrations above the assessment values in the aqueous eluate (determination limits usually 1 - 10 ng/L), eluate analyses are necessary for the investigations.

Currently, different elution methods are still being used in the individual German States, but it is foreseeable that the (W/S) 2:1 method (DIN 19529) and the column rapid test (DIN 19528) will find consensus or will be stipulated in the planned Mantle Ordinance.

Targeted investigations of PFAS-precursors are necessary for a complete risk assessment.

Precursors and sum parameters. Perfluorinated, mobile, and toxic PFAS can be formed from precursors (chapter 2.3). It is therefore necessary to consider the precursors in the investigation, even if there are no assessment criteria for them. As PFAS are a group of substances consisting of several thousand substances, neither now nor in the future will it be possible to analyze each single PFAS compound with respective assessment.

The analytical methods AOF, EOF and TOP-Assay[8] (Appendix A, chapter 4) are currently available. These methods indicate the total amount of adsorbable (AOF) or extractable organic fluorine compounds (EOF). If the known perfluorinated parameters are subtracted from the total, the proportion of previously unknown precursors can be approximately obtained. After the analysis, it remains unknown as to which precursor compounds are involved and with which potential or kinetics they can be degraded to mobile, perfluorinated, compounds. Nevertheless, the investigations are mandatory.

The reason is the determination of the quantity and spatial distribution of the contaminants, which is required by the BBodSchV §2 in the context of the detailed (phase III) site investigation. With respect to the statutory requirements according to §4 BBodSchG, the necessity of precursor investigation can be accordingly justified.

If no precursors are detected in the soil or groundwater, further evaluation of the propagation can be done by analyzing the standard or project-specific key parameters. If precursors are detected, they must be considered in the further risk assessment.

The evaluation of the precursors should be based on the perfluorinated PFAS behavior of release and should be used to determine the source strength or contaminant potential. The release capacity can be determined indirectly by observing the release of the perfluorinated PFAS through soil investigations or experimentally through degradation tests. A standardization of such degradation tests does not yet exist. The development of the tests based on current research projects and the current state of knowledge must be considered.

Depending on their molecular size and structure, some precursors can in-situ be very stable, while others are mobile and can occur in groundwater. Due to the fact that precursors only lead to the release of the perfluoroalkane acids when the groundwater becomes aerobic, in case of an extinguishing event it is necessary to analyze the existing co-contaminants (e.g. conventional surfactants) in addition to the individual PFAS compounds and the sum parameters. In addition to the contaminant-specific analyses, the parameter DOC (to detect any unknown organic constituents) and all redox indicators (dissolved oxygen, nitrate, dissolved manganese and iron, sulfate, and methane) should also be analyzed. This allows the redox conditions in the aquifer to be identified and assessed where precursor degradation is likely to occur. This can therefore take place with a time delay in a plume.

In case concentrations measured during the Phase II investigation of a suspected PFAS site (referred to as orienting investigations in Germany) are below the applicable assessment values, the test scheme in Figure 5 shall serve as an aid for further analysis with the aim to rule-out the presence of any significant precursor concentration that could later lead to the assessment values being exceeded after a microbial time-delayed transformation.

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[8] The AOF and EOF methods indicate the concentrations in μg/L fluoride, whereas in the TOP assay the precursors are converted to perfluorinated carboxylic acids and these are quantified. For comparison of results of AOF/EOF with results of TOP or conventional analysis, the concentrations of the individual compounds must always be converted into μg/L fluoride.

Figure 5   Test scheme (Phase II Investigation)
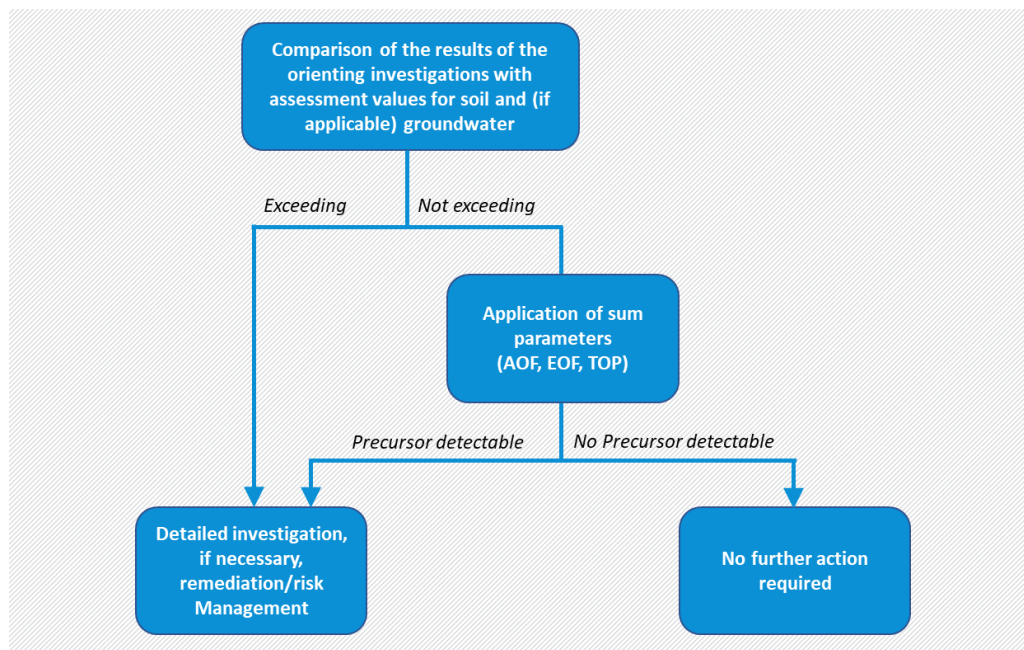
Source: Arcadis Germany GmbH, 2019

Quality assurance. PFAS tend to sorb on surfaces of laboratory vessels. Therefore, on the one hand, it can lead to reduced results and on the other hand, due to desorption in subsequent samples, to so-called memory effects. For this reason, blank samples (demonstrably PFAS-free samples of the same matrix) should be regularly integrated into the entire analysis program to provide indications of possible cross-contamination (approx. 10 % in relation to the total number of analyses). In addition, duplicate analysis of the sampled matrix should be performed regularly, starting with the sample preparation (approx. 10 %, see above). In the analytical reports, the implemented procedure for eluate preparation (incl. turbidity, etc.) should be clearly indicated.

Sampling, Key Parameters, Precursors and Quality Assurance

When taking samples, special conditions must be considered to avoid cross-contamination or loss of contaminants. As PFAS comprise more than 4,700 compounds, the single substance analysis must be limited to a small number of key parameters. The list of key parameters mainly contains perfluorinated carboxylic and sulfonic acids. These are also the end products of the microbial precursor transformation. To estimate the temporally and spatially varying extent of the new formation of perfluorinated carboxylic and sulfonic acids, the total concentration of the precursors and the redox conditions must be determined. Appropriate analytical methods are available for this purpose. The necessity for precursor analysis applies although the sum analyses have not yet been standardized and no evaluation values are available for the sum values.

Due to sorption and memory effects in laboratory equipment, blind and duplicate analyses must be performed regularly.

# 3 Remediation Management and Planning for Point Sources

3.1 Remediation Management

The management of the remediation of a point PFAS contamination can differ significantly from conventional remediation due to the complexity of PFAS damage.

Remediation strategy. After completion of the Phase III Investigation (in Germany referred to as detailed investigation) and final risk assessment, it is recommended to determine the strategic approach for remediation based on the conceptual site model. Due to the high mobility of PFAS, together with the lack of the possibility for microbial mineralization, a continuously expanding contaminant plume has often been the result, so that a temporal aspect of the contaminant expansion must be considered if the process shall be hindered. In the German Rhine Valley, for example, a spreading PFAS plume with a rate of 200 m/a has been confirmed at one site.

In complex cases, it may be necessary to prioritize remediation measures after evaluating the affected receptors, regarding their worthiness of protection. An example is shown in figure 6. For time reasons it is recommended to plan and execute the staged (partial) remediation measures one after the other and not in parallel. This is the only way to ensure the fastest possible entry into the remediation process.

Figure 6   Example of a remediation strategy
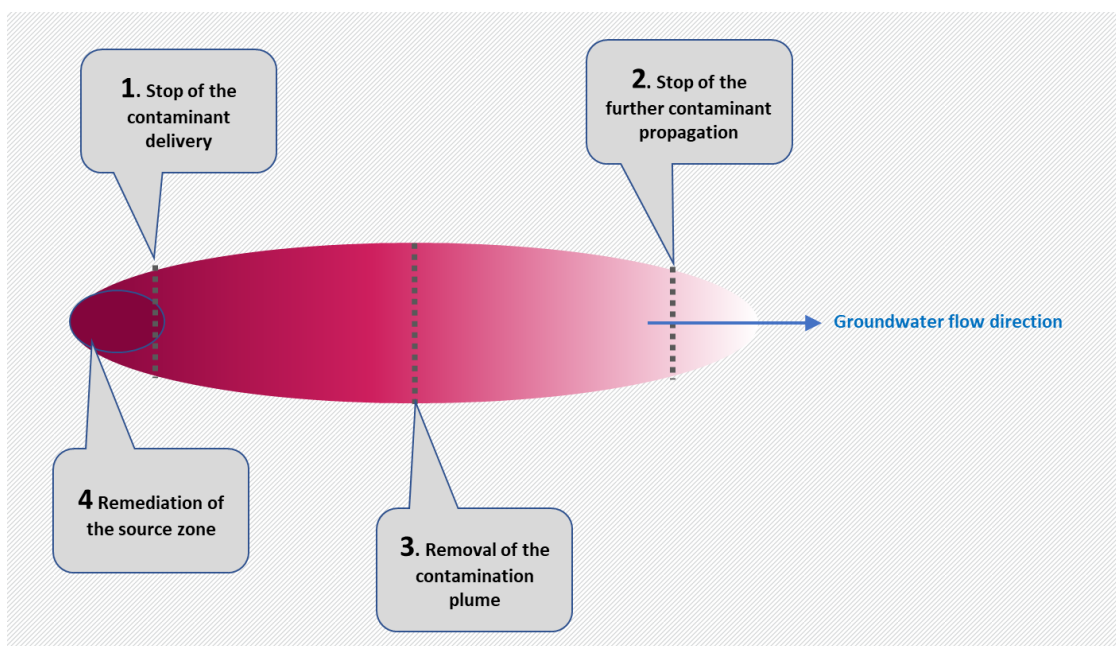
Source: Bantz, 2018

Protection and restriction measures (institutional controls). Prioritization may have as its result, in cases of successive remediation measures, for some (subordinately prioritized) receptors protective and restrictive measures must be defined until the actual remediation measures are taken. An example of protection and restriction measures is the prohibition of the extraction of groundwater and surface water for irrigation purposes without a permit within the framework of a general ruling. The legal basis for such a measure in Germany is the BBodSchG and the WHG. For example, watering gardens with PFAS-contaminated groundwater could lead to contamination of the soil. Accumulation in crops is a possibility (precautionary health protection) (see Appendix D).

The strategic sequence and prioritization of implementable measures is the result of a logical consequence from the conceptual site model and the evaluation of the affected receptors or objects of protection on a case-by-case basis.

Completeness checks. Once the remediation strategy has been determined, it is recommended in complex cases that a systematic completeness check of the previous investigations be carried out as part of the remediation investigation. The completeness check is not about pointing out deficits of the previous investigations (orienting investigation, detailed investigation), but rather the goal is to analyze which data are still missing and still needed for the selection of the most suitable remediation procedure.

Once the technologies and measures have been selected, the basics for technical planning must be determined. Further investigations are usually necessary for this as well.

Monitoring. Long-term monitoring is to be distinguished from monitoring following the completion of remediation measures. In particular, when remediation measures are prioritized and not started at the same time, the affected objects of protection (e.g. groundwater, lakes) must be included in a monitoring program. This also serves to be able to evaluate the basis for the assessment of possible future interventions in the water balance. When applying for anthropogenic interventions (water management), the applicant has to demonstrate to the competent authority in a comprehensible and verifiable way what effects the measure applied for will have, especially in the area of PFAS contamination. If necessary, additional countermeasures may be required for dewatering, in addition to the purification of groundwater that may be contaminated with PFAS, to prevent a migration of contaminants into areas that have not been contaminated so far. During and after the measure, the effects in the groundwater have to be monitored under an intensive monitoring program which must be planned accordingly.

Monitoring must also be continued after remediation. Residual PFAS contamination that is present after the completion of an active remediation phase requires a certain period of time to reach a state of "spatial immutability of residual contamination" (source and plume).

Remediation Management for Point Sources

In the case of a complex contamination with several receptors being affected, sites should be evaluated regarding their worthiness of protection for reasons pertaining to time and the remedial measures prioritized. It is recommended to plan and carry out the planned (partial) remediation measures one after the other and not in parallel. This is generally the only way to ensure the swiftest entry into the remediation process.

A prioritization can result in the fact that in the case of successive remediation measures, protective and restrictive measures (institutional controls) must be defined for some subordinated prioritized receptors until the subsequent remediation measures take place. These institutional controls must also be considered in the planning process.

Long-term monitoring and surveillance should be planned and started early to assess the future development of PFAS concentrations in groundwater.

3.2 Remedial Options Appraisal

3.2.1 Definition of Remediation Targets/Target Values

Basic investigations for remediation target definition. In the case of PFAS, various source/receptor pathways can be affected (Chapter 2.4). If not already done in the previous phases, additional investigations may be necessary when remediation targets/target values are set. For the source/receptor pathways soil → crop, transfer factors cannot yet be estimated. Research projects on this are currently (status 2020) underway. It is recommended that the currently known results are considered when investigating and evaluating the crop contamination. When evaluating home gardens, individual case and exposure assessments in the form of sensitivity calculations (Chapter 4.6) are recommended. For this purpose, it may be necessary to perform investigations of cultivated garden fruits or vegetables. The effect path soil → groundwater is evaluated in Germany by means of the seepage water prognosis. Thereby, the precursors are also to be considered and during the risk assessment the spatial distribution of precursors and redox conditions shall be clarified. With this, the question of whether a local potential for transformation of precursors to regulated mobile PFAS compounds exists can be answered. In the worst case, microbial transformation of contaminants (for example in the contaminant plume far downstream of the source area) can result in trigger values of regulated compounds being exceeded only after a time delay (for example, after completion of the site investigation). This must be considered both while defining remediation targets and while planning remediation.

Derivation of remediation targets. Generic remediation targets have not been defined by the legislator because any specified remedial target value must always be justifiable on a case-by-case basis. By defining remediation target values, verbally described remediation targets are able to be made specific. Any defined target value must be justified on an individual case-by-case basis and derived from initial verbal-argumentative remediation targets. For PFAS as well as for other contaminants, the following basic principles can be used as a basis for the derivation process in defining target values for remediation (Appendix B):

- ► groundwater: - insignificance threshold values
  - Drinking water guiding values of the Drinking Water Commission and health advisory levels (HAL)

- ► soil: - Seepage water trigger values
  - leachate prognosis for the location of assessment
  - TDI values

In 2020, nationwide uniform assessment values will be agreed for several PFAS compounds for:

- ► Groundwater (insignificance threshold values, HAL, sum quotient[9]),
- ► Landfilling and recycling of soil,
- ► Direct discharges into surface waters.

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[9] In most cases, the contamination of soil and groundwater is caused by several PFAS compounds. To record the sum effect of the entire PFAS, a sum quotient is calculated. The quotient of the analyzed concentration (e.g. in soil eluate) and the corresponding insignificance threshold value is calculated for each individual PFAS substance found. The individual quotients are then summed up to form the quotient sum. With a quotient sum ≤ 1, no harmful soil changes are to be assumed. If the sum quotient is > 1, it must be checked more closely whether there is a harmful soil change. Exceeding the quotient sum does not directly mean a hazard for the protected goods concerned, but serves as a threshold value, above which the responsible soil protection authorities must carry out more detailed investigations (https://rp.baden-wuerttemberg.de/rpk/Abt5/Ref541/PFC/Seiten/Boden_Grundwasser.aspx).

These are expected to be published soon. Remediation targets for PFAS contaminations are determined in a similar way as for other contaminations. In some German Federal States there are discretionary rules, which include, among other things, mass flux considerations downgradient of the contaminant source.

It should be noted that the insignificance threshold values, drinking water guiding values or health advisory values *do not normally* represent remediation targets. Investigation on an individual case-by-case basis is required. In various court cases the sole use of the insignificance threshold values as a remediation target has been declared inadmissible. A remediation target must therefore be derived and justified on a case-by-case basis under the principle of proportionality.

For other groups of contaminants, technical guidelines already exist that address the ways to determine proportionality (LABO, 2015, ITVA, 2018, LUBW 2012, HLNUG, 2018). These guidelines are not directly transferable but provide valuable information for the determination of remediation targets in light of a proportionality assessment. The implementation of a Federal/State guideline on this topic is considered desirable to achieve a basis, which is legally binding (e.g., by means of the Mantle Ordinance).

If necessary, institutional controls may be necessary within the framework of determining target values for remediation. This may be the case especially for instances of large PFAS soil contamination.

Suggested remediation target values are often derived by professional experts. The establishment of any target values for remediation that are provisional in character is carried out by the authorities considering each individual case. During remedial options appraisal, remediation methods are compared according to their suitability to achieve specified remediation targets. If necessary, remediation targets may be iteratively adjusted or a selected remediation technology may need to be changed.

Figure 7   Requirements for the remediation of soil and groundwater as part of hazard prevention
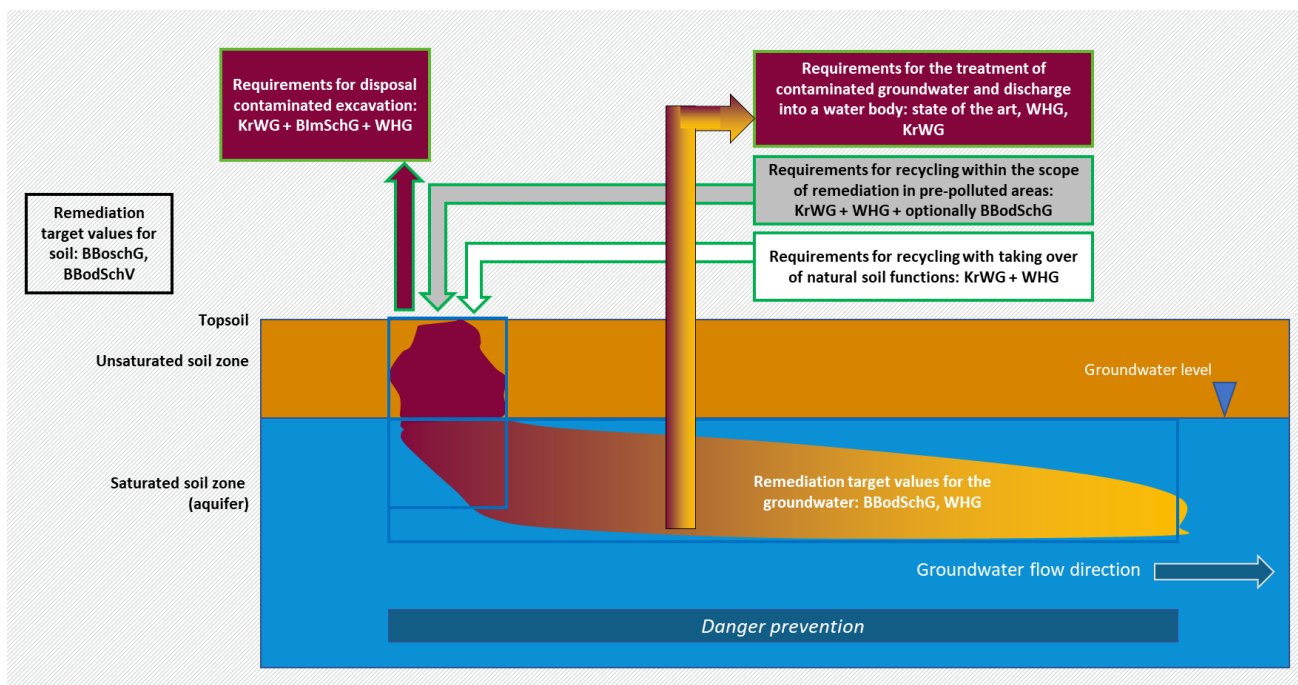
Source: Bantz, 2018

Also, while remediation is ongoing, remediation targets should be regularly reviewed in light of the assumed probability for remedial success. This is especially true if the contaminant concentrations approach asymptotic values and a proportionality investigation shows that a continuation of the remediation would not be appropriate (LUBW, 2012, HLNUG, 2018).

However, if the remediation is terminated at higher residual contamination levels, the consequences must be assessed and fully considered. Experiences from PFAS remediation projects for the achievement of remediation target values in the range of the insignificance threshold values or health advisory values are currently still missing. In addition to the remediation target values, further requirements for the remediation of soil and groundwater have to be considered (Figure 7).

> **Definition of Remediation Targets/Target Values**
>
> As with all other contaminants, remediation targets and remediation target values must be defined and justified on a case-by-case basis. They must be proportionate. Within the framework of the individual case-specific derivation process, the known assessment values (insignificance threshold values, health advisory values, drinking water guiding values) can be used for initial orientation.

3.2.2 Supplementary Investigations for Remediation Planning

For the final selection of a remediation technology, in many remediation projects, additional investigations are required. The following aspects particular to PFAS must be considered in these investigations.

Historical research (Phase I investigation). Usually, contaminated sites, which are subject to systematic remedial management, have already been officially registered as such and a historical research has generally already been documented. Prior to remediation, this documentation must be validated to minimize risk and to ensure that no further contamination is overlooked during remediation (Held, 2015). Especially when using fire extinguishing foams, for example, not only the known entry points (fire extinguishing places, training areas, fire stations) can play a role, but also other possible sources, such as storage areas for fire extinguishing foams, cleaning locations for used hoses and permanently installed extinguishing devices. Interviews and surveys involving contemporary witnesses are of very high value in cases of PFAS contamination. In comparison to other contamination, PFAS contaminations are usually comparatively young in age, so that reliable eyewitness testimonies are often still available.

Background contents in soils. Still not fully verified, but largely suspected, is the existence of a diffuse, exclusively anthropogenically caused PFAS background contamination of soils. This is explained by the following dispersion model. Even though PFAS (except FTOH) have a very low volatility, airborne transport is a relevant transport pathway for release from production sites. This is caused by the binding of PFAS to aerosols (liquid or particle phases). In air, some PFAS are subject to photo-oxidation to a small extent. After transport of the aerosols, atmospheric deposition can lead to measurable PFAS contamination in soil and surface waters (Young and Mabury, 2010, Ahrens and Bundschuh, 2014). Atmospheric deposition can occur as dry or wet precipitation-bound deposition (Barton et al., 2007, 2010, Dreyer et al., 2010, Taniyasu et al., 2013). During dry deposition, PFAS can be deposited naturally on surfaces by sedimentation, diffusion, or other processes. The leaching of PFAS-containing aerosols by precipitation is called wet deposition.

To differentiate between background contamination and PFAS contamination from a single source, it is recommended that the background levels be investigated at a suitable location. This is done by investigations of adjacent areas where no active contaminant input has been proven. As a rule, the remediation of background contaminations should be avoided.

It cannot be ruled out that the substitutes used in the recent past may still result in ubiquitous airborne input of PFAS into the soil, which would lead to a sustained increase in background contamination. This process still needs to be investigated and, if necessary, continuously monitored.

Investigations of source zone or of plume. With respect to investigations that are necessary for remediation planning, in addition to the PFAS, all potentially existing co-contaminations must be investigated. This is especially important for fire extinguishing foams and their places of application (e.g. extinguishing fuel fires).

As an on-site method for PFAS does not currently exist, adaptive methods for investigation (which immediately generate analysis data that could serve as a basis for determining the next sampling point) are not available. Differentiated, partly high-resolution groundwater investigations are applied as for sites with other contaminants. For example, direct-push methods (BAT sampler[10] or HPT, Hydraulic Profiling Tool) for depth-differentiated sampling of groundwater and for the delimitation of the typically long PFAS plumes may be applied, and the results can be used to determine the where best to locate new groundwater monitoring wells to be constructed for purposes of long-term monitoring.

Depending on the objective of the investigation, it may be important to determine the PFAS solids content in the water-saturated zone (aquifer). Due to the differences in PFAS properties and the parameters influencing sorption, it is usually not possible to back-calculate the sorbed amounts based on the contaminant concentrations in the groundwater. Therefore, only sampling and analysis of the aquifer sediment remains. It should be noted that the limits of quantification (LOQ) for the solid contents are often relatively high. Solids contents with the result "< LOQ" do not necessarily mean that no relevant, elutable PFAS contents are to be expected. Liner drillings are required for sampling the saturated soil.

Supplementary Investigations for Remediation Planning

Prior to any remediation, the existing historical investigation (phase I investigation) must be validated to minimize the risk of overlooking any additional contamination during the remediation. To differentiate between background contamination and PFAS contamination from a single source, it is recommended to investigate the background values at a suitable location. This then also allows the delineation of the point source contamination. The need for remediation depends on the hazardous situation and the discretion of the authority regarding the requirement of remediation.

Prior to remediation planning, investigations of concomitant contaminations are necessary. These play a role especially in cases where fire extinguishing foams and their places of application (e.g. extinguishing fuel fires) have caused the contamination. Precursors must be considered both in the determination of the remediation targets and in remediation planning.

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[10] At the BAT everything should be made of glass or stainless steel. If the HPT system has tubes made of PTFE, it is less suitable. For top-down sampling, new tubing should be used at each depth.

3.2.3 Selection and Evaluation of Remediation Technologies

For engineering and design of a feasible site-specific remediation technology, further factors specific to PFAS must be considered. These are listed in Table 6.

Table 6   Design criteria and considerations for PFAS remediation (supplemented and modified, according to NGWA, 2017)

Parameters	Justification	Crit. **
Concentration of critical PFAS compounds	Critical PFAS compounds are mainly those that have a low assessment value and/or high mobility and low remediability. The ionic form (neutral, anionic, or cationic) can also be decisive for the suitability of the remediation technology.	+++
PFAS chain length	If a PFAS mixture with strongly varying chain lengths is present, this significantly influences the choice of the remediation technology.	+++
Precursor Inventory	Are substantial amounts of precursor present? Is the mobilization of precursor a problem for the remediation site?	++
Presence and nature of co-contaminants*	Which co-contaminants are most problematic? Has a remediation been carried out on site that may have changed the PFAS distribution?	++
BOD (biological oxygen demand)	Products with polyfluorinated surfactants such as AFFF may have an increased BOD, which leads to a strong oxygen consumption and anaerobization of the aquifer, possibly with formation of soluble iron.	+
TSS (total amount of suspended solids)	Due to the surfactant nature of many PFAS, they tend to accumulate at interfaces such as suspended solids in an aquifer. This places additional demands on groundwater treatment.	++
Groundwater flow velocity	The flow velocity influences rates of diffusion. When PFAS desorb from available surfaces, slow flow velocities are likely to result in higher PFAS concentrations in the water.	+
PFAS remediation vs. hydraulic containment	Are both the source and the plume considered?	+++
pH	The pH value influences sorption processes.	+
Soil organic carbon content (TOC)	The quantity and quality of the soil-bound organic carbon influences the transport behavior of the PFAS. An increased TOC content leads to an increased sorption of the PFAS.	++
Are there naturally occurring processes that could affect the remediation?	Examples are clay lenses, elevated Ca^{2+} concentrations, high organic carbon content, rapid groundwater flow velocities, etc.	++
Overlay with other contaminants	In case of an overlap with other contaminants (CVOC, chrome, etc.), these can impair a targeted remediation of the PFAS.	++

*   Remediation procedures, which are aimed at the remediation of accompanying contamination, can influence the mobility of the PFAS. For example, enhancing aerobic microbial degradation or *in-situ* chemical oxidation (ISCO) can lead to rapid precursor oxidation. As a result, short-chain PFAS could possibly be formed preferentially, which are more mobile than the parental compounds. Also, remediation-related geochemical changes of the aquifer (e.g. redox potential, pH-value) could lead to a mobilization of the PFAS.

** Critical parameter: +++ very strong influence, ++ strong and + slight influence on the choice of the rehabilitation method

Further criteria for developing suitable approaches for a successful remediation are:

- ► Acceptable time frame for the remediation
- ► Technology acceptance and stakeholder participation
- ► Further contaminants to be considered in the area of the PFAS contamination
- ► Costs for remediation
- ► Proportionality and sustainability of the remediation concept
- ► Compatibility with daily site operations.

The advantages and disadvantages as well as the marketability of different remediation technologies are presented in Appendix C. They can be generally differentiated in:

- ► *Established technologies.* These are technologies whose effectiveness has been demonstrated under pilot conditions or on a technical scale and for which several applications are well documented in the literature.

- ► *Promising technologies.* These are technologies whose effectiveness has been demonstrated on a pilot or full-scale scale, but whose transferability to other sites has not yet been validated.

- ► *Experimental technologies* are those that are documented in the literature by several researchers or practitioners but have only been performed in the laboratory or are still under development.

Groundwater. For the remediation of groundwater, *pump-and-treat* with the sorption of PFAS on activated carbon are currently mainly used. All other technologies are, with a few exceptions, still in the design or development stage. Nevertheless, Appendix C not only describes those technologies that have already reached market maturity or are about to do so, but also other technologies for which the chances of establishing themselves on the market are considered comparatively low. Against the background that numerous technologies´ providers are currently active on the market, this compilation is intended to provide readers with the opportunity to better evaluate offered solutions regarding their chances of success. Appendix C therefore also describes the modes of operation of the technologies, the possible applications, the state of development and open questions.

Due to the lack of microbial degradability and the frequently large expansion of the plumes, there will probably be no or only very limited *in-situ* remediation technologies for groundwater available in the future. Therefore, site management will probably mostly result in hydraulic containment of the groundwater flow. *Pump-and-treat* technologies or barrier methods (e.g. *funnel-and-gate*) can be considered for containment.

Currently identified remediation options for groundwater are summarized in Figure 8 in terms of feasibility and development status according to the authors' assessment. Even if individual processes have been developed to market maturity, this is no guarantee that they will establish themselves on the market.

After appropriate development, *in-situ* foam fractionation would be the only decontamination process designed for *in-situ* application. However, even this is hardly suitable for the extensive decontamination of PFAS plumes of huge extent for cost reasons. However, it would be conceivable to use it as a barrier process, provided that the process is well-working. Electrochemical oxidation was also considered as a barrier process. However, due to the formation of harmful by-products, this will probably not be implemented in the foreseeable future.

Also, for *in-situ* application, the injection of activated carbon into the aquifer is used, but this is a reversible sorption process in the sense of a temporary protection.

Due to the rigid reaction conditions required in some cases, destructive processes are not likely to be used in the *in-situ* reactors of *funnel-and-gate barriers* (F&G). In most cases, the feasible processes will be limited to sorption on for instance activated carbon with all its advantages and disadvantages. Consumed sorbents must be replaced at regular intervals. The low loading capacities of most sorbents and the early breakthrough of the shorter-chain PFAS have so far inhibited considerations for the application of F&G in the field.

Figure 8   Possible remediation technologies for groundwater (blue: *in-situ* application)
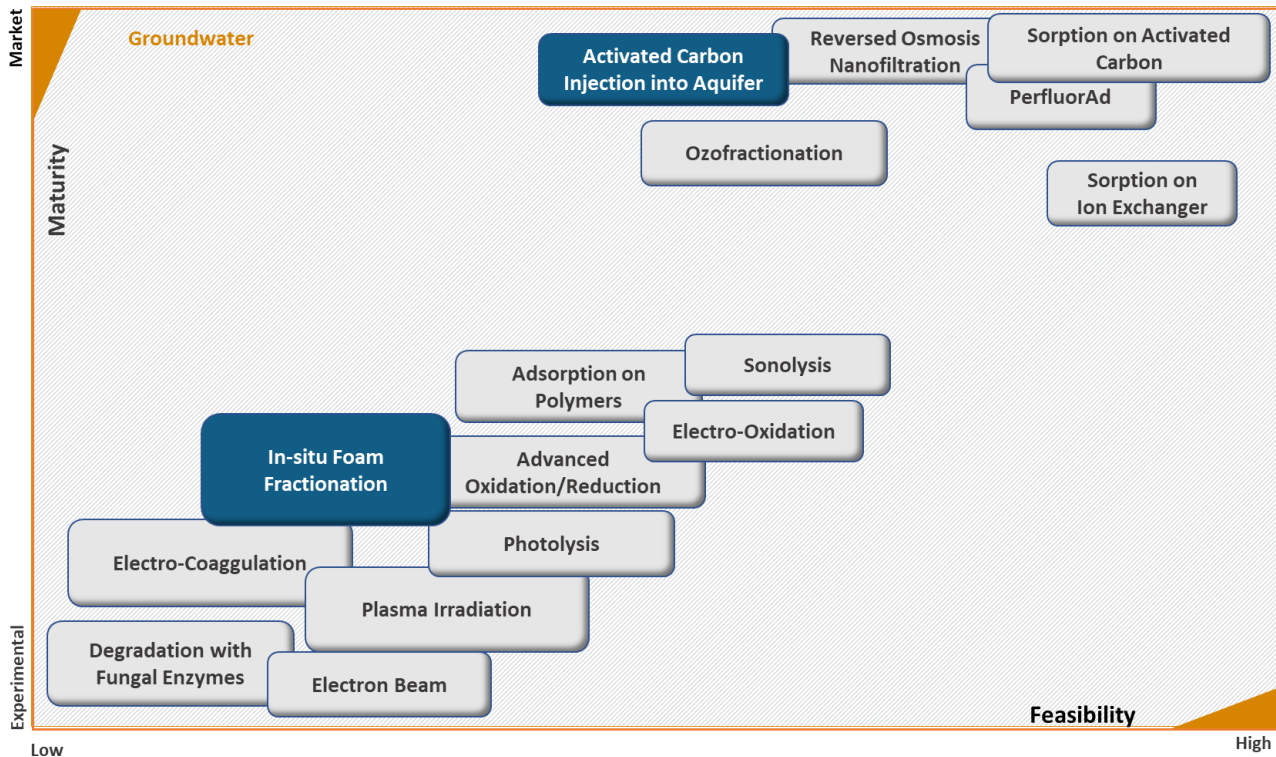
Source: Arcadis Germany GmbH, 2019

All other technologies are based on the extraction of groundwater with subsequent treatment of the PFAS-contaminated groundwater. A technology may be designated as being "*stand alone*" if associated reaction rates are so high that it can be used for continuous purification of pumped groundwater as part of a pump-and-treat measure. A distinction must then be made as to whether the "target effluent value" can be achieved continuously. This is true in most cases, however, the effort required may vary considerably. For example, ion exchangers require several reactors in a row to achieve the target effluent value. With other destructive processes, the treatment time must be extended accordingly to achieve the target effluent value. However, the treatment time becomes so long with different processes that it cannot be used for the continuous treatment of pumped groundwater. Instead, they could be used for the treatment of PFAS concentrates, which are mainly produced by sorption processes (assuming the feasibility of a mild desorption) or other separation processes.

Key factors for determining future applicability of the technologies that are shown in Figure 8 are probably the experiences themselves that still have yet to made with their application on a technical scale, and above all their costs in relation to conventional remediation technologies.

The methods are not always able to be considered as options. While some are primarily suitable for the treatment of slightly contaminated water without high concentrations of impurities, there are others (e.g. precipitation processes) which are suitable for removing higher concentrations of PFAS before using other adsorbents with the aim of extending the lifetime of the post-purifying adsorbent. However, because of product precipitation, a waste sludge is produced in this case which must be dewatered before disposal.

Table 7: Evaluation overview of remediation technologies for groundwater[*]

Procedure	Stand Alone[**] ?		Harmful by-products?	Formation of a concentrate?	In-situ applicable?
	Effluent value/remediation targets [***]	Treatment duration			
Sorption activated carbon	Yes	Yes	No	No	Yes (injection of activated carbon into the aquifer)
Sorption onto ion exchanger	(Yes)	Yes	No	(Yes)	No
Sorption on polymers	?	(Yes)	No	(Yes)	No
PerfluorAd	No	Yes	No	Yes (filter cake)	No
Reverse Osmosis	No	Yes	No	Yes	No
Nanofiltration	No	yes	No	Yes	No
Ozofractionation	No	Yes		Yes	Yes (in-situ foam-fractionation)
Sonolysis	(Yes)	No	No	No	No
Advanced Oxidation/Reduction	(No)	(No)	(Yes)	No	(Yes)
Electrochemical oxidation	(Yes)	(No)	Yes	No	(Yes)
Microbial degradation with fungal enzymes	No	No	?	No	(Yes)
Photolysis	(Yes)	No	No	No	No
Plasma Irradiation	(Yes)	(No)	No	No	No
Electron beam treatment	(Yes)	(No)	No	No	No
In -situ foam fractionation	(No)	Yes	No	Yes	Yes

(*) (Yes) means "probably yes", (No) means "probably not", ? = no information available

(**) Stand-alone processes are those that do not require additional processes (such as those to concentrate PFAS prior to further treatment) in continuous processes (such as *pump-and-treat*).

(***) At this point, the answer is "Yes" if this procedure can be used to comply with the discharge values of groundwater treatment plants usually specified by the authorities (see Appendix B) or the remediation target values with a moderate treatment duration.

The development of new adsorbents is based either on an adaptation of available materials to the removal of the PFAS or on the production of completely new materials. However, none of the adsorbents destroy the contaminants, but only lead to a rearrangement from one matrix to another.

The individual site factors of each remediation case must be considered separately. Thus, the treatment costs are highly dependent on the spectrum of PFAS individual compounds (fingerprint), possible competing adsorption of co-contaminants, possibly occurring interfering substances, as well as the officially defined remediation target values.

For use the classical *pump-and*-treat remediation, discussions have arisen on increasing the mobility of the PFAS in the aquifer by a specific modification of the redox milieu, for example by injection of oxidants. The effect of such processes of redox manipulation can be tested on a bench (laboratory) scale. It can also be investigated whether a forced transformation of the precursors leads to increased concentrations of perfluoroalkane acids. Furthermore, it must be investigated in each individual case whether the extent of mobilization is so high that the additional costs caused by this are worthwhile.

Table 7 summarizes the results the evaluation of various groundwater remediation methods that is provided in detail in Appendix C.

Soil. At present, soil remediation technologies focus on the replacement and recycling/disposal of contaminated soil (Figure 9).

Figure 9   Possible remediation technologies for soil (blue: *in-situ* application)
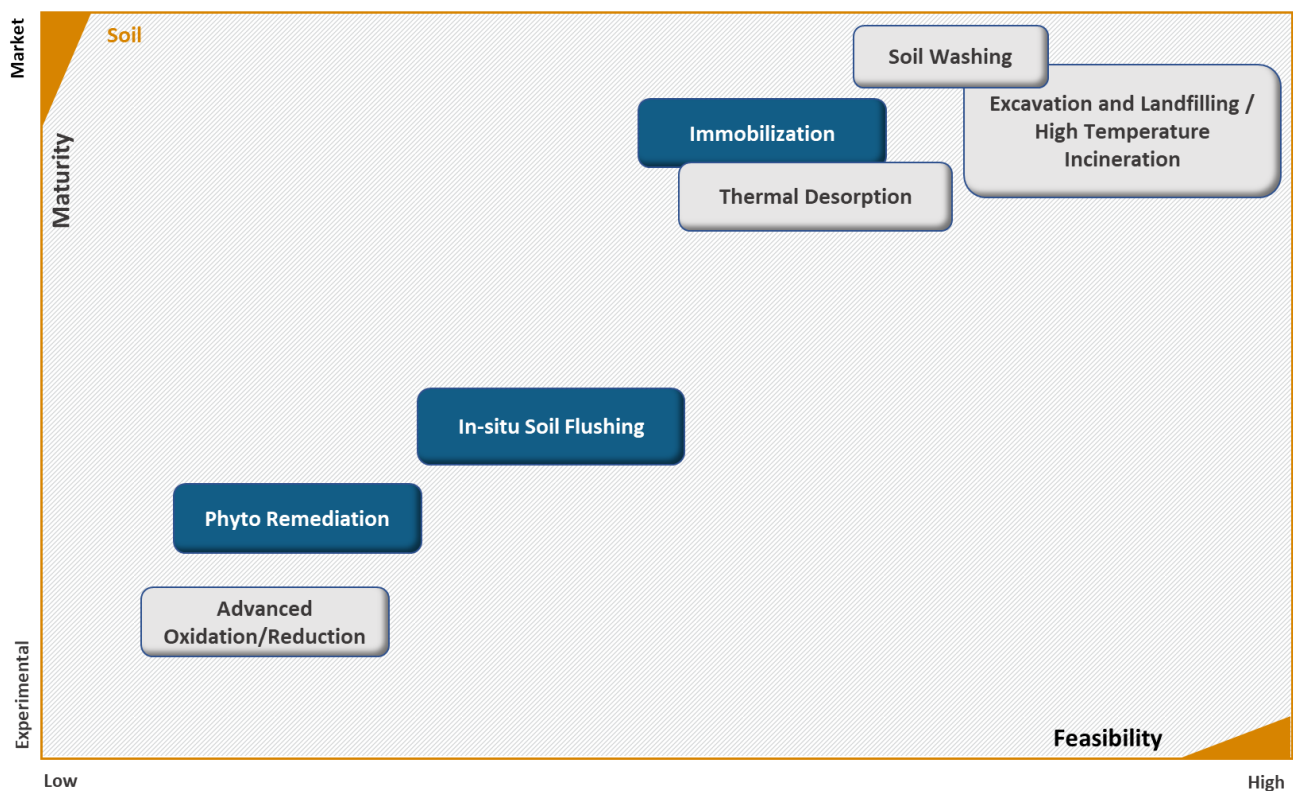
Source: Arcadis Germany GmbH, 2019

Due to limited landfill capacities, the deposition of PFAS-contaminated soils involves considerable effort and considerable costs, if a deposition possibility can be found at all. Due to the severely limited landfill space and the widespread concerns of landfill operators to accept PFAS-contaminated soil, alternatives to landfilling the contaminated soil are highly valued.

The long time contaminants take to naturally leach from the contaminant source, means that in the future the focus will probably be primarily on source remediation (i.e. treatment of unsaturated soil). Figure 9 shows an assessment of the market maturity and development status of soil remediation technologies. These are described in more detail in Appendix C. For newer technologies, experience (technical-organizational implementation, upper and lower limits of concentration, duration of effect and remediation, applicability in individual cases) and cost data for application on a technical scale are largely lacking.

Complete Containment. A further option for remediation is the containment of the site (sealing, encapsulation). Surface sealing prevents leaching of contaminants from the unsaturated soil. In many cases, vertical encapsulation, and management of the encapsulated area (groundwater extraction and purification) is also necessary. However, the contaminants remain permanently on site. In contrast to conventional contaminants, a significant change of the redox milieu in the hydraulically isolated area is not to be expected if no microbially degradable accompanying co-contaminants are present (e.g. non-fluorinated surfactants from fire extinguishing foams). Consequently, methane formation, which would require additional expenditures, is not to be expected. Otherwise, the technical construction of a containment measure for PFAS contaminations does not differ from that for other contaminants.

Effectiveness. The effectiveness of the discussed technologies regarding the elimination of precursor, non-precursor, and short-chain PFAS cannot be answered consistently. The corresponding data are almost always missing. This also applies to several other process parameters such as:

▶ Economic feasibility (estimation of specific process costs),

▶ Estimated total process costs and

▶ Sustainability (remediation duration, energy requirements, CO_2 emissions).

Preliminary tests are strongly recommended when selecting technologies during remedial options appraisal. The spectrum of PFAS compounds, accompanying substances, and impurities must be considered, as well as the quantities of residual waste materials (iron sludge, consumed activated carbon, etc.).

The remediation concepts implemented at several PFAS-contaminated sites currently under remediation are summarized in Appendix D.

Remediation Technologies

Due to the special characteristics of PFAS, the selection of applicable and available market-ready remediation technologies is limited. At present, remediation focuses on *pump-and-treat* and soil exchange as the main technologies. However, the landfilling of PFAS contaminated soil is hardly possible anymore because many landfills currently do not accept PFAS containing soil material. Therefore, alternative technologies, not only for soil but also for groundwater remediation, are of special interest. It should therefore always be checked whether these are applicable at a site and lead to lower remediation costs. The remediability of the precursors has to be considered. The applicability as well as advantages and disadvantages of innovative PFAS remediation methods are described in detail in appendix C.

Usually it is necessary to test the remediation technologies under site-specific conditions in the laboratory and, if necessary, in the field.

3.3   Remarks on Remediation Execution

Risk of cross contamination. The special properties of PFAS, especially the tendency for PFAS to accumulate on surfaces, should be taken into consideration when carrying out remediation. The danger of cross-contamination always exists. To avoid this, all equipment used for sampling and remediation should be completely cleaned after (or, if necessary, during) use. PFAS-contaminated cleaning solutions must be disposed of properly. Alternatively, the equipment or remediation technique should be used exclusively for the treatment of PFAS-contaminated sites.

Black-and-white areas must be defined and suitable cleaning options must be created to prevent the spread of contaminants. In groundwater purification plants, the risk of cross-contamination also exists in principle at sampling taps or pipes.

Immission control law. If soil material is to be provided or treated for relocation in the course of a remediation, it is recommended to check whether the waste plant term according to the laws KrWG and BImSchV applies and whether a time-consuming approval process according to BImSchG is required at all. A permit according to BImSchG often leads to a strong delay in the start of remediation. If necessary, the possibility to get an exemption according to §28 (2) KrWG should be examined.

Occupational safety. The health and safety requirements for PFAS-contaminated sites do not differ from those at conventional sites. In general, the German rules for working in contaminated areas (TRGS 524, 2011) apply. Exposures and hazards must be determined depending on the remediation. At present there are no occupational health and safety values. Alternatively, experts could try to derive provisional values for the soil → human source/receptor pathway, which could be used for occupational health and safety purposes. Estimates already exist for this purpose, which have been presented at technical lectures. According to these estimates, the values would be in the mg/kg range. However, whether these are robust must also be checked in light of the possibly changing TDI values. However, there are currently no binding calculations for preliminary assessment values for the source/receptor pathway soil → human (direct contact). This means that further action is urgently needed at this point.

In the case of high precursor contents, the determination of the resorption availability according to DIN 19738 should be checked if necessary.

Rebound. Through remediation, subsurface processes are anthropogenically changed. After completion of remediation, these processes return to natural conditions. The anthropogenic changes (e.g. P&T, soil exchange) can have an influence on the concentrations of the contaminants dissolved in the groundwater. Therefore, following an active remediation, the site must be monitored over a defined period and it has to be checked whether the PFAS concentrations stay permanently below the remediation target values.

Remarks on Remediation Execution

When remediating PFAS contaminations, special care must be taken to avoid cross-contamination and to consider occupational safety. Furthermore, a remediation is carried out according to the known requirements for design, monitoring, and remediation control. Required permits must be applied for in time to avoid time delays.

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4 Remediation Management for Extensive PFAS Contamination

4.1 Introduction

In a first approximation, extensive PFAS soil contaminations can be systematically distinguished into (a) coherent large areas and (b) non-contiguous accumulations of individual areas. Large areas are mainly due to PFAS inputs via the air from commercial or industrial emissions or flooding of surface water runoff from e.g. fire training areas or similar.

According to the current state of knowledge, accumulations of individual areas were caused by the application of PFAS-containing material (e.g. fertilizer, etc.) to individual areas. The individual areas cause overlapping individual contaminant plumes in the groundwater and overall large-area groundwater contamination (detrimental changes in the groundwater quality). In the following, the special features of remediation management are described, and possible courses of action are shown. In principle, active public-relations work should be carried out in the case of extensive PFAS contaminations with many affected stakeholder (Chapter 6).

4.2 Management of PFAS Impact on Groundwater (Source/Receptor Pathway Soil → Groundwater)

4.2.1 Orienting Investigation - Delimitation of the Contamination

In the case of extensive soil contamination, which can usually also cause extensive groundwater contamination, there is usually a very high level of public pressure and the demand to start immediate remediation measures. Nevertheless, it has proved to be reasonable to follow consecutively the basic management procedures fixed in the applicable state soil protection law.

The orienting (phase III) investigations are basically carried out depending on the corresponding individual case-related indications of harmful soil changes. The investigations are always carried out on a property-related basis or, if the source of contamination extends over several properties, on a source area-related basis.

With the orienting investigation, the sources of contaminants are to be identified and the leachate inputs into the groundwater are to be prognosed. Otherwise, the magnitude of the contamination of individual areas would remain unclear and a selection of the party liable to remediate would not be possible. In addition, all measures and use restrictions e.g. for agriculture would also affect uncontaminated land during further project processing. This could then lead to claims for compensation or only to additional expenditure (if, for example, pre-harvest monitoring is carried out).

Accumulation of individual areas. In the case of accumulations of individual areas, specific research must be carried out to clarify the question of which areas are those of concern. If it turns out that there are no or insufficient research possibilities and it is only known that contamination occurs within an area, the areas of concern can, if necessary, be delineated via the groundwater contamination, i.e. by tracing back the contaminant plumes. A purely integral approach for the delineation of soil contamination without reference to soil investigation is not possible in the phase of the orienting investigation, according to the current legal understanding (soil protection law).

If the source/receptor pathway soil → plant is affected, an investigation of each arable land parcel must be carried out, because otherwise no targeted evaluations and no definition of the resulting measures such as pre-harvest monitoring would be possible.

Coherent large area. In the case of large areas whose contamination results from commercial or industrial emissions, for example, air contaminant dispersion models can be used to theoretically delineate the areas affected by the primary source. Due to the interrelated contaminant situation, an integral, grid-like investigation of the secondary source can then be carried out on the basis of these data.

Use of databases. A special feature of the orienting investigation of PFAS-contaminations are the large amounts of data generated. Without the use of databases and spatial-based graphical information systems, goal-oriented analyses will usually not be possible. If the source/receptor pathway soil → groundwater is affected, it has proven to be useful to build up a hydraulic groundwater model or an instationary contaminant transport model at an early stage and to use it for the prognosis of contaminant transport.

Orienting Investigation and Delimitation of the Contamination

A purely integral approach in the phase of the orienting investigation is not possible according to the current legal understanding under soil protection law. Individual areas must be investigated. If an integral approach seems appropriate, it requires the approval of the responsible authority.

The use of databases and spatially based graphic information systems is necessary from the beginning and continuously in the case of extensive contamination.

4.2.2 Orienting Investigation - Integral Investigation and Evaluation

After the results of the orienting investigation with delineation of the contamination are available, it is useful to check which individual areas can be combined to clusters. Integral approaches are suitable for this purpose. The joint processing of clusters is useful if the groundwater contamination from the individual areas overlaps. In the context of this processing it is also to be evaluated whether a separate investigation of single areas or small clusters

▶ is at all professional, i.e. suitable to reach the investigation goal and/or

▶ would not lead to an economically high, unproportionate effort.

Area clusters can be worked on together as partial processing areas. The formation of partial processing areas can be useful not only in the case of accumulations of individual areas, but also for large areas. This is especially the case with heterogeneous hydrogeological conditions, especially if separate plumes have formed.

The following example shall clarify the background and the systematics.

Example

PFAS-containing substrates were applied to agricultural land. This led to an accumulation of many contaminated individual areas. The easily mobilizable individual PFAS substances are dissolved by percolating precipitation water starting from the source of the contamination in the upper soil layer and transported into deeper soil layers. With increasing PFAS chain length the transport is delayed. With an average groundwater recharge rate of about 300 to 400 mm/a in the example case, the precipitation (leachate) seeps through the unsaturated soil layer. The polluted leachate meets and mixes with the groundwater. Figure 10 shows a scheme of this exemplary situation.

Figure 10   Schematic of PFAS mixing process into aquifer
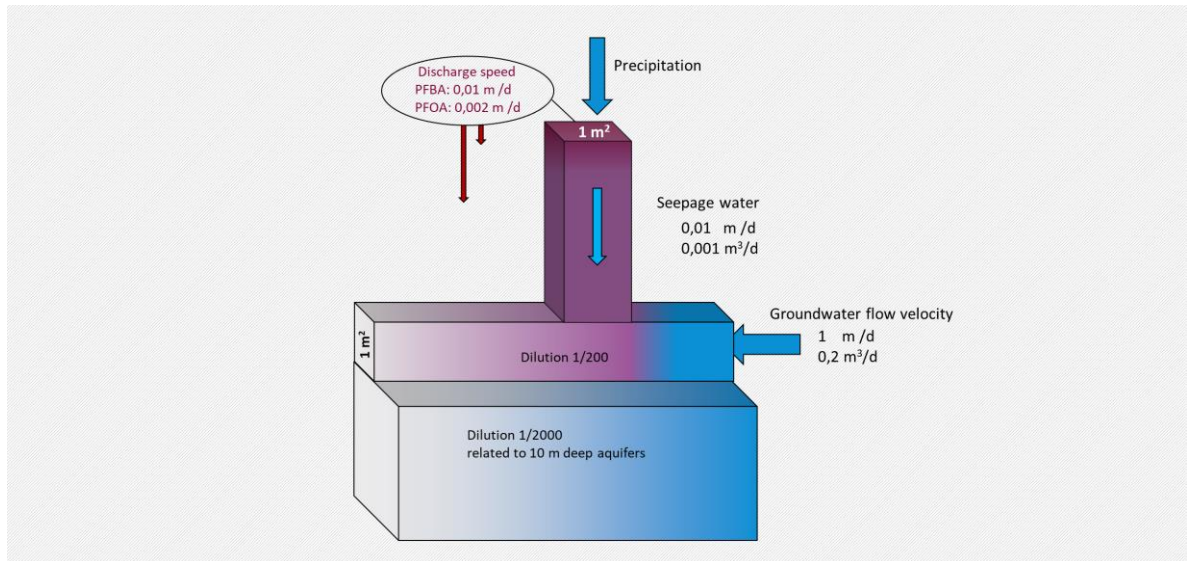
Source: Arcadis Germany GmbH, 2019

The amount of contaminant leachate fluctuates with time depending on the amount of percolating precipitation. It depends essentially on the seasonal amount of precipitation, evaporation, and water absorption by plants. In agricultural areas, the total amount of precipitation can sometimes be absorbed (evapotranspired) in summer. After harvesting, however, the water absorption of the plants can be completely eliminated. This depends on the type of plants cultivated. Added to this is the low evaporation in winter. Therefore, the amount of precipitation that seeps away is greatest in the winter months.

Figure 11 represents a real case. Here the contaminant input from a single area into the groundwater was simulated with a groundwater model. In winter months the contaminant input is highest and lowest in the summer months. The unexpected low concentrations in 2015 were not due to a decreasing contaminant discharge but is meteorologically caused.

Figure 11   Real example of a seasonally dependent, modeled PFOA input from a single area into the groundwater
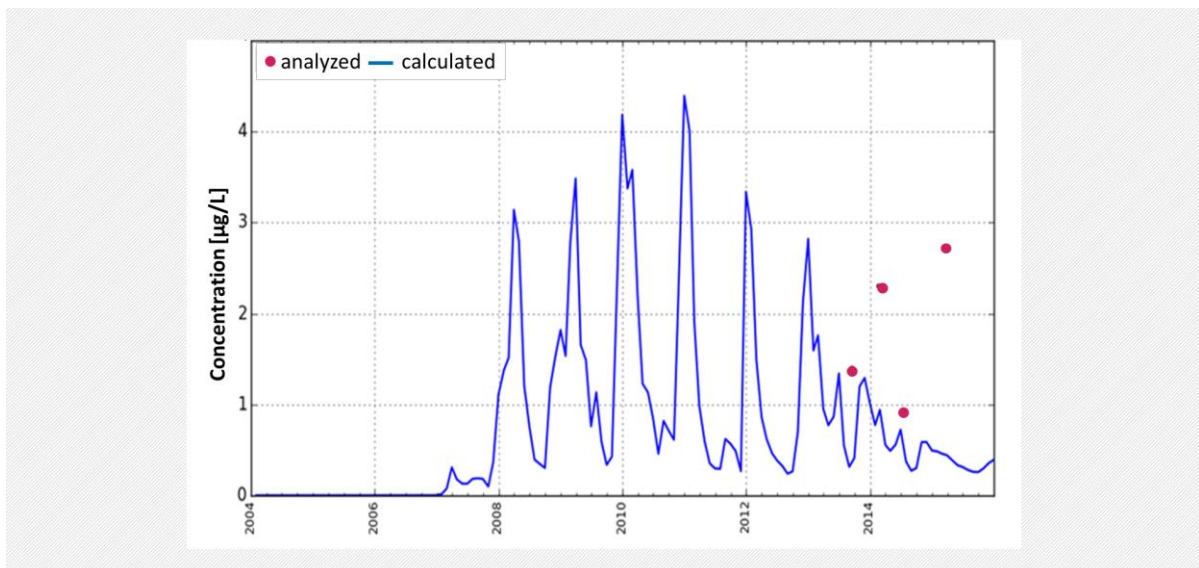

Source: Engineering Company Prof. Kobus and Partner GmbH

In this example the groundwater flows with a velocity of about 1 m/d. The retardation of the PFAS in the sandy gravel aquifer is very low. After a hundred days, it can be roughly estimated that the contaminants have migrated over a distance of about 30 to 100 m. In the example, the area sizes are about 1 hectare. If an area is now located downgradient of other contaminated areas, it is usually not possible to determine the exact proportion of the contaminant input from the specific area of concern into the groundwater by comparing the inflow and outflow concentrations.

This illustrates the scheme shown in Figure 12. In the investigation of an individual area the seemingly paradoxical situation can occur that despite a contaminant input occurring from the unsaturated zone, the inflow concentration to this area can be higher than the outflow concentration. As mentioned above, this situation is shown in the Figure 12 taking into account a retardation factor of 3 (e.g. for PFOA). In the example, the groundwater concentration in the monitoring well GMW A in the inflow from area 2 would be 3.5 and in GMM B in the outflow from area 2 would be 1.5 µg/L.

Figure 12   Schematic concentration curves of two overlapping PFOA plumes
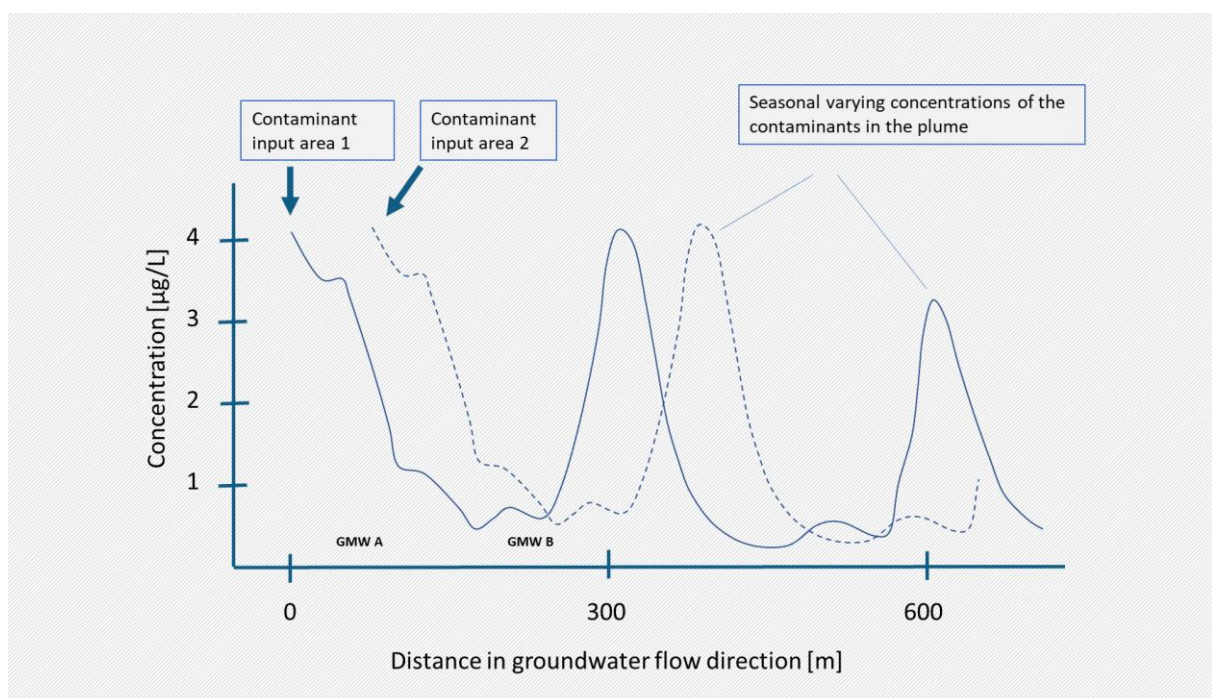
Source: Arcadis Germany GmbH; 2019

This example of a relatively simple situation with only two contaminated areas illustrates the problem of the investigation of single areas. Although the contaminant input would be determinable in principle with groundwater investigations, however for this purpose a narrow monitoring grid and investigations over many years would be necessary. In addition, declining and increasing contaminant inputs respectively from different areas would additionally complicate the evaluation.

In the example it was finally determined that an allocation of the individual PFAS contributions of the contaminated areas to the contaminant plume is not possible with a justifiable expenditure. Therefore, it was necessary to combine individual areas to an area cluster if they form a common contaminant plume by superimposing the outflowing contaminants.

Example End

Groundwater modelling. Groundwater models are suitable as a help for summarizing or delineating contaminated areas (area cluster, Figure 13) as partial processing areas. It has proven to be advantageous to model the dispersion of the newly formed groundwater, which has flowed through the contaminated areas as precipitation, in a transient manner over a longer period (for example 10 years). The actual spreading of the contaminant plumes, on the other hand, is usually retarded and thus slower. With this kind of model-like illustration it is possible to show the future contaminant transport paths and the overlaps of the individual plumes and to delineate area clusters or partial processing areas.

Figure 13   Delimitation of area cluster example and partial processing areas

Source: Arcadis Germany GmbH; 2019

Prioritization. The ultimately delineated sub-processing areas can be prioritized. In some Federal States there are technical specifications for the prioritization procedure. Prioritization has the advantage that in the case of extensive contamination, those sub-processing areas that cause a high level of concern are processed first. The prioritization can be based on affected water uses, estimated contaminant concentrations in groundwater, agricultural uses, etc.

In the case of very extensive partial processing areas, prioritization will be obligatory in many cases, because simultaneous processing of all partial processing areas by the responsible authorities and experts is often not affordable in terms of personnel. In addition, a graduated approach allows experience and information on hydrogeology, substance properties, etc. to be incorporated into the subsequent investigations.

Remediation concept. The orienting investigation is followed by the detailed (phase III) investigation specified in the Federal Soil Act (BBodSchG). The systematic and detailed investigation may be neglected if the dangers arising from contamination can be averted or otherwise eliminated by simple means. In the case of extensive soil contamination, it has proven to be helpful to check whether this is possible before starting the phase IIb investigation. It is often obvious at an early stage that, from a formal point of view, there is a need for remediation due to the very large, contaminated area or the fact that important drinking water production plants are affected.

Against the background of possible further risks due to time delays and the public interest in a quick solution, a remediation concept is sometimes already implemented at this point in time to avoid an unreasonable delay of a remediation. This is done during the orienting investigation of individual areas, but only at a time when a sufficient data basis for the remediation concept is already available. The remediation concept essentially comprises the following points:

► fundamental remediation considerations,

► overall visualization of the available investigation results with mass-flux considerations,

► assessment of the situation regarding special protection areas (e.g. water supply facilities) and

► evaluation of remediation options against the background of local constraints and costs.

The results of the remediation concept are used to check whether a quick technical solution or early hotspot remediation is possible or technically justifiable. The remediation concept will be updated in the following processing phase of the detailed investigation and is used as basics for the subsequent remedial options appraisal.

> **Orienting Investigation, Integral Investigation and Evaluation**
>
> In the case of PFAS contamination over a large area, an integral approach and the formation of partial processing areas makes sense, especially if plumes of contaminants can be separated from each other.
>
> A prioritization of the processing areas should be made if some areas are particularly affected.
>
> By a remediation conception already before the detailed investigation it is examined whether an advanced measure is possible and justifiable.

4.2.3 Integral Phase III Investigation of Partial Processing Areas (Detailed Investigation)

The detailed investigation (phase III) itself is carried out integrally for the respective partial processing areas. Representative data must be collected during the detailed investigation:

► Source/receptor pathway soil → plant.

- Survey of which plant species and varieties are realistically expected to be cultivated within the next few years. As a rule, the agricultural authorities are involved in this process.

- Assessment of the PFAS enrichment capacity of these plant species. For this purpose, the agricultural offices are also involved.

► Source/receptor pathway soil → groundwater. The results of the investigation should ensure the ability to

- perform a final risk assessment,

- describe the spatial distribution of contaminants in the soil and groundwater as comprehensively and in as much detail as necessary

- describe the spatial-temporal dispersion of the contaminants from the contaminant source in the groundwater to the protected property and

- set up a complete conceptual site model. This describes the dispersion of contaminants from the contaminant source to the affected receptors.

► Source/receptor pathway soil → human.

▪ Collection of data to be able to conclusively assess a possible hazard.

At the beginning of the detailed investigation, the groundwater contaminations are usually not yet exactly delineated. After completion of the integral detailed investigation, it must be possible to allocate the contribution of the individual areas to the total contamination of the partial processing area based on groundwater flow models. In addition, sufficient data must be available to be able to forecast the future distribution of the groundwater contamination in the aquifer in three dimensions.

> **Integral Phase III Investigation of Partial Processing Areas**
>
> The aim of the integral phase III investigation is to create the basis for a model-based analysis of the contribution of each individual area in the total contamination. In addition, sufficient data must be generated to be able to forecast the future distribution of the groundwater contamination in the aquifer in three dimensions and to be able to assess the impairment of identified valid receptors along the source/receptor pathways.

4.2.4 Integral Remedial Options Appraisal for Partial Processing Areas

During the subsequent remedial options appraisal, the remediation concept is supplemented with the results of the detailed (phase III) investigation. Furthermore, the remedial options appraisal is carried out in accordance with the requirements of the BBodSchV. The following shall be considered and processed, as deemed necessary:

► Recommendations for protection and restriction measures (institutional controls),

► Recommendations on monitoring concepts,

► Recommendations for the handling of contaminated excavated soil during construction measures, if an excavation measure is planned as remediation and

► model-based consideration and graduated presentation of which removal could be achieved with which extent of remediation. The reference level can be extended in addition to the usual procedure to the main affected parties (waterworks, etc.).

► If a total remediation would be disproportionate due to the magnitude of the contamination according to the BBodSchG, it should be examined whether partial measures could reduce the contaminant mass.

► Consideration of the contaminant plumes with regard to the use of groundwater for irrigation purposes (see also chapter 4.4)

Remedial options appraisal should be developed to the extent that it can form the basis for a proportionality assessment. As a result, protection and restriction measures (institutional controls) may be adopted. The proportionality assessment must be carried out on a case-by-case basis.

4.2.5 Integral Remediation Plan for Partial Processing Areas

If a complete remediation or partial measures are to be carried out, a remediation plan must be prepared. A remediation plan can describe not only the overall remediation but also measures that will lead to an improvement of the overall condition within a partial processing area in the future. Within the remediation plan, framework conditions for the handling of soils during future excavation or backfilling measures can also be defined, with which the overall condition within the partial processing area is to be improved.

There is currently no experience of the practical implementation of remediation plans for very extensive contaminations. A problem will be the large number of parties liable to remediate, so that the authority will probably have to take over the remediation plan and the remediation. Although this is possible in principle according to BBodSchG, the legislator was not able to know the extent of extensive PFAS contaminations with the discussed consequences when drafting the law. In future amendments of the BBodSchG or the BBodSchV, the authors believe that additional regulations on integral approaches to deal with this kind of contamination are useful.

> **Integral Remediation Plan for Partial Processing Areas**
>
> There is currently no practical experience of the practical implementation of remediation plans for very extensive contaminations. In future amendments of the BBodSchG or the BBodSchV, the authors believe that additional regulations on integral approaches to deal with this kind of contamination would be useful.

4.2.6 Institutional Controls (as Emergency Measures)

Considering the persistence of PFAS, e.g. irrigation with PFAS-contaminated groundwater can lead to a contamination of the topsoil. In addition, livestock watering or irrigation with contaminated water can lead to a contamination of farm animals or crops. In this case, it must be considered that agricultural and health protection concerns would also be affected. The recycling of PFAS-contaminated mowed material or plant residues from agriculture and home gardens as well as backfilling with contaminated soil material can lead to soil contamination and affect precautionary soil protection according to §10 BBodSchG.

This means that already during the investigations of the site, sometimes even in early phases of the investigation, it may become necessary to take institutional controls as immediate action or to make agreements as to such on a voluntary basis with the responsible parties. The institutional controls can also be temporary and bridge the time until remediation. For example, they can regulate the

- ► use of contaminated groundwater,

- ► utilization of mowed material or plant residues from agriculture,

- ► handling of soil material from large areas of concern and

- ► restriction of agricultural cultivation to certain non-PFAS-enriching crops (confirmed with so-called pre-harvest monitoring).

Institutional controls are either aimed at averting hazards or implementing precautionary soil protection. Material precautionary requirements in the form of precautionary values are not included for PFAS in the BBodSchV. Inputs of contaminants must be limited. Particularly long-chain PFAS have the property that they tend to accumulate in soils.

Therefore, a general decree prohibiting the extraction and use of groundwater for irrigation purposes can be justified by the enforcement of precautionary soil protection even without precautionary values for PFAS.

The institutional controls can also be formally implemented through preventive restrictions of use by those responsible for the area, such as in the case of real estate owned by the federal government (according to Chapter 8 in the PFC Guidelines for Federal Real Estate 2018).

A voluntary and cooperative agreement with the respective responsible persons should be the goal. This requires a stronger commitment from the authorities and will probably tie up human resources, but on the other hand promotes better enforcement. If no voluntary agreements are reached, the difficulty may arise that legally fixed precautionary values are currently lacking for many assessment cases. These must then be derived for the individual case.

Institutional Controls (as Emergency Measures)

Institutional controls (protection and restriction measures) can be determined at an early stage during the stage of investigation or planning. The aim is to react promptly and to bridge the period until remediation. These immediate measures can be aimed at averting danger or, in individual cases, also implement precautionary soil protection (e.g. prohibiting the use of PFAS-contaminated groundwater for irrigation purposes to take mitigate the effect of additional contaminations). Voluntary and cooperative agreements with the respective responsible parties should be sought.

4.3 Management of PFAS Impact on Groundwater and Surface water Uses (Source/Receptor Pathway Soil → Water Bodies)

In most cases, larger contaminant plumes have already formed in the case of PFAS contamination. At the beginning of the site investigation, however, only few data on the contamination situation will be available. Therefore, it is recommended to set up a hydraulic groundwater model at an early stage to simulate the possible contaminant migration paths. On the basis of the model, groundwater monitoring wells are then planned for investigation and the model is updated according to the increase in knowledge (see chapter 4.2).

With the help of the hydraulic model, it is also possible to identify at an early stage possibly affected groundwater areas and thus the possible impact on groundwater uses, e.g. drinking water production, fish farming, industrial water use, irrigation wells, etc. The responsible authorities (chapter 2.4) and groundwater users must be informed. It must be ensured that regular measurements of the contaminant situation are carried out during groundwater use.

If necessary, institutional controls can be ordered as immediate measures (chapter 4.2.6).

Affected water bodies with receiving water function must be considered and included in the investigations. Via contaminated waters, other groundwater areas may be affected laterally or vertically elsewhere. It is also possible that other uses (e.g. brook-fed fish farms, fishing waters, drinking water production) may be affected elsewhere via the contaminated receiving waters.

A PFAS contamination of a drinking water production area usually leads to a high priority in the treatment of the contamination. At the same time, however, the groundwater utilizer (in this case the operator of the waterworks) is responsible for the proper quality of the product (the drinking water) and must take the necessary measures to ensure this. If necessary, the operator concerned has the possibility to assert claims under civil law against the polluter regarding the damage suffered.

The authority responsible for processing the soil contamination will handle the case in accordance with the requirements of after-care soil protection and in accordance with the provisions of the relevant law. In this context, affected surface water uses, such as fish farming, or commercial uses as process or cooling water, etc., are also to be investigated about their impact on protected goods.

The soil protection authority, irrespective of its tasks and obligations to act, must ensure the flow of information to the users concerned and also to the competent authorities (Chapter 2.4). If many authorities are responsible, the establishment of a coordination office has proven to be ideal. This task can also be carried out by the higher-level authority.

> **Management of PFAS Impact on Groundwater and Surface Water Uses**
>
> Potentially affected groundwater uses must be identified and investigated at an early stage of the project. The soil protection authority must ensure the flow of information to users and also to the competent authorities. If many authorities are affected, the establishment of a coordination office has proven to be ideal.

4.4 Management of PFAS Effects on Crops (Source/Receptor Pathway Soil → Plant)

It is known that PFAS are enriched in different parts of the plant. This also applies to field crops that are to be marketed. Currently, intensive research is being conducted[11] to understand the processes and to identify crops that are less sensitive to PFAS uptake. In the future, the results of the research will have to be supplemented with binding guidelines. The ongoing development must be considered in the remediation management.

According to previous results of the vessel and field experiments of the German Agricultural Technology Center Augustenberg (LTZ) (RP KA, 2018a), the first experimental results have shown that there are great differences between the different plant species with regard to the incorporation of PFAS, especially in generative plant parts, e.g. flower, seed, fruit. This was also confirmed by the results of the pre-harvest monitoring of the crop. A small transfer of PFAS into generative plant parts is found in grain maize, winter barley, winter rye, grain rape, strawberries, and asparagus. A significantly stronger transfer of PFAS into the crop can be observed in wheat, triticale, and soya, as well as in crops where the vegetative plant parts, i.e. leaves, shoots, and roots are used, such as silage corn, forage or grass.

The Agricultural Technology Center also investigated the uptake of PFAS in typical energy crops such as *Miscanthus* and cup plant (*Silphium perfoliatum*) to see if such crops could be a potentially cultivated on moderately contaminated cropland. The results were not yet published at the time of reporting.

The extensive PFAS contamination in the Federal State of Baden-Wuerttemberg mainly affects agricultural land. As a result, the authorities have ordered that the harvested material be investigated prior to harvesting (so-called pre-harvest monitoring). The farmers then know for sure before the harvest whether they are allowed to market the field crops. This minimizes the cost risk and increases food safety. In addition, the confidence of the buyers increases to be able to consume the what are principally "quality-assured" field crops from a PFAS-contaminated area.

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[11] Among other things, a research project funded by the German Federal Environment Agency has been underway since 2019.

For short-chain PFAS in food, which are preferably accumulated in plants compared to long-chain PFAS, there are to date no toxicologically derived limit values worldwide. Therefore, the Ministry for Rural Areas and Consumer Protection of the State of Baden-Wuerttemberg had established transitional food law assessment values for these compounds, considering the findings of the Federal Environment Agency on drinking water.

Foodstuffs whose content of short-chain PFAS is analytically confirmed to be above these assessment values are not marketable. Such products may not be marketed to protect the consumer (RP KA, 2017).

Observations from pre-harvest monitoring indicate that the responsible state authorities have derived recommendations for cultivation and communicated them to farmers (RP KA, 2018b).

According to RP KA (2018a), the aim in Baden-Wuerttemberg is to develop a specific management and minimization concept together with each farm. This concept essentially includes the planning of crop rotations, which avoid the cultivation of PFAS-enriched crops on soils with PFAS content. The basis of the management and minimization concept is therefore the cultivation recommendation, which aims at minimizing the PFAS content in the crop by combining the PFAS content in the soil with the uptake behavior of the respective crop.

Irrespective of the fact that groundwater in Germany cannot be owned, PFAS groundwater contamination below uncontaminated or even contaminated farmland can be a major problem for farmers. Common agricultural practice in some regions is the local extraction of irrigation water from the aquifer. On the one hand, irrigation with contaminated groundwater can contaminate clean soil. On the other hand, it has been shown in many cases that the PFAS from irrigation water are preferably absorbed by the plants. This is especially true for greenhouse cultures. In the case of PFAS contaminations, the authorities can set specifications for such irrigation (RP KA, 2018c). This regulation "*must serve both the protective purpose and sufficiently meet the water requirements of the plants and be flexible enough to allow new findings on PFAS to be considered in the coming years. Depending on the crop, even the lowest PFAS contents in the soil or in irrigation water can be incorporated into the products and lead to the assessment values being exceeded (source/receptor pathway soil → plant). In addition, the effects on soil and groundwater must be minimized (source/receptor pathway soil → groundwater).* "

According to the specifications of the authorities (RP KA, 2018c), existing knowledge, especially about the transfer of short-chain PFAS via irrigation water or from contaminated soils into the plants, must be considered. For example, pre-harvest monitoring has shown that crops with a high water and protein content, such as tomatoes, zucchini, melons, and beans, particularly absorb and concentrate the PFAS contained in irrigation water very well. Nevertheless, there is still a considerable need for research to be able to answer open questions conclusively.

In cases of doubt, irrigation with water containing PFAS should be avoided. Irrigation should be adapted to the needs of the plants. The infiltration of irrigation water must be avoided in accordance with good professional practice. The amount of irrigation water must be minimized by selecting suitable irrigation methods.

Plant parts containing PFAS that leave the cultivation area must be disposed of as waste in Germany. Therefore, these are often left on the fields. In principle, the enrichment of PFAS in plants and their disposal could also serve to deplete PFAS in soils. For this purpose, however, the enrichment rates in the plants would have to be correspondingly high. This is however not the case according to present knowledge (see Appendix A and C).

If the groundwater cannot be used for irrigation, either another crop must be grown or the water supply must be changed. The latter often leads to further difficulties. Groundwater purification is usually uneconomical, and the supply of drinking water usually fails because of hygienic requirements for the pipe network, even if it is only used for irrigation.

Supply networks (ring pipelines etc.) are only possible if there is no uncontaminated groundwater at all in the wider surroundings. Therefore, it makes sense to consider this effect of the contaminant plume in the remedial options appraisal.

> **Management of PFAS Impact on Crops**
>
> For short-chain PFAS, transitional food law assessment values were established in Baden-Wuerttemberg. If foodstuffs exceed these values, they are not marketable. If PFAS-contaminated soils are used agriculturally, an investigation of the material prior to harvest is necessary (so-called pre-harvest monitoring). The farmers then know for sure before the harvest whether they are allowed to market the field crops. The cost risk is thus minimized, and food safety is increased. In addition, the confidence of the buyers rises with respect to the consumption of harmless field crops from an area with PFAS contamination.
>
> Reliable transfer factors, with which the contamination on plants can be calculated based on the contamination on the soil, will probably not be available soon.
>
> By irrigation with contaminated groundwater, PFAS can be absorbed into plants from the irrigation water. The authorities should provide applicable guidelines for irrigation.

4.5 Management of PFAS Impact on Areas Used by Humans (Source/Receptor Pathway Soil → Human)

Currently there are no calculations for preliminary assessment values for the source/receptor pathway soil → human (direct contact). Further action is therefore urgently needed at this point. There are only made estimations that have been presented at lectures. According to these, the values would be in the mg/kg range. However, whether these are robust estimates must be checked, also regarding the possibly changing TDI values.

In principle, preliminary assessment values may be derived for the source/receptor pathway soil → human (direct contact) if the safety factors and derivations used to derive the TDI values (or TWI values) were disclosed. Why this is not the case is unclear. Even preliminary values could help in the context of sensitivity considerations in individual cases.

The level of knowledge about the toxicology of the individual PFAS compounds varies. There is a need for further research. For the remediation management this means that the development of the state of knowledge must be continuously advanced.

When evaluating the source/receptor pathway soil → human, possibly occurring precursors must also be considered. At this stage it is still unclear whether precursors can be absorbed in the human body and converted into toxic PFAS. Therefore, it is recommended to test the resorption availability according to DIN 19738 in case of substantial precursor contents. With this standard, a test system for the mobilization of contaminants from contaminated soils with the help of synthetic digestive juices is standardized. The perfluorinated substances produced after oxidation of the precursors in the TOP assay can be used for toxicological sensitivity analysis or sensitivity estimation.

> **Management of PFAS Impact on Areas used by Humans (Source/Receptor Pathway Soil → Human)**
>
> There are currently no legal assessment values for the source/receptor pathway soil → human available. There is an urgent need for further action. Further developments in remediation management must be monitored. Precursors must also be considered when evaluating this source/receptor pathway.

4.6 Management of PFAS Impact on Home Gardens (Source/Receptor Pathway Soil → Human)

The consumption of self-cultivated contaminated garden fruits or vegetables from home gardens must be considered with the evaluation of the source/receptor pathway soil → human. With concentrations below the evaluation values for the source/receptor pathway soil → plant, consumption of home-grown crops would be possible without hesitation. At present, however, there are no evaluation values and these are not to be expected soon (chapter 4.4).

When considering vegetable or fruit cultivation in home gardens, the actual and possible planting must be considered. However, the enrichment rates of individual vegetable and fruit species and for each individual PFAS compound vary considerably. However, in the case of extensive PFAS contaminations, sensitivity analyses can be performed to check whether the uptake path may be relevant. These analyses can be based on available data or data from comparable cases on PFAS accumulations in the edible parts of vegetables or fruits. In selecting the data, it is less the level of soil contamination than the comparable fingerprint of the PFAS that is important.

One possibility for such a sensitivity analysis is, for example, the simulation of a worst-case scenario, in which it is assumed that only the vegetables and fruits with the highest intake rates are grown and consumed by the inhabitants on a defined, very large area. The consumption rates can be taken from the latest national consumption study published on the Internet. Harvest yields per area and procedures are described for example by LANUV North Rhine-Westphalia (2014). By means of such a sensitivity analysis it can be determined whether and, if so, from which size of area of a home garden the intake path via self-grown vegetables and fruits must be considered in individual cases. The evaluation itself must necessarily be carried out using TDI or TWI values. Here the same difficulty results, as with the effect path soil → human (direct contact) (chapter 4.6). The safety factors (if available) and derivations on which the TDI values (or TWI values) are based could be used to derive the corresponding values.

There is an urgent further need for action to derive values for the source/receptor pathway soil → human. Using these values, also the source/receptor pathway soil → human could be judged for house gardens.

In the case of home gardens, it must be considered that a high uptake rate in plants can be produced by watering with PFAS-contaminated groundwater. In this case, a substantial improvement of the overall situation in the relevant source/receptor pathway can be achieved by dispensing with or prohibiting the use of garden wells.

> **Management of PFAS Impact on Home Gardens**
>
> There is an urgent need for further action to derive values for the source/receptor pathway soil → human. Using these values, the source/receptor pathway soil → human could also be judged for house gardens.
>
> In the case of extensive PFAS contaminations, sensitivity analyses can be performed to check whether the PFAS uptake of plants may be relevant.

4.7   Management of PFAS-Contaminated Soils

The currently very limited and cost-intensive decontamination or disposal options for PFAS-contaminated soils make both remediation and site development measures difficult. In case of very extensive PFAS contaminations over a large area, municipal developments in designated areas for urban development or the expansion of commercial areas may be inhibited. Depending on the case-specific conditions, case-specific solutions for handling contaminated excavated soil or specific soil management concepts may be applied to overcome such obstacles. Irrespective of this, it is recommended to consider the creation of regional disposal possibilities on a mid-term basis for cases of extensive PFAS-contamination. Currently, treatment options or local landfills are generally not available.

In some cases, the applied solutions specified for handling contaminated excavated soil can also have a positive effect on contaminant mass flux of soil leachate. This is especially the case if surface sealing or the rearrangement of soils results in a reduction of the contaminant mass flux to groundwater. In the following, different possibilities to introduce soil management concepts are described. In principle, it must be examined for each individual case whether any of the described options are applicable.

Designated areas according to § 21 para. 3 BBodSchG. The designation of so-called soil protection areas or soil planning areas according to § 21 para. 3 BBodSchG aims at addressing extensive contaminations that occur or are expected to occur over a specified area (Hipp et al., 2000). Detailed solutions are to be proposed by the respective Federal States.

Designating areas to apply specific solutions for handling contaminated soil within areas of extensive PFAS contamination is a concept that is judged rather cautiously in currently ongoing discussions. One reason for this is that the BBodSchG does not specify any respective scope. State-specific solutions cannot replace federal laws or ordinances, they can only have a supplementary effect. Therefore, from the current point of view, § 21 has as its aim, either precautionary soil protection or the implementation of measures of access prohibition, measures of remediation (of soil contamination), or of institutional control.

For example, depending on the type of solution proposed by the state, in such areas, land-use may either be restricted or defined. Restrictions applicable to the handling of excavated materials are possible, as are acquiescence orders or instructions to the owners or land users.

Restrictions on use may at times be reason to invoke the right to monetary compensation by the local authority, according to some Federal States´ regulations. This is disadvantageous regarding the designation of soil protection or soil planning areas. Due to this, there is a risk of legal disputes regarding compensation claims.

In addition, implementation becomes difficult if there are disruptive parties involved. In the case of wide-spread PFAS contaminations, such disruptive parties actually exist, which is why conflicts can arise with regard to responsibilities or as to who is financially liable. Due to the overarching regulations and the resulting possible flaw that is officially attributed to an entire area, there is also the risk that owners of land that may actually be clean, yet which lies amongst individual contaminated areas comprising one designated large area may see the value of their land drastically reduced and legal disputes may arise.

In principle, however, it would be possible to designate soil protection or soil planning areas in the case of completely contiguous large areas, if a disruptive act can no longer be claimed and, for example, use and restriction measures are to be pronounced. Whether the instrument of a legislative decree for the designation of such areas is not too complex must be examined on a case-by-case basis.

General decree with specifications for soil management according to § 12 para. 10 BBodSchV.
One possibility to regulate the handling of contaminated soil material within extensive PFAS-contaminations is offered by § 12 para. 10 BBodSchV:

> *"In areas with elevated levels of contaminants in soils, relocation of soil material within the area is permissible if the soil functions mentioned in § 2 para. 2 No. 1 and 3 letters b and c of the Federal Soil Act are not additionally impaired and the contaminant situation at the place of application is not adversely affected. The areas of increased contaminant levels may be defined by the competent authority. In doing so, the competent authority may also permit deviations from paragraphs 3 and 4."*

The regulation in the BBodSchV allows the designation of areas where soil material can be relocated. A requirement for this is that the condition at the place of application is not worsened (*prohibition of worsening*). This requirement also fulfils the condition of the Waste Management Act of harmless recycling. In many Federal States there are specifications for classification values for the recycling of PFAS-contaminated excavated material. Exceptions to these regulations would therefore have to be defined within the designated area. The individual case-related deviation from the general regulations must be justified.

Together with the designation of the areas, a soil management plan must be drawn up in which the regulations for the reinstallation of contaminated soil, official permit procedures, documentation requirements, etc. are fixed. In addition, the soil relocations must be recorded in a separate cadaster to be able to document the constantly changing contamination situations in the entire area. This can be determined by the authorities within the framework of the general decree.

The described procedure may be suitable for large contiguous contaminated areas caused by emissions. In the case of accumulations of individual areas, the practical feasibility of the procedure is currently the subject of critical discussion, as it could be disadvantageous for any clean areas that are strewn in amongst the greater defined area. Such suspected clean areas would have to be proven to be clean and removed from the general decree.

In practice, in many cases the general ruling will only be possible after the entire process of soil protection law investigation and evaluation (selection of the party liable to remediate, remedial options appraisal, etc.) has been completed and the implementation of planned remediation measures has begun. If this is not the case and soil is already being relocated beforehand, this can lead to the fact that, e.g. during the remedial options appraisal, possible remediation options are made more difficult or impossible by the already realized soil relocation.

Integral remediation plan. For areas with a defined source and known party liable to remediate, the aftercare soil protection according to § 13(5) with the rules known from the BBodSchG and BBodSchV applies. According to these rules, a remediation plan must be drawn up for approval and declared binding. The remediation plan is drawn up on a case-by-case basis and can also be more comprehensive regarding the regulations contained therein. The regulations according to § 28 para. 1 sentence 1 of the Waste Management Act explicitly do not apply if it is ensured that the welfare of the public is not affected by soil redistribution within the remediation area. The designation of a remediation plan over a larger area, in which numerous point sources are located, corresponds to the principles of the soil protection law, and is referred to as an "integral remediation plan" (Grimski and König, 2010). Integral remediation plans are generally applicable if there is agreement among the parties responsible for remediation. There are basically two possible applications.

Case 1: Remediation is partially or wholly proportionate. If, during the remedial options appraisal, the remediation is judged to be proportionate, the integral remediation plan must be drawn up in accordance with BBodSchV. If there are different parties liable to remediate, the authority has the right to select a specific party or can prepare the remediation plan itself according to § 14 BBodSchG. The paragraph mentioned refers to abandoned contaminated sites, but the application to contaminated sites still in operation must be legally examined.

Case 2: Remediation is not proportionate. If, during the remedial options appraisal, the remediation of individual areas or sub-areas is generally judged to be disproportionate, a partial remediation can nevertheless be target-oriented and efficient in certain cases. This is the case if, on individual areas or sub-areas, measures take place anyway that allow for a proportionate remediation. Also, for the parties liable to remediate, conflicts of interest are resolved if there is a common interest, e.g. in the case of development areas or similar.

Regarding the consideration of individually PFAS-impacted areas within large extensive areas of soil contamination, different case constellations exist. An example case-study highlights the significance of a development area lying within an extensive soil contamination, whereafter completing the remediation concept it was determined that the treatment of individual areas is not proportionate or technically not reasonable.

Example

Combination of remediation and development measures. In this example, targeted soil management in the context of site development through synergies can enable proportionate remediation. This means that aversion or elimination of hazards (remediation) at a development site would then be possible with simple means (in the sense of BBodSchV § 3 (5) and § 7) or at least with proportional means. However, this is usually only feasible if an entire area that is designated for development is able to be considered as one single investigation area and a remedial options appraisal is carried out for this one defined area.

To be more precise and in context: within the framework of a remediation plan according to BBodSchG § 13 (5), relocation of polluted soils is generally possible if the welfare of the public is not affected. The Waste Management Act is not applicable in such a case. Areas located within a defined remediation area, yet which do not act as a significant source of PFAS input into groundwater, must be integrated into the scope of the remediation plan. Otherwise, the Waste Management Act would indeed be applicable and it would not be possible to conduct targeted soil management related to the remediation here, as transports across areas not in need of remediation would be ongoing. Measures taken for purposes of remediation and site development would, in such a case, not be able to be combined in an effective manner.

The area to be remediated is defined as the affected area of the soil management plan. In the figurative sense, the area affected by remediation is thus also extended to the (partial) areas that would not need remediation in the strict sense. However, this is also often the case with conventional larger remediations.

In soil management, the principle of prohibiting deterioration of unpolluted areas must be considered. The ownership structure must also be considered while conducting remedial options appraisal and for further site management.

Example End

Management of PFAS-Contaminated Soils

The currently very limited disposal possibilities for PFAS-contaminated soils complicate both remediation and development measures (leading to the inhibition of municipal developments and the expansion of commercial areas), which can be resolved by area-wide solutions (soil management concepts) if necessary.

Solutions include e.g. the designation of soil protection or soil planning areas to mitigate wide-spread impacts. This, however, can lead to conflicts regarding responsibilities and questions of financial liability amongst a variety of stakeholders.

An alternative is the general decree with specifications for soil management according to § 12 para. 10 BBodSchV, according to which a relocation of contaminated soil is permissible within designated areas with increased contaminant contents if the contaminant situation at the place of application is not adversely affected (prohibition of deterioration). Parallel to this, the relocation of soil must be recorded in a separate cadaster.

An integral remediation plan can also provide the framework for soil redistribution within the remediation area, where numerous point sources are located. Integral remediation plans are usually applicable if there is agreement among the parties responsible for remediation. Areas without any PFAS-input to groundwater must be integrated into the remediation area in order to derive remedially-based soil management.

5   Waste Management Act

Waste management. The German waste management concept is consistently geared to the goal of avoiding waste and to recycle. Disposal in landfills is intended as the possibility of last resort when all prioritized options like avoidance, recycling, or recovery are not possible. For this reason, the creation of new landfill capacities is consistently pursued on a subordinate basis, since strategic planning is always based on the assumption that materials in the economic cycle can be recycled.

At present, there are no proportionate decontamination possibilities for the very large soil volumes associated with extensive PFAS contaminations, but also from many local contaminations. At the same time, there are currently hardly any disposal possibilities in landfills.

For these reasons, either further landfill capacities would have to be created or an attempt would have to be made to strengthen the recycling possibilities of the PFAS-contaminated soils in the sense of the circular economy. This can also be done within the framework of the possibilities shown in chapter 0

When assessing the proportionality of measures in individual cases or when considering exemptions, it is recommended that special consideration be given to the economic priorities of waste prevention and recovery in the case of PFAS-contaminated soils. Recycling is carried out consistently and according to the legal requirements in the contaminated regions (prohibition of deterioration).

Removal of PFAS from the environment. In the sense of environmental protection, it is necessary to develop concepts and new solutions for the targeted and systematic removal of PFAS from the environment or human living environment. This is necessary in the long run, especially because of the very high persistence of the substances. For this purpose, it is recommended to develop concepts and approaches. Various scenarios are conceivable, such as systematic decontamination or landfilling of particularly high levels of contamination. Appropriate instruments and technical possibilities still need to be developed in this context.

Avoidance of waste. The generation of waste must be avoided as a priority. In each individual case, it must therefore be checked whether there is actually an obligation to dispose of the soil or whether PFAS-contaminated soil can be reinstalled or left in place. This should, if possible, result in a containment, i.e. in a better condition than before. An obligation to dispose of materials (as a basis for the definition of waste) exists according to § 3(4) Waste Management Act for materials (soils),

> *"...if these are no longer used in accordance with their original purpose, are suitable, on account of their specific condition, to endanger the public welfare, in particular the environment, at present or in the future, **and whose hazard potential can only be excluded by proper and harmless recycling or disposal in the public interest in** accordance with the provisions of this law and the statutory ordinances issued on the basis of this law. "*

If an area is managed according to the soil protection law, it can be assumed that either subsequent remediation will take place or that no remediation is necessary because there is no danger. If in this case construction measures involving the excavation of contaminated soil take place, the bold sentences of the above quotation would not normally apply and there would be no obligation to dispose of the soil as an exception to be agreed with the authorities in each individual case. The material could then be reinstalled on site if necessary.

Recycling. A working group commissioned by the German Conference of Environment Ministers is currently developing a nationwide guideline. Reference is made to this paper, which is expected to be published soon (Status Sept. 2020). Some additional, practice-relevant aspects of recycling are discussed below.

If soils with higher PFAS contents are recycled in technical structures and are exposed over a longer period of time, it is recommended to ensure that no contaminated seepage water can cause soil or groundwater contamination (e.g. temporary covering of the temporarily stored material, immobilization, sorption barrier, etc.) until the surface sealing is established.

Technical structures in which material with higher PFAS contents is recycled are generally not systematically recorded. In these cases, the recycling information is not permanently and reliably available across generations. It is therefore recommended to record these structures in the respective soil protection register.

The recycling of soils with very low PFAS contents is currently often rejected due to the uncertainty of many parties involved regarding the PFAS substance group. To avoid that anthropogenically caused background contamination is removed from this uncertainty, knowledge about it is essential. Clear evidence for the presence of background levels of PFAS, especially carboxylic acids with up to 8 C-atoms, is available from exemplary studies in several German states (Appendix A) and from the Environmental Sample Bank. All in all, there is a lack of further data and basics, which must be determined in the future.

Removal. The criteria for the disposal of PFAS-contaminated soil materials have so far been inconsistent throughout Germany. Regulations are existing only in a few Federal States which will not be discussed in the following. Within the scope of a 2018 research, only very few landfills could be identified that have accepted PFAS-contaminated soil. Moreover, these are not distributed throughout Germany, so that the transport route to these landfills associated with disposal is associated with considerable additional burdens (including contaminant emissions, CO_2 emissions).

For the parameter PFAS, the ability to landfill PFAS-contaminated soil depends not only on the acceptance criteria of the respective landfill, but above all on the suitability of the respective landfill-specific leachate treatment. Leachate treatment must be considered in each individual case regarding the necessary retention of contaminants. This concerns all landfill classes. In the nationwide uniform assessment guidelines, which are currently being drawn up by a working group of the Conference of Environment Ministers, the following statements are planned according to the state of discussion at the end of 2019:

> *According to EU Regulation No. 1342/2014, above-ground landfilling of PFOS contaminated soil material is permitted up to a content of 50 mg/kg. If the PFOS content exceeds this value, it must be treated or disposed of underground in accordance with Appendix V Part 1 of Regulation (EC) No 850/2004 (EC POP Regulation). It is recommended to apply the limit value of 50 mg/kg, which has so far only applied to PFOS, to the sum of the PFAS determined. Above-ground disposal of PFAS-containing excavated soil can be carried out up to a PFAS content (in total) of 50 mg/kg if the landfill fulfils the following technical requirements:*
>
> o *The deposition of PFAS-containing excavated soil in landfills must be carried out in special mono areas in the case of larger quantities in order to enable separate leachate collection, if morphologically feasible, and, if suitable cleaning methods are available, to enable the material to be retrieved if necessary. In addition, landfills must ensure that a suitable basic sealing component is available, e.g. in the form of a mineral seal or a convection barrier (plastic liner or landfill asphalt sealing component).*
>
> o *It must be ensured that when PFAS-containing excavated soil is deposited in a landfill, a suitable leachate treatment is carried out specifically for the respective PFAS, with which the PFAS can be sustainably removed from the material cycle.*
>
> o *The investigation program for leachate and groundwater is to be extended by the PFAS relevant to individual cases. Appropriate trigger thresholds according to the Landfill Ordinance for groundwater are to be determined by the competent authority.*

For landfills of the so-called class DK 0, which do not have a base sealing component and partly do not have a leachate collection system, the deposition of PFAS-containing soil material would therefore not be suitable.

If the PFAS-contaminated soils contain larger amounts of precursors, the microbial transformation of the precursors could be enhanced during excavation and landfilling after oxygen has been mixed into the contaminated soil. However, this risk would be covered by the planned leachate treatment.

Immobilization as a temporary technical aid in the waste management. Immobilization can be carried out as a temporary interim measure, even if a "semi-infinite" long-term stability cannot yet be proven. This can be used to temporarily prevent transport into deeper soil areas. In principle, immobilization is suitable as a technical aid, for example in the case of recycling or disposal at landfills where contaminated leachate otherwise could cause soil or groundwater contamination, but which are sealed after a specific period.

Currently, there are various efforts to develop methods for immobilization with high long-term stability. If this succeeds, a combination of immobilization and landfilling could be considered. Through immobilization, the properties of the waste (PFAS-contaminated soil) may be "improved" to such an extent that a simpler landfill with a lower demand on leachate treatment seems possible. The requirement for PFAS control in the monitoring phase would remain unaffected.

There are still several legal and technical questions regarding the immobilization procedure (Appendix E).

Waste Management Act

When examining the proportionality of measures in individual cases or when considering exemptions, it is recommended that special consideration be given to the economic priorities of waste prevention and recovery in the case of PFAS-contaminated soils.

In terms of environmental protection, it makes sense to develop concepts and new solutions for the targeted and systematic removal of PFAS from the environment or human living environment. For this purpose, it is recommended to work out concepts and approaches on the state or federal level.

The generation of waste must be avoided as a matter of priority. Therefore, it must be checked in each individual case whether there is actually a disposal obligation or whether PFAS-contaminated soils can be reinstalled or left on site.

At present, a working group commissioned by the Conference of Environment Ministers is developing uniform nationwide guidelines for recycling and disposal. Reference is made to this paper, which is expected to be published soon (Status: Sept. 2020).

6 Public Participation

6.1 Requirement for Public Participation and Basic Approach

At sites with extensive PFAS contaminations with many affected stakeholders there is a large interest of the public to understand the background of the contamination and the further planned proceeding. Although there is no legal obligation in Germany, it is strongly recommended to involve the public pro-actively, especially in larger projects. This serves to objectify the topic of PFAS, which also helps those parties affected, such as farmers who depend on local marketing of their products.

It has proven to be ideal to appoint an official contact person for public relations. The public relations work mainly consists of press releases, a citizen information page on the Internet with "frequently asked questions and answers" as well as citizen information events and the answering of inquiries from the political sphere. Experience shows that an interesting form of event is highly appreciated by the citizens. The current topics are introduced in short lectures. For each topic block, for example, information booths can be set up at which representatives of the authorities and external experts are available to answer questions. This form is much more elaborate than the usual podium form but allows for a greater and more individualized proximity to the citizens. It also prevents groups from using the citizen information for political agitation. Instead, the focus is on the individual citizen with his or her questions, which are answered on an equal footing.

The focus of public participation is thus on clear risk communication with the aim of explaining the risk assessments made and the management of the risks to those affected in an understandable way, especially against the background that those affected by the contamination usually perceive the risks very emotionally at first (NGWA, 2017; Slovic, 1987, 2003; UN-ISDR, 2002).

Effective risk communication involves all stakeholders in the process of risk assessment and management, communicates the actual risk, and facilitates participation in risk management decision-making processes by those affected. Supporting materials in preparation for risk communication are made freely available by a wide range of public institutions. Successful risk communication throughout the life cycle of a project increases community awareness of environmental hazards, strengthens the community through participation in risk mitigation activities, and contributes to improving the quality of life for stakeholders (Harclerode et al. 2016a, b).

Requirement for Public Participation

Especially in the case of PFAS contamination of large areas, there is great public interest in understanding the background of the contamination and the further planned procedure.

Although there is no legal obligation in Germany, it is strongly recommended, especially for larger projects, to continuously involve the public proactively from the beginning.

6.2   Participating interest groups (stakeholders)

Stakeholders can consist of any organization, group or individual who is interested in a project and who can influence the project results (Cundy et al. 2013, Reed, 2008). In the context of PFAS-contaminated sites, stakeholders are mainly

- ► parties potentially liable for remediation,
- ► competent authorities,
- ► affected water users,
- ► residents,
- ► farmers,
- ► consumers,
- ► municipalities and
- ► owner.

Considering the "context" of those involved can help professionals identify risk perception factors that contribute to community skepticism. Increased concern and skepticism about the communicated outcomes are sometimes based on distrust due to an initial lack of communication (Emmett et al., 2009, 2010). The "context" of those involved is defined by the demographics of the community:

- ► socio-cultural factors (e.g. views on environmental responsibility and remediation activities)
- ► psychosocial factors (e.g. diversity of beliefs, attitudes, values, and inhibitions of individuals, including trust in authorities)
- ► knowledge base (e.g. understanding PFAS exposure and safe concentration levels)
- ► The existence of mobility restrictions that may prevent adequate participation in public events.

Risk perception factors can be identified through surveys and interviews (Chappells et al., 2014).

6.3   Risk Communication

Risk communication is the process of informing stakeholders about health or environmental risks, risk assessment results and proposed risk management strategies. Risk communication should be a two-way process, where all stakeholders are informed of each other's needs and where the objectives are identified to address the concerns expressed (Cundy et al., 2013, US EPA, 2007).

In some cases, where decontamination cannot be achieved by proportionate means, security may be limited to institutional controls. In risk communication, it is important that this is presented transparently and truthfully to avoid erosion of credibility and to make decisions on how to manage the risk comprehensibly (US EPA, 2007).

The involvement of all stakeholders, if successful, can be a complex process. On the other hand, effective risk communication can simplify or accelerate the implementation of upcoming projects, increase transparency, and address stakeholder concerns.

It is advisable to identify frequently asked questions in advance and develop recommended answers. Examples are:

1st Question:	Why are there no laboratory methods available to determine whether PFAS are present (i.e. the detection limit is zero)?
Answer:	There is no method sensitive enough to determine a zero concentration (i.e. no single molecule is present) for any chemical. However, there are standardized methods that are sensitive enough to detect PFAS at concentrations lower than the current limits. Public health can therefore be protected.

2nd Question:	Does the presence of other contaminants and/or by-products increase the effects of exposure to PFAS on human health and the environment?
Answer:	The authorities have developed an approach to assess the potential effects of exposure to multiple PFAS compounds. However, each situation is different and depends on the amount and type of compounds that may be present and also whether the compound is in contact with humans or the environment. Furthermore, there are no known combinations of PFAS with other chemicals that aggravate the risks associated with exposure.

It can also be helpful to,

► create information sheets (*fact sheets*),

► develop a website containing presentations, research results, and frequently asked questions,

► set up a toll-free telephone number where experts can be contacted for any open questions,

► create clear site plans, so that the residents can classify their property in relation to the results of the investigation,

► develop a communication plan that describes how to involve and disseminate information to stakeholders.

It has been shown that the development of a communication plan and the right strategy significantly reduces the mistrust between those involved and the decision-makers (such as authorities and responsible parties). Such a communication plan could include the following chronological elements (Emmett et al., 2009):

► notifications of participants and authorities,

► shortly afterwards the sending of investigation results by mail,

► sending information material to decision-makers to ensure that appropriate responses to public inquiries can be made,

► press release and briefings. Important local and regional media are identified and informed early enough so that project management is the primary source of information for the press. Identified media representatives and national news agencies are invited to a press release.

Prior to public meetings, the agenda, comprehensibility of the slides, choice of wording, structure of the presentation and handling of probable questions should be clarified internally. It has proven to be ideal to hire external professional moderators to lead through the event and to objectify the discussion through neutral moderation. The implementation of effective risk communication is not without problems, especially in controversial situations where exposure routes and effects on human health have been identified.

These potential challenges include:

► ***Adjustments of evaluation bases and strategic remediation approaches.*** One of the tasks of risk communication is to support the affected stakeholders in understanding the process of risk assessment and risk management. Due to the nature of new contaminants such as PFAS and the number and complexity of PFAS compounds, current assessment criteria may conflict or change. Guidelines and criteria are also subject to change based on the development of analytical methods and risk assessments. In the context of risk communication, it is important to communicate these uncertainties and variabilities while maintaining the confidence of affected stakeholders and meeting their needs (US EPA, 2005, 2007; RESCUE Consortium, 2005).

► ***Misjudgment within the proposed risk management strategies.*** Effective risk communication depends on the ability of decision-makers to help affected stakeholders to form a scientifically based perception of their PFAS risk. Risk perception differs between expert and lay people (Pidgeon et al., 1992). Because the public is exposed to hazards, the community and society in general respond and directly influence the perceived risk of these hazards. A phenomenon known as "risk mitigation" occurs when experts classify hazards as relatively serious. Affected parties then often take the risk less seriously (risk perception). In contrast, a perceived "risk amplification" occurs when experts assess a hazard as low or moderate. This scenario often leads to a reduced acceptance of the proposed risk management strategies and to conflicts between stakeholders (e.g. the approval authority and the affected community). The degree of risk mitigation or risk amplification is also influenced by the assessment of the trustworthiness and expertise of the experts and compliance with guidelines and protective measures (Botzen et al., 2009; Lewis and Tyshenko, 2009; Kasperson and Kasperson, 1996).

► ***Lack of effective risk communication for all affected stakeholders.*** One of the main purposes of risk communication is to involve all affected stakeholders in the risk management decision-making process. Also understanding the perspective of affected stakeholders that do not have strong political support is essential for effective risk communication. It is therefore important to listen to the concerns of the public. People are often more interested in trust, credibility, competence, fairness, and empathy than in statistics and details. It is also important to meet the needs of the press media and to communicate accordingly in an understandable way.

► ***Different expectations of the affected stakeholders.*** It is not unusual to involve stakeholders with opposing views in risk communication. Stakeholders can be involved in the work (stakeholder engagement methods) to evaluate and prioritize multiple conflicting needs and communicate decisions (multi-criteria decision analysis and evaluation system) (Harclerode et al., 2015). Interactive workshops also provide opportunities to build trust and develop a common understanding of the problem from which solutions can be formulated.

Risk Communication

Risk communication is the process of providing transparent and truthful information to stakeholders about health or environmental risks, the results of risk assessments and proposed risk management strategies. All stakeholders should be informed of each other's needs and of measures to address the concerns expressed. Risk communication is important to avoid erosion of credibility and to simplify and accelerate upcoming actions. There are numerous tools available for risk communication.

It has proven to be a good idea to hire external professional moderators for information events to achieve an objectification of the discussion through a neutral moderation. The implementation of effective risk communication is challenging in contentious situations.

The task of risk communication is to support the stakeholders concerned in understanding the process of risk assessment and risk management against the background of changing conditions and different perceptions and to include them in decision-making processes on risk management. The phenomenon of "risk mitigation" occurs above all when experts classify hazards as relatively serious. People are often more interested in trust, credibility, competence, fairness, and empathy than in statistics and details.

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Appendix A:

Relevant Substance Properties

Table of Contents

List of Figures

List of Tables

1   Production

There are two established methods for the industrial production of poly- and perfluorinated compounds: electrochemical fluorination (ECF) according to J. H. Simons (1941) (cited in: Schmeisser and Sartori, 1964) (Figure 1) and fluorine telomerisation (Buck et al., 2011).

Figure 1   Electrochemical fluorination (ECF)

$$CH_3\text{-}(CH_2)_n\text{-}SH \qquad\qquad CH_3\text{-}(CH_2)_n\text{-}COCl$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$CH_3\text{-}(CH_2)_n\text{-}SO_2F \qquad\qquad CH_3\text{-}(CH_2)_n\text{-}COF$$

HF, e⁻ $\downarrow$ HF, e⁻ $\downarrow$

$$CF_3\text{-}(CF_2)_n\text{-}SO_2F \qquad\qquad CF_3\text{-}(CF_2)_n\text{-}COF$$

$$CF_3\text{-}(CF_2)_n\text{-}SO_3H \qquad CF_3\text{-}(CF_2)_n\text{-}SO_2X \qquad\qquad CF_3\text{-}(CF_2)_n\text{-}COOH \qquad CF_3\text{-}(CF_2)_n\text{-}COO^-M^+$$
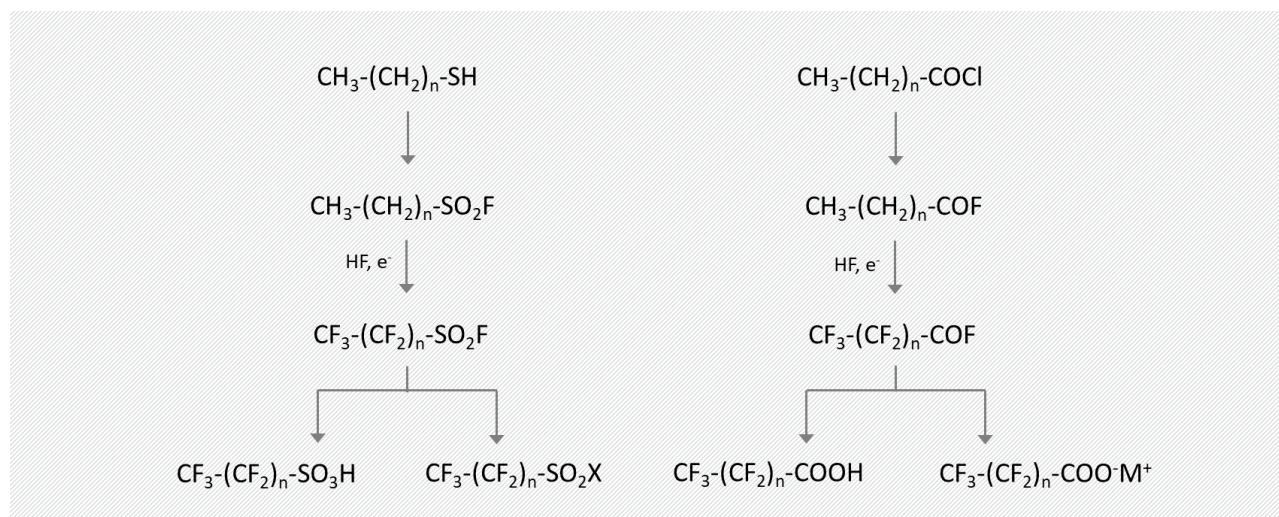
Source: Buck et al., 2011

In electrochemical fluorination (ECF), the starting substrate is converted in a water-free environment with the application of electricity using hydrogen fluoride. In this process, each hydrogen atom is replaced by fluorine (Schmeisser and Sartori, 1964).

Perfluoroalkylsulfonyl fluoride (PFOSF) and perfluoroalkylcarbonyl fluoride (PFOAF) are the central intermediates in the ECF. The respective hydrolysis at the end of the process finally replaces the fluorine at the acid group and leads to the known acids perfluorooctane sulfonic acid (PFOS) or perfluorooctanoic acid (PFOA), which can be converted into the corresponding salts by neutralization. The precursor compounds PFOAF and PFOSF are also important starting materials which can be derivatized by standard procedures. Instead of the fluorine atom at the carbonyl or sulfonyl group, a residue (X) is added to the molecule. Starting from PFOSF, two central intermediates are synthesized. The reaction with methyl- or ethyl-amine leads to N-methyl- or N-ethylperfluorooctanylsulfonamide (FOSA), which can be converted to N-methyl- or N-ethylperfluorooctylsulfonamide ethanol (N-MeFOSE or N-EtFOSE) (Fricke and Lahl, 2005). The intermediates themselves are used industrially only to a small extent (Bavarian State Office for Health and Food Safety, 2006), but the end products are important.

Since free radicals are formed in the ECF, the carbon chains can also break up and rearrangements can be formed. As a result, both linear and branched molecules are formed. The proportion of branched isomers in carboxylic acids is usually less than 20 %; in PFOS (perfluorooctane sulfonic acid) the proportion can be up to 30 %. Since many by-products are also formed, such as shorter-chain, longer-chain, and cyclic compounds, the yield of the main product with this cost-effective method is only 30 - 45 %. Typical chain lengths are in the range of 4 - 9 C atoms. Some of the by-products and impurities are removed in a purification step.

Telomerisation has been and still is predominantly used as a more modern process, as the product yield is higher, and the formation of by-products is lower. In telomerization, tetrafluoroethene is first reacted with iodine and iodine pentafluoride (IF$_5$) to form pentafluoroiodethane. Based on this, the target substance can be gradually built up.

Each further reaction with tetrafluoroethene increases the basic structure by two additional C atoms. One of these products is, for example, Capstone® 4-I (per-fluorobutyl iodide). The chain structure can be terminated by a reaction with ethene; this leads to the perfluoroalkylethyl iodides (general formula: $C_mF_{2m+1}(CH_2)_2I$), which are used as starting substances in the synthesis of fluortelomer alcohols (hydroxylation), sulfonates (after reaction with potassium thiocyanate), and carboxylates (Fricke and Lahl, 2005).

Figure 2   Telomerization

$$CF_2=CF_2$$

$$\downarrow \quad I_2, IF_5$$

$$F\text{-}(CF_2)_2\text{-}I$$

$$\downarrow \quad (n\text{-}2)/2\ CF_2=CF_2$$

$$F\text{-}(CF_2)_n\text{-}I$$

$$\downarrow \quad CH_2=CH_2$$

$$CF_3\text{-}(CF_2)_{n\text{-}1}\text{-}CH_2CH_2I$$

$$\downarrow$$

$$CF_3\text{-}(CF_2)_{n\text{-}1}\text{-}CH_2CH_2OH$$
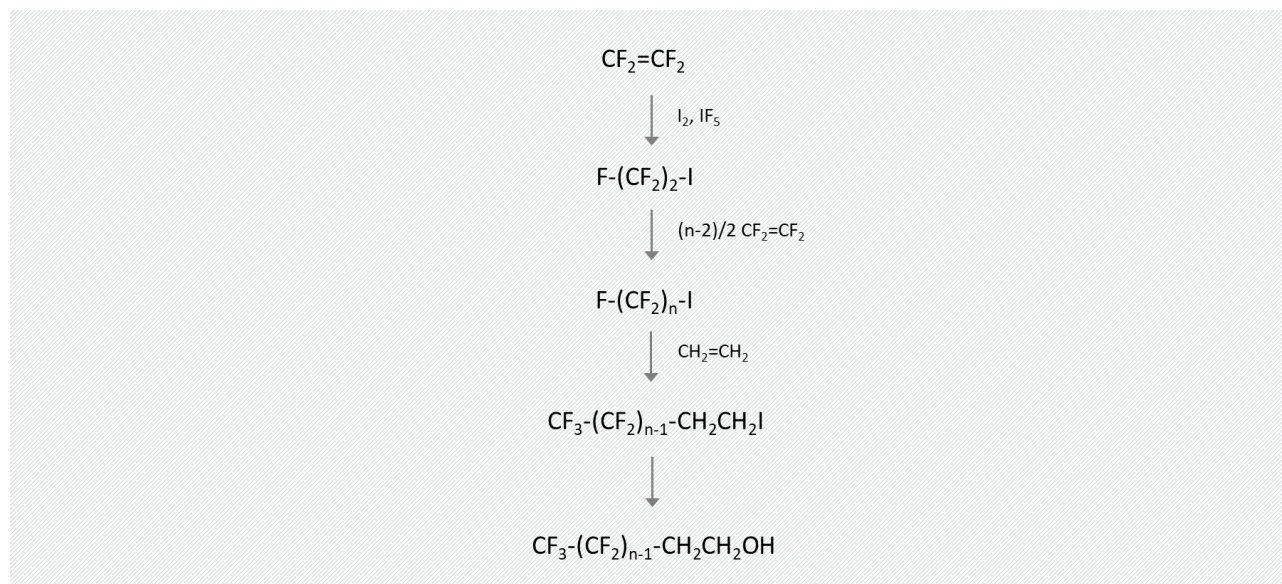
Source: Buck et al., 2011

Fluorine telomerization produces only linear molecules. In addition to the target molecule, however, several shorter or longer-chain compounds are always formed, which are removed as far as possible in a purification step. Branched or odd-numbered molecule lengths can, if desired, be synthesized by selecting starting products other than tetrafluoroethene, but are rather uncommon.

The number of PFAS known to date is very large; the OECD published a compilation of 1,070 PFAS in 2007 (OECD, 2007). However, the actual number of compounds used in industry is likely to exceed this figure. Currently, it is assumed that there are about 5,000 compounds produced.

PFAS production began in the 1950s (3M, DuPont), but more extensive use of the chemicals in industry did not occur until years later, from the early 1970s onwards. The following companies are considered the most important producers of polyfluorinated substances: DuPont, 3M/Dyneon, Clariant, Bayer, Ciba Speciality Chemicals, Daikin, Arkema, AGC Chemicals/Asahi Glass, Solvay Solexis and BASF SE (Danish Ministry of the Environment, 2008; 2010/2015 PFOA Stewardship Program).

PFAS Production (Summary)

There are two processes for the industrial production of poly- and perfluorinated compounds: Electrochemical fluorination (ECF) and fluorine telomerization. While ECF leads not only to linear but also to branched molecules, the more modern telomerisation, which has been mainly used later on, has a higher product yield and less by-product formation. The production of PFAS started in the 1950s, but it was not until about the beginning of the 1970s that the chemicals were used more extensively on an industrial scale.
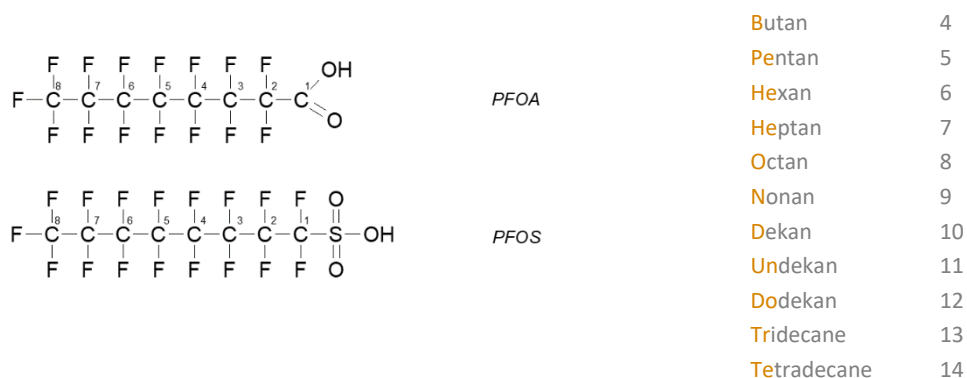
2 Overview of Substance Groups (Nomenclature)

The PFAS[1] (poly- and perfluorinated alkyl substances) comprise a large group of about 5,000 chemical substances (KEMI, 2015; Wang et al., 2017), each of which contains the common structural element of one or more fully fluorinated alkyl groups (referred to as perfluoroalkyl group) (C_nF_{2n+1}) (Buck et al., 2011). The whole PFAS molecule may be either partially (poly)- or fully (per)-fluorinated. However, each compound always contains a perfluoroalkyl group. The polyfluorinated PFAS are often referred to as **precursors** because they can be biotransformed microbially to the very perresistant perfluorinated compounds.

The nomenclature described below was published by Buck et al (2011). Because there is a high number of different PFAS compounds, it is not surprising that from time to time new classes of compounds are discovered in products and environmental samples. In this respect, a substance group overview can only ever be provisional.

The most prominent compounds are the perfluoroalkanoic acids (PFAA), which are subdivided into perfluoroalkane sulfonic acids (PFSA) such as PFOS and perfluoroalkane carboxylic acids (PFCA) such as PFOA.

In the nomenclature, the substance classes (carboxylic acid or sulfonic acid) are indicated at the end with "A" or "S", where A stands for acid and S for sulphonic acid. The third (or fourth) letter stands for the chain length (Figure 3, Figure 4). For example, in PFOA the "O" (octane) stands for the chain length of 8 carbon atoms.

Figure 3   Structural formula of PFOA and PFOS[2]

Butan	4
Pentan	5
Hexan	6
Heptan	7
Octan	8
Nonan	9
Dekan	10
Undekan	11
Dodekan	12
Tridecane	13
Tetradecane	14

It should be noted that in PFOS all 8 C atoms are perfluorinated, whereas in PFOA this is the case only for 7 C atoms, the 8th C atom is required for the formation of the carboxylic acid.

Regarding the chain length, the OECD (2014) divides PFAS into long-chain and short-chain compounds. The distinction was made because long-chain compounds are more toxic. It is unclear whether this "sharp" subdivision will prove useful as knowledge of toxicological effects increases. Long-chain compounds are, according to the OECD definition:

► Perfluorocarboxylic acids with a chain length ≥ C8 (e.g. PFOA),
► Perfluorosulfonic acids with a chain length ≥ C6 (e.g. PFHxS and PFOS),
► Precursor of perfluorocarboxylic and perfluorosulfonic acids

---

[1] Often referred to as PFC (poly- and perfluorinated chemicals).

[2] The acids are dissociated or present in salt form under environmental conditions; they are then called carboxylates and sulfonates.

Figure 4   Isomers of PFOS (linear and branched)
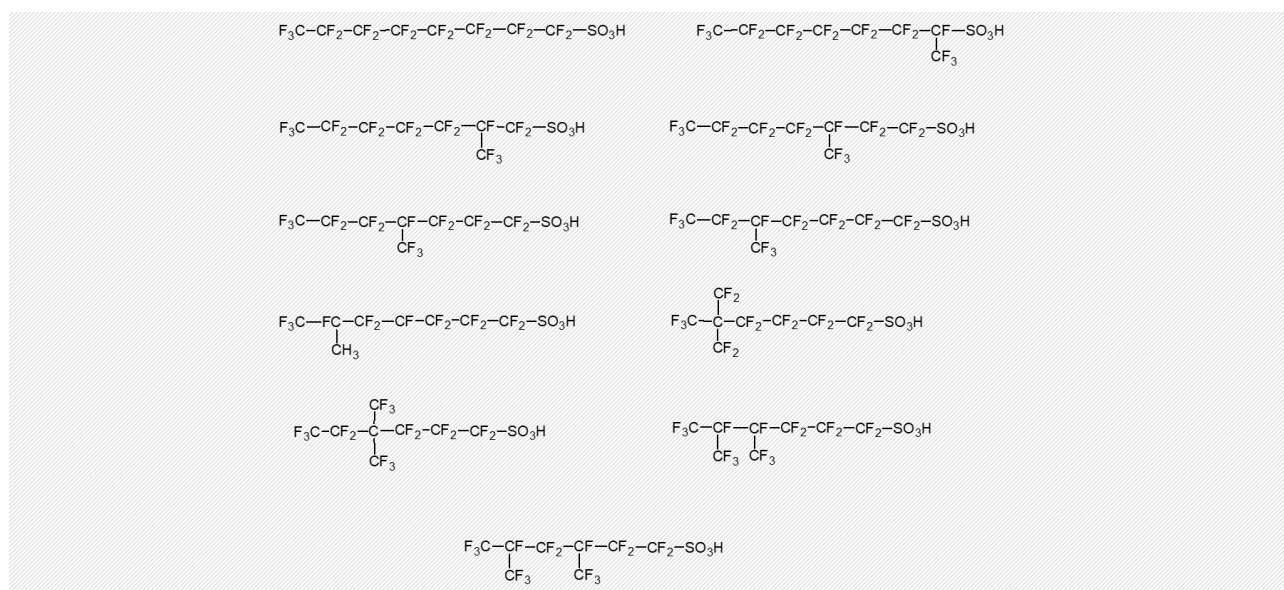
Source: NRW, 2011; Guo et al., 2009

Both substance classes, perfluoroalkane carboxylic and perfluoroalkane sulfonic acids, with chain lengths usually between 2 and 18 carbon atoms, are also called perfluorinated surfactants from a chain length of C_4. Various salts can be formed from PFOA ($F(CF_2)_7COO^-$) or PFOS ($F(CF_2)_8SO_3^-$) (Buck, 2011):

► $(F(CF_2)_7CO_2^-Y^+$ or

► $F(CF_2)_8SO_3^-Y^+$

where Y^+ represents the counter ion, for example with Y^+ =

► M^+ Metal salt,

► NH_4^+ Ammonium salt (e.g. APFO).

From the perfluorinated sulfonyl and carbonyl fluorides further compounds can be derivatized with Y =

► NR_2 Amid,

► R   Alkyl ester.

Electrochemical fluorination produces not only linear, but above all branched molecules (Figure 4).

Before the beginning of the 2000s, perfluorooctylsulfonyl fluoride (PFOSF) ($F(CF_2)_8SO_2F$) was the main starting substrate to produce a number of chemicals. Already in the presence of water, PFOSF hydrolyses to PFOS. By derivatization, for example, the compounds shown in Table 1 can be synthesized.

Table 1   Major derivatives of PFOSF

Substance Group	General Structural Formula	Chain length
Perfluoroalkylsulfonamides	$F(CF_2)_8SO_2NR^1R^2$	with R^1 and R^2 as alkyl groups of different lengths
Sulfonamide alcohols	$F(CF_2)_8SO_2N(C_nH_{2n+1})CH_2CH_2OH$	with n = 1 or 2
Sulfonamide acrylates	$F(CF_2)_8SO_2N(C_nH_{2n+1})CH_2CH_2OC(O)CH=CH_2$	with n = 1 or 2

The most important PFAS compound classes are summarized in Table 2 (Buck et al., 2011; Wang et al., 2013).

Table 2   Structure of the main chemical groups

Substance Group	Abbrevia-tion	General Structural Formula	Chain length
Perfluorinated alkanoic acids			
Perfluorinated carboxylic acids	PFCA	$F(CF_2)_xCOOH$	x = 2, 3, 4, …
Perfluorinated sulfonic acids	PFSA	$F(CF_2)_x\text{-}SO_3H$	x = 2, 3, 4, …
Perfluoroalkylsulfinic acids	PFSiA	$F(CF_2)_x\text{-}S(OH)O$	x = 4, 6, 8, …
Perfluorinated phosphoric acids	PFPA	$F(CF_2)_xPO(OH)_2$	x = 4, 6, 8, …
Perfluoroalkylphosphinic acids	PFPiA	$F(CF_2)_xPO(OH)(CF_2)_yCF_3$	x, y = 6, 8
Precursor			
Fluorotelomer alcohols	FTOH	$F(CF_2)_xCH_2CH_2OH$	x = 2, 4, 6, …
Fluorotelomer olefins	FTO	$F(CF_2)_xCH=CH_2$	x = 4, 6, 8, …
Fluorotelomer sulphonic acids	FTS	$F(CF_2)_xCH_2CH_2SO_3H$	x = 2, 4, 6, …
Fluorotelomer iodides	FTI	$F(CF_2)_xCH_2CH_2I$	x = 4, 6, 8, …
Perfluoroalkyl iodides	PFAI	$F(CF_2)_xI$	x = 4, 5, 6, …
Perfluoroalkylsulfonamides	FASA	$F(CF_2)_xSO_2NH_2$	x = 4, 5, 6, …
N-methyl perfluoroalkane sulfona-mides	MeFASA	$F(CF_2)_xSO_2NH(CH_3)$	x = 4, 5, 6, …
N-ethyl perfluoroalkane sulphona-mides	EtFASA	$F(CF_2)_xSO_2NHCH_2CH_3$	x = 4, 5, 6, …
Perfluoroalkylsulfonamidethanols	FASE	$F(CF_2)_xSO_2NHCH_2CH_2OH$	x = 4, 5, 6, …
N-methyl perfluoroalkanesulfonami-de ethanols	MeFASE	$F(CF_2)_xSO_2N(CH_3)CH_2CH_2OH,$	x = 3, 4, 5 …
N-Ethyl-Perfluoralkansulfonamid-ethanole	EtFASE	$F(CF_2)_xSO_2N(C_2H_5)CH_2CH_2OH$	x = 2, 3, 4 …
Fluorotelomer phosphate monoester	monoPAP	$F(CF_2)_xCH_2CH_2OP(O)(OH)_2$	x = 4, 6, 8, …
Fluortelomer phosphate diesters	diPAP	$F(CF_2)_xCH_2CH_2OP(OH)OCH_2CH_2(CF_2)_yF$	x = 4, 6, 8, …
Intermediates of biotransformation (see Chapter 6)			

Substance Group	Abbrevia-tion	General Structural Formula	Chain length
Fluorotelomercarboxylic acid	FTCA	$F(CF_2)_xCH_2COOH$	x = 2, 4, 6, …
Fluorotelomer unsaturated carboxylic acids	FTUCA	$F(CF_2)_xCF=CHCOOH$	x = 1, 3, 5, …
Fluoroelomeraldehyd	FTAL	$F(CF_2)_xCH2CHO$	x = 2, 4, 6, …
Fluorotelomer unsaturated aldehydes	FTUAL	$F(CF_2)_xCF=CHCHO$	x = 3, 5, 7, …
Perfluorinated aldehydes	PFAL	$F(CF_2)_xCHO$	x = 4, 5, 6, …

The non-fluorinated residue of the precursors can be negatively (anionically) charged (carboxylates, sulfonates, phosphates), positively (cationically) charged (quaternary ammonium compounds) or neutral (sulfonamides) (Figure 5).

Figure 5   Examples of differently charged precursors

Fluorotelomer alcohols (FTOH) represent an important group. They belong to the polyfluorinated compounds. FTOH consist of an even numbered chain of perfluorinated carbon atoms with a terminal ethanol group. FTOH are usually unbranched, contain an even number of carbon atoms and do not dissociate. The reason for the lack of branching is that the substances or the starting products were produced by fluorine telomerization. The general molecular formula of FTOH is $F(CF_2)_{2n}CH_2CH_2OH$. The designation of the fluorotelomer alcohols is based on the "X:Y FTOH" system. Here X denotes the number of perfluorinated and Y the number of non-fluorinated carbon atoms. The most important representative of the fluorotelomer alcohols is 8:2 FTOH (Figure 6).

Figure 6   Structure of 8:2 FTOH

Starting from FTOH, a large number of compounds can be produced, which are then also called fluortelomer-based compounds. Examples are perfluoroalkylbetaines[3], which are increasingly used in modern fire fighting foams.

Polyfluorinated alkyl phosphates (PAP) also belong to the group of telomer compounds. PAPs can occur as monoesters (monoPAP), diesters (diPAP) and triesters (triPAP). Industrial PAP mixtures consist mainly of diPAPs, monoPAPs and triPAPs. The nomenclature for PAP, similar to FTOH, is based on the number of perfluorinated carbon atoms in relation to the fluorine-free hydrocarbon bonds in the molecule. diPAPs with two perfluorinated carbon chains of different lengths are represented by the nomenclature x:2/y:2 diPAP; this is shown in Figure 7.

Figure 7   Structural formula of x:2/y:2 diPAP
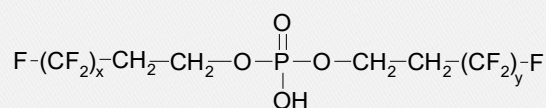
In addition to precursors, which can be biotransformed into analytically detectable compounds (Chapter 6), so-called non-precursors have been increasingly used in the recent past. Examples are GenX (ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate, CAS no. 62037-80-3) (Wang et al., 2013) and ADONA (ammonium 4,8-dioxa-3H-perfluoronanoate, CAS no. 958445-44-8) (Gordon, 2011) (Figure 8). Both compounds are polyfluoropolyether carboxylates. It can be assumed that the ether bond (oxygen bridge between two carbon atoms) is as stable as the CF_2-CF_2 bond. The substance Novec 1230 used in fire-fighting foams is also a non-precursor.

Figure 8   Structural formulae of Gen X, ADONA and Novec 1230 (from left to right)
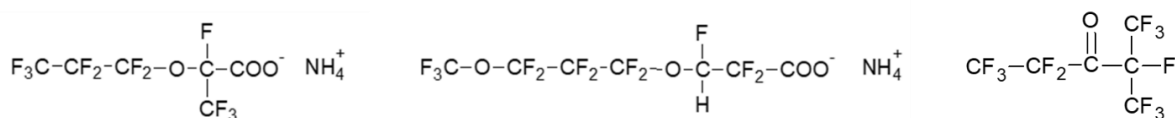
The non-precursors are mainly used as substitutes for PFAS, which are now regulated. For example, ADONA serves as a substitute for PFOA (Wang et al., 2017).

Recent studies have identified a number of other PFAS compounds (Baduel et al., 2017; Barzen-Hanson and Field, 2015). In this context, the ultra-short chain perfluoroalkanesulfonates seem to be particularly important:[4]

- ► Perfluoroethanesulfonates   (PFEtS)   (C_2)
- ► Perfluoropropane sulfonates   (PFPrS)   (C_3)

These were detected in five investigated fire extinguishing foams in concentrations of max. 13 mg/L (PFEtS) and 270 mg/L (PFPrS). In groundwater these compounds were already found in the double-digit µg/L range (Barzen-Hanson and Field, 2015). It cannot be excluded that the ultra-short chain compounds are formed as by-products in the production process (ECF). It can be assumed that these compounds do not show any sorption.

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[3]   Betaines are a quaternary ammonium compound (see Figure 5).

[4]   Analytical detection method: Liquid chromatography with quadrupole time-of-flight mass spectrometry without enrichment/purification steps (LC-QTOF-MS/MS).

Ericson Jogsten and Yeung (2017) showed that both compounds can be detected in comparatively high concentrations in the groundwater of Swedish airports and electroplating plants.

Baduel et al. (2017) have investigated extracts of concrete from a fire training pit and found 12 different classes of PFAS, including previously unknown classes such as:

► Chlorinated perfluoroalkylsulphonates $\quad$ $C_nF_{2n}Cl\text{-}SO_3^-$ / $C_nF_{2n-1}Cl_2\text{-}SO_3^-$

► Perfluoroalkene sulfonates $\quad$ $C_nF_{2n-1}SO_3^-$

► Ketone perfluoroalkylsulphonates $\quad$ $C_nF_{2n-1}SO_4^-$

In a study by Barzen-Hanson et al. (2017) as much as 40 PFAS classes were detected in groundwater affected by fire extinguishing foams. The occurrence of PFAS containing chlorine was confirmed. The most likely structure of one of these chlorine-containing compounds is shown in Figure 9.

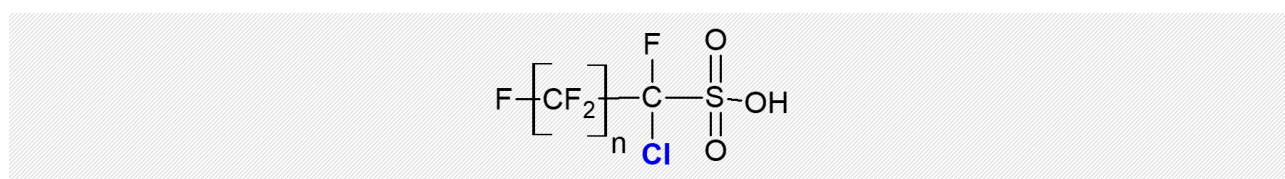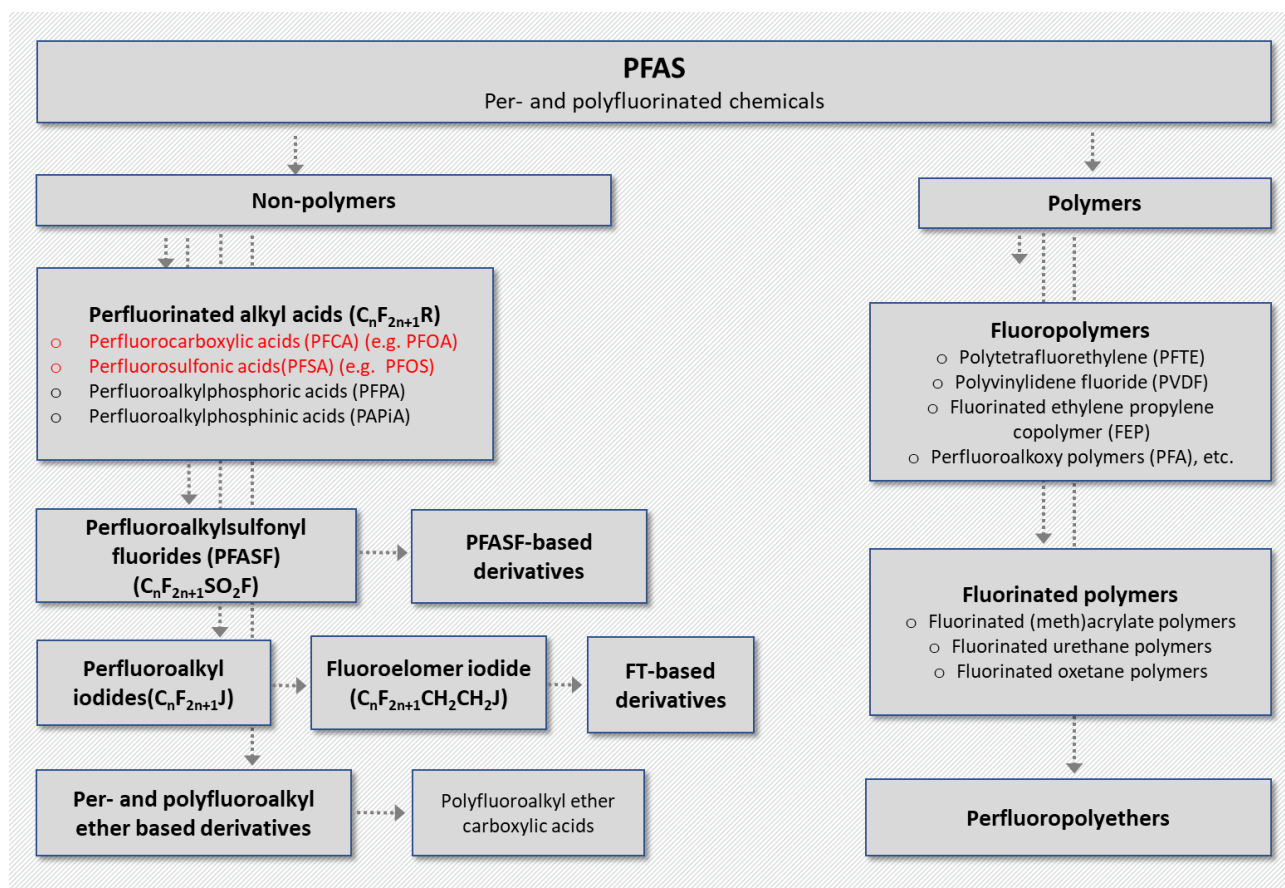Figure 9 $\qquad$ Structural formula of a chloro-perfluoro alkane sulfonate

Figure 10 $\qquad$ Classification of the PFAS

Source: Gellrich, 2014; Knepper et al., 2014

Furthermore, the presence of 2H-perfluorocarboxylic acids ($F(CF_2)_n$-CH_2-COOH) of different chain lengths (n = 3...16) was detected by means of non-target analysis on highly contaminated samples.

In addition to single molecules, polymers (e.g. Teflon: polytetrafluoroethylene; PTFE) also belong to the PFAS (Teng, 2012). Some fluorinated polymers, such as certain fluorinated polyacrylates (also known as fluorocarbon resins), are used for water and soil-repellent treatment of textiles. Neither PFOA nor PFOS are used in the production of these polymers. A summary classification of PFAS is shown in Figure 10.

Overview of the groups of substances and their nomenclature (Summary)

PFAS (poly- and perfluorinated alkyl substances) comprise about 5,000 chemical substances. The perfluorinated compounds can be divided into two classes: perfluorocarboxylic acids and perfluorosulfonic acids. The most important representatives of these two classes are PFOA and PFOS. The so-called precursors (precursor substances to perfluorinated compounds) have one or more non-fluorinated molecular residues of different sizes in addition to the perfluorinated chain of different lengths. The precursors can be non-ionic, anionic, cationic or zwitterionic in the neutral pH range. PFAS are also starting substances to produce polymers with Teflon as the most well-known product. Within polymers there are also numerous different classes of molecules.

3 PFOS/PFOA Substitutes

With the ban, phasing out of production and use of long-chain PFAS such as PFOA and PFOS, fluoro-chemical producers have switched their production to PFAS with shorter chains (e.g. perfluorocarbox-ylic acids with the chain length ≤ 6) and fluorinated substitutes such as GenX, ADONA and 9F53-B10 (Kemi, 2015; Wang et al., 2013). Many of these are perfluoroalkylether acids (PFEA) (C-O-C compounds), which are presumably as stable as the perfluorinated carbon chains (Figure 11).

Figure 11   Fluorinated substitutes in various industrial sectors
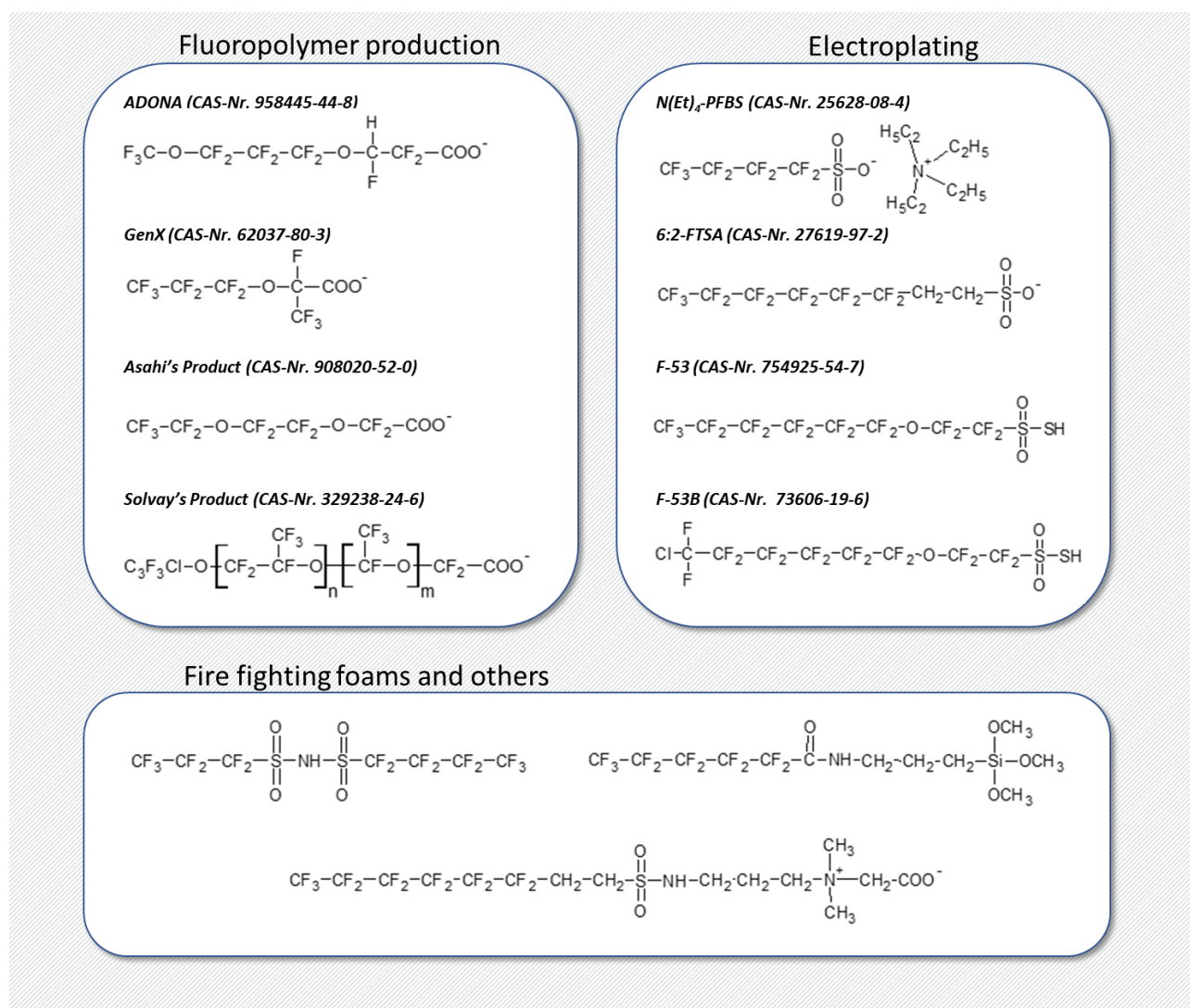
Source: Wang et al., 2013

ADONA has been used as a substitute product (processing aid) for PFOA since 2008. Based on the knowledge available to date on ADONA, a significantly more favourable toxicological profile than PFOA and PFOS must be assumed. Negative health effects, including long-term effects, are therefore not to be expected according to the current state of knowledge (Fromme et al., 2016).

GenX, as a substitute for PFOA, is apparently used quite frequently worldwide. It could be detected in a study of rivers in three countries (Germany: 108 ng/L, Netherlands: 91.5 ng/L, China: 3,830 ng/L). Detailed investigations of the Rhine near a fluorochemical production plant in the Netherlands revealed a maximum GenX concentration of 812 ng/L at the first sampling point downstream of the production plant (Gebbink et al., 2017).

In the US, GenX has been detected in drinking water supplied to the population at concentrations above the health orientation value (Hopkins et al., 2018).

GenX is the trade name for the ammonium salt of hexafluoropropylene oxide dimeric acid (HFPO-DA). GenX serves as a substitute for ammonium perfluorooctanoate, the ammonium salt of PFOA, and is used as a processing aid in the manufacture of fluoropolymers such as polytetrafluoroethylene (PTFE). GenX is also named as

► HFPO-DA (2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid) (CAS-13252-13-6) or

► (Ammonium) FRD-902 / FRD-903 (CAS-62037-80-3)

Since all compounds dissociate at neutral pH, only the anion is detected in the environment, as it is the case for most PFAS.

Figure 12   Ethercarboxylic acids as by-products of GenX production
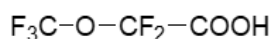
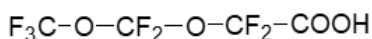| *Monoether carboxylic acids*	Example:
$F_3C-O-CF_2-COOH$	perfluoro-2-methoxyacetic acid (PFMOAA)
	$(C_3HF_5O_3)$
	Molecular weight: 180,0
	CAS-Nr. 674-13-5
Multiether carboxylic acids	Example:
$F_3C-O-CF_2-O-CF_2-COOH$	perfluoro-2-dioxahexanoic acid (PFO2HxA)
	Molecular weight: 246,0
	$(C_4HF_7O_4)$
	CAS-Nr. 39492-88-1-5
Multiether sulphonic acids	Example:
	Ethanesulfonic acid, 2-[1-[diflouro[(1,2,2-trifluoroethylene)-oxy]methyl]-1,2,2,2-tretafluoroethoxy]-1,2,2-tetrafluoro (Naphion by-product 1)
	$(C_7HF_{13}O_5S)$
	Molecular weight: 443,9
	CAS-Nr. 29311-67-9
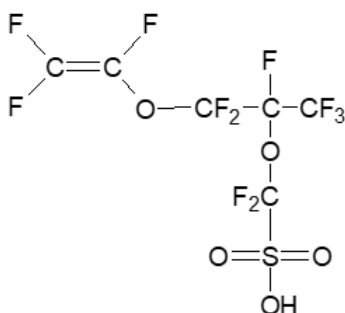
Source: Wang et al., 2013

While physicochemical parameters have been determined for the industrial products (acid, salts), almost no data are available for the anion. From the data it can be deduced that GenX is already completely dissociated at very low pH values, it is very soluble and hardly binds to the soil matrix. Like all perfluorinated compounds, GenX is not degradable. Overall, it exhibits high mobility in the aquifer (Hopkins et al., 2018).

The investigation of a highly polluted site in the USA revealed a number of other compounds that fall into the following three classes:

► Monoether carboxylic acids (C_{3-6}),

► Multiethercarboxylic acids (with up to four ether oxygen atoms),

► Multiethersulfonic acids.

Examples of these three groups are shown in Figure 12. It is assumed that these compounds are by-products of the production of GenX and Nafion[5] membranes.

Analytical standards for the analysis of GenX are available, but not for the compounds shown in Figure 12.

PFOS/PFOA Substitutes (Summary)

With the ban, the phasing out of production and use of long-chain PFAS such as PFOA and PFOS, manu-facturers have switched their production to PFAS with shorter chains (e.g. PFAA ≤C 6) and to fluorinated substitutes such as GenX and ADONA. The latter belong to the perfluoroalkylether acids (PFEA). There are also several other industrially used perfluoroalkyl ethers, such as perfluoroalkyl ether sulphonates.

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4 Analytical Detection

4.1 Sampling and Sample Preparation

The two German analytical standards for PFAS (DIN 38407-42 and DIN 38414-14) prescribe relatively little for sampling. However, because PFAS are present in many household products and in view of the low detection limits of PFAS analytic methods, there is a general that cross-contamination may occur during sampling. As a consequence, some international organisations have developed sampling regula-tions that have a very wide impact on the behaviour of the samplers (Table 3) (Environmental Scienc-es Group, 2015; NGWA, 2017; Transport Canada, 2016; MTM Research Centre, 2017). To be on the safe side, field personnel are advised to observe these regulations. In addition, the following measures should be taken:

► Change nitrile gloves frequently.

► Regular cleaning of the equipment used. All sampling equipment including multi-phase meter and groundwater leveling devices used at the sampling points should be cleaned between each sampling. Soaps that according to the relevant safety data sheets do not contain fluorine sur-factants are suitable for cleaning. The water used to decontaminate the sampling devices must have been declared "PFAS-free" by the laboratory.

► Larger equipment (e.g. drilling equipment) should first be cleaned with potable water under high pressure and then rinsed again.

Groundwater. According to the two PFAS analytical standards, methanol-cleaned and dried polypro-pylene centrifuge tubes (50 ml) [6] with polypropylene screw cap are suitable for water sampling. Glass bottles with suitable caps are approved by the standardised procedure (Chapter 4.2).

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[5] Nafion is a perfluorinated copolymer containing a sulfonic group as the ionic group. It was developed in the late 1960s as a modification of Teflon. Nafion belongs to the ionomers and it is a registered trademark.

A study carried out in 2019 (Woudneh et al., 2019) showed that not only glass but also HDPE sorb PFAS (although most official international guidelines require HDPE vessels). Therefore, the entire content of the sampling bottle should be processed.

The sampling container should be completely filled with the water sample and stored at +4 °C until further sample processing (not later than 14 days after sampling). A prolonged storage time may lead to losses due to increased adsorption of the PFAS to the sampling container wall. An additional 5 Vol.-% methanol to the sample reduces losses due to sorption. However, the dilution caused by this must be considered when evaluating the results. Furthermore, it could be shown that even at +4 °C an aerobic microbial transformation of the (partly commercially analyzed) precursors occured during sample storage (Woudneh et al., 2019). It is therefore recommended to preserve the sample by suppressing the microbial activity, for example, with sodium azide. It still must be checked whether this inactivation of the microbial activity interferes with subsequent preparation and analysis.

The two analytical standards do not prescribe the avoidance of exposure of the samples to sunlight. However, since some polyfluorinated PFAS can be photocatalytically converted, exposure to sunlight should be avoided by using brown-coloured sampling vessels.

In the presence of highly volatile substances (e.g. FTOH), air-tight sampling vessels should be used, and in case of water samples these should be filled completely without including gas phase (no bubbles) and sealed air-tight. Storage must be at +4 °C. Investigations have shown that 10 % loss due to storage can be expected after 24 h (Bavarian State Office for the Environment, 2012). If possible, the sampling containers should only be opened once, and the sample should be processed quickly.

Recent systematic studies (Denly et al., 2019) have used leaching tests (24 h, drinking water) to verify the extent to which the strict requirements given in Table 3 are necessary. Many materials (including aluminium foil, clay plugs, adhesive notes, bubble wrap, passive diffusion bags, PVC, certain tapes of groundwater level measuring devices, resealable plastic storage bags, silicone tubing and HDPE) did not elute PFAS. Other materials including field books (cover and pages), sample labels, nitrile gloves and PTFE (polytetrafluoroethylene) eluted PFAS. With a few exceptions (e.g. sampling tubes, material for well completion), the contact time between sampling equipment and sample is very short in classical groundwater sampling, so that the risk of cross-contamination is low, especially at high-yielding groundwater measuring points. However, caution is required, for example, when using passive samplers.

Soil. Soil samples are obtained by means of a ram core probe or liners and filled into methanol-rinsed wide-necked sampling containers with a screw cap and gaskets made of polyethylene. The edges of the vessels must be checked for particles before closing.

The required sample quantity depends on the particle size and must be sufficiently large to ensure laboratory analysis after sample pretreatment and, if necessary, the storage of backup samples.

Sampling for diffuse sources (e.g. wide-spread deposits in agriculture; based on the sampling scheme for agriculturally used areas; Barth et al., 2000) differs from sampling of point sources. As a rule, mixed samples are taken from several punctures within an area of a defined size.

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6   As a rule, 0.5 litre sample is taken.

For soil samples containing volatile PFAS, it is advisable to store them in screw-cap jars and to cover them with methanol after sampling (corresponding to the conservation of soil samples contaminated with volatile organic compounds). However, this method is not yet validated for PFAS.

Table 3   Overview of non-permissible and permissible objects in the PFAS sampling[7]

Non-permitted items	Permitted items
Equipment, field work	
Materials containing Teflon® (tubes, bailers, adhesive tapes, sanitary adhesives	Materials of polyethylene (HDPE) or silicone (also fluoride-free, suitable for AOF analysis)
Storage of samples in LDPE containers	Acetate liner (direct-push method), silicone piping
Waterproof notepads	Loose paper sheets
Plastic clipboards, fixed folders	Wood fibre or aluminium clipboards
Spiral blocks	Ballpoint pen
Eddings® and felt tip pens	Loose paper sheets
Post-It sticky notes	"Regular" ice
Clothing and personal protective equipment	
Clothing or water-repellent, waterproof or stain-resistant clothing containing Gore-Tex™	Clothing washed multiple times made of synthetic and natural fibres (preferably cotton)
Clothing treated with fabric softener	Clothing without the use of fabric softener
Gore-Tex™ shoes or jackets	Shoes containing polyurethane and polyvinyl chloride (PVC)
Tyvek®-Overalls	Cotton clothing
Cosmetics, moisturisers, hand creams or similar products in the morning of sampling for personal care/shower	Sun creams and insect sprays which have been shown not to contain PFAS.
Sampling container	
Container made of LDPE or glass	Container made of HDPE or polypropylene
Sealing caps with Teflon®	Uncoated polypropylene sealing caps
Rainfall	
Waterproof or water repellent rainwear	Rainwear made of PU and waxed materials. PFAS-free pavilion, which is only touched or moved before or after the sampling
Decontamination of equipment	
Decon 90	Alconox® and/or Liquinox®
Water from a well in the study area	Drinking water from the local supplier
Food	
All food and beverages (exceptions are listed in the right column)	Bottled water and isotonic drinks may only be taken and consumed in the lounge area

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[7]   Even if some of the requirements appear to be difficult to implement in practice, they have nevertheless been included here, particularly to identify possibilities for cross-contamination.

Eluate. The elutability of the PFAS from soil or other solid samples can be tested by the column method according to DIN 19528 or by shaking methods. However, the shaking method with a water/solid ratio of 2:1 according to DIN 19529 is generally recommended.

The DIN-compliant eluate preparation allows for a wide range of decisions depending on the laboratory equipment and the behaviour of the sample during preparation. It would therefore make sense for the future to establish clear instructions based on DIN for the preparation of eluates for PFAS analysis.

Soil Vapor. In principle, volatile telomer alcohols can also occur in soil vapor. Investigations on the relevance of PFAS in soil vapor or even protocols for taking soil air samples are not yet available. A sampling procedure is described for outdoor and indoor air, which can be adapted for soil vapor sampling if necessary. In this method, perfluoroalkane acids are sorbed onto polyurethane foams (PU) in stainless steel cartridges over methanol-rinsed glass fibre filters heated at 500 °C for 2 hours in a low-flow process. The filters are then eluted in the laboratory (Bayerisches Landesamt für Umwelt, 2012). Volatile compounds can also be sorbed on C_{18} solid phase extraction cartridges (SPE) or XAD-2 resins. Both sorbents have been shown to be highly effective in sampling volatile and semi-volatile PFAS from the air (Liu and Avendaño, 2013; Jahnke et al., 2007). Furthermore, PU foams are also suitable for the sorption of fluortelomer alcohols.

Using extraction with methanol and subsequent GC-PCI-MS analysis, determination limits of 0.2 - 2.5 pg/m^3 could be achieved depending on the PFAS compound investigated.

In the atmosphere, PFOA, PFOS, their homologues and probably also the majority of the more volatile PFAS are present (due to their high tendency to bind to soil) in particle-bound form. During air sampling, these particles are mainly retained on the glass fibre filter usually used. Therefore, an analysis of the filter is essential. As less strongly sorbing PFAS compounds are quickly desorbed from the particles, a comparatively short sampling time is recommended. Otherwise, the PU foam must also be extracted and analysed. According to the Bayerischen Landesamt für Umwelt (2010), the analysis of the glass fiber filter is sufficient for the determination of ≥ C7-perfluoroalkane carboxylic acids and the perfluoroalkane sulfonic acids.

Sample preparation. For soil samples the PFAS are extracted with methanol from the dry homogenized sample by ultrasonic assisted extraction. Samples with a higher water content (sediments, sewage sludge) should preferably be dried by freeze-drying. Alternatively, drying can also be carried out at 40 °C (more time required).

For homogenization, the dry sample is ground with an analytical mill to such an extent that 95 % of the ground material can pass through a 250 μm mesh sieve. Under these conditions homogeneous test samples are obtained from which representative subsamples are taken for analysis. To achieve the highest possible yield from extraction with methanol, ultrasonic treatment (1 h, 40 °C) is used. The supernatant (extract) is removed. It should be noted that prolonged digestion in the ball mill can lead to reduced PFAS results.

To analyze the non-polar PFAS, the water samples are subjected to liquid-liquid extraction with MTBE during sample preparation. The extract is dried with sodium sulfate and concentrated in a rotary evaporator at 40 °C and 400 mbar with acceptable losses (Bayerisches Landesamt für Umwelt, 2012). When telomeric acids are concentrated, the washing step is usually omitted because the losses are too high.

Biological tissue is extracted with a dichloromethane/methanol mixture. Plant extracts require a subsequent purification step to reduce the matrix effects (Jahnke et al., 2007). Other studies exclusively used methanol as an extraction agent (Theobald et al., 2007).

QA/QC. In order to ensure and control quality, in addition to appropriate sampling, the corresponding sample labels (chain of custody) must be generated, checked and documented completely.

Due to the high risk of cross-contamination, the analysis of quality control samples is particularly recommended for PFAS:

- ► *Background sample.* A background sample (usually a random sample) is taken from an area, water body or similar location compared to the site under investigation, but is located in an area that has been shown to be free of PFAS contamination attributable to a known input.

- ► *Washing water.* Washing water resulting from the decontamination of equipment is collected and analysed at the end of the decontamination process (once a day).

- ► *Double field sample.* When sampling, the double volume is first collected. After mixing, the material is divided into two sets of containers (split sample). Both sets of containers are submitted for analysis, one set is called the original sample and the other is called the partial sample. For large studies (more than 20 samples), approximately 5 % of all samples shall be taken as duplicate samples.

4.2 Standarized Methods (Overview)

For the analysis of polar poly- and perfluorinated compounds the following German DIN methods can be applied:

- ► Water samples: DIN 38407-42:2011-03 (F 42) Determination of selected polyfluorinated compounds (PFAS) in water - Method using high-performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS) after solid-liquid extraction (F42)[8].

- ► Soil: DIN 38414-14 (S14) German standard method for the analysis of water, waste water and sludge - Sludge and sediments (Group S) - Part 14: Determination of selected polyfluorinated compounds (PFAS) in sludge, compost and soil - Methods using high-performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS) (S14)[9].

The S14 method is suitable for analysis of sediment, sewage sludge, compost, and soil. The general analysis procedure of both methods is shown in Figure 13.

The method according to DIN 38407-42 is divided into three steps: SPE enrichment, HPLC separation and MS-MS detection. It is designed for the analysis of polar, lowly concentrated contaminants. In solid-liquid extraction (SPE, Solid Phase Extraction), the choice of the solid phase (here: anion exchanger) restricts the analysis to polar positively charged substances that bind to the anion exchanger and that are not volatile. The SPE is used for the selection, concentration of PFAS, and removal of interfering components. Other perfluorocompounds that do not contain an acid group in the molecule, such as perfluorooctane sulfonamide (PFOSA) and fluorine telomers, cannot be detected by this method if an an ion exchanger is used for enrichment. These compounds can only be analyzed from the non-concentrated solution.

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[8] Validation document for DIN 38407-42, October 2011.

[9] Validation document for DIN 38414-14, October 2011.

Figure 13   Analysis procedure according to DIN 38407-14 and DIN 38407-42 (IS: internal standard)
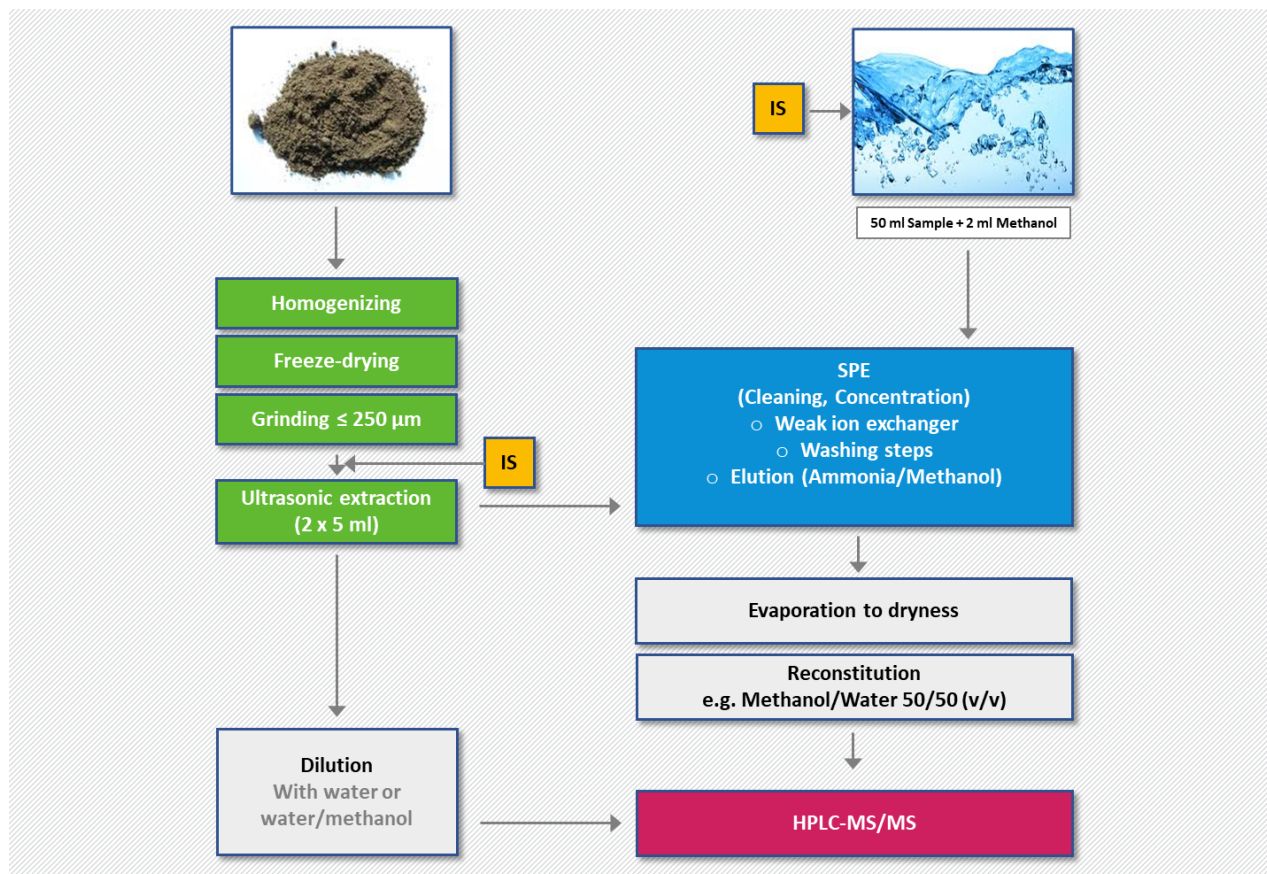
Soure: Lange., 2014, modified

According to DIN 38414-14 colourless and clear soil extracts or according to DIN 38407-42 highly concentrated water samples can be analysed without further cleaning and after appropriate dilution. If significant matrix influences of the sample are detected, the samples must be cleaned by SPE. The applicability of the standardised analytical method to other types of water, e.g. untreated wastewater, is not excluded, but must be checked in each individual case. The same applies to the analysis of solids. Also, in this case, the method is not excluded for other types of sample, e.g. fertilisers, but must be tested in each individual case. In combination with the solid phase extraction, the procedure can basically be extended to substances which have a polar functional group in the molecule, e.g. the substances PFUnA, PFDoA, PFHpS, PFDoS and H4PFOS.

In the analysis, losses of the analytes occur at different steps of the analysis. The "recovery rate" is therefore sometimes significantly lower than 100 %. Especially when analysing soils, the recovery rate also varies greatly from soil to soil. For this reason, an isotopically labelled reference standard (internal standard[10]) is usually added to the sample, e.g. $^{13}C_4$-PFBA. This means that four carbon atoms of the molecule are exchanged by the heavy ^{13}C isotope[11].

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[10] According to DIN 38407-42:2011-03 (F 42) only internal standardization is permitted for the analysis of samples. In this case, at least for the substances PFBA, PFHxA, PFOA and PFOS corresponding ^{13}C-labelled compounds must be used as internal standards. Substances for which no internal standard is used or for which no standard is available may be referred to other internal standards, provided that the recovery rates of the analytes are in the same range as those of the internal standards. However, this requirement is not always fulfilled, so that the use of other internal standards is generally recommended, especially for substances that are regularly found.

[11] As an alternative to carbon, oxygen can also be isotopically labelled. The most common ^{16}O isotope is then replaced by the heavier ^{18}O.

Both behave in the same way regarding losses during sample processing, chromatography, and ionization, but differ significantly in detection due to the different molecular weights.

The separation and quantitative determination of the PFAS is carried out by high-performance liquid chromatography coupled with mass spectrometric detection (HPLC-MS/MS). During quantification, the ratio of the area of the analyte in the sample to the corresponding internal standard is determined. According to the method standard only unbranched PFAS may be used for calibration[12]. In the evaluation, the total peak area of the linear and all branched, detected isomers of an analyte is determined by convention and evaluated by calibrating with the corresponding unbranched component.

For quantification, it is assumed that the non-linear isomers that elute immediately before the linear PFAS compound show the same response factor as the linear PFAS compound, although this is not one hundred percent the case. The analytical error is about 20 %.

This convention was agreed upon in order to be able to also consider the branched isomers in the quantification, since their proportions can be significant, especially for PFOS, and a chromatographic separation of all isomers is not possible under the conditions usually used in the analysis. In addition, the necessary pure substances for the calibration are not available for most isomers.

At present, commercial laboratories are able to analyse about 30 compounds, including the products Capstone A and Capstone B (quantification level 15 ng/l each), which are present in higher quantities in fire-fighting foams. In addition, several other polar compounds such as telomer acids (degradation metabolites of telomer alcohols) can be detected with this method (Trier et al., 2011; Bayerisches Landesamt für Umwelt, 2012). However, this has not yet found its way into commercial analyses.

In the meantime, there are also laboratories on the market that claim to be able to analyse PFAS (especially PFOS) with a limit of determination in the range of the AA-EQS (environmental quality standard, annual average) due to a higher enrichment. A detection level of 0.2 ng/L is specified for PFOS.

The analytical method can also be applied to eluates. The DIN standards do not specify how the eluate must be filtered; the regulations of the respective elution procedures apply. Most laboratories use centrifugation in glass beakers instead of filtration. The sorption to the glass beakers is balanced mathematically.

The indicated mass concentrations (in µg/L or µg/kg dry matter) are related to the respective acid. Other methods than the ones mentioned above have not yet been standardized.

4.3 Adsorbable Organic Bound Fluorine (AOF)

At present, only a very small number of PFAA precursors such as N-ethyl perfluorooctane sulfonamido acetic acid and N-methyl perfluorooctane sulfonamido acetic acid can be quantitatively analyzed by commercial laboratories. Therefore, there was special interest in a sum parameter similar to AOX[13]. The AOF method is based on the sorption of organic fluorine compounds on synthetic activated carbon with low fluorine content (Lange, 2014). The carbon is burned completely at 950 - 1,000 °C without soot formation by adding water in an oxygen atmosphere (hydropyrolysis). The combustion gases (HF, CO_2, etc.) are adsorbed in a neutral or alkaline solution which is fed to an ion chromatograph. The analysis in the ion chromatograph is performed for fluoride. This method, known as Combustion Ion Chromatography (Wagner et al., 2013; Lange, 2014, 2014A) achieves a limit of determination of 1.0 µg/L fluorine. This corresponds to a limit of quantitation of 1.54 µg/L for PFOS only.

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[12] Branched isomers occur especially in the compounds PFOA, PFHxS and PFOS.

[13] The AOX does not detect fluorine compounds.

This limit of determination is very high in relation to the currently discussed assessment criteria (the proposed lower insignificance value for PFOS is 0.23 µg/L). The method can be applied to soil eluates. The AOF with a detection level of ≤ 5 µg/L is already commercially available.

A draft DIN standard was already available in 1996 (DIN 38409-29:1996-01, German standard procedures for water, waste water and sludge investigation - Summarised effect and material parameters (Group H) - Part 29: Determination of dissolved, adsorbable organically bound fluorine compounds (AOF) (H 29) (German standard methods for the examination of water, waste water and sludge - General measures of effects and substances (group H) - Part 29: Determination of dissolved, absorbable organically bound fluorine (AOF) (H 29)) However, this draft was based on a slightly different procedure from that described above and was withdrawn.

The procedure described above is currently in the standardisation process. It is not yet clear when it will be completed. It can be expected that the new AOF procedure will quickly establish itself in commercial laboratories, at the latest after completion of the standardisation process, even though the analytical equipment required for this method is not part of the standard equipment and only a few laboratories are likely to have it already available at present. With increasing demand, the price of this analysis will probably also fall, so that it can be expected that it will be implementable as a routine screening analysis.

At present, the application is likely to be limited to selected samples with the aim of testing whether other PFAS, especially precursors, are present in addition to the commercially determinable compounds. However, regarding compliance with the (not yet legally binding) limit values, the analysis of single substances will always be necessary.

With respect to the corresponding parameter AOX (adsorbable organic halogenides), it is known that at least in organic-rich waters (e.g. landfill leachate) halogens are bound into the organic polymeric matrix (humic substances). As a result, the AOX value can become very high, although it is not matched by a corresponding concentration of individual substances. A similar situation can be assumed for the AOF. This means that the AOF in organic-rich waters may be of limited suitability for reliable detection of fluoroorganic compounds with small molecule size.

Since the first step is sorption to activated carbon, the AOF may underestimate the real concentration if the samples have a comparatively high proportion of short-chain PFAS (especially PFBA).

When taking samples and and conducting AOF analysis, attention must be paid to potential cross-contamination. Thus, all materials containing Teflon are not allowed. The materials used must not only be free of PFAS but also of fluorine. Silicones are suitable for the sampling tubes and for gaskets.

Due to the currently still comparatively high limit of quantitation (1 µg/L fluorine) and the fact that the individual PFAS compounds differ significantly in terms of their hazard potential, but are only recorded as a sum in the AOF, the AOF is intended to serve as a guiding value and not to replace individual substance analysis. Therefore, the AOF is not suitable for checking whether the assessment values have been exceeded.

4.4 Extractable Organic Bound Fluorine (EOF)

Like the AOF process, the EOF process has been developed for soils and other solid matrices. The fluorinated compounds are extracted from a soil sample with methanol. Inorganic fluoride is removed from the extract by ion exchange. The fluorine compounds are incinerated, and the fluorine is quantified by ion chromatography (Combustion Ion Chromatography). The limit of determination is currently 10 µg/kg. A deficit of the EOF analysis is the necessary pre-drying of the soil material, as volatile components such as fluortelomer alcohols are already removed from the sample.

The EOF analysis has already been adapted to the analysis of plant samples (BG: 25 mg/kg) (Nüren-berg et al., 2018b).

There are currently no efforts to standardise this method.

4.5 Precursor Oxidation

Another method for quantifying unanalyzable unknown PFAS (as a sum parameter) is the oxidation of all compounds by means of hydroxyl radicals (Houtz and Sedlak, 2012; Casson and Chiang, 2018) (Figure 14).

Figure 14   Analysis for total mass of oxidizable precursors
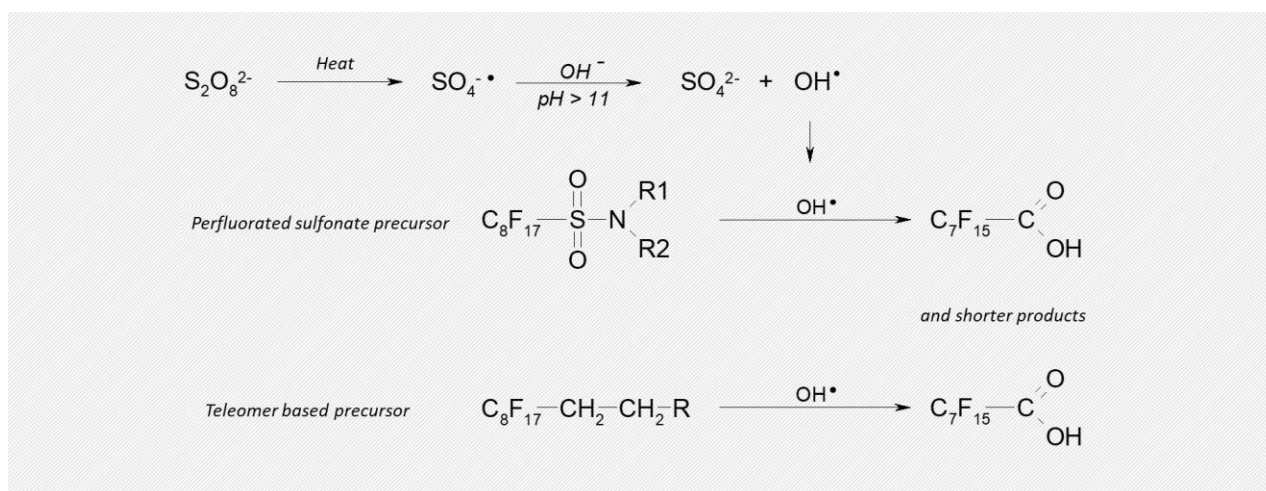
Source: Houtz u. Sedlak, 2012

This TOP assay (Total Oxidizable Precursor) is applicable to perfluoro carboxylic and sulfonic acid precursors. The hydroxyl radicals are generated by caustic thermolysis of persulfate. The radicals generated lead to the cleavage of all functional groups and non-fluorinated residues, forming perfluoro carboxylic acids. However, the CF_2-chain of the precursor can also be shortened in the oxidation step, so that several different compounds are formed which can be analyzed by conventional methods. The process requires the sample to be analysed once before and once after the oxidation. The process is suitable for both soil and water. The sample preparation and analysis procedure for soils comprises the following steps in summary:

► Addition of a ^{13}C-labelled PFAS reference substance ([13]C-6:2-FTS; internal standard).
► Addition of methanol, ultrasonic treatment.
► Centrifugation of the extract, concentration to dryness.
► Reconstitution with an acetonitrile-water mixture.
► Analysis with HPLC-MS/MS.

For oxidation, a part of the methanol extract is concentrated to dryness and subjected to the following treatment:

► Dissolve with aqueous persulfate/sodium hydroxide mixture (60 mM/125 mM).
► Heating (90 °C for 6 hours).
► Cooling down and neutralization (pH 7).
► Addition of acetonitrile and analysis.

The water samples are labelled with the internal standards, acetonitrile is added, and the solution is analysed directly. For oxidation, a part of the sample is mixed with persulfate/sodium hydroxide and heated like the soil sample. The sample is then neutralized, acetonitrile is added, and the solution is analyzed.

Only perfluoro carboxylic acids and no perfluoro sulfonic acids are formed by the oxidation.

In the mass balances of the TOP assay, only PFCA with chain lengths starting from C_4 have been recorded so far due to the analytical limitations. The fact that PFCA < C_4 are also formed has been analytically proven in the meantime. However, the formation of perfluoro propanoic acid (PFPrA) (C^3) and trifluoro acetic acid (TFA) (C_2) occurs only to a comparatively small extent. In any case, this leads to an underestimation of the concnetrations in the TOP analysis. Therefore, it is necessary to incorporate the short-chain PFAA into the analysis. However, this is not trivial, as the oxidative digestion produces high amounts of sulphate, which cause matrix effects that hinder the quantification of the very short-chain PFCA that elute early in the HPLC-MS/MS determination, so that a reliable quantification is not possible (Nürenberg et al., 2018b).

A check of the process with pure substances (Figure 15) revealed a higher concentration of perfluoro carboxylic acids than actually can be formed after PAP oxidation, presumably due to the poorer recovery of the PAPs themselves. For the FTS compounds the recovery was somewhat lower. These results show a high accuracy of the process and the fact that probably only a small proportion of the compounds are oxidized to < C_4-PFAA.

Figure 15   Recovery of PFAS after oxidation
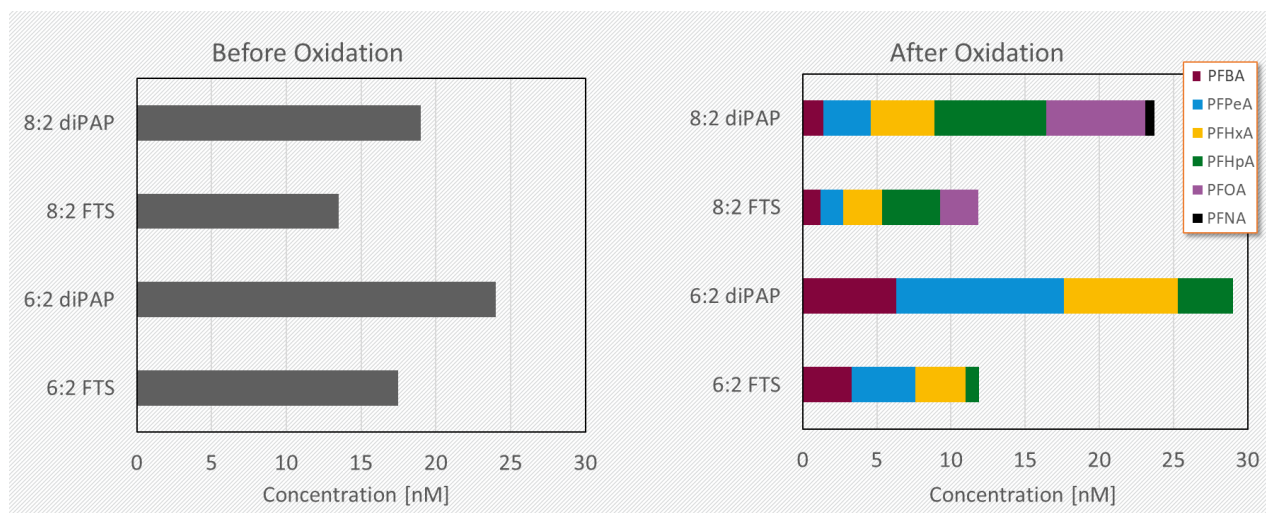
Source: Houtz u. Sedlak, 2012

The pH value should be > 3.5 after oxidation to ensure that the probability of chain shortening to < C_4 compounds remains low. Under certain circumstances, ^{13}C-labelled perfluoro octane carboxylic and sulphonic acids can be added to the sample (stability surrogates). If the ^{13}C label is completely recovered in the sum of the perfluoro alkane carboxylic and sulfonic acids (possibly after chain shortening), no < C_4 compounds are formed. The position of the ^{13}C-label (terminal) is important.

To check the completeness of the oxidation, the sample (soil or water) is marked with the internal standard [13]C-6:2 FTS (precursor). From the [13]C-6:2 FTS concentration remaining after oxidation, the extent of oxidation is calculated.

Matrix components of the samples (especially high C_{org} contents) can consume a significant portion of the oxidizing power. It may be necessary to repeat the oxidation step to achieve complete precursor oxidation. Advantages and disadvantages of the analytical method are summarized in Table 4.

Table 4   Advantages and disadvantages of the TOP method

Advantages	Disadvantages
The detection level is as high as with the standardised analytical methods	Non-precursors are not recorded
The method allows some statements about the length of the perfluorinated chain in the precursor	The oxidation partially leads to a shortening of the perfluorinated chain
Compared to the AOF, lower underestimation in the area of short-chain PFAS (C4)	Total losses are possible by shortening to < C_4, resulting in an underestimation of concentrations after oxidation

Figure 16 shows a good correlation of the AOF with the TOP, but the AOF systematically leads to an underestimation of the real concentration at elevated PFBA concentrations. The comparison TOP-assay with the EOF showed largely consistent results (Nürenberg et al., 2018b). With respect to the fluorine content the relation TOP = 1,05·EOF could be found.

Figure 16   Correlation AOF and TOP
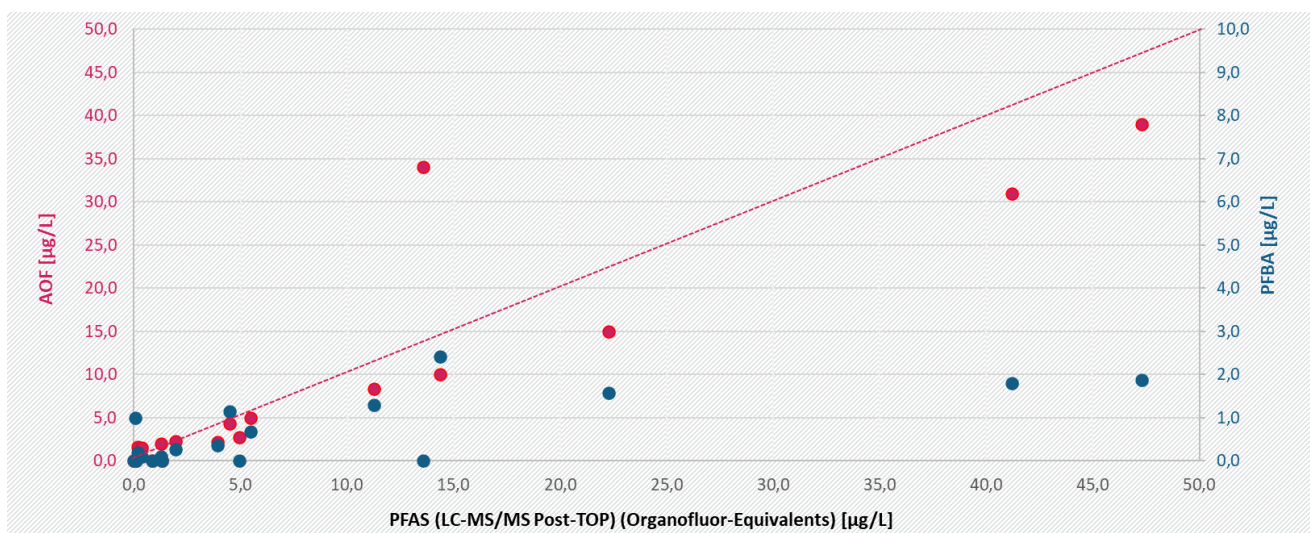
Source: Arcadis Germany GmbH, 2019

The TOP method has already been adapted to plant samples. Significant levels of precursors could thus be detected in the plant (Nürenberg et al., 2018b).

4.6   Additional Analytical Methods

Especially for the determination of the group of polyfluorinated alkyl phosphates (PAP) in soil extracts a semi-quantitative method was developed by TZW, Karlsruhe (Nürenberg et al., 2018a). With this method it is possible to extract the PAP from the soil matrix and analyse them by LC-MS-MS. The method can be applied to the compounds 6:2 di-PAP and 8:2 di-PAP (BG 5 µg/kg each). The internal standards ([13]C_4)-6:2 di-PAP and ([13]C_4)-8:2 di-PAP are used for quantification. Further details on the analysis can be found in Liu et al., 2013 and Gebbink et al., 2013.

A sensitive detection of mono-PAP from soil samples is not possible so far due to their unacceptable recovery rates. The reason for this is believed to be the susceptibility of these compounds to enzymatic hydrolysis, mainly through the activity of alkaline phosphatases (AP) (Jackson and Mabury, 2012). The enzyme inhibitors 4-nitrophenyl phosphate and bis(p-nitrophenyl)phosphate were used to determine the enzyme activity of AP with standard assays.

Telomer alcohols and other non-polar PFAS cannot be detected by the HPLC-MS/MS method. Firstly, they are not enriched under the given conditions of solid phase extraction. However, it is more important to note that the ionization procedure used in HPLC-MS/MS is not sufficient to ionize the telomer alcohols, in contrast to GC-MS. Gas chromatography with mass spectrometric detection (GC-MS) is therefore suitable for such compounds. Experience is available with the analysis of wastewater. Extraction and enrichment are carried out with good recovery rates using high-purity methyl tert-butyl ether (MTBE) (liquid/liquid extraction). According to Marzinkowski et al. (2013) the determination limits are 0.06 µg/L for 6:2-FTOH, 0.3 µg/L for 8:2 FTOH and 0.6 µg/L for 10:2 FTOH. With a more sensitive mass spectrometer these can be improved to a certen exent.

In addition, a headspace GC-MS method has been developed that does not require an enrichment step (Reagen, 2009). GC-PCI-MS (gas chromatography-mass spectrometry coupled with positive chemical ionization) is also suitable as a robust analytical method for volatile compounds such as FTOH, PFOSE and PFOSA. The ASE[14] method can also be used for the extraction of solids and pasty samples. After ASE extraction with DCM (dichormethane) (or with methanol) a sample cleanup can be performed via SPE. A concentration step should be avoided. The sample is filtered with a cellulose filter (0.45 µm) if necessary. Compounds detectable with the GC-PCI-MS are e.g:

- ► N-MeFOSA   N-methylperfluoro-1-octane sulfonamide
- ► N,N-Me2FOSA   N,N-Dimethylperfluoro-1-octane sulfonamid
- ► N-EtFOSA   N-Ethylperfluoro-1-octane sulfonamid
- ► N-MeFOSE   2-(N-Methylperfluoro-1-octane sulfonamid)ethanol
- ► N-EtFOSE   2-(N-Ethylperfluoro-1-octane sulfonamid)ethanol
- ► 4:2 FTOH   2-Perfluorobutylethanol
- ► 6:2 FTOH   2-Perfluorohexylethanol
- ► 8:2 FTOH   2-Perfluorooctylethanol
- ► 10:2 FTOH   2-Perfluorodecylethanol
- ► 7:2 sFTOH   1-Perfluoroheptylethanol.

In addition, there are several other methods for the quantification of fluoroorganic compounds. However, these are only used in research (Gruber, 2011), reference is made to the respective technical literature (Arsenault et al., 2008; Koc et al., 2011; Bavarian State Office for the Environment, 2012; CRC, 2013).

In the meantime, it has also been possible to extend the HPLC-MS/MS method so that shorter-chain perfluorocarboxylic acids (C_2, C_3) can also be detected (Nürenberg et al., 2018b).

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[14] ASE = *Accelerated Solvent Extraction* (extraction at elevated pressure and temperature) (liquid-solid extraction)

Analytical Detection (Summary)

A DIN method (HPLC-MS-MS) for soil and groundwater is available for the analysis of the PFAS. These methods have been extended so that currently about 30 compounds can be commercially analysed. Due to the large number of PFAS, sum parameters were developed such as the AOF method (adsorbable organic fluorine compounds) for groundwater and the EOF method (extractable organic fluorine compounds) for soil. In addition, the TOP-assay (Total Oxidizable Precursor) is available. Here the sample (soil or groundwater) is analysed before and after an oxidation step (which converts the precursors present into perfluorocarboxylic acids). The increase in concentration corresponds to the concentration of the precursors.

Numerous special problems require a continuous development of the methods. Most methods have already been adapted to the analysis of plants. In addition, a method for the quantitative determination of diPAP compounds was developed. The HPLC-MS/MS method was extended to also detect short-chain perfluorocarboxylic acids (C_2, C_3).

5 Physicochemical Parameters

5.1 Molecular Structure

Many PFAS consist of a hydrophobic poly- or perfluorinated carbon chain and a hydrophilic head (e.g. a sulphonate and/or carboxylate group) (Figure 17).

Figure 17   Surfactant structure of PFAS
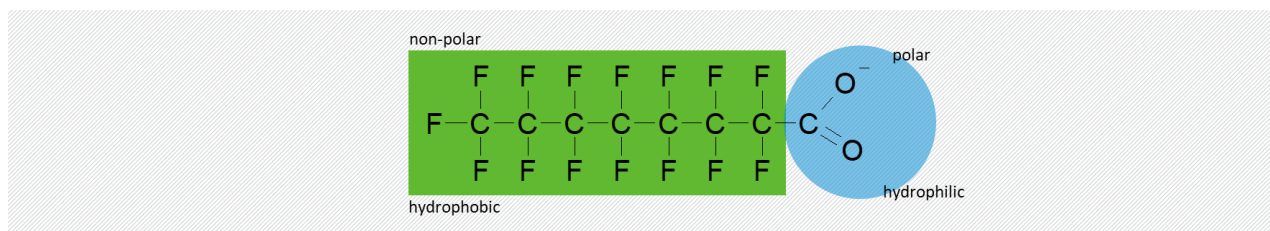
Source: LANUV NRW, 2011

This amphiphilic character results in its use as a surfactant. In contrast to the usual surfactants, the PFAS also have a lipophobic character. They therefore repel not only water but also oil, grease, and other non-polar compounds as well as dirt particles. For this reason and because of their stability they are interesting for industry and are used in numerous industrial and consumer products. The surface activity is higher than that of analogous hydrocarbon surfactants. This property is one of the reasons for a wide application of PFAS in industry (Fricke u. Lahl, 2005). Surface-active properties of polyfluorinated surfactants can be varied both along the length of the carbon chain and by the type of polar head group, resulting in a large number of different substances and properties (Albers, 2011).

But not all PFAS have surfactant properties. Perfluorosurfactants have the ability to accumulate at phase boundaries on the one hand and to form micelles on the other hand (LANUV NRW, 2011).

While PFOS and partly also PFOA are comparatively well investigated, physicochemical data on the remaining PFAS are available only sporadically, if at all[15].
It should be noted that the data in the literature sometimes vary considerably, since the measured values of the physicochemical properties depend substantially on the experimental conditions. Furthermore, it can often be observed that the physicochemical properties do not change exactly linearly within a homologous series (same substances with different CF_2 chain length). This is probably because with increasing chain length the geometry of the molecules changes and the steric hindrance caused by the larger fluorine atom compared to the hydrogen atom becomes more and more noticeable. With up to 8 fluorinated C-atoms the molecule preferentially remains in the linear stretched conformation, with more than 8 C-atoms a helix shaped molecule is formed. The resulting increase in electron density leads to a change in physicochemical properties (OECD, 2014). Such a change in physicochemical properties can also be caused by the formation of intramolecular hydrogen bonds, which mask the OH function, depending on the surrounding environment (Figure 18).

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[15] Some properties, e.g. the K_{OW}, cannot be determined experimentally for some substances due to their surface-active properties (emulsion formation).

Figure 18   Intramoleculare hydrogen bridges in fluorotelomer alcohols
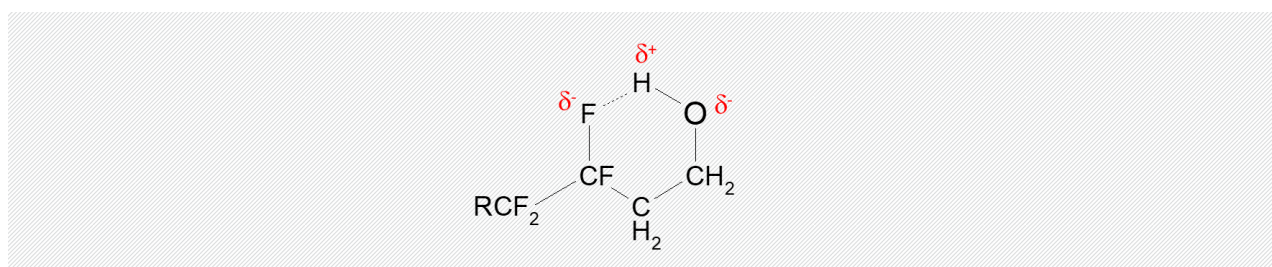
Source: Buck et al., 2011

Fluorine has the highest electronegativity of all atoms, a high ionization potential and a very low polarizability (due to the low deformability of the outer electrical sheath). Compared to hydrogen, the fluorine atom is larger; it has nine electrons distributed over a small space. Fluorine therefore has a higher charge density than hydrogen. Due to the effective overlapping of the orbitals involved in the bond, the covalent carbon-fluorine bond is one of the most stable bonds in organic chemistry (450 kJ/mol).

Figure 19   The role of the main physical and chemical properties (red) in PFAS substance distribution in different environmental compartments
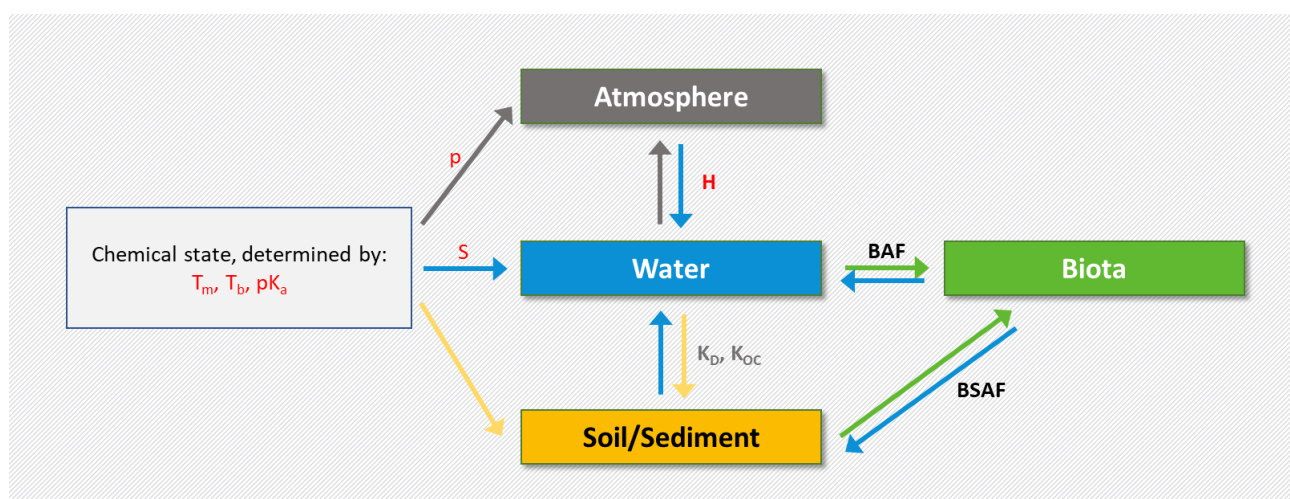
Important partition coefficients (in grey letters) are e.g. K_D, K_{OC} values. T_m = melting point, T_b = boiling point, pK_a = acid dissociation constant, p = vapour pressure, S = solubility, H = dimensionless Henry constant, BAF = bioaccumulation factor and BSAF = biota sediment accumulation factor. Source: Gellrich, 2014, modified

In addition, the dense electron packing of the fluorine acts as a kind of protective shield to protect the perfluorinated compounds from external attacks, thus causing the high thermal, chemical, photolytic (UV radiation) and biological stability of these substances. The oxidation potential of the fluoride (2 F- → F2 + 2e-) is extremely high (2.87 V). Despite their low tendency to participate in reactions, substance distribution processes play an important role in nature. An overview of the importance of the physicochemical parameters in the distribution of substances can be found in Figure 19.

5.2   Water Solubility, Dissociation and Physical State

Solubility. Short-chain perfluorinated sulphonic and carboxylic acids have a relatively good solubility in the g/L range. However, the solubility decreases drastically with increasing chain length. Fluorotelomer alcohols are dominated by the hydrophobic property, so they are less soluble in water and do not dissociate. Even perfluorobutylethanol (4:2 FTOH) only has a solubility of 0.97 g/L. With increasing length of the perfluorinated alkane chain the solubility decreases rapidly. The maximum solubility of 10:2 FTOH in water is only 11 µg/L (Liu and Lee, 2007).

As with hydrocarbon-based surfactants, it can be assumed that the composition of the ground water (especially the content of divalent ions) influences the solubility of the PFAS.

In an aqueous environment, the compounds with acid function can split off a proton and are then present as acid anions.

$$F_3C\text{-}CF_2\text{-}CF_2\text{-}COOH \;\longleftrightarrow\; F_3C\text{-}CF_2\text{-}CF_2\text{-}COO^- \;+\; H^+$$
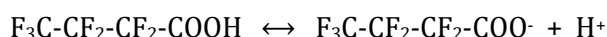
$$\text{Perfluorobutanoic acid} \;\longleftrightarrow\; \text{Perfluorobutanoate (+ dissociated proton)}$$

Dissociation. The extent of the dissociation is described by the dissociation constant (pKa). The smaller the pKa value and the more it deviates from the neutral point pH 7, the more strongly the compound is dissociated at pH 7. With a pKa of 0.5 (PFOA) or < 0.3 (PFOS) (Vierke et al., 2013)[16], both compounds are exclusively deprotonated in aqueous solutions at pH 7. The tendency to split off a proton is a typical property of an acid. The two compounds, PFOS and PFOA, can thus be considered strong acids (LANUV NRW, 2011).

Due to the dissociation, the molecules are well soluble in water despite the hydrophobic residue. In pH-neutral aquatic systems the perfluorinated alkanecarboxylic and alkanesulfonic acids are present as dissolved salt compounds. In contrast, fluorotelomer alcohols do not dissociate under environmental conditions.

The dissociation also has a further influence. The physicochemical properties of the salt compounds differ significantly from those of the free acid. For example, the acid PFOA has a melting point of 59 - 60 °C, the ammonium salt (APFO), on the other hand, has a melting point of 130 °C, and the solubility increases from 3.4 g/L to > 500 g/L for the salt. In contrast, the vapour pressure decreases from 2.3 Pa (acid, 20 °C) (European Chemicals Agency, 2013) to 0.0081 Pa (salt) (RPS Advies B.V., 2010), which means that the salt is not volatile, whereas the acid is. Similar conditions are present for the other dissociable PFAS.

This is clearly shown by the example of H4-perfluoro-n-octane sulfonic acid (6:2 FTS). The more the pH value falls below pH 7, i.e. the lower the dissociation, the more the solubility decreases (Figure 20) (Kawase et al., 2010).

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[16]   The pK$_a$ figures vary very strongly, with significantly higher values often being given. According to Vierke et al (2013), this is probably due to methodological difficulties. The authors estimated the pKa of C$_4$-C$_{11}$ perfluorocarboxylic acids to be < 1.6 throughout.

Figure 20   Solubility of 6:2 FTS (25 °C) depending on the pH value
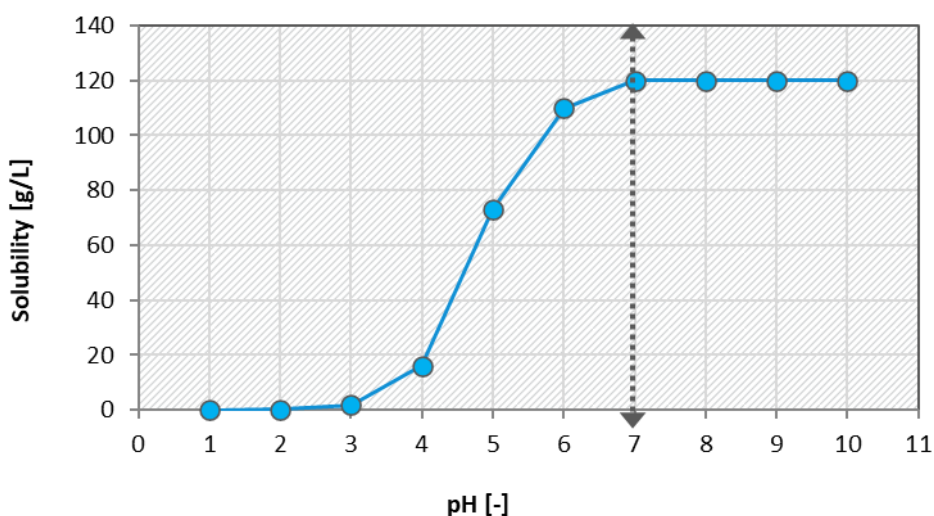
Source: Kawase et al., 2010

6:2 FTS has a pKa of 1.31 and is therefore already well below the neutral point (pH 7). It is almost completely dissociated or is present in salt form. Both forms, salt, and acid, differ in their solubility. In the present case, the increasing solubility with increasing pH value is probably not only due to the transition from acid to salt since the increase in solubility should then have already started at a much lower pH.

Physical state. At ambient temperature, the PFAS pure substances are mainly present as solids. Only the short-chain telomer alcohols (up to 6:2 FTOH) are liquid, longer-chain ones are solid. The melting and boiling points of PFAS are comparatively high. PFOA still has a relatively low melting (59 - 60 °C) and boiling point (192 °C). With PFOS the values are already considerably higher. The telomeric alcohol 8:2 FTOH is present as a solid at room temperature but can sublime from open vessels.

5.3   Volatility

Perfluorinated alkanecarboxylic and alkanesulfonic acids have a low to very low vapor pressure in their salt form present in the pH neutral range (Figure 21). However, PFOA in the non-dissociated form can sublimate at room temperature as well as 8:2-FTOH, for example. Thus, theoretically it is possible to spread this substance directly from the production process via the air path. For FTOH and many other PFAS, varying vapour pressures are given in the literature, but compared to perfluorinated alkylcarboxylic and alkylsulphonic acids, FTOH have much higher vapour pressures and are therefore to be classified as volatile (Liu and Lee, 2007).

It is therefore assumed that they can predominantly pass from the production/processing process into the atmospheric gas phase, where they spread and are deposited via precipitation. A direct entry into soil and groundwater at the place of production is therefore unlikely.

FTOH can be biotransformed to perfluorocarboxylic acids by various conversion processes (Chapter 6), which leads to a diffuse pollution of surface and groundwater with these compounds through precipitation. The conversion process is also accompanied by a significant decrease in vapour pressure.

Figure 21   Henry coefficient[17] of selected PFAS and commen contaminants at 20 °C
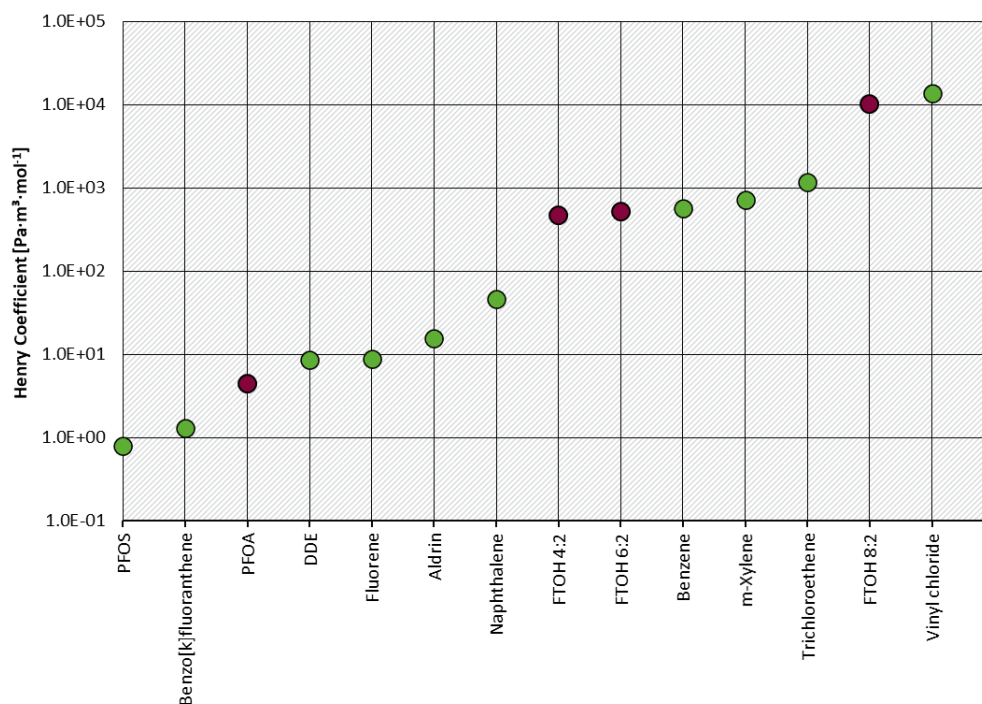
Source: Arcadis Germany GmbH, 2019

The tendency of the PFAS to change from the water to the gas phase (air) is described by the Henry coefficient (kH). This varies greatly within the PFAS (Figure 21) with PFOS (0.79 Pa·m^3·mol^{-1}) as a medium volatile[18] substance at the lower end and 8:2 FTOH as a substance with a higher volatility than TCE at the upper end of the scale. For PFOS, the transition to the gas phase is therefore not important, whereas FTOH is rather highly volatile.

The Henry coefficient is higher for fluorotelomer alcohols than for homologous hydrocarbon compounds. It increases non-linearly with the length of the C-chain.

Initial investigations are already looking into the question of whether PFAS can penetrate into interior spaces in sufficient concentration. The potential is regarded as low (Roth, 2019).

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[17]   Literature references to the Henry coefficient vary considerably, as do those for the other physicochemical parameters of the PFAS. Thus, differences of more than a factor of 10 were found for the Henry coefficient. The figure therefore does not show absolute values, but rather the volatility in relation to other known contaminants. For the figure, the Henry coefficient was calculated from molar mass, vapour pressure, water solubility and general gas constant. But also, for vapour pressure and water solubility of the PFAS strongly different values can be researched. Vapour pressures and water solubility for 4:2 FTOH were taken from Liu, and Lee, (2007), for 8:2 FTOH from Climate and Pollution Agency, Norway (2010), for PAH and for other compounds from ribs (2014).

[18]   Volatility levels: (a) slightly volatile: H < 0.003 Pa·m^3·mol^{-1}, (b) medium volatile: H = 0.003-100 Pa·m^3·mol^{-1}, (c) highly volatile: H > Pa·m^3·mol^{-1}.

5.4 Sorption

5.4.1 Overview

The hydrophilic and hydrophobic properties of PFAS influence the sorption behaviour. The molecular structures indicate that organic carbon is probably not the only factor influencing sorption. Li et al (2018) have evaluated numerous studies. According to these studies, the correlation of the sorption coefficient (K_D) of PFOA and PFOS with the content of organic material (f_{OC}) was weak ($R^2 = 0.05 - 0.07$).

Figure 22   Concept of the possible sorption mechanisms of PFAS on soils or sediments
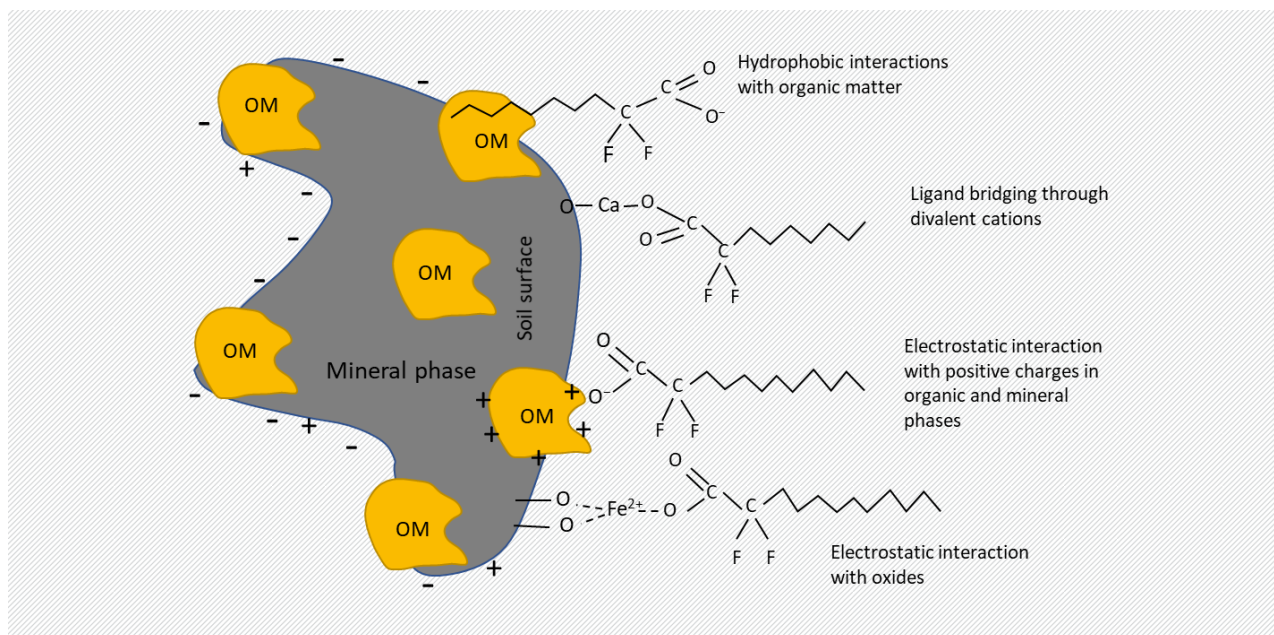
Source: Li et al., 2018. The mechanisms are shown for a carboxylic acid. They apply in the same way to a sulfonic acids.

For K_D values derived exclusively in the laboratory, R^2 values increased to 0.24 for PFOA, 0.38 for PFOS, 0.77 for PFNA and 0.78 for PFDA. Similarly, for PFOS and PFOA, there was no significant relationship between K_D values and pH over a wide range of environmentally relevant pH values. This shows that the sorption behaviour of several PFAS cannot be explained by a single soil or sediment property. Using different regression models, it could be shown that at least f_{OC}, pH and clay content together determine sorption. This was confirmed by the fact that the log K_{OC} values for perfluorocarboxylic acids obtained from the analysis of the solid/water distribution of analogous water and soil samples did not fully agree with the results of laboratory studies (McGuire, 2014). However, a correlation of the K_D with the mass of organic material in the soil was demonstrated in many other studies (see below). The conceptual illustration of possible sorption mechanisms of PFAS on soils or sediments is shown in Figure 22.

5.4.2 Hydrophobic Bonding

The surface-active properties of some PFAS influence their sorption to the soil matrix. However, the PFAS are found in relatively low concentrations in contaminated areas. Accordingly, most of the laboratory investigations were carried out under such conditions, i.e. at concentrations much lower than the critical micelle concentration. Only for such conditions the PFAS on the sorbent form monolayers and the effects described below are valid. At higher concentrations (> 1 mg/L) further effects occur, which can vary greatly depending on the physicochemical system (Tang et al., 2010).

Accompanying contaminants (non-aqueous product phases, non-fluorinated surfactants from fire extinguishing foams) also influence sorption in a way that is difficult to predict. The effects of non-fluorinated surfactants vary with the type of surfactant and soil, but also with the concentration of the PFAS. In contrast, Hydropobic Co-contaminants generally increase the sorption of PFAS for all soils (Guelfo and Higgins, 2013).

All investigations on the sorption of PFAS indicate the soil organic carbon content and the chain length of PFAS molecules as the dominant parameters determining sorption. Sorption is very rapid at the beginning and can then be described by a bi-exponential equation (kinetics). Overall, it takes a very long time (approx. 10 days) for a sorption equilibrium to be established for the longer-chain compounds. The sorption to the soil can be described with different models. At PFAS concentrations < 1 mg/L the adsorption isotherm is linear (Higgins and Luthy, 2006). The distribution coefficient (soil-water) (K_D) in the equilibrium has the unit [L/kg]:

$$K_D = \frac{C_B}{C_W}$$

C_B = Concentration in soil [µg/kg] and C_W = Concentration in water [µg/L].

Only at higher concentrations does the soil/water partition coefficient no longer increase linearly with increasing PFAS concentration and the curve flattens out. Normalized to the relative content of organic carbon (f_{OC}), the following applies

$$K_D = K_{OC} \cdot f_{OC}$$

with K_{OC} = Partition coefficient water-organic carbon [L/kg].

Most PFAS bind less to lipophilic than much more to proteinic structures. But these also occur in the organic material of the soil. For PFAS, a clear correlation of sorption with increasing organic carbon content has been observed, as shown for example with PFOS (Higgins and Luthy, 2006) or 8:2-FTOH (Liu and Lee, 2007). Within a homologous series (e.g. perfluoroalkanecarboxylic acids or perfluoroalkanesulfonic acids) the log K_{OC}[19] increases by 0.87 units per CF_2-group (Liu and Lee, 2007). Relative to the log K_D, the sorption of perfluorocarboxylic and perfluoroalkanoic acids increases by 0.5 - 0.6 units per CF_2-group (Higgins and Luthy, 2006). The sulphonic acid function increases the log K_D by 0.23 units compared to the carboxylic acid, presumably because the sulphonic acid is somewhat larger, thus having a lower charge density and a somewhat higher hydrophobicity. Other studies show a slightly different sorption strength (e.g. Vierke et al, 2014).

The functional group sulfonamide acetate significantly increases sorptivity. An amino group also increases sorption, e.g. PFOSA sorbs more strongly than PFOS. Lee and Mabury (2017) showed for perfluoroalkylphosphonates and perfluoroalkylphosphinates an increase in sorption strength with increasing number of fluorinated C atoms in the whole molecule.

In sorption, the CF_2-group is strongly dominant, and any CH_2-groups present play a clearly subordinate role. This becomes clear when comparing the two compounds 6:2 FTS and PFOS. Both have the same sulfonic acid group and the same number of C atoms in the chain with the difference that in 6:2 FTS two C atoms are not fluorinated. As a result, 6:2 FTS sorbs about 40 % less on average and is more similar to PFHxS in sorption strength, which has the same number of perfluorinated carbon atoms (Gellrich, 2014).

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[19]   The K_{OC} (in L/kg) is the ratio of the substance sorbed on the solid phase to the substance dissolved in water. It is usually standardized to the proportion of organic carbon (f_{OC}) in the solid phase and is referred to as K_D.

The competition of different PFAS compounds for the bonding sites on the soil is evaluated differently. In a study with PFAS compounds ≥ C_8, for example, the same K_D value was always measured, regardless of whether the substance was added individually or in a mixture (Higgins and Luthy, 2006). In another study, in which shorter-chain PFAS were also investigated, a higher K_D value was measured when the substance under investigation was used alone than in the mixture (Gellrich, 2014).

The predictions of sorption are further complicated by two additional effects. Firstly, the organically bound carbon molecules differ in their properties[20]. The organic carbon of soils has a higher polarity and thus lower lipophilicity than the organic carbon of sediments (Delle Site, 2001). Accordingly, soils also sorb better. Furthermore, the proportion of protein structures in the DOC also depends on the genesis of the DOC. Thus, the DOC does not exhibit uniform properties. Secondly, the adsorption strength also depends on the degree of branching of the perfluorinated chain. The branched isomers show lower sorption to soil than the corresponding linear molecules. Therefore, not only the number of CF_2-groups but also steric conditions are decisive for the sorptions.

In most studies short-chain compounds were not investigated. For the first time in 2013, C_3 to C_6 compounds were also examined (Guelfo and Higgins, 2013) (Figure 23).

Figure 23   Sorption of short- and long-chain perfluorocarboxylic acids on three different soils (A, B, C)
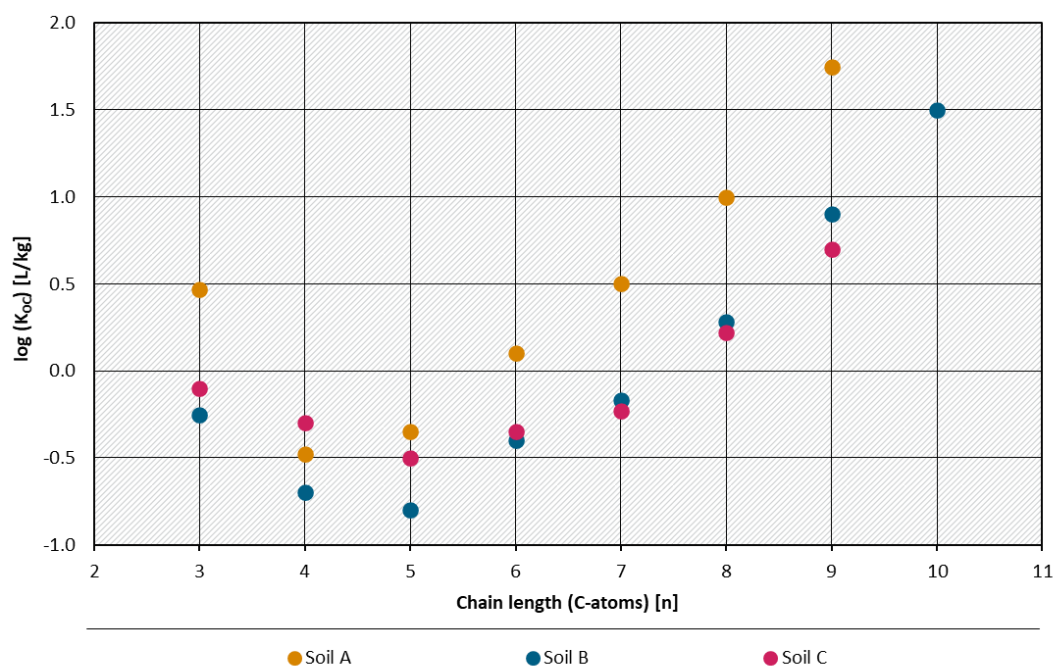
Source: Guelfo u. Higgins, 2013

The shorter-chain compounds (PFBA and PFPeA, among others) have a stronger sorption than would be expected after extrapolation of the sorption data of the longer-chain PFAS. It can be assumed that other sorption mechanisms (electrostatic bonding) play a greater role with these compounds than with the longer-chain, more hydrophobic PFAS.

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[20] This may affect the sorbability. While perfluorocarboxylic acids and sulfonic acids bind preferentially to protein structures (which also occur in natural organic material), the description of sorption via the K_{OC} model is likely to apply in particular to fluortelomer alcohols (e.g. 8:2 FTOH), where the hydrophobic properties have a stronger influence and which exhibit strong sorption to the soil matrix.

Indeed, the K_D values of PFPeA and PFHxA are higher in positively charged soils ($f_{OC} = 0.008$) than in negatively charged soils[21]. Another explanation would be that there is a subgroup of bonding sites accessible only to smaller molecules (steric effects) (Guelfo and Higgins, 2013). In other studies (e.g. Chen et al., 2016) this behaviour of the short-chain compounds could not be confirmed, no sorption was found for PFBA.

The mobility of PFAS in the aquifer can be quantified by determining the retardation factor (R). The factor is dimensionless and can be calculated as follows:

$$R = 1 + \frac{\rho_{Matrix} \cdot k_{OC} \cdot f_{OC}}{n_e}$$

ρ_{Matrix} = dry bulk density of the aquifer matrix, n_e = flow effective porosity, k_{OC} = partition coefficient between water and soil organic carbon, f_{OC} = soil organic matter content.

Some retardation values determined experimentally by Vierke et al. (2014) are summarized in Table 5. With a retardation factor of 1, a solute is transported at the same velocity as the groundwater, with a retardation factor of 2 only half as fast.

In summary, long-chain, lipophilic PFAS are preferentially found in solid matrices, and the more hydrophilic short-chain compounds mainly in aqueous matrices. This is confirmed by investigations on sediment cores and their pore water. Short-chain PFAS ($< C_7$) could only be detected in the pore water and long-chain PFAS ($> C_{11}$) only in the sediment (Ahrens et al., 2009). In a further investigation no PFAS with a chain length > C10 were found in groundwater. However, PFAS with up to 12 C atoms could be detected in river, lake, drinking or wastewater. The dominant compounds in the study were PFOA, PFBS and PFHxS (Rayne and Forest, 2009).

Table 5   Retardation factors for some PFAS (Vierke et al., 2014)[22]

Compound	Retardation Factor (R) [-]
PFBS	2.6
PFHxS	2.1
PFBA	1.9
PFHxA	9.9
PFOA	31.5
PFNA	23.5

Since PFAS are predominantly only slightly retarded during groundwater transport, long plumes can form. The maximum achievable length of the plume depends mainly on the input quantity and the reduction of concentration by hydrodynamic dispersion and diffusion into hydraulically hardly conductive soil layers (matrix diffusion). The Contaminants are transported until they are diluted to concentrations below the limit of quantification or reduced by sorption.

Since the limit of quantification of PFAS are at least one order of magnitude lower than those of many other organic contaminants, correspondingly longer plumes are also detected. At least at one highly contaminated site of a production plant in Italy a plume length of > 45 km was reported.

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[21] Almost all soil particles of the mineral and organic soil substance are electrically charged at their surfaces or interfaces. Oxides and hydroxides cause negative charges, whereas iron minerals cause positive charges. In the case of clay minerals and humic substances, which are regarded as essential charge carriers and ion exchangers, negative charges predominate.

[22] Mean value of two analyzes.

Chromatographic effects occur along the plume propagation. Mobile shorter-chain compounds are transported more rapidly, as well as those less strongly than the linear molecule on soil sorbing sorbing branched PFOS isomers. But PFOS also arrives at the plume end, albeit with a time delay (Bavarian State Office for the Environment, 2012).

At very high concentrations of PFAS in groundwater, there is in principle the possibility of micell formation. The critical micelle concentration (CMC) for lithium perfluorooctane sulfonate, for example, is $6.5 \cdot 10^{-3}$ mol/L (corresponding to 3.3 g/L). At this concentration, the transport of accompanying contaminants is accelerated, but to a lesser extent than with non-fluorinated surfactants (Simmons and McGuffin, 2007). In real cases of damage, such high concentrations usually do not occur.

Since the use of PFAS in fire extinguishing foams can also introduce other contaminants (from the thermal decomposition of the combustible material) into the aquifer during extinguishing work, it was investigated to what extent accompanying contaminants influence the transport of PFAS below the CMC. However, no clear correlation was found (Guelfo and Higgins, 2013).

Barzen-Hanson et al (2017) investigated the sorption of anionic, zwitterionic and cationic PFAS on soils. The compounds listed in Table 6 were used as model substances. The sorption took the form of a log-transformed Freundlich isotherm, but showed no substantial correlation with DOC, effective cation exchange capacity, anion exchange capacity or pH of the soil.

Table 6   Model compounds

Compound	Abbrev.	Chemical Formula	Length	Ion	pKa [-]
Fluorotelomer sulfonate	FTS	$F\text{-}(CF_2)_n\text{-}(CH_2)_2\text{-}SO_3^-$	n = 6,8	Anion	2,0
Fluortelomer-sulfonamidbetaine	FTSaB	$F\text{-}(CF_2)_n\text{-}(CH_2)_2\text{-}SO_2\text{-}NH\text{-}(CH_2)_3\text{-}(NH_2)^+\text{-}CH_2\text{-}CO_2^-$	n = 6,8,10,12	Zwitter ion	1,8
6:2 Fluorotelomer sulfonamidamine	FTSaAm	$F\text{-}(CF_2)_n\text{-}(CH_2)_2\text{-}SO_2\text{-}NH\text{-}(CH_2)_3\text{-}(NH)^+\text{-}(CO_3)_2$	n = 6	Cation	9,2

6:2 FTSaAm was completely sorbed except for one soil, indicating a combination of electrostatic and hydrophobic interactions. The sorption of the FTS is controlled by hydrophobic interactions, whereas the FTSaB behave more like cations binding to the soil. Therefore, the sorption mechanisms of FTS, FTSaBs and 6:2 FtSaAm are more complex than expected and cannot be predicted by general soil properties.

Since natural soils have negative charges and the cation FTSaAm is completely sorbed, it can be assumed that cationic soils are generally much more retarded than anionic PFAS.

There are currently almost no data available on the sorption of other precursors. The available knowledge was derived from the transport of precursors in groundwater and their desorption behaviour. According to Weber et al. (2017) the precursors are transported in a similar way as the perfluoroalkanecarboxylic acids. Although previous studies (Azzolini, 2014) suggested that precursors are less mobile than PFAA, investigations at a real contaminated site showed that the precursors were distributed similarly to PFOS.

Precursors desorbed more slowly than PFAA in column experiments with rate constants 3 to 15 times lower than PFAA (Azzolini, 2014). The poorer dislocation of precursors was also confirmed by site investigations (Chapter 5.4.5). Despite slower desorption rates, precursors can represent a significant proportion of potentially mobile PFAS at a site.

5.4.3 Electrostatic Bonding

Electrical charge of the sorbent. The perfluoroalkanecarbon and -sulfonic acid molecules, which are almost completely negatively charged under environmental conditions, can also be bound electrostatically to the soil. Clay minerals and organic carbon predominantly have a negative surface charge and thus repel negatively charged PFAS (anions). Electrostatic bonding, which nevertheless occurs in small quantities, is obviously to iron oxides, which have a positive charge. Electrostatic bonds obviously only play a noticeable role when the f_{OC} is very low (Johnson et al., 2007).

Obviously, electrostatic bonding is more pronounced for PFAS with low to moderate sorption (C_5-C_8-PFCA) than for longer-chain ones. Electrostatic bonding is influenced by the pH and the cation content in the aquifer, as both change the net charge of surfaces (soil, DOC). From the results of the investigations it was concluded that most long-chain PFAS, similar to other hydrophobic organic compounds, are preferentially sorbed to the highly concentrated domains of the humic fraction, while shorter-chain PFAS are bound to a greater extent to humic acid and fulvic acid (Pereira et al., 2017).

5.4.4 Influence of pH-Value and Salinity on Bonding

pH value. Sorption tests with PFDS, PFUnA and N-EtFOSAA showed a decrease of sorption in the range of pH 5.7 - 7.5 with increasing pH value. The log K_D value decreases by 0.37 units with an increase in pH by 1 unit. Since the pK_a value (dissociation constant) of the compounds is so low that the compounds in the investigated pH range are almost exclusively deprotonated, dissociation is excluded as the cause of this effect (Higgins and Luthy, 2006). Presumably, the decreasing pH-value (accompanied by an increase in the H^+ concentration) leads to a reduction of the negative charge of the sorbing material and thus to a reduction of the electrostatic repulsion between the organic carbon and the PFAS, which are also negatively charged.

It should be noted, however, that the change in pH also changes other parameters than just the surface charge of the organic carbon. For example, the Ca^{2+} concentration decreased from 22 mM at pH 5.9 by sorption to the soil to 1.1 mM at pH 7.5, so that it cannot be excluded that the pH-value has only an indirect influence on the sorption strength, especially since monovalent cations (Na^+) do not show any effect.

Ionic strength. The concentration of dissolved cations influences the distribution of the anionic PFAS between soil and water. In the sorption experiments with PFDS, PFUnA and N-EtFOSAA, an increase in sorption strength (K_D value) with increasing Ca^{2+} concentration was observed (Higgins and Luthy, 2006). The log K_D value increased on average by 0.36 ± 0.04 units with an increase in Ca^{2+} concentration (log Ca^{2+}) of 1 unit. This is attributed by Higgins and Luthy (2006) to a reduction of the negative surface charge of the organic carbon (similar to the effect of protons; H^+). However, Na^+ has no effect on sorption.

Another explanation lies in the same electrostatic charge of the sorbing molecules. Since the PFAS molecules repel each other electrostatically (PFAS-PFAS electrostatic interaction), two adjacent molecules on the sorbent occupy the bonding sites at a comparatively long distance from each other. Bivalent cations such as calcium form a molecular bridge (PFAS-Ca-PFAS), so that the distance between two sorbing molecules decreases significantly and more PFAS can be sorbed.

It should be noted that the charges on the surface of the fluorine atoms are negative compared to the positive charge of the hydrogen atoms of the hydrocarbon (fatty acid) analogues. This results in a total negative charge of the PFAS molecule surfaces. The electrostatic interactions are therefore not limited to the acid group alone (Johnson, 2007). Overall, a solution with high ion strength tends to promote the adsorption of the PFAS by suppressing the electrostatic repulsion force (Tang et al., 2010).

Figure 24   Partition coefficient of PFOS and PFOA depending on salinity
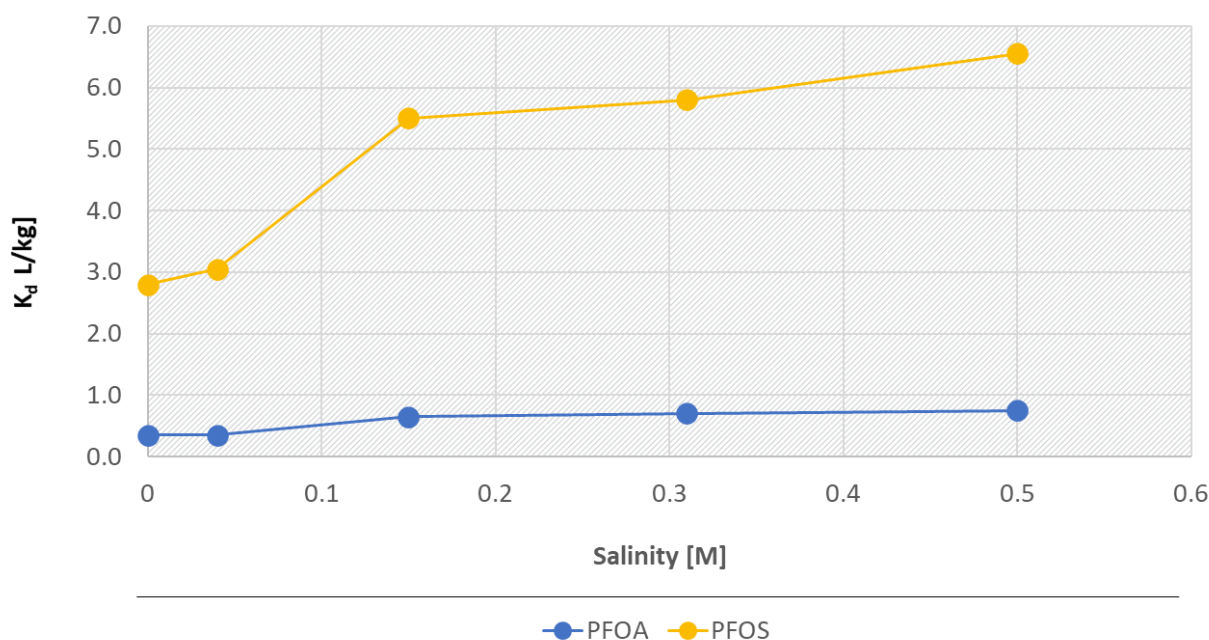
Source: Jeon et al., 2011

Studies with kaolinite (clay) showed that the increase in the partition coefficient with increasing salinity is much more significant for PFOS than for PFOA (Jeon et al., 2011) (Figure 24).

5.4.5 Elution

Elution or desorption is not just the simple reversal of sorption. Gellrich (2014) already noted that in experiments with sorption and subsequent desorption, smaller quantities desorb than sorb before. The tendency of the PFAS to sorb to the soil is therefore obviously greater than the tendency to go back into solution (sorption hysteresis). According to Guelfo and Higgins (2013), previously derived organic carbon normalized partition coefficients are not accurate predictors of desorption of long-chain PFAA from soils. According to them, desorption is mainly characterized by a non-equilibrium behavior, especially in soils with significant organic carbon content and for longer-chain PFAA. In addition, accompanying contaminants from fire extinguishing foams can influence the desorption.

A systematic investigation of the reversible and irreversible sorption (more precisely: kinetically restringing desorption) of several PFAS (C_4-, C_6-, C_8-, C_9- and C_{10}-perfluoroalkanoates as well as PFOS and PFHxS) was carried out by Chen et al (2016). Although all sorption isotherms were nearly linear, desorption experiments showed that some of the sorbed PFAS did not desorb. The hysteresis desorption curves were approximately linear (Figure 25).

The irreversibility increased with the chain length and was almost complete for PFDA. For the weaker sorbing compounds PFOA and PFHxS, sorption was largely reversible. Data suggest that:

►   for the strongly sorbing PFAS (e.g. PFNA, PFDA and PFOS) the sediments act as irreversible sinks,

►   aqueous concentrations of moderately sorbing PFAS (PFOA and PFHxS) are buffered by reversible sorption on solids

►   and the short-chain PFA (PFBA and PFHxA) are not significantly sorbed.

For irreversibly sorbed contaminants, field based K_D values are higher than the K_D values derived from the laboratory sorption tests.

Figure 25   Isotherm of the linear PFOS sorption (solid line) and the subsequent desorption (dashed lines)
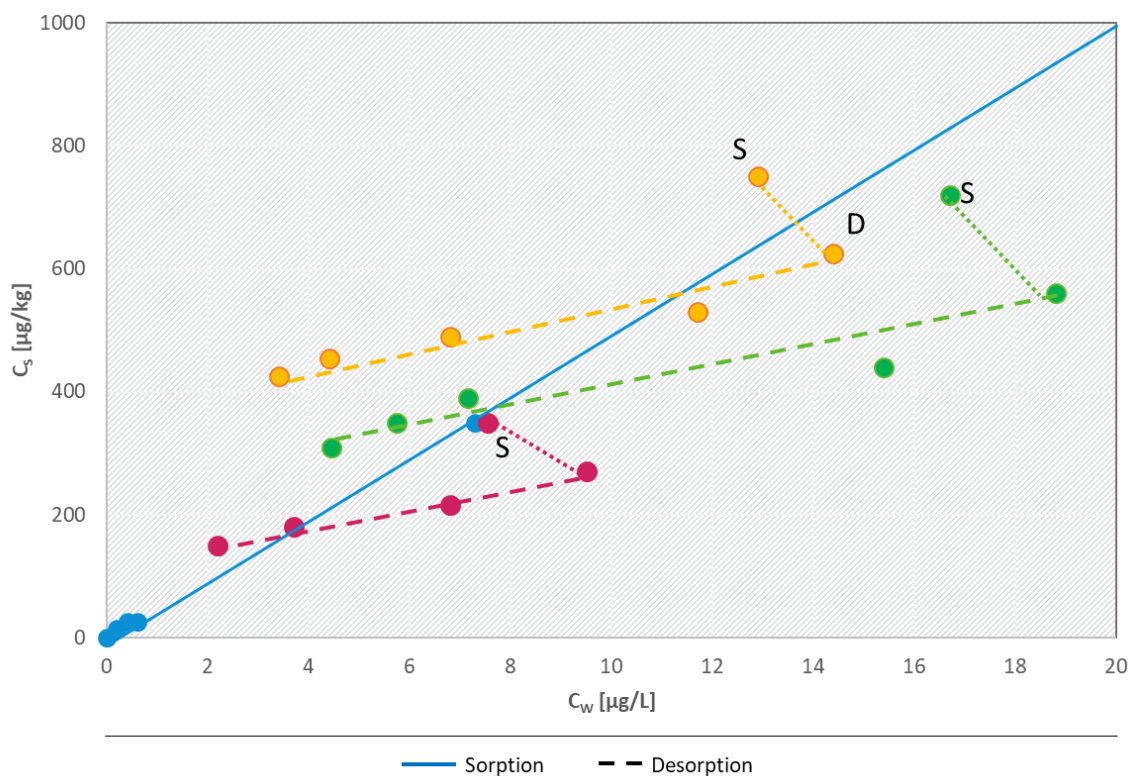
Dotted lines: Shift from the sorption point (S) to the desorption isothermal point (D) by replacing the aqueous supernatant with a fresh solution. Long dotted lines: linear desorption isotherm. Source: Chen et al., 2016, modified

A first, early approach to describe the transport of PFAS in soil and groundwater was provided by experimental investigations. Elution experiments were carried out with highly contaminated material from the site Scharfenberg in the Germany Federal State Northrhine-Westphalia, simulating annual precipitation of 600 and 800 mm/a (NRW, 2011). In the result, the sorption behaviour of the materials was primarily dependent on the f_{OC} value. The upper soil layer, richer in humus and organic compounds, generally shows a higher sorptivity than the lower, more mineral soil layer.

In the elution experiment, PFOA is released more rapidly than PFOS and transferred to the groundwater. The composition of the PFAS in the soil and in the groundwater changes accordingly over time.

It can be assumed that shortly after the occurrence of a PFAS spill, the less sorbing compounds are preferentially found in the groundwater (with a corresponding impoverishment in the soil). At a later point in time, these compounds displaced into the groundwater have already largely flown away and the better sorbing, longer-chain PFAS compounds are preferentially found in the soil and groundwater of the contaminant source. Although the data obtained are specific to the soil investigated, Table 7 shows that PFOS can still be detected in the soil eluate and thus in the soil itself many years after the damage occurred. A PFOS fraction of the total content that decreases with depth indicates a comparatively small, time-delayed displacement of this substance.

Table 7   Prognosed leaching from PFAS high-contaminated soils (NRW, 2011)[23]

Relative PFAS-concentration in soil leachate [%]	PFOA [µg/L]	PFOS [µg/L]	Time to reach a defined residual leaching [a] depending on irrigation			
			600 mm		800 mm	
			PFOA	PFOS	PFOA	PFOS
100	400	650	0.0	0.0	0.0	0.0
50	200	325	2.3	10.6	1.7	7.9
10	20	65	4.9	21.8	3.6	16.3
1	4,0	6.5	8.3	37.3	6.2	27.9

Extensive investigations have also been carried out on a site at which compost mixed with paper sludge was applied to the soil as a fertiliser. The soil-bound PFAS contamination was mainly related to the processing horizon (down to a depth of 30 - 40 cm). The paper borne PFAS contamination includes not only the perfluoroalkan acids (sum PFAS), but also several PAP compounds and a large proportion of unknown PFAS detectable by the AOF method (mainly precursors) (Figure 26).

Figure 26   Transport of PFAS to depth within the unsaturated soil (left: soil bound PFAS, right: PFAS in the soil eluate)
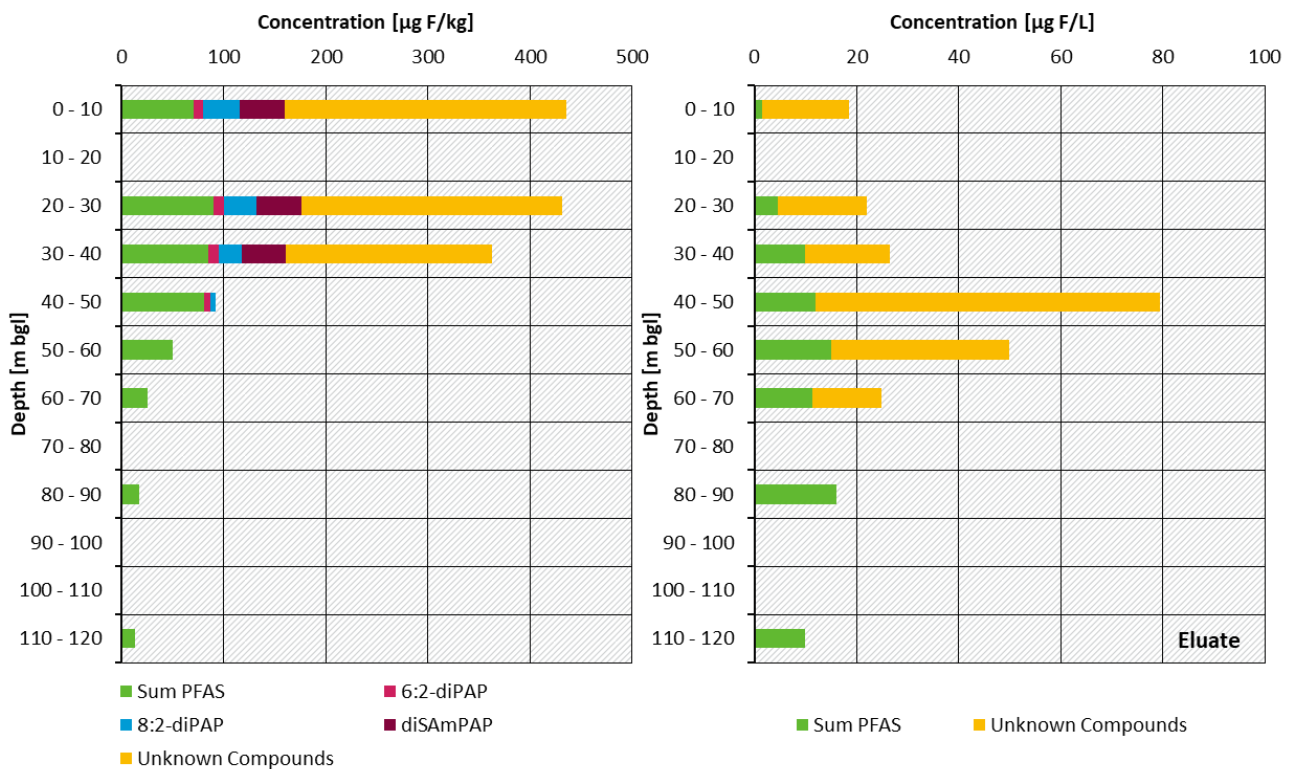
Up to a depth of 150 cm, soil samples were taken in 10 cm increments. Selected soil samples were analysed for individual PFAS compounds in the solid and eluate, individual analysable precursor compounds from the group of polyfluorinated phosphate esters (6:2 diPAP, 8:2 di-PAP and diSAmPAP) and for the sum parameters AOF. Source: Landkreis Rastatt, 2019.

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23 To what extent precursors have influenced the elution process was not investigated.

While the perfluoroalkan acids are transported to a lesser extent to greater depths with the precipitation, this is not the case with PAP. Precursors are only transported to a minor extent and are not detectable in the soil, but in the soil eluate. PAP were not detectable in the eluate throughout (District of Rastatt, 2019). In case of a different input characteristic (e.g. fire extinguishing water) precursors may well enter the groundwater

Further elution experiments (Gellrich, 2014) showed that branched PFOS elute faster than unbranched isomers. With a PFOS-spiked soil and a simulated (discontinuous) precipitation of 850 mm/a, PFOS (exclusively branched isomers) was detectable in the eluate for the first time 70 weeks after the start of the experiment; the unbranched PFOS molecules were still not detectable in the eluate even after 160 weeks. PFOA was completely eluted after about 60 weeks. Short-chain compounds (PFBA, PFBS) eluted just as quickly as an added conservative tracer, although PFBS was retained on the soil column to approx. 43 %, in contrast to PFBA.

Figure 27   PFAS fingerprints in soil (top) and groundwater (bottom) (mean values)
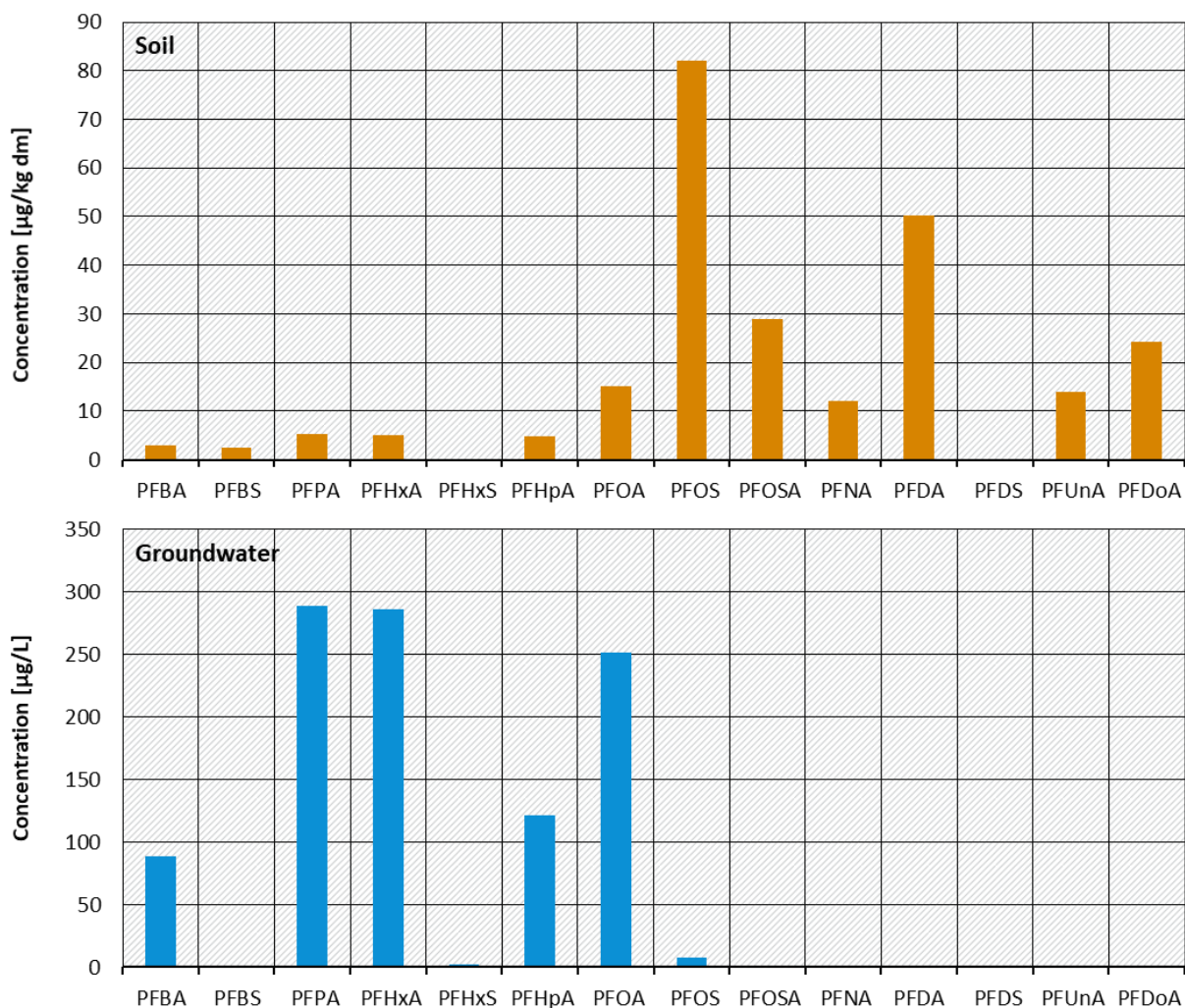
Source: Arcadis Germany GmbH, 2019

These findings are also confirmed by experiments on doped and planted outdoor lysimeters. After 5 years of continuous elution of PFOA and PFOS (whereby the concentration of PFOS in the eluate increased continuously during the test period) only 3.12 % of the PFOA and 0.013 % of the PFOS inventory were removed by elution. The low molecular weight PFAS eluted faster. PFHxA, PFHxS, PFHpA were completely eluted after 3 years.

On the other hand, PFBS was still detectable in the eluate after 5 years (Stahl et al., 2013). The cause for the long lasting PFBS elution is unclear. It is possible that PFBS was displaced into deeper layers of the lysimeter, where it was bound and only displaced from its bonding position over time.

Investigations at a real contaminated site also largely confirmed the findings of the laboratory tests. While the longer-chain PFAS were found in higher concentrations in soil-bound form, the shorter-chain PFAS were found in groundwater in higher concentrations (Figure 27). Due to the higher mobility of these compounds in comparison to the higher molecular weight PFAS, these compounds are found in groundwater in higher concentrations, whereas PFOS and longer-chain molecules are more retarded.

Similar experiences were made at other locations. The elution of a flood clay sample by means of a column test according to DIN 19528 showed a clearly different PFAS composition in the eluate than in the soil. While PFHxA and approx. 5 % PFOA were almost exclusively detectable in the soil, PFHxS and PFOS dominated in the eluate. At a water-to-solid ratio of 32 L/kg, about 58 % of the original contamination was eluted. Even from soil samples in which the solid concentrations of PFAS were below the limit of determination (10 µg/kg), PFAS up to 4.4 µg per 1 kg of solid could be eluted with the 2:1 shaking method (DIN 19529) (Bantz et al., 2011). For the evaluation of the pathway soil → groundwater, the determination of the solid concentrations is therefore not sufficient, but eluates (liquid:solid of 2:1) are required.

5.4.6 Enrichment at the Air-Water Interface

PFOS, PFOA and related PFAS are surfactants and will naturally accumulate at air-water interfaces, with air acting as the hydrophobic phase. It is therefore expected that adsorption at these interfaces can provide a significant retardation mechanism for these PFAS in the unsaturated soil zone[24]. The retardation (R) is given as :

$$R = 1 + \frac{K_{ai} \cdot A_{ai}}{\theta_W}$$

with K_{ai} = air-water adsorption coefficient [cm^3/cm^2], A_{ai} = specific air-water interface [cm^2/cm^3], θ_w = volumetric water content [-]. Typical values are for K_{ai} = 0,0005 cm, A_{ai} = 80 cm^{-1} and θ_w = 0,26.

The surface activity and the air-water interface adsorption potential respectively is influenced by the length of the perfluorinated chain (Brusseau, 2018).

Lyu et al (2018) investigated the retardation in partially unsaturated soil columns. The retardation of PFAS increased with decreasing water saturation and grain diameters (i.e. increasing size of the air-water interface). Retardation was higher at low PFOA concentrations. This indicates a nonlinear interface adsorption. The results showed that adsorption at the air-water interface is a significant retention source for PFOA and is responsible for about 50 – 75 % of the total retention in the soil column.

The adsorption of the PFAS at the air-water interface also depends on the ionic strength of the soil solution. The soorption increased from 0 to 6 mM ionic strength, after which further adsorption increase was low (Silva et al., 2019).

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[24] This process is an adsorption mechanism, not a distribution between air and water.

Physicochemical Properties (Summary)

The perfluoralkane acids are completely dissociated at neutral pH values. Their solubility is moderate and decreases strongly with increasing chain length. Except for the fluortelomer alcohols, the PFAS are non-volatile.

Sorption takes place preferentially at the TOC of the soil. In contrast to conventional contaminants, they sorb less to hydrophobic and more to proteinic structures. The sorption increases with increasing chain length. Sulfonates sorb more strongly than carbonates with the same chain length. Only at very low TOC do electrostatic interactions play a role. Electrostatic bonding is also more important with shorter-chain PFAS than with longer-chain ones. Furthermore, pH-value and salinity influence sorption.

Desorption is not complete, especially with longer-chain PFAS. Some of the PFAS desorb much worse and may possibly remain irreversibly bound. PFAS can also accumulate at the water-air interface with air as the hydrophobic compartment. This process is also dependent on several parameters and can account for up to 75 % of the total sorption.

Therefore, the chances of predicting the PFAS being released into the groundwater are low.

6 Microbial Biotransformation

PFAS are not fully biodegradable[25], i.e. mineralisable (Colosi et al., 2009; Ochoa-Herrera et al., 2008, 2016). Perfluorinated alkane acids are not subject to any microbial changes. Only polyfluorinated compounds are subject to microbial biotransformation. Similar processes also occur in higher organisms. In this case, the precursors are biotransformed by the attack of cytochrome P450 enzymes (Vestergren et al., 2008).

The precursors are transformed into perfluoroalkane acids as final products which do not transform further under environmental conditions and are very persistent. It should be emphasized that none of the more than 5,000 PFAS compounds are biologically mineralizable.

Due to their high oxidation state, PFAS should be usable for microorganisms as electron acceptors for energy production in anaerobic processes (similar to the reductive dechlorination of volatile chlorinated hydrocarbons). Although this defluorination is thermodynamically possible, it has not yet been detected. Reasons for this could be the lack of suitable enzymes, the high binding strength of the C-F bond or the lack of structures suitable for electrophilic or nucleophilic attack. The non-degradability was confirmed by a series of degradation experiments with ^{14}C-labelled PFOA ($C_7F_{15}^{14}COOH$) and with different bacterial mixed cultures and different electron donors. In all experiments, neither biodegradation nor biotransformation of PFOA could be detected (Liu and Avendaño, 2013)[26].

Polyfluorinated compounds on the other hand are subject to biotransformation. These reactions can be very different. During hydrolysis, parts of the molecule are split off at certain points within the molecule (functional groups such as esters, ethers, urethanes etc.) by the addition of water. The stability of these bonds determines the biotransformability of PFAS by hydrolysis. Figure 28 shows the hypothetical cleavage of an ester bond in a fluorotelomer derivative. The cleavage product, here 8:2 FTOH, is further transformed via complex biological reactions to PFOA and other products (see below).

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[25] Degradation at this point means a complete ^degradation to the mineral end products, thus a mineralization. The microbial conversion of the precursors to the perfluoroalkanoic acids as stable end products should therefore always be called biotransformation.

[26] Degradation by fungal enzymes is discussed in Appendix B.

Comparable hydrolytic cleavages with subsequent more complex degradation reactions are expected for EtFOSE derivatives containing hydrolysable functional groups (Figure 28, below).

Figure 28   Scheme of the biotransformation of 8:2 fluorotelomer derivatives (top) and selected perfluorooctane sulfonamide derivatives.
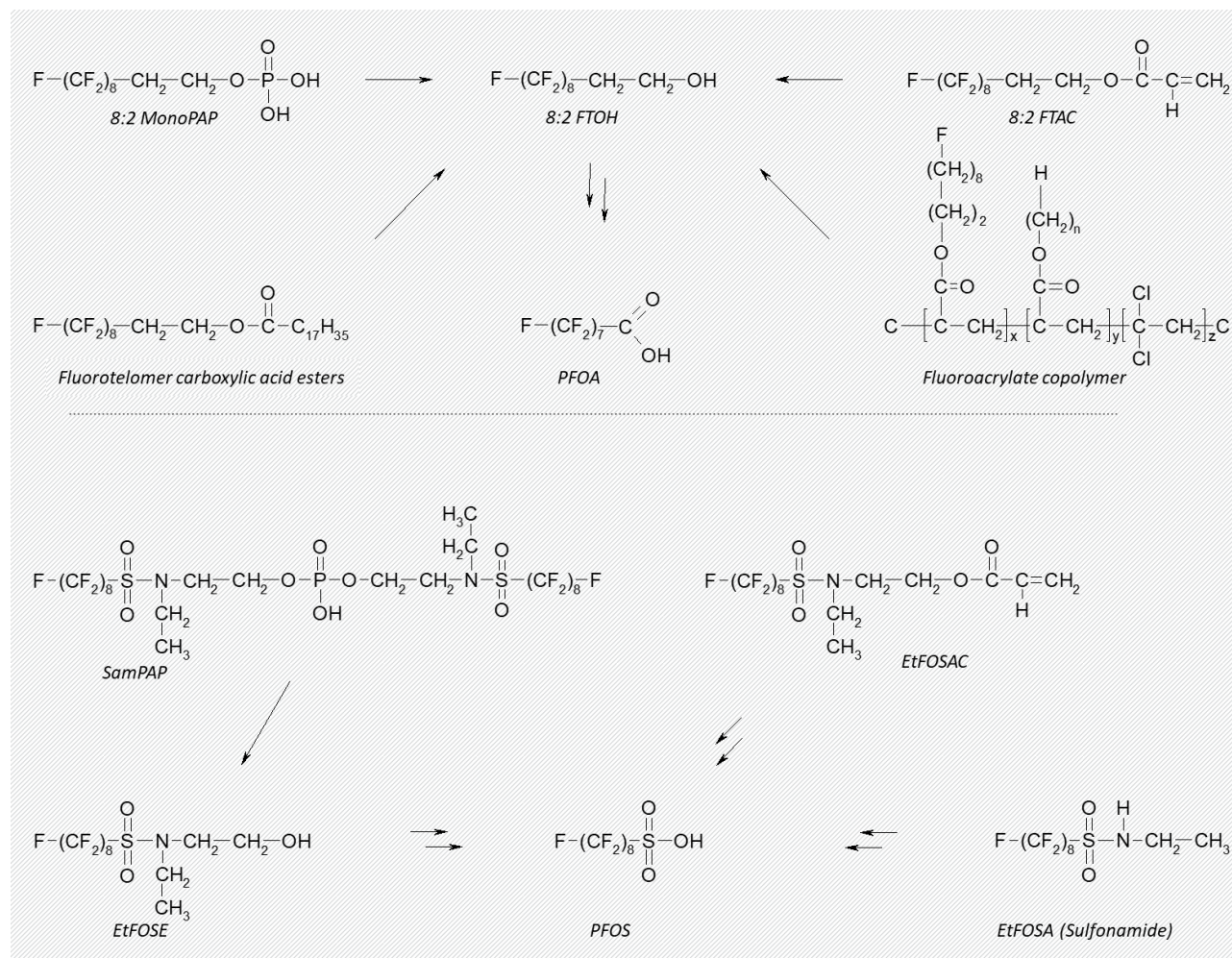
Initial hydrolysis reactions of the ester bonds are marked by simple arrows, complex transformation paths by double arrows. The biotransformation of EtFOSAC is hypothetical, that of EtFOSA has so far only been demonstrated in mammals. Source: Liu and Avendaño, 2013.

In addition to hydrolysis, a successive removal of terminal non-fluorinated carbon atoms takes place (Benskin et al., 2013; D'Agostino and Mabury, 2017; Dasu et al., 2013; Dasu et al, 2012; Dinglasan et al., 2004; Frömel and Knepper, 2010; D'Eon and Mabury, 2010; Lee et al, 2014; Liu et al., 2010; Russell et al., 2010; Wang et al., 2005, 2009; Weiner et al., 2013). To achieve biotransformation of PFAS, the transforming bacteria require at least one hydrogen atom on the α-carbon atom adjacent to the perfluoroalkyl chain for initial attack (Key et al. 1998). Many polyfluorinated precursors are biotransformed to PFAA, which contain a perfluoroalkane chain that is shorter at the end than in the starting compound (Harding-Marjanovic et al., 2015; Liu and Avendaño, 2013). The CF_2-groups are therefore not completely microbially inert. If CH_2-groups are found in the molecule in the immediate vicinity of the CF_2-groups, the fluorine can be split off from at least one of the CF_2-groups in the C-chain. Obviously, in order to break the C-F bond, it is necessary for adjacent, non-fluorinated alkyl residues to be present, via which the molecule can be activated to such an extent that the carbon-halogen bond can be cleaved. The entire biotransformation takes place via complex mechanisms.

For example, investigations on various telomeric alcohols (2n:2 FTOH) have shown that they are bio-transformable without restrictions (Butt el al., 2014). The transformation path is shown below for the compound 6:2 FTOH (Figure 29) (Kim et al., 2013). The transformation of 6:2 FTOH differs significantly from the degradation of the analogue non-fluorinated hydrocarbon compound. While in the latter case the oxidation takes place at the second C atom (oxidation) and C_2-bodies (activated acetyl residues: acetyl-CoA) are split off one after the other, in the case of FTOH there is an oxidation at the first C-atom (oxidation) and C_1-bodies are split off one after the other. These one-carbon removal pathways represent a novel reaction in microbial metabolism. The entire biotransformation and defluorination takes place in several individual steps.

While the PFAS pathway (II) is the main degradation pathway in the biotransformation of 6:2 FTOH with the formation of PFHxA and is followed by all bacteria studied, the remaining reactions (X:3 pathway)[27] (I) are only catalyzed by certain bacteria (Figure 29).

Only recently, further novel degradation products have been detected. For example, the saturation of the 6:2-FUCA (III; Figure 29) with H_2 leads to 3-fluoro-5:3 acid. Starting from 5:2-ketone, over 3F-5:2-ketone ultimately 2H-PFHxA is formed. A number of such 2H-perfluoroalkane acids with very different chain lengths have already been detected by non-target analysis.

While the initial substance was rapidly converted (t½: approx. 2 days; for 8:2 FTOH t½ is approx. 7 days; Wang et al., 2009, 2005), the metabolites could still be detected for a very long time. The main biotransformation pathway of 6:2 FTOH leads to PFPeA and 5:3 acid (15 %) (after 180 days incubation). The yield of the main product PFPeA ranges from 0.5 % in a mixed bacterial culture, 10.4 % in an aerobic river sediment to 30 % in aerobic soils. The biotransformation of 8:2 FTOH occurs in a very similar way (Parsons el al., 2008, Wang et al., 2009).

Transformation studies using the radioactively labelled compounds [3-^{14}C] 8:2 FTOH showed a number of other important results (Wang et al., 2009). After 7 months, up to 35 % of ^{14}C was irreversibly bound to the soil and could only be removed by burning the soil. This part of the PFAS, presumably covalently incorporated into the soil matrix as so-called *bound residues*, lost its toxicological potential and its chemical identity. The formation of the boundary residues is usually linked to a microbial enzymatic catalysis. The formation of boundary residues is confirmed by the fact that free fluoride (F-) counts only partly for the "mass loss" (Dinglasan et al., 2004). In addition to PFOS, shorter-chain perfluorocarboxylic acids such as PFHxA (approx. 4 %) also occurred.

The detection of the ^{14}C label in [14]CO$_2$ (6.8 % of the initial amount) as well as in shorter-chain PFAS compounds provided direct evidence that several CF_2 groups were microbially removed and mineralized from 8:2 FTOH.

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[27] X stands for an indefinite number of perfluorinated carbon atoms.

Figure 29   Proposed aerobic biotransformation pathway of 6:2 FTOH
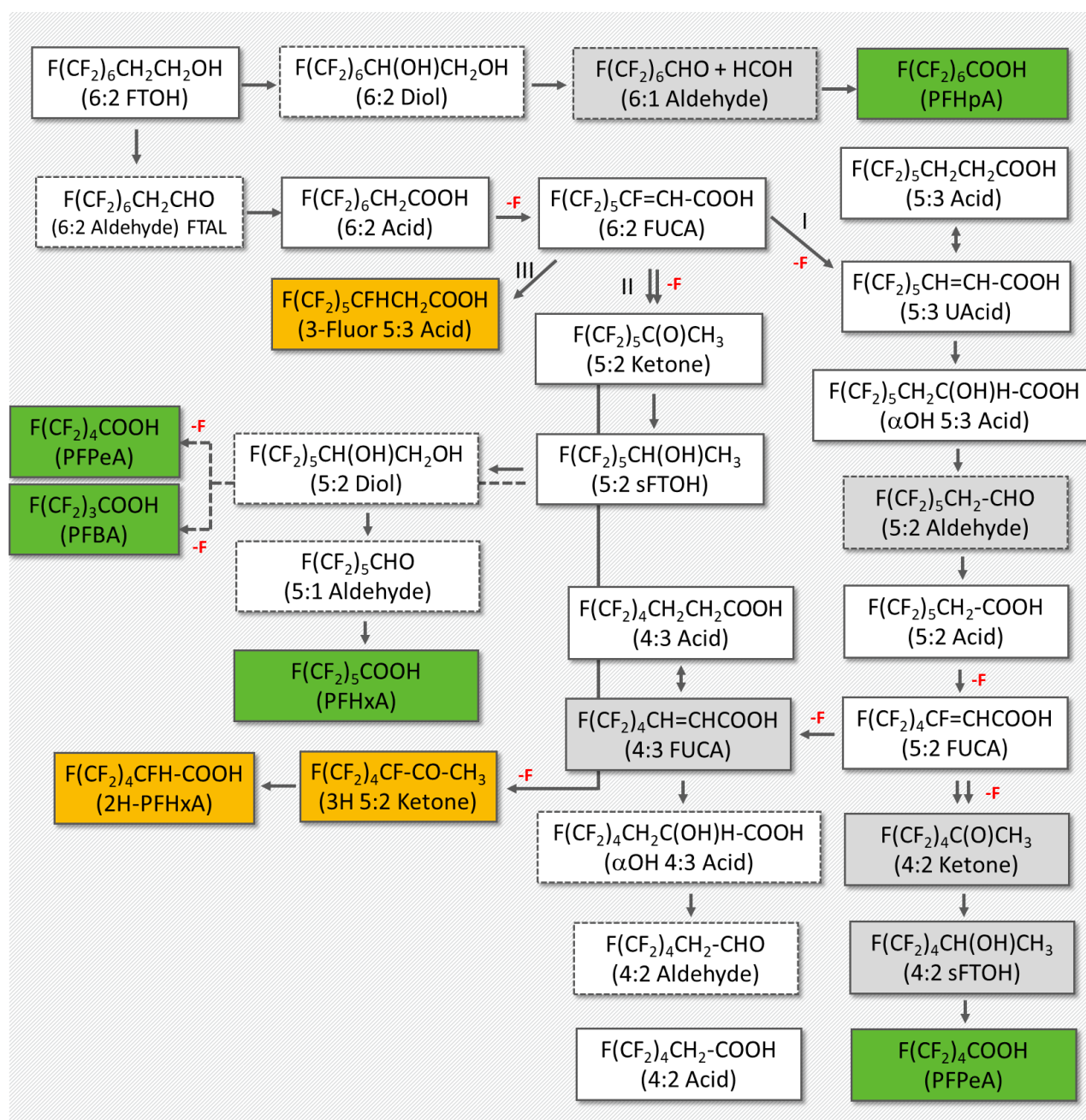
The dark grey-shaded compounds are suspected but not proven. Perfluoroalkanecarboxylic acids as end products have a green background and novel metabolites are purple, -F characterize the steps in which fluorine is cleaved off. Double arrows indicate reactions consisting of several steps. Dotted boxes and arrows are suspected but not detected metabolites or reactions. sFTOH = secondary fluorotelomer alcohol, FTAL = fluorotelomer aldehyde, FTUCA = unsaturated fluorotelomer carboxylic acids, 5:3 UAcid denotes a compound with 5 fully fluorinated C atoms and 3 non-fluorinated C atoms. The last C-atom represents the carboxylic acid function. "U" stands for unsaturated (C-C double bond). The remaining designations are self-explanatory. Source: Butt et al 2014, Liu et al., 2010, modified.

During the biotransformation of 2n:2 FTOH, a number of metabolites occur, which show different rates of conversion. Among the secondary alcohols, 5:2-sFTOH shows a faster transformability than 7:2-sFTOH. Also among the starting compounds (6:2 FTOH or 8:2 FTOH) the shorter molecule is more rapidly transformed. The faster biotransformability was therefore generally attributed to the smaller size of the molecules to be transformed or the greater bioavailability due to the higher solubility (Liu and Avendaño, 2013).

In the transformation pathway of fluortelomer-based compounds, x:2-sFTOH[28] and above all x:3 acids occur. Compared to other transient metabolites they are relatively stable and can therefore be used as indicator substances for the identification of the starting products.

Among the central metabolites, 7:3 acid (7:3 acid) and 5:3 acid were investigated in more detail with regard to their further biotransformation. While 7:3 acid was hardly converted with activated sludge in 90 days (product in small amount: PFHxA), 5:3 acid was rapidly transformed to 4:3 acid, 3:3 acid, PFPeA, and PFBA (Wang et al., 2012).

Contrary to previous investigations, the transformation of the unsaturated 4:3 acid (4:3 UAcid) does not end with the 4:3 acid, but a further cleavage of a CF_2-group takes place according to the same mechanism as with longer-chain acids to form a 3:3 acid (Figure 30). This suggests that, in principle, mineralization of FTOH is possible, although no proof of this has yet been provided. The assumption that telomer alcohols (after biotransformation) are a source of perfluorocarboxylic acids (Wang et al., 2009) is therefore only partially correct, since the predominant proportion of molecules is transformed to saturated and unsaturated fluorotelomer acids.

Figure 30   Proposed aerobic biotransformation pathway of 4:3 UAcid
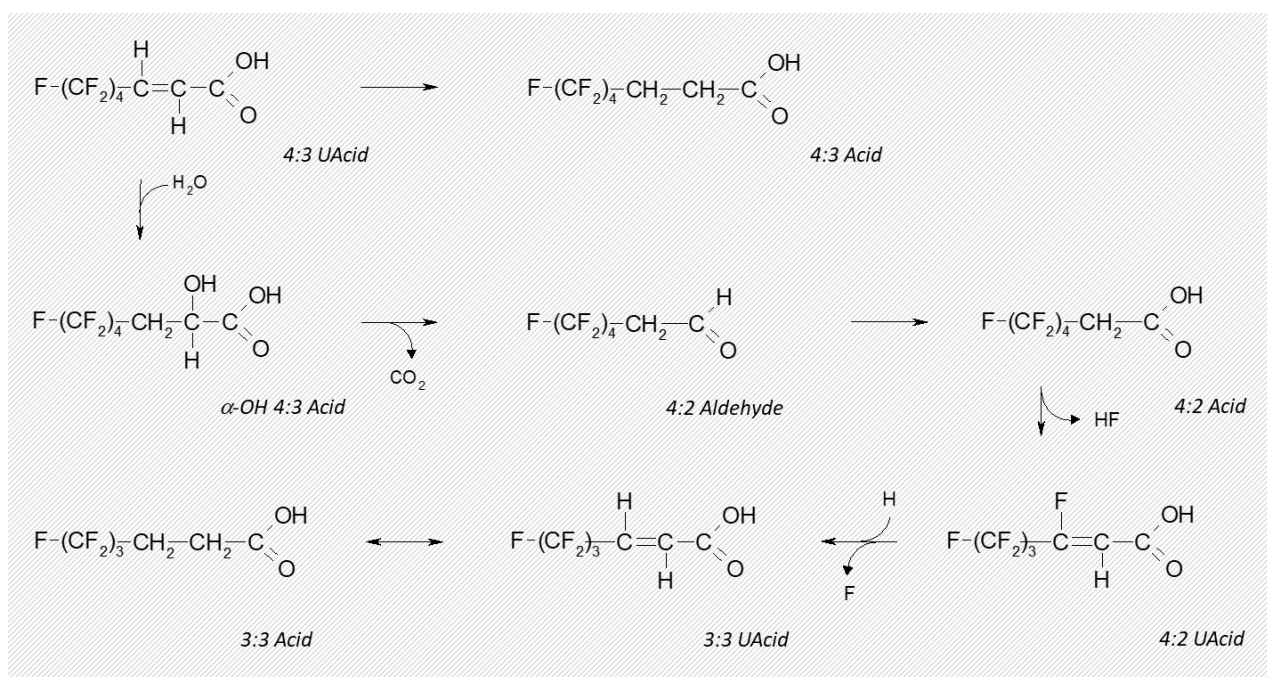
The aldehydes were suspected, but not proven. Source: Wang et al., 2012.

Investigations with single alkane-oxidizing bacteria (*Pseudomonas sp., Mycobacteriaum sp.*) and a fluoroacetate-degrading bacterium (*Pseudomonas sp.*) showed that these strains can transform 4:2, 6:2 and 8:2 FTOH, but no growth was found with these substrates as the only carbon source. From this it can be concluded that the biotransformation of FTOH was cometabolic. This also appears to be supported by the fact that up to a concentration of 2 g/L, FTOH does not inhibit microbial respiration in the activated sludge, so the PFAS do not interfere with microbial metabolism (Liu and Avendaño, 2013).

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[28]   x:3-acids are polyfluorinated carboxylic acids with x fully fluorinated carbon atoms with (in this case) 3 non-fluorinated carbon atoms, for the sFTOH the s stands for secondary alcohols (R-COH-CH$_3$).

While the microbial PFAS-transformation takes place exclusively under aerobic conditions, under anaerobic (methanogenic) conditions a biotransformation of 6:2 and 8:2 FTOH was detected for the first time in 2013. The FTOH were mainly transformed to polyfluoroalkane acids such as FTCA's, FTUCA's and X:3 acids. Perfluorocarboxylic acids only accounted for ≤ 0.4 % of the original substrate mass. Biotransformation was much slower compared to aerobic conditions (Liu and Avendaño, 2013).

The transformation is also accompanied by a substantial change in the physicochemical properties of the compounds. For example, with 8:2 FTOH the vapour pressure of the parental compound is 20,000 times higher than that of the transformation product PFOS. In contrast, the water solubility of the parental compound is lower by a factor of 100.

Studies on the biotransformation of 8:2 FTOH by higher organisms (rat, mouse, trout), human hepatocytes, human liver microsomes and cytosol indicate that 8:2 FTOH is only slightly transformed in humans, unlike in lower organisms, and 8:2 FTOH is therefore not a significant source for the formation of PFOA or other perfluorocarboxylic acids (Nabb et al., 2007).

Higher substituted compounds such as N-EtFOSE (N-ethyl-perfluorooctane sulfonamide ethanol) and N-MeFOSES are under aerobic conditions subject to a biotransformation typical for the non-fluorinated structural elements (Figure 31), beginning with an oxidation of the alcohol residue to acid. Accordingly, 2-(N-ethyl-perfluorooctane sulfonamide)acetate (N-EtFOSAA) is detected as the main transformation product. However, this can be metabolized by further oxidation steps. As a result, the amino function and the aliphatic non-fluorinated chain are removed from the molecule to form a perfluorosulfonic acid (here: PFOS). If the sulphate group is also eliminated, a perfluorocarboxylic acid (here: PFOA) is formed. Since the limiting step is the transformation of EtFOSAA, instead of PFOS EtFOSAA appears as the main product (Liu and Avenda-ño, 2013). N-EtFOSE is not transformable under anaerobic conditions.

With the phase-out of PFOS, it appeared necessary to quantify the potential release of PFOS from precursors previously emitted to the environment. The aerobic biotransformation of EtFOSE was investigated in two soils (forest silt loam, agricultural soil) for about 200 days. The transformation rate (t½) of the initial product ranged from a few days to one month. The PFOS yields at the end of the experiment were in the range of 1.1 - 5.5 mol-% (Zhang et al., 2017). This shows that after the end of the experiment PFOS can still be generated in soils contaminated with the precursors.

The aerobic microbial transformation of the polyfluorinated alkyl phosphates (PAP) takes place by hydrolysis of the phosphoric acid ester bond and release of the respective FTOH, which can then be converted according to the known transformation pathways (Lee et al., 2010). The rate of hydrolysis of the ester bond decreases continuously with increasing chain length of the perfluoroalkane residue. While in laboratory experiments short-chain PAP was completely transformed within a few days, in 10:2 mono-PAP no complete transformation could be observed even after 90 days. PAPs can obviously be transformed in higher organisms in the same way as experiments with rats have shown (D' Eon and Mabury, 2007).

The fact that some precursors hydrolyse to FTOH suggests that some of the contaminants may be lost by outgassing into the unsaturated soil zone or into the atmosphere. This was confirmed by microbial column experiments (Arcadis, 2018).

Figure 31   Proposed biotransformation pathway of N-EtFOSE
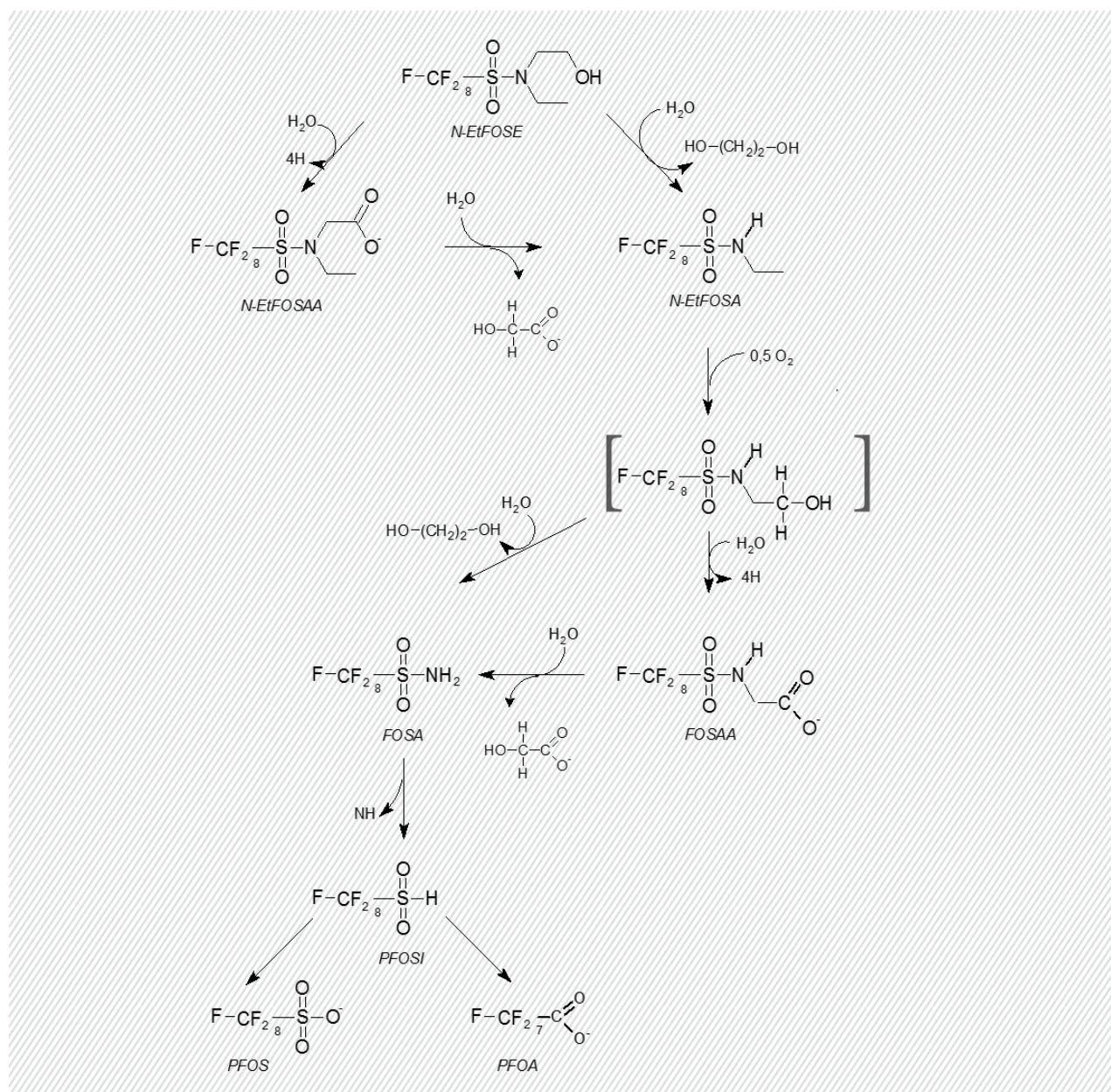
Connection in brackets were suspected but not proven. PFOSi = perfluorooctane sulfinate, reductive NH-elimination under aerobic conditions seems unlikely at first. Presumably, this step, which is shortened here, is based on a much more complex transformation reaction. Source: Parsons et al., 2008.

The question of degradation rates was addressed in a series of laboratory experiments. A compilation of precursor degradation rates can be found in Held and Reinhard (2016). Under optimal aerobic laboratory conditions, the half-lives for many compounds range from days to a few months. In summary, monomeric compounds are usually aerobically quickly biotransformable, whereby the speed generally decreases with increasing chain length. Only 6:2 FTS is biotransformed comparatively slowly. Dimers, such as 6:2-di-PAP, are transformed much more slowly than the corresponding monomers (here 6:2-PAP). The comparison of 8:2-FTSME with 8:2-FTCTE shows that the trimer (triester) can be transformed much more slowly than the monoester.

In this context, the question arises why precursors can still be detected in the unsaturated (aerobic) soil many years after the PFAS spill has occurred. One of the reasons for the detection of precursor long after the spill has occurred could be the formation of long-lived metabolites. It is suspected that a large proportion of the metabolites are not detected with the available analytical methods. However, numerous TOP analyses also show the presence of precursors and indicate that under environmental conditions the precursors are not rapidly transformed.

From the available data, it is not yet possible to draw conclusions about the duration until a complete transformation to the perfluoroalkanoic acids. For example, the biotransformation of 8:2 fluorote-lomer stearate (t½ = 28.4 d) resulted in the formation of only 4 mol-% PFOA at the end of the test period (94th day), although the formation process had not yet reached a plateau. During the aerobic transformation of 8:2 FTOH, less than 50 mol-% were found again as perfluoroalkane carboxylic acids after 7 months. Apparently, one or the other step in the transformation cascade leading to the stable end products is quite slow, which is especially true for the intermediately formed 5:3 acids. All in all, these data prove that the PFAS probably remain "hidden" in metabolites (which are not analysed so far) for a long period of time.

Figure 32   Degradation of the precursor in the groundwater
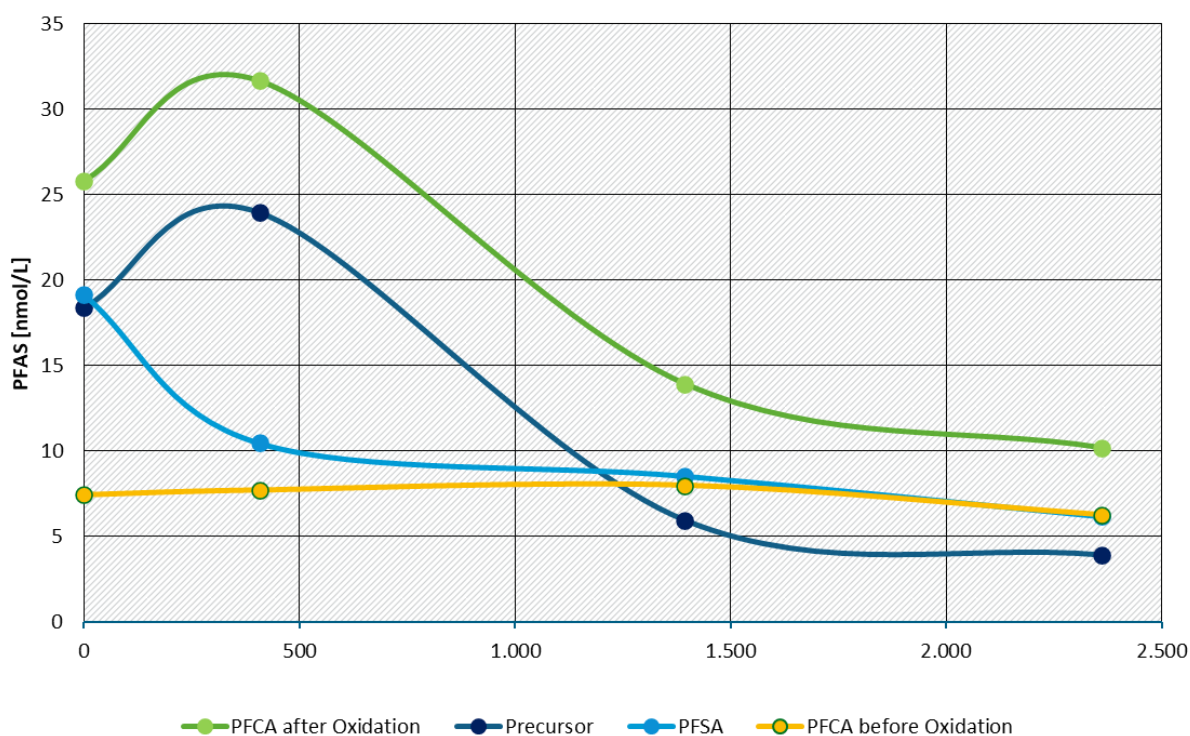
The TOP assay only leads to the formation of PFCA. From the PFCA concentration before and after oxidation, the concentration of the precursor can be calculated. It is assumed for simplification that 1 molecule of precursor degrades to one molecule of PFSA[29]. This allows the precursor concentration [in µMol/L] along the groundwater flow direction to be calculated and thus also the transformation rate constant (1st order transformation). The dilution is deducted from the transformation rate. Source: Arcadis Germany, 2019.

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[29] There are also exceptions to this rule. For example, two perfluoroalkanoic acids can be formed from diPAPs. However, this is negligible in most cases (with the exception of those in which the PFAS originate from paper finishing).

The transformation products also show a partly very strong sorption to the soil matrix, which significantly reduces their bioavailability and probably their biotransformability. In addition, some compounds such as SAmPAP (sulfonamide-based polyfluoroalkyl-phosphate diesters) have very long half-lives. N-EtFOSE also showed a reduced transformation rate in the presence of soil.

Presumably, the high hydrophobicity of these compounds leads to a strong sorption at the soil and thus to a low bioavailability that reduces biotransformation. This effect is believed to be responsible for the longevity of many precursors in sediments and soils. These results can be proved by the fact that considerable precursor contents were still detected at fire extinguishing training areas more than 20 years after the end of the trainings. This shows that isolated investigations in the laboratory on the degradability of precursor single substances under analysis of only their disappearance are of little help.

If the PFAS precursors enter the groundwater after desorption and transport, substantial further degradation is only possible if the groundwater is aerobic and has not been anaerobicised by the accompanying input of other organic contaminants. Using the TOP assay, the 1st order degradation rate of precursors at a defined aerobic site was determined to be 0.0003 d^{-1} (Figure 32).

Polymers. The investigation of the biotransformation of polymeric compounds poses a particular challenge. Essentially, the detection is only possible by the formation and analysis of expected metabolites, which can lead to the fact that other transformation reactions and also the splitting of the polymer backbone remain undetected. To study the biotransformation of fluoropolymers, a synthetic fluoroacrylate polymer with FTOH side chains of different lengths was synthesized (Figure 33) and aerobically incubated in soil for more than 2 years.

Figure 33   Schematic polymer backbone and release of N-MeFOSE
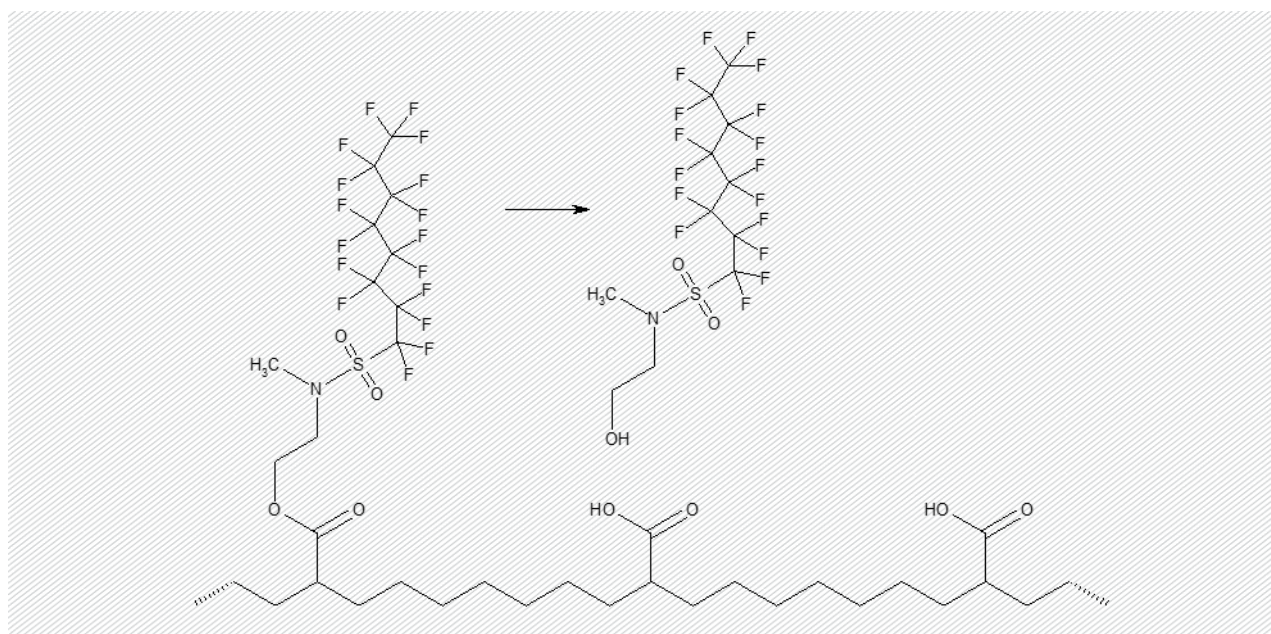
Source: Fricke und Lahl, 2005

The half-life for the cleavage of the ester bond was prognosed to be 1,200 - 1,700 years (Russel et al., 2008). Other studies come to half-lives of only about 10 - 17 years for fine-grained polymers. Overall, the microbial transformation of polymers only plays a minor role with regard to the release of PFAS into the environment.

Other authors suspect that the release of excess, unbound monomers may occur during surface finishing and may occur. Also, in the further course of the process, for example through abiotic degradation of the PFAS-containing polymers during cleaning or wear of the polymer-coated materials, a release of monomers may be possible. To what extent this plays a significant role with regard to the released masses has still not been conclusively determined.

Polymers such as fluorotelomer acrylates and methacrylates (8:2 FTAC and 8:2 FTMAC) can be hydrolysed to release 8:2 FTOH. The urethane bond (-NH-CO-O-) is another bond often used to produce fluortelomer polymers. Although the microbial hydrolysis of the urethane bond is similar to the hydrolysis of the ester bond, perfluorocarboxylic acids are formed only to a very small extent ($\leq$ 1 mol-%). The main degradation products of the fluorotelomer ethoxylates (FTEO, $F(CF_2CF_2)_x(CH_2CH_2O)_yH$ with x = 2 to 6, y = 0 - 18) are the corresponding carboxylates (FTEOC, $F(CF_2CF_2)_x(CH_2CH_2O)_{y-1}CH_2COOH$).

Besides microbial transformation, abiotic transformation also takes place, especially in the atmosphere. Especially volatile compounds, such as FTOH, react with chlorine atoms, oxygen molecules or photochemically produced OH-radicals and are thereby oxidized. Photooxidation with chlorine atoms results mainly in fluortelomercarboxylic acids (FTCA), -aldehydes (FTAL), perfluoroaldehydes (PFAL), carbonyl fluoride (CF_2O), PFOA and PFNA. Photooxidation of FTOH with OH-radicals lead to FTAL, PFAL and carbonyl fluoride (Houtz and Sedlak, 2012).

Stable metabolites. Many biotransformation pathways proceed via X:3 acids as central metabolites (e.g. 5:3-fluorotelomeric acid in the degradation of 6:2-FTSA). Even if the developed schemes (e.g. Figure 29) postulate a further biotransformation to the stable perfluorocarboxylic acids, investigations have shown that these metabolites obviously show a high stability. With the biotransformation of 6:2-FTSA, an almost continuous increase in the concentration of the 5:3 acid was observed over the entire experimental period (90 d) parallel to the increasing formation of the end products (PFPeA, PFHxA, PFHpA) (Zhang et al., 2017).

Figure 34   Degradation of 6:2-FTSAS
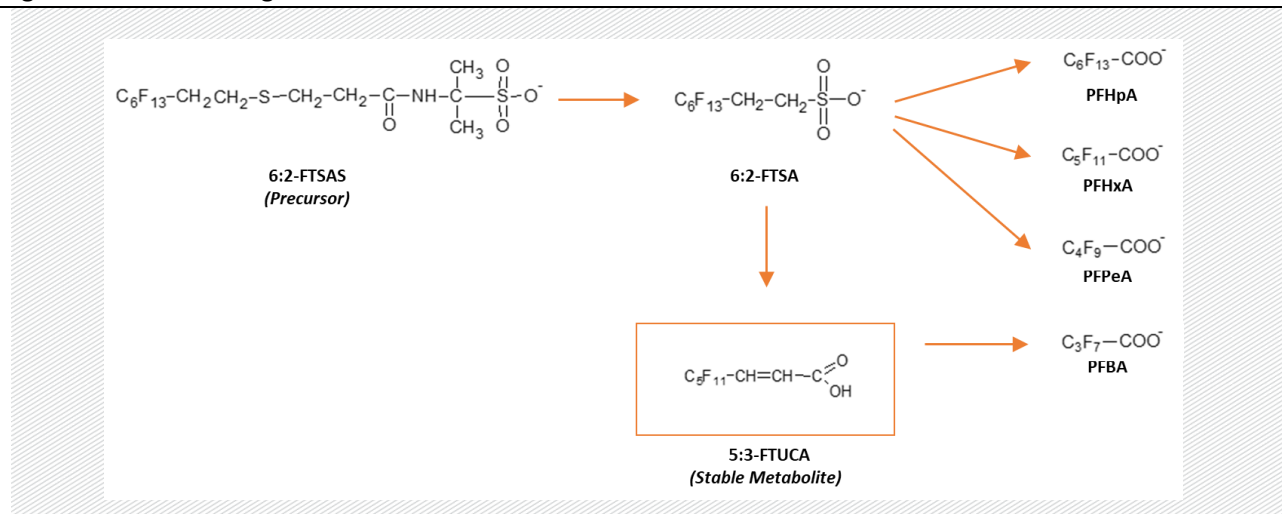
Source: Weiner et al., 2013

Weiner at al (2013) found an accumulation of 6:3-FTUCA (6:3-fluortelomer-unsaturated carboxylic acid) as stable metabolites during the biotransformation of 6:2-FTSAS (6:2-fluortelomer-mercapto-alkylamidosulfonate), a component of AFFF foams.

Biotransformation (Summary)

Perfluorinated compounds are not degradable in the sense that they can be subject to mineralization or biotransformation. Precursors can be biotransformed into perfluorinated compounds. The end products are persistent perfluoroalkane carboxylic acids and perfluoroalkane sulfonic acids. In addition, other products (not yet available for commercial analysis) can be produced as stable end products. The transformation essentially takes place only under aerobic conditions; under methanogenic conditions, the degradation is extremely slow.

Biotransformation seems to be retarded in nature, probably due to the low bioavailability of the compounds (including metabolites). The transformation rates and kinetics as well as the accumulation of different end products are thus not only dependent on the chemical structure but also on the environmental conditions. Over long periods of time, the compounds remain hidden as non-analyzed "metabolites". A part of the transformed compounds is irreversibly bound to the soil (Bound Residues), a very small part is mineralized to CO_2. If FTOHs are released during the precursor transformation, they can, in principle, be released as vapor into the unsaturated soil zone or the atmosphere.

During precursor biotransformation, the perfluorinated chain is shortened. Thus, mineralization of the FTOH-based compounds seems possible in principle but has not yet been proven.

The biotransformation leads to metabolites with substantially different physicochemical properties. Some metabolites seem to be very stable.

7   Plant Uptake and Effects on Plants

The studies carried out so far on the transfer of PFAS from soils and aqueous solutions to plants have shown that PFAS are taken up in plants and can thus enter the food chain either directly or indirectly via the path soil - feed - animal. The average dietary exposure to PFAS (7 substances) of adults and children is ≤ 1 ng/d per kilogram body weight. There are different dietary exposure patterns from region to region due to different dietary habits and contaminations. Plant foods (e.g. fruits and vegetables) are most important for the dietary intake of PFHxA, PFOA and PFHxS, while consumption of foods of animal origin (especially fish and seafood) leads mainly to the intake of PFDA and PFUnDA. PFNA and PFOS are equally absorbed with animal and plant foods (Klenow et al., 2013).

The accumulation of PFAS in plants does not only depend on the type of plant and the PFAS compound, but several factors (such as soil properties) can influence uptake from the soil. Therefore, in addition to experiments on transfer from soils to plants, experiments on transfer from PFAS-containing nutrient solutions were also carried out to eliminate soil-specific effects. Some commonalities can be deduced from all experiments.

The PFAS are taken up from the soil solution with the water via the root system, transported within the plant with the transpiration water current (systemic uptake) and accumulate preferentially in the leaves. Since potatoes showed a higher concentration of PFAS (here: PFOS and PFOA) in the skin than the potato body, it was assumed that the PFAS first sorb to the root surface tissue and then are absorbed. In carrots, however, no increased PFAS contents were detected in the skin. In contrast to the potato, the carrot is not only a storage organ but also has the function of a root. It was therefore assumed that the PFAS initially sorbed on the root surface are also absorbed into the plant and do not accumulate there as in the potato (Lechner and Knapp, 2011).

This adsorption thus appears to be particularly important for the longer-chain non-polar PFAS, while polar PFAS compounds are able to penetrate the natural barriers of plants (Blaine et al., 2014). Once they have penetrated the epidermis of the root, they are transported within the plant. To do so, they must penetrate a cell membrane (the so-called Casparian strip) (Figure 35).

The mechanisms for this are different. While PFOA is actively transported, PFOS is transported passively (Wen et al. 2013). Accordingly, a lower uptake of PFOS than of PFOA was found (Chen et al., 2012).

Figure 35   Conceptual model of the intake of perfluorocarboxylic acids on a tomato plant
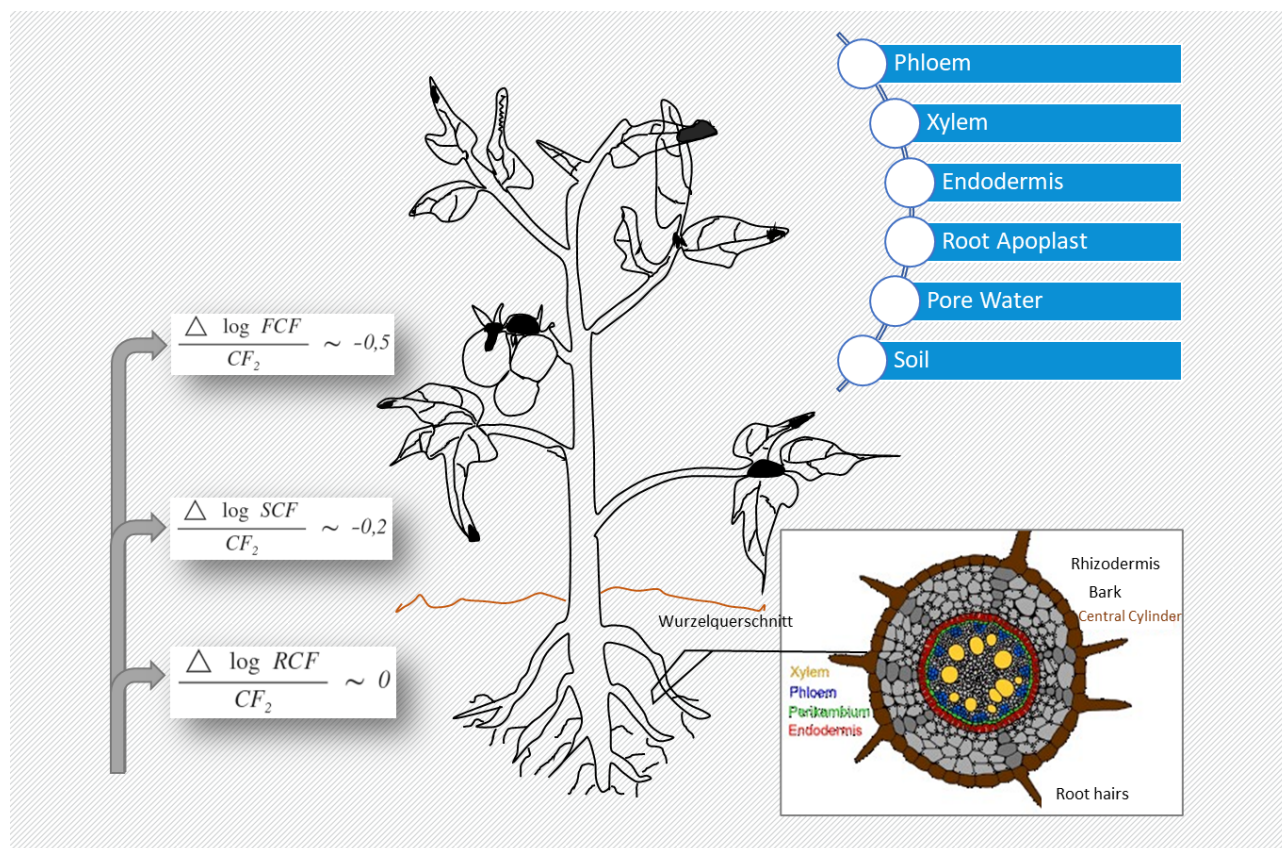
The approximate values are given in log BCF per CF$_2$ group. RCF, SCF and FCF denote root, shoot, and fruit concentration. The exposure pathway is shown at the top right. Source: Blaine et al., 2013.

Experiments with wheat seedlings showed that with the beginning of exposure, the concentration in the plant increases rapidly up to an asymptotic value (Zhao et al., 2013). Other authors find a linear increase in the concetrations in the plant with increasing PFAS load in the soil.

However, very high concentrations can also have negative effects. For example, at high soil PFOA/PFOS concentrations, yellowing, reduced growth and necroses were observed in plants[30] (oats and potatoes from 25 mg/kg soil PFOA/PFOS). Maize showed no significant reactions up to 50 mg/kg PFOA/PFOS in soil (LAUV NRW, 2011). Above 50 mg/kg a significant decrease in yields was observed in maize and spring wheat, in potatoes already from 25 mg/kg. An influence of soil content on oat yields was not discernible (Stahl et al., 2009), oats thus appear to be less sensitive. Apparently, PFOS has a beneficial effect in soil in low concentrations.

While chlorophyll formation is stimulated at concentrations < 10 mg/L, above this level inhibition is observed. PFOS affects biomass and the lengthening of roots and leaf formation (Zhao et al., 2010). Overall, significant plant species-specific differences were found with respect to growth impairments and plant damage and the accumulation and distribution within the exposed plant.

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[30]   Investigated were wheat, oats, potatoes, corn, and ryegrass

The uptake in plants is characterized by different parameters. The bioaccumulation factor (BAF) describes the concentration ratio of soil to plant (Beek, 1991, Gobelius et al., 2016, Jørgensen et al., 1998). Sometimes this quantity is also called transfer factor.

$$BAF_{Plant} = \frac{C_{Plant}}{C_{Soil}}$$

The term transfer factor (TF) can also refer to the roots alone (RTF = root transfer factor) or to the distribution in different tissues of the plant.

$$TF = \frac{C_{Root}}{C_{Stem}}$$

In the following the term, BAF is used for uptake from the soil and transfer factor for distribution within the plant.

PFAS chain length. Short chain PFAS with a molecular weight < 300 g/mol can be easily absorbed by the roots. They show a high uptake rate in leaves, stems, and fruits (Wang & Cousins 2015). As the number of biological barriers increases during transport within the plant (from the roots to the shoots and finally to the fruits), the retardation becomes more and more pronounced with increasing hydrophobicity (i.e. chain length) (Felizeter et al., 2014). Presumably, the higher uptake of short-chain PFAS is also due to their lower sorption to the soil matrix.

This has been demonstrated by studies on lettuce (*Lactuca sativa*) and tomatoes (*Lycopersicon lycopersicum*) (Figure 36). Concentrations of up to 266 ng/g PFBA and 236 ng/g PFPeA (lettuce) were detected in soils treated with sewage sludge. In tomatoes the concentrations were 56 ng/g PFBA and 211ng/g PFPeA. Field studies have shown that in a single application of sewage sludge the concentrations of most PFAS in the plants remained below the limit of determination (Blaine et al., 2013, 2014).

Figure 36   Correlation between log BAF and PFAS chain length
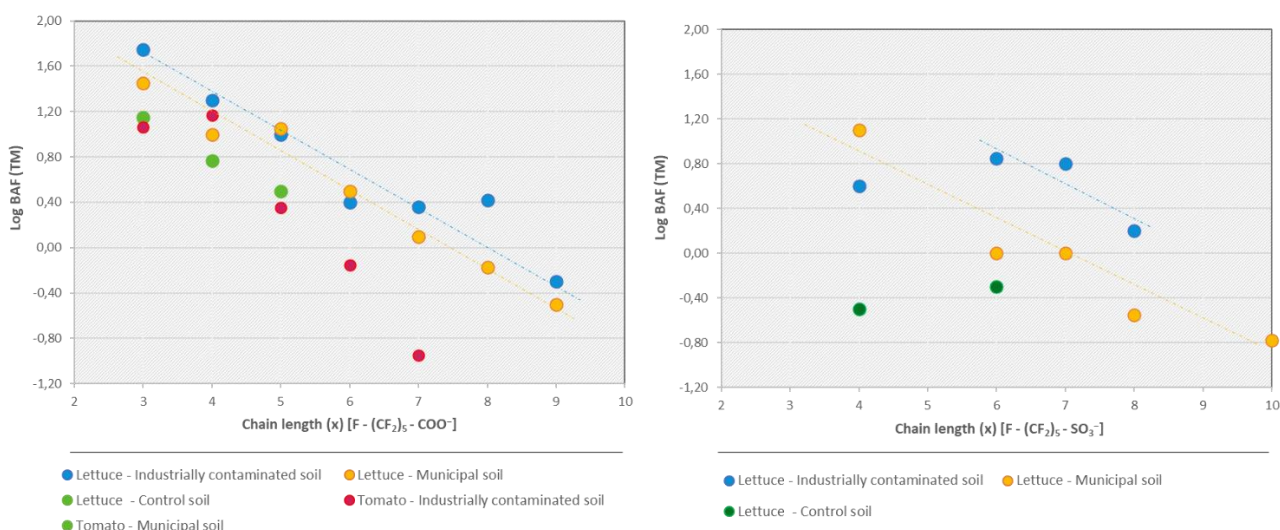
Source: Blaine et al., 2013

The results of the investigations on transfer in plants have shown that perfluorosulphonic acids accumulate by a factor of 2 - 3 more than perfluorocarboxylic acids of the same chain length and that in vascular experiments the contents of PFOS and PFOA in the plants (and presumably of all other PFAS) increase linearly with their concentration in the soil (Stahl et al., 2009).

Essentially, three properties of PFAS determine their ability to pass through a membrane (Krippner et al., 2014):

► Type of functional groups,
► Position of the functional groups,
► Size and polarity of the molecule.

The composition of the soil can also have a great influence on the bioavailability of the PFAS.

Underwater plants behave fundamentally different. The BAF increased with increasing chain length. In general, aquatic plants have the absorption preference for long-chain PFAS, especially PFOS. This emphasizes sorption as a major effect on uptake (Zhou et al., 2017). When the matrix has no or very low adsorption power, as is the case with water, adsorption to the plant dominates the uptake.

pH value. The influence of the pH-value was investigated in the range pH 5 - 7 on maize. For most compounds (PFPeA, PFHpA, PFOA, PFNA, PFBS, PFHxS and PFOS) no pH-dependent uptake was found. However, soil acidity affected the uptake rate of PFDA, which decreased with increasing pH. The authors postulated that PFDA is more protonated at low pH values, which forces its uptake (Krippner et al., 2014). Other studies on wheat showed an increase in PFOS uptake rates as pH decreased to pH 6 (Zhao et al., 2013). The reason for the effects of pH is the bioavailability of the contaminants (Higgins and Luthy, 2006). As the Ca^{2+} concentration increased, the sorption of PFAS sediments to the soil increased, while the pH value decreased

Sorption to the soil. Most POPs (*Persistent Organic Polutants*) are expected to sorb to soil organic matter, which reduces their bioavailability and uptake in plants (Higgins et al. 2007, Higgins and Luthy 2006, Jeon et al. 2011). Accordingly, it can be expected that this is also true for PFAS. In this respect, the concentrations of the bivalent cations (Ca^{2+}, Mg^{2+}) and the pH value of the soil also have an influence (Ullberg, 2015) (Chapter 5.4).

Temperature. The influence of temperature was investigated with wheat (*Triticum aestivum L.*) for two PFAS compounds with different enrichment sites (PFOA: roots, PFBA: stem) (Figure 37).

Figure 37   Influence of the temoerature in the uptake of PFBA and PFOA
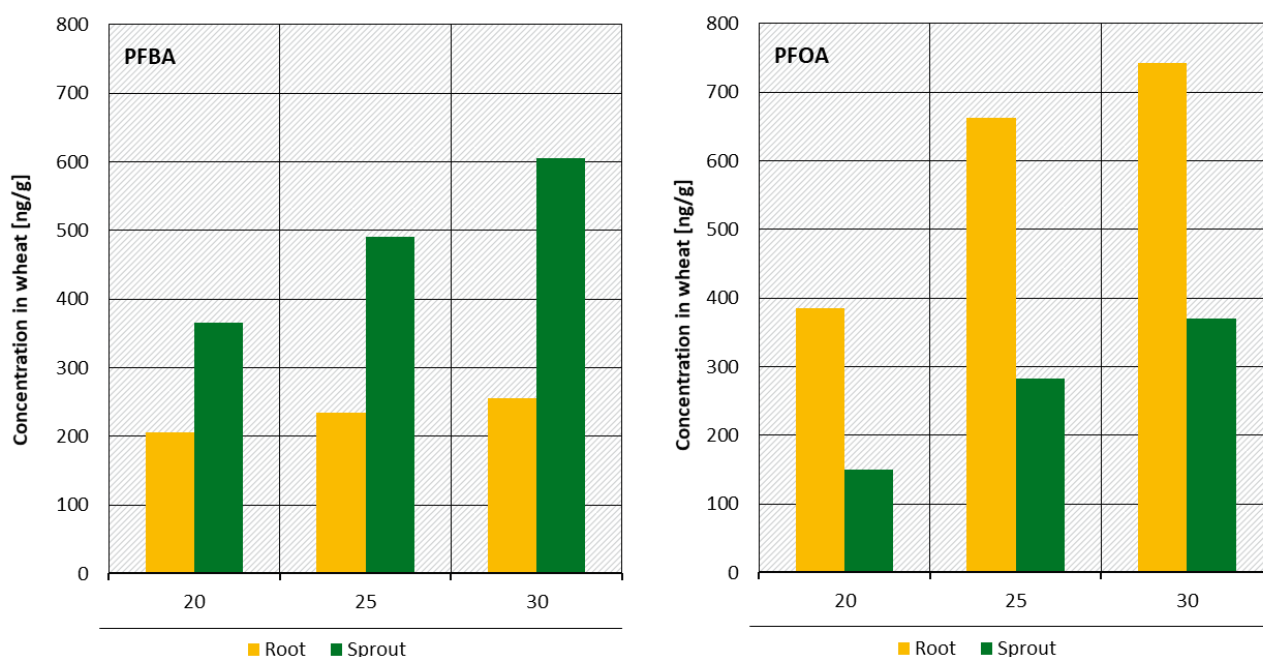
Source: Zhao et al. 2013

The temperature increase from 20 °C to 30 °C doubled the PFAS concentrations in the plant. This also applies to the transfer factor, which for PFBA increases from 0.7 to 1.2 at a temperature difference of ten degrees (Zhao et al. 2013). Temperature thus significantly influences the uptake efficiency of roots and shoots.

Accumulation in different organs. After uptake by the roots, the transport takes place through the plants by means of the transpiration current. The first organs in which PFAS is stored are the leaves and the stem. Fruits are the last storage organ (Blaine et al. 2014). The investigation of agricultural crops showed a higher accumulation of PFAS in vegetative parts of plants compared to storage organs (grains) (Stahl et al. 2009). This was confirmed for PFOA and PFOS in some vegetables (Lechner and Knapp, 2011)**.**

In a study with PFAS-contaminated solutions (14 compounds) and tomato plants, cabbage and courgettes, it was found that, despite some differences in uptake efficiency, uptake from the solution into the roots and further distribution within the different parts of the plant was quite similar. In some studies, PFOA and PFOS were found in significantly higher concentrations in the vegetative parts of the plant than in the storage organs (fruit). In a study on the transfer of a mixture with several PFAS compounds, only PFAS to C_{11} were transported into the storage organs, but in comparably low concentrations. This is understandable as the storage organs hardly contribute to transpiration (Felizeter et al., 2014). The concentrations of the contaminants in the plant parts show (exemplary given for tomato plants in Table 8) that uptake (or storage) in the root of the plant predominates over transfer to the vegetative plant parts and storage organs.

Table 8   Distribution of PFAS in different parts of tomato plants (in % of the total amount taken up) (Felizeter et al., 2014)

Compound	Roots	Stem	Branches	Leaves	Fruits
PFBA	3	4	10	43	40
PFPeA	5	8	7	20	60
PFHxA	12	8	9	42	30
PFHpA	12	8	9	67	4
PFOA	29	7	9	53	1
PFNA	56	5	7	32	0
PFDA	72	5	5	17	0
PFUnA	88	4	5	5	0
PFDoA	90	5	3	2	0
PFTrA	96	2	1	1	0
PFTeA	98	1	0	1	0
PFBS	21	4	9	65	1
PFHxS	38	5	7	49	0
PFOS, branched	68	6	5	21	0
PFOS, linear	71	5	4	19	0

Edible plants. The uptake of PFAS depends strongly on the plant species. Regarding human health, it is important to be able to quantify the risks from the consumption of vegetables or plants. Furthermore, the identification of vegetables or fruits with a low bioconcentration factor can help to find possible uses for PFAS-contaminated soils and to avoid the risks to humans from consumption.

Contaminated sites include not only agricultural land affected by contaminated sewage sludge or compost, but also, where appropriate, vegetable gardens. Table 9 summarises bioconcentration and transfer factors for several plant species used in agriculture and kitchen gardens. As already discussed, PFAS are stored particularly in the vegetative parts and not so much in fruits or grains (Stahl et al. 2009). A plant with a high bioconcentration factor would therefore not pose a high risk for human or animal consumption if PFAS accumulate exclusively in the roots and only the shoots are edible. This is not the case with cabbage and tomatoes, which accumulate PFAS in the edible parts. Strawberries are particularly rich in PFAS (Landkreis Rastatt, 2017).

Table 9   Ability of plants and vegetables to absorb and concentrate PFAS

Plant	Use	PFAS	BCF*	TF**	Experimental design	Reference
Alfalfa (*Medicago sativa*)	Agriculture	PFOS	S/S = 0.407	R/S = 0.131	Laboratory [1]	Wen et al., 2016
		PFOA	S/S = 3.15	R/S = 0.304		
Cabbage (Brassica oleracea)	Kitchen garden	PFBA	S/E = 7.0 - 8.0		Laboratory [2]	Felizeter et al., 2014
		PFeA	S/E = 7.0 – 8.1			
		PFOA	S/E = 1.0 – 2.0			
Carrot (*Daucus carota*)	Kitchen garden	PFOS	S/E = 0.04		Laboratory [1]	Lechner u. Knapp, 2011
		PFOA	S/E = 0.05			
Cucumber (*Cucumis Sativus*)	Kitchen garden	PFOS	S/E = < 0.01		Laboratory [1]	Lechner u. Knapp, 2011
		PFOA	S/S = 0.03			
Lettuce (*Lactuca sativa*)	Kitchen garden	PFOS	S/S = 0.396 S/P = 0.1	R/S = 0.102	Laboratory [1] Field trials	Wen et al., 2016, Blaine et al., 2013
		PFOA	S/S = 1.18	R/S = 0.196	Laboratory [1]	
		PFPeA	S/P = 16.3		Field trials	
		PFBA	S/F = 40.0			
Maize (*Zea mays*)	Agriculture	PFOS	S/S = 0.17-0.80	R/S= 0.0624	Laboratory [1]	Wen et al., 2016, Navarro et al., 2017, Liu et al., 2017, Blaine et al., 2013
		PFOA	S/S = 0.206 S/S = 0.02	R/S = 0.122	Field trials	
		PFHxS	S/L = 9.39		Laboratory [1]	
		PFBS	S/L = 4.0			
		PFBA	S/P = 64.8 S/P = 2.5		Field trials	
Mung beans (*Vigna radiat*)	Kitchen garden	PFOS	S/S = 0.683	R/S = 0.165	Laboratory [1]	Wen et al., 2016
		PFOA	S/S = 8.40	R/S = 1.08		
Potato (*Solanum tuberosum*)	Agriculture	PFOS	S/E = < 0.01		Laboratory [1]	Lechner u. Knapp, 2011
		PFOA	S/E = 0.01			
Radish (*Raphnus sativus*)	Kitchen garden	PFOS	S/S = 0.468 S/S = 2.61	R/S = 0.179	Laboratory [1]	Wen et al., 2016
		PFOA	S/S = 5.34 S/S = 3.00	R/S = 1.78		
Strawberry	Kitchen garden	PFBA	S/F = 202.56		Laboratory [2]	Blaine et al.,

Plant	Use	PFAS	BCF*	TF**	Experimental design	Reference
(Fragaria ananassa)	den					2014
		PFPeA	S/F = 242.52			
		PFOA	S/F = 1.95			
Soja bean *(Glycine max)*	Kitchen garden	PFOS	S/S = 0.251	R/S = 0.0551	Laboratory [2]	Wen et al., 2016
		PFOA	S/S = 0.296	R/S = 0.093		
Tomato *(Lycopersicon lycopersicum)*	Kitchen garden	PFBA	S/P = 18.2		Field sampling	Blaine et al., 2013
			S/E = 7.0 - 8.0		Laboratory [2]	Felizeter et al, 2014
		PFPeA	S/P = 14.9		Field sampling	Blaine et al., 2013
			S/E = 7.0 – 8.0		Laboratory [2]	Felizeter et al, 2014
		PFOA	S/E = 0.4 – 0.5			
Wheat *(Triticum aestivum)*	Agriculture	PFAS		R/St = 0.2 -0.84	Laboratory [1]	Wen et al., 2014
		PFSA		R/St = 0.19 -0.37		
		PFAA	S/F= 0.06-1.00			
		PFBA	S/F = 33.1		Field sampling	Liu et al., 2017
Zucchini *(Cucurbita pepo)*	Kitchen garden	PFBA	S/E = 0.7 – 0.8		Laboratory [2]	Felizeter et al., 2014
		PFeA	S/E = 1.0 – 2.0			
		PFOA	S/E = 0.4 – 0.5			

*   S/S = Soil-Stem S/E = Soil-Edible part of plants, S/F = Soil-Fruit, S/P = Soil/Plant, S/L = Soil-Leaves

**   R/S = Root-Stem, R/St = Root-Straw

(1) Soil mixed with sewage sludge

(2) Hydro culture

Based on the available data on the concentration of PFAS in plants, a possible risk to humans from the consumption of these plants can be assumed. The current tolerable daily intake (TDI) is 0.15 µg/kg body weight/day for PFOS and 1.5 µg/kg body weight/day for PFOA (Annex B). If, for example, the analysis data of maize grown on PFAS-heavy soils (max. 6.4 µg/kg TS PFOA, max. 94 µg/kg TS PFOS), wheat grain (max. 43 µg/kg TS PFOA, max. 4.3 µg/kg TS PFOS) and potatoes (peeled) (max. 15 µg/kg TS PFOA, max. 6 µg/kg TS PFOS), a person weighing 70 kg would have to consume about 1.7 kg potato or 2.4 kg wheat products (both based on dry matter; TS) daily to exceed the TDI for PFOS (or PFOA), assuming this is the only route of intake. In the case of maize, however, 110 g would already be sufficient to exceed the TDI for PFOS. However, the TDI should not be exhausted by a single food as humans usually ingest several foods containing PFAS.

The risk of exceeding the TDI for PFOA or PFOS by the consumption of contaminated plants can be considered relatively low. On the other hand, it has been shown that especially the vegetative parts of the plants absorb PFAS from the soil. As a result, animal feed could be a major source of input into the food chain.

Non-edible plants. Non-edible plants were investigated mainly regarding the decontamination of contaminated areas (phytoremediation). In a pilot test (wetland) in Taiwan the phytoextractability of PFAS was investigated with four different species (temperature: 28 - 32 °C):

- ► *Hygrophila pogonocalyx Hayata,*
- ► *Ipomoea aquatic Forssk,*
- ► *Ludwigia (x) taiwanensis,*
- ► *Eleocharis dulcis.*

These plants are mainly found in wetlands. The uptake capacity was highest in *Hygrophila pogonocalyx Hayata*. This species has only a small, flatly distributed root biomass, but it is very common and grows faster than the other species. The uptake was 11.6 µg/g PFOA and 46 µg/g PFOS in 15 days. The worst intake was obtained with *Eleocharis dulcis*, the only plant with tuber roots. Previous studies show that in wetlands, uptake of contaminants correlates with root density and size (Chen et al., 2012). The comparatively high uptake rates were achieved in a small experimental scale (0.5 kg plant mass in 4 tanks, 0.1 kg soil per tank, addition of 90 litres water per tank (5 mg/L PFOS/PFOA) under rigid conditions.

PFOA accumulation was investigated in a study with several different riparian wetland plants including reeds. The highest accumulation was achieved with the thick-stemmed water hyacinthe (*Eichhornia crassipes*), which has a fibrous rooting system (38 ng/g, BAF = 0.37; Mudumbi et al., 2014).

In a previous study, wastewater from a sewage treatment plant was discharged into an artificial wetland. The total concentration was 100 - 170 ng/L, main compounds were N-EtFOSAA, PFDS and PFOS. No significant removal of PFAS was observed. (Plumlee et al., 2008).

To evaluate the uptake capacity of PFAS, small plants and trees were sampled at a fire extinguishing training site in Sweden. Σ_{26}PFAS were detected in soil and groundwater in the range of 16 - 160 µg/kg and 1.2 -34 µg/L respectively. Samples of different plant species and tissues (roots, stem, kernels, branches, leaves, needles) of the species silver birch (*Betula pendula*), spruce (*Picea abies*), bird cherry (*Prunus padus*), rowan (*Sorbus aucuparia*), European mountain ash (*Aegopodium podagraria*), long beech (*Phegopteris connectilis*) and wild strawberry (*Fragaria vesca*) were examined. The plants showed a high variability of the concentrations with the highest Σ_{26}PFAS concentrations in vegetative parts of plants with up to 97 ng/g wet weight (FG) and up to 94 ng/g FG in birch leaves and spruce needles, respectively. The bioconcentration factors were highest for foliage. These trees can form deep roots and thus absorb PFAS also from groundwater (Gobelius et al., 2017). The disadvantage is that birch shed its leaves every autumn and this part of the tree is exactly the one with the higher PFAS concentration. The annual leaf collection must be managed in such a way that no recontamination of the soil occurs (Gobelius et al., 2016).

Considering a mixed stock of silver birch and spruce in combination with a regular harvest of leaves and birch sap, it is possible to remove 1.4 g Σ_{26}PFAS per year and hectare from (heavily) contaminated areas. An alternative approach consists in felling the birch trees in combination with removal of the underwood. It is estimated that 0.65 g/a/ha Σ_{26}PFAS would have to be removed. A simple meadow with ground elder would remove 0.55 g/a/ha Σ_{26}PFAS.

With the above-mentioned Σ_{26}PFAS contamination, 1 ha shows an inventory of 0.8 - 8.0 g (remark.: height of the contaminanted layer: 0.5 m). The decontamination rate would thus be in a manageable range. Nevertheless, the technical feasibility still rises considerable questions.

Other studies have shown that the uptake in plants does not lead to a significant decontamination of the soil. A long-term test with planted outdoor lysimeters, which were spiked with a technical PFOS/PFOA mixture, which also contained shorter-chain perfluoralkanoic acids as a contaminant, showed a depletion of 0.001 % PFOA and 0.004 % PFOS after 5 years by the growth of the plants. The plants were harvested regularly so that the decomposition of the biomass did not lead to recontamination (Stahl et al., 2013).

The investigations in the German Federal State Baden-Wuerttemberg on PFAS uptake by different crops were summarized as shown in Figure 38.

Figure 38 PFAS uptak through various crops
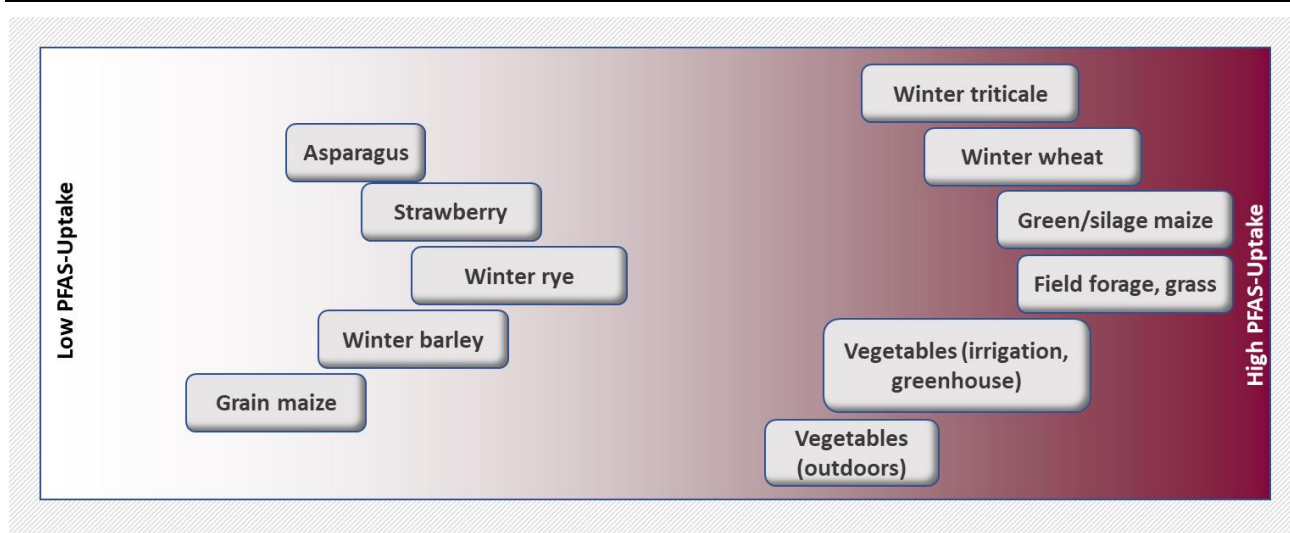
Source: https://rp.baden-wuerttemberg.de/rpk/Abt5/Ref541/PFAS/PublishingImages/pfc_anbauempfehlu. ng_gross.jpg

Plants as indicators. With investigations of plants in the vicinity of a PFAS production site it could be shown that PFAS are transported as aerosols and accumulates with precipitation deposited in plants (here: wheat and corn). The concentration in the plants decreased logarithmically with the distance to the PFAS source. The wheat grain showed a higher contamination by a factor of 11.3 than the corn grain. Presumably, the higher transpiration rate of wheat by a factor of about 2 contributes to the higher PFAS accumulation (Liu et al., 2017).

Precursor. Using the TOP assay, it could be shown that precursors are also taken up in plants (Nürenberg et al., 2018b).

Uptake in Plants (Summary)

The ability of plants to absorb PFAS depends on several factors. The essential factor is the length of the PFAS carbon chain. The shorter it is, the better the PFAS are absorbed by the plants. This is mainly due to the sorption capacity of the soil (bioavailability). If PFAS bind better to the soil, they are less well absorbed. Therefore, aquatic plants show the opposite preference: Longer-chain, better sorptive PFAS are better absorbed than short-chain ones. In terrestrial plants, the longer-chain ones preferably sorb in the root area while the shorter-chain ones are transported within the plant.

Several other factors play a role, such as temperature and plant species. This leads to different accumulations in different parts of the plant. The investigation of agricultural crops showed a higher accumulation of PFAS in vegetative plant parts compared to the storage organs (grains).

In the end, the PFAS concentration in the plants (recycled fractions) can hardly be predicted by other easier to measure parameters (e.g. PFAS contamination of the soil).

Investigations on non-edible plants have so far been limited to the question pertaining to the extent of which depletion of PFAS in soil is possible through the accumulation of PFAS in plants. Depletion seems to occur only in cases where original soil contamination is low.

8 Bioaccumulation and Biomagnification

In addition to accumulation in plants, there is also accumulation in animal/human organisms. Data are available mainly for PFOS and PFOA. In contrast to most persistent organic pollutants (POPs), there is less accumulation in fat and muscle tissue than there is binding to protein (plasma proteins and β-lipo-proteins; Jones et al., 2003) and thus accumulation in protein-rich compartments such as blood and well supplied organs such as the liver, kidneys and spleen, but also in the testicles and brain. In animals as well as in humans, PFAS penetrate the placenta and are excreted with breast milk, but also, for example, in urine (Stahl et al., 2011). Overall, they accumulate along the food chain (bioaccumulation). It has been shown that animals at the upper end of the food chain have higher PFAS concentrations than animals at the lower end.

Bioaccumulation is thus the accumulation of a substance in an organism through absorption from the surrounding medium (establishment of equilibrium) or through food (accumulation). Due to the lack of knowledge of the exact binding sites, bioaccumulation was related to the PFAS concentration in the wet weight of the organnism (Haukas et al., 2007). Long-chain PFAS in particular have a higher potential for bioaccumulation across trophic levels (Asher et al., 2012; Awad et al., 2011). Bioaccumulation is described by the bioaccumulation factor (BAF):

$$BAF = \frac{C_O}{C_W}$$

with C_O = PFAS concnetration in the organism (µg/kg) and C_W = PFAS concentration in water.

The BAF thus has the unit L/kg. Since enrichment in fish is well known, many studies have concentrated on its investigation. The log BAF fish (bright fish) ranged from 1.9 - 3.2 for PFSA and from 0.88 - 3.47 for PFAS, while the log BAF fish liver was higher from 2.1 - 4.3 for PFAS and from 1.0 - 5.0 for PFSA. The PFA fingerprint in fish was different from that in water. The short-chain PFCA and PFSA such as PFHxS, PFHpA and PFOA were not detected in fish compared to water or only in very low concentrations. In general, the PFAS profile in the fish liver was similar to that of the whole fish. The accumulation of PFAS in fish liver was attributed to certain protein families. However, the exact mechanism of bioaccumulation and binding sites of PFAS in organisms is unclear (Awad et al., 2011).

Liu et al (2011) investigated the bioaccumulation of PFOS, PFOA, PFNA and PFDA in green mussels (*Perna viridis*). For all compounds, the BAF was higher at lower PFAS concentrations in the water phase, which was explained by a nonlinear adsorption mechanism. Based on the results, a new kinetic model for adsorption was proposed. Furthermore, a linear relationship between the BAF and the chain length or binding affinity was found (Figure 39).

The bioaccumulation of PFAS varies between species (Giesy et al., 2010). This shows that not only the binding of PFAS to proteins, but probably also the hydrophobicity of the substances plays an important role. Among others, fish, mussels, crustaceans, gastropods, shrimp, starfish and polychaetes were investigated with respect to strength and substance distribution. While fish and shrimp preferred to accumulate PFOS, other species showed a more even distribution of accumulated PFAS. Regarding the organ-specific distributions, larger PFAS concentrations were found in the intestine of fish (green eel).

Figure 39   Relationship between Δlog BAF and binding affinity (blue curve) or with the perfluori-
                   nated chain length (orange curve)
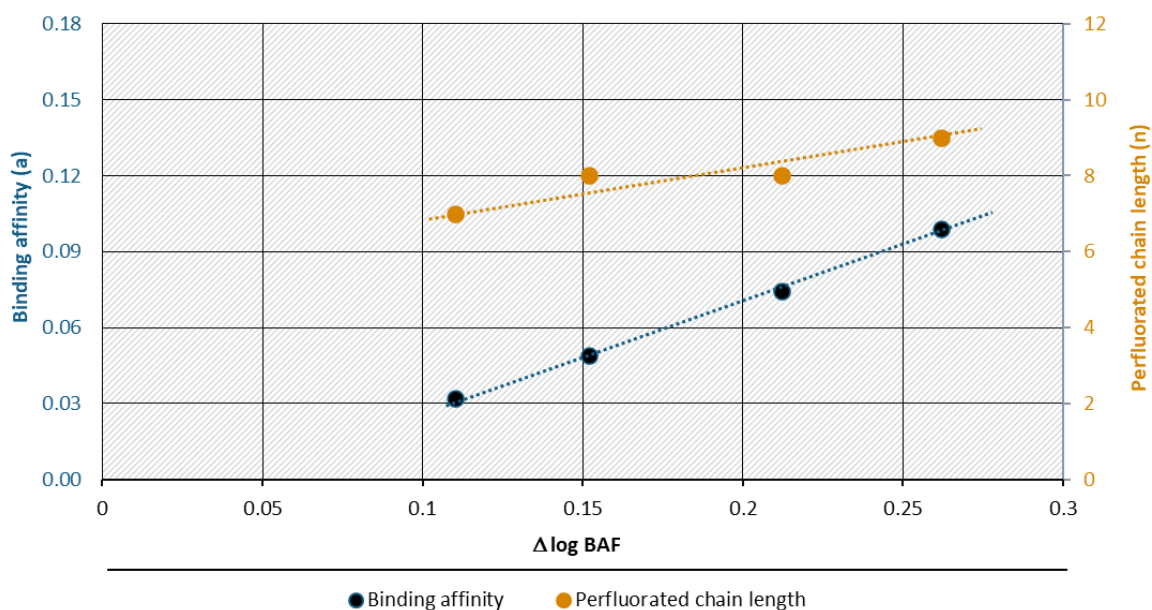
Source: Liu et al., 2011

This result suggests that PFAS are accumulated mainly via dietary exposure. In contrast, increased PFAS concentrations were found in mussels (oysters) not only in the intestine but also in the gills, suggesting that intake was both through water and food. The intestines of fish contained higher PFAS concentrations compared to other organs and tissues such as liver, gills, and fillet. In mussels, however, PFAS concentrations in gills and gut were comparable and relatively low concentrations were detected in the mantle. In crabs, the highest PFAS concentrations were found in the soft tissues, but also shell and legs contained about half of the PFAS concentrations of the soft tissues, indicating a possible direct absorption from the surrounding waters (Hong et al., 2015).

Also due to the fact that long-chain perfluorocarboxylic acids (C_{14}-C_{15}) in particular have been detected far from possible sources in fish, invertebrates and predators at the top of the food chain (seals, polar bears), a bioaccumulation potential for these compounds can be deduced (US EPA, 2009). Accordingly, C_{11}-C_{14}-PFAS have been included in the REACH Candidate List[31] because of their vPvB (very persistent, very bioaccumulative) characteristics

The log BAFs for PFOS described in the literature vary between 2.85 and 4.0 and are thus partly below the limit value of 3.7 (BAF = 5,000), above which substances are classified as very bioaccumulative (vB) (Stockholm Convention, 2009, Stockholm Convention on Persistent Organic Contaminants, 2006). Nevertheless, PFOS is referred to as vB in the European Directive 2006/122/EC, mainly because the "classical" determination of the bioaccumulation rate in the fatty tissue of organisms is insufficient for PFOS, as this substance mainly binds to proteins and thus the accumulation rates were initially underestimated.

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[31] http://echa.europa.eu/de/candidate-list-table.

It also meets the criteria P (persistent) and T (toxic) and is listed in Annex XVII (Restrictions) of the REACH regulation (Commission Regulation (EC) No. 552/2009). The classification of PFOA (PBT substance) as bioaccumulative (B) was based on weight-of-evidence studies, as this substance was detected in organisms at the top of the food chain. The classification of P and T was based on different data (ECHA, 2013, Vierke et al., 2013, 2014).

A systematic study with perfluorocarboxylic and sulfonic acids of chain length C_4 - C_{13} and three test organisms (rainbow trout, sunfish, bullhead carrot) showed a logarithmic increase of the bioconcentration factor (BCF[32]) with chain length, whereby perfluorosulfonic acids accumulate somewhat more. In summary (Conder et al., 2008):

► The bioaccumulation and thus the concentration of perfluoroalkane acids in the organisms depends directly on the length of the perfluorinated carbon chain,

► PFSA bioaccumulate more than PFCA of the same length of the perfluorinated carbon chain,

► PFAS with ≤ 7 fluorinated carbon atoms (PFOA and shorter-chain PFCA) can be described as non-bioaccumulative (BCF < 5,000 L/kg). The BAF of C_{4-6}-PFCA and PFBS is < 1, that of PFHxS is 10 and of PFOA 2 - 570 (Conder et al., 2008),

► PFAS with ≤ 7 fluorinated carbon atoms have a low potential for biomagnification in the food chain,

► The processes underlying bioaccumulation, especially those for long-chain compounds (> 7 CF_2-groups), are not yet sufficiently understood.

The terrestrial food chain showed about two times less enrichment than the marine food chain (Müller et al., 2011). Therefore, PFAS accumulate especially in marine animals. PFAS enter humans via the food chain (biomagnification) (Danish Ministry of the Environment, 2013). Hence, the two lead substances, PFOS and PFOA, are detectable in human blood, both in the general population and in infants (Commission Human Biomonitoring, 2009).

Biomagnification is thus a partial aspect of bioaccumulation. It describes the accumulation of pollutants in living organisms only through food via the unitless biomagnification factor (BMF):

$$BMF = \frac{C_{Consumer}}{C_{Food}}$$

This is done either with reference to the entire body or with reference to individual tissues. In this case, the concentration of the entire body is the sum of the concentrations of the individual tissues multiplied by their proportion ($f_{tissue,n}$):

$$C_{Body} = \sum_{n=1} C_{Tissue,n} \times f_{Tissue,n}$$

In the context of the investigation of the biomagnification of perfluorinated alkane acids in the terrestrial food chain (lichens → plants → caribous → wolves) C_8-C_{13}-PFCA and PFOS were regularly detected in all species. The lowest concentrations were found for vegetation. Wolf liver showed the highest concentrations, followed by caribou liver. The BMF were highly tissue and substance specific.

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[32] The Bioaccumulation Factor (BAF) is a dimensionless parameter that represents the ratio of concentrations in the organism to water. In fish tests, for example, the BAF is defined as the ratio between the concentration of the test substance in the test fish and the concentration in test water under equilibrium conditions (uptake rate by diffusion over body surfaces is equal to the elimination rate: excretion, outward diffusion or degradation). Compounds with a BCF of > 2000 L/kg or > 5000 L/kg for aquatic species fulfil the partial criterion for PBT- or vPvB-substances under REACH.

Therefore, individual whole-body concentrations were calculated and used for biomagnification and trophic magnification (Müller et al., 2011).

The trophic magnification factor (TMF[33]) was highest for C_9-C_{11} PFCA[34] (TMF = 2.2 - 2.9) and PFOS (TMF = 2.3 - 2.6). TMF values increase with PFAS chain length up to C_{10}-PFAS, and decrease thereafter (Müller et al., 2011). Houde et al. (2008) could show that the TMF for linear PFOS (4.6) is higher than that for the single-branched molecule (0.17 - 2.6). Dimethyl-PFOS showed no biomagnification.

Bioaccumulation and Biomagnifikation (Summary)

Bioaccumulation is the accumulation of a substance in an organism (animal, human) by absorption from the surrounding medium (after achieving equilibrium) or through food. It is described by the bioaccumulation factor (BAF). Long-chain PFAS have a higher potential for bioaccumulation across trophic levels. PFAS bind to protein structures rather than lipids.

The accumulation within a food chain is called biomagnification, it is described by the unitless bio-magnification factor (BMF). Biomagnification is thus a partial aspect of bioaccumulation.

The terrestrial food chain showed an enrichment about two times lower than the marine food chain. As a result, PFAS accumulates especially in marine animals. The PFAS reach humans via the food chain.

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9 Ecotoxicology and Human Toxicology

Due to the ubiquitous detection of PFAS in the environment, the toxicological effects of PFAS are being investigated more and more intensively. Due to its bioaccumulative property, there is increasing concern that long-term exposure could have adverse effects on the environment and humans. However, there is currently little toxicological and ecotoxicological data available for many compounds, apart from the lead substances PFOS and PFOA.

Ecotoxicology. Most studies on the ecotoxicity of PFAS have been performed using aquatic (fish invertebrates, algae) and less using terrestrial organisms (Bayerisches Landesamt für Umwelt, 2011). The studies showed clear differences between acute and chronic toxicity.

PFOS shows overall moderate acute toxicity to aquatic species (LC_{50} in the range of 33 - 91 mg/L for *Daphnia magna* (large water flea) after 48 h incubation; Giesy et al., 2010). Other studies come to similar orders of magnitude. PFOA also has moderate acute toxicity in animal models (Bundesinstitut für Risikobewertung, 2008).

In short-term exposures experiments (acute toxicity), marine fish and invertebrates are more sensitive to PFOS exposure than freshwater organisms. Regarding acute toxicity, duckweed in the sublethal area showed a death of the roots and a curvature of the leaves below the water surface in general. IC_{50} was reported to be 46-144 mg PFOS/L at 7 d exposure[35]. Frogs, frog embryos and tadpoles showed concentration-dependent malformations of the intestinal convolutions, edema and malformations of the *Chorda dorsalis* [36]and face when exposed to different PFOS concentrations. (Giesy et al., 2010)

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[33] The TMF provides information on the average change in contaminant concentration per relative trophic level and is calculated from the natural logarithm of the concentration of each organism relative to its trophic level.

[34] No enrichment for PFOA.

[35] IC_{50} refers to a mean inhibitory concentration of an inhibitor at which half maximum inhibition is observed.

[36] The *chorda dorsalis* is the original inner axial skeleton in the back of all so-called chordates. In all vertebrates it is created embryonally and usually recedes completely during the course of individual development.

PFOA shows moderate to low toxicity to aquatic species such as fish in short-term studies (LC_{50} in the range of 70 to 2,470 mg/L).

In general, although PFOS appears to be more toxic to aquatic organisms by a factor of about 10 than PFOA, PFOS, PFOA, their salts and the longer homologues can be classified as not very toxic to aquatic and other organisms overall in terms of acute toxicity. The lowest known NOAEL (*No Observed Adverse Effect Level*) for PFOS is 2.3 µg/L for the sugar mosquito *Chironimus* (Moermond et al., 2010). On the other hand, both PFOS and PFOA have been classified as toxic under REACH. For PFOA, this classification was based on the fact that the substance is toxic for reproduction. PFOS was classified as toxic due to its chronic toxicity. There are indications that some compounds may also act as endocrine disruptors (Danish Ministry of the Environment, 2013).

Based on the PFOS concentrations in groundwater commonly measured in environmental PFAS spills, PFOS is not expected to affect microbial communities. For example, an EC_{50} of 131 mg/L was determined for the cyanobacterium *Anabaena flos aquae* (96 h incubation, reference: cell density) (Giesy et al., 2010).

However, the composition of the zooplankton community has shown chronic toxic effects after exposure to PFOS and a decrease in total numbers. Fish exposed to PFOS did not show a significant reduction in egg hatching time and breeding success. Mortality and growth were also unaffected (Giesy et al., 2010).

A value commonly used in ecotoxicology is the PNEC (*predicted no effect concentration*, the concentration below which, in all probability, no adverse effects of an environmentally hazardous substance on the respective ecosystem occur). The PNEC is derived from toxicity studies. For the two compounds PFOS and PFOA, PNEC values for the aquatic system are already available within the framework of the European and international chemical evaluation. This value is 0.23 µg/L for PFOS (EU, 2011) and 570 µg/L for PFOA (OECD, 2008). The German authority working group LAWA-LABO (2017) also derived aquatic PNEC values for eight other PFAS compounds in the course of the "Derivation of insignificance threshold values for groundwater - Per and polyfluorinated compounds" after extensive data research and according to the rules of the TGD (2011). These are shown in Table 10.

Table 10   PNEC Concentrations

Compound	Abbreviation	PNEC [µg/L]
Perfluorobutanoic acid	PFBA	1,260
Perfluoropentanoic acid	PFPeA	320
Perfluorohexanoic acid	PFHxA	1,000
Perfluorononanoic acid	PFNA	8
Perfluorodecanoic acid	PFDA	10
Perfluorobutanesulfonic acid	PFBS	3,700
Perfluorohexanesulfonic acid	PFHxS	250
H4-Perfluorooctanesulfonic acid	H4PFOS	870
Perfluoropentanesulfonic acid	PFPeS	320

Toxicity studies in terrestrial ecosystems show strongly varying effects with effects on internal organ systems (increased liver weight), endocrine system disorders (decreased serum cholesterol concentration), and embryonic development (Goosey, 2010).

The LD_{50} value in rats was achieved by oral intake of 250 mg/kg PFOS or 550 mg/kg PFOA (OECD, 2002). A 90-day feeding experiment on the subchronic toxicity of PFOS in rats showed liver changes already at doses of 2 mg/kg/d. From a dose of 6 mg/kg/d mortality was between 50 and 100 %. In most studies, the liver was the primary target organ of toxic effects. NOAEL values were observed in the range of 0.06 to 0.3 mg/kg/d. The lowest NOAEL for aquatic organisms was 0.25 mg/L for PFOS.

NOEC values determined in birds were 10 mg/kg for most PFAS (Theobald et al., 2007). The results of the animal studies suggest that PFOS and PFOA have moderately acute oral toxicity with gastrointestinal effects. The primary target organ for PFOS and PFOA in rodents is the liver. Because PFAS are analogous ligands to natural long-chain fatty acids, they can displace them in biochemical processes. This interference can increase the toxicity of these chemicals (Danish Ministry of the Environment, 2013).

Short-chain PFAS presumably exhibit the same toxicity mechanisms as longer-chain PFAS, but at a significantly lower level due to the lower bioaccumulation capacity, since the effect-causing effect lies in the chemical structure of the perfluorinated carbon chain and not in the functional group (Liao et al., 2009). However, there are only few studies available on the shorter-chain compounds. In one of them it was shown that PFBS is not very toxic to freshwater organisms. Effects could only be observed at a concentration of > 700 mg/L PFBS. The LC_{50} value for the thick-headed gouge is 1,938 mg/L PFBS (Gisey et al., 2010).

Human toxicology. The most comprehensive findings on toxicological effects of PFAS on humans are available from a study conducted by an Australian expert panel (Australian Government, 2018a, 2018b). Numerous international publications have been evaluated in this study. In summary, although the scientific evidence for the relationship between PFAS exposure and health effects is limited, there is largely consistent evidence for the following health effects of PFAS:

► increased cholesterol levels in the blood,

► increased uric acid levels in the blood,

► reduced kidney function,

► changes in the immune response,

► altered levels of thyroid hormones and sex hormones,

► reduction of fertility in women,

► later age for the beginning of menstruation in girls and earlier menopause and

► lower birth weight of infants.

For the effects mentioned above, the differences documented in the scientific studies between persons with the highest PFAS exposure and persons with low exposure are generally small. Even the persons with the highest PFAS exposure generally showed only effects comparable to those of the general population. From this, no or only a limited correlation between the level of PFAS exposure and a human disease could be deduced. However, despite the very weak and inconsistent evidence of health effects after PFAS exposure, health effects cannot be excluded. Many of the evaluated studies were judged to be technically inadequate and, overall, the evaluated studies showed numerous methodological flaws. For example, it could not be excluded that a reverse causality existed (i.e., a health effect causes an apparent increased exposure) or that third factors (e.g., age, smoking, or socioeconomic status) influenced the study results. Also, the groups studied were too small to make statistically sound statements and there are concerns about the selection of the study groups. Another complicating factor is that there are many different PFAS compounds and different environmental or working conditions with possible interacting effects, making it difficult to determine exactly which compound is responsible for which outcome.

In these studies, PFOS and PFOA were found to have endocrine and toxic effects on liver function, development, and immune response in laboratory animals (Lau, 2012). PFOA and PFOS also caused birth defects, delayed development, and neonatal deaths in laboratory animals. There are both similarities and differences in the toxicological effects of different PFAS. In general, the longer-chain PFAS are more toxic than the shorter-chain compounds (Dickenson and Higgins, 2016; Lau, 2012). However, humans and animals react differently to PFAS and not all effects observed in laboratory animals may also occur in humans. However, the data do provide opportunities to assess the extent to which exposure and effects in animals are comparable to those in humans (Australian Government, 2018b).

The US National Toxicology Program has classified the two compounds PFOA and PFOS as *presumed to be immune hazards to humans* (NTP, 2016). For PFAS compounds other than PFOS and PFOA, relatively little data is available. The Dutch National Institute of Public Health and Environment (RIVM) has derived relative potency factors (RPFs) for a number of PFAS compounds (C_4-C_{16}) from literature data on liver toxicity in rats, taking into account additive toxicity in the presence of several compounds. PFNA, for example, has a 10-fold higher potency to cause liver effects than PFOA (Figure 40).

Figure 40   RPF (and 90 % confidence interval) for PFAS
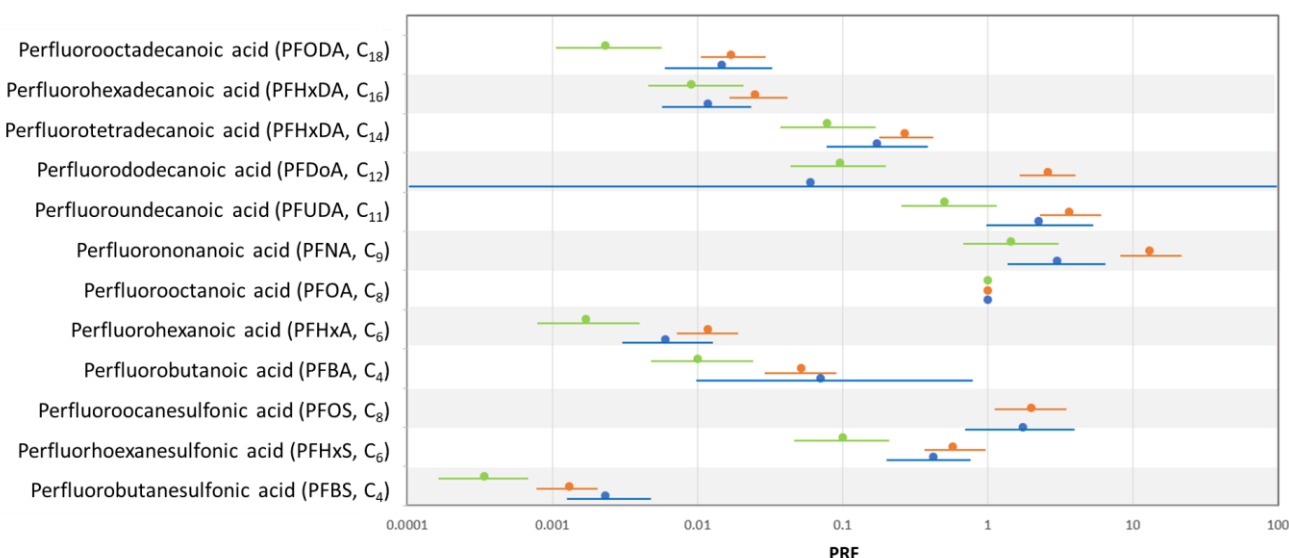
PFOA was selected as the reference substance (RPF = 1). Three RPFs were derived for each PFAS compound: based on absolute liver weight (blue), relative liver weight (orange) and hypertrophy[37] (green). PFDoA showed no dose-dependent response in absolute liver weight, therefore the confidence interval is very large. Source: Zeilmaker et al., 2018.

The Human Biomonitoring Commission at the Federal Environment Agency has derived so-called HBM-I values for PFOS and PFOA. The HBM-I value corresponds to the concentration of a substance in a body medium above which, according to the current state of expert assessment, no health impairment is to be expected. This value is 5 for PFOS and 2 µg/L blood plasma for PFOA (Federal Environment Agency, 2018).

Carcinogenicity. Regarding cancer, there is currently no conclusive evidence to suggest an increased risk of cancer. However, there is a possible association with PFAS exposure and an increased risk for two rare cancers: testicular cancer and renal cancer. This association is believed to relate to PFOA rather than PFOS and is not yet statistically proven, mainly because other factors such as smoking have not been studied (Australian Government, 2018a, 2018b).

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[37] Excessive enlargement of tissues and organs due to enlargement (not proliferation) of cells, especially because of increased stress.

In addition, chronic toxicological studies on PFOA and PFOS have been conducted, with both compounds leading to cancer of the liver, testes, pancreas, and thyroid in rats (ATSDR 2009; Lau 2012). However, some scientists doubt that humans develop the same cancers as animals.

Finally, the International Agency for Research on Cancer states that PFAS are multisystem toxins, i.e. exposure to PFAS is associated with toxicological findings in many types of tissues and systems. In fact, the evidence for PFOA is sufficiently strong to classify it as potentially carcinogenic to humans (Group 2B) (IARC, 2018). Other PFAS compounds have not yet been evaluated in this regard.

Tolerable Daily Intake (TDI). The TDI (Tolerable Daily Intake of Contaminants) is the derivation of the amount (exposure) of a substance that can be ingested per day over a lifetime without any noticeable effect on the health of the consumer. To determine the TDI, a NOAEL (No observed adverse effect level) is determined from animal experiments or epidemiological data. This value is divided by a safety factor (usually 100), which should consider the different sensitivities between humans and animals and between individuals in the human population.

The TDI values for PFOS and PFOA have been repeatedly adjusted internationally in recent years (Figure 41). Most recently, they were reduced by the EFSA in 2018 to a value of 1.8 ng/kg BW/d for PFOS and 0.8 ng/kg BW/d for PFOA.

Figure 41   International adaption of the TDI for PFOS and PFOA
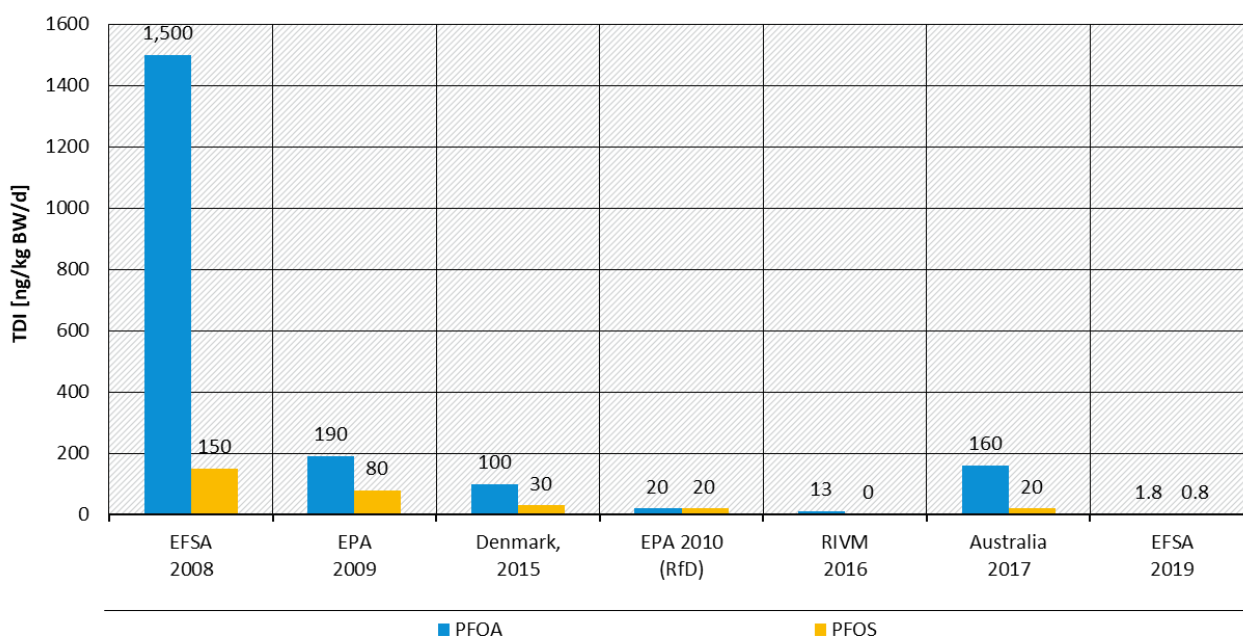
Source: EFSA, 2008; RIVM, 2017; Australian Government 2017; EFSA, 2018.

The last reduction was based on observations in humans. The association with elevated concentrations of PFOS/PFOA in serum with multiple health effects was considered causal. Health impairments included (i) increased serum cholesterol, (ii) increased antibody response after vaccination and (iii) decreased birth weight. The human toxicological data studies included evaluations of several PFAS. The effects of the individual compounds could not be assessed separately. Therefore, the effect attributed to PFOS may include the effects of other PFAS. No additional safety factor was applied as the studies were based on a general population, including potentially sensitive subgroups.

Food chain. Based on the individual contaminanted environmental compartments, PFAS can also enter the food chain. PFOS and PFOA have already been found in seabirds, polar bears, seals, otters, marine mammals, and fish along the coasts of many countries[38] (Jahnke, 2007). For PFOA, the daily intake of the total adult population was calculated (Table 11). This shows that PFAS intake is mainly dietary and other sources are negligible.

Table 11   Calculated PFOA intake (total adult population) (Fromme et al., 2009)

Recording pathway	Daily Intake [ng PFOA/kg body weight]	
	Mean Value	Maximum
Indoor Air	0.0009	0.0009
Fresh air	0.0013	0.012
House dust	0.016	1.03
Food	2.82	11.5
Drinking water	0.022	0.087
Total recording	**2.9**	**12.6**

A simple one-compartment toxicokinetics model showed that the intake correlated well with PFOA concentrations in the plasma of the same population.

Excretion rates. PFAS can be detected in the blood of almost all people. Studies of 13 PFAS compounds in the serum of 786 adult Koreans over 10 years showed that PFAS concentrations increased from 2006 to 2013 and decreased thereafter. PFAS concentrations were higher in men than in women (Seo et al., 2018).

The German Federal Environment Agency derived reference values for PFOS and PFOA. The reference value is formed from measured values of a sample of a defined population group and describes the concentration of a substance in a certain body medium at the time of the investigation. The reference value is a purely statistically defined value which per se has no health significance. For PFOA, the reference value for women and men is 10 (for children 3) µg/L blood plasma. For PFOS, the reference value for men is 25, for women 20 and for children 5 µg/L blood plasma (Umweltbundesamt, 2019).

In terms of toxicokinetics (including excretion rates), there are differences between species (mice, rats, monkeys, and humans), gender differences and differences in PFAS chain length (Bull et al., 2014). PFOS is excreted mainly in urine and to a lesser extent in faeces (Kommission Human-Biomonitoring, 2009), whereas FTOH is excreted primarily in faeces. During excretion (with reference to the PFAS concentration in the blood), the half-lives of PFAS are:

► longer for sulfonates than for carboxylates,

► shorter for branched than for linear isomers,

► often shorter in women (men generally have higher PFAS blood concentrations than women) and

► increasing with the chain length.

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[38] Of course, the PFAS are also found in offshore waters, but most studies are limited to the coastal areas.

The biological half-lifes were determined for pensioners who worked with fluorochemicals until retirement. The half-lives for PFOS were 5.4 years, for PFHxS 8.5 years and for PFOA 3.8 years (Olsen et al, 2007). Later studies have reported half-lives for the short chain compounds of about 1 month for PFBS and 2 - 4 days for PFBA. A compilation of human half-lives compared to animals is shown in Table 12.

Table 12   Estimates half-lives for selected PFAS (ATSDR, 2018)

Compound	Human	Non-human Primates	Rat	Mouse
PFOA	8 Years	$20.1 - 32.6$ Days	$\male$: $44 - 322$ Hours $\female$: $1.9 - 16.2$ Hours	
PFOS	5,4 Years	$110 - 170$ Days	$179 - 1968$ Hours	$731 - 1{,}027$ Hours
PFHxS	8,5 Years	$87 - 141$ Days	$\male$: $382 - 688$ Hours $\female$: $1.0 - 41.3$ Hours	$597 - 643$ Hours
PFBS	665 Hours	$8 - 95.2$ Hours	$2.1 - 7.2$ Hours	
PFBA	72 Hours	$40.3 - 41$ Hours	$1.0 - 9.2$ Hours	$2.8 - 13.3$ Hours

Precursor transformation. Abiotic and metabolic transformation of precursor to PFOS in animals may also contribute to distribution and accumulation. For example, precursor transformation in liver microsomes and liver cytosol has been demonstrated in rats. The end product was usually PFOS (Stahl et al., 2011).

Obviously 6:2-FTOH is transformed in the human body and a 5:3 acid is accumulated. The detection of this acid can be used as a biomarker for internal 6:2-FTOH exposure.

Relatively little is known about the toxicity of precursors. However, since they can be degraded to perfluorocarboxylic and sulfonic acids, it can be assumed in a simplified way that they have the toxicity of the final product, unless better evaluation methods are available.

GenX. Since 2000, long-chain perfluoroalkane acids (PFAA) and their respective precursors have been replaced by numerous fluorinated alternatives. The main reason for this industrial transition was that these alternatives were considered less bioaccumulative and less toxic than their predecessors.

One study investigated to what extent differences in toxicological effect thresholds (dose) for PFAA and fluorinated alternatives were influenced by differences in distribution and elimination kinetics. Studies in male rats were performed using the compounds PFBA, PFHxA, PFBS, PFOA, PFOS and GenX. The toxicity ranking was as follows for the serum: GenX > PFOA > PFHxA > PFBA and for the liver: GenX > PFOA ≈ PFHxA ≈ PFBA. It was concluded that GenX as fluorinated alternatives have a similar or higher toxic potency than their precursor substances (Gomis et al., 2018).

For GenX, a TDI of 21 ng/kg/d was derived using an overall correction factor of 4,752 (for comparison, the TDI for PFOA is 0.8 ng/(kg BW·d). This value is based on a NOAEL of 0.1 mg/kg/d for the disturbance of the serum albumin/globulin ratio. The NOAEL for liver toxicity in this study was 1 mg/kg/d (RIVM, 2017a). GenX has an RPF of 0.06 based on liver toxicity. In rodents, the so-called "tumor triad" (presence of tumors in the liver, pancreas, and testicles) was detected after exposure to GenX (Rae et al. 2015).

Ecotoxicology and Human Toxicology (Summary)

So far, the data situation on ecotoxicological and toxicological effects of PFAS is still insufficient. Only the two compounds PFOS and PFOA are sufficiently characterized in this respect. However, there is growing evidence of numerous negative effects of PFAS on human health.

Accordingly, the TDI (tolerable daily intake) has been steadily reduced over the years to 1.8 ng/kg BW/d (PFOS) and 0.8 ng/kg BW/d (PFOA) (2018).

PFOA has been classified as potentially carcinogenic to humans (Group 2B). Other PFAS compounds have not yet been evaluated in this regard.

10 Precursor

The precursors topic has already been addressed in various chapters. All precursors have in common that they have a perfluorinated chain of different length and a non-fluorinated molecular residue[39]. In the following, additional information relevant for the remediation management is given with respect to precursors. In summary, precursors are compounds that have the potential to be biotransformed to perfluoroalkanecarboxylic and sulfonic acids[40] (collectively referred to as perfluoroalkane acids) as stable degradation end products (Nielsen, 2014). Precursors account for the largest amount of all the different PFAS compounds. There are no exact figures for this, but an estimation of the distribution is given in Figure 42.

Figure 42   Distribution of the PFAS
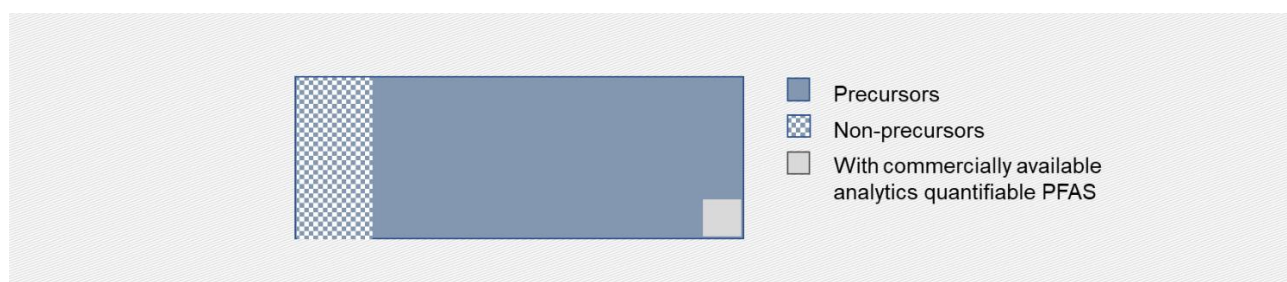
Source: Held and Reinhard, 2016

The main reason to care about precursors was probably the fact that higher concentrations of perfluoroalkane acids were found in the outlet of PFAS-contaminated wastewater treatment plants than in the inlet. In addition, potential precursors such as fluortelomer alcohols (FTOH) and 6:2 FTS were detected in the influent, whereas transformation metabolites such as unsaturated fluortelomer carboxylic acids (FTUCA) and x:3 acids were detected in the effluent (Chapter 6). The transformation metabolites are precursors *per se* and can be converted into perfluoroalkane acids, fwhat can be shown for example with the help of TOP analysis (Chapter 4.5).

In addition, precursors can also occur in the air. In one study FTOH was detected in all investigated air samples (indoor air) (Frömel et al., 2015). This also shows that the emission of volatile FTOH is a serious path of propagation.

[39]   Does not refer to the functional groups (carboxylic and sulfonic acids).

[40]   In contrast to microbial biotransformation, TOP analysis only produces perfluorocarboxylic acids. TOP analysis and microbial biotransformation do not necessarily yield exactly the same products.

Various authors have also found precursors in environmental samples. For example, precursors (e.g. 8:2-diPAP) could be detected in sediment in the San Francisco estuary (Benskin et al., 2013) and in water in Japanese rivers (Ye et al., 2014). In a German study, water samples from the rivers Rhine and Körsch were analysed using AOF analysis (Chapter 4.3). The 17 detected PFAS single substances accounted for only about 5 % of the AOF, 95 % were unknown. It has been speculated that this is partly due to exposure to fluoride pesticides (Willach et al., 2016). According to Jeschke (2004) more than half of the fluorinated agrochemicals are used as herbicides, usually containing three to five fluorine atoms. Typical representatives are flurtamone, diflufenican and flufenacet.

According to Ross et al (2018), precursors for longer-chain perfluoroalkane acids are preferably detected in soils and biosludges (*biosolids*) and those for shorter-chain perfluoroalkane acids are preferably detected in aqueous samples.

Houtz et al. (2013) investigated various AFFF products. On a molar basis, the precursors accounted for 41 – 100 % of the total concentration of PFAS in the AFFF formulations (Figure 43).

Figure 43   Formation of ferfluoroalkane acids out of AFFF
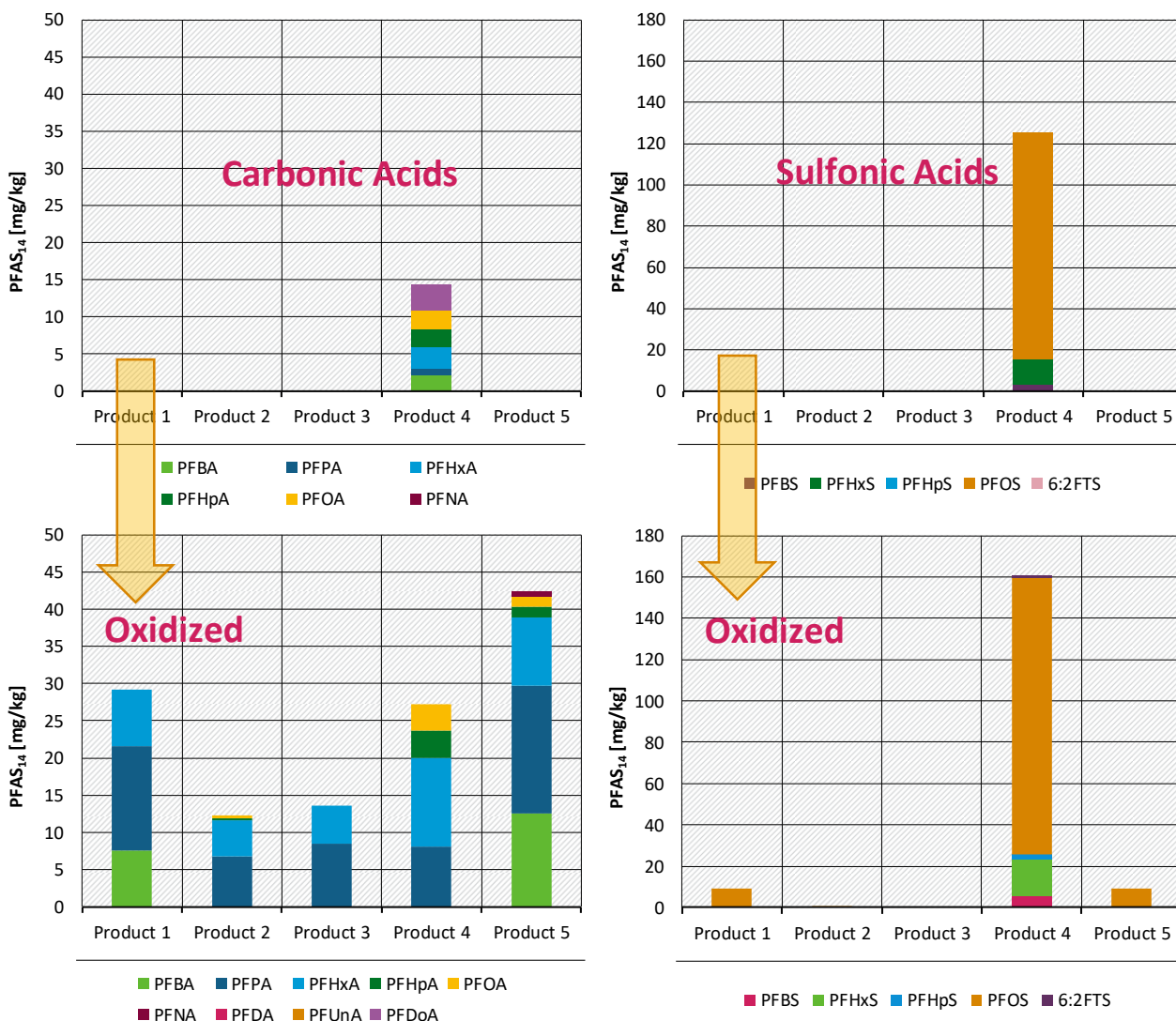
Source: Houtz et al., 2013, modified

In the area of a fire extinguishing training place, precursors represented only an average of 23 % (groundwater samples) and 28 % (soil samples) of the total PFAS. Suspected and analytically determined metabolites of precursor biotransformation were responsible for about half of the precursors in the investigated groundwater and soil samples. The relative proportion of perfluorocarboxylic and sulphonic acids in the total PFAS content was higher in the environmental samples than in the AFFF products used at the site, suggesting that a large proportion of the precursors released at the site had already been converted into perfluorinated carboxylates and sulphonates.

Remediation measures, especially those involving aerobization or oxidation of the groundwater, can lead to a forced release of the perfluorinated carboxylic and sulfonic acids from the precursors. McGuire (2014), for example, observed a significantly increased PFHxS : PFOS ratio in groundwater in the vicinity of air sparging measures. A differential transport of the two substances cannot be responsible for this, since PFHxS (log K_{OC} = 2.28) is retarded less than PFOS (log K_{OC} = 3.14 for PFOS). Furthermore, the concentration of a possible PFHxS precursor in the aerobicized area was strongly reduced compared to the surroundings.

Precursor (Summary)

Precursors can release perfluoroalkane acids into the subsurface due to natural biological transformation processes in cases where the aquifer is aerobic. It is therefore evident that remediation measures, which are accompanied by an aerobization or oxidation of the groundwater, lead to a forced release of the perfluorinated carboxylic and sulfonic acids from any precursors that may be present. The effect becomes particularly clear with fluorine-containing fire extinguishing foams (AFFF). Some modern AFFFs do not contain PFAS detectable via commercial analysis. Rather, only after some time upon release and corresponding biological transformation, do detectable PFAS gradually appear in groundwater.

There is currently hardly any information available on the non-precursors.

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11 Application Quantities and Usage

11.1 Introduction

Compared to many other environmentally relevant chemicals, PFAS are not mass products. In most areas of application, only a few kilograms or tons of PFAS are used. Exact figures are not available. As far as information on the quantities used is available, these are compiled in Held (2015). The main areas of application for PFAS are in surface finishing, paper coating, and specialty chemicals. Thus, PFAS or PFAS formulations are used in numerous industrial products and processes as well as in household products:

▶ Fire extinguishing agents,

▶ Galvanic industry (wetting agents, mist inhibitors),

▶ Paper industry (surface-treated papers),

▶ Textile industry (waterproof, breathable membranes, functional clothing, shoes, dirt-repellent carpets, wallpaper, leather furniture),

▶ Semiconductor industry (electronic circuit boards),

▶ Photo industry (films, photo papers and photo plates),

▶ Paint and varnish production (special wall paints),

▶ High-performance hydraulic fluids (e.g. for aviation),

► Detergents and cosmetics,

► Chemical industry (e.g. grease-repellent food packaging for fast food as well as baking paper, non-stick coated cookware, popcorn bags, pesticides, inks, lacquers, waxes (e.g. also ski wax), pesticides, water-repellent medical products in surgery, surface finishing/impregnating agents for furniture, textiles, leather, carpets)

► Plastic production (emulsifier).

A compilation of the PFAS compounds used in each industry can be found in Held (2015). The example of the simple compound perfluorobutyliodide (PFBJ), which is marketed under the product name Capstone® 4-I (DuPont™), clearly shows the extraordinarily wide (patented) range of applications for this compound alone in a large number of industrial processes and products (Table 13). However, no figures are available on the application quantities. The range of applications suggests that fluorine chemistry has penetrated wide areas of modern manufacturing processes and products.

Table 13   Application examples for Capstone I-4® (DuPont™)[41]

Application	Patent No.
Surfactants	
Sulfinic and sulfonic acids as surfactants and detergents	US4866190
Surfactants for liquid or supercritical carbon dioxide reactions	JP2003238473
Aromatic sulfate as surfactant	JP2001097943, US5491257
Tertiary perfluoroalkoxy surfactants in the PTFE dispersion polymerization process	US456466
Lubricants	
Fluorocarbon waxes	US3956000
Phosphine as oil additives	US3956000
Spirobiindan derivative as oil additive	JP3824339
Fluoroalkylsilanes as hydraulic fluids	US5196614
Carboxylate salts as wear protection additives	US5202038
Carboxylic acid ester or amide for magnetic recording media	JP09104881
Medical and biological Application	
Steroid	US7148213, US5719159, WO9313123
Peptidyl-perfluoroalkyl ketones as inhibitors of elastase	US6008196
Carboxamides as surfactant intermediates and as medicines	FR2623497
Triazole antifungals	US4727159
Hydroximic acid derivatives as pesticides	WO9967209
Phthalamides as insecticides	WO2005095351
Perfluoroalkylanilines for insecticides	US6717013
Aniline derivatives as agricultural chemicals	WO2002096882
Fluorinated polysiloxanes for cosmetics	JP09291010, JP09104757, JP3558410
Perfluorocarbon emulsions as blood substitutes	US2004057906
Modified lipids for drug delivery systems	US6090800, US6537246

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[41] Caprstone®-Produktinfoblatt. http://www2.dupont.com/Capstone/en_US/assets/downloads/Capstone(R)_4-I_K20131-1.pdf

Application	Patent No.
Optoacoustic contrast media for medical diagnostics	US6123923
Cosmetic skin or hair care compositions	US5851544
Fluorinated amphiphilic or steroid containing prodrug	WO9850041
Surfactant for perfluorocarbon microemulsions for blood substitutes	US4975468
Novel materials	
Maleimide polymers as photoresist compositions	US2002164541
Sulfonates and polycarbonates as refractory agents	JP2002265432
Fluoroelastomers	WO2001081464
Fluorinated azo dyes for thermal transfer printing	JP3009267
Fluoropolymer Ion Exchange Membranes	JP58127738
Sulphates as thermally stable gel compositions	JP2006241379
Imidazolium compounds As ionic liquids	WO2006051897
Phosphonic acids for the treatment of metal-coated silicon wafers	US6824882
Functionalization of carbon nanotubes	US2006257556
Poly(organosiloxanes) for organic-inorganic hybrid dielectrics	US714482
Organic-inorganic hybrid materials for optical devices	US2003235933
Phosphinic acid salts for optical devices	WO2003082884
Fluoroalkyl substituted styrene polymers for gas separation membranes	JP63097215

By far the largest quantities of PFAS are discharged into the environment through the use of fire-fighting foams, probably followed by electroplating. In third place is probably the paper industry, not because of local inputs, but mainly because of the currently still controversially discussed widespread use of paper industry residues in composts for fertilization. Fire extinguishing foams containing PFAS are mainly used to extinguish fires of liquid media. Sensitive areas for this are mainly the mineral oil industry and airports. Due to the outstanding importance of the three sectors, fire extinguishing foams, electroplating and paper industry, the use of PFAS in these fields is explained in more detail below.

11.2   Extinguishing Media

History. There are two main classes of fire fighting foams: Class A and Class B. In the 1980s, Class A fire-fighting foams were developed to fight forest fires. Class B foams are all foams designed to effectively extinguish flammable and combustible liquids and gases such as petroleum oils, greases, tars, gasoline, solvents, and alcohols (ITRC, 2019)[42].

All foams marked as AFFF or AR-AFFF contain perfluoroalkyl or polyfluoroalkyl compounds or both as active ingredients. These foams were manufactured and sold in the U.S. from the 1970s through 2016 and include all other AFFF brands in addition to 3M Lightwater. Although not manufactured with PFOA, they contain precursors that can release PFOA and other PFCA in the natural environment. They may contain traces of PFOA as an unavoidable by-product of the manufacturing process.

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[42]   There are also fluorine-free class B extinguishing foams.

In the past, fluorotelomer-based AFFF foams have predominantly contained short-chain C_6-PFAS of about 50-98 %, the remainder being long-chain PFAS that may release PFOA and other PFCA in the environment, but not PFOS or other PFSA. Modern AFFF products contain only short-chain PFAS (ITRC, 2019).

In response to the voluntary PFOA stewardship program of the US Environmental Protection Agency (US EPA), most manufacturers have now switched to the production of short-chain C_6-PFAS. These contain no PFOS and no other long-chain PFAS such as PFHxS and PFOA. Although some long-chain PFAS are regulated or phased out, short-chain PFAS with similar structures or compounds with fluorinated segments linked by ether bonds are the most common substitutes.

AFFF. In summary, extinguishing agents are complex mixtures consisting of several different substances. The extinguishing agents, which include fluorine compounds, are divided according to the terminology of DIN EN 1568 (2010) into

- ▶ AFFF   Water film forming foaming agents
- ▶ AFFF (AR)   Alcohol resistant water film forming foaming agents
- ▶ FP   Fluorine protein foaming agent
- ▶ FP (AR)   alcohol-resistant fluorine protein foaming agents
- ▶ FFFP   Water film forming fluorine protein foaming agents
- ▶ FFFP (AR)   alcohol-resistant water film forming fluorine protein foaming agents

with AFFF = *Aqueous Film Forming Foam,* FFFP = *Film Forming Fluoroprotein Foam* FP = Fluor-Protein Foamand AR = *Alcohol Resistant*. In addition, there is a range of fluorine-free foaming agents available. Foam extinguishing agents containing fluorine are primarily used for fire fighting of flammable liquids such as fuels and melting solids. Liquid fires can spread very quickly compared to solid fires. In addition, the formation of large quantities of toxic combustion gases can make such fires very dangerous. PFAS in the AFFF foams ensure that an aqueous liquid film is formed between the flammable liquid and the applied extinguishing foam, which is quickly distributed on the burning liquid due to the lowering of the surface tension by the PFAS. In addition to the AFFF foams, the non-fluorinated surfactants are essential in these products for the formation of a film between the hydrophobic flammable liquid and the water. The fluorosurfactants, on the other hand, have their polar group oriented towards the surface of the water and their perfluorinated carbon chain oriented towards the air. This creates a film on the surface of the flammable liquid that seals the fire airtight. This also prevents the flammable liquid from continuing to outgas. As a result, faster extinguishing success can be achieved, and the risk of re-ignition is minimized. Extinguishing foams containing PFAS are used in fire-fighting trucks, stationary extinguishing systems and hand-held extinguishers. Since 1963, PFAS have been the main component of high-performance foam extinguishing agents (Tuve and Jablonski, 1963). Further details can be found at Held (2015).

For many years (until the year 2000) the best-known product in the field of PFOS-containing AFFF fire extinguishing foams was *Lightwater*.

AFFF composition. Despite extensive analyses, the exact composition of AFFF, which is treated as a company secret, is not known. In addition, the components can vary not only from manufacturer to manufacturer, but also over time for a given product. Even though the composition of AFFF is protected, there are several studies that provide information about the compositions.

The investigation for commercially detectable PFAS showed that a number of the shorter-chain perfluoroalkane carboxylic and sulfonic acids are detectable in the groundwater of various sites in addition to PFOS (Figure 44). However, a typical fingerprint for groundwater containing extinguishing foam cannot be derived. Similar results have been found by investigations at Norwegian airports. The compounds PFOS and PFHxS dominated in groundwater. In lower concentrations PFHxA and PFBS were detectable. Longer-chain compounds or sulfonamides were not detectable (Posner et al., 2013).

Perfluoroalkanoic acids were found in elevated concentrations in the subsurface of numerous AFFF-contaminated sites (Moody et al., 2003; de Solla et al., 2012). However, information from AFFF manufacturers also indicates precursors. The prepared safety data sheets allow only limited conclusions about the ingredients.

Figure 44   Composition of the PFAS distribution in the groundwater after the use of extinguishing agent (scope of analysis: 10 substances according to DIN; sorted according to increasing concentration)
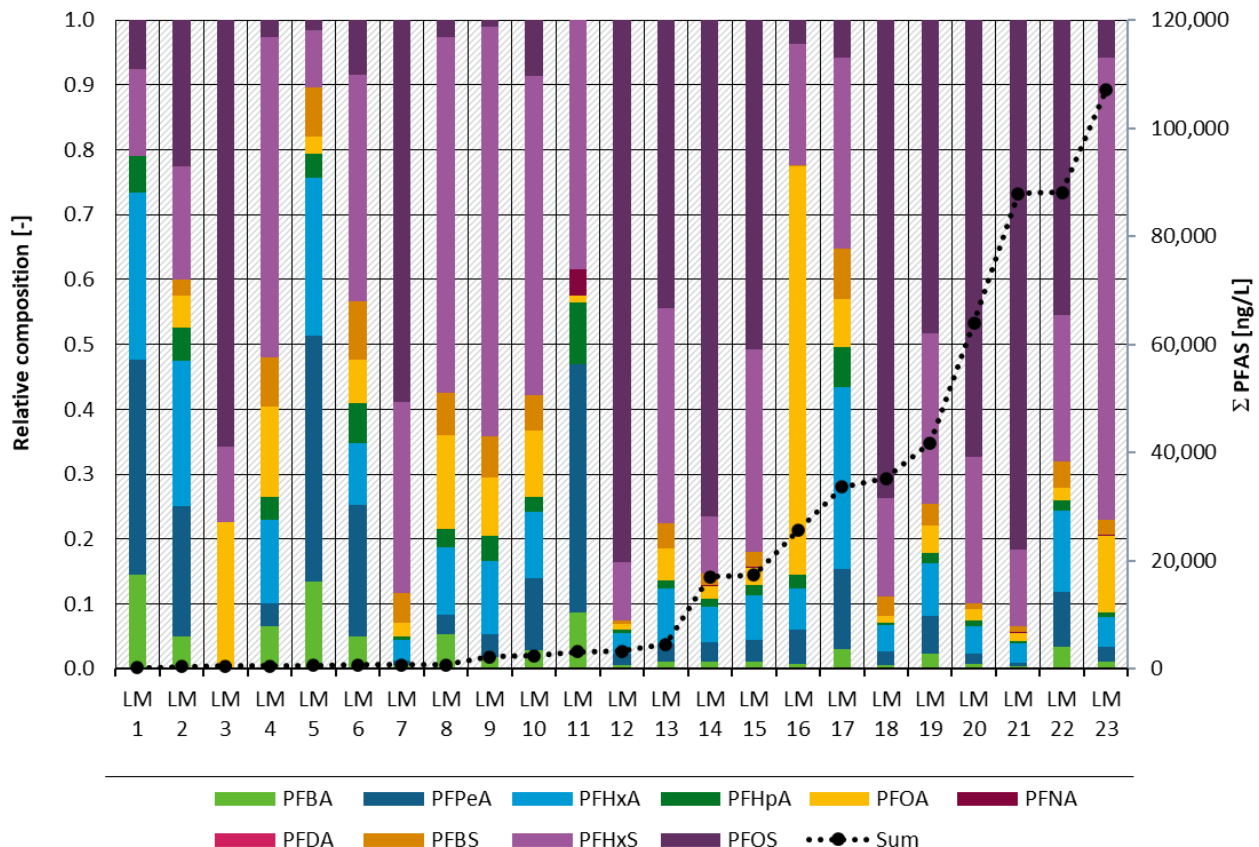
Source: Schroers, 2015

In one of the university studies, the ingredients of 19 AFFF foams produced before 2001 were examined by five manufacturers. As a result, it was found that only the 3M products contained perfluorinated carbonic (PFCA) and sulfonic acids (PFSA). Branched as well as linear isomers could be detected, indicating electrochemical fluorination as a production process.

After 2001, telomerization is found almost exclusively as a production process. In contrast, betaines with an odd-numbered CF_2-chain were detected in the products of one company (Place and Field, 2012). The remaining products contained fluorotelomer derivatives (FTS, FTSA, fluorotelomer thioether) before all (Houtz et al., 2013). This shows that only a small part of the compounds is currently directly detected by the available chemical analysis within the scope of contaminated site management.

PFOA was used in AFFF until about 1975 and may occur as a by-product in PFOS-based AFFF. Following the phase-out of PFOS production in the 2000s, foaming agents now contain virtually no PFOS, except for products manufactured in China. However, a maximum of 0.001% PFOS is still allowed, which corresponds to a concentration of approx. 300 µg/L PFOS in a 3 % solution, for example.

However, PFOA and shorter-chain PFAS may be present in the AFFF formulations as impurities in non-negligible amounts.

As the harmful properties of long-chain PFAS became known, the new generation of AFFF extinguishers used shorter-chain PFAS, mainly fluortelomer or fluortelomer-based compounds (mainly fluortelomer sulfates and perfluorocarboxybetaines) with 6 fully fluorinated carbon atoms (e.g. 6:2-FTS) instead of PFOS. Some newer AFFF formulations contain up to 90 % of these C_6 perfluorosurfactants (Place and Field, 2012). Furthermore, AFFF products contain numerous other PFAS classes (Herzke et al., 2012; D'Agostino and Mabury, 2014) (Chapter 2).

In addition to the strongly substituted compounds, 6:2 FTS (= H_4PFOS) is considered the main substitute for PFOS in extinguishing foams. The AFFF fire-extinguishing foams of the products frequently used in Germany contain, in addition to some perfluorocarboxylic and sulfonic acids, the compound 6:2 FTS in low concentrations and, above all, in high proportions the two betaines listed in Table 14 (see also Figure 45).

Table 14   Quantitatively dominating substances in the AFFF products of a German supplier

| Compound	Chemical Formula	CAS No.
Capstone A	$C_{13}H_{17}F_{13}N_2O_3S$	80475-32-7
Capstone B	$C_{15}H_{19}F_{13}N_2O_4S$	34455-29-3

According to the manufacturer, the addition of perfluoroethyl-carboxybetainsulfonic acid compared to PFOS-based AFFF reduces the necessary total amount of expensive fluorinated compounds to achieve the desired equal reduction of surface tension in the extinguishing foams (Bock and Pabon, 2009). All newer AFFF extinguishing agents thus contain 30 - 60 % less fluorine.

Figure 45   Chemical structure of the Capstone™ Product A (top) and B (bottom)
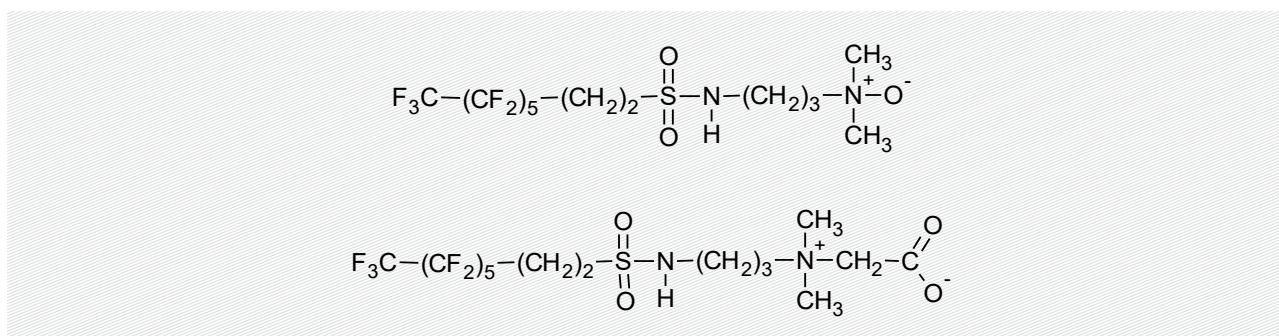
In addition, a number of other novel substances are used which have an oxygen function, especially in the fluorinated carbon chain. For example, one of the manufacturers uses the non-precursor dodecafluoro-2-methylpentan-3-one (CF_3-CF_2-C(O)-CF(CF_3)$_2$) as a replacement for PFOS (RPS Advies B.V. , 2010). The new fire extinguishing agent Novec™ 1230 (3M, 2015), which is intended for use in stationary extinguishing systems, i.e. in closed rooms, is also not a precursor (non-precursor) (Figure 46).

Figure 46   Chemical structure of Novec™ 1230 (CAS No. 756-13-8)
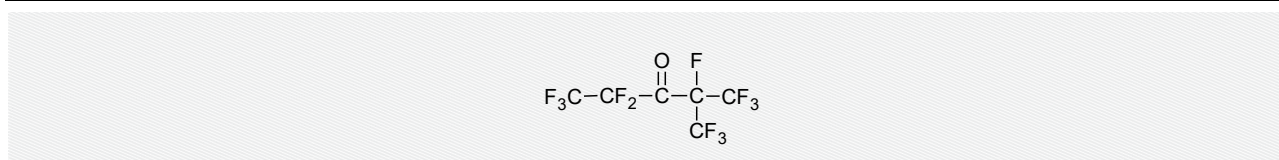
In addition to the fluorinated surfactants, AFFF extinguishing foams contain a number of other organic compounds that can enter the substrate when the extinguishing foams are used. The components are listed in Table 15 for four exemplary products.

Table 15   Organic non-fluorinated components of AFFF foams [% by weight] (according to the safety data sheets)

Compound	AFFF 1% F-15	Fomtec AFFF 1 % A, 3 % A	Fomtec AFFF 6 % A	EXPYROL AFFF 3 % F
1,2-Ethanediol	< 15			25 – 50
2-(2-Butoxyethoxy)ethanol	< 10	10 - 25	1 - 10	5 - 10
Octyl sulphates	< 10			
Decyl sulphates	< 10			
Sodium alkyl ether sulphate	< 5			
Alkylpolyglycosides	< 5			
Alkylamidobetaines	< 5			
Hydrocarbon surfactants		5 - 15	2-5	
Polyethylene glycol		1 - 12	< 5	
Monopropylene glycol		1 - 13	< 5	

11.3   Electroplating

Electroplating is the electrochemical surface treatment of metal or plastic workpieces with the aim of improving material properties. PFAS is used to improve the electroplating process and a fast dripping of solutions from the workpieces with the aim of minimizing the mixing of the liquids of the individual baths. Another important effect is the prevention of the formation of toxic chromium aerosols. The annual PFOS quantities formerly used in German electroplating plants amount to approx. 3.4 t/a (Held, 2015).

PFOS (as tetraethylammonium perfluorooctane sulfonate, CAS No. 56773-42-3) was mainly used for electroplating, since the aggressive conditions of the process solutions would destroy non-fluorinated or only partially fluorinated compounds very quickly (UNIDO, 2012). PFOS was also used in various other salt forms (K-PFOS, lithium, diethanolamine or ammonium salt).

Presumably, a larger number of other substances were and are used in addition to those mentioned above. In an exemplary investigation in the German Federal State Nortrhine-Westphalia, only PFOS, PFBS and traces of PFHxS could be detected in the groundwater of real contaminated electroplating sites under 10 analysed PFAS. PFBS is added as a formulation aid by the manufacturer of the process solutions (Schwarz et al., 2011).

After the ban on PFOS, substitutes such as 6:2 FTS were increasingly used, but this is only applicable for decorative chrome plating. Other substitutes include (Danish Ministry of the Environment, 2013):

► PFBS

► Potassium 1,1,2,2-tetra-fluoro-2-(perfluorohexyloxy)ethane sulfonate
  ($KO-(SO_2)-(CF_2)_2-O-(CF_2)_6-F$)[43]

► Potassium-2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluorethane sulfonate ($KO-(SO_2)-(CF_2)_2-O-(CF_2)_4-CFCl-CF_3$)

► 1H,1H, 2H,2H-perfluorooctane sulfonic acid ($HO-SO_2-(CH_2)_2-(CF_2)_6-F$)

Today, PFOS and its derivative are still used in the field of hard chrome plating (special permit).

11.4   Paper Industry

The surface finishing of papers serves to make them water, grease, and dirt repellent. Such properties are almost exclusively required for food contact papers. According to the Association of German Paper Factories (VDP)[44], PFAS are only used for this purpose. Within the EU, approximately 160 tons of PFOS-related compounds were used in the paper industry in 2000 (Rudiger et al, 2000). Today only substances listed in the recommendation of the German Federal Institute for Risk Assessment (BfR) are used (Bundesinstitutes für Risikobewertung, 2016a). These are polymers of the groups:

► Phosphoric acid ester of ethoxylated perfluoropolyether diol,
► Modified polyethylene terephthalates,
► Highly complex fluorinated polymers[45],
► Perfluoropolyether dicarboxylic acid, ammonium salt.

In the past, however, other compounds were used. At agricultural areas treated with compost containing paper sludge PFBA, PFPA, PFHxA, PFHpA, PFOA and PFOS could be found in soil eluates. PFBS, PFNA and PFHxS could also be measured except for a few samples. In addition, traces of PFDA and PFPeS were found in some eluates (LUBW, 2017).

In further investigations of selected soils presumably contaminated with paper waste, it could be shown with the help of the EOF method that the detectable individual substances perfluoroalkane acids and 6:2/8:2-diPAP made up only about 10 - 90 % of the organic fluorine compounds (Nürenberg et al., 2018b). Therefore, it can be assumed that precursors are predominantly present.

From the 1960s onwards, polyfluorinated alkyl phosphates (PAP including N-EtFOSE) were mainly used as starting materials. Mono-, di- and tri-PAP (mono-, di- and tri-esterified phosphoric acids) were used, usually in the form of mixtures (Department of Environment England and Wales, 2004; Posner et. al., 2013). PFOS and PFOA are not used directly in the paper industry but occur together with FTOH as impurities or as conversion products in the products.

While N-EtFOSE and comparable compounds were used until about 2002, the PAP and diPAP compounds were available on the market until about 2012 (Fraunhofer, 2018).

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[43] The two potassium salts are non-precursors.

[44] VDP (Association of German *Paper* Mills) (2015). http://www.vdp-online.de/de/

[45] For example copolymer of acrylic acid 2-methyl-2-(dimethylamino)ethyl ester and γ,ω–perfluoro (C_8-C_{14}) alkyl acrylate, N-oxide, acetate or copolymer of acrylic acid 2-methyl-2-(dimethylamino)ethyl ester and γ,ω-perfluoro -(C_8-C_{14}) alkyl acrylate, N-oxide.

Zonyl® RP (*Paper Fluoridizer*) was used as a technical product for paper finishing. Analysis of this product revealed a range of mono, di- and tri-PAP congeners, including all quantifiable PAPs up to 12:2 monoPAP. SAmPAP was not included in Zonyl® RP (Nürenberg, 2018b).

The application of the analytical method to a soil sample which was supposed to be contaminated with PFAS-containing paper sludge showed that 6:2- and 8:2-diPAP represented an important fraction of the total amount of diPAP, 6:2-triPAP was detectable only in low concentrations. The compound 6:2-triPAP was the smallest representative of the detectable triPAP congeners. The monoPAP (12:2 and 14:2), which can only be detected qualitatively, probably represent an important compound in the soil samples in terms of quantity. In addition, diSAmPAP was found in several soil samples. These samples also contained its degradation product PFOS and in some samples also the degradation product FOSA (sulfonic acid amide). It can therefore be assumed that monoPAP is hardly detected by the EOF analysis either, but this still needs to be verified (Nürenberg, 2018b).

EtFOSE-based phosphate esters (sulfonamide ethanol-based phosphates, SAmPAP) are a second group of substances in the family of perfluoroalkyl phosphates, which belongs to the precursors. SAmPAP (Figure 47) have been used since 1974 for papers which were approved for food contact applications and were produced in high volumes in North America until production was phased out in 2002. Formulations usually consisted of 10 % mono-, 85 % di-, and 5 % trisubstituted phosphate esters of N-ethyl perfluorooctane sulfonamide ethanol, collectively referred to as SAmPAP. SAmPAP can be transformed to PFOS in the environment via several intermediates. In laboratory experiments with marine sediment, however, no degradation of diSAmPAP could be detected over 120 days (Nürenberg et al., 2018a). As a rule, they are no longer used since 2011. In addition, polymers such as polyfluorinated polyethers (PFPE) have been used since 2010 (LUBW, 2017). These are fluorinated polyether chains of different lengths, whose ends can have different functional groups.

Figure 47   Chemical structure of SAmPAP

Fluoroalkyl acrylate polymers (also called fluorocarbon resins) are polymers of acrylic acid whose side chains (carboxyl groups) are esterified with polyfluorinated alcohols or similar. They have been in use since the 1960s (Posner et al., 2013; Reichart, 2009). In 2012, manufacturers of paper auxiliaries with fluorine-containing side chain polymers with chain lengths of C_8 or longer voluntarily abandoned the use of such polymers. Short chain fluoroalkyl acrylate polymers, however, are still in use.

Recent investigations in Denmark on papers and board materials intended to come into contact with food at high temperatures revealed more than 115 different PFAS compounds, which can be assigned to homologous series of the following classes (Trier et al., 2011):

► x:2 FTOH

► monoPAP, diPAP, triPAP

► S-diPAP (x:2/y:2 FTOH disubstituted thioethers)

► SN-diPAP di(N-ethyl-2-perfluorooctane sulfonamide ethyl phosphate)

► Alkyl-PAP (Perfluoroalkyl organic phosphates)

► 3-[2-(perfluoroalkyl)ethylthio]propionate

► PFSA (perfluoroalkylsulfonate, tetraethylammonium salt)

► PFOSF (perfluorooctane sulfonate fluoride)

► PFOSA (perfluorooctane sulfonamide)

► Et-PFOSA (perfluorooctane sulfonamide N-ethyl ester)

► Alkyl-PFOSA (alkylperfluorooctane sulfonamide)

► Fluoroalkoxylates (perfluoroalkyl polyethoxylate alcohol)

► Fluoroacrylates

► Polyfluoropolyethers (PFPE)

Apart from polymers, all other compounds belong to the precursors. According to the Bundesinstitutes für Risikobewertung (2016b), baking papers contain a number of complex polymeric PFAS:

► Ammonium salts of perfluoroalkyl substituted phosphoric acid esters (reaction product of 2,2-bis(α,ω-perfluoro-C4-C20-alkylthio)methyl]-l,3-propanediol, polyphosphoric acid and ammonium hydroxide)

► Diethanolamine salts of 4,4-bis[(γ,ω-perfluoro-C8-C20-alkyl)thio]pentanoic acid.

► Copolymer of perfluoroalkylethyl acrylate, vinyl acetate and N,N-dimethylaminoethyl methacrylate.

► A mixture of bis(diethanolammonium) mono-1H-1H, 2H-2H-perfluoroalkyl orthophosphate and diethanolammonium bis(1H-1H, 2H-2H-perfluoroalkyl) orthophosphate.

Application Quantities and Usage (Summary)

The use of PFAS in fire-fighting foams (AFFF) represents largest amount of PFAS used. Upon the use of fire extinguishing foams, PFAS are released into the environment. The foams pose a special challenge for analysis, evaluation, and remediation. On the one hand, they contain large amounts of different PFAS compounds and compound classes, especially precursors, and on the other hand, they also contain other non-fluorinated surfactants.

The second greatest use of PFAS is their use at electroplating shops. Many of these plants have led to contamination with PFAS and other pollutants in the soil and groundwater. It should be noted, however, that PFAS were not used in Germany until about the 1970s.

The extensive contamination of soils and groundwater with PFAS, which is believed to have originated from paper sludge, is likely to be a circumstance which, according to current knowledge, is primarily limited to Germany.

12 PFAS in Concrete

The release of PFAS into the environment not only contaminates soil and groundwater. Above all, it is to be expected that the PFAS in aqueous solution will penetrate the concrete via micro and macro pores. A product (X55) is available on the Australian market that is intended to seal the concrete surface and pores and thus prevent elution of the PFAS. However, its effectiveness has not yet been independently confirmed.

In a study of the product supplier, PFAS was shown to penetrate the concrete of an extinguishing training basin to a depth of 12 cm. Elution tests (diffusion tests) showed a considerable re-solution (Baduel et al., 2015). A mass balance showed that this will continue for decades.

However, the PFAS are particularly important in connection with dismantling measures. PFAS-contaminated concrete floors cannot be disposed of in inert landfills but must be disposed of separately. Elution tests (NEN 7355) help to assess the elutability of the PFAS. The elutability of organic contaminants can be tested according to this standard. The elution time is 64 days. Wipe tests can be carried out to identify those areas of the concrete floor where higher PFAS contaminations are present.

13 Background Concentrations and Causes

The widespread use of PFAS has resulted in a significant release of PFAS into the environment. Today, PFAS are ubiquitously distributed and can be detected in the entire water cycle (precipitation water - surface water - ground water - drinking water). Due to their lack of degradability, PFAS accumulate globally in the environment. For example, PFAS could be detected in water of the Swiss mountains up to 2.25 ng/L (Greenpeace, 2015). The yet unexplained processes and physical-chemical mechanisms that cause and have caused the global spread of these substances are very complex. All per- and polyfluorinated compounds found in the environment have an anthropogenic origin. In the end, the only possible process for reducing the excess of the contamination is dilution.

In the environment PFAS can be diffusely distributed via many pathways and lead to background contamination caused exclusively by anthropogenic activities (Figure 48). The extent of the background contamination is of great importance when deriving remediation target values.

Figure 48   Possible distribution routes of the PFAS in the environment
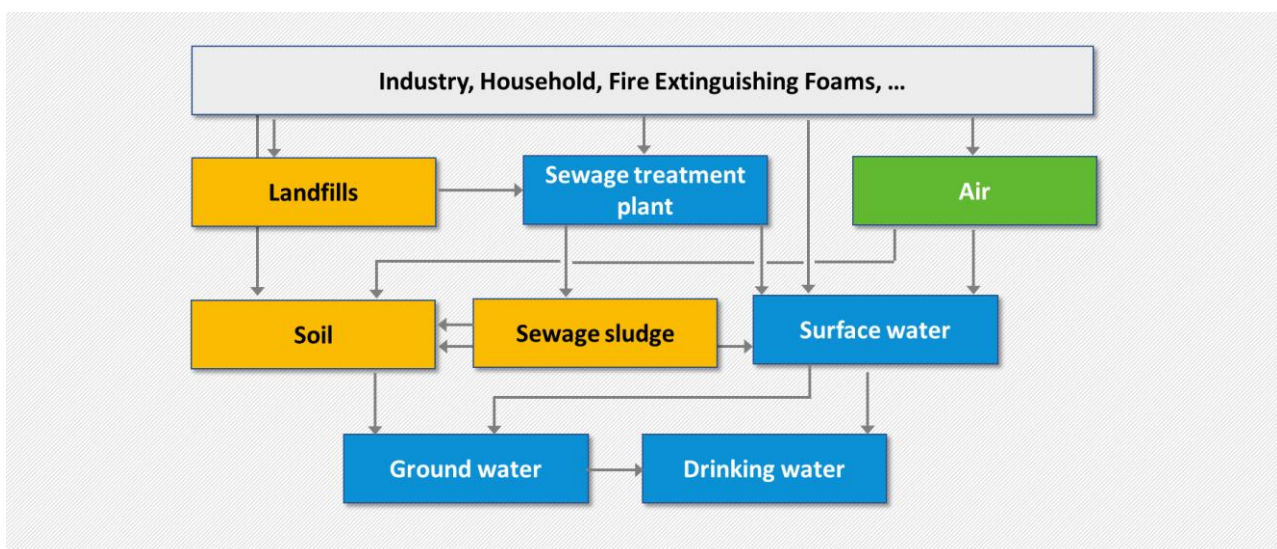
Source: Gellrich u. Knepper, 2012, modified

Landfills. Since PFAS are used for a wide range of purposes, many residual materials from households and industry are sent to landfill as waste. One example is PAP, which is often used for coating food packaging. After disposal, they can end up in the environment where they can be broken down into PFOA. Therefore, landfills are usually also sources of PFAS. If landfills are not completely sealed, the PFAS can be introduced directly into the groundwater via the leachate (LANUV, 2011). In the case of sealed landfills, the PFAS reach the local or municipal sewage treatment plant via the leachate collection and from there the surface water, if no or no sufficiently effective treatment process is installed.

Sewage treatment plants. In addition to domestic wastewater, municipal wastewater treatment plants also collect and purify wastewater from indirectly discharging commercial enterprises. If commercial wastewater contains PFAS, it is discharged into the sewage treatment plants. PFAS are only partially retained in state-of-the-art mechanical-biological sewage treatment plants and can therefore be detected in both sewage plant effluents and sludge[46]. Private households can also be considered as PFAS sources, as PFAS are contained in many consumer products. In wastewater treatment, PFAS precursors can also be biotransformed to the stable end products. For example, an increase of PFAS, especially of perfluorocarboxylic acids within a sewage treatment plant with textile wastewater could be proven, i.e. the effluent values were partly higher than the inflow values. Investigations at five larger municipal wastewater treatment plants[47] revealed the following concentrations:

- ▶ PFOA 5 - 32 ng/L
- ▶ PFOS 9 - 26 ng/L.

PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFDoA and shorter chain PFAS were present in only low concentrations (1-7 ng/L). The maximum PFAS value in the effluent of the wastewater treatment plant was approx. 54,000 ng/L (Bayerisches Landesamt für Umwelt, 2010).

Sewage sludge. Sewage sludge accumulates PFAS and thus allows a statement about long-term contamination. The investigation of 66 sewage treatment plants (2007), in whose catchment area indirectly discharging commercial enterprises are located which possibly handle PFAS, showed that 14 sewage sludges exceeded the precautionary limit of 100 µg/kg PFAS dry matter sewage sludge (max. 6,700 µg/kg dry matter) (Figure 49).

The PFAS contamination of the sewage sludge consists mainly of PFDA, PFOA and PFOS. Because of its high nutrient content, sewage sludge is used as a fertilizer in agriculture, provided that defined limit values for contaminants are not exceeded. PFAS could thus be diffusely distributed in low concentrations through the soil and enter the groundwater. Since 2008, for example, in Bavaria (Germany), PFAS must be investigated in the case of an intended recycling of sewage sludge on soil. The precautionary guideline value is 100 µg/kg dry matter (plus 25 % tolerance). If this value is exceeded, the sewage sludge may only be disposed of thermally.

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[46]   https://www.lfu.bayern.de/analytik_stoffe/analytik_org_stoffe_perfluorierte_chemikalien/pfc_belastung_abwasser_klaerschlamm/index.htm

[47]   24-hour composite samples, 2006

Figure 49   Distribution of the PFAS contamination in sewage sludge (in µg/kg dm) (investigation period 11/06 - 12/09)
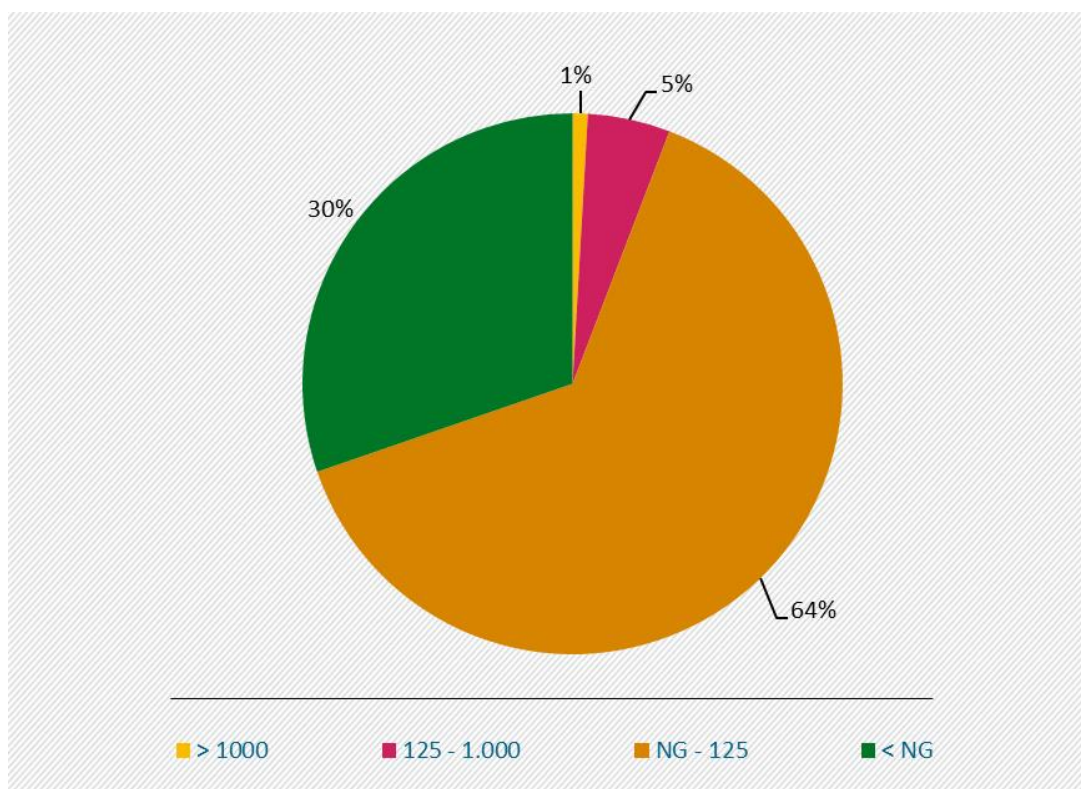
Source: Bayerisches Landesamt für Umwelt, 2010

Compost. Compost or biomass residues from biogas production can also have a PFAS contamination, they mainly contain PFOS (LANUV, 2011). Biowaste composts investigated in Bavaria (Germany) had a maximum content of 40 µg/kg PFAS. However, their elution only leads to a contamination of surface and ground water in the trace range (Bayerisches Landesamt für Umwelt, 2012).

Atmosphere. PFAS are also transported via the atmosphere. Despite their low volatility, the two lead compounds PFOS and PFOA are globally distributed, especially in remote areas such as the Arctic. Since the volatile fluorotelomer alcohols can also be detected in the Arctic atmosphere, it is assumed that the PFAS distribution in the atmosphere takes place in the form of volatile precursors, which are then transformed in the air under abiotic and biotic conditions to the persistent, highly water-soluble perfluorocarboxylic acids. These are then washed out of the air with the precipitation and enter surface waters and groundwater. However, model calculations have shown that the slow transport of PFAS-contaminanted waters via rivers into the oceans and their distribution there by ocean currents over the entire world's oceans to the Arctic, which takes years to decades, is more likely to contribute to global distribution than airborne transport, even the latter is by orders of magnitude faster (Armitage et al., 2009).

Nevertheless, deposition via the atmosphere does not appear to be negligible. This is particularly the case in the vicinity of PFAS production plants. PFAS can be adsorbed on particles in gaseous form or dissolved in water droplets emitted into the atmosphere. Non-volatile PFAS can also be emitted into the atmosphere in large proportions as aerosols when used in industry (Barber et al. 2007). Investigations at two sites near the Germany city Hamburg allowed the detection of mainly FTOH and 8:2 FTOH in the gas phase in concentrations up to 600 pg/m^3 (Dreyer et al., 2009). In the particulate phase PFOS was detected with up to 13 pg/m^3.

Investigations in the US have shown that PFAS in the atmosphere can reach the groundwater via precipitation and seepage water and cause diffuse large-area contaminations (Prevedouros et al., 2006). The background concentration of PFOA in rainwater was 2 - 53 ng/L (Baton et al., 2007).

Studies in rural areas (Germany, 2007) showed precipitation-related deposit rates (in $ng·m^{-2}·d^{-1}$) of max. 16 for PFHxA, 12 for PFHpA and 46 for PFOA. PFOS was not detectable. Near a PFOA emitter, PFOA deposition increased to 2,000 - 5,000 $ng·m^{-2}·d^{-1}$. In addition, significantly higher values for PFHxA and PFHpA were measured (Bayerisches Landesamt für Umwelt, 2010). More recent studies show 1.6 - 48.6 ng/L PFAS (34 compounds) in precipitation. PFOS could be detected in all rainwater samples, PFOA in 90 % of the samples. The corresponding deposition rates (wet deposition) varied for PFOS from 0.1 - 11.9 $ng·m^{-2}·d^{-1}$, the average was 3.3 $ng·m^{-2}·d^{-1}$. For PFOA they were between 0.8 and 13.9 $ng·m^{-2}·d^{-1}$, averaged at 4.0 $ng·m^{-2}·d^{-1}$. The calculated deposition rate for the sum of all analysed PFAS compunds was 2 - 91 $ng·m^{-2}·d^{-1}$ (LUBW, 2016).

Soils. Based on the application of sewage sludge, compost, and the deposition from the atmosphere, PFAS contamination can occur in the soil. In a study in the German Feral State Baden-Wuerttemberg only 6 of 43 areas treated with compost PFOS could be detected in very low concentrations (max. 4 µg/kg dry matter) in the soil horizon 0 - 30 cm. A state-wide PFAS screening in Bavaria (Germany) (2006) showed that biowaste compost did not cause significant PFOS and PFOA inputs on the investigated areas. PFOS (max. 6.5 µg/kg dry matter) and PFOA (max. 4.5 µg/kg dry matter) were detected in the topsoil of only 2 of the 13 areas treated with biowaste compost (LfU, 2010). However, it should be noted that in the eluate of these soils significantly more positive findings were detected, but regularly in low concentrations. The highest concentrations in the eluates were measured with values up to about 0.1 µg/L for the perfluorocarboxylic acids PFBA, PFPA, PFHxA, PFHpA and PFOA. Similar conditions are found in the case of surfaces treated with sewage sludge (LUBW, 2017).

Furthermore, reserve samples from nationwide distributed measuring areas (soil duration monitoring in the German Federal State Baden-Wuerttemberg with the main soil uses arable land, grassland and forest in areas far from settlement and industry and which showed a farming history without the use of waste-borne fertilizers such as compost or sewage sludge) were analyzed. The analysis (soil, eluate) showed PFOS concentrations above the limit quantification of 1 µg/kg in the solid matter in 17 of 28 samples (1 grassland soil, all 16 forest soils). In some forest soil samples PFOA and PFDA were also quantifiable. In the aqueous shaking eluate, the carboxylic acids PFBA, PFPA, PFHxA, PFHpA and PFOA as well as PFOS above the limit of quantification of 1 ng/L were detected. The results thus indicate a very low areal background content of PFAS in soils, probably due to deposition.

Surface water. PFAS detectable in surface waters can originate from various sources, such as effluents from wastewater treatment plants, atmospheric deposition, or surface runoff of PFAS-contaminated soil[48]. Due to the expected low PFAS concentrations and the high bioaccumulation, the analysis of fish or other aquatic organisms are preferred over surface waters. For example, investigations of carp in 2008 from fishponds in the vicinity of a PFAS source revealed a maximum concentration of 666 µg/kg PFOS in the fish. The concentration of PFOA and PFHxS was below the limit of quantification (LANUV, 2008). Investigations in Bavaria (Germany) on fish from different rivers showed a varying basic contamination with PFOS (max. 140 µg/kg in muscle tissue). Only in fishes caught below the discharge point of a production site a contamination of the fish with PFOA (max. 48 µg/kg in muscle tissue) was observed in addition to PFOS[49].

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[48] Excluded at this point is the application of fertilizer/soil improvers that have been illegally mixed with PFAS-contaminated industrial waste.

[49] https://www.lfu.bayern.de/analytik_stoffe/analytik_org_stoffe_perfluorierte_chemikalien/pfc_belastung_fische_muscheln/index.htm.

Investigations of the Germayn rivers Rhine, Weser, Ems, and the Elbe estuary revealed a maximum of approx. 110 ng/L PFAS in an area north of Cologne (Rhine) and approx. 17 ng/L in the Elbe estuary. Especially north of Cologne the non-precursor HFPO-DA[50] accounted for the largest part of the PFAS contamination. Further downstream it was no longer detectable. Otherwise, all perfluorinated carboxylic acids, from PFBA to PFDA as well as PFBS, PFHxS and PFOS, were detectable in the watercourses in changing compositions.

The PFAS can enter the groundwater, crops, livestock and thus ultimately reach humans via the food chain via contaminated soil and surface water.

Background Concentrations and Causes (Summary)

Due to the wide range of applications of PFAS and their non-degradability in the environment, PFAS have spread almost ubiquitously. They are found in low background concentrations in surface waters and partly in groundwater and soil.

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[50] 2,3,3,3-Tetrafluor-2-(1,1,2,2,3,3,3-heptafluorpropoxy)propansäure = GenX

14   Sources of Contamination

Point contaminant sources can always occur where PFAS were handled in large quantities (Chapter 11). However, the probability of contamination is not the same for all industries.

Figure 50   PFAS cases in Northrhine Westphalia (status: 04/2017) according to causes (top, n = 93) and extinguishing agent differentiated (bottom, n = 66)
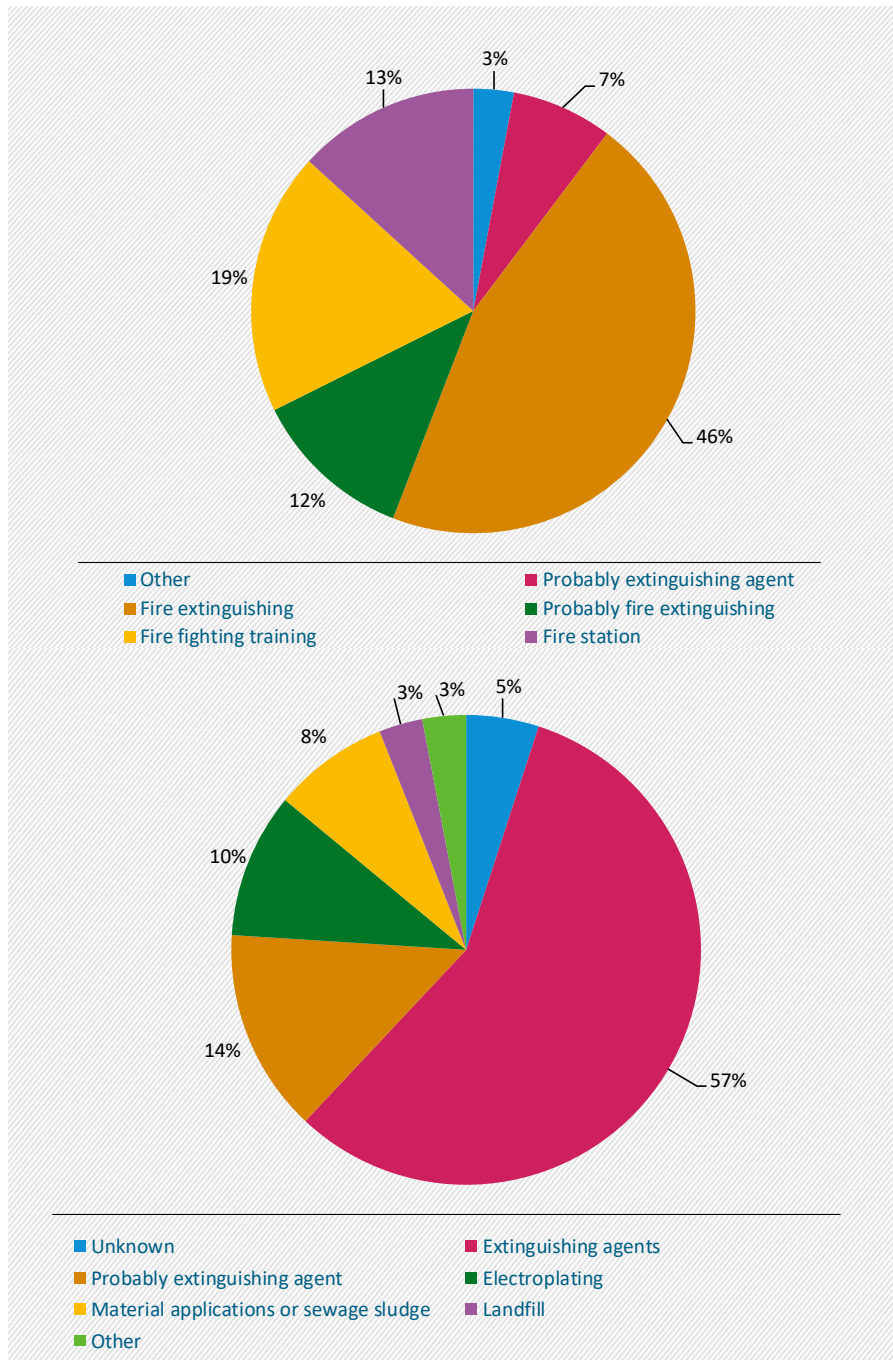
Source: LANUV NRW, 2017, modified

As Figure 50 shows, the vast majority of contamination is caused using extinguishing agents and electroplating; among the extinguishing agent uses, cases with fire extinguishing dominate.

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Appendix B:

Assessment and Documents Leading to the Assessment (as of December 2019)

Table of Contents

List of Tables

General remark Appendix B:

Unless otherwise stated, this Appendix B compiles the legal basis in the Federal Republic of Germany. These are based on European specifications and are, however, largely determined by German legislation. In this respect, this Appendix is only intended as an orientation for other legal systems, although the implementation in the member states of the EU is comparable.

1.   Regulatory Environment

In 2006, the European Parliament adopted its first restriction on the use of PFAS with the EU Directive 2006/122/EC. This restriction of use concerned the single substance PFOS and its derivatives (EU, 2006). According to this directive, PFOS may no longer be placed as a product on the market or used as a substance or constituent of preparations with a concentration of ≥ 0.005 mass-%. Semi-finished products, articles or components may not be placed on the market if the PFOS concentration is ≥ 0.1 % by mass. For textiles or other coated materials, the limit value of 1 µg/m^2 PFOS of the coated material applies. Very limited exemptions apply to, inter alia, photographic coatings for films, papers, and anti-fogging agents for non-decorative hard chromium plating in electroplating and hydraulic fluids for aerospace applications.

In 2007, the regulation was implemented in German law (Bundesregierung, 2007).

Two years later, in 2009, PFOS was included in the list of substances to be restricted worldwide under the Stockholm Convention (REACH, 2019). In the meantime, 6 further perfluorinated compounds have been included in the REACH candidate list as substances of very high concern, including PFHxS, PFOA, PFNA, and PFDA.

On 14 June 2017 the EU published measures to regulate PFOA, its salts, and precursors in a wide range of products according to Annex XVII of REACH. The new law will be implemented in stages from 4 July 2020 (REACH, 2017) onward.

Under the EU REACH regulation, foaming agents containing more than 25 µg/L PFOA for PFOA and its salts and 1,000 µg/L precursor compounds may no longer be sold in the European Union (EU) after 4 July 2020.

Today, the production and/or use of PFOS and PFOA (the so-called C$_8$ compounds) in Europe have been almost completely discontinued. As a result, both compounds are being actively replaced by other PFAS. Known substitutes include PFHxS, 6:2 FTS, PFBS and ether compounds such as ADONA and GenX. Short-chain PFAS compounds are regarded as less toxic and bio-accumulative, but are still very persistent. Another problem is that the substitutes often must be used in higher concentrations to achieve the desired properties in the application.

In 2017 the German Federal Environment Agency (UBA), together with KEMI (Swedish Chemicals Agency) and the European Chemicals Agency (ECHA), submitted a proposal to ban six highly fluorinated PFAS (PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA) in the EU from 2020. The proposal also covers all other PFAS that can be degraded to any of these six compounds (precursors). This means that the total ban will apply to a group of about 200 highly fluorinated compounds. The reason for the Swedish-German proposal is that the substances are extremely poorly degradable in the environment and accumulate in living organisms. The quantities of substances currently used in the EU are small. ECHA is currently (as of 2019) conducting a public consultation on this proposal. There are many other international organizations (e.g. Organization for Economic Co-operation and Development; OECD and the Global PFC Group of the United Nations Environment Program; UNEP) that have a similar influence on the regulation of PFAS.

For the intake of PFAS by humans, the German Federal Institute for Risk Assessment (BfR) had already derived a provisional TDI (tolerable daily intake) of 0.1 µg/kg body weight (bw) for PFOS and PFOA in 2006 (BfR, 2006). In 2008, the TDI was initially increased to 0.15 µg/kg bw for PFOS and 1.5 µg/kg bw for PFOA (BfR, 2008). In December 2018, the European Food Safety Authority (EFSA) published a re-evaluation of health risks from PFOS and PFOA in food. The tolerable weekly intakes (TWI) were reduced to 6 ng/kg bw for PFOA and 13 ng/kg bw for PFOS (BfR, 2018).

In 2019, the BfR recommended that the derived tolerable daily intake values (TWI) be used to assess the health risk of PFOS and PFOA intakes from food and that measures be taken to further minimize consumer exposure to PFOS and PFOA via food. In principle, it was recommended that drinking water should be considered as a source of exposure. However, scientific uncertainties have been identified and further research needs have been formulated regarding current chemical evaluations (BfR, 2019).

2. Federally Unified Basis of Assessment Bases in Germany

On the basis of the resolution of the 88th German Conference of Environment Ministers of May 2017, uniform nationwide requirements for the assessment and remediation of soil and water pollution and for the disposal of materials containing PFAS are currently (as of 09/2019) being derived by a working group that spans the federal states. After consultation with the Ministry, it is expected that the German Conference of Environment Ministers will issue a recommendation to the federal states to apply these requirements. In the next step, the requirements should then be introduced in each federal state by decree. For this reason, no information on country-specific regulations is given below.

3. Direct Pathway Soil → Human

Currently there are no calculations for preliminary trigger values for the source/receptor-pathway soil → human (direct contact). There are only estimations that were presented at technical lectures. According to these, the values would be in the mg/kg range. However, whether these are reliable must also be checked regarding the possibility of changing TDI values.

In case that PFAS have already been taken up into the human body, the German Commission on Human Biomonitoring (HBM) has derived two types of assessment values (UBA, 2020):

► Reference values from a series of measured values from a sample of a defined population group according to a given statistical procedure. The reference values allow, among other things, the description of the actual state (so-called background exposure) of a defined population group with or without recognizable specific exposure at the time of the study and the determination of a specific exposure of individuals or groups of persons to substances. The reference values are purely statistically defined values which per se have no health significance (UBA, 2020).

► Toxicologically justified HBM values to tolerable (HBM-I) or just tolerable (HBM-II) substance concentrations in blood or urine. These values were derived based on toxicological and epidemiological studies. The HBM-I value can be regarded as a test or control value. The HBM-II value corresponds to the concentration of a substance in a body medium above which, according to the current state of assessment, a health impairment that is to be considered relevant is possible, so that there is a need for action to reduce the exposure and environmental medical care (counselling) must be arranged. The HBM-II value is therefore to be regarded as an intervention and measure value. An HBM-II value has not yet been established for PFAS. For PFOS and PFOA (blood plasma, general population), however, there is an HBM-I value (as of February 2017):

PFOS   5 µg/L
PFOA   2 µg/L.

4. Pathway Soil → Plant and Pre-Harvest Monitoring

There is currently still a need for the derivation of trigger values for the source/receptor pathway soil → plant. Recent studies indicate that the uptake of PFAS by plants (transfer factors) is influenced by many parameters (including local plant composition) that often change over time. Research projects are currently underway on the uptake routes and mechanisms.

As long as no values have been developed for the soil → plant pathway, an assessment can be made only with the help of so-called pre-harvest monitoring. In pre-harvest monitoring, the plants are sampled and analyzed for PFAS before harvesting. The Ministry of Rural Areas and Consumer Protection of German Feral State Baden-Wuerttemberg has defined so-called assessment values (the values that can be tolerated for foodstuffs), considering the precautionary and minimization principle (Table 1).

Table 1   Assessment values for foodstuffs (status 9/2019) (in µg/kg) (Regierungspräsidium Karlsruhe, 2019)

Product	PFBA	PFPeA	PFHxA	PFHpA	PFBS	PFHxS
Fruit and vegetables	9.4	2.8	5.7	< 2.0	5.7	< 1.0
Cereals	21	6.5	13	< 2.0	13	< 1.0
Meat, fish, offal	100	30	60	3.0	60	1.0

In the German Federal State Baden-Wuerttemberg, the assessment values are used as a basis for decisions on the marketability of plants, for use as foodstuffs and for meat, fish, and offal. The assessment values are used both in pre-harvest monitoring and in food monitoring.

Pre-harvest monitoring is also used in animal feed (official feed monitoring) to ensure that only safe feed is fed, and that safe animal food can be produced even after feeding. Basically, it is true that crops that comply with the assessment values specified for food (Table 1) are also suitable as animal feed (Landtag von Baden-Württemberg, 2016). Due to these manifold aspects, the safety of feedstuffs with increased PFAS contents can usually only be achieved by individual case decisions, considering the available information.

In addition to the individual case decision, the information is sent to the food control authorities in order to carry out additional investigations in food of animal origin.

Despite the continuing need for research, the BfR recommends that the preliminary health-related guide values (TDI) of the EFSA be used in future evaluations of PFOS and PFOA in food.

5. Drinking Water

The joint German working group of LAWA and LABO[1] has identified 13 PFAS as priorities for groundwater based on information on occurrence and distribution as well as individual case reports. For seven of these compounds insignificance threshold values could be derived based on human toxicological data (LAWA, 2017). The Drinking Water Commission at the German Federal Environment Agency has assessed the data situation as sufficient to establish the seven derived insignificance threshold values also as guiding values according to the Drinking Water Ordinance (DW$_{GV}$). For a further six PFAS,

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[1]   LAWA: Federal/State Working Group Water, LABO: Federal/State Working Group on Soil Protection

the LAWA-LABO working group has given lifetime Health Advisory Level (HAL) for a further six PFAS due to the limited data available (Table 2).

Table 2 Drinking water guidance values and GOW (UBA, 2017) (UBA, 2017)

No.	Name	Abk.	CAS No.	DW_{GV} [µg/L]	HAL [µg/L]
1	Perfluorobutanoic acid	PFBA	375-22-4	10	-
2	Perfluoropentanoic acid	PFPeA	2706-90-3	-	3.0
3	Perfluorohexanoic acid	PFHxA	307-24-2	6	-
4	Perfluoroheptanoic acid	PFHpA	375-85-9	-	0.3
5	Perfluorooctanoic acid	PFOA	335-67-1	0.1	-
6	Perfluorononanoic acid	PFNA	375-95-1	0.06	-
7	Perfluorodekanoic acid	PFDA	375-95-2	-	0.1
8	Perfluorobutanesulfonic acid	PFBS	375-73-5	6	-
9	Perfluorohexanesulfonic acid	PFHxS	355-46-4	0.1	-
10	Perfluoroheptanesulfonic acid	PFHpS	375-92-8	-	0.3
11	Perfluorooctanesulfonic acid	PFOS	1763-23-2	0.1	-
12	H_4-Perfluorooctanesulfonic acid	H4PFOS	27619-97-2	-	0.1
13	Perfluorooctanesulfonamidw	PFOSA	754-91-6	-	0.1

The Drinking Water Commission has not expressed an opinion on the application of the quotient ratio sum; in some federal states it is currently used for drinking water assessment, but there is not yet a nationwide uniform procedure. In addition, the EU Commission has proposed to include PFAS in the substances to be monitored in the new Drinking Water Directive (EU, 2018). The proposal, which has been the subject of much controversy, provides for a regulation for the PFAS group as defined by the OECD and recommends the following limit values:

0.1 µg/l for each individual substance

0,5 µg/l for the sum of all PFAS

6. Surface Waters

The daughter directive "Priority Substances" (EU, 2013) to the Water Framework Directive (WFD) defines environmental quality standards (EQS) for PFOS in surface waters. This directive was transposed into German law in 2016 with the Regulation for the Protection of Surface Waters (Bundesministerium der Justiz und für Verbraucherschutz, 2016). According to this publication the following EQS values apply:

► 0.65 ng/L as annual average value

► 36 µg/L as maximum allowable concentration

For coastal waters, an EQS of 0,13 ng/L apply.

In the German Surface Water Ordinance (OGewV of 20.06.2016) there are currently environmental quality standards (EQS) available for PFOS for the protection of humans consuming fish as the most sensitive object of protection (assumption: fish consumption of 115 g/d and a contribution of 10 % to the TDI from fish consumption). For fish, the PFOS-biota-EQS is therefore 9.1 µg/kg fish. The calculation of the EQS is based on the effect on the biota. The water EQS was calculated based on the fish EQS. According to the OGewV, biota values should always be used for PFOS evaluation. Only if these cannot be determined should water samples be analyzed. The low EQA for water can be determined analytically, but only with great effort.

The EQS will apply from 2018. If these EQS are exceeded in a surface water, suitable measures must be taken to ensure compliance by 2027 at the latest.

7.   Fertilizer Ordinance

The German Fertilizer Application Ordinance (DüMV, 2012) sets a limit value for the sum of PFOA and PFOS of 100 µg/kg. The DüMV also applies to sewage sludge. In the currently valid German Sewage Sludge Ordinance (AbfKlärV) of 27 September 2017, no limit values for PFAS are specified, since the AbfKlärV refers to the DüMV.

8.   PFAS Regulations Abroad

In many countries outside Germany, limit or trigger values for PFAS (primarily for PFOS and, where appropriate, PFOA) have been derived. In the following, only some of the findings are listed as examples. A complete description of the current global situation is not appropriate for this guideline, especially since the regulations are still subject to frequent changes.

In the USA, values for exposure to PFOS and PFOA were first set by the US Environmental Protection Agency (EPA) in 2006. According to this, a lifetime Health Advisory Level (HAL) for drinking water of 0.07 µg/L applies to the sum of PFOS/PFOA. In other US states, values have been set for other media and other PFAS compounds (EPA, 2019). In 2018, the U.S. Department of Health published a draft proposal to lower the limit for PFOS to 0.007 µg/L and for PFOA to 0.011 µg/L (ATSDR, 2018).

For soil in residential areas a soil screening level of 6 mg/kg PFOS and 16 mg/kg PFOA was recommended regionally.

In the US state of North Carolina, a HAL value for GenX of 0.14 µg/L was derived in July 2017 for the most endangered population group in coordination with the US EPA. This health target is a non-regulatory value below which no harmful effects on health are to be expected over the entire exposure period (Water Online, 2017).

Australia adopted the American limit values for drinking water in April 2017, but added PFHxS to the sum, so that the limit value of 0.07 µg/L now applies to the sum of PFOS and PFHxS (Australian Government, Department of Health, 2017a, b).

In Europe, the strictest drinking water limits apply in Scandinavia. In Denmark, the limit value for the sum of 12 PFAS is 0.1 µg/L (Danish Ministry of the Environment, 2015) and in Sweden the limit value for the sum of 11 PFAS is 0.09 µg/L (Gobelius et al., 2018).

9. Available Methodological and Discretionary Guidance Documents

Methodological and discretionary guidelines are available in the individual German Federal States. However, these are soon to be replaced by the nationally uniform assessments and regulations. In addition, methodological guidelines have been prepared for

► Recording and exploratory investigation (project stage 1) (LABO, 2015)

► Recording and exploratory investigation (project stage 2) (LABO, 2017).

In project stage 1, the basic principles for the recording, historical investigation, and orienting investigation (phase 1 investigation) not only of contaminations with fire extinguishing foams, but of all industrial sectors in which PFAS were used, were formulated. In project stage 2, the elaborated basics were checked for their applicability in practice.

In addition, "PFC Guidelines for Federal Real Estate" are available at the federal level, published by the Federal Office for Infrastructure, Environmental Protection and Services of the German Armed Forces together with the Federal Agency for Real Estate Tasks as part of the Construction Guidelines for Soil and Groundwater Protection (Bundesamt für Infrastruktur, Umweltschutz und Dienstleistungen der Bundeswehr, 2018).

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Appendix C:

Remediation Technologies

Table of Contents

List of Figures

List of Tables

1 Introduction

1.1 Current Status

From an economic point of view, the remediation methods described below are almost without exception applicable only to local contaminations. The few technologies that can be applied over a wide area have not yet been developed to market maturity or still have numerous open questions.

Altogether, apart from the *pump-and-treat* technology with the sorption of PFAS on activated carbon or soil exchange (both referred to in the following as standard technology), all other remediation technologies are still at the design or development stage with only a few exceptions.

The following chapters not only describe the technologies that have already reached market maturity or are about to do so, but also those for which the chances of establishing themselves on the market are comparatively low. Against the background that numerous technology providers are currently active on the market, this compilation is intended to give readers the opportunity to better evaluate offered solutions regarding their chances of success. The mode of operation of the processes is described in detail (section *Description*). In the section *Outlook* the possible applications, development status, practical relevance as well as the status of application and open questions are discussed. A graphical summary of the feasibility in relation to market maturity is given in Chapter 0 at the end of this Appendix.

At present, intensive efforts are being made to remove PFAS from the environment in a sustainable manner using comparatively mild methods. However, the degradation of PFAS using conventional biological and chemical processes is an almost insurmountable challenge due to the strength of the CF-bonds and the high electronegativity of fluorine (Jin, 2015). Many conventional technologies used to remediate "classical" organic contaminants are ineffective due to the chemical and biological stability of PFAS and their low volatility. Processes such as aerobization and some forms of chemical oxidation only lead to a transformation of the precursors to stable perfluoroalkane acids, but not to their mineralization (Dauchy et al., 2017a, b; McGuire et al., 2014). Typical PFAS-contaminated sites exhibit the following properties:

▶ The average plume length is > 1,5 km.

▶ More than 75 % of the plume are contaminated with < 10 µg/L PFAS.

▶ Large plumes (with mostly low PFAS concentrations) do not necessarily originate from source areas with high PFAS concentrations.

1.2 Groundwater Remediation

1.2.1 Optional Treatment Technologies

There will be no cost-efficient *in-situ* remediation technology for groundwater because of the large area of the contamination. Therefore, site management will always result in hydraulic containment. Pump-and-treat or sorbing barrier technologies (e.g. funnel-and-gate, F&G; permeable reactive barriers, PRB) can be considered for protection of the downgradient groundwater. For the decontamination of the pumped groundwater, the methods shown in Figure 1 are generally applicable.

The use of pump-and-treat technologies for remediation has long been regarded to be potentially open-ended, as the contaminants are back-diffusing from less permeable groundwater horizons.

Figure 1   Possible groundwater treatment technologies
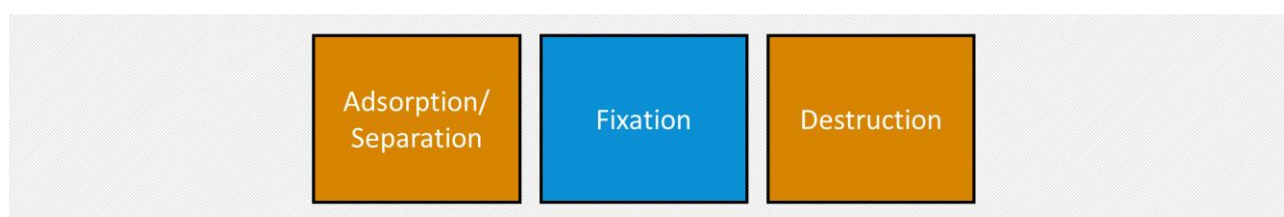
Source: Arcadis Germany, GmbH

The very low remediation targets for PFAS, combined with the relatively high solubility of many PFAS and the presence of extensive diffuse plumes, raises questions about the long-term success of pump-and-treat technologies for the removal of PFAS from groundwater. Due to the extensive diffuse contaminant plumes, in-situ remediation technologies cannot be realized in a cost-effective manner.

The available remediation technologies for groundwater are discussed in detail in Chapter 2 few exceptions, the procedures are based on pump-and-treat with different methods of decontaminating the pumped groundwater.

1.2.2   Barrier Technologies

Due to the, in most cases, necessary rigid reaction conditions, destructive technologies or membrane technologies (separation) are rather not used in F&G in-situ reactors. The feasible options are limited to sorption processes such as sorption on activated carbon with all its advantages and disadvantages (Chapter 2.2.1.2). Consumed sorbents must be replaced at regular intervals. The low sorption capacities of most sorbents and the early breakthrough of the shorter-chain PFAS have so far inhibited considerations of F&G and PRB applications in the field. There is currently no published practical experience in this area. However, this remediation approach is generally feasible and is already being pursued in the research field.

Optionally, commercially available sorbents such as RemBind™ or MatCare™ can also be used.

1.2.3   Redox Environment

To increase the efficiency of the pump-and-treat technology, considerations have been made to increase the mobility of the PFAS in the aquifer by forcing specific modification of the redox milieu. The approach resulted from the observation that activated persulfate reduced PFAA transport in the aquifer, while permanganate and catalyzed hydrogen peroxide increased[1] PFAA transport. PFAA sorption also increased in the presence of higher concentrations of polyvalent cations or decreased pH. The direction (increased or decreased transport) and the magnitude of mobilization during in situ chemical oxidation will probably depend on several parameters (PFAA properties, oxidant properties, site specific factors, degradation of the sorbent natural DOC).

In general, PFCA are more amenable to mobilization by redox milieu changes than PFSA, presumably because the latter bind overall more strongly to the soil (McKenzie et al., 2015, Arvaniti et al., 2015). The extent to which the enhancement of reducing conditions affects PFAS mobility has not been investigated.

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[1] It can be assumed that the release of perfluorinated acids from the precursors after application of the oxidizing agents was not considered in these studies.

Methods of redox manipulation have hardly been tested beyond laboratory scale, as there are concerns that enhanced transformation of the precursors releases elevated concentrations of perfluoro-alkane acids. On the other hand, precisely this should be desirable. The precursors are then converted into a form that is easier to monitor and removable from the aquifer with the available remediation technologies.

However, it remains to be checked whether, in individual cases, the extent of mobilization is so high that the additional costs incurred are worthwhile. The quantity of reagents required is likely to be high, as they may also react with other components of the aquifer system which are presumably not directly involved in the mobilization of the PFAS. However, as long as a source is still emitting contaminants from the unsaturated soil zone into the aquifer, the method is unlikely to have any additional benefit.

1.3 Soil Remediation

1.3.1 Disposal on landfills

Due to the long time required for the natural leaching of the contaminant source, the focus in future will therefore be primarily on source remediation (i.e. treatment or removal of the soil and the unsaturated zone). Classically, the most frequent used technology for this is soil exchange and landfilling of the contaminated soil and subsequent backfilling of the excavation area with uncontaminated soil. Apart from the fact that the accepting landfill must have a sufficiently effective leachate treatment plant, soil exchange at PFAS-contaminated sites is a standard procedure that does not differ from the soil exchange at other contaminated sites.

Due to the very limited landfill space available and the widespread concern of landfill operators to accept PFAS contaminated soil, alternatives to landfilling the contaminated soil, such as for instance on-site containment, are highly valued. In the case of extensive contamination, monetary and above all ecological aspects also prevent the clearing of the landscape.

1.3.2 Complete Containment

Another issue is the containment of the site (sealing, encapsulation). Surface sealing prevents the leaching of contaminants from the unsaturated soil. In many cases, vertical encapsulation and dewatering in the encapsulated area is also necessary. However, the contaminants remain permanently on site. In contrast to conventional contaminants, a significant change of the redox milieu in the hydraulically isolated area is not to be expected in the event of contamination with the non-mineralizable PFAS, provided that no microbially degradable accompanying contaminants are present (e.g. non-fluorinated surfactants from the fire extinguishing foams). Consequently, methane formation is not to be expected. Otherwise, the constructional safety procedure for PFAS contamination does not differ from that of other contaminants and is therefore not discussed further.

1.4 Technology Assessment

The aim of the following compilation is a technical examination of the feasibility of the respective technologies, considering both the chemistry of the PFAS and the geological and hydrogeological site factors when implementing the remediation technologies.

Since most of the technologies are not yet ready for the market, there are considerable problems in assessing the effectiveness and costs of the processes compared to the standard pump-and-treat or soil exchange/landfill technologies.

However, the costs of the standard technologies can also vary considerably. Therefore, first of all such a pump-and-treat remediation was evaluated (Chapter 2.1) in order to elucidate the costs of such a standard remediation technology. As these remediation measures were carried out immediately after the PFAS entry in form of fire extinguishing foams, a further spread of the PFAS was minimized and the remediation can be considered as being a best case.

2   Groundwater Remediation Technologies

2.1   Standard Technology Pump-and-Treat

For the standard technology pump-and-treat, a case study is presented below. During a major fire on a company site (Figure 2) in October of the late 2000s, fire-fighting foams containing PFAS were used. As a result, a considerable PFAS contamination of the building fabric occurred and, due to the infiltration of the extinguishing agents, also of the soil and groundwater. The quantities of extinguishing agent or PFAS used are unknown.

Figure 2   Site map
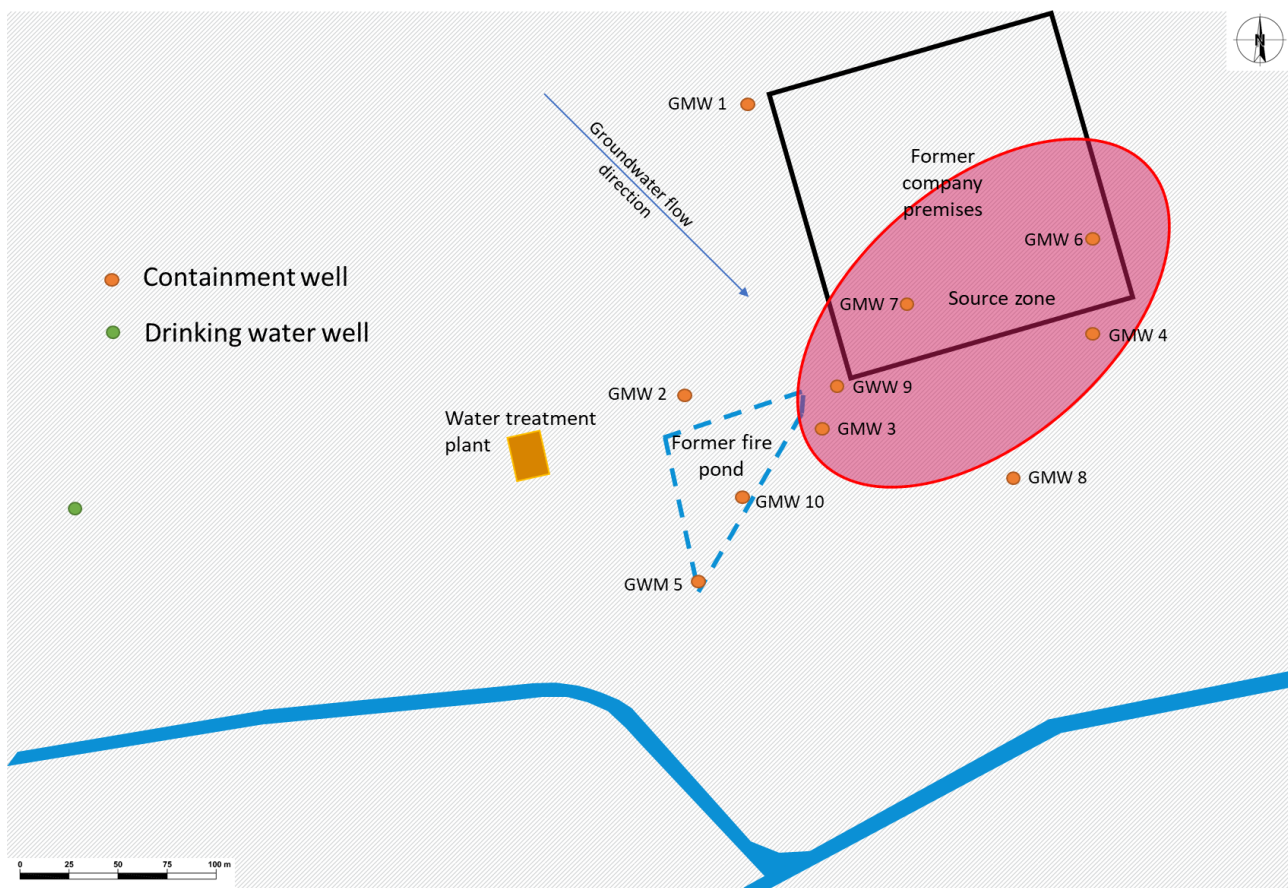
Source: Arcadis Germany GmbH, 2019

Quaternary weathering products and Lower Buntsandstein bedrock comprise the site geology. The groundwater level is less than 3 m below ground. The aquifer is within the fractured bedrock with an extensive network of prevalent faults and joints resulting in a coefficient of hydraulic conductivity of(k_f value) approx. $4.7 \cdot 10^{-5}$ m/s over a thickness of approx. 50 m.

To the southwest of the site there was a "fire pond" into which extinguishing water flowed during fire-fighting, both directly and via a drainage system. In the same month, immediately after the fire, the pond water contaminated with extinguishing water was removed by tankers and disposed of via a sewage treatment plant. Since the site's sewer system continued to drain into the former fire pond, a permanent catchment basin was constructed in the area of the pond to collect surface water that ran off. Over a period of 2.5 years, the water collected in this catchment basin at the site was cleaned separately via an activated carbon system with upstream gravel filter and discharged into the public sewage system.

During the ongoing fire-fighting operations due to the infiltration of the fire-fighting foams containing PFAS, an influence on the groundwater was detected in the form of foam formation in the groundwater monitoring well (GMW) 1 (i.e. upstream of the actual contaminant source). As the affected area is located in zone III of a water protection area and in the catchment area of several drinking water wells (the distance to the nearest well is approx. 400 m), the contaminated groundwater at GMW 1 was pumped out, temporarily stored, and disposed of to a sewage treatment plant as an immediate measure while the fire was still being fought. In addition, boreholes were drilled in the presumed main contaminated area and these were completed as containment wells (GMW 2 to GMW 5). GMW 2 and GMW 3 were put into operation at the end of October, i.e. shortly after the fire, after further disposal capacities became available. With these three wells a total groundwater extraction rate of 36 m^3/h was achieved.

Two months after the fire event, a three-stage groundwater treatment plant using PFAS sorption on activated carbon was put into operation. At the same time, groundwater pumping began at two other wells (GMW 4 and GMW 5). By the beginning of the following year, the containment measures had been gradually built up. In three further drilling campaigns, GMW 6 to GMW 8 as well as control monitoring wells and monitoring wells in the inflow were constructed.

In May/June of the following year the plant technology was moved to a new plant site. As part of these measures, the third activated carbon filter for water cleaning was removed. Since then, the extracted groundwater has been treated in a 2-stage plant using activated carbon for water with a total of approx. 24 m^3 activated carbon. The consumed activated carbon is regenerated off-site and is then available for a new use at the same site. The purified water is discharged into a surface water body.

In the first six months after the fire, the contamination source with PFAS-containing extinguishing agent was partly remediated by soil exchange (approx. 12,000 tons of contaminated soil) as part of a danger prevention measure. The soil was excavated at least to the depth of the solid bedrock (maximum 3.0 m below ground level, average 1.2 m below ground level) and disposed of. Thus, a total of 20 kg PFAS was removed from the subsoil. A second soil exchange at the site was intended to remove the contamination still present within the near-surface layers of loose rock. Further 30,000 tons of PFAS-contaminated soil, also down to solid bedrock, was excavated. As a result, a further 15.7 kg PFAS were removed. Below the former soil remediation level, however, there are still high quantities of contaminants present which should be removed via the drainage system after being discharged into the groundwater.

During these measures, groundwater with streaks and foaming was discovered at the southwestern boundary of the property. Therefore, two shallow wells (GMW 9 and GMW 10, depth 4,5 m) were constructed and connected to the water treatment plant.

The achievable groundwater extraction rate of the containment wells and in particular the two shallow wells is strongly dependent on the precipitation quantities occurring and therefore shows fluctuations. On average, an extraction rate of 43 m^3/h was achieved, with a maximum achievable extraction rate of 60 m^3/h. The development of the PFAS concentration in the raw water (inflow water treatment plant) is shown in Figure 3.

Figure 3   Change of PFAS substance concentrations at treatment plant inflow (top) and the cumu-lative PFAS total removal (bottom). The dotted line indicates the period of soil exchange
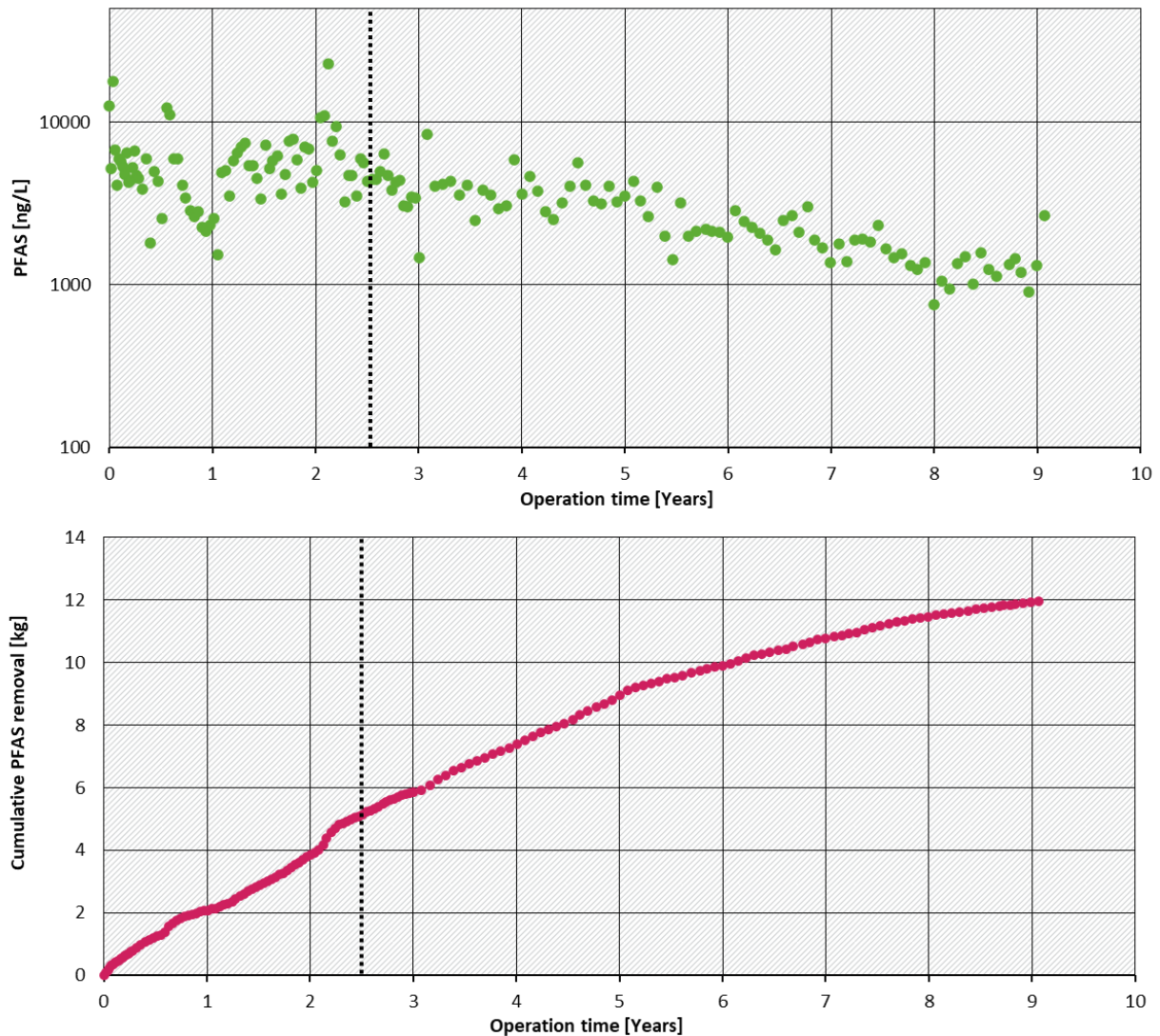
Source: Arcadis Germany GmbH, 2019

The analysed PFAS parameters[2] was extended from 9 to 10 parameters[3] after about 3 years of operation. All 10 individual parameters can be detected in larger concentrations in the inflow of the water treatment plant. In addition, 22 PFAS compounds[4] were analyzed every three months until the time of the survey (2018). Despite the extension of the scope of analysis to the mainly occurring parameters, the PFAS sum is decreasing in trend.

The discharge limit is 100 ng/L total PFAS. Since the start of operation, approx. 12 kg PFAS have been removed from the aquifer.

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[2]   PFOS, PFOA, PFBS, PFHxS, PFHxA, PFHpA, PFOSA, PFNoA, PFDeA

[3]   PFOS, PFOA, PFBS, PFHxS, PFHxA, PFHpA, PFBA, PFPeA, PFHpS, H4PFOS

[4]   PFOS, PFOA, PFBS, PFHxS, PFHxA, PFHpA, PFBA, PFPeA, PFHpS, H4PFOS, PFOSA, PFNoA, PfDeA, PFTrA, PFDeS, PFDoA, PFTA, PFUnA

After a few years of remediation, the slope of the cumulative PFAS recovery flattens out, in part due of the performed soil exchange. In total, approx. 3,500,000 m^3 groundwater was treated by the end of the 9th remediation year.

The total cost of the remediation so far consists of the investment costs for the treatment plant as well as the operation and maintenance costs and the costs for the activated carbon. The investment costs for this plant are approx. 350,000 € with operating costs of approx. 50,000 €/year and costs for the activated carbon of approx. 33,000 €/year (as of 2018).

According to the current status, this results in an amount of approx. 3.10 € per 1 m^3 treated groundwater or approx. 92,000 € per 1 kg removed PFAS. If only the operating costs and the costs for the activated carbon are considered, these amounts fall to approx. 0.20 € per 1 m^3 treated groundwater or approx. 62,500 € per 1 kg removed PFAS.

While the costs for the treatment (without activated carbon) remain the same, the concentration of PFAS in the extracted water and thus the removed mass of contaminants generally decreases with increasing remediation time. This results in increasing costs per kg of PFAS removed. This increase is particularly noticeable after the completion of soil remediation in year 5. The costs per cleaned m^3 of groundwater remain relatively constant in the first remediation period (Figure 4).

Figure 4   Cumulated and specific clean-up costs and cumulated PFAS removal
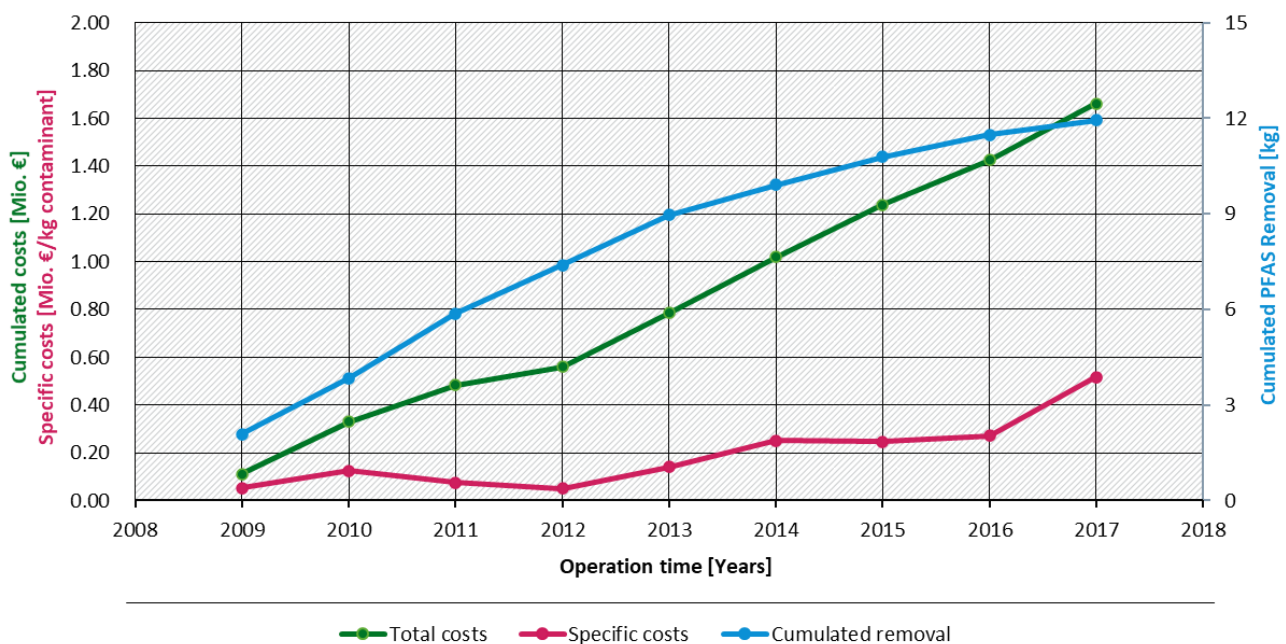
Source: Arcadis Germany GmbH, 2019

For an estimation of the entire remediation time needed, the previous course of PFAS concentration can be extrapolated. Using an exponential function (1st order concentration attenuation rate, starting after the end of soil remediation; R^2 = 0.73) the remediation target value is expected to be achieved after a total of 22 years of remediation.

The behavior of the precursors has not been considered at the site so far. *The pump-and-treat technology* was designed as an emergency measure, so the groundwater extraction wells may not be in the optimal locations.

To be able to better estimate the residual remediation time, an estimation of the contaminant inventory and thus an investigation of the precursors has been recommended.

In the following chapter 2.2 several technologies for the removal of contaminants from the process water stream are described.

<div style="background-color:#5aa832; color:white; padding:4px 8px;">

Standard Procedure Pump-and-Treat (Summary)

</div>

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P&T is used for the remediation of most local PFAS contamination. Although the technology is established quickly after the occurrence of contamination, long remediation times and high overall remediation costs result, even if partial source remediation has been carried out. Relative to the kilograms of contaminant removed, the costs are generally very high. If remediation has been set up as an immediate relief measure, it is always advisable to carry out a subsequent review of the efficiency of groundwater extraction.

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2.2 Technologies for the Decontamination of the Extracted Groundwater

2.2.1 Sorption on Carrier Materials

2.2.1.1 Overview

Sorption[5] on carrier materials (sorbents) is an equilibrium process. Since the equilibrium is strongly on the side of the sorbed form, there are significantly more contaminant molecules bound to the sorbent in the reactor in a time-integrated manner than dissolved in the process water. Where exactly the sorption equilibrium lies depends on the sorption strength of the sorbent for certain contaminants and, in the case of non-linear sorption, on the contaminant concentrations of the compounds to be eliminated. Thus, poorly binding compounds in very high concentrations can displace better binding compounds in low concentrations.

For a single molecule (sorbate) it is true that it constantly changes from dissolved to sorbed. As a result, better sorbing compounds can occupy the binding sites and the worse sorbing compounds therefore stay statistically more often in the water phase. In a sorption reactor, the poorly binding contaminants are transported further towards the outlet and can there bind again, assuming an overall low loading rate. This leads to the formation of a layer in the sorption reactor in which poorly sorbing compounds are concentrated. During remediation, this layer is increasingly shifted by displacement towards the outlet in the reactor. As a result, the poorly sorbing compounds break through more quickly. Due to the concentration in the reactor, their concentration in the outlet can then be significantly higher than in the raw water. Sorption is therefore in principle a reversible process.

2.2.1.2 Sorption on Activated Carbon Activated Carbon

Description. The sorption of PFAS on activated carbon is currently the most common process for the removal of PFAS from contaminated groundwater. Accordingly, numerous studies have been carried out (Szabo et al., 2017; Woodard et al., 2017 and others). The activated carbon is filled into a continuously flowed through fixed-bed reactor. The reactors (at least two) are generally operated in series (sorption filter - backup filter configuration).

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[5] Sorption is a collective term for processes that lead to an accumulation of a substance within a phase or on an interface between two phases. The accumulation within a phase is more precisely called absorption, the accumulation at the interface is called adsorption. Sorption is the generic term for processes in which it is not possible to differentiate clearly between adsorption and absorption.
The sorbing substance is called sorbent or sorbing agent. The substance that has not yet been sorbed is called a sorptive. The system of sorbed substance together with the sorbent is called sorbate (following Wikipedia, 2019).

Sorption is a phenomenon of surface chemistry in which a substance dissolved in the aqueous phase adheres to the surface of a granular medium but does not penetrate this solid matrix. The activated carbon binds the organic compounds at its surface[6] by physical attraction (sorption). Although the exact mechanism of action depends on the type of contaminant to be bound, the sorption process mainly involves Van-der-Waals forces (hydrophobic binding). Electrostatic binding can also occur (Figure 5).

Figure 5   PFAS sorption on activated carbon
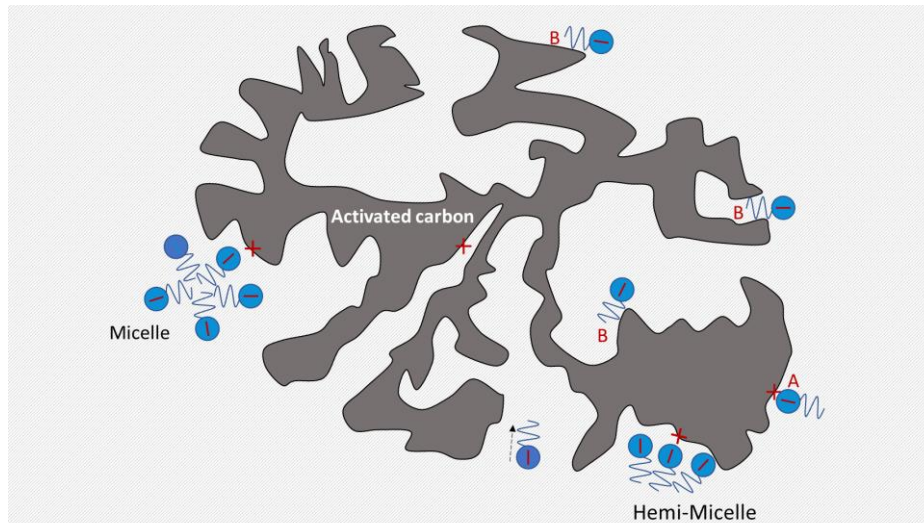
A: Electrostatic interaction, B: Hydrophobic binding[7]. Source: Yu, 2009.

Due to its porosity and the relatively large inner surface area of the pores, activated carbon is the most used sorbent. The sorption of the contaminants can vary considerably and can be influenced by the following factors:

► the type of activated carbon[8] and its properties (area of the inner surface, pore structure, chemical composition)

► reaction conditions (temperature, composition of the solution, pH),

► retention time in the reactor[9],

► concentration of the contaminant to be removed,

► competitive sorption by other substances,

► chemical properties of the molecule to be sorbed (molecule size, hydrophilicity, polarity).

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[6]   Activated carbon for water purification usually have a BET surface area of 500 - 1500 m^2/g. The inner surface area of activated carbon is determined by the BET method (Brunauer-Emmert-Teller). For this purpose, the nitrogen isotherm is measured at -196 °C and, assuming a monomolecular occupancy of nitrogen molecules on the inner surface of the activated carbon, the surface area is calculated using the surface area of an N_2 molecule (approx. 0.16 nm^2) (DIN 66131).

[7]   Micelles, also known as association colloids, are aggregated molecular complexes (aggregates) of amphiphilic molecules or surface-active substances (according to Wikipedia, 2019). Monolayer arrangements are called hemimicelles.

[8]   Activated carbon is made from hard coal, coconut shell, bitumen, brown coal, peat, or wood.

[9]   Indicated as EBCT (Empty Bed Contact Time). EBCT is defined as the total volume of the activated carbon reactor divided by the flow rate, expressed in minutes.

The sorption capacity in equilibrium is described as follows (Freundlich isotherm):

$$\frac{X}{M} = KC^{\frac{1}{n}}$$

where X/M = quantity of contaminants (X) sorbed per unit of activated carbon (M) [weight %], C = concentration of contaminants in the water phase, K, n = empirical, contaminant-specific constants (determined from the sorption isotherm).

From the sorption isotherms, the equilibrium concentrations (in the effluent) can be derived at certain inflow concentrations. If the sorption is not sufficient, i.e. the concentration in the effluent is above the permissible residual concentration, a multi-stage sorption plant is required. Usually, sorption isotherms are determined in batch tests which do not consider the sorption kinetics. With these results it is difficult to predict which activated carbon is most suitable. Therefore, fast small-scale column experiments (RSSCT[10]) are usually carried out under conditions that are as realistic as possible, with which various parameters (including activated carbon product, sorption, residence time, and others) can be tested (Poddar et al., 2013, Crittenden et al., 1991). Thus, case-specific data for the design of the sorption process such as minimum residence time in the reactor (contact time) including the required frequency of activated carbon exchange can be determined. The performance of RSSCT is essential if multi-component mixtures are present and/or substances more difficult to sorb are present. The best sorbent material cannot be determined without preliminary tests, it depends on the site-specific PFAS distribution and characteristics of the site water. For example, an activated carbon may show the best results at one site but be less suitable at another. These tests can also be used to check the effectiveness of reactivated activated carbon[11]. Inadequate preparation and implementation of activated carbon sorption entails increased risks of poor efficiencies, incomplete purification, and excessive operating costs (Edel et al., 2018).

However, the best sorbing activated carbon does not necessarily have to be the most economical. Based on the project-specific sorption capacity and material costs, specific costs (in € per m^3 of treated groundwater) can be calculated in relation to the consumption of activated carbon. These can vary considerably, for example from 0.40 - 2.30 €/m^3 in a pilot test (Bayerisches Landesamt für Umwelt, 2014). In another case, costs of < 0.06 €/m^3 to 0.68 €/m^3 were found (Haist-Gulde et al., 2017). Another study indicates the costs of sorption on activated carbon in the range of 0.24 €/m^3 (10 µg/L PFAS in raw water) to 0.78 € (100 µg/L PFAS in raw water) (Q = 25 m^3/h). This includes electrical energy, maintenance, and activated carbon consumption (Edel et al., 2015).

By means of activated carbon, the PFAS concentration in the pure water can be reduced to very low concentrations (ng/L or below the limit of determination) with efficiencies from 90 % to > 99 %. However, the sorption capacity varies greatly for individual PFAS (Appleman et al., 2014):

► In general, shorter-chain PFAS are less easily sorbed than longer-chain[12] PFAS (Eschauzier et al., 2012). Breakthrough occurs in the order PFBA << PFHxA < PFBS < PFOA < PFHxS < PFOS (Figure 6).

► Perfluorosulfonic acids sorb better than perfluorocarboxylic acids of the same chain length.

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[10] Rapid Small-Scale Column Tests

[11] Triple reactivated coconut-based activated carbon showed significantly better treatment efficiency than fresh carbon. Reactivated activated carbon based on hard coal, on the other hand, showed no such behavior and differed less strongly or not at all from fresh carbon. The reactivation obviously burns additional pores into the activated carbon and positively influences the pore size (Keldenich et al., 2012).

[12] The breakthrough time for short chain PFAS is about 5 times less than for long chain PFAS.

Figure 6   Breakthrough curves of different sorption materials (AC = activated carbon, IX = ion exchanger)
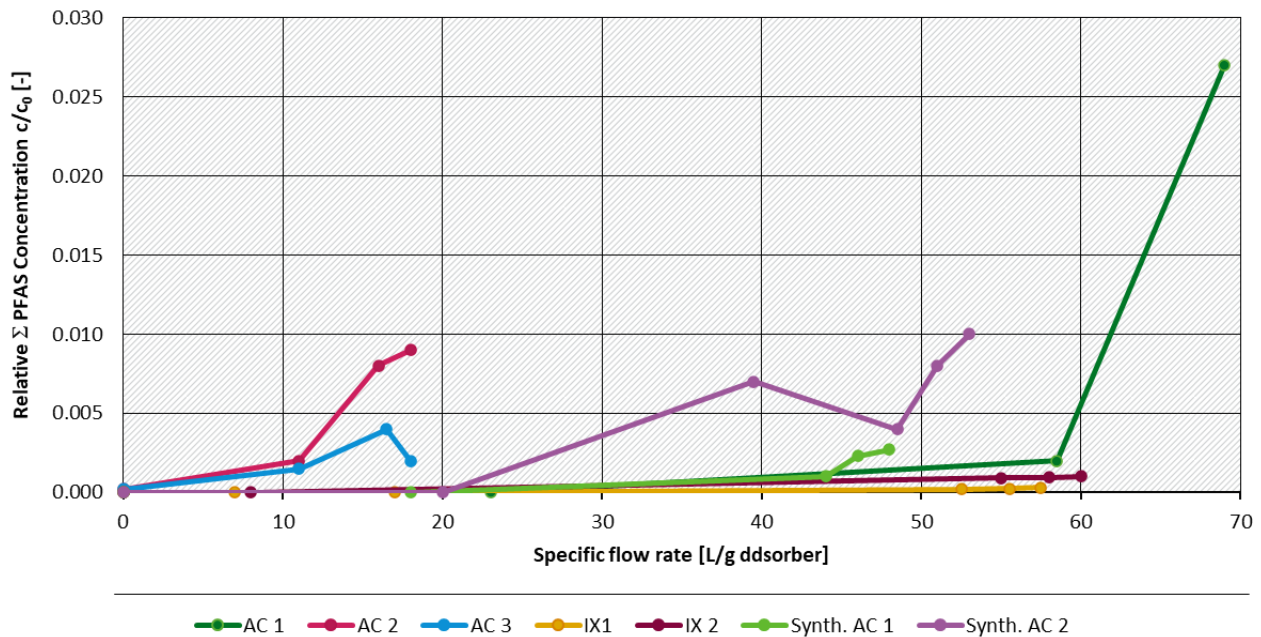
The PFAS sorption at a discharge value of 1 μg/L for the sum of short-chain and 0.3 μg/L long-chain PFAS is about 0.12 - 0.15 wt.% for the sum PFAS, depending on the product (tests with groundwater). Source: Bavarian State Office for the Environment, 2014.

Accordingly, the breakthrough times (increase of the concentration in the purified water) for individual compounds are very different (Figure 7).

Figure 7   Breakthrough curves for various PFAS compounds
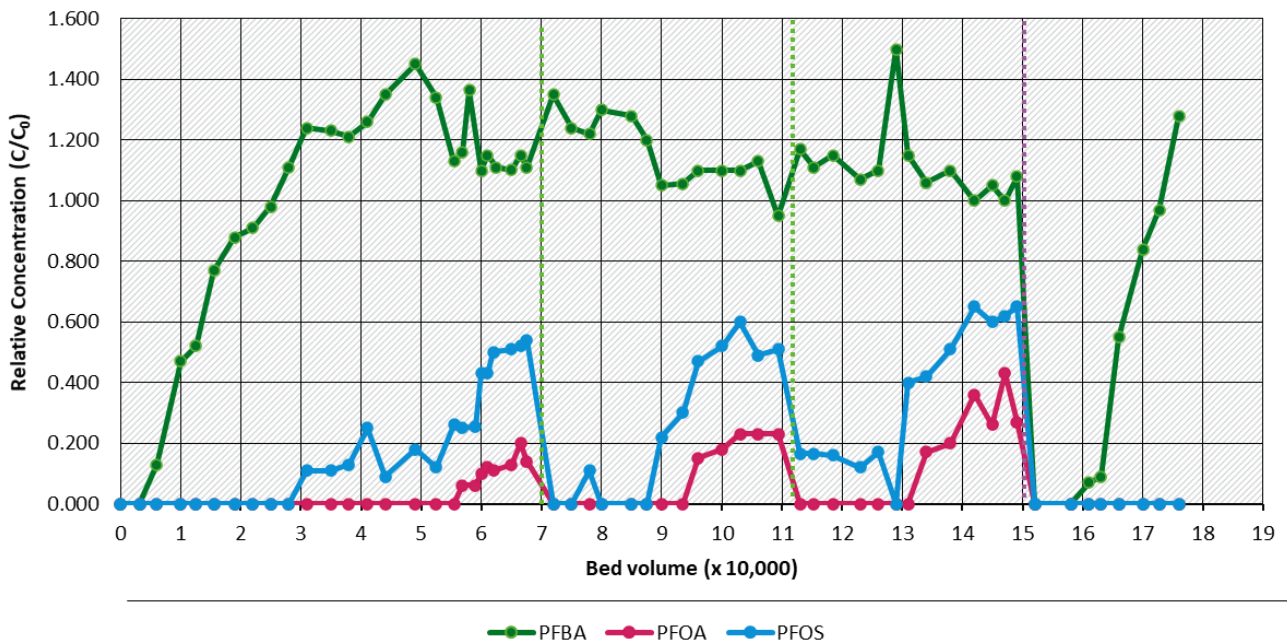
The green lines show the times of renewal of the activated carbon (1st filter), on the purple line the activated carbon of the 1st and 2nd filter of the two-stage plant was renewed. The short-chain PFBA regularly breaks through first. A concentration of $C/C_0 > 1$ shows the accumulation on the activated carbon before the breakthrough. Source: Appleman et al., 2014.

The sorption of PFAS onto the activated carbon is kinetically controlled. The values vary greatly. For some types of activated carbon it has been determined that a sorption equilibrium is reached after 4 h, for others only after to 168 h (Yu et al., 2009). A selection is shown in The green lines show the times of renewal of the activated carbon (1st filter), on the purple line the activated carbon of the 1st and 2nd filter of the two-stage plant was renewed. The short-chain PFBA regularly breaks through first. A concentration of C/C0 > 1 shows the accumulation on the activated carbon before the breakthrough. Source: Appleman et al., 2014.

The sorption follows a reaction that is pseudo 2nd order.

Based on the initial sorption rate, the contact time is selected for the technical scale. The minimum value was 10 minutes (EBCT) and the default value 30 - 60 minutes.

The sorption capacity for PFAS is quite low, in the range of 0,1 % by weight and in some cases significantly lower. Details for some activated carbons are given in Table 1. The sorption of precursors has not yet been studied in detail. Based on theoretical considerations, it has been assumed that these are removed moderately, some not very effectively (Figure 9; Xiao et al., 2017). For GenX, a 30 % removal was achieved with a powdered activated carbon (60 mg/L). The same amount of activated carbon resulted in 80 % PFOA and > 80 % PFOS removal.

Figure 8   Time dependent adjustment of the sorption equilibrium for PFOS at different activated carbons
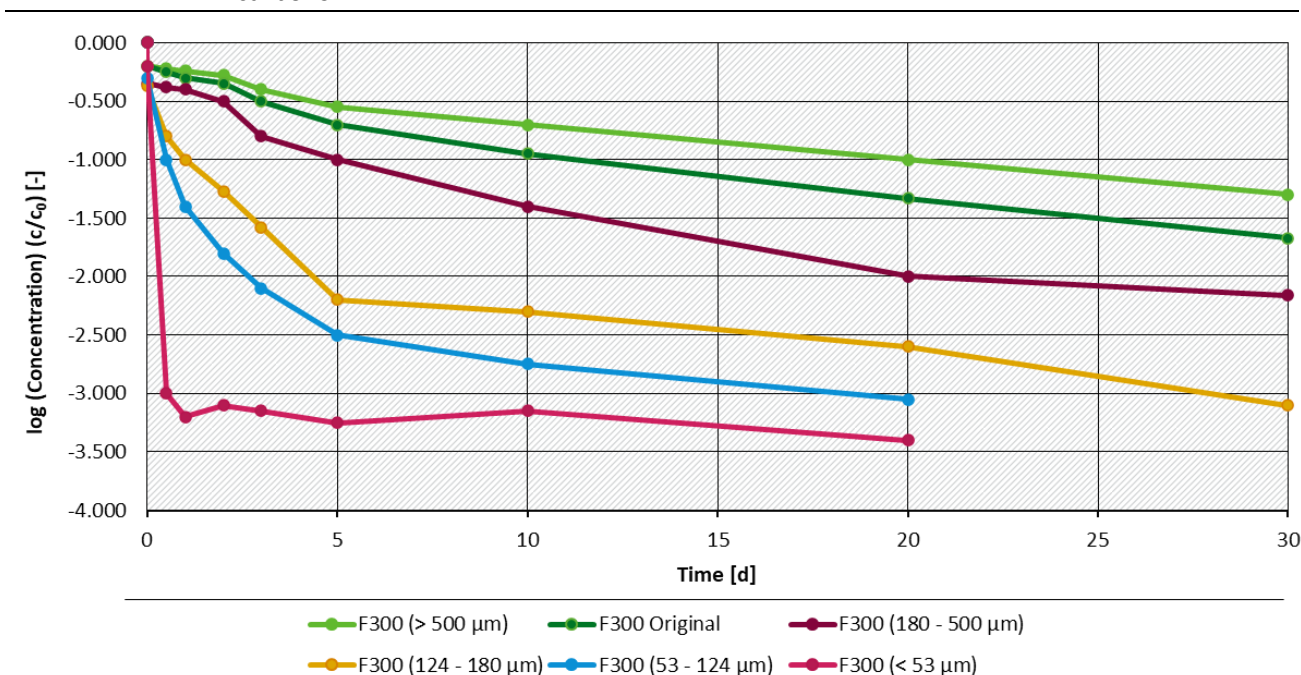
Source: Xiao et al., 2017

Short chain GenX by-products (perfluoroether acids) such as PFMOPrA and PFO2HxA were essentially not sorbable. Due to the poor sorption and the formation of an enrichment front, the GenX by-product PFMOAA had a 10-fold higher concentration in pure water than in raw water after the breakthrough (Hopkins et al., 2018).

Most studies refer to laboratory tests. Documentation of long-term remediation on a full scale is found only rarely. In one plant the removal of PFAA was monitored on a technical scale over a period of five years (Q = approx. 1.5 m^3/h, EBCT = 13 min.). The number of bed volumes (BV) treated before PFAA breakthrough was (Appleman et al., 2014):

► 60,000 BV for PFOS

► 30,000 BV for PFHxA and PFOA and
► 5,000 BV for PFBA.

Table 1   Sorption data for activated carbon

Type of activated carbon	Characterization	Sorption equilibrium [h]	Sorption function	Sorption capacity [mg/g]	Reference
Coal-based granular activated carbon	Surface: 712 m²/g, Micropores: 313 m²/g, Meso-/ Macropores: 399 m²/g, pH 7.5 Isotherm C_0 = 20 - 250 mg/L	168	Langmuir, pseudo 2nd order	PFOS: 199 PFOA: 170	Yu, 2009
Coal-based activated carbon powder	Surface: 812 m²/g, Micropores: 466 m²/g, Meso-/ Macropores: 812 m²/g, pH 7.5 Isotherm C_0 = 20 - 250 mg/L	4	Langmuir, pseudo 2nd order	PFOS: 560 PFOA: 292	
Activated carbon powder (probably Norit CA1)	Isotherm-Study: C_0 = 1 - 1.48 h equilibrium, pH 7, no pH control, 48 h equilibrium, pH 7	5 min 4	Langmuir, pseudo 2nd order	PFOS: 440 PFOA: 426	Rattanaoudom, 2012
Activated carbon	Surface: 1.553 m²/g, Micropores: 0.58 cm²/g, Mesopores: 0.61 cm²/g, pH 7.5 Isotherm C_0 = 1 - 1000 mg/L	Approx. 12	no information	PFOS: about 1,200	Schuricht et al., 2014
URV-MOD1	Pore volume 0.64 ml/g, Micropores 0,37 ml/g, Mesopores: no information, Isotherm C_0 = 15 - 150 mg/L, pH 7.2	> 48 h	Langmuir	PFOS: 212	Ochoa-Herrera, 2008
Filtrasorb 300 (Coal)	Pore volume 0.709 ml/g, Micropores 0.378 - 0.408 ml/g, Mesopores 0.063 - 0.378 ml/g, Isotherm C_0 = 15 -150 mg/l, pH 7.2	> 48 h	Langmuir	PFOS: 196	
Filtrasorb 400 (Coal)	Surface 948 m²/g, Pore volume 0,77 ml/g, Micropores 0,31 - 0,39 ml/g, Mesopores 0,07 - 0.17 ml/g, pH = 8,3, Isotherm C_0 = 15 -150 mg/L	> 48 h	Langmuir	PFOS: 236 PFOA: 112 PFBS: 98.7	
	Surface 948 m²/g, Pore volume 0.61 ml/g, macropores 0.04 ml/g, Mesopores 0.09 ml/g, Micropores 0.48 ml/g, pH=8.3, Isotherm C_0 = 15 -5000 µg/L	4	Freundlich K_f = 28.4, n = 2.2	Not specified	Senevirathna, 2010
Filtrasorb CC60 (Coal)	Unknown	Unknown	Not calculated	PFOS: ~240 PFOA: ~80 PFBS: ~75	CPL carbon link
Filtrasorb CC50 (Coal)	Unknown	Unknown	Not calculated	PFOS: ~210	
Filtrasorb CC50R (coal)	Unknown	Unknown	Not calculated	PFOS: ~175	

Due to the low sorption capacity of activated carbon for PFAS, development activities are currently focused on improving the activated carbon surface. For example, the basicity of the surface could be increased by ammonia gas treatments, which was accompanied by an improved sorption affinity for PFOS and PFOA. The effectiveness of surface modification to improve sorption varied with the carbon raw material. Charcoal and activated carbon fibers showed an improvement in sorption by one to three orders of magnitude, while other materials even showed a reduction in sorption (Zhi and Liu, 2016).

Figure 9   Sorption coefficient for different PFAS
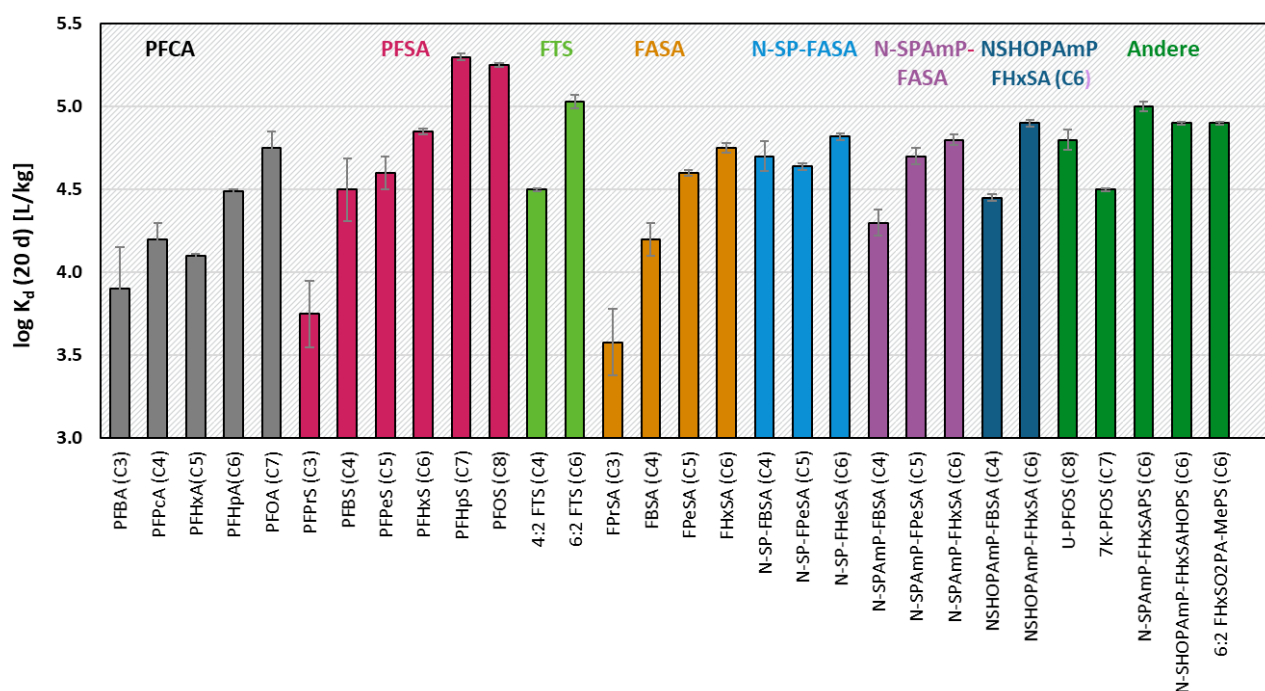
Log K_d (linear sorption) after 20 days of sorption of the analysed PFAS on granular activated carbon (F300) For 6:2-FHxSO2PA-MePS, the K_d value is given after 10 days because this compound was no longer detectable in the water phase after 20 days. Source: Xiao et al., 2017.

In another approach, an attempt was made to increase the sorption capacity by using powdered activated carbon with a substantially larger binding surface compared to granular activated carbon. For this purpose, ultrafine magnetic activated carbon (consisting of Fe_3O_4 and powdered activated carbon in a ratio of 1:3) was added to water containing PFAS (2 h incubation time). This resulted in a high binding capacity for PFAS. The consumed magnetic activated carbon could easily be separated with a magnet and regenerated with a small amount of methanol. Regenerated magnetic activated carbon could be reused more than five times and maintained a stable sorption capacity for PFOS after three cycles (Meng, et al., 2019).

The sorption on activated carbon is negatively influenced by impurities (dissolved Fe and Mn, DOC, water hardness, suspended solids, additional contaminants) (Siriwardena, 2019). It is therefore essential to characterize the groundwater to be treated chemically in detail. Often a pre-treatment of the raw water is then necessary. Especially the DOC, which binds better to activated carbon than PFAS and occurs in concentrations that are orders of magnitude higher, can significantly impair sorption. A first activated carbon sorption stage is therefore only used to retain the DOC. Alternatively, the DOC can be degraded in an oxidation stage (UV light, H_2O_2). Preliminary tests showed a degradation of the DOC in the solution of > 98 % (from 99.1 mg/L to < 2 mg/L) (Dyson, 2018). Dissolved iron and manganese are removed by flocculation and precipitation. The resulting thin sludge (4 - 6 % TS) can be thickened to approx. 30 % TS in a chamber filter press (Edel et al., 2018). However, the filter cake contains considerable amounts of PFAS and must be disposed of accordingly.

To achieve optimum loading of the activated carbon with PFAS, all other conventional contaminants that have a higher affinity to activated carbon than PFAS must first be removed.

Consumed activated carbons are either disposed of by high-temperature incineration or thermally regenerated at 600 °C. The activated carbon is then free of PFAS (Watanabe et al., 2016). The desorbed PFAS (gas phase) are destroyed in the high temperature range (afterburner). The gas stream is then treated in a gas scrubber (removal of the acid HF). It can be assumed that under these rigid conditions all precursors and non-precursors are also eliminated. The resulting burnup of 10 - 15 % is replaced by fresh coal. The regenerated activated carbon can be reused for PFAS sorption. Column tests have shown that regenerated activated carbon charges are not less effective (Brewer 2017). Data for estimating the sustainability of activated carbon regeneration (energy demand, CO_2 emission) are not available.

The sorption capacity of biochar was also investigated. Biochar is a carbon-rich, porous solid that is synthesized by heating biomass such as wood or manure in an oxygen-deficient environment (pyrolysis). The properties of biochar (e.g. pore size, chemical composition, and hydrophobicity) can be influenced by the pyrolysis temperature and the composition of the biomass. The sorption properties of biochar are comparable to those of activated carbon. The application of the biochar to AFFF-contaminated water in a laboratory test gave sorption results comparable to those of activated carbon. However, the variability of the properties of biochar compared to granular activated carbon may influence the reliability of this material (Xiao et al., 2017). Rahman et al. (2014b) also found that biochar is not sufficiently effective. A reactivation of biochar is currently not possible, which requires combustion of the spent biomass.

Outlook. The sorption of PFAS on activated carbon is currently the most used process on a full scale. It is a well-developed technology that is applicable in almost all areas. Even though the sorption capacity is low, activated carbon is currently even more economical than other sorbents due to the comparatively low material costs. A disadvantage is that elimination of the PFAS (after high-temperature regeneration of the activated carbon) requires very high temperatures, which means that the process has only a low sustainability. In addition, the activated carbon is only slightly effective with short-chain PFAS. It is possible that the ultra-short chain PFAS are not sorbed to activated carbon at all.

The time to reach sorption equilibrium is significantly longer than the sorption duration (EBCT) that is realized in the technical application. On the other hand, most molecules sorb within the first minutes to a sufficiently high degree. The EBCT realized on a technical scale is therefore a compromise between the actual adsorption kinetics and the economic efficiency of sorption on a technical scale. If it is wanted to exploit a higher sorption, the EBCT would be much longer and the reactors much larger.

Sorption of PFAS on Activated Carbon (Summary)

The adsorption of PFAS on activated carbon has been very well studied. This is the most used process on a technical scale. As types of activated carbon differ significantly in terms of cost and adsorptive capacity, preliminary tests are recommended to determine the most economical type of activated carbon. Small-scale column tests are best suited for this purpose. The shorter the chain length of the PFAS molecules, the lower the adsorption of the PFAS. Therefore short-chain PFAS break through first. If the spent activated carbon is thermally regenerated, it must be ensured that the desorbed PFAS are destroyed in the high temperature range. Regeneration of the activated carbon usually does not lead to any deterioration, in some cases even to an improvement of the sorption capacity. High-temperature combustion of the spent activated carbon is the safer way to prevent PFAS from being released into the environment.
Impurities must be removed in a first plant unit prior to PFAS sorption. There are proven procedures available for this task. In most cases the impurities lead to increased PFAS-contaminated waste quantities and thus to increased water treatment costs.

Current research is aimed at improving the sorption properties of activated carbon and minimizing the amount of waste when removing impurities.

2.2.1.3   Sorption on Ion Exchanger

Description. Ion exchangers are solid materials (usually small porous resin beads)[13] consisting of an immobile skeleton (cross-linked polymer matrix) with charge-carrying functional groups and freely movable counterions. They are capable of reversibly exchanging dissolved ions with the free ions of the ion exchange matrix (Figure 10). Many naturally occurring substances such as organic humus are also capable of ion exchange. In water treatment, mainly synthetically produced ion exchangers based on polystyrene or polyacrylate are used in the form of porous plastic beads with a diameter of 0.3 - 1.3 mm, which contain about 50 % water (Edel et al., 2018).

Figure 10   Principle of anion exchangers
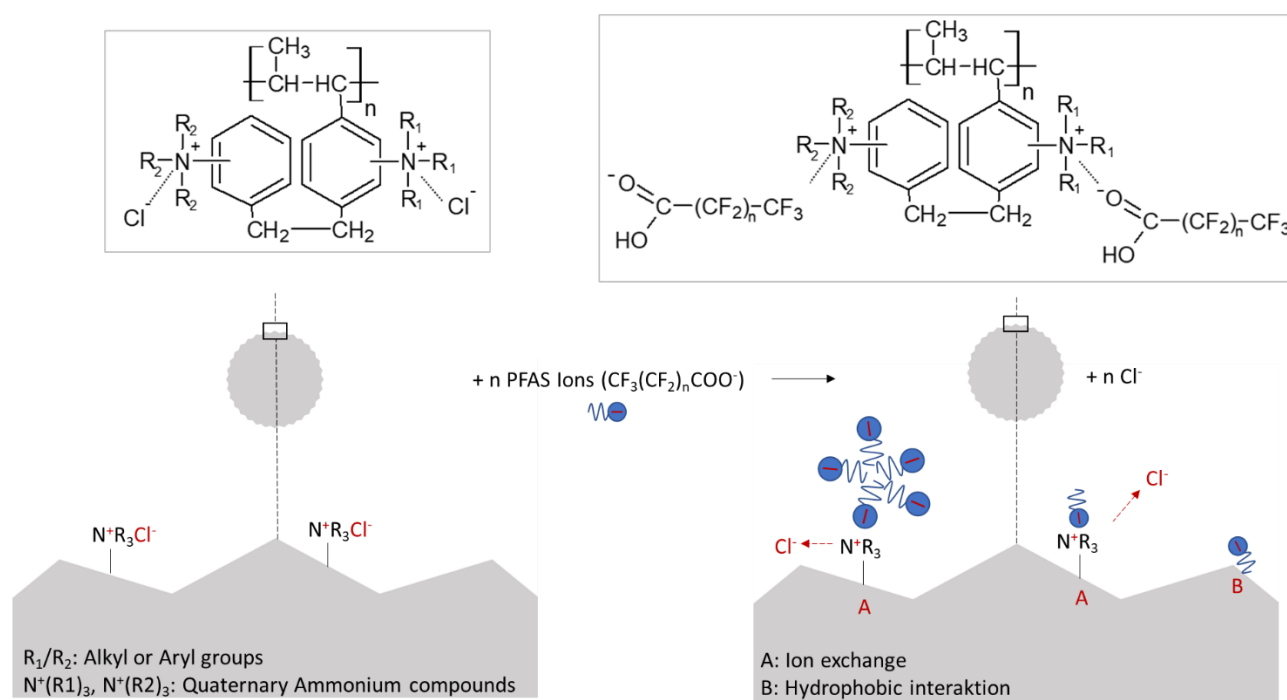
Source: Dow Liquid Separations, 2000

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[13]   For this reason, ion exchangers are also referred to briefly as "resins".

A distinction is made between cation and anion exchangers. For the removal of PFAS compounds, however, anion exchangers (AIX) were preferably investigated. These carry positively charged functional groups that interact with anions:[14]

$$AIX\text{-}Cl^- + PFAS^- \quad \leftrightarrow \quad AIX\text{-}PFAS^- + Cl^-$$
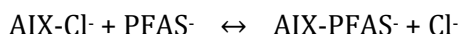
Depending on the structure of the functional group, a distinction is made between weakly and strongly basic anion exchangers (Table 2). The rate of removal depends on the following factors:

- ► concentration of the contaminants to be removed in the raw water,
- ► concentration of competing ions,
- ► process design (z. B. flow rate, resin bead size),
- ► properties of the ion exchangers (e.g. stability, sorption capacity, selectivity, sorption kinetics)

Table 2   Anion exchanger (Edel et al., 2018)

Exchanger type	Functional group	Effective application range (pH)
Weakly basic	$-N\text{-}R_2\cdot H_2O$	0 - 7
Strongly basic, Type 1	$-N{+}(CH_3)_3$	1 - 12
Strongly basic, Type 2	$-N{+}(CH_3)_2(CH_2CH_2OH)$	1 - 12

Selectivity. Depending on the type of ions used for the ion exchanger, the binding to the functional group is stronger or weaker. Weaker bound ions are exchanged with stronger bound ions, i.e. these have a higher selectivity. The stronger the binding to the ion exchanger, the

- ► higher is the charge of the ion,
- ► smaller the ion is in the hydrated state,
- ► the more polarizable the ion,
- ► more the specific interactions are that the ion enters with the poly-ions of the matrix and
- ► the lower the complex formation of the ion to the components of the solution.

Accordingly, the following selectivity series apply to

- ► strongly alkaline exchangers: $SO_4^{2-} > NO_3^- > Cl^- > HCO_3^- > OH^-$
- ► weakly basic exchangers: $OH^- >> SO_4^{2-} > NO_3^- > Cl^-$

This shows that especially high sulphate contents disturb the binding of the PFAS. The binding of an ion to the functional group of the ion exchanger also depends on the concentration of the other ion types with the same charge sign.

Weaker binding ion species in higher concentrations can displace stronger binding ions in lower concentrations (law of mass action).

As a rule, groundwater contains not only cations but also anions such as sulphate, chloride, or hydrogen carbonate and, in some cases, humic and fulvic acids in the higher mg/L range, which compete for the exchange sites with the perfluoroalkane acid anions, which are only present in the µg/L range (Edel et al., 2018).

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[14]   At this point it should be noted that in addition to the mostly anionic PFAS, cationic, neutral or zwitterionic polyfluorinated compounds may also be present, which bind to an anion exchanger only to a reduced extent.

Binding. Material balances (a smaller quantity of counter ions is desorbed than PFAS are sorbed) have shown that, in addition to the electrostatic bonding of PFAS to the functional group of the ion exchanger, the non-polar alkane residue of the substances additionally binds to the polymer backbone via Van-der-Waals forces. Longer-chain perfluoroalkane acids with a higher hydrophobicity therefore bind more strongly to anion exchangers than short-chain PFAS. On the other hand, this hydrophobic bonding is necessary to achieve a sufficient removal of the PFAS. Tests with non-hydrophobic resins (A600E) showed a significantly reduced sorption capacity compared to hydrophobic resins (Zaggia et al., 2016).

Macroscopic PFAS aggregates may form in the intraparticle pores of the resin, suggesting that other mechanisms may play an additional role in PFAS removal (Zaggia et al., 2016).

Precursor compounds without charge can only attach to the polymer backbone via Van-der-Waals forces. It is still open how zwitterionic PFAS behave. Cationic PFAS probably are not removed by the anion-exchanger or show to a great extent reduced electrostatically hindered hydrophobic bonding to the polymer backbone.

PFAS elimination. Compared to granular activated carbon (GAC), ion exchangers have a higher sorption capacity for some PFAS and the reaction kinetics for ion exchangers is significantly faster than for GAC[15]. The combination of these properties results in a much smaller ion exchanger system compared to an equivalent GAC system. Compared to a conventional contact time[16] of five minutes, the resin was able to purify eight times as much bed volume (BV) PFOS contaminated groundwater (or six times as much BV for PFOA) as GAC. On a mass-to-mass basis, four times as much PFAS per gram of sorption material was removed by the resin up to the breakthrough point as by GAC (Woodard et al., 2017). Under certain circumstances, this can make sorption on ion exchangers cheaper than on activated carbon, even if regeneration of the ion exchangers is more expensive or even if the ion exchanger is only used once and disposed of after consumption.

The sorption of the PFAS to the ion exchanger is only after several hours in its equilibrium. Some ion exchange resins require even longer than the time shown in Figure 11 (Yu et al., 2009). As a rule, the residence time in the ion exchanger, which is realized on a technical scale, is only a few minutes to keep the process stage on an economic scale.

Studies on the effectiveness of PFAS elimination by defined anion exchange resins (A-714) resulted in > 99 % removal of PFOA and PFOS after 25 h contact time. Another ion exchange resin (A-244) showed only 33 % removal in the same time. Both resins bound PFOS better than PFOA (Lampert et al., 2007). The resin Amberlite® IRA-400 has a higher binding capacity for PFOS and PFOA than granular activated carbon (Yu et al., 2009).

Polyacrylic resins showed faster binding kinetics and higher binding capacities for PFOS and PFBS in batch tests than polystyrene resins. PFBS was also removed with faster kinetics and higher capacities than PFOS (Deng et al., 2010). However, this contrasts with the results of Carter et al. (2010), where PFOS was removed more effectively than PFBS, presumably due to stronger hydrophobic interactions between the resin polymer backbone and the longer carbon chain.

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[15] For Sorbix A3F IX resin 2 Min. EBCT has been applied.

[16] Specified as EBCT (Empty Bed Contact Time).

Figure 11   Sorption of PFOA on Purolite A532E
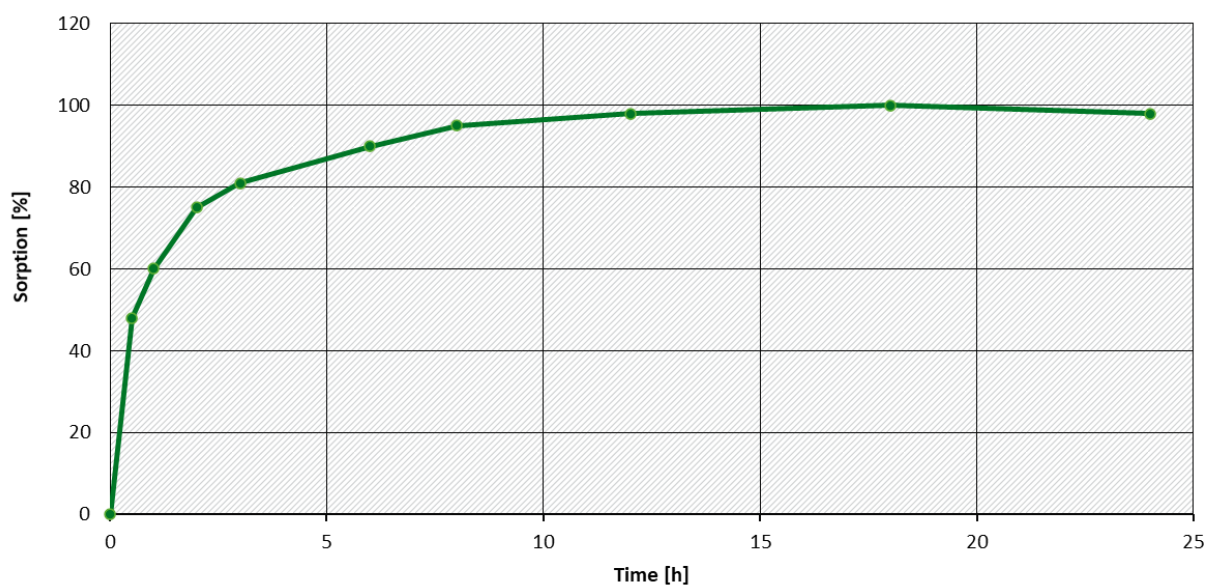
Source: Yu et al., 2009

A systematic investigation of eight PFCA and PFSA and four different resins showed that the acrylic macroporous resin shows faster PFAS removal than other resins. However, polystyrene resin (strong base) showed a higher PFAS removal than polyacrylic resin. All resins showed a higher affinity for longer chain PFAS and for perfluoroalkane sulfonic acids with the same chain length. During purification, shorter-chain PFAS can be displaced by better binding longer-chain PFAS. In addition, the removal of long-chain PFAS was increased at the end of the experiment, indicating agglomeration or micelle development. Linear molecules were removed better than branched ones (McCleaf et al., 2017). Some ion exchangers cannot remove shorter-chain PFAS (Appleman et al., 2014).

Like GAC, the exchange capacities and the corresponding breakthrough times ultimately vary depending on PFAS functional groups and chain lengths. In addition, PFAS have been removed more effectively from natural waters than from laboratory waters, possibly due to interactions between PFAS and natural organic matter (Dudley, 2012).

The strongly basic ion exchanger Sorbix A3F has proven to be particularly effective. With a raw water concentration of approx. 12 µg/L PFOA, the pure water concentration after 20,000 BV (EBCT: 5 Min.) was still approx. 0.5 µg/L. PFOS (raw water: approx. 27 µg/L) and was still below the detection limit at the same point. However, the behavior towards short-chain PFAS was comparable to GAC. The material is completely (> 99 %) regenerable by a salt/solvent mixture.

Nonionic resin sorbents are significantly less effective than ionic ones (Senevirathna et al., 2010).

Ion exchange processes are particularly suitable for the treatment of diluted solutions. The concentration of the ions to be removed should not exceed 300 mg/L. Depending on the quality of the groundwater, multi-stage ion exchange plants achieve purification efficiencies with 20 - 100 µg/L PFAS in the effluent. These values are too high in view of the remediation target values to be achieved for PFAS compounds. Therefore, a post-treatment of the purified water with an activated carbon absorption step is necessary. Compared to activated carbon absorption, ion exchangers require a shorter contact time.

Regeneration of the ion exchangers. The electrostatic binding of an ion to the functional group is reversible, so that a bound ion can be displaced or exchanged by an ion dissolved in water in very high concentrations (according to the principle of the law of mass action).

Acids, bases, or salts are normally used for regeneration. Due to the hydrostatic bonding of the PFAS to the polymer backbone, this type of regeneration of the ion exchanger is not possible. Only by using combined regenerants such as NaCl or HCl solutions containing organic solvents (preferably methanol or ethanol) in a concentration of 45 % was it possible to achieve extensive regeneration of the ion exchangers, where the weakly basic anion exchangers were easier to regenerate than the strongly basic exchangers (Janda et al., 2017).

Due to the use of high concentrations of organic solvents and the associated high technical safety requirements, on-site regeneration is rarely implemented. Instead, special plants are required for this purpose. The regenerated ion exchanger is then ready for reuse. Due to the limited economic efficiency of regeneration with organic solvents, PFAS-loaded ion exchangers are often disposed of or incinerated off-site in the high temperature range.

Spend regeneration solution (regenerate). In addition to the components of the regenerating solution (usually high salt and methanol concentrations), the regenerate produced contains the eliminated PFAS in increased concentration and must therefore be further processed or disposed of. The ethanol in the regenerating solution can be recovered by distillation and reused. The PFAS-containing residue must be fed to destructive processes (e.g. high temperature combustion or possibly sonolysis). The volume of the regenerate can be efficiently reduced by more than 96.5 % by using reverse osmosis coupled with evaporation under vacuum (Zaggia et al., 2016).

Full-scale operation. The inflow should be free of suspended solids, solvents, and oxidizing agents. Strong mechanical stress and pressure surges of the resin bed of 1.5 bar are to be avoided as well as strong fluctuations of the salt concentration and the pH-value. Frost leads to irreversible damage to the ion exchange resin (Edel et al., 2018). During operation, the absorption capacity of the ion exchange resin decreases over time. Finally, it cannot be used any further.

Compared to activated carbon, higher sorption capacities for PFAS with shorter chain length were identified for certain disposable ion exchangers. This suggests the use of several process stages consisting of both single-use and regenerable ion exchangers. This optimizes the overall performance of the purification process and reduces the operating costs for contamination with a mixture of shorter and longer PFAS.

Outlook. The investigations have shown a good suitability of different ion exchangers, some of them are particularly suitable for the removal of short-chain PFAS, which is not the case with most other processes. However, the technology still has some challenges. Ion exchangers are sensitive to geochemical influences. High concentrations of dissolved cations make it difficult to eliminate the PFAS. Redox-sensitive substances such as dissolved iron and manganese can be removed in first process stages, but it is more difficult in the presence of high sulphate concentrations. Currently there is no effective method to selectively remove these anions from the water. In additional first stages the removal of particulate matter is necessary.

This ultimately means that various ion exchangers must be tested with the site water to be treated within the framework of preliminary tests.

Due to the selectivity of the anion exchangers to negatively charged substances, there is a risk that zwitterionic and especially cationic precursor-PFAS are not retained. Uncharged PFAS are bound to the polymer backbone of the ion exchanger at least by hydrophobic interactions. This would also have to be checked in each individual case using analytical sum parameters.

Whether disposable ion exchangers or regenerable ion exchangers can be used must be based on site-specific economic calculations. Which of the two processes is more sustainable in terms of energy balance and CO_2 footprint, cannot be determined without detailed data. In any case, the total costs compete with the costs for the sorption of the PFAS on activated carbon. Even if the activated carbon process is less efficient and requires more sorption material, in the end it could be cheaper.

To avoid the use of ethanol for regeneration of the ion exchangers, it was proposed to treat the raw water successively by means of activated carbon filtration and ion exchange. The activated carbon should preferably remove longer-chain PFAS over a longer period of time. Short-chain PFAS, which are no longer retained by the activated carbon after a short operation time, should be removed by means of ion exchange. Afterwards, the exchanger should be regenerated with standard regeneration agents (salts, acids) to extract the short-chain PFAS from the exchanger. However, even short-chain PFAS cannot be completely desorbed without organic solvents.

Groundwater purification by means of ion exchangers are common and widely used technologies. However, they have only rarely been used for the remediation of PFAS contamination, mainly because of the effort involved in regeneration.

Sorption on Ion Exchanger (Summary)

The ion exchangers differ in terms of cost and adsorptive capacity. Therefore, preliminary tests are recommended to determine the most economical ion exchanger. The binding of PFAS to ion exchangers is not only affected by the intended electrostatic interactions, but also by hydrophobic interactions with the backbone of the ion exchanger. This makes it difficult to regenerate the ion exchanger. As a rule, an organic solvent (usually methanol) is required in addition to highly concentrated salt.

Due to the large number of ion exchangers available, it is not possible to make general statements as to its performability. Many ion exchangers have a higher sorption capacity than activated carbon. The contact time is sometimes considerably shorter. In individual cases, this can lead to ion exchangers being more economical than activated carbon, even if regeneration is expensive or even if the ion exchangers are disposed of after consumption and are not regenerated.

However, ion exchangers are sensitive to water quality. For example, the water to be treated must not have too high a sulphate concentration. The feasibility must therefore be investigated in each individual case.

Groundwater purification by means of ion exchangers is a common and widely used process. However, they have only rarely been used in Germany for the remediation of PFAS contamination. Accordingly, only limited experience is available from remediation on a technical scale. Due to the growing experience with this process, especially in Australia, it can be expected that ion exchangers will be used more frequently in the future.

2.2.1.4 Sorption on Polymers or Other Materials

Description. In addition to binding PFAS to activated carbon and ion exchangers, several other sorption materials were tested for their ability to sorb PFAS. These include carbon, ash and carbon nanotubes (Cheng et al., 2011), activated carbon fibers (Zhi, 2017), hydrotalcite (Rattanaoudom et al., 2012), Ambersorb (Zhi and Liu, 2015), coated polymers (Yu et al, 2008), modified cotton and rice husks (Deng et al., 2012), porous aromatic solids (Luo et al., 2016) and cross-linked cyclodextrins (Xiao et al., 2017). Some of the sorbents are mixed into the soil with the intension to immobilize PFAS, as explained further in Chapter 3.3. Other sorption materials are suitable both for use in soil and for water purification. Only those sorbents that are intended for use in water purification are discussed here.

Hydrotalcite, a layered double hydroxide (mineral from the carbonate class) with the molecular formula $Mg_6Al_2CO_3(OH)_{16} \cdot 4(H_2O)$, has proven to be a well-suited sorbent at high PFOS/PFOA concentrations (> 97 % elimination). The sorption equilibrium is reached within one hour and thus quite quickly (Rattanaoudom et al., 2012).

It is presumed that hydrotalcite sorbs the anionic PFAS in its intermediate layer by ion exchange processes. After sorption, the space of this intermediate layer increases according to the size of the sorbed compound. Figure 12 shows the postulated sorption mechanism of hydrotalcite: exchange of charged molecules (CO_3^{2-}) against anionic PFAS in hydrotalcite. The sorption on hydrotalcite was not reduced by the formation of hemi-micelles (Rattanaoudom et al., 2012).

Figure 12   Sorption of PFOS on Hydrotalcite
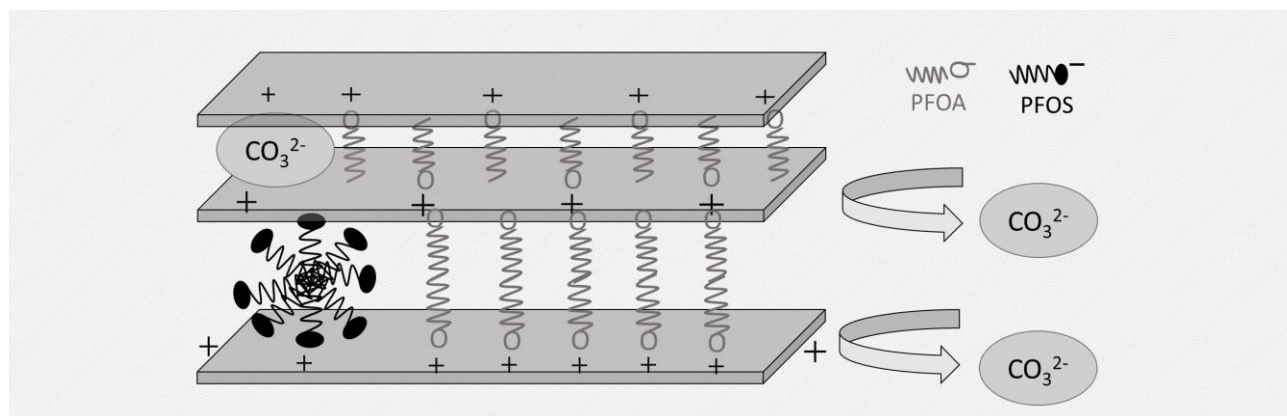
Sourec: Rattanaoudom et al. (2012)

Quaternized cotton. In the production of quaternized[17] cotton, long polymers with a high density of quaternary ammonium cations were produced. This quaternized cotton showed rapid sorption and high sorption capacity for PFOS and PFOA. The sorption equilibrium of PFOA and PFOS on quaternized cotton was achieved after 4 h and 12 h respectively. The obtained maximum sorption capacities of PFOS and PFOA on quaternized cotton at pH 5.0 were 1,650 mg/g PFOS and 1,360 mg/g PFOA. The pH of the solution had only a small effect on sorption in the range of 3 - 10 (Deng et al., 2012).

Ambersorb. In contrast to the physical properties of sorbents, surface chemistry plays a decisive role in the sorption on carbon-based surfaces. The sorption affinity correlates positively with the basicity of the surface, indicating that the anion exchange capacity is critical for the sorption of PFOS and PFOA. The hydrophobicity had a small effect on the degree of sorption, unlike in ion exchangers. The synthetic polymer Ambersorb was more effective than activated carbon (Zhi, 2017; Zhi & Liu, 2015).

The aromatic polymer PAF-45 (PAF = *Porous Aromatic Framework*) with a particle size of 200 - 500 nm showed a fast sorption of PFOS, the sorption equilibrium was reached after 30 minutes and the sorption capacity was 5,847 µg/g at pH 3. The PFOS sorption amount increased significantly with increasing cation concentration (Na^+, Mg^{2+} or Fe^{3+}), probably due to the fact that the cations enhanced the interactions between the negatively charged PFOS molecules and the positively charged PAF-45 surface. The cations thereby formed complexes with PFOS anions in solution. However, the main mechanism of sorption was probably based on hydrophobic interactions with the very hydrophobic surface of PAF-45, where the pH has a significant effect on the amount of PFOS sorbed. The composition of the water also influenced the amount of sorbed PFOS and the kinetics of the sorption process (Luo et al., 2016).

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[17] In chemistry, quaternization describes the transformation of suitable atoms (here: nitrogen) into a quaternary substitution degree with four organic substitutions. Quaternization is thus a subgroup of alkylation. Here the central atom receives four equal or different organic substituents and a positive charge, so a cation is formed. Since halogen alkanes are frequently used as alkylating agents, the counterion (anion) is usually a halide, e.g. chloride, bromide, or iodide.

β-Cyclodextrin. For a porous, powdery polymer based on β-cyclodextrin[18] (β-CD) (crosslinking via tet-rafluoro terephthalic acid dinitrile) it could be shown that it has a higher affinity, but similar capacity and kinetics to GAC for PFOS. The β-CD polymer was able to reduce PFOA concentrations from 1 µg/L to < 10 ng/L. The sorption equilibrium is reached after approx. 13 h; the sorption capacity is at 34 mg/g. Sorption is not affected by humic acids. It can be regenerated with methanol and reused (Xiao et al., 2017).

Osorb can be used for both soil (Chapter 3.3) and groundwater remediation. It is intended to support both sorption and absorption of the PFAS. Osorb has a silicate polymer structure consisting of cross-linked alkoxy silicanes. After binding organic molecules, the Osorb structure expands to three to five times its initial volume, which has the effect of absorbing (rather than sorbing) the organic compounds into the primarily microporous matrix. Osorb does not expand in water. At present, Osorb is either available as a pure material or applied to silica (→ Purasorb), which is probably more suitable for re-mediation processes. Initial studies show that Osorb is similarly effective in removing PFOS and PFOA and more effective than GAC in removing PFBA. It shows little competition with natural organic matter and little influence by pH. Osorb can be regenerated to > 95 percent using methanol (Edmiston, 2017).

Outlook. The investigations of alternative sorbents are almost exclusively limited to laboratory tests with PFOS and PFOA. Some of the sorbents seem to show quite good properties, so that further inves-tigations are desirable. As with most processes, there is a lack of studies on the removal of short-chain PFAS, various precursors and on the effectiveness in real contaminated groundwater. The environ-mental compatibility of the products must also be investigated. For example, β-cyclodextrin itself is an organic fluorine compound and its disposal could be problematic. The state of development of alterna-tive sorbents is still so low that it is not possible at present to assess whether one or the other product will reach market maturity.

> ### Sorption on Polymers or Other Materials (Summary)
>
> In the past, numerous materials have been investigated and identified for their ability to sorb PFAS. The aim is to find materials that have high sorption capacities, require short contact times, and can be regen-erated. However, almost all the investigations are still on a laboratory scale, i.e. they take place under simply defined conditions. Consequently, there is a lack of information on the decontamination perfor-mance of real groundwater, especially those that also contain short-chain PFAS, precursors and impuri-ties. The sorbents themselves are generally not allowed to represent contaminants, however this is not always the case. Furthermore, no statement can yet be made as to whether the use of such materials will be more economical than activated carbon.
>
> Hence, at present there is no full-scale applicability in sight. Nevertheless, the further development of such cost-effective sorption materials is desirable.

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[18] Cyclodextrins are compounds that belong to the cyclic oligosaccharides. They are ring-shaped degradation products of starch. They con-sist of linked glucose molecules.

2.2.2 PerfluorAd

Description. The PerfluorAd® process is a precipitation process. The biodegradable reagent PerfluorAd®, a liquid cationic polymer, is continuously added to the groundwater to be treated in a stirred tank (Figure 13). Experience to date has shown that a polymer dosage of 5 - 50 g/m³ is sufficient (Cornelsen, 2015). The addition as a liquid product into the flowing water stream allows a high contact frequency between the reagent and the contaminant and thus a rapid reaction. PerfluorAd® forms a weak ionic bond with anionic PFAS. Cationic or zwitterionic PFAS are probably not precipitable. The bond creates a macromolecule (Figure 14) whose solubility is lower than that of the starting product and the adduct flocculates within about 10 - 30 minutes. If necessary, powdered activated carbon is added additionally.

Figure 13   PerfluorAd®-Process scheme
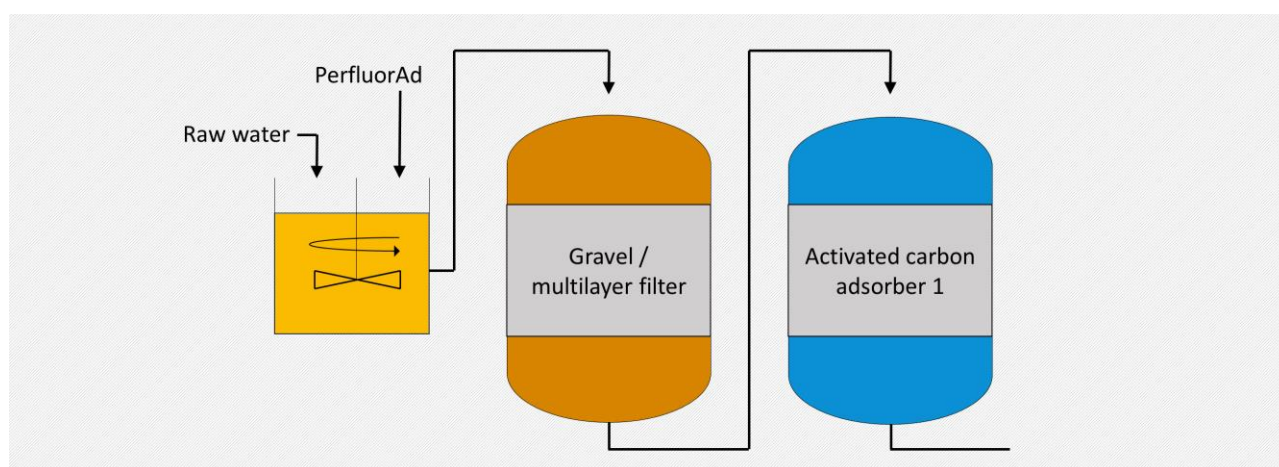
Source: Cornelsen, 2015

Depending on the quality of the groundwater to be treated, it may be necessary to add further flocculants. These serve to improve flocculation and consist of linear, water-soluble polymers. After flocculation, the solid phase is separated by sedimentation and/or filtration through a sand filter. The discharge from the sand filter is done by backwashing. The dry matter content of the resulting thin sludge (approx. 3 - 4 %) can be dewatered to approx. 30 - 40 % solids content in the filter cake by means of a chamber filter press.

The resulting water is returned to the process. The PFAS-containing residues from flocculation must be disposed of in a suitable high-temperature incinerator.

Figure 14   PerfluorAd®-PFAS-binding
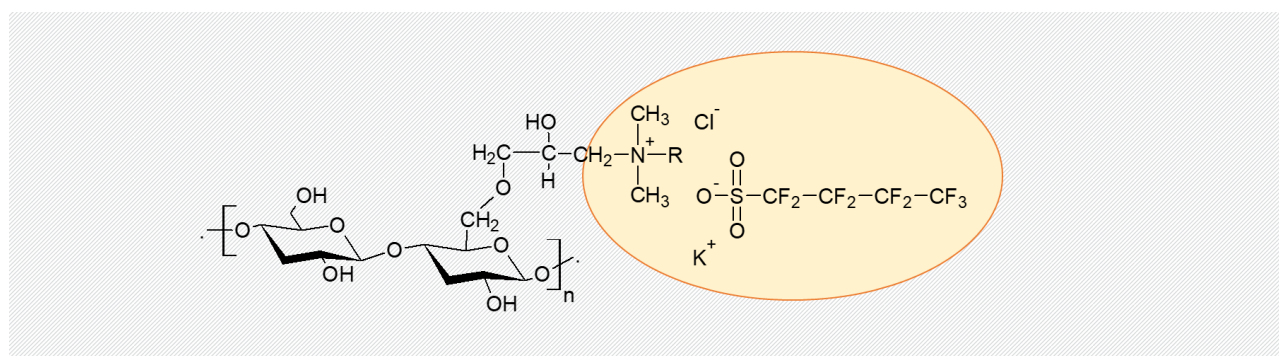
Source: Somborn-Schulz et al., 2012

The method is particularly suitable for higher PFAS concentrations (in the µg/L range) but is less suitable for lower concentrations. Furthermore, short-chain PFAS are precipitated less effectively (e.g. PFBA: 6 - 30 %). However, very high concentrations of the polymer (2 kg/m^3) can significantly improve precipitation (to approx. 77 %). To maintain the usually very low PFAS concentrations in the effluent, a one- or two-stage activated carbon absorber is usually installed downstream of the PerfluorAd® precipitation.

In the case of complex groundwaters with numerous impurities, the procedure can become more complicated. Although flocculation is hardly influenced by other organic water constituents, this must be considered in the downstream activated carbon absorption. A multi-stage process is then essential (Chapter 2.2.1.2). Other water constituents such as iron, manganese or heavy metals can be simultaneously precipitated in the stirred reactor without major additional plant engineering effort. Only additional dosing stations are required (Cornelsen et al., 2018).

In the case of complex contaminated sites, it is recommended to determine the optimum dosage and process combination as well as the need for additional reagents in preliminary pilot tests. This allows a reliable operating cost forecast to be made. The basic prerequisite is a comprehensive chemical-analytical characterization of the groundwater to be treated.

Investigations within the framework of a research project with a very complex groundwater chemistry (high DOC and Fe concentrations (approx. 20 mg/L DOC, 3 mg/L Fe), detection of precursors by AOF analyses) showed that in particular longer-chain sulfonic acids (e.g. PFHxS, PFHpS and PFOS) are largely removed with PerfluorAd®, while the concentrations of short-chain sulfonic acids (e.g. PFBS) and carboxylic acids (e.g. PFBA) remained almost unchanged. Also, regarding the sum parameter AOF only a small elimination was observed. After about 6 months of operation of the pilot test, the PerfluorAd® stage showed almost no effectiveness, which was attributed to the low temperatures (winter) and the resulting reduction in the dosage quantity of the polymer due to increased viscosity.

For the entire PerfluorAd®/activated carbon system, operating costs (depending on the activated carbon used) amounted to < 0.055 - 0.68 € per m^3 of treated water, of which[19] approx. 0.04 €/m^3 is attributable to the PerfluorAd® requirement. For this particular case, a cost saving of 0.04 €/m^3 was calculated for the use of the precipitant compared to pure activated carbon absorption (Haist-Gulde et al., 2017).

Outlook. The PerfluorAd® process can be described as being fully developed. The main objective of using PerfluorAd® is to save costs compared to pure sorption on activated carbon. The operating cost advantages to be expected from the use of PerfluorAd® are lower at low PFAS initial concentrations and higher at high PFAS concentrations. Due to the complexity of groundwater that is treated, a generalized estimate on savings potential is not determinable. As a rule, a pilot test is required to provide the data for a more detailed cost calculation.

PerfluorAd® (Summary)

The use of PerfluorAd® is intended to remove as much PFAS as possible from the water before treatment with activated carbon. PerfluorAd® is a liquid substrate which leads to precipitation of PFAS after its addition to contaminated groundwater. The precipitation product is then separated, thickened, and disposed of. The process is well established and has been used in several instances, at least on a pilot scale. It is relatively insensitive to impurities.

[19]   Probably without energy costs.

In most cases, however, PerfluorAd® must be combined with an activated carbon sorption stage to achieve low effluent value requirements. Short-chain PFAS in particular are poorly removed by Perfluo-rAd®. The use of PerfluorAd® together with activated carbon is not always cheaper than a standalone activated carbon system. Therefore, a pilot test is almost always necessary to determine the economic efficiency of PerfluorAd® use. Furthermore, reports on its practical use are currently not yet available.

2.2.3   Membrane Filtration

2.2.3.1   Overview

Description. Membrane filtration is a pressure-driven process[20] that retains and concentrates dissolved molecules of a certain size (separation limit) on one side of the membrane. The concentrate is called retentate. Water and smaller molecules can pass the membrane (Figure 15).

Figure 15   Principle of Membrane Filtration
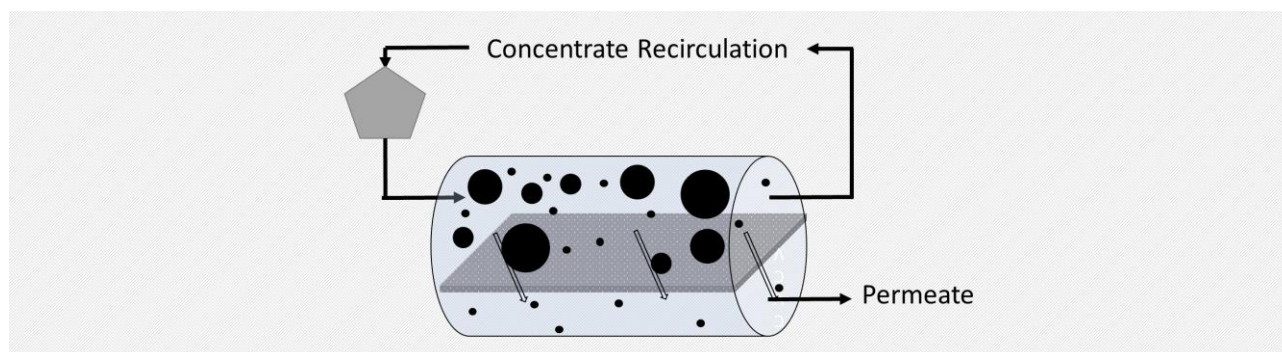
Source: Rahman et al. 2014a

In the passage of charged molecules, not only the separation size of the membranes, as probably the most important factor, plays a role, but also the electrostatic repulsion of the substances to be separated from the surface of the membranes (i.e. ion charge of the substances to be separated) and the formation of cover layers. The decontaminated water (permeate) collects on the other side of the membrane. Membrane filtration refers to a variety of separation technologies, the main difference being the nominal size of the membrane pores. Membrane types suitable for the purification of water containing PFAS include reverse osmosis (RO) and nanofiltration (NF) (Rahman et al. 2014a). The latter also removes short-chain PFBA with a molecular weight of 214.04 g/mol (Table 3).

Table 3   Parameters for nanofiltration and reverse osmosis (Edel et al., 2018)

Parameters	Nanofiltration	Reverse osmosis
Operating pressure	2 - 40 bar	5 - 70 bar
Separation limit (dissolved substances)	≥ 200 - 300 g/mol	< 200 g/mol

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[20]   The applied pressure must be high enough to overcome the osmotic counterpressure.

Especially the formation of cover layers on the membranes can influence the performance of the separation processes. Causes of these layers are biofouling (with high contents of organic water constituents), colloidal fouling or scaling. In biofouling a biofilm grows on the membrane surface, in colloidal fouling colloidally dissolved substances are deposited. Inorganic precipitation on the membrane that occurs due to excess solubility is called scaling. Cover layers reduce the permeate flow. The formation of cover layers can be reduced by (i) pretreatment of the raw water, (ii) increasing the overflow velocity, (iii) membrane and module properties and (iv) cleaning of the membranes.

When membrane processes are used, a high yield is aimed for to keep the concentrate as small as possible. However, to prevent the formation of cover layers on the membrane surface by scaling, a high overflow velocity is required, which is accompanied by a reduction in membrane penetration. Therefore, the yields of reverse osmosis and nanofiltration are only in the range of 75 - 85 %. This means that 15 - 25 % of the treated raw water accumulates as retentate, which must be treated or disposed of (Edel et al., 2018).

Membrane filtration processes are sometimes not able to achieve the low treatment target for short and long chain PFAS that is usually required. The treated groundwater must then be treated by means of activated carbon absorption (Rahman et al., 2014a).

As with all treatment processes, laboratory-scale and pilot-scale tests are required for membrane processes to verify the applicability of the process and to determine detailed design criteria and cost-effectiveness.

First comparative tests showed a degree of purification for reverse osmosis of 99 % (4,99 µg/L PFAS in the permeate) while nanofiltration only led to a degree of purification of 87 – 95 % (84 µg/L PFAS in the retentate) (LfU Bayern, 2014).

Outlook. In general, reverse osmosis seems to be more suitable than nanofiltration. Membrane processes leave behind large amounts of retentate, whose further treatment usually results in high costs. For the treatment of the retentate, processes such as activated carbon absorption and ion exchange are mentioned (LfU Bayern, 2014). However, the question then arises as to what economic advantage membrane filtration offers over pure sorption on activated carbon.

Even though membrane processes have been established for a long time for the purification of water, they are generally not economical for the decontamination of PFAS-containing groundwater. Only if, for example, membrane processes are already established in drinking water production plants, can they be used for this purpose in the event that PFAS contamination may occur.

Membrane Filtration (Summary)

Membrane processes (nanofiltration and reverse osmosis) are established processes and generally suitable for the removal of PFAS. In most cases the achievable purification levels are not sufficient, so that they must be combined with activated carbon sorbents. A large amount of retentate is produced, the treatment of which causes additional costs. Membrane processes are more expensive than standard processes (like sorption to activated carbon) and are therefore only used in special cases.

2.2.3.2 Reverse Osmosis

Description. Reverse osmosis was investigated with respect to the elimination of PFAS from wastewater and drinking water on bench and pilot-study scales. Reverse osmosis membranes are very susceptible to fouling, therefore a pre-treatment of the raw water is essential.

PFOS can be eliminated at raw water concentrations of 0.5 - 1500 mg/L with an efficiency of > 99 %. PFOS removal was better for denser membranes but was not influenced by the surface charge of the membrane. The permeate volume decreased with increasing PFOS concentration. At a very high PFOS concentration in raw water (> 500 mg/L) all membranes showed identical permeate amounts (Tang et al. 2006).

In a further study (raw water: 10 mg/L PFOS) an improvement in PFOS separation was observed with a longer operation time and slightly lower flow rates. It is suspected that some of the PFOS molecules were retained in the polyamide layer of the composite membranes, which reduced the further passage of water and PFOS molecules (Tang et al. 2007).

In a technical scale reverse osmosis plant, PFOS, PFHxS, PFHxA, and PFOA were the dominating PFAS in the raw water. All existing PFAS were removed except for concentrations below the detection limits (0.4 - 1.5 ng/L) (Thompson et al. 2011).

The treatment of high AFFF-contaminated water poses a challenge. With the help of electrocoagulation and filtration, the water was prepared to such an extent that it could be treated by reverse osmosis (degree of purification approx. 99.9 %). The PFAS concentrations in the permeate were 10 - 16 µg/L The achievable flow rate decreased over time (Baudequin et al., 2011).

Outlook. Reverse osmosis can separate the PFAS to a high degree. This even applies to short-chain PFAS like PFBA. On the other hand, the process is sensitive (fouling, reduction of the permeate for-mation rate). The unavoidable removal of minerals from the treated water can increase its corrosive-ness, which in most cases requires a post-treatment of the treated water to reduce its corrosive prop-erties.

In addition, the process requires high amounts of energy (high-pressure pumps). For the treatment of the retentate, destructive methods (e.g. sonolysis) are most likely to be recommended.

From the results of the investigations of nanofiltration (Chapter 2.2.3.3), it can be concluded that the deposition of PFAS at the membrane is influenced by several other factors in addition to the formation of the cover layers in extraordinarily complex processes. This also applies to reverse osmosis. Essen-tial is the surface charge of the membrane in relation to the charge of the PFAS under the given condi-tions in real groundwater. This can either lead to an electrostatic repulsion of the PFAS or alternatively to an accumulation on the membrane surface, which influences the permeability of the membrane.

Reversed Osmosis (Summary)

Reverse osmosis can lead to a relatively high degree of purification, even for short-chain PFAS such as PFBA. However, the process requires high amounts of energy and is quite sensitive. Often, blocking of the membranes occurs, which can only be avoided to a limited extent by additional process stages. The ap-plicability of reverse osmosis must be tested with real site water. As a rule, the process is more expensive than, for example, sorption to activated carbon and is therefore only used in special cases.

2.2.3.3 Nano Filtration

Description. Although nano filtration (NF) has been shown to be less effective than reverse osmosis, there are some studies on the effectiveness of NF for PFAS elimination. However, these are limited to laboratory tests throughout. Therefore, no data are available on performance variations due to fouling or flow/concentration variations under real conditions.

The purification levels determined were mostly > 95 % for PFAS with molecular weights of 214 - 713 g/mol (Appleman et al., 2013). The investigation of the removal of 15 PFAS (5 PFSA, 9 PFCA and FOSA) resulted in removal rates of > 95 % for compounds with molecular weights (MW) > 300 g/mol. FOSA (MW: 499 g/mol), which is uncharged at the pH of deionized water (pH 5.6), had a retention of only 42 %. Short-chain PFAS (for example PFBS and PFHxA) were eliminated at a significantly lower rate (Steinle-Darling and Reinhard, 2008).

The comparison of the separation of PFOS and PFBS also showed that PFBS was only separated at < 69 %, but PFOS at > 88 %. The authors attributed this mainly to the greater hydrophobicity of PFOS (Wang et al., 2018).

In addition, fouling influences the separation rates, but the reported results are contradictory. Steinle-Darling and Reinhard (2008) showed that a fouling layer reduced the separation efficiency.

In the membranes that were used, charged PFAS were rapidly sorbed to the membrane surface, whereas the uncharged FOSA absorbed into the membrane matrix at a much slower rate (Steinle-Darling and Reinhard, 2008). In another experiment, the removal rate at a constant permeate flow (17 - 75 L·m^{-2}·h^{-1}) was > 93 % for all PFAS under all tested conditions, regardless of the degree of contamination of the membrane by humic acid (PFAS dissolved in deionized water or artificial groundwater; Appleman et al., 2013). Wang et al. (2018) showed that before fouling, the sorption of PFOS to the membrane dominated the removal, and after formation of the fouling layer, an improved size exclusion led to PFOS deposition (Wang et al., 2018).

The concentration of bivalent ions also has an influence on the separation efficiency. For example, an increase in the Ca_2Cl concentration from 0.1 to 1.0 mM Ca^{2+} improved the PFOS removal rate from 94.0 % to 99.3 %, which was attributed to the fact that calcium connects two PFAS molecules via electrostatic bonds (calcium bridges). This however leads to larger molecules that can potentially block the pores. Furthermore, the addition of calcium leads to increased precipitation and surface roughness as well as PFOS accumulation on the membrane, resulting in a reduction in permeate flow (Zhao et al., 2013). This was confirmed in another experiment for PFOS. However, the removal efficiency for PFBS decreased from 48.9 % to 20.5 % with an increase in dissolved ionic concentrations from 0 to 100 mM (Wang et al., 2018).

The pH value had a significant effect on the PFOS separation efficiency. With an increase in pH from 3 to 9, deposition increased from 86 % to 95 % (0.1 mM Ca^{2+}; Zhao et al., 2013).

The attempt to increase the permeate flow and salt transmission by using membranes with a large pore diameter (separation size: 27,000 Da) showed that PFHxA (100 - 300 ng/L) could still be separated to 95 % in pure water. This indicates that PFHxA separation is less dependent on the separation size of the membrane than on its negative surface charge (zeta potential) and the resulting electrostatic repulsion of the PFAS. Membranes with a stronger negative surface charge tend to show a higher removal rate for PFHxA (Zeng et al., 2017).

Nano filtration can also be used in *treatment trains.* For example, PFHxA (60 - 20 mg/L) was eliminated to 96 - 99 % at high pressures (20 bar). The retentate (20 % of the feed stream) was then purified by electrooxidation (98 % degradation). The energy requirement in laboratory tests for the electrooxidation was 15.2 kWh/m^3 treated concentrate (Soriano et al., 2017).

As with other membrane processes, a pre-treatment of the raw water is necessary to avoid fouling.

Outlook. At present, basic research on the applicability of nano filtration is the main focus. However, real water cannot be modified to the same extent as in the laboratory tests without significantly increased process costs or undesirable side effects (salination of the treated water). Due to the significantly lower effectiveness of nano filtration compared to reverse osmosis and the fact that these systems are expensive, nano filtration is considered to have little market potential. On the other hand, the results of basic research can also be used to evaluate the effectiveness of nano filtration.

Nano Filtration (Summary)

Due to the inferior cleaning properties compared to reverse osmosis, nano filtration is not important for the purification of water containing PFAS. Nevertheless, there are numerous studies on the separation of PFAS by nano filtration. In particular, groundwater properties (including pH value, salt content, concentration of divalent ions) have been investigated. The results help to better understand and assess the influence of groundwater properties on the purification performance of all membrane processes.

## 2.2.4 Ultrasound Treatment (Sonolysis)

Description. Ultrasonic treatment is a process with already established practical applicability for use in many applications (e.g. in the digestion of biosludges to increase biogas production) (Cheng et al., 2012). Ultrasound is generated and transferred to the water phase via a transducer. Factors such as energy intensity and frequency can be influenced by the type of transducer. The number of transducers required in a vessel depends on the reaction kinetics, the flow rate to be treated, and the sound field to be achieved for uniform cavitation.

Sonolysis uses sound waves with frequencies generally between 20 and 1,100 kilohertz (kHz). As sound waves travel through water, oscillating cycles of dilution and compression occur, creating cavitation (cavitation is the formation and dissolution of vapor-filled cavities in liquids) in the water. Due to the sound waves, at ambient temperatures and pressures, existing bubbles begin to grow and eventually collapse. The collapse of cavitation bubbles is quasi-adiabatic[21] and heats up the vapor phase within the cavity to temperatures of 4,000 - 5,000 °C (Campbell et al., 2009), resulting in a pressure on the order of 1,000 bar. The temperatures of the bubble-water interface are estimated at 800 - 1.200 °C (Gole et al., 2018). As a direct consequence of these transient, locally limited high temperatures and pressures, dissolved substances accumulated in the vapor phase or at the bubble-water interface are pyrolytically decomposed. The water vapor within the collapsing cavity is homolytically split, generating hydroxyl radicals as well as oxygen and hydrogen atoms. The radicals can decompose organic substances in the bubble vapor, at the bubble-water interface and even in the aqueous solution (Figure 16).

PFAS are sonolytically quite well degradable, the application of sonolysis on PFAS is patented (Mader et al., 2010). Scientific investigations focused on the optimization of the conditions (u. a. sound field distribution, pH value, pressure) and the determination of the influence of interfering substances (Cheng et al., 2010; Fernandez et al., 2016).

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[21] An adiabatic change of state is a thermodynamic process in which a system is transferred from one state to another without exchanging heat with its environment.

Figure 16   Principle of sonolysis of PFOS
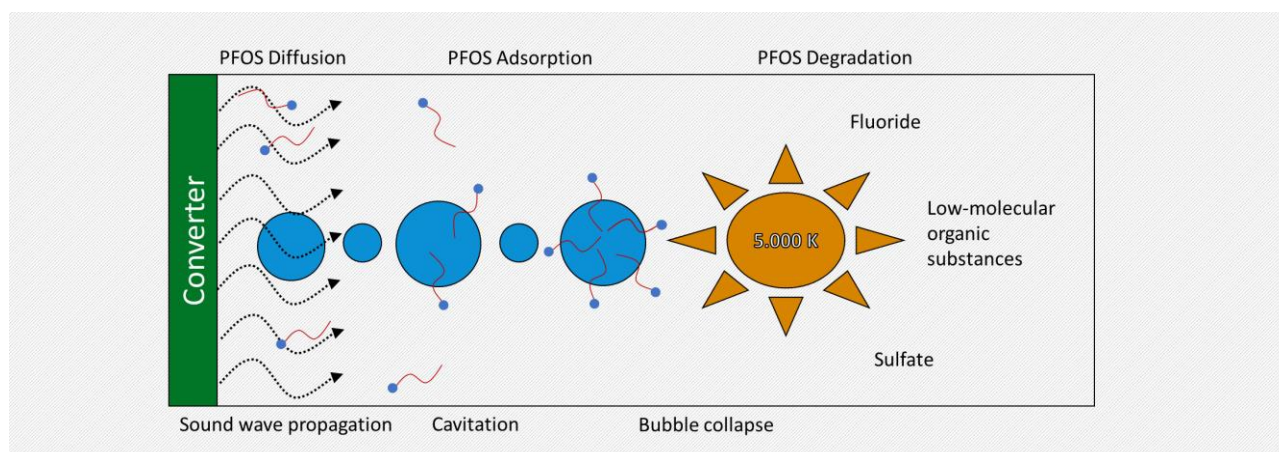
Source: Rodriguez-Freire et al., 2015

PFAS Degradation. The degradation of PFAS probably occurs via a pyrolysis mechanism acting over the bubble-water interface. Thus, a key factor in the sonolytic treatment of PFAS is sorption on the surface of these microbubbles since the dominant process is thermal decomposition at the bubble surface or in the bubble itself. The hydrophobic part of the PFAS is (depending on the specific molecule) preferably attracted by the gas phase and the hydrophilic functional group (e.g. carboxylate or sulfonate group) preferably remains dissolved in the liquid phase. Therefore, the gas-liquid interface of a bubble is ideal for the agglomeration of PFAS.

Sonolysis appears to destroy a wide range of PFAS compounds, both long chain and short chain. The degradation follows pseudo-1st order kinetics and is faster for perfluorinated than for polyfluorinated compounds. PFOS degrades 2.3 times faster than the polyfluorinated compound of the same chain length 6:2 fluorotelomer sulfonate (Fernandez et al., 2016, Rodriguez-Freire et al., 2016). For per-fluoroalkyl sulfonates it was shown that the degradation rates also decrease with decreasing chain length. PFBS was degraded at a rate about 1.9 times slower than PFOS. A similar trend applies to the sonolysis of perfluoroalkyl carboxylates: PFBA was degraded at a rate about 2.3 times slower than PFOA (Fernandez et al., 2016).

PFOS, PFOA, PFBA, PFBS could be completely degraded to fluoride in a laboratory test in 180 min, PFOA is degraded at a rate slightly faster than PFOS.

The intensity of cavitation activity depends on the initial PFAS concentration of the solution, so that the selection of the optimum concentration of a contaminant is highly significant. The fastest degradation rate was found at 2.6 mM PFOS (1,300 mg/L) (Cole et al., 2018). Sonolysis can also be effectively used for environmentally relevant concentrations and matrices (Cheng et al., 2008, Vecitis et al., 2008a, Vecitis et al., 2010).

Rodriguez-Freire et al. (2015) found that increasing PFOS concentrations correlate to increasing degradation rates, offering the causal explanation of a higher availability of sorbed PFOS molecules at the bubble-water interface. A further causal effect is an increase in electrostatic repulsion between bubbles, which prevents bubbles from merging.

At the beginning, the C-C or C-S bond between the last CF_2 group and the carboxylate or sulfonate group is cleaved, resulting in the formation of an intermediate product (1H-fluoroalkane) with high volatility. This migrates to the bubble nucleus for further thermal and radical decomposition. The fluorochemical intermediates undergo a series of pyrolytic reactions in the bubble vapor, which leads to C_1-fluorine radicals. Secondary bimolecular vapor phase reactions coupled with simultaneous hydrolysis convert the C_1-fluorine radicals into end products.

The PFAS are thus completely mineralized to their inorganic components (F^-, SO_4^{2-}, CO and CO_2) during the ultrasonic treatment (Campbell et al., 2009, Vecitis et al., 2008b).

pH value. Based on laboratory tests, the fastest degradation was achieved at pH 4.0. At this lower pH value, the charge of the bubble-water interface becomes more positive and the negatively charged hydrophobic PFAS are therefore better attracted to the bubble surface, which ultimately increases the degradation rate under acidic conditions. In addition, bubble coalescence is reduced and the frequency of bubble collapse is increased (Cheng et al., 2010).

On the other hand, at pH 4, fluoride is already largely present as hydrofluoric acid (HF) (pKa = 3.2). Possibly, a treatment at neutral pH value, at which HF is largely dissociated, is more advantageous.

Frequency. The ultrasound frequency plays an important role in the extent and speed of PFAS degradation. For the destruction of PFAS it has been observed that ultrasound with higher frequency is better. Campbell et al (2009) found the fastest degradation for PFHpA and PFHpS at a frequency of 358 kHz, similar to PFOS. In contrast, PFBA/PFBS degradation was best at 610 kHz.

Lower frequencies produce larger bubbles with higher energy formation and higher frequencies produce smaller bubbles with an overall larger surface but less energy formation (Drees, 2005). The degradation of PFAS requires a higher frequency range compared to other contaminants (> 200 kHz; Fernandez et al., 2016; Rodriguez-Freire et al., 2016). Since PFAS degradation depends mainly on sorption at the bubble-water interface, it is obvious that higher frequency sonolysis is more advantageous. Mader et al (2010) stated 400 kHz as the frequency with the best degradation rate.

In general, the degradation rate increases linearly with increasing ultrasonic energy density (W/L; Mader et al., 2010).

Organic and inorganic accompanying substances. High concentrations of organic concomitants (typical for AFFF-contaminated waters or landfill eluates; Vecitis et al., 2010) reduce the PFAS degradation rate due to competitive reactions for binding sites at the bubble-water interface or by lowering the average interface temperatures during bubble collapse. The effect of individual organic compounds depends on their sorption constant, the Henry coefficient, and the specific heat capacity. Especially volatile organic compounds contribute to the reduction of PFAS degradation, but the effect of dissolved natural organic material is not significant (Cheng et al., 2010). Mader et al (2010) therefore found the same degradation rates for groundwater as for PFAS dissolved in distilled water.

Under certain circumstances, this effect can be eliminated by pre-treating the water (for example by chemical oxidation) before sonolysis. It still needs to be tested whether the resulting oxidation products affect the effectiveness of the sonolysis.

The reduction in degradation rates is mainly caused by bicarbonate. It is assumed that the observed inorganic effects are due to the splitting of the ions and interactions with the bubble-water interface (radical scavenging) (Cheng et al., 2010). Bicarbonate can be easily removed from the raw water.

Energy. The energy requirements for sonolysis are in the range of 1.32 kWh/m^3 to 3 kWh/m^3 (for DOC degradation).

Outlook. Sonolysis has been demonstrated on a laboratory scale for PFAS degradation but has not been used on a technical scale. The scale-up is probably still associated with design challenges (Gole et al., 2018). A significant advantage is that the decomposition of PFAS by ultrasound does not produce any undesirable secondary substances.

Due to the required treatment time of several hours, sonolysis is also not a process suitable for the continuous purification of pumped groundwater. In addition, most studies have been conducted with very high PFAS concentrations. The question is whether it is possible to achieve such low final PFAS concentrations with sonolysis that the treated water can be discharged into the sewerage system.

Since the degradation follows a pseudo 1st order reaction, it is probably not economical to degrade the PFAS completely. The residues of the PFAS should be removed with activated carbon. Possible applications of sonolysis are:

► treatment of landfill eluates (optionally after pre-treatment),

► treatment of concentrates from soil washing,

► treatment of ozone fractionation concentrates,

► treatment of water highly contaminated with AFFF.

Usually these are complex matrices and further research is required to optimize sonolysis for them. Finally, sonolysis is considered a high priority in PFAS management. Further investigations are therefore recommended.

The question was also discussed whether sonolysis on activated carbon can destroy PFAS sorbed to activated carbon (Lim and Okada, 2005). However, this has not yet been tested at this stage. The treatment of large material flows with low PFAS concentrations is not cost-effective.

Sonolysis (Summary)

In sonolysis, gas bubbles are formed by means of ultrasound. When these bubbles collapse (cavitation), high local temperatures (up to 5,000 °C) and pressures are generated and these destroy the PFAS pyrolytically. In addition, cavitation also produces radicals (especially hydroxide radicals), which additionally contribute to PFAS degradation. The shorter the PFAS chain, the longer the treatment time. Due to the generally required treatment time of several hours, sonolysis is not a process suitable for continuous purification of pumped groundwater for technical reasons alone, but only for the treatment of aqueous PFAS concentrates. The treatment of large streams with low PFAS concentrations is not cost-effective. It is still unclear whether final PFAS concentrations in the range of desired discharge values can be achieved with this process.

A significant advantage is that no undesirable by-products are produced during the degradation of the PFAS by ultrasound. The process is sensitive to elevated bicarbonate concentrations and increased concentrations of highly volatile organic compounds.

All in all, sonolysis is a technology that has been developed to technical maturity. However, regarding the treatment of water containing PFAS, it is still necessary to adapt and optimize the process parameters. Even though sonolysis is not yet used for PFAS destruction in real remediation projects, the process has a high development potential, mainly because it can completely destroy PFAS without any undesired by-products.

2.2.5   Advanced Oxidation/Reduction

Description. The aim of advanced oxidation/reduction is to convert harmful substances into harmless end products by means of chemical oxidation or reduction. The chemical oxidation of PFOS and PFOA is very slow due to the high electronegativity of the fluorine atoms and the complete substitution of carbon atoms by fluorine. The perfluorinated backbone also reduces the oxidizability of the functional group ($-SO_3^-$, $-CO_2^-$). If other organic compounds are present in addition to PFAS, these are preferentially degraded by the oxidizing agents and regarding PFAS, there is also a competitive inhibition of oxidation.

Several laboratory studies demonstrate the general feasibility of chemical oxidation of PFOA and partially PFOS (Table 4). So-called advanced oxidative processes (AOP) (Merino et al., 2016)) have been shown to be effective for the degradation of PFAS.

Table 4   Results of PFAS degradation tests with activated persulfate in batch experiments (Crimi et al., 2017)

Contaminant	Activation	Concentrations	Results
PFOA and short-chain PFASA	Thermal (80 °C)	PFOA (0.9 µg/L) Persulfate (50 mM)	Complete degradation with 77 – 88 % fluoride-release
PFOA	Thermal (20 - 80 °C)	PFOA (0.58 µg/L) Persulfate (20 - 200 mM)	Complete degradation after 72 h at 40 °C (67 % F$^-$-release), after 215 h at 30 °C 69 % F$^-$-release
PFOA	Thermal (85 °C), buffered to pH 7,1	PFOA (1 ng/L) Persulfate (10 mM)	93,5 % degradation with 43,6 % F$^-$-release in 30 h
PFOA	Thermal (60 °C)	PFOA (68 ng/L) PFOS (2 ng/L) Persulfate (24 - 84 mM)	Complete degradation of PFOA despite the presence of BTEX, no degradation of PFOS
PFOS	UV light at 20 °C	PFOS (372 ng/L) Persulfate (18.5 mM)	Approx. 65 - 85 % defluorination

This also applies in part to reductive processes, especially those in which solvated electrons are formed. However, solvated electrons are quickly neutralized by oxygen and anions. Various oxidation processes using persulfate show promising results for the degradation of PFOA (Table 5). Persulfate can generate hydroxyl (OH$^•$) and free sulfate radicals (SO$_4^{•-}$). PFOA was also effectively destroyed by UV-activated Fenton oxidation (Tang et al., 2012).

Table 5   Second order rate constants for the chemical degradation of PFOA and PFOS with selected radicals and hydrated electrons (Trojanowicz et al., 2018)

Contaminant	Form of the contaminant	Radical	Rate constant [M-1s-1]
PFOA	Ammonium salt	$^•$OH	$\leq 3 \cdot 10^7$
	Ammonium salt	e_{aq}^-	$1,3 \cdot 10^7 – 5,1 \cdot 10^7$
	sodium salt	e_{aq}^-	$1,7 \cdot 10^7$
	Acid	$^•$H	$9,0 \cdot 10^7$
	-	SO$_4^•$	$2,6 \cdot 10^7, \leq 5,0 \cdot 10^4$
	-	NO$_3^•$	$\leq 5,0 \cdot 10^4$
PFOS	Ammonium salt	$^•$OH	$\leq 3 \cdot 10^7$
	N$_{(C2H5)4\ salt}$	$^•$OH	no reaction
	N$_{(C2H5)4\ salt}$	e_{aq}^-	$7,3 \cdot 10^7$

Although the hydroxyl radical itself does not break down PFOA, such oxidation systems produce other radical species that are active against PFOA. In a degradation experiment using 1 M H$_2$O$_2$ and 0.5 mM iron (III), PFOA was degraded by 89 % within 150 minutes. Hydroxyl radicals do not react with PFOA, but systems that only produce superoxide allowed 68 % PFOA degradation. Hydrogen peroxide caused 80 % degradation, all in the same time. The absence of detectable degradation products and the formation of near stoichiometric equivalents of fluoride suggest that PFOA has been fully mineralized (Mitchell et al., 2014).

The oxidant persulfate ($S_2O_8{}^{2-}$) itself has only a weak effect on the defluorination of PFOS, but the sulfate radicals formed with activators are quite reactive. Activation led to different results in the order thermal > UV light > Fe^{2+}. An increase in persulfate concentration had a positive effect on the defluorination of PFOS only up to a certain point, after which autocatalytic persulfate degradation probably occurred. Presumably PFOS becomes a sulfate radical by splitting off an electron, which is then further desulfonated to a C_8F_{17}-radical.

During the degradation reaction, long-chain PFAS are decomposed step by step so that all shorter-chain perfluoroalkane carbonic acids could be detected in lower concentrations as intermediates of PFOS degradation. From this it was concluded that mineralization of PFOS is generally also possible (Yang et al., 2013). A lower pH value produced higher degradation rates than a higher pH value.

Persulfate is used for PFAS degradation in quite high concentrations. Hori et al (2008) report the use of 12 g/L for the degradation of up to 56 mg/L PFOA. To degrade 155 mg/L PFOA, 6 h of ongoing thermal activation (80 °C) were required. Fluorine was formed at 77.5 % of the stoichiometrically possible concentration. In general, PFAS degradation requires extreme chemical conditions (environment, dosages) and PFOS is often only incompletely degraded (Kingshott, 2008). The investigation of the degradation of precursors (FTOH, PFSA-based compounds in AFFF-contaminated waters) with heat-activated persulfate, resulted in a conversion into perfluoroalkane carbonic acids, which were then further degraded (Figure 17). The presence of soils reduced the efficiency of the remediation process but did not change the transformation pathways. At high concentrations of contaminants, the presence of non-fluorinated organic compounds, as present in AFFF formulations, inhibited the degradation of, for example, PFOA. PFOS and PFHxS could not be degraded under any conditions (Bruton and Sedlak, 2017).

Figure 17   Degradation of a defined AFFF product, dissolved in water
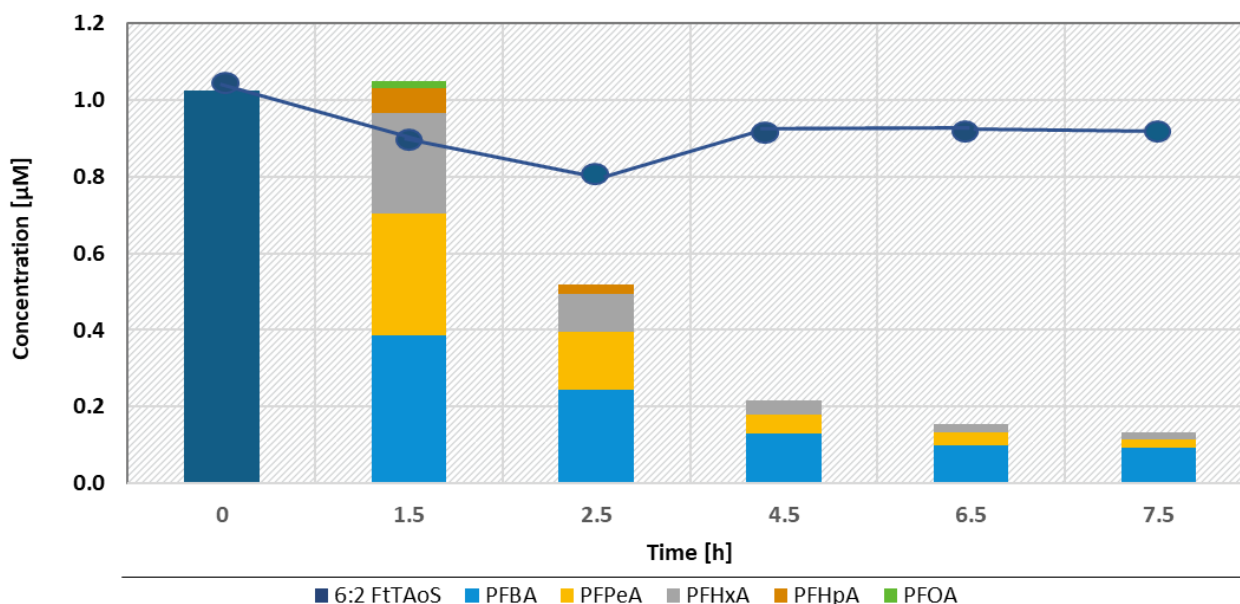
Initial persulfate concentration = 50 mM, pH_0 = 3.5, T = 85 °C. Bars represent the mean value of triple measurements. The solid line with circles represents 6:2 FtTAoS in a persulfate free control. Source: Rodriguez-Freire et al., 2015.

Only a few field tests on the ISCO (in-situ chemical oxidation) of PFAS have been documented. In one of the experiments PFAS were to be degraded with peroxone-activated (O_3/H_2O_2) persulfate. Decreases in PFAA concentrations were observed in analyzed soil and groundwater samples, but the final concentrations were still far above any target values.

In groundwater, no increase in concentration was observed, which led to the conclusion that oxidation did not lead to a mobilization of PFAA. Whether precursors that could have been released were present at this site was not investigated. Laboratory scale tests using this method show up to 99.9 % PFAS degradation and up to 86 % fluoride released (Eberle et al., 2017).

As the fluorine atoms are very electronegative, it was investigated whether reductive processes could possibly be used for the degradation of PFAA. Attempts to defluorinate PFOS and PFOA with vitamin B_{12} (260 µM) as the catalyst in a reducing environment generated by Ti(III) citrate (36 mM) at 70° C and pH 9 resulted in only moderate fluorine release.

Branched PFAS were more readily degradable than linear molecules (Ochoa-Herrera et al., 2008). The hydrated electron acts as a reducing agent and allows the attack on the C-F bonds (α position) instead of the C-C bonds, thus initiating a defluorination process (Qu et al., 2010b, Song et al., 2013). Hydrated electrons are non-selective and strong reducing agents and are used in many other processes described in the following chapters. Because of their sensitivity to oxygen, anaerobic treatment processes are more advantageous. Zero-valent iron is not suitable for PFAS degradation (Blotevogel et al., 2018).

Outlook. The chemical oxidation studies are mainly focused on the treatment of PFOA and subordinate PFOS. There are also studies that show no degradation for PFOS (Dombrowski et al., 2018). Overall, the degradation of perfluoroalkane sulfonic acids appears to be significantly more difficult than that of perfluoroalkane carbonic acids. In particular, the degradation of short-chain PFAS is not or only insufficiently validated. There are major concerns regarding the formation of significant concentrations of more mobile short-chain PFAS.

In particular, the complex compositions of contaminated media (soil, water) can pose a major challenge. First results show that the degradation systems functioning in the laboratory can hardly be transferred to real environmental conditions (Dombrowski et al., 2018). The additional oxidant requirement for the oxidation of natural organic compounds and the inactivation by radical scavengers present in groundwater (Bruton and Sedlak, 2017) are not different from the remediation of conventional contaminants. Especially groundwater contaminated with AFFF is likely to have a very high DOC and thus an unusually high oxidant requirement. For this reason, field tests are essential (Crimi et al., 2017).

In principle, oxidation processes can also lead to the preferential transformation of precursors, if these are present, which results in significantly increasing PFCA concentrations in groundwater (Houtz and Sedlak 2012). This partial transformation is accompanied by a change in the physical, chemical, and toxicological properties of PFAS. However, basic data for the evaluation of these changes are currently still missing.

At present, chemical oxidation can be classified as not yet sufficiently developed for the field scale. There is a lack of fundamental investigations why processes that largely work in the laboratory cannot be transferred to the field scale. However, the question also arises as to whether the processes would still be competitive in view of the high concentrations of expensive oxidizing agents required and whether the high concentrations of formed end products (e.g. sulphate when using persulfate) can be accepted in individual cases. Sulphate is limited by the German Drinking Water Ordinance to maximum concentrations of 250 mg/L. The ISCO processes would generate many times this amount. The chemical reduction requires extreme reaction conditions, therefore there is no practical application so far.

> ### Chemical Oxidation/Reduction (Summary)
>
> The chemical oxidation of PFCA has been proven in laboratory tests. For PFSA, however, the results are contradictory. It appears that these (especially PFOS) are much more difficult or impossible to degrade by chemical oxidation. Reductive methods have proven to be largely unsuitable.
>
> Chemical oxidation requires very high concentrations of oxidants and rigid reaction conditions and is very sensitive to impurities in the aquifer (including increased DOC concentrations or increased concentrations of radical scavengers such as bicarbonate or chloride). The process has not yet been used on a technical scale for the remediation of aquifers. It seems questionable whether the still existing problems can be solved technically. There are, however, special cases in which chemical oxidation appears promising. Further developments are still pending.

2.2.6   Ozofractionation

Description. The process combines the property of PFAS to accumulate at gas-water interfaces (Figure 18) with the property of ozone to form particularly small gas bubbles and to lead to a chemical transformation of the precursors to the perfluoroalkane carbonic and sulfonic acids.

Figure 18   Concept of foam fractionation
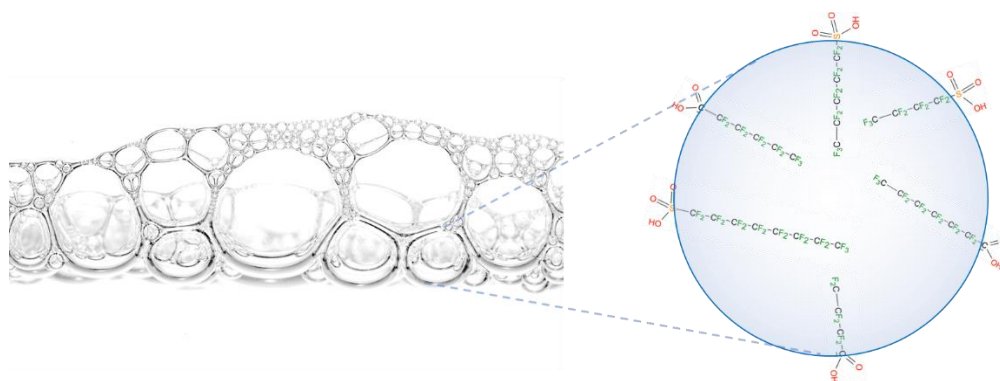
Source: Arcadis Germany GmbH, 2019

Ozone bubbles are not only small, but also remain stable in the groundwater to be treated and on the surface within the treatment reactor. Ozone is more soluble in water than oxygen but decomposes rapidly. It can directly oxidize the contaminants in the water phase, but this occurs slowly and contaminant-specifically. Effective is the autocatalytic decomposition with formation of hydroxyl radicals (OH•), which cause a very fast and non-selective oxidation of the precursors. The transformation of the precursors to perfluoroalkane carbonic and sulfonic acids improves the removal rate, as the perfluoroalkane carbonic and sulfonic acids have a higher surfactant character and therefore accumulate better at the gas-water interface. The mass ratio of ozone to water should not exceed 13 % (v/v), otherwise the ozone bubbles will combine to form larger bubbles and the process will be less effective (Dickson, 2014).

In terms of process technology, ozofractionation is also known as the *Ozofractionative Catalysed Reagent Addition* Process (OCRA). Since only the precursors are oxidized to the perfluoroalkane carbonic and sulfonic acids, these remain in the system, but are concentrated and discharged in the gas bubbles.

Ozone can also promote the degradation of accompanying organic contaminants. Due to the small size of the gas bubbles (diameter < 200 μm), the total mass of the ozone bubbles has a large gas-water interface. At the surface of the water phase in the reactor, the PFAS are therefore concentrated in a small, separable volume.

On a technical scale (Figure 19), the ozone fractionation consists of several reactors connected in series with continuous flow, into which ozone is introduced as bubbles. The PFAS concentrate as highly contaminated foam on the liquid surface in each reactor. There they are drawn off (vacuum extraction) and further concentrated, and can be fed to a further destructive treatment (such as sonolysis: Chapter 2.2.4 or thermal).

The gas phase is released into the atmosphere via an activated carbon absorber. As a rule, the last process stage of the water phase is an activated carbon absorber, with which the residues of the PFAS that have not yet been removed can be retained in order to achieve the required discharge values. If impurities are present, the process can be extended by further process stages if required.

Figure 19   Ozofractionation process concept
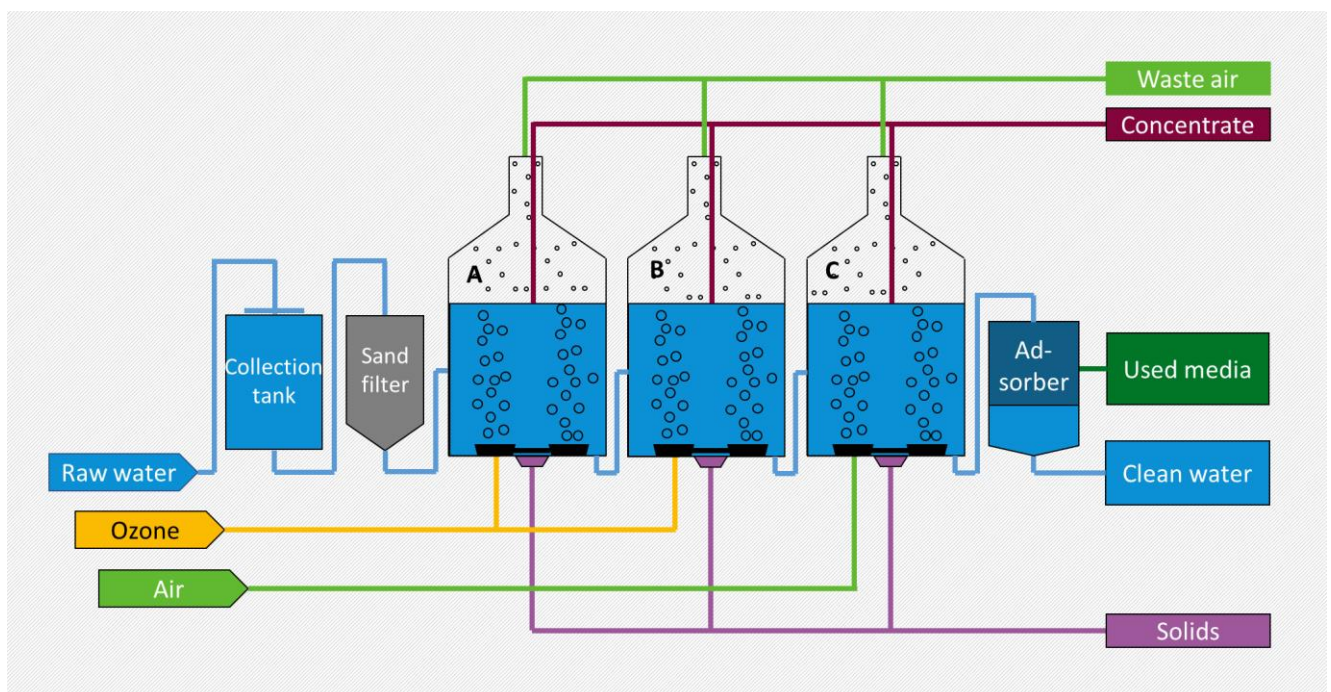
A - C: "Ozofractionator" steps. Source: Evocra, 2016, modified

The process is not only suitable for the treatment of groundwater, but also for sludge with a solids content of up to 20 %. The fractionation reactors separate the liquid from the solid phase. Smallest particles get into the foam concentrate and are removed with it. Coarse particles sediment at the bottom of the reactors and are removed there.

A similar process has been investigated on a laboratory scale in Germany. Here, the gas bubbles were generated electrolytically. The bubbles collapse on the surface of the water phase to be treated and an aerosols strongly enriched with PFAS are formed. Tests with 6:2 FTSA resulted in a degree of purification of 99.8 % (recovery in the aerosol, 60 minutes treatment time). Similarly high purification levels were found for PFOA and PFOS.

The degree of purification is significantly dependent on the salinity of the fluid to be treated. When using pure water, the efficiency was significantly lower. It is possible that the salinity reduces the solubility of the PFAS so that they have a higher affinity for the gas-water interface[22]. The separation of short-chain perfluoroalkane carbonic acids was significantly worse (PFBA: approx. 10 %, PFPeS: approx. 20 %, PFHxA: approx. 45 %; gas surface flow: 5 ml/(min·cm^2); Ebersbach et al., 2016).

The ozofractionation process has already been tested on a technical scale in Australia. For long-chain PFAS such as PFOS and PFOA, a purification level of 99.9 % has been achieved (Evocra, 2017). For the ozofractionation stages alone, a purification level of > 98.7 % was always achieved. The short-chain PFAS can be removed better with ozone than with air (Ross et al., 2017).

When applying the process to waters with a high concentration of organic molecules and high precursor content, a significantly lower degree of purification (approx. 66 %) was found for ≤ C_6-PFCA. It was therefore suspected that this was due to formation from the precursors during ozone treatment. This can be justified by the mass balance shown in Figure 20. A considerable concentration of precursors was present in the feed (proven with the TOP assay). Already after the first oxidation step, the precursor concentration was clearly reduced along with the concentration of the long-chain PFAS. However, the concentration of the short-chain PFAS had increased, indicating a release from the precursors. In total > 97 % PFAS were removed at varying raw water concentrations between 100 and 5,400 μg/L PFAS (28 compounds after TOP oxidation) (Ross et al., 2017).

Figure 20   Ozofractionation: Results of the treatment on a technical scale
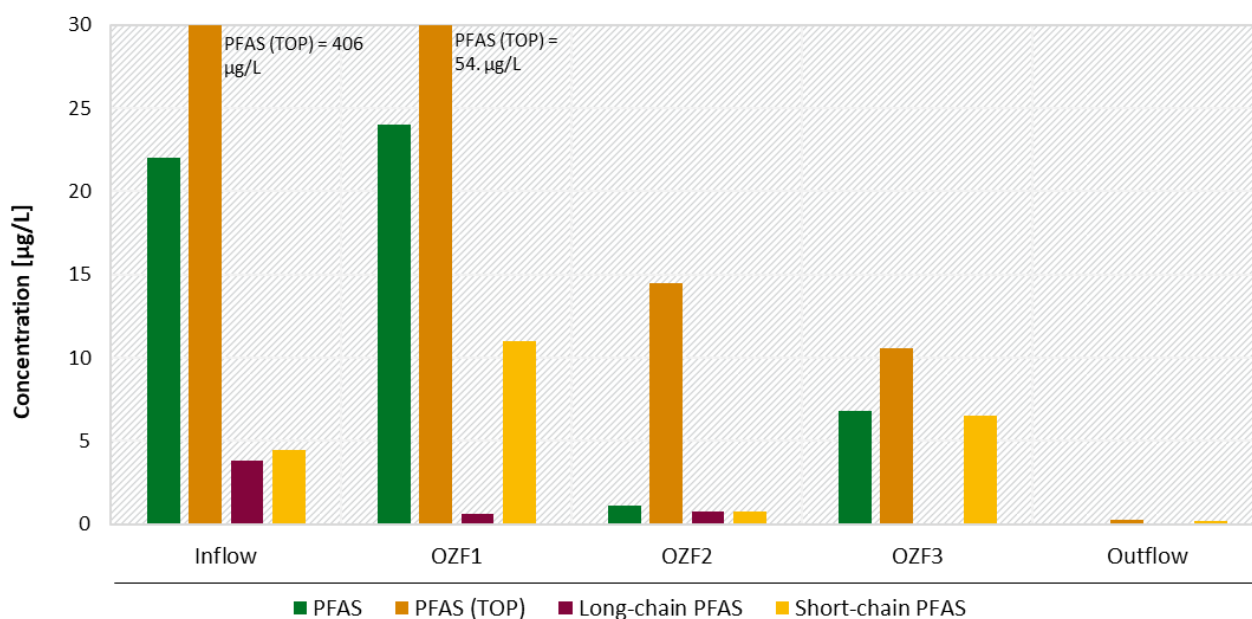
Source: Arcadis Germany GmbH, 2019

Unlike many other processes, the degradation of an accompanying organic contamination does not significantly affect the PFAS removal level. The disadvantage is that a waste product (PFAS foam concentrate) is produced which must be disposed of separately. The volume of the concentrate is 0.5 - 2 % of the inflow volume. With the ozofractionation process alone, the required PFAS concentrations in the outlet cannot be achieved, a supplementary process stage is therefore necessary (*treatment train*).

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[22]   The solubility of PFOS decreased from 570 mg/L in pure water to 25 mg/L in sea water (3M Company, 2000).

The process requires a higher operating effort than simpler processes such as the sole sorption of activated carbon, but this can usually be achieved by remote monitoring. (Dickson, 2013, Dickson, 2014).

Outlook. According to the available documentation, the process appears to be ready for the market. However, as is the case with most newer technologies, there is a lack of supplier-independent studies to verify its effectiveness. It is also a relatively complex technology whose operating costs are significantly higher than those of alternative market-ready technologies, but this cannot be assessed due to lacking data. The competing process to the ozofractionation technology is probably the precipitation with PerfluorAd®. Both processes are most likely to have their economic advantages at very high PFAS concentrations.

Ozofractionation (Summary)

The ozofractionation technology has already been successfully applied on a technical scale in Australia. However, there is a lack of data for a general assessment of its applicability in relation to raw water quality.

In this process ozone bubbles are introduced into a reactor. PFAS separation is based on the accumulation of PFAS on the gas-water surface. With the gas bubbles, the PFAS enter the head space of the reactor where they are removed as a concentrate. The concentrate is further treated accordingly. Ozone leads to a destruction of accompanying organic substances, which has little disturbing effect on the process and contributes to the degradation of the precursors to PFAA. These have a stronger surfactant character and are therefore easier to separate with this process. Ozofractionation is less effective for short-chain PFAS (not yet finally clarified) and for waters with low salt content. The process must be combined with an activated carbon adsorber stage to achieve the usually low target discharge values.

Ozofractionation is significantly more expensive than the standard procedure (sorption on activated carbon) for moderately contaminated groundwater. It can only prove to be economically viable for very highly contaminated water. However, there are no independent process reports to be able to conclusively assess the applicability and market opportunities of this process.

2.2.7   Electrochemical Technologies

2.2.7.1   Electrochemical Oxidation

Description. Degradation by electrochemical oxidation is achieved by direct electron transfer on the surface of the anode (Zhuo et al., 2011; Figure 21). This takes place in two different ways:

- ► Indirect electrochemical oxidation, in which strong oxidants (hydroxyl radical) are generated on the anode, which then trigger the chemical oxidation
- ► Direct electrochemical oxidation, where the electro-oxidation takes place directly at the anode by the production of physically sorbed "active oxygen" (sorbed hydroxyl radicals).

It is assumed that PFAS degradation occurs mainly via decarboxylation (Niu et al., 2013), releasing fluoride and sulphate in advance and producing PFAS with shorter chains (Zhuo et al., 2012). The sulfonic acids are converted into carboxylic acids shortened by one perfluorinated carbon atom and then further degraded. Material balances show that, in addition to the short-chain PFAS, other metabolites must also be formed, since not all degraded molecules are found as fluoride. With longer treatment duration, the metabolites are also broken down (Gomez-Ruiz et al., 2017). The analysis of the AOF showed that precursors are also degraded to a large extent (Trautmann et al., 2015). This also applies to the natural DOC.

Laboratory tests with increased concentrations of the hydroxyl radical scavengers chloride and tert-butyl alcohol (TBA) showed that these had only minimal effects on PFOA/PFOS degradation in the range of the current densities used (3 - 50 mA/cm^2) and contaminant concentrations (low/high) (reduction of rates by < 20 %). As a result, degradation occurs via direct oxidation at the electrode surface rather than via hydroxyl radicals (Schaefer et al., 2015). On the other hand, Urtiaga et al. (2015) showed that with a higher current density more hydroxyl radicals were formed, which was associated with faster PFOA degradation. Ultimately, the predominant degradation mechanism has not yet been conclusively determined.

Figure 21   Principle of electrochemical oxidation
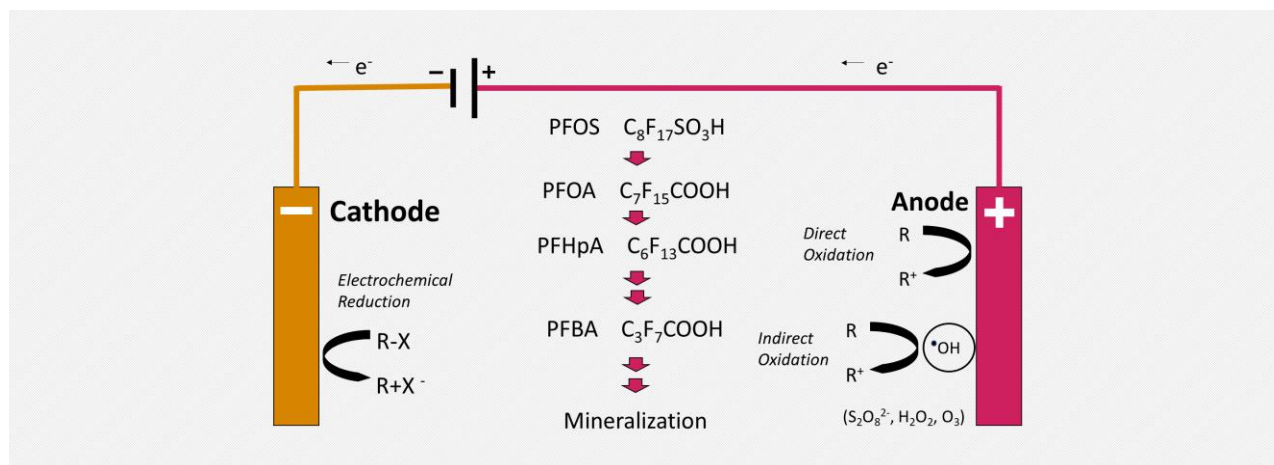
Source: Zhuo et al., 2012

Due to their high chemical, mechanical, and thermal stability as well as their high degradation efficiency due to the high overvoltage for oxygen evolution, boron-spiked diamond electrodes are generally used. Comparatively good degradation performance has been achieved in laboratory tests:

► Various groundwaters from a former fire training area as well as concentrates from the membrane filtration experiments spiked with PFOS, PFHxS and PFBS were subjected to electrochemical degradation. In all groundwater samples used, depending on the energy input (current intensity and test duration; here: approx. 42 h), up to 97 % of the total PFAS could be degraded. The extent of degradation was higher for longer-chain than for shorter-chain PFAS. The DOC concentration was 13 mg/L (Trautmann et al., 2015).

► With an ultra-nano crystalline boron-spiked conductive diamond electrode, even greater mineralization of PFOA was obtained (Urtiaga et al., 2015).

► PFOS is significantly less degradable than PFOA (Schaefer et al., 2015).

► Degradation of PFOA, PFBA, PFHxA, PFDA, PFBS, PFHxS and PFOS under optimized conditions; the PFOA concentration was reduced by 97% within two hours with 60 % fluoride yield (Zhuo et al., 2012)

► Electrochemical treatment of the effluent of an industrial wastewater treatment plant (8 PFAS compounds, max. 1,652 µg/L, mainly fluorotelomer sulfonamide alkyl betaine, 6:2-FTAB and fluorotelomer sulfonate, 6:2-FTSA) resulted in 99.7 % PFAS removal (50 mA/cm^2, 10 h). The energy input of 0.15 kWh/L led to a 98 % removal; at 0.26 kWh/L it was 99.7 %. At low current densities (< 50 mA/cm^2), short-chain PFAS appear to be persistent (Gomez-Ruiz et al., 2017).

▶ The application of a titanium suboxide (Ti_4O_7) electrode degrades both PFOS and PFOA (Huang, 2017) to CO_2 and F^-, with only traces of intermediate organofluorine compounds formed. The destruction of both PFOS and PFOA by electrochemical oxidation using this Ti_4O_7 electrode sounds very promising, since conventional electrochemical oxidation has to struggle with perfluoroalkyl sulfonic acids. This was confirmed by Liang et al (2018): Using a Ti_4O_7 electrode, within 3 h 96 % PFOA and 98.9 % PFOS (starting concentration 10 mg/L each) were degraded. The degradation followed a pseudo 1st order reaction. In the mixture PFOA was degraded faster than PFOS. Obviously PFOA inhibits PFOS degradation.

▶ Schaefer et al (2015) showed that electrochemical degradation also works in groundwater contaminated with AFFF foams.

In some less successful studies, PFOA degradation took much longer (Carter and Farrell, 2008). Short-chain PFAS are only degraded with less efficacy (Merino et al., 2016).

Depending on the composition of the groundwater and the content of co-contaminants, undesirable toxic by-products are formed, such as hydrogen fluoride, chlorine gas, as well as the strong oxidizing agents bromate (BrO_3^-), perchlorate (ClO_4^-), and absorbable organic halides (AOX) via the halogenation of natural DOC. In one test up to 5.3 mg/L, AOX were formed. The amount of AOX formed did not correlate with the initial DOC concentrations (Trautmann et al. 2015, Gomez-Ruiz et al., 2017).

Outlook. The process is very energy intensive. For a reduction of 99.7 % PFAS, an energy demand of 260 kWh/m^3 is necessary (see above). This causes costs of 52 €/m^3 for the energy alone[23]. This means that the process can only be used economically for the treatment of highly contaminated concentrates, although it is still unclear whether the usually required low remediation target values can be achieved with this process alone. Presumably, post-treatment, e.g. with activated carbon, is necessary. However, due to the generation of undesirable by-products, a practical implementation of this technology cannot yet be carried out at present, as further treatment steps for the removal of the transformation products still needs to be developed. It remains questionable whether the process will then still be economical.

Currently, there are even considerations to use the electrooxidation process *in-situ* as a barrier process, for example in a control plane perpendicular to the PFAS plume. However, this will not be feasible as long as the problem of the formation of unwanted by-products is not solved.

Electrochemical Oxidation (Summary)

In electrochemical oxidation, electricity is applied to the PFAS-contaminated groundwater to be treated in a reactor. PFAS degradation is carried out either by indirect oxidation (generation of radicals at the anode, which trigger the chemical oxidation of the PFAS) or by direct electrochemical oxidation, whereby the electrooxidation takes place directly at the anode. The degradation works comparatively well. However, the process takes so much time that it can only be used as a batch process. In addition, the process is very energy intensive, so that continuous treatment of pumped groundwater is not possible for economic reasons alone.

Since numerous undesirable by-products are produced, electrochemical oxidation cannot be used at present. It is questionable whether further developments will lead to a functional and economical process.

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[23] Assumption: Costs for electricity of 0,20 €/kWh.

2.2.7.2 Electrocoagulation

Description. One of the electrochemical methods propagated is so-called electrocoagulation. By applying a current, the charge of the suspended particles is changed, allowing them to form an agglomeration[24] which can be separated. Coagulation is one of the most important physical-chemical reactions in water treatment. Ions and colloids are usually kept in solution by electrical charges. The addition of ions with opposite charges destabilizes the colloids, allowing them to coagulate. Coagulation can be achieved by a chemical coagulant or by electrical processes.

PFAS can also be removed from the solution in this way. By adding zinc (< 150 mg/L) and after applying a current (energy consumption < 0.18 kWh/m^3), zinc hydroxide flakes are formed which sorb PFAA via hydrophobic forces (Lin et al., 2015).

Supplementary studies have shown that PFOA and PFOS in the µg/L to mg/L range can be effectively separated from the aqueous solution (> 95 % removal, 20 minutes). The sorption capacity of PFOA/PFOS on the zinc hydroxide flakes was > 2 mg/g Zn. The electrokinetically produced zinc hydroxide flakes have a much higher sorption capacity and a faster sorption rate than other sorbents investigated so far, such as externally added zinc hydroxide.

In contrast to the other sorbents, zinc hydroxide flakes can be easily dissolved in acidic solution by a simple pH adjustment, so that the sorbed PFAA are released again in concentrated form in solution, where they are accessible for other destructive processes. The dissolved zinc ions can be precipitated by adding e.g. PO_4^{3-} and thus separated from PFAA.

Experiments to optimize the electrocoagulation process using the Fe-electrode resulted in the following optimal operating parameters:

- ► current density: 25 mA/cm^2,
- ► stirring speed: 180 rpm,
- ► conducting electrolyte: 2 g/L NaCl,
- ► thus > 99 % of PFOS (125 mg/L initial concentration) could be removed after 50 minutes of treatment (Yang et al., 2016).

Based on the studies described above, a three-stage treatment (*treatment train*) was designed to remove PFAA from the water and break it down: (i) electrocoagulation to separate PFAA from pumped groundwater and pre-enrichment on zinc hydroxide flocs, (ii) separation of PFAA from the flocs via pH adjustment and concentration of PFAA in a small volume of water and (iii) destruction of PFAA via electrochemical oxidation. The coagulant produced in the electrocoagulation process is highly hydrophobic and highly porous and thus not only suitable for sorption of PFAA but also for many other organic contaminants. These organic contaminants can also be effectively broken down by electrochemical oxidation (Chiang, 2018).

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[24] It is generally assumed that coagulation is primarily caused by the reduction of the net surface charge to a point where the colloidal particles, previously stabilized by electrostatic repulsion, can come close enough to the Van-der-Waals forces to allow aggregation. The reduction in surface charge is a consequence of the decrease in the repulsion potential of the electric layer due to the presence of an electrolyte with opposite charge. In the electrocoagulation process, the coagulant is produced by electrolytic oxidation of a suitable anode material. In this process, charged ionic species (PFAS) are removed from the wastewater by reacting them with metal hydroxides of opposite charge.

Outlook. At present, there are still not enough results available to be able to make a final assessment of the process. The most important question will be how effectively the process removes short-chain PFAS. A disadvantage is that the solution has a high salt content after treatment, so that the purified water cannot be easily re-filtered into the aquifer. Overall, the process (especially as a *treatment train*) does not appear to be very cost-effective. This still needs to be evaluated by further studies.

Electrocoagulation (Summary)

Electrocoagulation has so far only been investigated in the laboratory. At present, not enough results are available to be able to conclusively evaluate the method. No substantial progress is expected in the next few years.

2.3   *In-situ*-Technologies: Injection of Activated Carbon into the Aquifer

Description. The basic concept of this containment technology is that "liquid" activated carbon[25] is injected at low pressure (< 2 bar), via for example by direct push into the aquifer (Fan et al., 2017). The injected colloidal activated carbon should be evenly distributed (Regenesis, 2017). The product consists of very fine particles of activated carbon (1-2 µm), which are dispersed in water and surface-coated to make them more mobile and prevent the suspension from clumping together. Once in the subsurface, the product is intended to bind to the aquifer matrix and thus provide a sorption barrier for dissolved contaminants. The sorbed activated carbon quantities can[26] be determined by means of soil analyses (TOC/TIC before and after injection). According to the manufacturers, a PFOA/PFOS plume could thus be substantially cut off.

The product can be applied either as single or multiple barriers, which decontaminate the groundwater flowing through. It can also be used as a protective screen around individual groundwater extraction wells if the PFAS plume is so extensive that a barrier would be too expensive.

Modelling (three-dimensional reactive transport models) showed that PFAS binding is effective over decades. The modelling was mainly based on the use of sorption coefficients and did not consider displacement by DOC (Carey et al., 2019).

In a field application (but with an anaerobic aquifer of very low thickness) a radius of influence of about 5 m was achieved. Into the aquifer (780 m^2 area, 0.8 m thick), a total mass of 290 kg colloidal activated carbon was injected via 20 temporary direct-push probes with a pressure < 21.4 bar. Concentrations of PFOA (max. 3.2 µg/L) and PFOS (max. 1.45 µg/L) were reduced to a total of < 0.03 µg/L (BG), which remained constant over the entire follow-up period (18 months) (McGregor, 2018).

A laboratory attempt using a soil column to "regenerate" a PFAS-loaded granular activated carbon *in-situ* by chemical oxidation with heat-activated persulfate failed. In the experiment, PFOS showed no transformation even with an increased activated persulfate oxidant dose. Dissolved PFOA was subject to degradation, but only to shorter-chain compounds.

Sorbed PFOA was stable against oxidative attack. Persulfate treatment changed the surface polarity of the activated carbon resulting in improved sorption, making the PFAS even less available for oxidative degradation (Crimi et al., 2017).

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[25] For instance, PlumeStop® Liquid Activated Carbon™ or BOS 100. Both are colloidal suspensions.

[26] In a field example, a coal enrichment of about 0.13 g/kg soil was achieved (measured immediately after injection) (McGregor, 2018).

In other studies (Sun et al., 2016) a new route for the removal of PFOA was observed in a thermally activated PFAS degradation with persulfate in the presence of powdered activated carbon (PAC) under environmentally neutral pH conditions. Under these conditions, the removal of PFOA was attributed to chemisorption, a process in which PAC catalyzed persulfate decomposition and reacted with the transformation products to form covalently bound PFOA. At PAC concentrations between 200 and 1,000 mg/L and an initial PFOA concentration of 0.5 µM the covalent binding led to the removal of 10 – 40 % of PFOA.

Outlook. Since PFAS are not subject to biological degradation, there is no "regeneration" of the sorption medium. This means that, as soon as the total mass of activated carbon is loaded with PFAS to the sorption equilibrium, the contaminants break through and can be detected again undiminished in the barrier's outflow. As a result, enough activated carbon must be injected into the aquifer so that the time-integrated total mass expected at a barrier can be completely sorbed. Repeated dosing of the colloidal activated carbon may not solve the problem, as blocking of the aquifer then becomes increasingly probable, with the result that the PFAS-contaminated groundwater flows around the sorption area. This must then be checked in each individual case. Alternatively, it is possible to additionally inject the activated carbon further downstream to increase the length of the sorption barrier.

The question of whether higher soil-bound activated carbon concentrations can be achieved during the first injection with higher concentrations of colloidal activated carbon in the injection fluid, or whether the "surplus" is washed out with the natural groundwater flow, also remains to be examined. Groundwater samples are suitable for this purpose. If the colloidal activated carbon is moved with the flowing groundwater, it should be detectable in the groundwater sample. This should be checked at regular intervals, starting with the first injection.

A possible breakthrough will be achieved comparatively quickly for short-chain PFAS. These are first bound to the activated carbon and later displaced from their binding sites by the better binding longer-chain PFAS, presumably in higher concentrations than in the inflow to the barrier. Moreover, as with conventional activated carbon, precursors as well as shorter-chain PFAS are probably also retained less effectively (Xiao et al., 2017). However, other components of groundwater, especially the natural DOC, also sorb on the activated carbon and increasingly reduce its sorption capacity for PFAS over time. In the "worst case" the natural DOC sorbs continuously to the activated carbon (which remains in the aquifer forever) and leads to a complete desorption of the PFAS.

Finally, the binding capacity of the colloidal activated carbon is also strongly dependent on the f_{OC} content of the aquifer sediments. With increasing f_{OC}, PFAS sorption to activated carbon decreases.

In addition, as soon as the contaminant concentrations in the inflow decrease in the late lifetime phase of the contamination (due to a source remediation or the fact that the source has naturally completely eluted), desorption of the activated carbon takes place. Due to the high sorption power, the distribution equilibrium is strongly on the side of the activated carbon, so that in the water phase probably only low PFAS concentrations (possibly even below the determination limit) will be measured. Consequently, the activated carbon elutes the PFAS over very long periods of time and in low concentrations. To prove that the PFAS concentrations remain below the remediation target values, very long-term groundwater monitoring is therefore required.

Since the contaminants are not removed from the subsoil, the process has only a low sustainability.

The effectiveness of the process is also strongly dependent on the uniform distribution of the colloidal product in the regularly heterogeneous aquifer matrix (as a prerequisite for complete sorption of the PFAS in the groundwater) and, above all, on the retention of the product within the aquifer matrix. It is not always certain that the aquifer can be charged with colloidal activated carbon over the entire area. There are also reports of applications where injection into a sand/gravel aquifer has failed (Broholm et al., 2019).

After injection, the injected particles must, on the one hand, have sufficient mobility to migrate sufficiently far from the injection site and, on the other hand, the mobility must not be so high that the particles are completely washed out with the natural groundwater flow. This should be avoided by the sorption of the particles to the soil matrix after injection.

Various approaches have been discussed to avoid unwanted desorption (NGWA, 2017):

- ▶ digging out the PFAS-loaded activated carbon,
- ▶ inject strongly desorbing reagents (e.g. methanol) and pump off the highly concentrated solution,
- ▶ new injection of activated carbon downstream of the existing barrier.

Whether such solutions are advantageous must be determined in site-specific cost-benefit analyses. In summary, a much better understanding of the distribution and effectiveness of injectable particulate activated carbon for the retention of PFAS is required. This includes manufacturer-independent feasibility studies, which are currently still lacking and are therefore strongly recommended. The research needs are further detailed in Annex E.

Injection of Activated Carbon into the Aquifer (Summary)

The injection of colloidal activated carbon into the aquifer with subsequent sorption of the PFAS to the carbon is a relatively simple process. The products are commercially available on the market and are already used in practice, mostly outside Germany.

Apart from a few positive reports on experience, however, there are a number of open questions (above all regarding the full-scale supply of the aquifer with sufficient quantities of colloidal activated carbon and the time-dependent behavior of the sorbed PFAS) which would have to be answered in order to increase the approvability of the process and to be able to use it as a sustainable solution.

2.4 Additional Technologies

2.4.1 Overview

In addition to the procedures discussed in the previous chapters, there are several more or less intensively investigated technologies for decontaminating the water phase, which are, however, mostly at the beginning of development. Of these, only the foam fractionation technology is designed to be applied *in-situ:*

- ▶ microbial degradation with fungal enzymes,
- ▶ photolysis,
- ▶ plasma irradiation,
- ▶ electron beam process (eBeam),
- ▶ In-situ foam fractionation.

For purposes of completeness, these technologies are briefly described below.

2.4.2   Microbial Degradation with Fungal Enzymes

Description. The considerations are based on the fact that fungi form lignolytic (wood-decomposing) enzymes under aerobic conditions, which initiate the decomposition of substances via the formation of non-specific radicals and should thus be able to decompose perfluorinated compounds. Therefore, corresponding fungi were investigated for their PFAS degradation potential (Wang et al., 2014, Tseng, 2014). It could be shown that PFOA is converted by fungi. Treatment with the enzyme horseradish peroxidase showed a 30 % reduction of PFOA concentrations with a phenolic co-substrate. Short-chain compounds were formed as products (Colosi et al., 2009).

Using 1-hydroxybenzotriazole as primary substrate, the oxidation enzyme laccase transformed PFOA to partially fluorinated shorter-chain alcohols and aldehydes (1st order reaction) under idealized laboratory conditions in 157 days. Short-chain PFAS were not detectable. About 28 % of the fluoride was released, which corresponds to a mineralization rate of the same level (Luo et al., 2015).

Biotransformation of 6:2-FTOH over 28 days by a white rot fungus (*Phanerochaete chrysosporium*) resulted in a mixture of 5:3-fluortelomeric acid, PFPeA and PFHxA as the main transformation products (Tseng et al., 2014). 6:2-FTOH was transformed only about 50 % during this period, no further transformation seems to occur. A degradation of PFSA like PFOS has not been observed so far.

Since such fungi do not occur in the aquifer, attempts were made to produce the degradation enzymes with genetically modified cell lines and then encapsulate them in organic protein capsules of about 100 nm in size. These capsules ensure that the enzymes are protected against rapid degradation and thus make them more durable. However, successful PFAS degradation has not yet been achieved (Mahendra et al., 2016).

Outlook. For a practical application, the technology of degradation with the help of enzymes is not suitable for ex-situ processes, the achievable degradation rates are far too low. For an in-situ application the addition of co-substrates would be necessary. Wood is usually used for this purpose (soluble chemical analogues are themselves contaminants), which can at best be incorporated into upper soil areas. Short-chain PFAS are then formed during the long periods of decomposition, which are more mobile and can be more easily washed out into the groundwater. A complete mineralization of the entire mass of contaminants has not been proven.

Furthermore, PFSA cannot be degraded. Also, the attempt to integrate the degradation enzymes in shells and thus protect them was not successful.

Nevertheless, white rot fungi continue to be intensively investigated regarding their decontamination performance (Gao et al., 2010). In principle, there seems to be a potential to overcome the PFAS-specific challenges. However, the development of a rapid, practicable, cost-effective fungal treatment technology for commercial PFAS remediation projects is not expected in the foreseeable future.

| Microbial Degradation with Fungal Enzymes (Summary) |
| --- |
| PFAS degradation by fungal enzymes is incomplete and too slow. The process is therefore currently not suitable for the remediation of PFAS contamination. |

2.4.3 Photolysis

Description. In photolysis, the groundwater is irradiated with high-energy light (UV). As a rule, mediators are required with the help of which hydrated electrons (e_{aq}^-) (Qu et al., 2010b) or radicals can be formed. The highly reactive electrons lead to an oxidation of the PFAS and in the best case to a mineralization to CO_2 and release of F^-.

Photolysis has probably only been investigated in the laboratory until now. It has been proven that PFOA can be degraded with iodide as a mediator. Short-chain compounds such as PFHpA, PFHxA, PFPeA, PFBA as well as pentafluoropropione acid and trifluoroacetic acid were detected as intermediates. With an increase in temperature from 20 °C to 40 °C in the reaction solution, the degradation of PFOA also increased (from 48 % to 81 %, both according to 6 h; Zhang et al., 2016). CO_2 and F^- were detected as end products. The use of H_2O_2 as a mediator proved to be less effective (Hori et al., 2004). In another study In_2O_3, Ga_2O_3 and TiO_2 were used as mediators. PFOA (100 %) was best reduced with In_2O_3 (t ½ = 0.16 Min). Natural organic material reduces the effectiveness of photolysis (Xu et al., 2017). On the other hand, there are also indications that the photolysis of humic and fulvic acids in natural waters leads to the formation of hydrated electrons, which should promote PFAS degradation.

Since the methods discussed above always require very rigid reaction environments, it was investigated whether photolysis is also possible with milder agents and at low PFOA concentrations (as found at contaminated sites). After irradiation with two wavelengths (185 nm and 254 nm) PFOA was almost completely degraded in 4 h. Since degradation occurs according to a 1st order reaction, degradation rates are also lower at low PFOA concentrations. Formic and acetic acid have been identified as products (Giri et al., 2011).
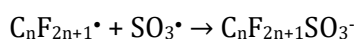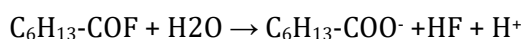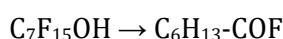
In addition, metabolites can be short chain perfluoroalkane carboxylic acids down to C_1 acids. Other metabolites were CF_3H and C_2F_6 in low concentrations. In an anaerobic system ($UV-SO_3^{2-}-N_2$) the degradation mechanism shown in the Figure 21 was postulated.

Figure 22   Postulated PFAS degradation mechanism (photolysis)
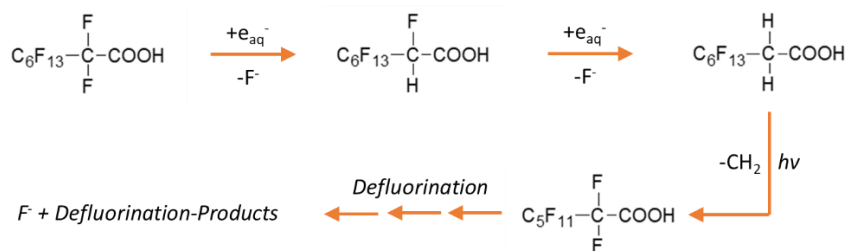
Source: Songa et al., 2013

The formation of hydrated electrons plays the central role in this process: $SO_3^{2-} + h\nu \rightarrow SO_3^{\bullet-} + e_{aq}^-$ (Songa et al., 2013). This leads to a direct cleavage of the C-F bond after attack by the nucleophilic hydrated electron with subsequent CH_2-elimination. Perfluorinated sulfonic acids of different chain lengths can also be formed as by-products in this reaction system, but these can be broken down again in the further course of the reaction:

$C_7F_{15}COOH + h\nu \rightarrow C_7F_{15}{}^\bullet + {}^\bullet COOH$

$C_7F_{15}{}^\bullet + H_2O \rightarrow C_7F_{15}OH + H^\bullet$

$C_7F_{15}OH \rightarrow C_6H_{13}-COF$

$C_6H_{13}-COF + H2O \rightarrow C_6H_{13}-COO^- + HF + H^+$

$C_nF_{2n+1}{}^\bullet + SO_3{}^\bullet \rightarrow C_nF_{2n+1}SO_3^-$
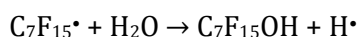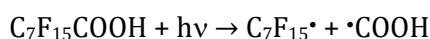
Furthermore, C_8HF_{17} and $C_8F_{17}OH$ compounds which were shorter by one CF_2 group were also detected. Hence, it was assumed that stepwise CF_2 cleavage is possible (Yamato et al., 2007).

In a comprehensive study with 34 PFAS compounds and UV-generated hydrated electrons, PFCA with chain lengths from 2 to 10 were degraded at a similar rate. The degradation of FTOH and PFSA showed a dependence on the length of the fluoroalkyl chain (Bentel et al., 2019). This was confirmed by Taniyasu et al. (2013). According to this, shorter-chain compounds are significantly less degradable by photolysis than long-chain, and perfluoroalkyl sulfonic acids are less degradable than perfluoroalkyl carbonic acids. Precursors are also degradable.

PFCA can be degraded in two ways when reacting with e_{aq}^-. Besides the above described way of shortening the PFAS chain, a repeated F → H exchange at the α-position can lead to the poorly degradable compound $C_{n-1}F_{2n-1}CH_2COO^-$. If the perfluorinated carbon chain is sufficiently long, additional F-atoms can also be split off from the middle CF_2-groups (Bentel et al., 2019).

In the anaerobic system (UV-SO_3^{2-}-N_2) the degradation of PFOA was complete within one hour, but only after 24 h 88.5 % of fluoride was released.

Like all radical reactions, photolysis is highly sensitive to increased concentrations of radical scavengers such as bicarbonate.

Outlook. The investigation of photolysis has so far concentrated mainly on laboratory experiments. The treatment time for a complete mineralization with release of all organically bound fluoride is in the range of several hours. This requires a high energy demand and rigid reaction conditions. This means that the process can be applied to aqueous PFAS concentrates at best. But even after removal of the PFAS, the water phase cannot be disposed of without further treatment steps. All in all, photolysis could be more expensive than the thermal disposal of concentrates. In this case the process would be uneconomical.

Photolysis has been investigated several times in the past for other compounds on a pilot and technical scale.

Photolysis (Summary)

Photolysis has already been investigated in the past for other contaminants, some of which are difficult to degrade. So far it has not become generally accepted, mainly because of technical problems (contamination of the UV lamps) and the incompleteness of the reactions, which made a post-treatment with activated carbon necessary. The long treatment time of several hours plays a major role in the PFAS remediation. Therefore, the process cannot be used for the continuous purification of water streams generated by P&T. Other processes are more successful for the batch approach. It can be assumed that the photolysis of PFAS will not reach market maturity.

2.4.4 Plasma Radiation

Description. The degradation of PFAS (especially PFOA and PFOS) at low initial concentrations in water (< 1 µg/L) is achieved by irradiation with a non-thermal atmospheric plasma[27]. The plasma is generated from air. Laboratory tests have shown that a 3-5-minute treatment of the water samples resulted in a decrease of the PFOA/PFOS concentration by a maximum of 90 %. It is assumed that mainly the hydrated electrons formed in the plasma are responsible for the PFAS degradation.

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[27] A plasma is a fully or partially ionized gas made up of electrons, ions, free radicals, and neutral species.

The efficiency of the process depends very much on the selected reactor nozzle geometry (sizes of the plasma nozzle in relation to the reactor size). During the treatment time, the pH decreases rapidly from neutral values to final values of pH 2.3 - 2.6. This is most likely the reason why PFAS degradation comes to a standstill after a short time in the reactor and remains incomplete (Jovicic et al., 2018).

Outlook. In principle, it should be possible to neutralize the adverse pH value effect by regulating the pH value in the reactor. Because of the speed of the reaction, pH regulation is likely to be a demanding process. At present, too few results are available to assess whether the process is ultimately economically viable. However, if complete destruction of the PFAS can be demonstrated (which is not yet the case), the process could at least be sustainable and permanently remove the contaminants from the environment.

Plasma Radiation (Summary)

Plasma irradiation has only been studied infrequently and only on a laboratory scale. PFAS degradation remains incomplete. It can be assumed that this process will not reach market maturity, at least in the medium term.

2.4.5   Electron-Beam Radiation

Description. The irradiation of synthetic wastewater with a high-energy electron beam[28] (generated by a linear accelerator[29]) in a laboratory experiment under oxygen-free conditions (eBeam) led to a degradation of PFOA. The process can quickly generate high temperatures (> 400 °C) and lead to the formation of three primary reactive species: Hydrated electrons, strongly reducing hydrogen radicals and strongly oxidizing hydroxyl radicals.

This leads to a combined reduction and oxidation process without the addition of chemicals involved in the destruction of PFOA. The absolute concentration of radicals formed during irradiation depends on the dose and water quality. The higher the absorbed dose[30] (dose rate), the higher the degradation rate, total degradation, and concentration of free fluoride. From experimental data, a model with a postulated formation of partially defluorinated intermediates was developed. According to this model, the degradation of PFOA takes place in a two-step mechanism (Figure 23). In a first step, the formation of two different intermediates (I_1, I_2) in different fractions is possible. While I_2 acts as a stable final product, I_1 is completely de-fluorinated.

Figure 23   PFOA degradation model
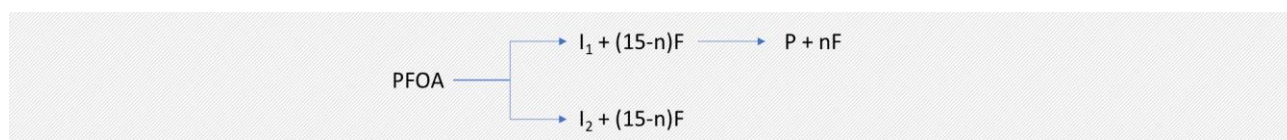
Source: Wang et al., 2016

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28 Non-radioactive

29 10 MeV, 18 kW Electron beam linear accelerator (LINAC).

30 The amount of energy from eBeam that is absorbed by an irradiated material per unit of mass is called the dose.

PFOA degradation is probably the result of a reaction with reducing radicals generated by eBeam irradiation, such as for instance hydrogenated electrons (e_{aq}^-) and H. With increasing nitrate concentrations, the degradation of PFOA also increases. This is probably because nitrate is an e_{aq}^--scavenger and leads to the formation of the nitrate radical ($NO_3^{2-}\cdot$), which effectively breaks down PFOA.

Higher alkalinity also increases PFOA degradation. This is probably accompanied by the formation of the carbonate radical ($CO_3^{-\cdot}$). This is an oxidant and could react with the PFOA anion. Although bicarbonate/carbonate also reacts with e_{aq}^-, the reaction is much slower than with $OH^\cdot$. In the presence of oxygen, PFOA was degraded less efficiently and showed more complex degradation patterns, probably due to scavenging of the radicals e_{aq}^- and $H^\cdot$ required for the reaction. A similar scavenging effect is probably caused by the natural DOC (fulvic acid). A pre-treatment to remove dissolved oxygen would probably be necessary to use eBeam in practice for the degradation of PFOA and other PFAS (Wang et al., 2016).

Outlook. In principle, the technology is mature and is used worldwide amongst others for the pasteurization of food, the sterilization of medical equipment or the remediation of organic compounds in water (EPA, 1997). However, knowledge of PFAS degradation is currently still very limited. The degradation was investigated in synthetic treated wastewater. The question arises to what extent other water constituents influence the reaction. Furthermore, the method´s efficacy to degrade other compounds, especially perfluoroalkane sulfonic acids and short-chain compounds, is still unclear.

Electron-Beam Radiation (Summary)
Although the process is already being used on a technical scale in other areas, the data available on PFAS degradation is too limited to assess whether this process can be developed into a marketable technology.

2.4.6   *In Situ* Foam Fractionation

Description. With the so-called *Downhole Foam Fractionation System,* the PFAS are to be removed by foaming in specially designed groundwater wells. The wells can be positioned at strategic points of the contaminated aquifer, for example.

Many surfactant-reacting PFAS compounds have a natural tendency to foam or accumulate at the gas-water interface. The remediation technology concept exploits this property of rapid foaming. Compressed air is injected through a diffuser at the bottom of the well. The ascending bubble column acts as a mammoth pump and generates an upward flow of groundwater. As a result, groundwater is drawn into the well at the bottom and flows out again at the upper edge of the well. A radially circulating groundwater flow is created in the aquifer according to the principle of groundwater circulation wells. The diffuser for air injection is selected in a way that optimally sized bubbles are created that rise through the water column in the well. The dense bubble column and the large surface area of the bubble interfaces generate a water movement in the well and provide a strong attraction surface for PFAS in the solution. They are thus quickly removed from the groundwater and transported to the upper part of the water column. The foam that forms at the well head is highly enriched in PFAS and co-contaminants and, before collapsing again, can be optimally collected, sucked off and discharged into a centralized collection tank by using a specially designed patented extraction head. The foam extraction head is variable in height and automatically adjusted according to the site requirements (Figure 24). The PFAS foam is concentrated in further process steps until only a PFAS hyper-concentrate remains for disposal (OPEC-Systems, 2018a,b). So far, this process is only a concept, it has not yet been tested in the field according to current author's knowledge.

Figure 24   Principle of the in situ-foam fractionation technology
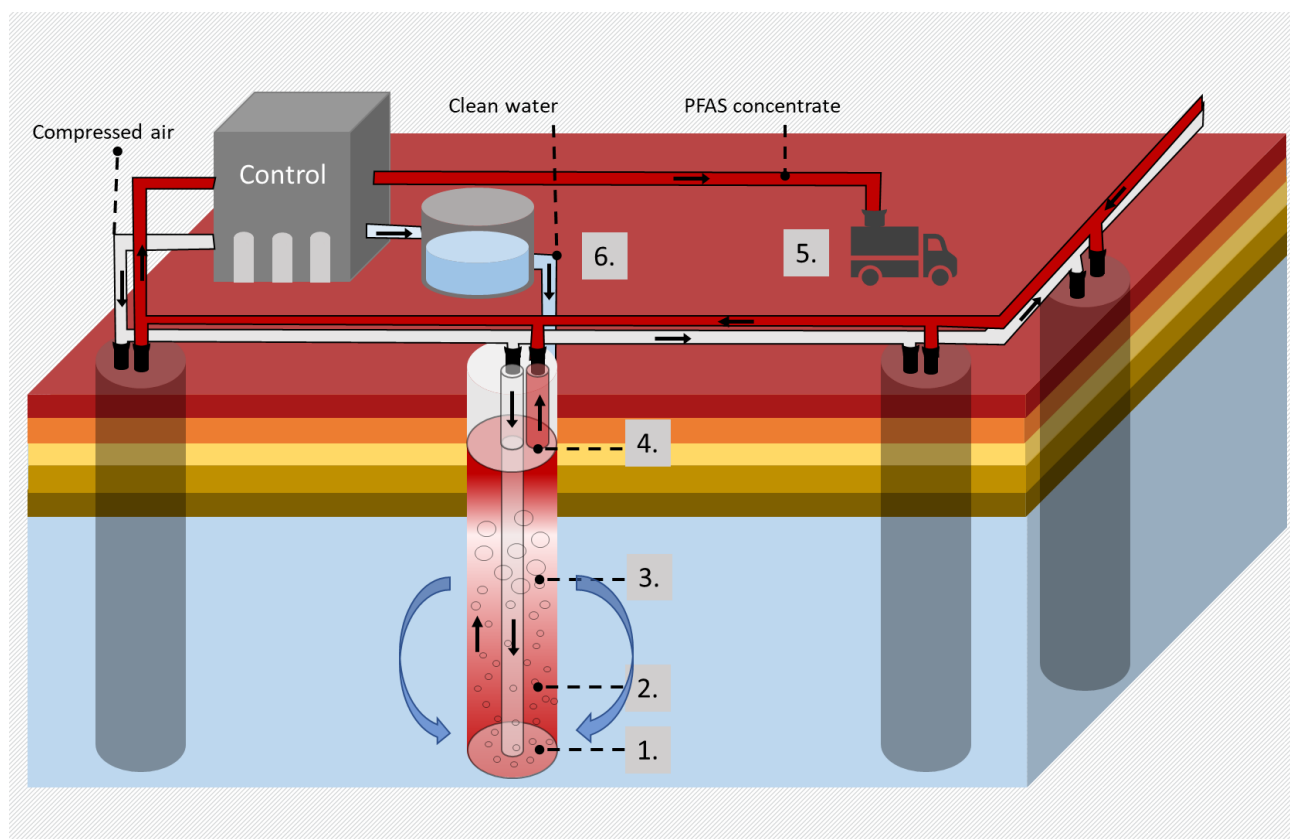
1: Compressed air is introduced at the base of the well. 2: PFAS foams out of the ground water, 3: Air bubbles carry the foam to the surface. 4: Foam is extracted by a special device and pumped to the plant where further concentration takes place. 5: Concentrated PFAS solution is removed for complete external degradation, 6: Purified water is pumped back into the aquifer. Source: OPEC-Systems, 2018a

The effectiveness of this process depends on the hydraulic permeability of the aquifer, the size of the induced water/foam interface above the static groundwater level and the effectiveness of the groundwater circulation. The concept is similar to ozofractionation (Chapter 0), but is carried out *in-situ.*

The general feasibility of PFAS removal from a water column (of what in the field would be the well) could be demonstrated on a bench-scale. A wide range of PFAS compounds (including PFOS, PFOA, PFHxS and 6:2FTS) in high concentrations (> 400 µg/L) was almost completely removed from the water column within a few minutes.

Outlook. The process is already offered (OPEC system, Australia), but there is neither any verification of its technological concept nor is any independent review available. Major limitations could be the effectiveness of the groundwater circulation and the achievable radius of influence. The basis of the procedure is that the cleaned groundwater, which is re-injected into the aquifer at the well head, is reloaded after dissolution/desorption processes with contaminants and returns to the well at its bottom. Short-circuit groundwater flow and insufficient influence radii would greatly limit the groundwater circulation process (Allmon, 1999).

Furthermore, the effectiveness of the foam extraction head is of decisive importance. If the foam extraction at the well head were incomplete, the PFAS foam would be distributed radially around the well at the groundwater surface.

The use of compressed air can lead to rapid biomass formation in the well itself if aerobically degradable compounds, such as non-fluorinated surfactants from fire extinguishing foams, are present. If reduced Fe/Mn compounds are present in the aquifer, they will also precipitate in the well under aerobic conditions. Such blocking reactions have the potential to stop the groundwater circulation within a few days/weeks. One possible option would be to seal the well against the atmosphere and initiate foaming with an inert gas (e.g. nitrogen). The nitrogen could be circulated in a closed system. However, a certain proportion of the gas dissolves in the groundwater, so that it must be continuously replenished. In general, the process seems to have a certain potential after appropriate adjustments. However, independent tests are still missing.

In situ Foam Fractionation (Summary)

The process of in-situ foam fractionation is based on the principle of groundwater circulation wells, whereby the groundwater circulation is kept going by a mammoth pump (injection of air bubbles at the bottom of the wells). From the groundwater flowing into these wells, the PFAS are removed by foaming and accumulating at the gas-water interfaces with subsequent accumulation at the wellhead. There the foam is removed, thickened, and further treated. Although the removal of the PFAS from the water column works as could be shown, the in-situ approach is currently only developed at the conceptual level.

There are still many unanswered questions in this process, especially regarding the effectiveness of groundwater circulation. It is therefore unlikely that this method will be ready for the market in the near future.

3 Technologies for Soil Remediation

3.1 Excavation and Landfill

Description. All soil treatment technologies discussed below are based on initial soil excavation and subsequent ex-situ "treatment". The methods of soil excavation do not differ from the excavation of classical contaminants, so excavation will not be discussed in further detail.

The simplest form of "treatment" is landfilling. Presumably there will be no nationwide uniform requirements (PFAS concentration values) for landfilling in the future. This means that within the framework of individual case decisions, it must be examined whether and to which degree of contamination the landfills accept PFAS-contaminated soil. Further details can be found in the main part of this guideline.

> **Excavation and Landfill (Summary)**
>
> The excavation of PFAS-contaminated soil and subsequent landfilling is a standard procedure in the remediation of contaminated sites or in the case of local contamination. The problem is that many landfills do not have adequate leachate treatment facilities and therefore do not accept the contaminated soil.

3.2 Technologies for the Treatment of Excavated Soil

3.2.1 High Temperature Incineration

Description. High-temperature combustion usually takes place in a reactor. The PFAS are transferred from the soil into the gas phase and destroyed directly in the reactor at a sufficiently high temperature. Alternatively, the PFAS are transferred to the gas phase at about 600 °C. The gas phase can be discharged and the PFAS are destroyed in a waste gas reactor at a significantly higher temperature (Chapter 3.2.2).

For high temperature combustion, temperatures > 1,100 °C and 2 seconds contact time are required. Under these conditions PFAS are evidently completely thermolytic destroyed (Yamada et al., 2005). It has been shown that thermolysis (here of PFOA) occurs at very different rates depending on the concentration of the contaminant and the physical and chemical environment. Thermolysis probably begins with the following reaction (Krusic et al., 2005):

$$CF_3(CF_2)_4CF_2CF_2COONa \rightarrow CF_3(CF_2)_4CF=CF_2 + CO_2 + NaF$$

The sulphonic acid group is mainly emitted as SO_2. At lower temperatures, a release of C_1- and C_2-fluoroalkanane compounds (CHF_3, CF_4, C_2F_6) and difluoroethene takes place. Higher molecular weight fluorinated PAHs were not formed (Yamada and Taylor, 2003).

The investigation of the thermal regeneration of activated carbon loaded with PFOA, PFHxA and PFOS showed that at a temperature of 700 °C, 13.2 % of the PFOA was still detectable as volatile organic fluorine (VOF); for PFHxA it was 4.8 % VOF and for PFOS 5.9 % VOF. If the temperature in the exhaust gas was increase to 1,000 °C, the VOF decreased to 0.1%. The activated carbon was PFAS-free at temperatures of 700 °C and above. In the temperature range 800 - 900 °C short-chain PFAS were detected in low concentrations in the exhaust gas scrubbing water.
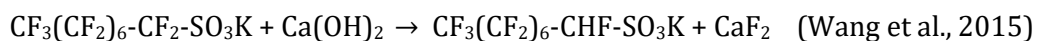
The mass balance (Figure 25) showed an almost complete conversion to fluoride for PFOA at a furnace temperature of 1,000 °C. For PFHxA and PFOS, the conversion rate was higher, even at lower temperatures.

Figure 25   Mass balance of thermal treatment of PFOA in an N_2 stream
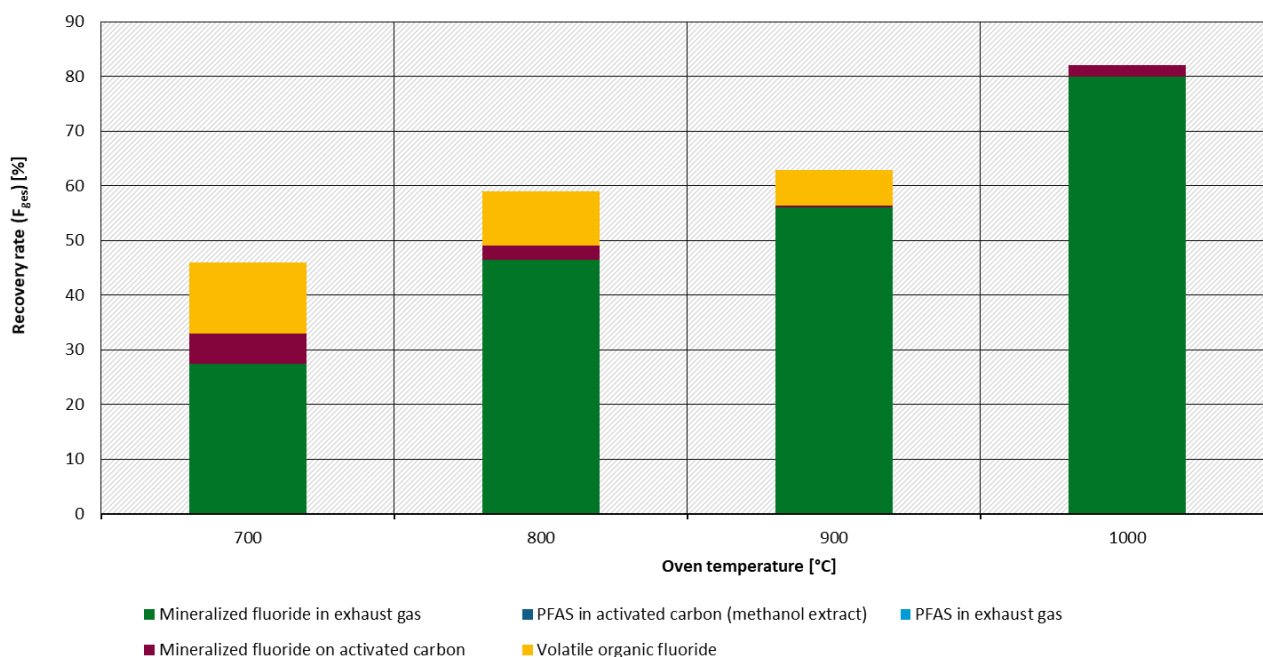
Source: Watanabe et al., 2016

Oxidative thermal processes under oxygen supply have a higher mineralization capacity than the anaerobic process under investigation (Watanabe et al., 2016). Dioxins and furans are not formed at such high temperatures either.

The addition of inexpensive calcium compounds (e.g. $Ca(OH)_2$) to the soil leads to a thermal reaction between PFOS and $Ca(OH)_2$ already at lower temperatures and thus to a mineralization of the PFAS to CaF_2 which reduces the formation of gaseous PFAS:

$$CF_3(CF_2)_6\text{-}CF_2\text{-}SO_3K + Ca(OH)_2 \ \rightarrow \ CF_3(CF_2)_6\text{-}CHF\text{-}SO_3K + CaF_2 \quad \text{(Wang et al., 2015)}$$

Outlook. With the available investigations, it has been shown that the desorption of PFAS from activated carbon is complete at temperatures of 700 °C and that complete mineralization is also possible at the temperature of 1,100 °C which is usually used for the thermal treatment of soils. Harmful by-products are not formed. Therefore, the process is well applicable, but has a high energy demand, is expensive and therefore only suitable for relatively small amounts of soil. It can be assumed, although not explicitly investigated, that PFAS precursors and non-precursor sare completely destroyed in the same way. The treated soil is then present as slag and no longer has any soil functions.

High Temperature Incineration (Summary)

Ex-situ high-temperature combustion has long been used for classical contaminants on a technical scale and can also be used for PFAS-contaminated soils. It is state of the art. Due to the high costs of the process, it is only applied to very highly contaminated soils. Accordingly, there are relatively few suppliers.

3.2.2 Thermal Desorption (TD)

Description. In contrast to high-temperature combustion, the thermal desorption process aims at de-sorbing the PFAS at a lower temperature in the rotary kiln and treating the resulting PFAS-contaminated exhaust gas at a high temperature for pyrolysis of the PFAS (Endpoint Consulting 2016, Enviropacific 2017, Nolan et al., 2015). The advantage over high-temperature combustion is that no slag is produced, but rather usable purified soil.

In thermal desorption, the excavated soil is heated to about 500 - 600 °C in large ex-situ treatment plants by introducing steam. A maximum temperature of 950 °C is possible. The desorbed PFAS are then destroyed by catalytic oxidation in the afterburner at > 1,000 °C (Figure 26).

Figure 26   Structure of the patented „VEG Vapor Generator "
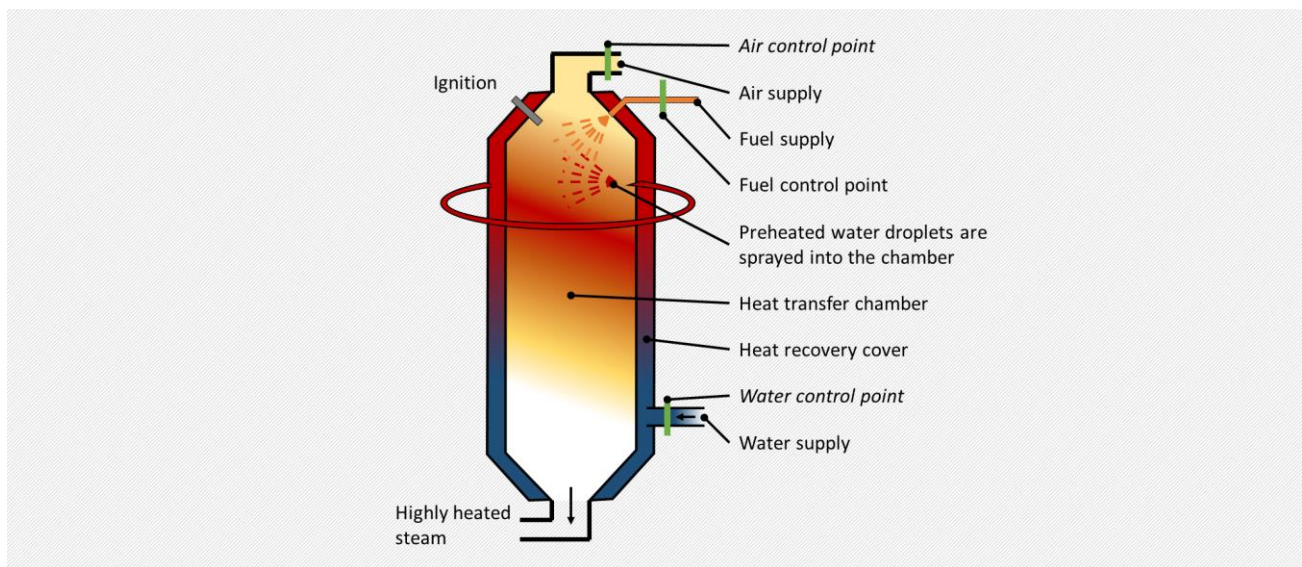
Source: Endpoint Consulting, 2016

Figure 27   Results of the thermal desorption at 590 °C and 950 °C
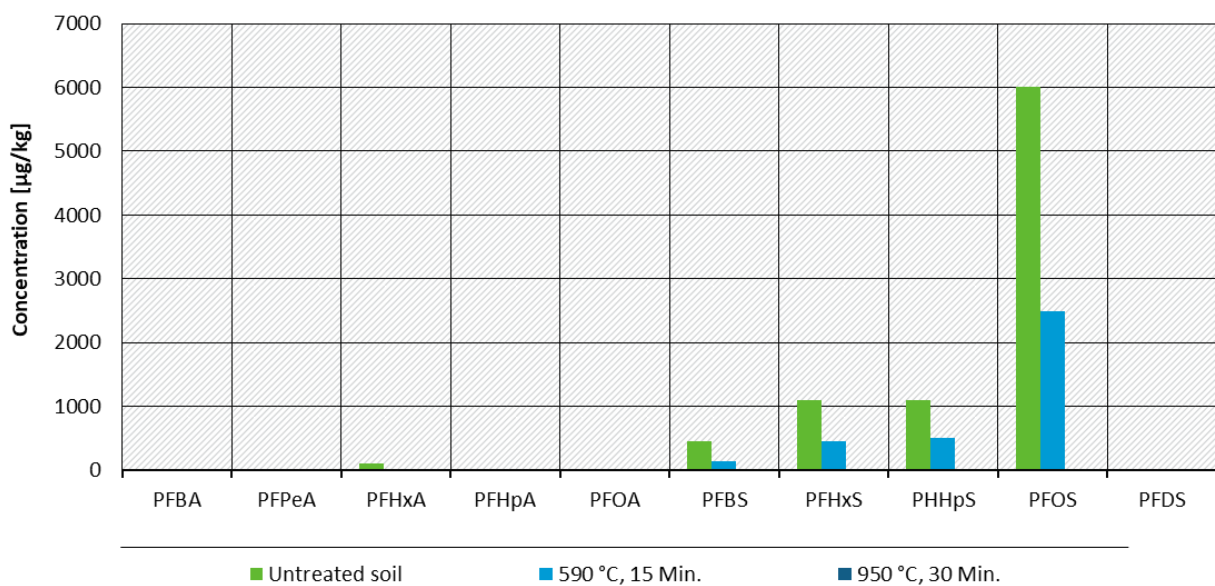
Source: Endpoint Consulting, 2016

In laboratory scale tests, three approaches were run at different temperatures (480 °C, 15 min, 590 °C, 15 min and 950 °C, 30 min). At the medium temperature, about 60 % of the PFAS were desorbed, whereas at the higher temperature > 99 % were desorbed. The optimum temperature is probably > 600 °C and the treatment time > 15 minutes (Figure 27).

In a pilot test, nine PFAS compounds were completely removed within 30 minutes. However, this required relatively high temperatures (> 954 °C) (Endpoint Consulting, 2016).

In another pilot project the concentrations of 20 PFAS compounds in the soil were reduced to the limit of quantification, corresponding to 99.9 % degradation (Enviropacific 2017). It is not known whether the pilot test led to a complete destruction of the PFAS, it was carried out at relatively lower temperatures (approx. 450 °C). The question of whether the process only mobilizes or destroys the PFAS has yet to be substantiated by material balances. Typical throughput rates are around 200 m^3/d (depending on the residence time required by the soil).

Recently, another process has been launched on the market that removes PFAS at higher temperatures in a vacuum (VacuDry®) (Econindustries, 2018).

Outlook. A few questions are still open regarding this technology, such as the behavior of short-chain PFAS or precursors in the remediation process. However, it can be assumed that there will be no restrictions on the feasibility of the technology in this respect. Furthermore, there is a lack of data to evaluate the economic viability of the process (even for different contaminated soil types). There should be no restrictions on the eligibility for approval of this technology. In the end, however, the costs of the process will probably be significantly higher than the costs for landfilling. The competitiveness of the technology will presumably only increase when no more landfill space is available. Advantages are likely to be found in the treatment of higher contaminated soils that can no longer be deposited in a comparatively simple way. The advantage that soil and no slag is left over will probably only be accepted if the process is cheaper or at best the same price as conventional high-temperature thermal treatment.

> **Thermal Desorption (Summary)**
>
> In thermal desorption, the PFAS move to the gas phase at a moderately high temperature. This gas is drawn off and further heated for complete thermal destruction of the PFAS. The advantage over high-temperature incineration is that soil and no slag remain at the end. The process is already offered for practical application. However, no data are available to evaluate the feasibility and economic viability of the technology. Due to the significantly longer treatment time compared to high-temperature incineration, it can be assumed that it is more expensive than the competitive technology.

3.2.3 Soil Washing

Description. Soil washing serves to remove the PFAS or the highly contaminated fine grain fraction from the rest of the sand fraction. Due to the very large surfaces of the fine grains in the soil in relation to their volume, the main remediation performance consists in the separation of the larger, only minor contaminated soil components from a smaller, highly contaminated fine grain fraction (grain size classification). An additional cleaning effect is achieved by transferring the contaminants into the process water, from which they are removed with downstream treatment technology.

Soil washing with water as a flushing medium is primarily a physical process, with chemical processes only being of secondary importance. During the separation process, the purified soil and a residual material with the concentrated contaminants are produced. While the purified soil is intended to be used as backfill material, the contaminant fraction must be disposed of as hazardous waste at high

costs. It can either be deposited in landfills or thermally treated. Without a closed concept for the treatment or disposal/recycling of residual materials, soil washing processes cannot be used effectively (LfU, 1993).

The contaminated soil is first excavated and temporarily stored. Then a pre-treatment is carried out, e.g. in the form of crushing and/or separation of non-soil materials (e.g. iron, plastic). The soil is then slurried with water. If necessary, additives such as surfactants can be added to the water. However, this makes the treatment of the process water more difficult. It should also be noted that some surfactants have the opposite effect and increase the sorption of the PFAS by binding to the soil matrix and thus increasing the fraction of soil organic carbon (f_{OC}), which serves for PFAS sorption (Pan et al., 2009). The selection of the suitable surfactant is therefore of great importance.

Energy is supplied to the system to separate the contaminants from the soil particles. The resulting acceleration, shear, and friction forces cause the contaminants to pass more and more into the washing liquid. It is also possible that the contaminants are transferred from the coarse to the fine grain. Furthermore, it is conceivable that special chemicals could be added to accelerate the desorption of the PFAS from the soil matrix.

For example, the addition of oxalate increased PFOS desorption by a factor of 1.4 to 17 and significantly increased the release of dissolved organic carbon and inorganic ions from the soils investigated. The effects of root exudates were similar to those of oxalate. The addition of low molecular weight dissolved organic carbon caused a partial dissolution of the soil structure (e.g. by formation of organo-mineral complexes), which resulted in the release of organic carbon and metal ions and subsequently increased PFOS desorption. The effects of oxalate on PFOS desorption were influenced by the content of dissolved organic carbon and the formation of calcium oxalate (Tang et al., 2017). However, oxalate can have a negative effect on PFAS sorption on activated carbon and must ultimately be removed from the water solution (for example by microbial degradation).

In the next step of the soil washing process, separation into the batches (i) coarse grain, (ii) fine grain and (iii) process water takes place. Both soil batches are dewatered. The cleaned coarse soil is separated by sieving. Furthermore, a separation of the particulate contaminants from the wash water follows, e.g. by sieving, density separation or flotation. The wash water is then cleaned usually using PFAS sorption on activated carbon and the cleaned water is returned to the process cycle. As an option, it would be conceivable to pre-clean the wash water with PerfluorAd®, for example. The separated particulate contaminants and the highly contaminated fine fraction are solidified. Finally, the cleaned soil is reinstalled or otherwise recycled.

Mobile plants of the suppliers of the remediation process on a technical scale[31] have a throughput of 20 - 50 t/h (power supply: 400 KVA). The process water is circulated. A clay filter cake is produced as a residue concentrate. An alternative plant has a throughput of 20 - 40 t/h (240 kW). If the plant is operated continuously at full capacity, the washing of 1 t soil consumes 6 - 12 kWh. This corresponds to a CO_2 emission of 1.2 - 2.4 kg CO_2/t. The energy costs are correspondingly high. In 2018 the first soil washing on a technical scale started in Southern Germany with a mobile plant (throughput approx. 180 t soil/h). The water throughput is 350 m^3/h, whereby the water is circulated. The water treatment contains the steps: flocculation, sedimentation, filtration, sorption on activated carbon, sludge treatment, chamber filter press (Edel et al., 2018). Operating data are not yet available.

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[31] All data are company data.

Outlook. Early experiments with soil washing on a laboratory/ pilot plant scale have already been quite successful (Arcadis, 2018). However, it is still open how soil washing affects cationic and zwitterionic precursors. In any case, planning a soil wash requires the performance of preliminary tests (test washes), in which all open questions can be investigated.

In principle, the process is economical if soils with a low fine grain content (< 20 % of the fraction < 0.063 mm) and low f_{OC} are treated. Since the soil absorbs water during the washing, the mass of the fines to be disposed of is about twice as high as the fines determined in the original soil. The amount of the highly contaminated fines to be disposed of is a decisive factor in the total costs of the entire soil washing process. The disposal costs determine to a large extent up to which fine grain proportion of the contaminated soil that soil washing may still be considered to be economical.

PFAS are more difficult to elute if the f_{OC} is high. This also applies to soils that are predominantly contaminated with longer-chain PFAS that are more difficult to elute.

Soil washing can be done *off-site* (useful for small soil volumes) or *on-site* with a mobile unit. Due to the comparatively high costs for the mobilization/demobilization of the soil washing and water treatment plant, an *on-site process* is only cost-effective when treating correspondingly large soil masses.

Soil washing only makes sense if the cleaned soil has such low residual contamination that it can be recycled without additional costs. This is in Germany the case, for example, if the decontaminated soils have a maximum residual contamination in accordance with the respective allocation values (Z values; Appendix B). The washed soil could then be sent for recycling. If the washed soil had to be deposited in a landfill, the process would presumably be cost-inefficient.

The estimated costs for soil washing are in the range of the costs for landfilling and thus in a range that makes the soil washing competitive. Only when reliable operational data, including a corresponding remediation success on a technical scale, are available can the economic efficiency of this process be assessed. It is expected that the economic efficiency for defined contamination cases can be achieved.

Soil Washing (Summary)

Soil washing is a process that is already available on the market on a technical scale. The success and economic efficiency of soil washing depends on the fraction of soil organic carbon (f_{OC}) and fines content of the soil to be washed. Only if the conditions are favorable and the washed soil can be reused free of charge, soil washing is competitive for local contaminations. For economic and ecological reasons, the use of soil washing in the case of extensive contamination is not yet a viable option. Future efforts will focus on improving the applicability of the process for higher f_{OC} and fine grain content.

3.3   *In-situ*-Technologies for Soil Treatment

3.3.1   Solidification/Stabilization

Description. The S/S process (*solidification/stabilization*) involves mixing cementitious binder and/or additives into the contaminated soil matrix. This is done either *in-situ* or *ex-situ*, and aims to reduce elution of the contaminants from the soil by

► physical protection (solidification of the matrix, which reduces the hydraulic conductivity and reduces the exposure of contaminants to leaching)

► chemical protection (stabilization of contaminants by reducing their solubility in water: precipitation, change in oxidation state or sorption).

Immobilization of PFAS refers to the mixing of reagents into the unsaturated soil with the goal of reducing the mobility of PFAS to such an extent that the source/receptor pathway soil → groundwater is no longer relevant (ITRC, 2011). The methods of immobilization are usually sorption. Reagents for sorption include

► activated carbon (granular or powdered) with amorphous AlOH and kaolinite (for example Rembind-Plus) or similar products,

► modified organic clays (for example Fluoro-Sorb, CETCO),

► carbon nanotubes[32] (Kwadijk et al., 2013, Bei et al., 2014),

► ion exchanger,

► minerals.

It is also possible to consolidate the contaminated soil by adding reagents to form low-permeability monoliths in which only the outer surface is exposed to the seeping precipitation water. This significantly reduces the leaching of contaminants. The consolidation process requires a reagent that allows geotechnical stability to be achieved. Nevertheless, additives are necessary to achieve the binding of the contaminants. Initial tests have shown that consolidation with cement alone (5 %) can lead to a complete reduction in PFAS elution (Arcadis, 2018).

In most technologies, both processes (sorption and solidification) are used jointly. The field of solidification/stabilization is highly dynamic at the time of writing this guideline. New products are coming onto the market on a regular basis. The following explanations can therefore only shed light on a small section of the numerous products.

The products for immobilization are applied by mixing near the surface soil with constructional milling or agricultural machines. In the case of deeper-reaching contaminant sources, the so-called *in-situ soil mixing* technology can be applied (Figure 28). This technology has the advantage that it homogenizes geological heterogeneities and that it can also be used in the water saturated soil zone.

Figure 28   Principle of the *In-Situ-Soil-Mixing*-Technology

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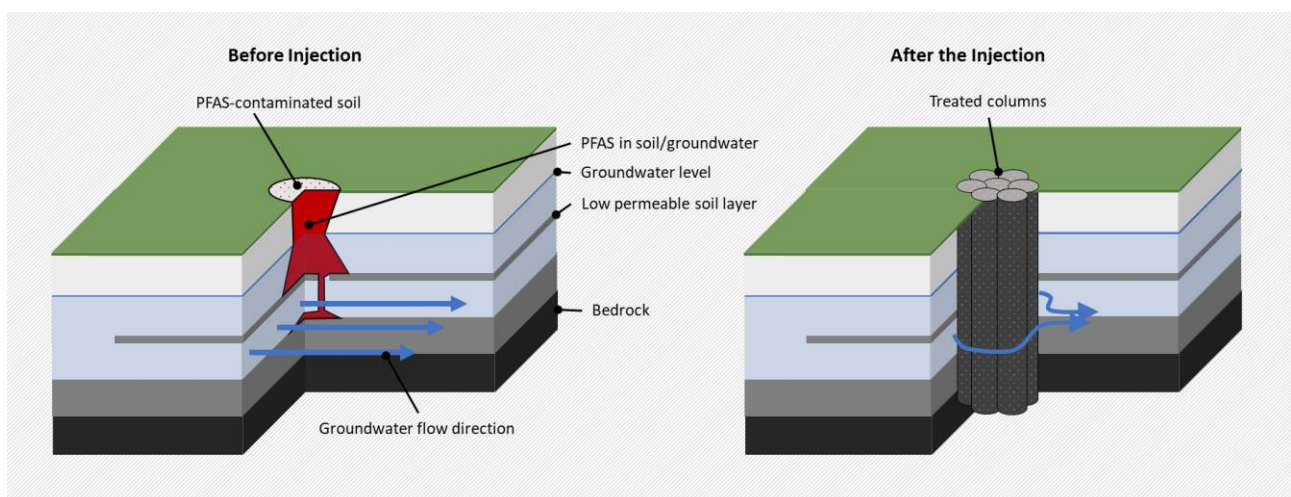
[32] Carbon nanotubes, also known as CNTs, are microscopically small tubular structures (molecular nanotubes) made of carbon. Their walls consist only of carbon, with the carbon atoms taking on a honeycomb-like structure with hexagons and three binding partners each. The diameter of the tubes is usually in the range of 1 to 50 nm.

Source: Olsen et al., 2018

The general feasibility of the technology (here sorption of PFAS) has already been demonstrated. As a rule, these technologies are cheaper and faster than excavation and disposal and have a better CO_2 footprint. On the other hand, the treated soils cannot be used until it has been reliably clarified that the PFAS are permanently and sufficiently removed from the relevant soil/receptor pathways. At this point, legal questions are still open (see Annex E).

Sorbent materials that are mixed into the soil (Ruffing et al., 2013) can significantly reduce the availability of PFAS for transfer to groundwater (Du et al., 2014). However, their effectiveness is reduced in the presence of organic co-contaminants (NGWA, 2017) and also depends on the PFAS chain length and the functional group of the compound (Xiao et al., 2017). Therefore, it is usually necessary to first carry out laboratory tests using site-specific soils and the intended sorption reagent.

Activated carbon-based products. On the market already several powdered products based on activated carbon are available. One of the patented products contains, in addition to activated carbon, amorphous aluminum hydroxide, kaolin clay and other protected substances, thus creating a large surface with different charges. Aluminum hydroxide in an amorphous form lacks a crystalline structure. This leads to an irregular, charged and relatively large inner surface, which makes it suitable for electrostatically binding of charged compounds.

When the product was added to the soil (25 % by weight), almost complete sorption (99.9 %) was achieved. The concentration of PFOS in the eluate was < 0.5 µg/L. The effectiveness was higher for longer-chain PFAS than for shorter-chain compounds. In addition, the bioaccumulation of fixed PFAS in plants (wheat grass) and animals (worms) was investigated. The product was found to reduce accumulation for worms in the range 0 - 98 % and for wheatgrass in the range 94 - 97 % for PFOS and 30 - 60 % for PFBA. In general, it was confirmed what is already known for bioaccumulation: There is a higher accumulation of shorter-chain PFAA and a higher accumulation of carboxylic acids in plants compared to sulphonic acids (Bräunig et al., 2017).

The addition of activated carbon alone (3 %) reduced the elution by 94 - 99.9 %. Compost alone also showed an effect, but this was significantly less pronounced (Hale et al., 2017).

According to the manufacturer's instructions, the substrate is added to the soil (moisture approx. 30 %) in a concentration of 5 – 20 % by weight. The binding should take place within 48 h after mixing the soil. Two of these treated soils were investigated in leaching tests. They behaved very differently. In one soil (5 wt.-% substrate) the PFOS concentration in the eluate (pH 7) was 0.05 µg/L, in the other soils even with 30 wt.-% substrate only a PFOS concentration in eluate of 0.74 µg/L could be achieved. In tendency, the elution for PFOS at pH 5 is somewhat lower than at pH 7 (Steward et al., 2018).

Resins. The product Osorb (Edmiston, 2010) is a polysilsesquioxane, i.e. an organic/inorganic hybrid material (silicone resin) with a Si-O-Si backbone and organic side chains. Probably the sorption takes place via a hydrophobic binding to the side chain. Little information is available on Osorb.

Mineral-based products. Sorption processes based on the use of substances such as iron oxide minerals, organically modified clay minerals (for example montmorillonite) or minerals such as a two-layer hydroxide (hydrotalcite; $Mg_6Al_2[(OH)_{16}|CO_3]\cdot4H_2O$ and palygorskite; $Mg,Al)_4[OH|(Si,Al)_4O_{10}]_2\cdot(4+4)H_2O)$; Kambala and Maidu, 2013) are promising. However, only limited studies with PFAS have been performed. Minerals such as clay minerals, silica, iron oxides and zeolites have been used as sorbents to remove contaminants from groundwater and soil (Zhu et al., 2016; Zhou et al., 2013). The surface of organic clays can also be modified for improved PFOS and PFOA sorption (Zhu et al., 2016). Organic clays are used because they are environmentally friendly, have a high sorption capacity and can be easily modified to improve their sorption capacity. Their surface is hydrophilic and therefore initially

ineffective for the sorption of hydrophobic organic compounds such as long-chain PFAS, but only a modification with cations (e.g. sodium) changes the surface to a lipophilic property.

MatCare, another modified clay, also has good sorption properties (Naidu, 2015). No data are available on the sorption of shorter-chain compounds. In addition, other organic clays (CETCO, Organoclay SS-199) are on the market as sorption materials, but there is almost no information available on this product.

In a comparative experiment, the substrates powdered activated carbon, commercial activated carbon-based product, pulverized zeolites, chitosan, hydrotalcite, bentonite and calcium chloride were investigated (each added in 2 wt.-%), with activated carbon-based substrates proving to be most suitable for PFAS sorption (Sörengård et al., 2019). The effect was dependent on the length of the PFAS compounds and the type of the functional group. For example, sorption increased by an average of 11 - 15 % per CF_2-unit and was on average 49 % higher for PFSA than for PFCA.

Further tests with different products (AlOH/activated carbon, 15 wt.-%, pyrolysis cellulose, 25 wt.-% and modified clay, 10 wt.-%) showed that the clay had the highest sorption capacity (38 µg/g). AlOH/activated carbon proved to be better for short chain PFAS. Leaching tests showed that the clay released < 1 % of the sorbed mass (Arcadis, 2018).

The effectiveness of immobilization also differs according to the conditions of the site conditions. High concentrations of organic compounds in the soil compete with the available binding sites on the substrates.

Cement. The extent to which PFAS can be immobilized by consolidation with cement has not yet been conclusively clarified. First attempts (see above) were quite successful. If the produced concrete is impermeable to water, no elution of the PFAS takes place. A prerequisite, however, is that the non-eluting of the PFAS can be proven in a laboratory test (see below). If the concrete is used for building structures, it would not be possible to dispose of it without restriction if the concrete were to be demolished and broken later. It is likely that additional disposal costs, which cannot be predicted at this stage, will then have to be considered. However, conventional concrete does not seem to meet the necessary criteria for immobilization.

Outlook. At first glance, the solidification/stabilization procedure appears to be simple and, compared to soil exchange, more cost-effective. In view of the postulated financial advantage of the technology, an application for extensive contaminations could be considered. First applications on a technical scale are already available. However, due to the various site-specific parameters that influence the binding capacity, it is advisable to test different products in different quantities (e.g. 1 - 15 wt.-%) in laboratory tests. This also applies if cement is added to the soil to consolidate the soil and to increase the immobilization of the PFAS. In this case, the influence of the high pH value on sorption as well as a possibly undesired increased Al release of products containing aluminum must be tested. The behavior of the precursors must always be checked with the help of appropriate analytical methods as part of the analytical sorption investigation. The results of the laboratory tests can then be used to check whether the technology using the required product masses is still cost-effective.

The information available so far still leaves many questions unanswered. It is important to note that independent studies on the efficacy of the various products are currently still lacking. Almost all studies were initiated by manufacturers. Due to the composition of the products, it can be assumed that no chemically stable binding of the PFAS occurs. Even if the in principle reversible binding of the contaminants is initially very strong, a later desorption of the PFAS takes place (probably over long periods of time). This may be so low that the concentrations of the PFAS in the eluate remain below the respective limit of quantification (see comprehensive description in Chapter 2.2.7). Because of this risk, the immobilization products are critically evaluated by the authorities and it is unclear whether the delayed leaching will be eligible for approval.

Since the PFAS are not destroyed using solidification/stabilization but remain on site, the long-term stability of the immobilized PFAS is of great importance. The success of the immobilization is often proven in the investigations of the manufacturers with a commercially available leaching test (Toxicity Characteristic Leaching Procedure (EPA, 2015)). According to this method, non-volatile compounds (here: PFAS) are leached under acidic conditions (pH 2.88 ± 0.05). Under these acidic conditions, however, the electrostatic charges on the sorbent are altered and the sorption of anionic PFAA is supported, artificially reducing the leaching of the PFAS. Alternatively, tests for the investigation of concrete, which are however quite time-consuming, could be used. The following steps would be necessary:

1 Production of a sample to be tested using a PFAS-contaminated soil sample from the site and the selected sorbent (DIN EN 13892, 2003).

2 To the best of our knowledge, there is no standardized procedure for ageing the sample. For this reason, the procedure of Wägener (1997) could be used. This involves artificially ageing the test sample under various conditions for a maximum of 120 days.

3 The diffusion test method NEN 7345 (1995) is available for testing the contaminant elution on a monolith. The elution of organic contaminants can be tested according to this standard. The elution time is 64 days.

During the tests, care must be taken to ensure that the natural pH value is not changed by the test (except by adding the necessary products).

Furthermore, the effectiveness proofs of the suppliers are mostly based on laboratory work and are therefore not subject to the influences of non-ideal mixing of the substrates in the field or weathering in the natural environment. Field trials are therefore essential. Consequently, a four-year leaching study with a natural neutral pH in soil was started in 2018. The monitoring includes TOP-assay analyses to check the behavior of the precursors (Arcadis, 2018). Further open questions are addressed in Annex E.

Stabilization/Immobilization (Summary)

The immobilization of PFAS by mixing substrates into the soil is a procedure that is already available on the market today. Many different substrates are offered. There is still a lack of experience with the application on a technical scale. Questions regarding the long-term behavior of the sorbed PFAS and possible secondary effects are also open. However, it is expected that these questions will be answered soon. It is expected that the immobilization of PFAS will be used more frequently in the future.

3.1.2 *In-situ* Flushing

Description. Against the background of the frequently very extensive PFAS contaminations, for which complete decontamination with conventional methods would lead to disproportionately high costs, low-cost remediation technologies are required with which decontamination of the contaminant source can be achieved at least in some areas. Pump-and-treat system for hydraulic containment are already in operation at most sites. The concept of supplementary *in-situ flushing* consists of actively and intensively irrigating the soil surface in the source zone so that natural elution via precipitation is increased many times and the PFAS are washed out into the groundwater area as quickly as possible. There the PFAS are collected and cleaned by the installed pump-and-treat. Part of the extracted water is used for infiltration via sprinklers, while another part must be drained off after purification to maintain the water balance in the aquifer. In exceptional cases, the water content in the unsaturated soil zone can be increased up to 100 %.

The precipitation of decades could theoretically be applied within months. The influence of the heterogeneity of the unsaturated soil zone is thus substantially reduced. Nevertheless, the heterogeneity and the preferred flow paths can have a strongly prolonging effect on the duration of remediation.

Near-surface silty layers or soils with a high proportion of organic material (and thus a high sorption capacity), such as topsoil or loamy arable soils, must be removed beforehand. *In-situ flushing* may be suitable for permeable sandy soils. The efficiency of the process can be increased considerably if desorption can be accelerated. It is known that pH changes (saturation of soil charges), hydrogen peroxide (to increase DOC degradation while increasing the polarity of the DOC and thus reducing the sorption capacity on the soil) or surfactants can lead to preferential desorption. However, an increase in the pH value can have a negative effect on the elution of the cationic and zwitterionic PFAS. These are better to elute at low pH, but anionic perfluoralkane acids bind better to the soil. An investigation of the influence of the pH-value is still pending.

Since in deeper soil layers of the unsaturated zone a largely reversible sorption occurs again before the contaminants are finally transported into the groundwater, *in-situ flushing is* particularly suitable for sites with an unsaturated zone of comparatively low extension (e.g. 3 - 5 m).

The increased irrigation means that higher quantities of groundwater must be extracted by the P&T to avoid a lateral run-off of the mobilized PFAS in the groundwater. In addition, to achieve a water circulation, not all the extracted and cleaned water must be re-infiltrated. Some must be drained or infiltrated in the effluent or lateral flow. Under certain circumstances, bypassing the saturated area may reduce the amount of water to be pumped around. Modelling is required to optimize the water balance. In any case, however, the cost-related influence of dewatering and water purification on the overall process must be evaluated.

Outlook. Simple model calculations (1D models using published K_D values) and column desorption experiments can be carried out for initial testing of the process. The PFAS mass (incl. precursor) present in the unsaturated soil zone plays an essential role for the duration of remediation. The preliminary investigations show increased uncertainties especially in the range of low concentrations (at the end of the remediation after an initially rapid exponential decrease of PFAS concentrations).

The process is economical if it is possible to decontaminate the soil within a reasonable period to such an extent that no more significant amounts of PFAS are released into the groundwater. This applies to all differently charged PFAS (precursor). These must also be washed out sufficiently in the same way. To date (as of 2019), there have been no studies on *in-situ flushing*, so that this technology cannot be further evaluated.


In-situ Flushing (Summary)

The process of *in-situ flushing is* based on an enhanced leaching of the PFAS into the groundwater. There they are caught by a hydraulic containment (which is necessary in most cases anyway) and removed from the subsurface. After cleaning, the groundwater can be reused for flushing (via sprinkling of the surface) (recirculation). The success of the process depends mainly on the organic carbon content of the unsaturated soil and the type of contamination. If the contamination is primarily longer-chain PFAS, leaching is likely to be less efficient. The applicability of the technology is therefore limited to a specific number of sites.

This concept is already being discussed in many cases of remediation, but it has not yet been applied on a technical scale at any site. In this respect, there is a lack of data for a final assessment of the technology. However, it is expected that *in-situ flushing* will be used more often in the future, mainly because of the low costs of the flushing itself.

3.4 Additional Technologies

3.4.1 Smoldering

Description. During the smoldering process, the PFAS are thermally destroyed directly in the ground under limited oxygen supply. This requires the addition of a fuel and the injection of oxygen. Due to the thermal stability of the PFAS, temperatures of at least 1,000 °C are required for pyrolytic degradation of these compounds in order to additionally minimize the production of short-chain volatile organic fluorine compounds (VOF) and possibly fluorinated dioxins and furans (PFDD/F). Smoldering is carried out according to the following equation:

$$\text{Fuel} + \text{PFAS} + O_2 \rightarrow CO_2 + CO + H_2O + HF + VOF + PFDD/F$$
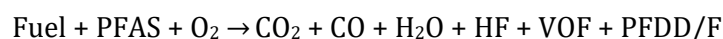
With increasing completeness of PFAS combustion, VOF and PFDD/F are produced in only very low concentrations and, above all, hydrofluoric acid (HF) is formed as the final PFAS degradation product.

The ideal fuel is either a waste product which itself requires disposal (e.g. PFAS-contaminated activated carbon) or an easily available, inexpensive substrate (e.g. coal). As the calorific value of the fuel increases, more energy can be released per unit time, provided that sufficient oxygen is available. This leads to higher average peak temperatures.

The self-sustaining smoldering makes the process very energy-efficient and therefore cost-effective. External energy is only required for the ignition process at the beginning of the remediation. This is in contrast to the high-temperature combustion processes (Chapter 3.2), which require continuous energy input. During the smoldering process, a hot, self-perpetuating, smoldering front is formed which spreads from the ignition point through the contaminated matrix in the direction of the air flow. The reaction front is relatively thin in the direction of migration (a few millimeters to centimeters) in which complex reactions such as pyrolysis (i.e. endothermic, thermal decomposition) and oxidation (exothermic conversion of carbon compounds into CO_2 and H_2O) take place. The smoldering process is controllable and can be stopped at any time by interrupting the air flow. Although most of the fuel is consumed for oxidative reactions, some of the contaminants can be volatilized during the pyrolysis reactions and by the heat generated, which arrives before the smoldering front. This means that the pyrolysis reactor must always be followed by a stage for treating the waste gas. The emitted PFAS could be sorbed to activated carbon and the spent activated carbon could be reused as fuel. The addition of limestone to the soil to be smoldered can reduce the HF emission.

In principle, the method should also be applicable for *in-situ remediation.* For this purpose, the fuel would have to be injected into the subsoil using the *in-situ soil mixing* technology (Chapter 3.3).

The method has so far only been tested on a laboratory scale (column experiment) (Major, 2019). For this purpose, sand was mixed with granular activated carbon (40 g/kg sand). The activated carbon was ignited selectively with a piezo element. The smoldering front migrated at a speed of 0.7 cm/min. A maximum temperature of 900 °C was reached. After smoldering, the concentrations of all PFAS compounds (PFOA, PFOS, PFHxS, in total about 1 mg/kg) were below the limit of quantification (0.4 µg/kg). The degradation end-product HF was detected in the gaseous column emission. At least 82 % of the available fluorine was recovered as HF. PFAS (C_4 - C_{12}, mainly PFCA) were also detected in the exhaust gas in small quantities. With a proportion of 50 g activated carbon per kg soil the target temperature of > 1,000 °C could be reached.

Outlook. The smoldering process was developed for the remediation of mineral oil phases, but even there, only a few projects have been realized so far. As an ex-situ process it is quite complex, as it requires large amounts of fuel and a complex cleaning process of the exhaust gas. In addition, the process management to avoid the formation of fluorinated dioxins and furans is complicated. Data are not yet available to assess whether smoldering is more favorable than high-temperature incineration.

The *in-situ* application has not yet been tested (status: 2019). It is therefore not yet clear whether the concept will work.

Smoldering (Summary)

Smoldering is a technology introduced at least for the remediation of mineral oil phases and applied on a technical scale, even though relatively few applications have been documented. As an *ex-situ* technology*,* it is also commercially available for the remediation of PFAS contaminated soils. However, it has only been tested in the laboratory and not yet on a technical scale.

Due to the high process engineering costs (waste gas purification), it is probably only competitive to high-temperature incineration if the necessary fuel is available as waste that must be disposed of anyway. The use of this technology will probably be limited to exceptional cases.

The application of this procedure for *in-situ* remediation is still in the conceptual stage. If the technology is one day functional, presumably it will not be more cost effective than competing technologies.

3.4.2   Ball Mill Technology

Description. During research, it was discovered that PFAS degradation can be achieved applying soil in a ball mill (with stainless steel balls of 5 - 10 mm diameter, as used in conventional planetary ball mills). In the ball mill that is operating at high speed, many collisions of the non-deformable steel balls with the deformable solids to be treated occur. The deformation of the solid phase leads to a short-term increase in temperature or to the generation of triboplasms (d. h. highly ionized neutral gas; Heinicke, 1984) on the surface of the solid phase.

In some ball milling processes, auxiliary agents such as potassium hydroxide (KOH), lime (CaO), silicon dioxide (SiO_2) and sodium hydroxide (NaOH) can be added to enable the generation of the hydroxyl radical (OH•) and thus a simultaneous chemical destruction of the PFAS. Zhang et al. (2013) used the addition of KOH and were able to achieve the destruction of PFOA and PFOS. A decrease in PFOA and PFOS concentrations of ≥ 90 percent could be demonstrated in about 6 hours with a fluoride and sulfate release of ≥ 95 percent. Although auxiliary agents were added, there is evidence that the dominant mechanism was thermal rather than chemical destruction.

Outlook. The method has not been investigated for its applicability to short-chain compounds and precursors. However, if thermal destruction is the main mechanism, the process should not be restricted in this respect, provided that the PFAS-specific thermal destruction temperatures are reached.

Whether mobilization of sufficiently large planetary ball mills to sites with high PFAS contaminations (depending on the amount of soil to be treated) is a viable option and economically advantageous in comparison to other technologies (e.g. *off-site* combustion) cannot be assessed at present. There are no planetary ball mills of an appropriate dimension for a reasonable soil throughput available. Up-scaling requires further research, and the practical aspects of its implementation on a larger scale still need to be studied in detail.

Ball Mill Technology (Summary)

During the treatment of soils in ball mills, such high temperatures are probably generated locally, which can in comparatively long treatment periods cause pyrolytic destruction of the PFAS. It is not expected that this can be developed into a marketable technology.

3.4.3   Phyto Remediation

Description. Phytoremediation refers to the decontamination of soil or groundwater with the help of plants. Phytoremediation is the generic term for numerous individual processes: (i) phytoextraction, (ii) phytodegradation or (iii) phytovolatilization. Regarding the properties of the PFAS, only phytoextraction comes into consideration. For this purpose, plants are used which absorb contaminants from the soil to a greater extent and accumulate them in high concentrations in their biomass (so-called hyperaccumulators). The contaminants can be stored both in the roots and in the above-ground biomass. These plant parts are then removed after the vegetation period (harvesting) and, depending on the degree of pollution, are sent for appropriate disposal (e.g. B. incineration).

The knowledge on the accumulation of PFAS in cultivated plants (short-chain PFAS accumulate mainly in fruits, long-chain PFAS in roots and the shoot) is of limited use for phytoremediation. Investigations on phytoremediation in case of PFAS contamination are relatively sparse. In general, phytoremediation requires:

▶   fast plant growth and high PFAS enrichment rate,

▶   low sensitivity of the plants to higher concentrations of contaminants (often high concentrations cause poisoning symptoms such as necroses, which significantly limits the efficiency of phytoremediation),

▶   low demands of the plants on soil properties such as pH value, type of fertilization and microclimate conditions, which can only be influenced to a limited extent.

In an investigation at a fire extinguishing training site (PFAS max. 160 µg/kg soil) the ability of several plants to accumulate PFAS (26 individual compounds) was tested. A variety of tree species and local plants including silver birch (*Betula pendula*), spruce (*Picea abies*), bird cherry (*Prunus padus*), rowan *(Sorbus aucuparia)*, goutweed (*Aegopodium podagraria*), long beech (*Phegopteris connectilis*), and wild strawberry (*Fragaria vesca*) were examined (Gobelius et al. , 2017). The bioconcentration factors (BKF; plant/soil ratio) were highest in foliage. They were maximally 906 for PFOS (beech) and 41 for PFOA (spruce). The total tree contamination of Σ_{26}PFAS per tree was only up to 11 mg for birch and 1.8 mg for spruce. This study shows that PFAS do not accumulate in tree species at concentrations known to be associated with metals (e.g. max. 26 % nickel (reference: TS), Jaffré, 1979; Gobelius et al., 2017).

In a forest with mixed planting of silver birch and spruce in combination with a regular harvest of leaves and birch sap and an undergrowth layer, it is possible to remove 1.4 g/(a·ha). An alternative approach is to harvest the birch in combination with an undergrowth layer, which is expected to remove 0.65 g/(a·ha) PFAS, while a simple meadow with ginger can remove 0.55 g/(a·ha) PFAS.

Outlook. Phytoremediation will probably not play a major role in the remediation of PFAS contaminated soils. The accumulation rates are too low, so that the procedure will take many years. During this time, the PFAS are continuously transported with the precipitation into the deeper soil layers and into the groundwater, so that phytoremediation does not result in a substantial advantage. However, the topic has not been conclusively terminated. Trees are, because they shed PFAS contaminated leaves or needles and because of their slow growth, certainly not the most suitable plants. However, they can theoretically be used to intercept PFAS groundwater plumes, provided the water uptake rate is sufficiently high and the thickness of the aquifer and the water compartment sufficiently low.

The question of thermal utilization of PFAS-enriching plants also arises. Here it would still have to be clarified whether the plants can be fed into technical, energy-supplying processes that take place at temperatures so high that the PFAS are destroyed. This is not the case with most processes.

> **Phytoremediation (Summary)**
>
> Phytoremediation (uptake of the PFAS in plants with subsequent thermal disposal of the plants) is not a sufficiently effective process. The uptake rates in plants are too low. The process can therefore not be used for soil remediation.

3.4.4   PFAS Contaminated Soil as Additive in Cement Production

Description. In principle, it is conceivable to use mineral raw materials (PFAS-contaminated soil) directly as additive for cement production. PFAS are destroyed at production temperatures of over 1,250 °C.

Outlook. At present, the interest of the cement industry seems to be rather restrained. In addition, there are procedural problems in adding the PFAS-contaminated soil to the process without outgassing losses. No such trials are known, at least in Germany.

> **PFAS Contaminated Soil as Additive in Cement Production (Summary)**
>
> In principle, the addition of PFAS-contaminated soil to the cement production process could lead to thermal destruction of the PFAS. However, there are currently no efforts to investigate this route in Germany.

3.4.5   *Ex-situ* Soil Flushing

Description. Another possibility is to excavate the soil, lay it out over a large area in a special plant and leave the elution of the PFAS to natural precipitation. The plant is sealed to the side and to the bottom, whereby the leachate is collected and cleaned before it can be discharged (Yao et al., 2015).

Outlook. In view of the large quantities of PFAS-contaminated soil to be disposed of, this approach seems to be an attractive option. The disadvantage is that extensive areas are required for this and the turnaround per plant is in the range of several years (to decades). Whether the process is economical (high investment costs, continuous operating costs over long periods of time) has yet to be determined by comparative calculations. An alternative would be to erect the construction at the site of the contamination. Furthermore, the legal framework conditions still must be clarified (clarification whether it is containment or remediation according to German Soil Protection Act and if there is a necessity for approval according to German Immission Control Act).

> **Ex-situ Soil Flushing (Summary)**
>
> *Ex-situ soil elution* refers to a structure (*on-site* or *off-site*) in which the soil is exposed to natural precipitation over a long period of time and the PFAS are eluted as a result. The eluate is collected and cleaned. Due to the long treatment times in which large areas cannot be used for other purposes, the high costs and the unclear legal situation, this procedure has hardly been discussed in the past. The technical implementation, however, is comparatively simple.

4 Summary and Outlook

4.1 Overview

The overview presented in the preceding chapters considers established and innovative methods for the remediation of PFAS in soil and groundwater, whereby the new alternative methods differ from many conventional approaches.

Table 6   Summary of the technology evaluation for groundwater remediation

Procedure	Stand Alone(**) ?		Harmful by-products?	Formation of a concentrate?	In-situ applicable?
	Effluent value/remediation targets (***)	Treatment duration			
Sorption activated carbon	Yes	Yes	No	No	Yes (as injection of activated carbon into the aquifer)
Sorption on ion ex-changer	(Yes)*	Yes	No	(Yes)	No
Sorption on polymers	?	(Yes)	No	(Yes)	No
PerfluorAd	No	Yes	No	Yes (filter cake)	No
Reverse Osmosis	No	Yes	No	Yes	No
Nanofiltration	No	yes	No	Yes	No
Ozofractionation	No	Yes		Yes	Yes (as in-situ foam fractionation)
Sonolysis	(Yes)	No	No	No	No
Advanced Oxidation/Reduction	(No)	(No)	(Yes)	No	(Yes)
Electrochemical oxidation	(Yes)	(No)	Yes	No	(Yes)
Microbial degradation with fungal enzymes	No	No	?	No	(Yes)
Photolysis	(Yes)	No	No	No	No
Plasma Irradiation	(Yes)	(No)	No	No	No
Electron beam treatment	(Yes)	(No)	No	No	No
In -situ foam frac-tionation	(No)	Yes	No	Yes	Yes

(*)   (Yes) means "probably yes", (No) means "probably not", ? = no information available

(**)   Stand-alone processes are those that do not require additional processes (such as concentration of PFAS prior further treatment) in continuous processes (such as *pump-and-treat*).

(***)   At this point, the answer is "Yes" if this procedure can be used to comply with the discharge values of groundwater treatment plants usually specified by the authorities (see Appendix B) or the remediation target values with a moderate treatment duration.

Some procedures focus on separating the PFAS from the environmental compartment, others on immobilizing or even destroying the contaminants. While numerous technologies have already been discussed in this guideline from a practical perspective, the list of PFAS remediation technologies is growing and includes many new technologies that are currently still being investigated exclusively on a laboratory scale. This compilation can therefore not be a complete list of all technologies under development.

Table 6 summarizes the results of the above technology descriptions for the purification of groundwater. For all processes, as far as known, the process impurities, (undesired) by-products, and end products were listed. The effectiveness of the technologies on the elimination of precursors, non-precursors, and short-chain PFAS cannot be answered consistently. The relevant data are almost always missing. This also applies to a few other process parameters such as:

► economic feasibility (estimation of specific process costs),

► estimated total remediation cost and

► Sustainability (duration of remediation, energy requirements, CO_2 emissions).

Many processes are already prohibited by theoretical considerations for cost reasons, or they are very energy-intensive or produce toxic by-products.

Also, the eligibility for approval of some technologies, such as chemical oxidation, is likely to be very questionable, as very high concentrations of reaction end products (mostly sulphate in this case) are released into the aquifer. It has also not been investigated for all processes whether harmful by-products are produced. Finally, it must also be decided whether a temporary sorption followed by very slow desorption is acceptable, even if the resulting concentration remains below the remediation target values.

4.2 Groundwater

According to the authors' assessment, the currently identified remediation options for groundwater are summarized in Figure 29 with regard to feasibility and development status. Even if individual technologies have been developed to market maturity, this is no guarantee that they will be established on the market.

In-situ foam fractionation is the only decontamination process designed for in-situ application. However, even this method is hardly suitable for the area-wide decontamination of the usually extensive PFAS plumes due to cost reasons, but an application (assuming the functionality of the method) as a barrier method is conceivable. Electrochemical oxidation was also considered as a barrier process. However, due to the formation of harmful by-products, this will probably not be implemented in the foreseeable future.

For *in-situ* application, the injection of activated carbon into the aquifer is also used, but this is a largely reversible sorption process in the sense of a temporary protection.

All other technologies are based on the extraction of ground water with subsequent treatment of the PFAS-contaminated groundwater. A technology is described as "stand alone" if the reaction rates are so high that it can be used for continuous purification as part of the *pump-and-treat* measures (Chapter 2.1). A distinction must then be made as to whether the target effluent value can be achieved. This can be achieved in most cases, but the effort to achieve this goal varies. For example, ion exchangers require several process stages. With other destructive processes, the treatment time must be extended accordingly to achieve the desired effluent value. However, the duration of treatment is then usually so long that the technology cannot be used for the continuous treatment of pumped groundwater.

Instead, they are more suitable for the treatment of PFAS concentrates, which are mainly produced by sorption processes or other separation processes (e.g. *in-situ foam fractionation*). For *in-situ* processes, the remediation target value for groundwater applies instead.

Figure 29   Possible remediation methods for groundwater (blue: in-situ application)
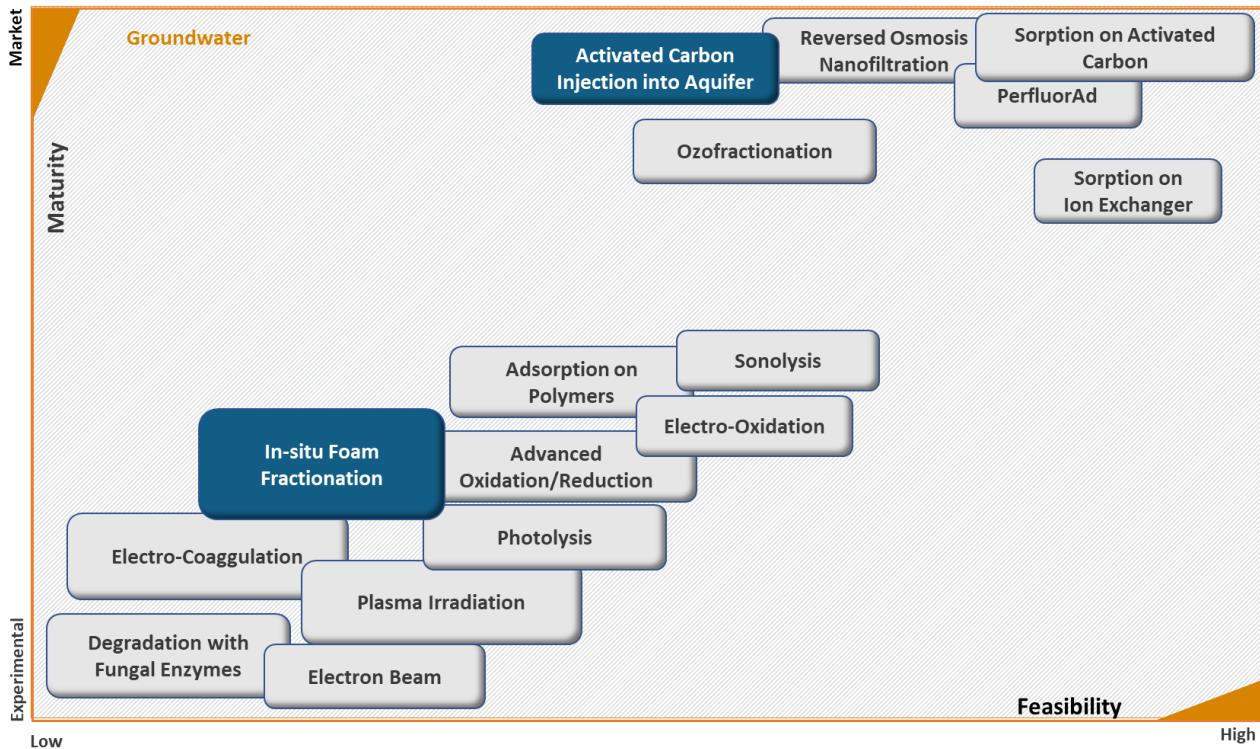
Source: Arcadis Germany GmbH, 2019

Harmful by-products (not meant in this case are shorter-chain PFAS compounds) are according to present knowledge only generated during the electrochemical process.

The applicability of the techniques is likely to depend on the experience still to be gained from their use on a technical scale and, above all, on their costs in relation to conventional remediation methods.

The technologies are not always optional. While some are particularly suitable for the treatment of low contaminated water without high concentrations of impurities, there are others (e.g. precipitation processes) which are suitable for removing higher concentrations of PFAS before using other sorbents with the aim of extending the service life of the sorbent as last stage. However, precipitation processes produce a waste sludge from precipitation and the need for dewatering.

New sorbents are created either by adapting available materials to the removal of the PFAS or by university development of completely new materials. None of the sorbents, however, destroys the contaminants, but only leads to a rearrangement from one matrix to another. Therefore, more and more processes are being investigated which claim to be able to destroy PFAS, possibly only in combination with other processes (*treatment train*).

The individual site parameters of each remediation case must be considered separately. Thus, the treatment costs are highly dependent on the spectrum of individual PFAS compounds (fingerprint), possible competitive sorption, possibly existing interfering substances (impurities) as well as the officially defined clean-up target values.

4.3   Soil

Figure 30 shows an estimation of the market maturity and development status of soil remediation technologies.

Figure 30   Possible remediation methods for soil (blue: *In-situ* application)
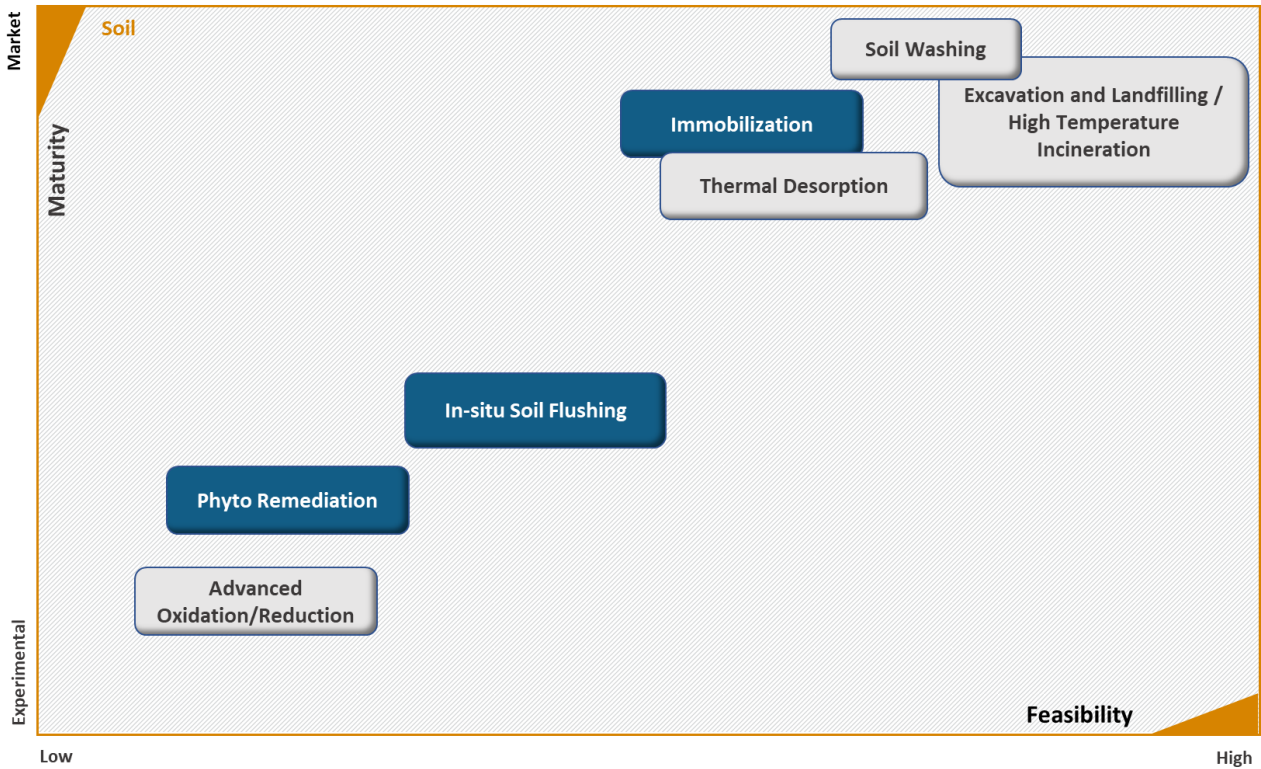
Source: Arcadis Germany GmbH, 2019

In addition to soil excavation, several other methods have meanwhile become established. However, up to now, experience (technical-organizational implementation, upper and lower concentration limits, duration of effect and remediation, applicability across individual cases) and cost data for application on a technical scale are largely lacking.

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Appendix D:

Project Case Studies

Table of Contents

1   Objective

The handling of PFAS-contaminations requires, due to their special features, numerous new approaches, be it increased protection and restriction measures (institutional controls), immediate measures or innovative measures to manage large masses of PFAS-contaminated soil. Even though there are still very few remediation projects in Germany, and those that are already underway focus almost exclusively on the conventional processes of pump and treat (P&T) and soil exchange, there is a great possibility that the solutions found in the individual cases can be used to derive procedures and knowledge that are of more far-reaching significance and must therefore be included in the this technical guideline. For this reason, several cases were identified while preparing this technical guideline, in which at least one agreed remedial options appraisal, but better still, initial experience with the success of the remediation is already available. In the next step, a telephone interview was conducted with the respective responsible authority representative. In particular, we asked for management decisions of the party liable for remediation and the competent authorities, which are not normally included in the technical reports for documentation. The results of the interviews are summarized in Chapter 2, and the insights gained from these interviews have been incorporated into this technical guideline.

2   Project Case Studies

2.1   Application of Fire Extinguishing Foams (Case 1)

In 2010 a fire was extinguished in a company for reform goods (warehouse trade). The company had a multi-trench system for the infiltration of surface water run-off. The percolating water was discharged into the groundwater via these trenches. Overflow pipes went directly into the trenches below the systems, thus short-circuiting the topsoil passage.

Immediately after the fire, the extinguishing water in the multi-trench system was analyzed for the content of PFAS, which were promptly detected. The main PFAS entry into the groundwater was via infiltration and overflow pipes. A groundwater monitoring well (GMW) was immediately installed downstream of each of the two multi-trench systems. Their sampling and analysis revealed high concentrations of PFAS, but also of PAHs and increased toxicity (luminescent bacteria test). However, PAH concentrations and toxicity decreased rapidly over the time.

The detailed site investigation was carried out in two phases. Since the current PFAS plume ended in an area below a highway, a GMW was installed beyond the highway and sampled regularly (1st phase). PFAS concentrations increased continuously. In a 2nd phase, the PFAS plume in the groundwater was delineated using direct-push sampling in two transects.

A formal remedial option appraisal was not carried out as there was no alternative to pump-and-treat (P&T) at that time. The location of the extraction wells and the extraction rates were determined using a groundwater flow model. The P&T measure at the plume tip were taken into operation about one year after the PFAS contamination occurred. The soil of the PFAS-contaminated multi-trench systems was excavated after prior investigation of the soil contamination shortly before the start of the P&T measures (partial remediation, as the PFAS contamination could not be completely excavated beneath an existing building).

The strategy was to explore the site quickly but thoroughly and to put the remediation measures into operation quickly in order to avoid further spreading to a nature reserve located further downstream.

It was clear at an early stage that PFAS had already migrated to an area beneath the highway and that pumping the contaminated groundwater only made sense on the other side of the highway. This left sufficient time for a careful investigation and greater legal certainty for the ordering of remedial measures.

As a rule, it is hardly possible to decide whether an immediate measure would have removed more contaminants and more quickly from the subsoil. An obstacle to immediate measures is the question of the extent to which the measures can be targeted in the situation of limited data availability. In the worst case, a subsequent detailed investigation would have shown that the emergency measure was not sufficiently suitable, and that the authority would have had to bear the costs in case that they had ordered the remediation or performed by themselves as substitute performance.

Additional institutional controls were not necessary in this case. The goal of the remediation was to stop the spread of the plume. The target value upgradient of the groundwater extraction wells was set to max. 0.3 µg/L (sum of PFBS, PFHxS, PFHxA, PFHpS, PFOA, and PFOS). This value also had to be maintained for the purified water that was re-injected into the aquifer (discharge value). Later, the in-significance threshold value, including the sum quotient was set as the remedial target. This was advantageous regarding the holding life of the activated carbon adsorber, and it corresponded to a tightening of the limit values regarding the evaluation of the inflowing water.

Since currently only a few hundred grams of PFAS per year are removed from the aquifer in the area of the PFAS plume, it is to be examined within the framework of a proportionality analysis whether it is appropriate to continue the remediation. This examination is based on the intention (not the individual values) of the guidelines for the termination of long-term P&T measures in the case of CVOC contamination (LUBW, 2015). It must be shown in form of a prognosis what happens after the groundwater extraction is stopped (extension of the plume?). Precursors (sampled and analyzed at the plant inlet and outlet) will also be included in the prognosis. It will probably be necessary to allow a short section-stretch of acceptable contamination in front of the current plume, but in which no groundwater use is currently taking place.

2.2   Application of Fire Extinguishing Foams, Test Field (Case 2)

At the site of a fire engine manufacturer, PFAS was spilled into the soil and groundwater in two areas (sources zones). The first source zone represents a so-called test field for the fire-fighting vehicles in test operations, which according to the current state of knowledge did not have any regular drainage system or at least did not have a drainage system designed according to the state of the art. Here, primarily PFOS and H_4PFOS contamination occurred (PFAS were initially analyzed first according to DIN, but after confirmation of the suspected contamination, 24 individual substances were routinely analyzed). The second source zone, which is almost directly located downstream of the first source zone, showed mainly PFOS, the cause of the damage could not be determined. The entire operation of the manufacturer was shut down in 2013.

The site was then to be sold. For this purpose, a historical investigation, and a phase 1 investigation were carried out. In this process, attention was drawn to possible PFAS contamination. In the following detailed investigation, the PFAS contamination was delineated. The contaminant plume has also been delineated as far as possible. At a distance of approx. 130 m downgradient of the source zone (centerline), a considerable PFAS contamination remains, but with a magnitude that is lower than that of the source zone. PFAS could be detected at trace concentrations a greater distance further downgradient (at about 280 m). In groundwater, the precursors were also analyzed using the AOF method. The results gave no indication for any other compounds apart from those identified by single substance analysis.

The remedial option appraisal was completed in 2018. The authorities have requested that this needs to be done by an expert certified according to §18 BBodSchG (German Federal Soil Act).

Besides P&T and soil exchange, the following remediation options were also considered: hydraulic containment via groundwater circulation wells, different variants of soil exchange (including exchange of the clay top soil and in-situ flushing of the PFAS-contaminated coarse-grained subsoil of the unsaturated soil zone by trickling), soil washing and encapsulation of the source zone. The following approach was chosen as the preferred remediation option:

- o Partial soil exchange in the hot-spot areas (unsaturated soil zone with a PFAS contamination > 10 x sum quotient, using the insignificance threshold value or health-oriented guidance value of 13 compounds),

- o P&T immediately downstream of the 2nd source zone with three groundwater extraction wells and four upstream infiltration wells (hydraulic source containment).

The hydraulic source zone containment shall be set up first. If efficacy is proven (i.e. the PFAS concentrations at a groundwater monitoring well downstream of the containment zone reach the remediation target level), soil exchange will be carried out. It is expected that there will be a period of six months between the two measures.

The PFAS plume, from which no danger emanates and therefore no remediation is necessary, is set to dissolve on its own by dilution. There is no groundwater use within the plume area, so that protection and restriction measures (institutional controls) are not necessary. An exception is a groundwater heat pump system located in the immediate downstream area. However, it is a closed system that has no direct contact with the groundwater. Furthermore, the geohydraulic model calculation measure shows that the P&T has no negative impact on the heat pump system.

The effectiveness of the hydraulic barrier to be installed at the site boundary is given if the insignificance threshold values or health-oriented guidance values (including quotient ration sum) are met downstream of the barrier (status: 2018). The hydraulic measure can be terminated if the PFAS concentrations in the area upgradient from the extraction wells are below the above-mentioned values. A formal decision on the remediation target values will be issued after completion of the remediation plan, which is still to be drawn up.

The disposal of PFAS-contaminated soil materials is still unsettled. It is expected that this will be difficult. Due to the persistence of the PFAS, high demands on wastewater treatment must be made. Apart from that, the management of this contaminated site did not show any special features compared to the management of site contaminated with conventional contaminants.

The site is currently a brownfield site. Part of the site is owned by the municipality. The aim is to bring the site to a rapid subsequent use. The time periods required for this are still uncertain. This will probably only be possible once the remediation measures (here only soil replacement) have been completed.

2.3 Application of Fire Extinguishing Foams (Case 3)

The fire at this site occurred in 2007. The affected area was completely sealed, and the site had a firefighting water retention system. Therefore, there was initially no reason to investigate the soil and groundwater in more detail. In 2012, elevated levels of PFAS were found in the water of a drinking water production plant about 7 km downstream. The causal analysis identified the fire as the cause of the contamination.

During the following investigation, no explicit hotspots could be identified. Throughout the property, areas with increased PFAS contamination in the groundwater could not be connected to corresponding instances of contamination in soil and vice versa.

It was therefore assumed that the fire-fighting foams entered the subsoil via a defective sewer system and via cracks that had formed in the concrete slab during the fire. Smaller entries were theoretically also conceivable when handling the extinguishing foam during the extinguishing process. The soil contamination has been delineated to a large extent, and further groundwater monitoring wells are currently being installed downstream of the source area to consolidate the information on PFAS distribution in the groundwater. The PFAS plume is currently about 8 km long and probably stationary in its extension. The plume is also largely delineated. Within the scope of the site investigation, 18 PFAS single compounds were analyzed. Precursors were only analyzed in the pilot study (see below). The PFAS accumulate in the groundwater fluctuation zone.

Within the scope of a pilot study, the feasibility of three different remediation methods that seemed to be promising (precipitation with PerfluorAd, enrichment on an ion exchanger in conjunction with chemical degradation of the PFAS in the desorbate, and sorption on activated carbon or ion exchanger) was tested in laboratory and partly on a pilot-plant scale. Within the scope of the pilot study, the precursors (as AOF) were partly analyzed and detected. For some processes, the groundwater to be treated had a complicated matrix (high DOC and dissolved iron concentrations). The source of the DOC was not determined, the groundwater inflow to the site was not investigated. It is therefore not clear whether the DOC flows from upgradient.

Within the scope of the remedial options appraisal for the contaminated area, in addition to the classical methods, mainly containment methods were considered. The selected remediation technologies included the elements of partial pile walls (to minimize the flow rate), extraction of the contaminated groundwater and purification with PerflurAd and subsequent sorption on activated carbon and re-infiltration of part of the purified water in the upstream area to improve hydraulic leaching, especially in the groundwater fluctuation zone.

Protection and restriction measures (institutional controls) were not necessary for the PFAS plume area in the groundwater.

As provisional remediation target values, the insignificance threshold values were determined, the final remediation target values are still to be derived by the experts within the framework of the preparation of the remediation plan.

2.4 Application of Fire Extinguishing Foams, Airport (Case 4)

On the premises of an airport there are a total of 5 source areas with PFAS from the use of fire extinguishing foams. The source areas are fire training areas (large, walled basin east and smaller basin west), the fire brigade parking area, as well as a larger biotope, and a smaller area in the north. The main damage is at the former fire training area east. The PFAS seeped away from the entry areas and entered the groundwater. At the same time, the PFAS contaminated topsoil was eluted via draining surface waters and spread into the surrounding area. Ultimately, all the contaminated surface water and groundwater drains into a ditch as a receiving watercourse. The PFAS reach the receiving water via near-surface soil layers and the groundwater. The annual PFAS mass flux, which is transported further via the receiving watercourse, is currently 1.5 - 3.5 kg/a PFAS.

A remediation project has been underway for several years at the East Fire Training Area. This began in 2014, initially as a pilot test. The groundwater that is extracted within the scope of a P&T (originally max. 1 m^3/h) is mixed with an active liquid substance which is brought to a precipitation reaction with the PFAS compounds.

In a second step, decontamination is carried out via sorption on activated carbon. After some plant modifications and hydraulic optimizations to completely capture the effluent, the remediation now runs with a volume flow of 2 m^3/h.

The treated water is discharged into a ditch. A concentration of 20 ng/L PFOS is the target value for purification and for other PFAS the insignificance threshold values apply. According to the binding remediation plan, AOF and precursor substances are to be analyzed once in the raw and clean water of the treatment plant.

The contamination has been delineated to a large extent and a historical investigation (phase 1 investigation) has been carried out. As a result, no cause could be determined for the area "North". It is assumed that the contamination in this area is due to soil that was previously relocated. Otherwise, all contaminants´ transport paths can be explained, and a conceptual site model is available for the site. A groundwater model was created for the entire site. Integral investigation methods (such as immission pumping tests or similar) were carried out.

Based on the results of the investigation, a remediation concept was developed. In addition to P&T (a depth-differentiated investigation showed that in the source zone groundwater extraction is only effective in the upper part of the aquifer) and soil exchange in the most diverse variants, soil relocation was also considered. A remediation plan drawn up by a consultant was declared binding by the competent authority.

The remediation plan describes the extension of the P&T measure to technical scale. The cleaning procedure in the main source zone will be retained until further notice. The groundwater extraction will be designed in such a way that the groundwater depression in the hot-spot area is very low. This will ensure a continuous elution of the contaminants into the groundwater and into the P&T system. In addition, the surface drainage is to be redesigned so that the water does not run into highly contaminated areas. Part of the treated water should be channeled into the biotope to maintain the water level and thus the biotope itself.

In the downstream part of the biotope, a drainage system and a well gallery will be built to collect the contaminated surface water that runs off, but also the effluent from the biotope. The collected water will be fed into a groundwater treatment plant.

In addition, the PFAS-contaminated soil is to be excavated in all contaminated areas and deposited in the area of the eastern fire training area in a large embankment body that is secured and controlled with regard to the inflow of precipitation water and the outflow of leachate. The intervention value determining the excavation is 0.3 µg/L in the eluate for the sum of PFOS, PFOA and PFHxS. The deposition takes place in an area where high soil contamination already exists (compliance with the prohibition of deterioration). This area is sealed off from the surface by the deposit. In the hotspot area, soil is to be excavated down to the groundwater fluctuation zone. Since the entire airport has been declared a remediation area, the transfer of contaminated soil within the entire area is permitted.

The airport operator has already made adequate financial provisions.

Remediation target values for the groundwater have not yet been set due to the lack of legal certainty. This is to be done at a later date, taking into account the principle of proportionality.

In addition to groundwater and surface water, defined receptors are the fish in the fishponds in the surrounding area. An urgent recommendation has been made to refrain from eating fish. In the groundwater sphere of influence there are also allotment gardens. For the allotment gardeners it was urgently recommended not to use the groundwater that can be pumped via garden wells for irrigation.

Furthermore, there are irrigation wells in agricultural areas, industrial water wells and wells to produce drinking water (public and private users) in the area further downstream. Their water must be monitored regularly.

Up to now, only traces of PFAS have been found in some industrial water, which do not require any further measures. It is expected that the concentrations will decrease after the remediation of the source zone. However, if monitoring shows a deterioration of the situation, restrictions cannot be ruled out (e.g. restrictions in the groundwater extraction rate).

In the PFAS plume area, the construction of a motorway connection with intensive groundwater dewatering was planned. The groundwater in this area was intensively investigated. Due to the PFAS contamination, the project has been postponed for the foreseeable future.

The grass cuttings on contaminated soils are being analyzed. If determined to be polluted, grass should not be used for animal feed or used in a biogas plant. If possible, the grass clippings can be dug under or must be disposed of properly. Pre-harvest monitoring is carried out for crops. Up to now, this has only resulted in low PFAS contents and therefore no need for action.

The results are communicated transparently in a comprehensive public relations campaign.

2.5 Fire Extinguishing Trainings in the Mineral Oil Industry (Case 5)

During the operation of a site of the mineral oil industry, fire extinguishing trainings were carried out at various locations. At these locations, as well as at the site of the company´s fire brigade, PFAS were released in soil and groundwater. Only after the dismantling of the site, did PFAS become a general topic of concern, so that only at this point investigations into potential PFAS could begin. After completing a phase I environmental site assessment, investigations were conducted which could determine and delineate contaminant source areas (soil) as well as groundwater contamination.

Since the PFAS plume extended beyond the property and into the area of a floodplain forest, a down-gradient groundwater containment system was quickly installed as an immediate measure. After the sale of the property, the new owner overplanned the hydraulic containment, using the results of the conducted investigations. Target discharge values of 20 ng/L PFOS and 200 ng/L for total PFAS were set, according to the state of the art. During operation of the containment system, the concentrations of the individual PFAS compounds fell below the respective limit of quantification (10 ng/L). The purified water is re-infiltrated in the side stream, in which no PFAS contamination exists. The hydraulic containment can be terminated when the concentrations are below the level 1 values valid in the German Federal State Bavaria. The basis for these values were specifications of the Bavarian State Office for the Environment. Precursors have not yet been investigated.

At this site, the affected source/receptor pathway is exclusively soil → groundwater. Protection and restriction measures (institutional controls) were therefore not necessary.

For remedial options appraisal, various remediation options were examined. However, since the site was to be quickly put to new use, it was decided to wash the soil in the source zone, mainly because the possibilities for depositing the PFAS-contaminated soil on landfills are very limited. This soil washing is still ongoing at the end of 2019.

The cleaned soil will be backfilled on site, provided it meets the quality requirements for reuse according to the reuse class Z 0. If the soil does not have meet this classification, which is not unlikely for the sand fraction, it will be washed again. According to the notification, in accordance with LAGA M20 (status 06. November 1997), recycling of material with quality requirements of reuse class Z1.1 or lower, is possible if implemented as "restricted open backfill" in technical structures.

Highly contaminated fine-grained material is only produced in small quantities and is deposited in landfills.

The polluter was selected as the party liable for remediation. However, the remediation obligation was transferred to the new owner in a remediation contract between the old and new owner and the city´s administration.

2.6 Application of Fire Extinguishing Foams, Airport (Case 6)

Several PFAS spills have been identified at an airport, which could be attributed to the use of PFAS-containing fire-fighting foams. After the detection of PFAS contaminations in the main application areas (fire training basin, fire station), an extended historical (phase 1) investigation regarding additional possible PFAS entries preceded the further investigation of the PFAS contaminations. Suspected areas were fire training areas, the fire station, the location of the fire trucks, extinguished fires, crash, storage, and trans-shipment areas for PFAS, piles of material with suspected PFAS as well as the complete drainage system of the property.

The main source zone known so far is located in the area of the former fire training area and in the area of the fire station. Within the scope of the current investigations, however, further suspected PFAS areas are still being investigated.

In the area of the former fire extinguishing training basin, even more detailed investigations are planned to clarify the distribution of the contaminants in the soil and groundwater. The PFAS plume in the groundwater emanating from the site has been largely investigated, but additional investigations are still required, especially in the area beyond the site. The background to this is that the groundwater in the low yielding aquifer of minor thickness has an unexpected flow regime, whereby the PFAS plume is divided into two differently directed flow tubes or sub-plumes due to the special morphology of the bottom of the aquifer. During the investigation, individual PFAS compounds were analyzed, an analysis for precursor (sum parameter) was not carried out.

The affected source/receptor pathway is mainly soil → groundwater. One of the two PFAS sub-plumes flows towards a former drinking water production area. Due to the PFAS contamination, however, operations here were stopped several years ago. The second PFAS sub-plume flows in the direction of a still used drinking water production area. At the time of the survey, it was not yet conclusively determined how great the risk potential is to this designated drinking water area, but this is being investigated further.

A wastewater treatment plan had been receiving PFAS-contaminated wastewater from the site and farmers have been spreading associated PFAS-contaminated sewage sludge onto their fields for fertilization. Control investigations are being carried out by the authorities.

For the former fire extinguishing training basin, the authorities have demanded an immediate measure for containment/remediation. The owner of the property has so far refused to do so because the area is located in the airport entry lane, making it difficult to install a surface seal from the point of view of air traffic control, and because the site has not yet been fully investigated. It was then mutually agreed with the environmental authorities to wait for the investigation and a formal remedial options appraisal. In the meantime, the flight operations have been suspended.

Rainwater that collects within the fire training basin can be drained off via outlet drains. In the event of a large water influx, the outlets become overflown and the PFAS-contaminated water may enter the groundwater. Therefore, the water accumulating in the basin should be pumped out and cleaned in the future. A pilot test to the containment on the site was implemented in spring 2019. This is intended to prevent any overflow and release of PFAS.

Some of the precipitation water that accumulates at the site is discharged into rivers and some is seeping into the groundwater. At the time of this survey, the site-specific wastewater management plan is currently being updated. The update includes PFAS monitoring within the drainage system.

So far, no protection and restriction measures have been implemented. Drinking water production facilities located downgradient to the north have ceased operations in 2013. The airport operator does not consider itself responsible for the application of PFAS-contaminated sewage sludge on arable land, especially since the PFAS contamination on the arable land could also come from other sources (other sewage sludge, other PFAS inputs to the sewage treatment plant). Investigations of the arable land are arranged by the environmental authority (official investigation).

2.7 Application of Fire Extinguishing Foams, Airport (Case 7)

At an airport, the use of fire-fighting foams at several locations resulted in the release of PFAS to the underground, the groundwater, and subsequently to surface waters. Upon completion of a historical investigation of the site, several suspected areas were identified, including fire training areas, the fire station and its surroundings (presumably testing of extinguishing equipment), storage areas, operational areas, parking areas for fire engines in certain flight situations, and foam carpets in accidents and during trainings.

Orienting (phase 2A) investigations of the suspected areas have been carried out. For three more heavily contaminated areas, a detailed investigation (phase 2B), including a final risk assessment, has also been completed and contamination to soil and groundwater has thereby been sufficiently investigated. Classical methods were used for the investigation and groundwater samples were partly obtained by direct-push drillings. During the investigation, the existing network of groundwater monitoring wells was further completed.

The fire station has so far proved to be the main contaminated area. A small diffuse contamination was also found on the property, probably due to soil redistribution. The extension of the PFAS plume in groundwater and surface waters is also known. The plume flows out of the airport over a large area. The analysis focuses on the 13 compounds specified in the official guideline; precursors were not analyzed.

The source/receptor pathway soil → water bodies and above all the pathway soil → crop are relevant to this study. In the area of the PFAS plume outside the property, there are groundwater extraction wells in use for private gardens and agricultural irrigation. On the garden areas, the use of contaminated groundwater has led to PFAS enrichment in the soil. First studies were carried out to evaluate the consequences of agricultural irrigation. Monitoring areas are being established on a permanent basis. Near-surface PFAS contamination was found in agricultural areas in the immediate vicinity of the airport. Higher concentrations were detected in the groundwater fluctuation zone, presumably due to accumulation from the contaminated groundwater. The process is still being monitored.

Furthermore, there are fire-fighting wells on the site from which extinguishing water may be extracted in the event of a fire. To ensure that they can be used if needed, function tests were carried out regularly. These tests are currently suspended. A concept for future functional tests is being developed.

As a protection and restriction measure in the contaminated groundwater outside the property, the extraction of groundwater and surface water for irrigation purposes was prohibited by general ordinance. The basis for this was the German Federal Water Law (prevention) in conjunction with precautionary soil protection according to German Federal Soil Act (BBodSchG).

For the operation of the agriculturally used wells, no protection and restriction measures are currently necessary. In the immediate vicinity of the airport, however, protection and restriction measures may become necessary in the future. When applying for the renewal of the permits for the operation of these wells (usually for 10 years), it must be proven that the operation of the wells does not cause harmful soil changes.

After the final risk assessment, a remedial options appraisal and remediation planning was required by the authorities for the contamination areas investigated so far. As an early measure, a groundwater containment system for the fire station area is currently being examined in combination with a possible source-related measure.

Two sources are currently known at the site. Due to the PFAS-contaminated groundwater runoff from some suspected areas, the properties of the two polluters are mutually influenced. The responsibilities will be clarified internally. One polluter has declared responsibility for the PFAS outflow from the fire station area.

2.8 Application of Fire Extinguishing Foams, Refinery (Case 8)

At the site of a refinery still in operation, fire extinguishing foams were used in several training areas. This led to contamination of soil and groundwater, as shown by orienting investigations in 2009. In addition to the training area, fire extinguishing agents were probably also the cause of further PFAS contaminations. Today, the site is diffusely contaminated in many areas. This has been shown by area-wide investigations. It cannot be ruled out that individual contaminated areas were built over after the contamination had developed. This cannot be analytically verified at present. The list of PFAS compounds specified by the state authority were analyzed, but no precursor analysis has been carried out to date.

A groundwater flow model was created as part of the investigation. The aim of the model was actually to depict the groundwater situation of the upper quaternary aquifer of the site, including its receiving waters. During validation of the model, the high likelihood of an additional PFAS source was determined. A further source was then confirmed by conducting subsequent investigations.

The site investigation was mainly based on conventional sampling of soil (2 - 4 m unsaturated soil area) and groundwater. The plume is largely delineated in its thickness (but not depth-differentiated) and in the groundwater flow direction. It extends about 1.3 km beyond the approximately 1 km long refinery site. In the area of the plume, a smaller settlement can be found. Several small ponds are located downstream from the source. A part of the plots covered by the PFAS plume already belong to the refinery, another part, the pond plots, was bought by the refinery to prevent potentially contaminated fish from circulating uncontrollably.

Process water is taken from the refinery premises. This water is discharged via the plant's own sewage treatment plant. In the past, drainage water was discharged into the nearby creek, but this discharge has since been stopped. The drainage water is now also discharged into the plant's own sewage treatment plant. Once the discharge of drainage water into the surface water has been stopped, the situation there has improved considerably, and the surface water is now hardly contaminated at all.

The ponds located downstream were sampled and analyzed for PFAS (water, sediment, and fish). The water samples showed PFAS in different concentrations. PFAS could also be detected in fish. These fish were assessed as unsafe to eat in the sense of Article 14 (2) (b) in connection with Article 5 of Regulation VO (EC) 178/2002.

The fish may be taken from the ponds in accordance with Article 14(1)(i) in conjunction with Article 14(6) of Regulation VO (EC) No 178/2002, fish from the ponds may not be placed on the market without proof of food safety. The pond operators were informed accordingly by the District Office at the time.

Furthermore, the wells used for garden irrigation in the settlement are currently being investigated, but no results are yet available.

This shows that at this site only the source/receptor pathways soil → groundwater and groundwater → surface water → fish → human are relevant. The extent to which the source/receptor pathway soil → crop is relevant cannot yet be answered.

Since the PFAS plume extends beyond the property boundary, it was essential to install a hydraulic containment. This is currently being planned in detail and should be put into operation shortly. In addition, detailed remedial options appraisal is yet to be conducted. The aim would be to determine available options for source remediation of the individual hotspots. The refinery was obligated to carry out the investigation and remediation as the liable party.

Remediation targets, including values for the hydraulic containment, are currently being discussed and have not yet been finally determined.

2.9 Application of Fire Extinguishing Foams, Airport (Case 9)

At an airport, PFAS contaminated areas are known (fire station, practice area, fire event). The contamination to soil and groundwater has been delineated to a large extent. Within the groundwater plume that stems from the fire station, higher PFAS concentrations were determined at locations further from the identified source as compared to the immediate vicinity. The suspicion that there might have been another PFAS source zone could not be confirmed. The PFAS plumes partially enter lakes and then flow off along the entire width of the lakes. Finally, they flow into the nearest stream (surface water).

Soil and groundwater contamination were delineated using classical methods (soil and groundwater samples). Groundwater sampling was carried out by means of direct-push methods in several transects in order to determine suitable locations for the later construction of the groundwater monitoring wells. The investigations mostly comprised 10 PFAS compounds. Occasionally all detectable compounds (approx. 25) including Capstone were analyzed later. Capstone was only detected at one location. A TOP analysis showed that precursors were also present, but the analysis results still need to be checked.

The affected source/receptor pathways are soil → groundwater, groundwater → drinking water and others. Drinking water use rights of a medical institution were not extended after expiration. A waterworks had to be closed. Discussions are currently underway with the operator as to whether the waterworks can be put back into operation if suitable means are implemented to eliminate the PFAS in the raw water, or what measures can be taken to protect the other drinking water production plants directly connected to it.

The contaminated lakes (former gravel extraction) with connection to groundwater in the area of the PFAS plume were used as fishing ponds. The public health department recommended not to consume the fish from the lakes. An agreement was made with the fishing club that the lakes should not be restocked with fish. Lake residents had previously used the lake water as service water (not drinking water), and this too was prohibited. Furthermore, the use of lake water for agricultural purposes (horse farm) was discontinued, the corresponding right of use was not extended.

A general decree was issued in accordance with the German Federal Soil Act (BBodSchG) to prevent the use of groundwater via wells for garden irrigation. The reason given is that watering the gardens with PFAS-contaminated groundwater would lead to harmful soil contamination. An accumulation in crop plants could also not be excluded (precautionary health protection) applying irrigation.

For source remediation (direct measure), the training basin and about 0.5 m of soil below it were removed and a foil was installed to separate the clean refill soil from the contaminated soil below the excavation pit. The contaminated soil is, however, larger in its surface area, since in earlier times the fire brigade already approached the training basin with fire extinguishing cannons switched on.

In the area of the fire (an airplane had gone over the runway and caught fire) the soil was only excavated to a small extent. For safety reasons, it is not possible to exchange soil in the vicinity of the runways. Therefore, the possibility of soil decontamination by soil flushing was investigated more intensively. Some preliminary tests have been carried out, but the entire investigation is still in its infancy. First results show that silty areas are worse and sandy areas can be decontaminated better with this method.

The excavated soil was deposited in landfills and partly installed in separate cassettes at the landfill.

Furthermore, there are many construction measures at the airport. What is currently still missing is a general remediation framework plan that regulates the handling of soil. This will be finished soon (status: mid-2019).

A hydraulic containment barrier has been installed directly downstream of each source zone. The purified water is discharged into a surface water, which after a short distance flows into a stream. The discharge values are 200 ng/L sum of PFAS and 20 ng/L PFOS. It has been shown that the prohibition of deterioration of surface waters is thus in compliance. For this purpose, numerous samples of the surface waters were analyzed for PFAS.

Remediation target values for groundwater have not yet been set but are currently being derived.

Several hydraulic barriers have been put into operation for the remediation of the plumes. This should also stop the inflow to the area of the drinking water production so that it could be put back into operation.

Intensive coordination between all stakeholders occurred. In addition to regular update meetings with the party responsible for remediation, the public is regularly informed, including at citizen information events. Further information is provided via the Internet.

2.10   Application of Fire Extinguishing Foams, Major Fire (Case 10)

In a major fire caused by arson in a warehouse for plastic crates for beverage bottles, various professional and plant fire brigades were deployed. It can therefore be assumed that various extinguishing foams were also used. The private property was later purchased by the city without knowledge of the PFAS contamination. Today the site is a wasteland, a plan for its subsequent use is not yet available. In this respect, the city, as the owner of the land, is liable for the remediation. The polluter (arsonist) could not be identified.

The contamination in soil and groundwater was delineated using classical methods (soil and groundwater samples). Groundwater sampling was carried out by direct push to determine suitable locations for the subsequent construction of the groundwater monitoring wells. The approximately 3 km long plume is currently still expanding rapidly (200 m/a) and converges at the tip with a chlorinated hydrocarbons plume.

Precursors have been sporadically investigated and detected, Capstone was also investigated, but only small amounts were found.

No secondary contaminants from burning plastic were found. However, the site is located on a several meter thick layer of fill, containing the usual contaminants found in historic fill soils.

The affected source/receptor pathway is mainly soil → groundwater. To prevent the use of groundwater for garden irrigation, a general decree was issued in accordance with the German Federal Soil Act (BBodSchG). The reason for this is that irrigation of the gardens with PFAS contaminated groundwater would lead to harmful soil changes. An accumulation in crop plants would not be excluded either (precautionary health protection).

For the remediation of the source area (soil), preliminary tests were carried out with the aim of assigning the PFAS contamination to defined grain sizes. Then the highly contaminated material could have been separated by wet classification. Due to the inhomogeneity of the contaminated backfill, the results were not suitable for developing an economical remediation technology. Currently there are no further plans for soil remediation.

A hydraulic barrier (pump-and-treat) with a removal rate of 30 m^3/h, distributed over two cleaning lines within the plant, was installed downstream of the source zone. It is planned to use PerfluorAd additionally in one of the two cleaning lines and to operate the stage until the breakthrough of the following activated carbon filter. The monitoring data will then be used to determine whether and to what extent the additional use of PerfluorAd will lead to cost savings.

Prior to the establishment of the hydraulic containment, several column tests were carried out as part of a funded research project to determine the best activated carbon and the achievable water quality.

Pump-and-treat measures for the remediation of a chlorinated hydrocarbons plume are already in operation at two locations, including at the plume tip. The party liable for remediation of the CVOCs must also remove the PFAS from the exfiltrated water. Since the measure has attracted the PFAS plume in the past, the groundwater pumping regime has been modified to minimize this process. The city is currently discussing whether one of the groundwater treatment plants can be taken over by the private stakeholder to clean up the PFAS plume tip and thus prevent a further extension of the plume.

The target discharge value is 200 ng/L total PFAS or 20 ng/L PFOS. Remediation target values for the groundwater have not yet been set.

3   References

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Appendix E:

Research Needs

Table of Contents

1   Introduction

During the preparation of this guideline, but also in the two parallel expert workshops and from the international literature, a number of open questions from all areas of contaminated site management have arisen which cannot be answered at first and are therefore formulated below as a need for research. There is also a considerable need for research according to the German *Bund/Länder Fachgruppe PFC* (2019) in the following topics:

► for most of the substances there is a lack of detection methods; their behavior in the environment, such as mobility in soil or uptake by plants, is largely unclear,

► the human and ecotoxicological evaluation is still inconclusive, especially for cases of mixed toxicity, where several substances from the PFAS family interact,

► technologies for removal of PFAS from the environment are lacking, with current instances of remediation being very complex, costly, or technically impossible, and

► the industrial development of PFAS-free substitutes is still in its infancy in some areas.

In general, the discussion on further needs for research can be subdivided into legal and technical issues. General needs for research have been outlined in the main part of this guideline and here those needs are explained in further detail.

PFAS comprise almost 5,000 different compounds. For only a few of them, sufficient data are available to assess their toxicological potential, including their bioavailability, and to derive assessment values. This is certainly the area where the greatest need for research exists, however this will not be discussed any further.

Rather, in addition to legal issues, the following topics will be addressed (Stroo et al. 2017):

► transport properties and natural sinks

► investigation methods

► remediation technologies

► Use of contaminated sites

For all research and development, the specific costs for a full-scale application must be determined. Only in this way, will it be possible to arrive at more cost-effective and sustainable solutions in comparison to the established technologies.

It is already becoming clear that only through targeted research coordination, e.g. in a joint research project, can sufficient knowledge be gained for future strategies of avoidance, precaution, and risk mitigation. Further open questions are addressed in the publication of the *Bund/Länder Fachgruppe PFC* (2019).

2   Legal Issues in Germany

In the case of large areas of PFAS-contaminated, questions regularly arise regarding the handling of excavated material, as part of infrastructure management. The administrative handling of these questions varies, depending on the responsible German Federal State. In some cases, the impression is given that out of concern of making wrong decisions with respect to waste legislation, the path chosen is more often than not direct disposal, although direct disposal as a cure-all solution is by no means always the best solution.

In effect, an unnecessary burden is imposed on existing disposal facilities that already are fighting with the issue of limited space and resources. It is therefore imperative that legal guidelines for handling of such wastes are created that encompass a variety of scenarios of PFAS-contamination.

For cases of wide-spread PFAS contamination, further legal issues and questions, concerning their handling shall be addressed and clarified. To this end, the existing German Federal Soil Act (BBodSchG) may serve as the basis for assessing various possibilities, such as the relocation of soil material within contaminated areas according to §12(10) BBodSchG. This existing regulation, for example, is yet not specific enough for the application to cases of wide-spread PFAS contamination. Rather, for cases of wide-spread PFAS contamination, the regulations of the BBodSchG should serve as the basis for more detailed specifications of mitigation.

Furthermore, there is a lack of working aids or guidelines for the legal evaluation of the source/receptor-pathways soil → human and soil → crop (including home gardens for home-grown fruits and vegetables). Despite there being the lack of a valid basis for trigger value derivation, nevertheless, on an everyday basis, the issues described above are the subject of professional and administrative judgment. At the same time, scientific data is lacking, such as basic human-toxicological data and information on transfer processes and factors.

Legal questions arise not only with respect to the management of PFAS-contaminated sites, but also in the application of the individual remediation technologies. Regarding the remediation technologies, open questions remain, in particular those regarding the immobilization of PFAS, a current topic of intense discussion. Discretionary criteria for the application of immobilization technologies are largely lacking. The process of immobilization comprises the deliberate leaving of contaminants onsite in an immobilized bounded state. An example of one open question is: to what extent can land that has an immobilized PFAS impact in soil even be used?

3 Technical Issues

3.1 Chemical Analysis

Considering the very high number of PFAS in existence, it would certainly not be best to continually extend the list of analyzable compounds more and more and without any defined limit (exceptions are new special compounds such as ADONA). Rather, sum parameters, that can effectively summarize contamination levels, shall become more relevant factors to be considered in the assessment. The following points highlight current pertinent issues:

- ► the set of individual PFAS substances to be analyzed must be clearly defined (derivation of a "PFAS list" according to the relevance of each individual substance),
- ► high-resolution methods to identify previously unknown PFAS (non-target methods) must be developed,
- ► development of standard methods for new PFAS, such as ADONA, GenX, cyclic PFAS, etc.,
- ► further development and, if necessary, standardization of the TOP assay for the detection of precursor compounds,
- ► research on AOF, TOP assay and EOF to explain differences in AOF/EOF (total fluorine content) and TOP (PFAS after oxidation of precursors determined by LC/MS),
- ► Evaluation standards for AOF, EOF and PFAS contents from the TOP assay.

3.2   Background Concentrations

As PFAS are ubiquitously distributed, a low background level of detectable concentrations that is caused exclusively by anthropogenic activities is to be expected over the entire nation. This background level however is likely to vary depending on the historical and present use of the general area. It cannot be ruled out that the substitutes used in the recent past may contribute to a current ubiquitous airborne input of PFAS into the soil, which if the case, would lead to a sustained increase in background contamination. In addition, the presumably slow biotransformation of precursors can cause an increasing proportion of perfluorated carboxylic and sulphonic acids over time. These processes must be investigated in the context of an area-wide monitoring program and if necessary, regularly monitored.

3.3   Transport Properties and Natural Sinks

3.3.1   Overview

A detailed understanding of the transport and fate of PFAS in the environment is essential to assess the risks resulting from contamination and to develop reliable conceptual site models. Such derivations are complicated by the large number of different PFAS compounds in AFFF[1] formulations. Moreover, different isomers (linear or branched forms of a molecule) behave differently with respect to their transport properties (Prevodorous et al., 2006), their bioaccumulation potential (Houde et al., 2008), and their remediability (Rahman et al., 2014). Data to predict transport and fate are not available for most PFAS, and investigated PFAS show a wide range of physicochemical properties.

In addition, there are likely to be significant mixing effects and interactions with co-contaminants, which may alter the behavior and transport properties of the PFAS and further complicate the problem. Furthermore, a variety of abiotic and biotic processes can convert PFAS precursors into regulated PFAS compounds (e.g. PFOA and PFOS) under specific environmental conditions. These processes should be considered in risk assessments, model predictions, and conceptual site models.

3.3.2   Transport Behavior

A better understanding of the transport and long-term fate of PFAS, including precursors in unsaturated soil and groundwater would improve the prediction of contaminant migration and thus the management of PFAS-contaminated sites. Ideally, this would allow prioritization for further site investigation and remediation. Furthermore, with this knowledge, more efficient site characterizations could be carried out.

Reliable predictions on the period of "bleeding" of PFAS in unsaturated soil sources zones and aquifers are currently not possible. Consequently, the kinetics of the source strength are difficult to measure and model. For example, cationic and zwitterionic PFAS tend to remain in the source zones due to relatively strong sorption, but it is not known whether they persist permanently or whether and to what extent they may be degraded or transformed.

Transformations of the precursors could occur in contaminated aquifers preferably near and within the capillary fringe, but under certain conditions PFAS can penetrate deeper into the aquifer.

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[1]   AFFF stands for Aqueous Film Forming Foam, a synthetic PFAS-containing foaming agent which is added to water to produce foam, especially to extinguish liquid fires.

Of particular interest are also processes responsible for the long-term sorption and desorption of PFAS in fractured aquifers (sources and plumes).

The evaluation of precursors also raises numerous questions. Their transformation pathways, but especially their transformation rates are not sufficiently understood in real contaminated soils and aquifers, especially in the presence of co-contaminants and under the specific biogeochemical conditions that usually occur at contaminated sites. Extensive studies on the biotransformation of precursors could significantly improve the risk assessment and characterization of PFAS-contaminated sites.

3.3.3 PFAS-Distribution in Different Compartments

PFAS are surface-active substances and therefore tend to accumulate at interfaces (e.g. air-water, water-product phases, or soil-groundwater). Depending on their concentration and composition, PFAS can be present predominantly as monomers, hemicelles or micelles, which influences the characteristics of their fate and transport.

The distribution of the PFAS in different environmental compartments (water, soil, soil air) is extremely complex and has a particular influence on the transport and fate of the PFAS in the environment as well as the characterization and remediation of the site. The distribution of PFAS in solids, water and air can affect the choice of remediation technology and the success of the remediation. Certain remediation methods can also have an impact on PFAS mobility. Understanding the factors that control PFAS partitioning in aquifers is also critical to the management of contaminated sites. Basic data on the occurring partitioning processes are not available for many PFAS.

3.3.4 Prognosis Models

Pollutant transport models to predict the future spread of PFAS are required above all to assess the risks caused by these contaminants in all environmental compartments. Such models must be capable of predicting the potential migration pathways of PFAS as well as changes in concentrations and compositions over time. In a next step, these models should be extended to reactive contaminant transport models, including the transformation of precursors and the effects of environmental conditions (including redox potential, pH, C_{org} content and the presence of co-contaminants) on the transport and fate of PFAS. Identification and quantification of the key parameters (e.g. soil parameters, contaminant transformation kinetics) that control these models are also still required. After development and validation of such models, conceptual site designs and decisions on the need for further investigation and/or remediation can be improved.

It is still unknown whether fingerprints exist for PFAS as they do for CVOCs and whether transformation rates can be deduced from the pattern shift. Such information can be of essential importance for model calibrations.

3.3.5 Precursor Transformation

The apparent slow biotransformation of precursors to stable end-products (perfluorinated carboxylic and sulfonic acids), leads to the formation of very long-lived metabolites. The question arises as to whether these are further transformed into end products over the long term or whether they are transported into the groundwater as metabolites. There is hardly any toxicological data available for these metabolites, so that they currently elude evaluation. Of particular interest are the transformation kinetics and the biogeochemical prerequisites for transformation in the environment. Only with knowledge of these data, can the process of precursor biotransformation be evaluated.

3.3.6   PFAS-Uptake in Crops

Intensive research efforts are currently underway to understand the processes and identify crops that are not sensitive to PFAS uptake. Pre-harvest monitoring has shown that crops with a high water and protein content, such as tomatoes, zucchini, melons, and beans, are particularly good at absorbing and concentrating PFAS that are contained in irrigation water. Further research is still needed in this area.

3.4   Site Investigation

3.4.1   Leaching Methods

Given the complexity of PFAS mixtures, the range of operating histories of most contaminated sites, and the difficulty of predicting PFAS mobility, it is important to develop methods to measure and predict the extent of PFAS migration in unsaturated or saturated zones. This is particularly important for assessing the potential for PFAS migration from residual contaminants in the unsaturated zone to groundwater. The assessment of whether residual sources pose a persistent risk after natural elution of the most mobile components requires validated elution methods for soils and sediments. Laboratory methods for determining the elutability of PFAS mixtures in environmental samples would be as valuable as methods for measuring elution and mass flux in-situ. A reliable elution method should consider the effects of co-contaminants, PFAS precursors, and geochemical soil and groundwater conditions. Basic research on the effects of soil and contaminant parameters on transport is also required.

3.4.2   Mass Flux Determination

Mass fluxes, if determined for the unsaturated zone and for groundwater would lead to several improvements, such as:

> ► Improved understanding of conceptual site models
> ► Evaluation of the detected PFAS concentrations
> ► Communication of technical information between technical and non-technical interest groups.

The determination of mass flux is complicated due to the slow transformation of precursors.

4   Remediation Technologies

4.1   Overview

The development of improved PFAS remediation technologies will have to meet several requirements, such as:

> ► development of methodologies that eliminate PFAS without causing the production of harmful by-products (destructive processes),
> ► applicability to (ultra)short-chain compounds and to precursors,
> ► ability to meet the required target values, usually in the ng/L range,
> ► total energy efficiency, sustainability, and cost-effectiveness.

It is quite apparent that these challenges along with the wide range of contaminant compounds, will not be able to be solved with one single process, but rather treatment trains will be required. Regardless of whether the processes involve degradation, separation, or both, they must meet the typical requirements for remediation. These include consideration of geochemistry, the presence of likely co-contaminants (in terms of co-contaminant removal and interactions with PFAS elimination), and relatively low initial PFAS concentrations at many sites.

Degradation-based processes require careful preparation of mass balances to assess the risks associated with the final products. Since typically aggressive reaction conditions are required to degrade PFAS, research should also focus on avoiding the potential formation of toxic by-products.

4.2   *In-situ* Technologies

In-situ remediation technologies for PFAS are urgently needed for both the unsaturated soil (source zone) and the groundwater (source zone and/or plume). An effective remediation of the unsaturated zone, where usually most of the PFAS of a source area is located, is of particular interest. Technologies for the unsaturated soil zone must consider the distribution equilibria of the PFAS (solid/aqueous), which are influenced by increased concentrations of soil organic matter and the size of fluid-fluid interfaces. Source remediation techniques may include PFAS transformation, flushing, or immobilization/stabilization. Initial and sometimes failed approaches are included:

- ► enzyme-based methods
- ► coagulant-enhanced sorption
- ► permeable Sorption Barriers
- ► persulfate oxidation coupled with biodegradation
- ► thermally activated persulfate oxidation coupled with pump-and-treat

For in-situ technologies that enhance PFAS transformation, mass balances are also required regarding the proof of sufficient longevity of the added reagents and the maintenance of the reaction rate. In-situ methods based on sequestration/immobilization must be able to guarantee (almost complete) irreversibility and long-term stability.

Cost-effective in-situ technologies for contaminant plumes are also required. However, technologies that attack the PFAS-impact source are more likely to be considered as key technologies. The effects of PFAS source reduction on the long-term behavior of plumes are not known at present.

4.3   Ex-situ Technologies

4.3.1   Overview

Pump-and-treat technologies for groundwater remediation, which use activated carbon and/or ion exchange resins, are already being used at full scale at many sites. These processes have their limitations in terms of their ability to efficiently remove short chain and hydrophilic PFAS. In addition, the PFAS sorbed on activated carbon or the resins must be disposed of together with the sorbent or separately after sorbent regeneration at high costs. Ex-situ technologies capable of degrading PFAS would be desirable. Initial approaches such as electrochemical degradation, degradation by means of generated hydrated electrons or PFAS separation via membrane filtration are promising. However, there are still challenges in terms of formed oxidation by-products, waste/concentrate streams and energy demand, which currently represent substantial obstacles to the implementation and acceptance of these technologies. Urgently necessary are therefore:

- ► alternative, low-cost, and easily regenerated sorbents with a longer service life and higher selectivity also for short-chain PFAS.
- ► Improvements of activated carbons and ion exchange resins in terms of sorption capacity (including short chain PFAS) and/or regenerability.
- ► Treatment trains with precursor transformation for the remediation of complex PFAS mixtures.
- ► Improving electrochemical processes and the generation of hydrated electrons.
- ► Development of novel processes for effective and efficient conversion/defluorination of PFAS.

All of the above mentioned approaches must take into account the energy requirements, degradation/elimination rates, the longevity of the reagents and apparatus used, the ability to handle a wide variety of PFAS compounds (including precursors), and the life cycle costs of the processes. Finally, the quality of the water to be treated (e.g. salinity, turbidity, pH-value) must also be considered with regard to the discharge of the treated water.

There are also many open questions regarding soil treatment methods.

4.3.2 Treatment of Concentrated PFAS-Waste Streams

Concentrated waste streams (PFAS-loaded activated carbons or ion exchangers) are a result of the most widely used technologies for the remediation of PFAS-contaminated waters (P&T). Concentrated waste streams can also result from several other processes (e.g. membrane filtration, soil washing). Each of these technologies generate one or more types of concentrated waste streams (e.g. contaminated iron sludge or gravel filters from groundwater pre-treatment) that require careful further treatment, which usually significantly increases the total cost of the remediation technology.

Current approaches to eliminate these concentrated material streams are energy intensive. Usually, thermal regeneration of activated carbons at high temperatures and/or combustion at high temperature ($\geq 1,000 °C$) with subsequent reuse or disposal is used. However, there is little data on residual contaminants and other potentially toxic by-products that could remain in the reactivated material.

There is therefore a great need to develop cost-effective and sustainable approaches to concentrate material streams from ex-situ remediation processes and thus simplify the management of residues. As with all methods, the wide range of PFAS and critical compounds (short-chain PFAS, precursors) must be considered. Furthermore, possible transformation products must be identified and the (complete) defluorination-cause by the individual technologies must be confirmed analytically. Other reaction by-products not containing PFAS (e.g. perchlorate formation from chloride present in the waste stream) should be fully identified. Finally, life cycle cost and environmental impact assessments of residual waste streams are also of interest. Ideally, the technologies for the elimination of the high-concentration waste streams can be applied on site as part of the process.

4.3.3   Activated Carbon

For activated carbons and other carbon-based sorbents, a better understanding of PFAS fate during thermal reactivation is required, as well as the extent to which reactivation affects the long-term effectiveness of the sorbent. Questions like:

- ► What is the permit situation for such plants?
- ► Are the temperatures used sufficient to fully mineralize the PFAS?
- ► Are there investigations of the exhaust air (emission) and with what result?
- ► Are there investigations of the soils in the vicinity of the plants?
- ► Which measurement methods were used for emissions monitoring?

should at least in principle be clarified. Furthermore, it should be investigated whether toxic products are formed during thermal reactivation and subsequently released from the sorbent.

In addition, new or modified sorbents should be developed which can be regenerated on-site under milder conditions and with less energy input. Finally, the development of improved adsorbents can also contribute to the concentration of PFAS waste in small media volumes.

Whether there will be alternatives to sorption on activated carbon in the future is controversially discussed. In addition to the assumption that presumably no new economic purification processes for extracted groundwater will emerge, there is (at least according to basic research) the possibility to control (at least according to basic research) whether the activated carbon sorbs or desorbs via selected electrical potentials. This would provide the possibility of on-site regeneration. The regenerate (concentrate) would then preferably have to be fed into a non-thermal PFAS mineralization process. All in all, the process should require a significantly lower total energy input and would then be significantly more sustainable.

4.3.4   Ion Exchange Resins

The same applies to ion exchangers as to activated carbon. Ion exchange resins that better bind the PFAS (including problematic substances) and that can be regenerated easily and completely are needed. In addition, processes are required to prepare the regeneration solutions (consisting of PFAS, brine, alcohol, etc.) so that they can be reused. These processes may include the development of novel regeneration solutions and processes and/or new processes for the conversion or separation of PFAS from the regeneration liquid. The influence of the regeneration process on the long-term effectiveness of the ion exchange resin must also be tested for ion exchange resins. Under certain circumstances, the development of improved cost-effective disposable ion exchange resins may also be useful.

4.3.5   Membrane Filtration

Membrane filtration technologies such as reverse osmosis or nanofiltration generate a waste stream with a high content of salts and PFAS that requires further treatment. For the treatment of this concentrate, a technology is required that can ideally be applied on-site. These technologies should include a reduction in the volume of the PFAS concentrate or the development of improved technology to eliminate the PFAS in the concentrate.

4.3.6   Oxidative and Reductive Technologies

Up to now, oxidative processes for PFAS transformation (defluorination) have been the focus of research. Oxidative methods may be less effective for PFSA than for PFCA (Park et al., 2016), while reductive approaches may be more suitable for eliminating PFSA (Park et al., 2009; Arvaniti et al., 2015). Furthermore, oxidative processes often generate undesired reaction by-products such as perchlorate and short-chain PFAS and are retarded in-situ by high levels of organic carbon. Therefore, the development of reductive PFAS transformation technologies is of particular interest. Relatively little is currently known about this. Possible procedures are:

▶ cathodic electrochemical treatment, including cathodically produced coagulants (electrocoagulation)

▶ catalysts/zero valent metals

▶ hydrated electrons

▶ treatment trains with a sequence of reductive and oxidative processes

The transformation processes of the reductive technologies must be understood as clearly as the impact of the reductive processes on water chemistry and other potential co-contaminants.

4.3.7   Soil Washing

For full-scale ex-situ decontamination of soil, only soil washing has been carried out so far. The procedure is limited to sandy and gravelly soils. There is still a need for clarification and optimization with regard to recycling of washed soil. Agricultural use of the washed soil is unwarranted. Questions of recycling washed soils and soils separated according to grain size (declaration as recycling material, re-installation according to waste law, substitute building material properties) have still not been conclusively answered.

4.4   Immobilization Technologies (Soil Stabilization)

The immobilization of PFAS as an ex-situ or in-situ-applicable procedure is a current topic of intensive discussion. Since processes associated with in-situ technologies applied to unsaturated and saturated soils are not fully the same, they must be considered as separate procedures. Aspects of both may be identical, yet, there is a need for a greater detailed process understanding, which is significantly higher for immobilization within an aquifer.

PFAS immobilization within aquifer

▶ Do the groundwater hydraulics (e.g. groundwater flow bypassing the contaminated area due to blocking) change after injection of the reagents?

▶ Are the environmental conditions (pH, redox-oxidation-potential, etc.) changed by the injection of the reagents? This can be expected if organic substances are injected together with the reagents. How do the changes in environmental conditions affect the conditions within the aquifer?

▶ What should be done when the maximum sorption capacity is reached (breakthrough)?

▶ Is it possible that PFAS-loaded colloids are transported with natural groundwater flow (long-term particle transport)?

► In urban areas, contaminants plumes comprising only one contaminant group are rare. What happens to any existing PFAS when remediation-promoting reagents targeted for other contaminants are injected into the aquifer?

PFAS immobilization in unsaturated soil

► Does immobilization prevent transfer and uptake of the PFAS into the food chain?

► What influence does immobilization have on plant growth and nutrient supply?

Compartment-independent PFAS immobilization

► For complete sorption, the quantity and concentration of the adsorbent must be determined. The corresponding methods must be developed.

► Which soil/groundwater parameters influence efficiency of immobilization?

► How are the short-chain PFAS immobilized? Is there a release of these compounds in increased concentrations when they are displaced by better binding substances?

► Are the PFAS displaced and remobilized by natural organic substances (DOC)? If this occurs, what are the concentrations that the mobilized PFAS can reach?

► Activated carbons are very good growth surfaces for microorganisms. What effect does the formation of a biofilm have on immobilized PFAS?

► What contaminant concentrations in leachate or groundwater occur when the process returns to the desorption phase? Do the PFAS concentrations remain below the respective limit values?

► The appropriate test methods for checking the long-term stability still need to be developed. These must be agreed with the approval authority so that the test methods are accepted. In addition to laboratory tests, large-scale tests in lysimeters can also be useful. In the event of an increased release, at what point in the release process must the authority intervene? Which options would be available?

► How do costs, benefits, and sustainability compare with decontamination technologies?

In addition, the introduction of substances into the aquifer is an act that generally requires a permit. The competent authority may require additional hydraulic safety measures downgradient of the treatment zone, which can only be removed if the processes in the aquifer remain unchanged and an effluent of increased PFAS concentrations is considered unlikely.

Modelling the underground processes over long periods of time would help to increase the safety of the immobilization technology.

In addition to immobilization, the authorities will likely require a monitoring program that must be approved in order to record and evaluate both short-term (complete immobilization in the reaction area) and long-term (remobilization) effects.

4.5   Comparison of Treatment Technologies

Numerous technologies for the remediation of PFAS-contaminated sites are currently under development. Applicable full-scale technologies were tested at individual real contaminated sites with different properties (e.g. PFAS sources, groundwater chemistry, hydrogeology). It is therefore difficult to compare the costs and performance of the technologies. Often the documented performance is also based on provider information and was not determined by independent bodies.

To facilitate an efficient technology selection and to identify the most promising remediation solutions for different types of sites, direct comparisons of promising remediation technologies should be carried out. Comparisons could include the following issues:

- ▶ Ex-situ groundwater treatment processes
- ▶ Treatment of PFAS concentrates
- ▶ Methods to improve PFAS extraction from soils (e.g. soil washing) with different reagents

Comparative studies should include costs, the feasibility of achieving low remediation targets and the ability to remove precursors and short-chain PFAS compounds. Where possible, demonstration sites should have the same co-contaminants and conditions typical of most PFAS-contaminated sites.

5 Use of Contaminated Sites

The risk to the environment caused by the PFAS is currently hardly assessable. Due to the high water solubility of PFAS and their moderate to high mobility in soils and sediments, PFAS persist in aquatic and terrestrial environments and accumulate in fish and wildlife. The management of sites contaminated with PFAS requires ecological risk assessments for listed and non-listed cultural and wild species (plants, animals).

Ecological risk assessments at PFAS-contaminated sites are complicated by the fact that PFAS often occur in complex mixtures.

Biota are exposed to a mix of PFAS. Therefore, a continuing need for research on bioaccumulation and biomagnification exits. This results in the following basic research tasks, among others:

- ▶ Determination of the toxicity of PFAS mixtures based on available data including effects on population density in aquatic and terrestrial ecosystems.

- ▶ Fundamentals of bioaccumulation and biomagnification pathways from soil and sediment organisms to higher trophic levels including the development and validation of corresponding models.

- ▶ Assessment of exposure pathways to threatened and endangered species.

Specifically, the question arises as to whether large areas of agricultural land contaminated with PFAS can be put back into use. Various approaches are conceivable. On the one hand, crops can be cultivated that hardly accumulate PFAS (neither in the parts of the plant that can be used for food nor in the remaining parts of the plant, in order to avoid diffuse PFAS spreading through plant waste). On the other hand, plants can be cultivated which enrich PFAS to a high degree. To derive an economic benefit from cultivation, these plants must be usable. Recycling of the plants for energy generation is also conceivable, provided the process temperatures are high enough to destroy the PFAS

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