

State of the Art PFAS

**An overview of knowledge gaps and research needs
soil and groundwater**

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T +31 88 xxx xx xx
M +31 6 xx xx xx xx
E ...@arcadis.com

Arcadis Nederland B.V.
P.O. Box 264
6800 AG Arnhem
The Netherlands

Contents

| | |
|--|-----------|
| Management samenvatting | 5 |
| 1 Introduction and scope | 7 |
| 2 Types, uses and presence in the environment | 8 |
| 2.1 Definition and types of PFAS | 8 |
| 2.2 Uses and presence in applications and products | 11 |
| 2.3 PFAS in the environment | 12 |
| 2.3.1 Presence in different environmental compartments | 12 |
| 2.3.2 Diffuse contamination and source sites | 13 |
| 2.4 Knowledge gaps and research needs | 13 |
| 3 Behavior, fate and transport | 14 |
| 3.1 Characteristics | 14 |
| 3.1.1 General properties | 14 |
| 3.1.2 Functional group and chain length | 14 |
| 3.2 Conceptual site model | 16 |
| 3.2.1 Transport into the environment | 16 |
| 3.2.2 Subsurface zoning | 17 |
| 3.3 Behavior in unsaturated and saturated zone | 17 |
| 3.3.1 Unsaturated zone | 18 |
| 3.3.2 Saturated zone and solute transport modelling | 18 |
| 3.4 Knowledge gaps and research needs | 19 |
| 4 Risk assessment, legislation and policy | 20 |
| 4.1 Risk assessment and health advisory levels | 20 |
| 4.2 RPFs and RBFs | 21 |
| 4.3 Legislation and policy the Netherlands | 22 |
| 4.3.1 Soil reuse | 22 |
| 4.3.2 Risk based advisory levels | 22 |
| 4.4 International legislation and policy | 23 |
| 4.4.1 European Union | 23 |
| 4.4.2 Other Countries | 24 |
| 4.5 Knowledge gaps and research needs | 26 |

| | | |
|-----------|---|-----------|
| 5 | Site investigation | 28 |
| 5.1 | Sampling | 28 |
| 5.2 | Chemical analyses | 28 |
| 5.2.1 | Standard Analytical Techniques (LC-MS/MS) | 28 |
| 5.2.2 | Advanced Analytical Techniques | 29 |
| 5.2.3 | Resumé analytical technologies | 30 |
| 5.3 | Knowledge gaps and research needs | 31 |
| 6 | Soil remediation | 32 |
| 6.1 | Technologies and challenges | 32 |
| 6.1.1 | Structuring technologies | 32 |
| 6.1.2 | Overview available technologies soil | 32 |
| 6.1.3 | Waste disposal and discharge | 34 |
| 6.2 | Knowledge gaps and research needs | 34 |
| 7 | Water treatment | 35 |
| 7.1 | Technologies and criteria | 35 |
| 7.1.1 | Inventories | 35 |
| 7.1.2 | Structuring technologies | 35 |
| 7.1.3 | Overview available technologies water | 36 |
| 7.1.4 | Waste and disposal | 36 |
| 7.2 | Knowledge gaps and research needs | 37 |
| 8 | Sustainability and circularity | 38 |
| 8.1 | Sustainability | 38 |
| 8.2 | Circularity | 38 |
| 9 | Resumé | 40 |
| 10 | References | 42 |
| | Appendix A: Overview of Treatment Techniques (Dutch) | 46 |
| | Colophon | 47 |

Management samenvatting

Inleiding en kader

Op initiatief van Rijkswaterstaat, zijn gedurende de zomer gesprekken gevoerd tussen Rijkswaterstaat en het Ministerie van Infrastructuur en Waterstaat over de aanpak van PFAS in de bodem. De conclusies waren dat Nederland aan een aantal internationale afspraken gehouden is, dat het probleem te groot is om individueel op te lossen en dat er eigenlijk al langere tijd een kennisinfrastructuur wordt gemist waar kennisvragen in kunnen worden geadresseerd en opgelost. Het onderzoek wordt versnipperd uitgevoerd. De gezamenlijke en geprogrammeerde kennisontwikkeling die noodzakelijk is voor het oplossen van een dergelijk groot probleem wordt gemist.

De samenwerking in een kennisprogramma tussen praktijk, onderzoek en beleid is in het verleden succesvol gebleken. Vanuit het werkveld is er een roep om een gezamenlijke aanpak en gezamenlijk onderzoek. Ook uit Rijksgelden die nu suboptimaal worden ingezet, kan meer (kennis-) rendement worden gerealiseerd. Dit alles heeft geleid tot een eerste verkenning om te kijken of een gezamenlijk kennisprogramma over PFAS breed gedragen wordt.

In de periode van november 2022 tot januari 2023 is een 'State of the Art' onderzoek uitgevoerd om de ontwikkelde kennis en daaruit volgende kennisleemtes en onderzoeksvragen in kaart te brengen. De resultaten zijn gereviewed en onderschreven door nationale en internationale experts. Het is een waardevol referentie document dat de basis vormt voor een kennisprogramma en waarmee de huidige praktijk zijn voordeel kan doen. Parallel aan het opstellen van de State of the Art hebben gesprekken met stakeholders plaatsgevonden om de behoefte aan en interesse voor een nationaal kennisprogramma voor de aanpak van PFAS in de bodem te peilen.

Voorliggend document bevat een samenvatting van de resultaten en conclusies van de State of the Art inventarisatie.

Conclusies State of The Art

PFAS is een verzamelnaam voor een grote groep (duizenden) chemisch geproduceerde stoffen met zeer uiteenlopende eigenschappen. Veel stoffen van deze groep kennen we niet omdat ze niet kunnen worden geanalyseerd. Van de stoffen die we kennen (tientallen) weten we dat ze schadelijk zijn voor milieu en mens. Deze bekende PFAS zijn alomtegenwoordig in ons (Nederlandse) milieu: oppervlaktewater, bodem, grondwater, stof en lucht.

Door de Europese voedselautoriteit (EFSA, 2021) is een opinie geschreven over acceptabele waarden (van een aantal PFAS stoffen) waar de mens via voedsel aan zou mogen worden blootgesteld. Door een aantal relevante internationale instanties wordt aangegeven dat de onzekerheden in afleiding van deze acceptabele waarden te groot zijn. Op basis van deze EFSA-waarden zijn in Nederland risicowaarden voor een aantal PFAS stoffen in bodem en grondwater afgeleid. Deze waarden liggen lager dan de (achtergrond-) waarden die alomtegenwoordig in het Nederlandse milieu worden aangetroffen.

Landen grenzend aan Nederland hebben een ander bodembeleid voor PFAS, deels door een andere wetgeving en deels gebaseerd op andere wetenschappelijke uitgangspunten of berekeningsmethoden. Veel landen in Europa hebben geen beleid voor PFAS. Europese wetgeving schrijdt voort. Ontwikkeling van een sterk aangescherpte normering voor meer PFAS stoffen dan tot nu toe, is al aangekondigd in de herziening van de Kaderrichtlijn Water en de Grondwater Richtlijn. De (neergaande) ontwikkeling van normering leidt tot nadering (en overschrijding) van grenzen van analysetechnieken voor grond en grondwater.

Door de complexe en resistente eigenschappen van PFAS zijn er weinig technieken om PFAS uit bodem en grondwater te verwijderen. De meeste van deze technieken zijn gebaseerd op het principe van concentreren van de PFAS in een kleiner volume en storten. Een gering aantal technieken verwijdert de PFAS, waarbij onzeker is of deze zijn verwijderd dan wel verplaatst naar een ander milieucompartiment. Zeker is dat bij deze technieken zeer veel energie nodig is zodat bij de uiteindelijke milieuwinst vraagtekens mogen worden geplaatst.

Op basis van de huidige stand der techniek wordt geconcludeerd dat er behoefte is aan:

- Onderzoek, communicatie en begeleiding om risico's van PFAS in perspectief te plaatsen.
- Onderzoek naar de herkomst van (onbekende) PFAS uit productieprocessen om zicht te krijgen op mogelijke bronnen en andere parameters noodzakelijk voor het bepalen van het conceptueel model van de verontreiniging in bodem en ondergrond.
- Onderzoek naar (verspreidings-) gedrag en risico's van vele (onbekende) PFAS, ook voor de PFAS met korte ketens, die doorgaans mobieler zijn.
- Onderzoek en kennisoverdracht over stoftransport en -modellering van PFAS.
- Ontwikkeling van analysemethoden voor PFAS die nu nog niet kunnen worden geanalyseerd.
- Ontwikkeling van de methodiek om de verschillen in toxiciteit van de verschillende PFAS-stoffen te kunnen evalueren ("RPF-methodiek").
- Onderzoek en realisatie van duurzame technieken voor de destructie van PFAS.
- Ontwikkeling van in-situ technieken voor bodem en grondwatersanering.
- Ontwikkeling en optimalisatie van (grond-)water zuiveringstechnieken met minder energiebehoefte en minder afvalproductie.
- Ontwikkeling van (duurzame) grondreinigingstechnieken.
- Ontwikkeling van afvalverwerkingsinstallaties met een gesloten massabalans voor PFAS (rest) afval van de huidige grond en water reinigingsinstallaties zodanig dat geen ongecontroleerde overheveling van PFAS naar andere milieucompartmenten plaatsvindt.

1 Introduction and scope

At the initiative of Rijkswaterstaat, conversations have been held during the summer and fall 2022 between Rijkswaterstaat and the Ministry of Infrastructure and Water Management about the approach to PFAS¹ in soil and groundwater in the Netherlands. The conclusion was that the Netherlands is bound by a number of international agreements, that the problem is too big to solve individually by stakeholders and that a knowledge infrastructure has been missing for some time in which knowledge questions can be addressed and solved. The research is carried out in a fragmented manner. The joint and programmed knowledge development that is necessary for solving such a major problem, is missing.

The collaboration in a knowledge program between practice, research and policy has proved successful in the past. There is also a call in the Netherlands from the professional field for a joint approach and joint research. All this has led to an initial exploration to see whether a joint knowledge program about PFAS will be broadly supported by stakeholders.

In the period from November 2022 to January 2023, a 'State of the Art' study was carried out to map out the knowledge (inter-)nationally developed regarding PFAS. And a number of discussions have taken place with stakeholders to evaluate the need for and interest in a national knowledge program for tackling PFAS in the soil. This report reflects the outcome of the 'State of the Art' study.

State of the Art PFAS

This document aims to draft an overview on the State of the Art on PFAS in soil and groundwater. It is not the outcome of an extensive study but rather a rapid inventory to derive the major knowledge gaps, research needs and technical challenges. It focusses on the Netherlands, with an eye on Europe and the wider world. The inventory is based upon publicly available information and expertise. A lot of research and development is ongoing, and results are not yet published or available. The state of the art will always be under evolution.

In parallel with this inventory, a separate stakeholder consultation is being carried out in the Netherlands. Together with the outcome of the consultation, this State of the document will be the basis for the development of a knowledge program on PFAS in Soil and Groundwater in the Netherlands.

¹ PFAS: poly- and perfluoroalkyl substances

2 Types, uses and presence in the environment

There is a wide variety of different PFAS and the knowledge concerning occurrence, environmental behavior and toxicological relevance is growing fast. Most part of the knowledge is limited to only a certain number of PFAS. This report focuses on the most well-known PFAS. Furthermore, the definition as to which substances classify as PFAS has changed over time. Therefore, we consider it important to state what definition of PFAS is used in this report, as well as a short explanation of the different subgroups of the PFAS chemical family including information about the occurrence of certain PFAS in the environment.

2.1 Definition and types of PFAS

Definition of PFAS

In this report, the focus is largely on the (non-polymeric) perfluoroalkyl acids (PFAA) and their precursors, as we consider these PFAS most relevant for soils and groundwater, regarding use and environmental levels. However, the definition of PFAS is much broader. In the REACH restriction proposal PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl (CF₃) or methylene (CF₂) carbon atom (without any H/Cl/Br/I atom attached to this carbon atom) (ECHA, 2022). This is the same definition of PFAS that is being used by the OECD (OECD, 2021) and it is a broad definition that includes many different types of PFAS with different properties regarding their environmental behavior and toxicology.

When this report mentions PFAS (e.g. concerning PFAS properties), this refers mainly to perfluoroalkyl acids (PFAAs) and their precursors. If this is not the case, it will be clearly indicated.

Types of PFAS

There are thousands of different PFAS which comprise both per- and polyfluorinated substances. The first includes fully fluorinated molecules, whereas the latter includes molecules that are not fully fluorinated.

PFAS can be non-polymeric and polymeric:

- Non-polymeric are of most concern for their environmental risks (Bell et al. 2019). They can be divided into the following groups:
 - o Perfluoroalkyl acids (PFAAs), which have been most investigated for their environmental behavior, fate and risks.
 - o PFAA-precursors, which can degrade to PFCAs (perfluoroalkyl carboxylic acids) or PFSAs (perfluoroalkyl sulfonic acids).
 - o Other PFAS, per- and polyfluorinated compounds.
- Polymeric PFAS can be divided into:
 - o Fluoropolymers (polymers with a fluorinated backbone)
 - o Side-chain fluorinated polymers, which have a hydrocarbon backbone and a fluorinated side chain. Side-chain fluorinated polymers can biotransform into PFAAs
 - o Other fluorinated polymers with perfluorocarbons built into the backbone (e.g. perfluoropolyethers).

An overview of the different PFAS families and subgroups is given in Figure 1. Molecular structures of a selection of PFAS are given in Figure 2.

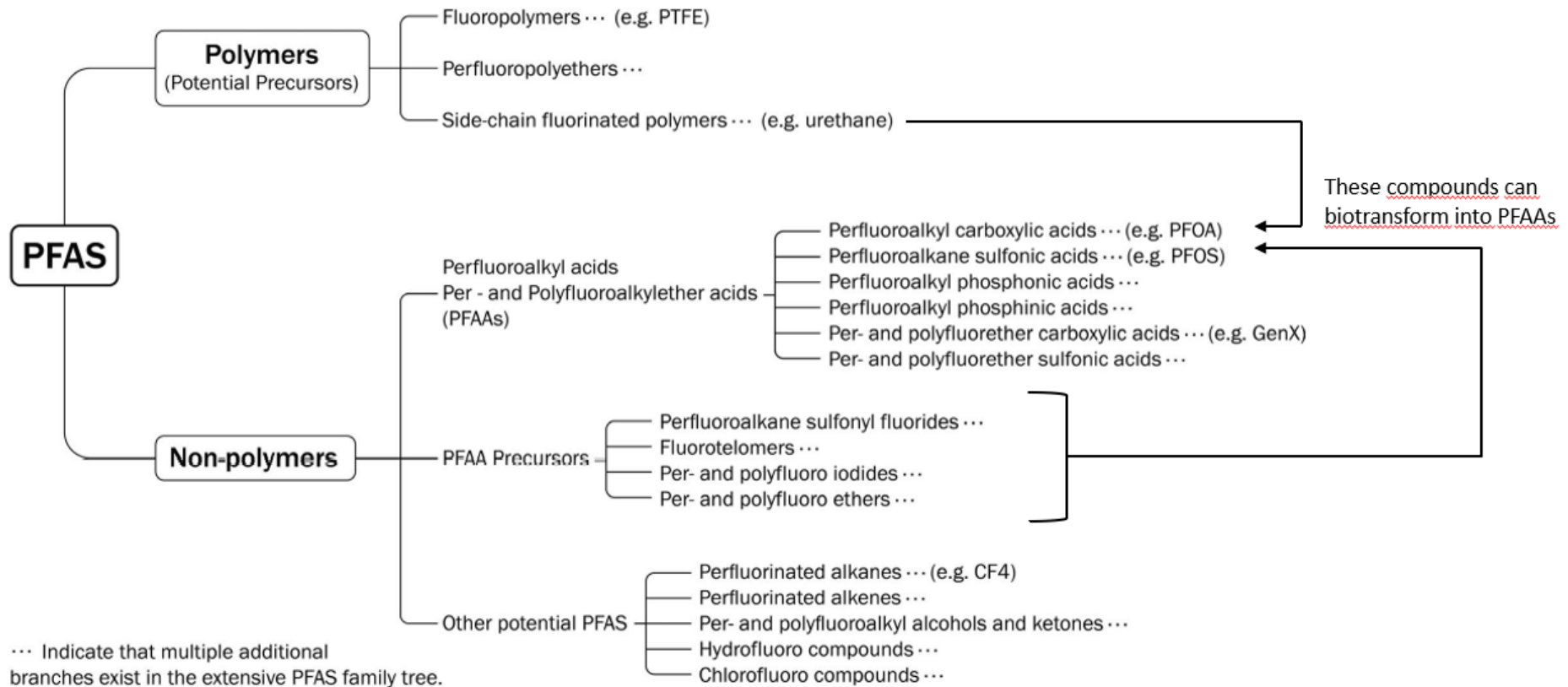


Figure 1. PFAS family and subgroups, based on: Winchell et al., 2021, with biotransformation paths from precursors to PFAAs.

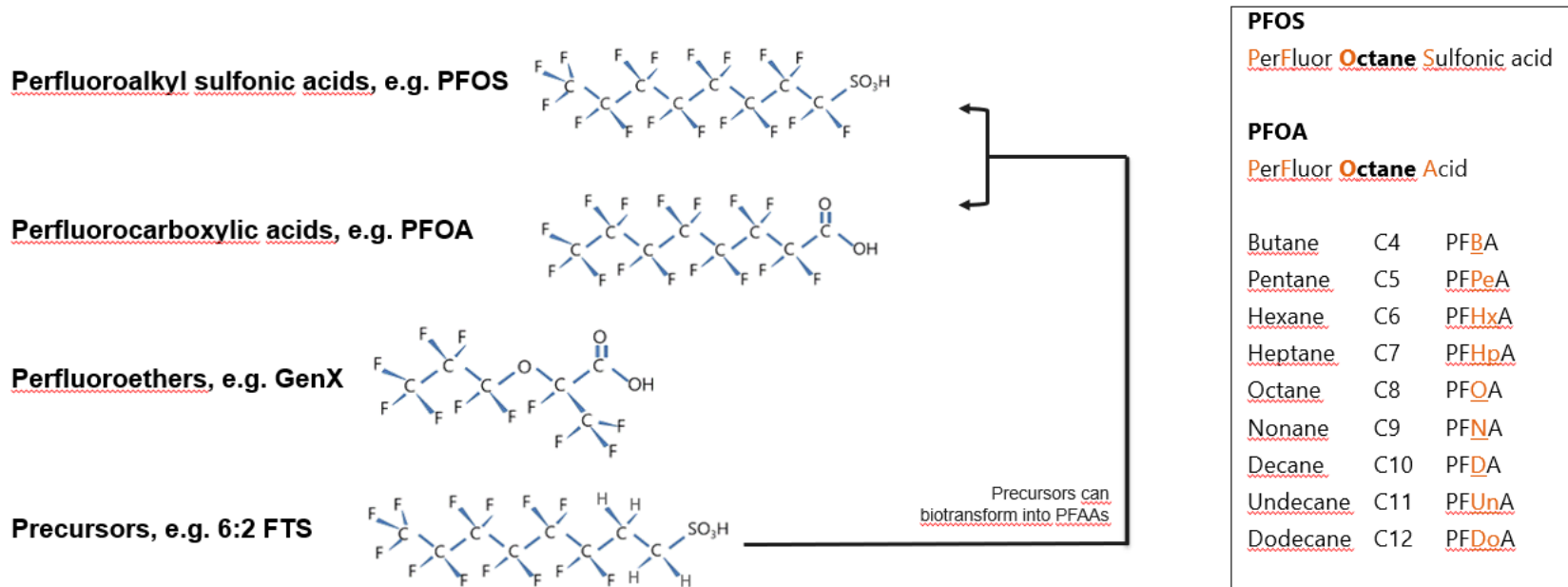


Figure 2. Molecular structures for a selection of PFAS.

PFCA and PFSA

The perfluoroalkyl carboxylic acids (PFCA, including PFOA, PFHxA and PFBA) and perfluoroalkyl sulfonic acids (PFSA, including PFOS and PFHxS) are the group most studied for their environmental dispersion and risks.

PFCAs with a chain length of 2 up to 18 carbon atoms and longer have been reported. PFOA is the most commonly reported PFCA. PFCA can occur as a mixture of linear and branched isomers when they are produced by electrochemical fluorination process (Riddell et al., 2009; Rayne & Friesen, 2008; Pancras et al., 2016). When a fluorotelomerization process has been used, usually only straight chain isomers are present in a mixture. Environmental samples containing PFCA often contain a range of PFCA chain lengths. Shorter chain lengths are increasingly being used as the production of longer perfluoroalkyl chain carboxylates is being phased out (Bell et al., 2019; Ritter, 2010).

For PFSAs, chain lengths of 1 to 18 carbon atoms have been reported. The most common PFSA is PFOS, which is usually present as a mixture of linear (70%) and branched (30%) isomers due to the production process (usually ECF; electrochemical fluorination). As for PFCA, shorter chain lengths (C4, C6) have been introduced as alternatives. For PFOS, perfluorobutanesulfonic acid (PFBS) is an important replacement substance (Bell et al., 2019; Ritter, 2010). Other replacement products are fluorotelomers with a fluorinated alkyl chain with 6 fully fluorinated carbon atoms (e.g. 6:2 FTS, a fluorotelomersulfonate).

Biotransformation of PFAS

PFAA precursors can biotransform in the environment to PFAAs:

- ECF based precursors, such as EtFOSAA, can biotransform to PFSA, such as PFOS.
- Fluorotelomer-based substances, such as FTOHs, can biotransform to PFCA, such as PFOA.

Biotransformation to PFAAs can occur via multiple intermediates. A very large suite of PFAS- precursors is used (Barzen-Hanson et al., 2017). When analysis of environmental samples is performed on solely PFAAs, the precursors of PFAAs are not detected. These precursors can act as long-term sources of PFAAs as they can gradually degrade into these compounds via multiple intermediates. This phenomenon is often observed in wastewater treatment plants (Derksen and Baltussen, 2021), and can also occur at other places. Thus, when analyzing environmental samples, it is important to take into account the PFAA precursors.

Biotransformation of polymeric PFAS to PFAAs is possible via the breakdown of side-chain fluoropolymers. Perfluoropolyethers (PFPEs) cannot degrade to PFAAs, but might be present in environmental samples as impurities, possibly because they are used in manufacturing of PFAAs (Bell et al., 2019; DTSC, 2018; Washington et al., 2014; Washington et al., 2015). PFOA has been used as processing agent for polytetrafluoroethylene (PTFE) in the Netherlands up to 2012. Nowadays perfluoroalkyl ethers are often used as replacement chemistry for long-chain PFAS (Bell et al., 2019; Prevedouros et al., 2006).

2.2 Uses and presence in applications and products

Due to their unique properties, PFAS are used in a wide range of industrial applications and commercial products. PFAS have specific surface tension and levelling properties, and are water, dirt and grease repellent. They are amongst others used in:

- Firefighting foams;
- Non-stick cookware and food containers;
- Surface treatments for textiles, upholstery, leather, masonry, paper and board;
- Leveling agents in paints, coatings and waxes;
- Plastics;
- Lubricants and greases;
- Aerosol propellants;
- Solvents;
- Pesticides;

An overview of the more than 200 use categories for more than 1400 PFAS have been identified and published by Glüge et al. in 2020. In 2021 Arcadis finalized a study on PFAS in products and waste (Pancras, 2021).

The main conclusion was that most products contained PFAS in medium to high levels, whilst the biggest part of organic fluorine content could not be identified by targeted chemical analyses and remains “dark matter”. Very high concentrations were found in dust of production sites, but also in dust of households. This indicates the widespread use and presence of PFAS.

Although much is known about the use of PFAS in applications and products, it can be assumed that even more is unknown because of complex production chains, maximum allowable concentrations in products, and difficulties in identifying specific PFAS compounds outside the chemical analysis library. In MSDS (material safety data sheets) the actual type of PFAS being used is often not mentioned, and only SVHC (substances of very high concern) with a concentration higher than 0.1% must be mentioned (0.1% is 1 g/kg). Note that the SVHC list currently only mentions specific types of PFAS, not all PFAS. Furthermore, many of the products that are produced outside the European Union are to some extent outside the control of EU-policies and legislation. For example, whereas the production and use of PFOS and PFOA has strongly decreased in the western world before 2010, the last decade still saw an increase in India, Russia and China. In the EU, there is a shift towards replacement products that do not contain PFAS, stimulated by the proposal for the restriction of PFAS under REACH (the EU chemicals regulation). This proposal has recently been submitted at the ECHA (European Chemicals Agency) (ECHA, 2023).

2.3 PFAS in the environment

2.3.1 Presence in different environmental compartments

PFAS do not occur naturally in our environment. However, due to its wide range of applications and persistence, PFAS are present in all environmental compartments. In the Netherlands, ambient levels of PFAS in the topsoil of 1.4 and 1.9 µg/kg dry matter² for PFOS and PFOA respectively have been identified (Wintersen et al., 2020b). The term “ambient” is used because background might suggest that these levels have a natural origin, which they do not have.

Data show that concentrations are usually higher in urban areas than in the rural environment (Wintersen, 2020b). So called ‘hotspots’ for PFAS occurrence include fire training areas (due to the use of PFAS containing aqueous film forming foam (AFFF)) and PFAS or polytetrafluoroethylene (Teflon) production. Other sites with potentially high PFAS concentrations are airports, landfills, paint and textile industry, chemical and metal industry (Pancras, 2021), and all sites with AFFF-based fire extinguishing systems. However, the nationwide overview of PFAS contaminated sites is still growing, and many sites still remain to be identified.

To provide some context for which concentrations can be found in the environment in the Netherlands and globally (for rain), Table 1 shows a number of environmental concentrations, presented in nanograms (per kg or liter) in order to reflect these values to advisory risk- and health levels (see chapter 4).

Table 1. Indication of PFAS concentrations found in (environmental) media in the Netherlands and globally (rain).

| | |
|----------------------------------|---|
| Soil | ~ 1,000-2,000 ng/kg dry matter for PFOS and PFOA ³ |
| Phreatic groundwater | ~ 30 ng/l for sum of PFAS ⁴ |
| Surface water of Rhine and Meuse | ~ 10 ng/l for sum of EFSA-4 PFAS ^{5 6} |
| Rain | ~ 1-2 ng/l for sum of EFSA-4 PFAS ⁷ |
| Dust in households and offices | ~ 100,000- 1,000,000 ng/kg for sum of PFAS |
| Consumer goods | ~ 100,000 ng/kg for sum of PFAS ⁸ |

Note: In line with high concentrations of PFAS in our environment, extractable organic fluorine (EOF) levels in human blood plasma of 15,000 - 20,000 ng F/l are common, based on research in German and Chinese cities (Yeung and Marbury, 2016).

² The background concentrations were based on the 95th percentile of weighed concentrations, which were based on surface areas of agricultural and nature areas in the Netherlands.

³ Wintersen et al., 2020.

⁴ Wintersen et al., 2021.

⁵ The EFSA-4 PFAS are the PFAS for which the European Food Safety Authority (EFSA) set a tolerable weekly intake in its opinion of 2020. These PFAS are perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS).

⁶ Notitie Expertisecentrum PFAS voor VEWIN 2021: “Vervolgvragen inzake EFSA opinie: bronnen van PFAS voor oppervlaktewater”

⁷ Cousins et al., 2022.

⁸ Pancras, 2021.

Temporal changes in environmental PFAS concentrations

Falling concentrations have been reported in the levels in both the environment and blood plasma of the EFSA-4 PFAS (the four PFAS included in the latest TWI of the European Food Safety Authority) in recent years. Most probably because of restrictions for PFOS and PFOA. In general, the concentrations of PFOS, PFOA, PFNA and PFHxS have been shown to have decreased over the last decade (Göckener et al., 2020). The downside is that an increase of their replacement compounds is found or can be expected, whereas many replacement compounds are expected not to be detected with common analytical methods (see chapter 5).

2.3.2 Diffuse contamination and source sites

Ambient levels

Half a century of PFAS use has led to the fact that the northern hemisphere has ambient levels in surface soil everywhere (Cousins et al., 2022). It is important to distinguish ambient levels from concentrations at locations with a PFAS source; concentrations that are obviously locally elevated above ambient levels because of a specific activity.

Availability of data of ambient levels in soil and groundwater is important for policy making and the reflection against advisory levels and remediation levels. So far little energy has been invested in the appraisal of the cost-effectiveness and sustainability of interventions close to ambient levels, however, compared with the rest of the world, the knowledge on ambient levels of PFAS in soil and water in the Netherlands is high.

Source sites

Whereas intervention measures to reduce the concentrations of PFAS in areas with ambient levels will not be meaningful in most cases, tackling source sites will be more effective. In both 2021 and 2022 studies on potential source sites (aandachtslocaties) in the Netherlands were completed (Expertisecentrum PFAS, 2020; TAUW et al., 2021; Koster et al., 2022). In many provinces (Drenthe, Gelderland, Flevoland, etc.) regional projects are started to further refine the outcomes of these studies and to try to identify these sites.

2.4 Knowledge gaps and research needs

Knowledge on PFAS is large and expanding for the common types of PFAS, but a lot is still unknown. The following gaps and research needs are identified regarding the use and occurrence of PFAS:

- The overview of processes and products in which PFAS are being or have been used is far from complete.
- Knowledge on which PFAS are used in products is in its infancy, and moreover, due to the lack of technologies that can identify specific compounds we don't know how much PFAS are present in products and processes.
- As a consequence the identification of source sites is not complete. Refinement of the identification of potential source sites is needed. The number of potential sites in previous inventories is found to be extensive (TAUW et al. 2021), whilst when refining too much, it is certain that some sources of PFAS are missed. This also includes the assessment which types of uses of PFAS are actually a source towards soil and groundwater. There is a need for an overarching, and specifically more founded view on which sites represent the biggest risk on soil and groundwater contamination. A study in which relations are made between real field data and former site use.
- The group of PFAS compounds is very big and complex, PFAS like PFOS and PFOA are well studied, but for the other PFAS, and most certainly also for the unknown PFAS, a lot less is known about these compounds considering their behavior in the environment and toxicity.
- There is need for more insight into the question of whether ambient levels in soil are likely to generate an unacceptable risk to human or ecological health.

3 Behavior, fate and transport

The behavior of PFAS in the soil groundwater system is very complex and our understanding is limited, though developing rapidly. Therefore, more focus is given for some explanation of the knowns of the behavior of PFAS, which is needed to recognize the critical gaps in knowledge, uncertainties and priorities for additional research and guidance.

3.1 Characteristics

3.1.1 General properties

PFAS molecules usually contain a fluorinated carbon chain ('tail') which is hydrophobic and a hydrophilic functional group ('head'). This tail and head can be either linked directly to each other or via an intermediate ethyl or propyl group. The combination of hydrophobic and hydrophilic properties enables PFAS to act as surfactants, concentrating on the interfaces of air-water and oil-water (Figure 3). Unlike more conventional surfactants the tail of PFAS molecules can have lipophobic properties as well making PFAS not only water repellent, but also resistant to oil, fat and other non-polar substances. Some PFAS are characterized as persistent, bioaccumulative and toxic (PBT). The strong carbon-fluor bond requires a lot of energy to dissociate and the complete breakdown of these molecules therefore only occurs at very high temperatures (at least 1000 °C, potentially as high as 1400 °C) (Yamada et al., 2005; Ryan and Gullett, 2020). Due to these properties PFAS are highly resistant to biotic or abiotic degradation in the environment.

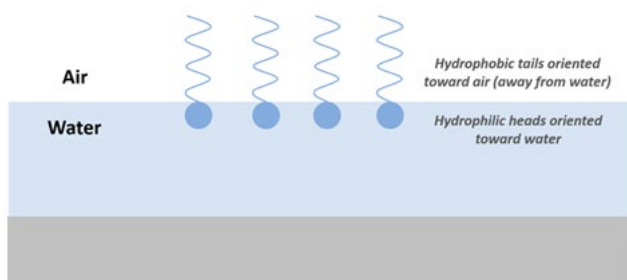
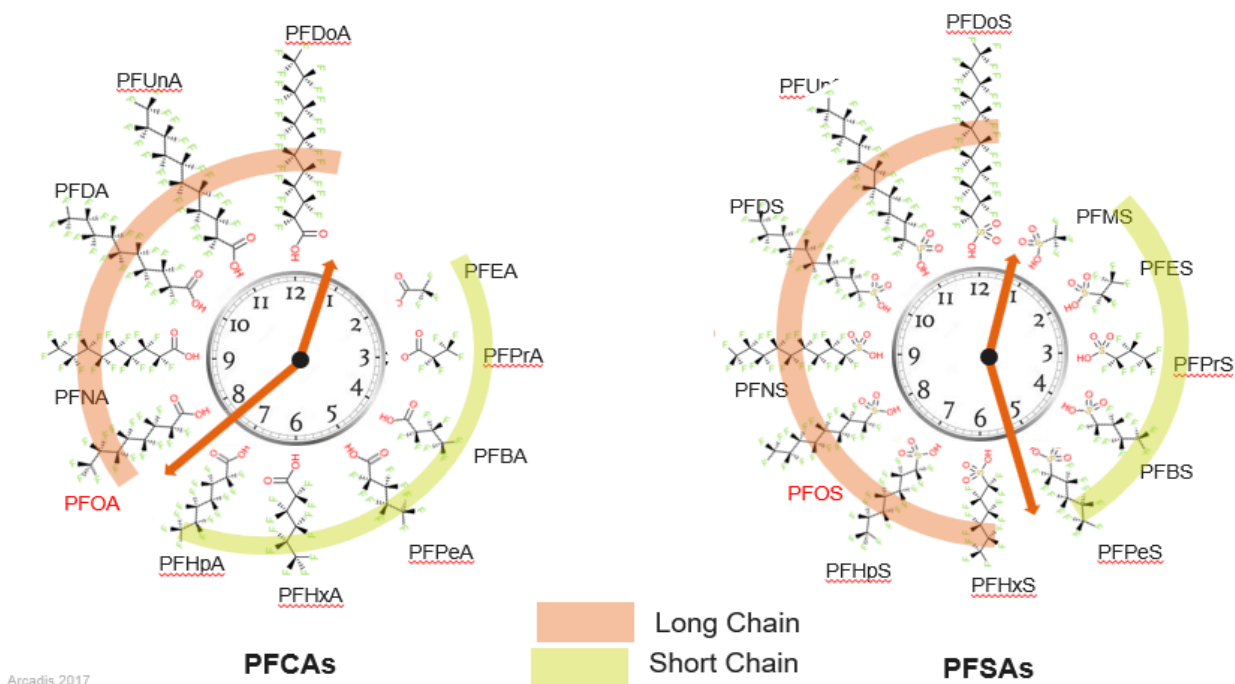


Figure 3. PFAS molecules concentrating on the interface of air and water, acting as surfactants (ITRC, 2022a).

PFAS can behave very differently in the soil and groundwater depending on their specific characteristics such as chain length and the type of PFAS. Besides this, local environmental circumstances are of influence. Understanding the characteristics of PFAS and the way they interact with the environmental characteristics is fundamental for understanding the fate and transport in the environment. This, in turn, is of major importance to the investigation and remediation of any contaminated site.

3.1.2 Functional group and chain length

The adsorption of PFAS to soil and sediment is hard to predict in the absence of appropriate laboratory experimentation. All too often attempts are made to predict PFAS behavior by reference to standard advection-dispersion models, which don't adequately describe PFAS processes. Additionally, different types of PFAS can behave differently. For example, PFOS with sulfonic acid as a functional group adsorbs more strongly to organic matter than PFOA having a carboxylic acid as a functional group. However, also the chain length is of influence, with longer chain PFAS generally showing greater adsorption to soil than shorter chain PFAS. Retardation during groundwater transport is therefore typically larger as the fluorinated chain length of PFAS increases and as the amount of organic matter present in the soil increases (Higgins & Luthy, 2006). Shorter chain PFAS, like PFBA, PFHxA and PFBS are only weakly sorbed to soil. Also, molecular geometry plays a role. Branched isomers appear to have less solid phase sorption than linear isomers (Expertisecentrum PFAS, 2018; Higgins & Luthy, 2006; ITRC, 2022b). Figure 4 gives an overview of the distinction between short and long chain PFCAs and PFSAs.



Arcadis 2017

Figure 4. Distinction in short and long chain PFAS for PFCAs and PFASs (Arcadis, 2017).

Next to molecular characteristics, the adsorption of PFAS to soil and sediment and their water solubility is influenced by environmental factors, such as pH, the presence of organic matter and several minerals. The PFASs and PFCAs make up the group of PFAAs that have been studied most intensively for their distribution in the environment. At the usual pH (5-9) of soil, groundwater and surface water PFASs and PFCAs are present as anions and the extent to which they adsorb to soil and sediment is limited due to the usual negative charge of soil particles (Higgins and Luthy, 2006). PFAS occurring as cations or zwitterions⁹ are expected to have a higher adsorption to soil¹⁰. PFAS Adsorption of PFASs and PFCAs increases as the pH decreases. Also, the concentration of PFAS can be of influence on their adsorption to soil. Above certain concentrations, the hydrophobic tails interact with each other in such a way that micelles, hemi-micelles or bilayers are created (Figure 5). There is evidence that PFAS in such a case show higher adsorption to organic material. Other factors of influence on the adsorption to soil is the extent of fluorination and the calcium concentrations present, with an increase of calcium concentrations causing more adsorption (Expertisecentrum PFAS, 2018; ITRC, 2022a).

⁹ Zwitterions contain both a cationic and anionic group in a single molecule.

¹⁰ Note that the regular types of analyses for PFAS do not include cationic and zwitterionic PFAS, since the solid phase extraction in the analysis focusses at anionic compounds (like PFCAs and PFASs).

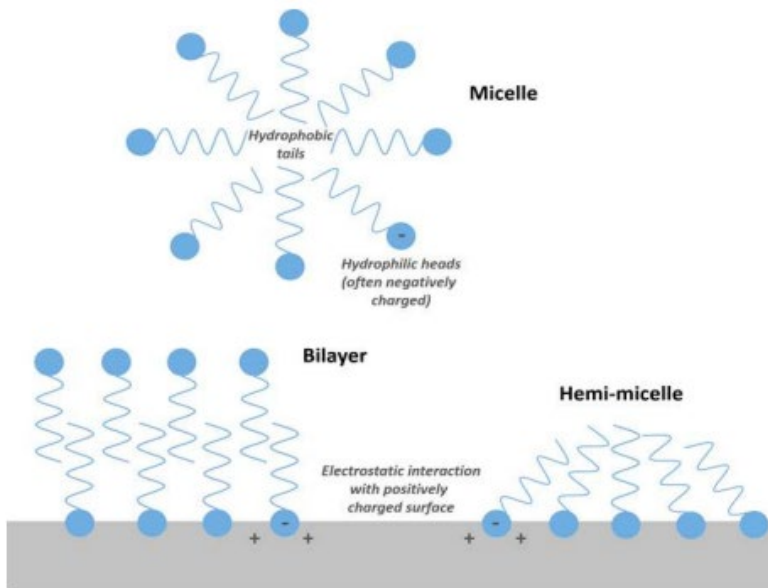


Figure 5. Illustration of the formation of PFAS micelles, hemi-micelles, and bilayers. Also shown is an example of aggregation at a positively charged surface. Note that the opposite effect (electrostatic repulsion of PFAS) can occur if the surface is negatively charged (ITRC, 2022).

3.2 Conceptual site model

3.2.1 Transport into the environment

PFAS can be found in the soil and water system in different capacities:

1. As diffuse contamination, a result of transport through the air, followed by deposition of PFAS on the soil or surface water.
2. As a concentrated source zone, via spills at facilities or firefighting activities, or because of the use or relocation of PFAS contaminated sludge or soil.

In the soil, PFAS can leach to the groundwater, from where a plume disperses in the direction of the groundwater flow, potentially ending up in surface water or drinking water areas. During the dispersion of PFAS to different environmental compartments, it can undergo uptake by biota and transformation. The specifics concerning the fate and transport of PFAS depend on the interaction between the compound characteristics and local environmental characteristics which can vary greatly. The principal types of sites of concern regarding potential PFAS contamination may include:

- industrial facilities undertaking primary and secondary manufacturing, as well as facilities that use PFAS-containing materials in their industrial process (Lyons, 2007);
- sites handling firefighting foams;
- Wastewater treatment plants and biosolids application areas;
- landfills (Bell et al, 2019; ITRC, 2022).

Figure 6 gives a general conceptual site model showing the different transport routes of PFAS in the environment.

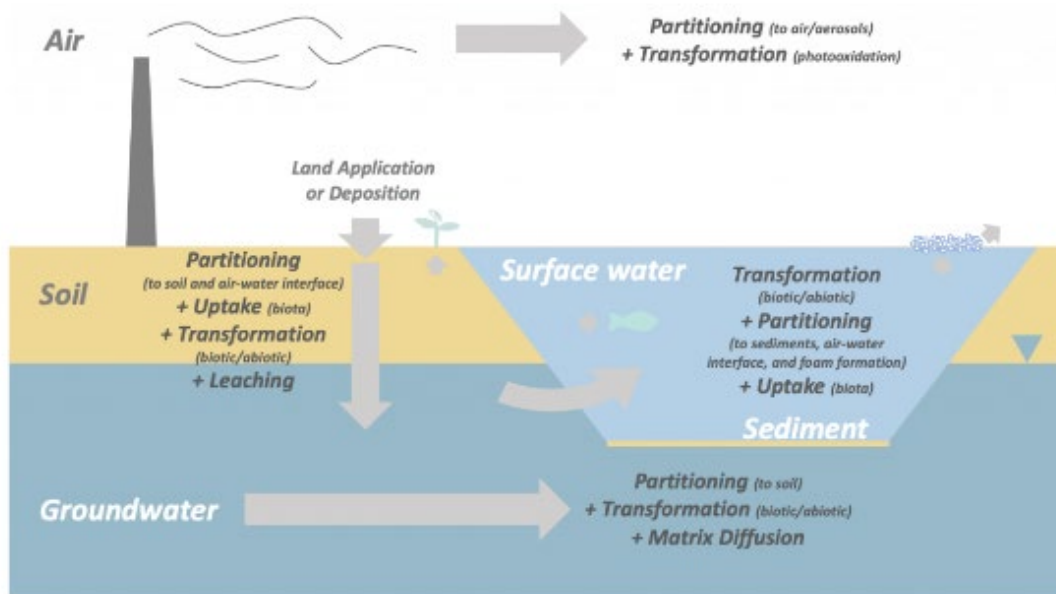


Figure 6. General conceptual site model (CSM) of PFAS dispersion in the environment (ITRC, 2022a).

The quantity and types of PFAS that enter the environment depend highly on the type of the source and the way in which PFAS enter the environment and can differ strongly between different sources. The PFAS contamination and dispersion will for example be different for an industrial production site of PFAS than for a firefighting training area (FTA) where PFAS containing firefighting foams have been used. Aviation, industrial and waste management facilities can release PFAS to the environment via wastewater discharges to surface water or via wastewater treatment plants. PFAS and precursors are also released into the air and end up in the soil and surface water via atmospheric deposition. Thus, when assessing a PFAS contamination a location specific conceptual site model (CSM) is needed.

3.2.2 Subsurface zoning

PFAS that has entered the top layer of the soil can infiltrate the different zones of the soil:

- Unsaturated zone, the layer in which the pores in between the soil particles contain both air and water (unsaturated zone).
- Saturated zone (also called phreatic zone), in which the pores only contain water.

There is no clear boundary between the saturated and unsaturated zone. Although a groundwater level can clearly be determined in monitoring wells, pore water can be found throughout the unsaturated zone, to near full saturation in the capillary fringe, which can be capricious because of different pore sizes and sedimentology.

3.3 Behavior in unsaturated and saturated zone

All too often field measurements seem to be out of line with calculations based on lab data for linear sorption, both in the saturated and unsaturated zone (also termed vadose zone). It is necessary to account for other processes that PFAS are subject to. PFAS tend to accumulate at interfaces, and especially the unsaturated zone has many different interfaces with a huge surface area. The behavior and leaching of PFAS is difficult to predict in this zone with differing grain sizes, moisture and carbon content. Leaching- and column tests often or perhaps mostly underestimate these phenomena. Retardation in the unsaturated zone is much greater than in the saturated zone, and as a result, contamination within the unsaturated zone can be a source of groundwater pollution for decades to come. Whereas PFAS transport in the unsaturated zone is often slower than expected (based on linear isotherms), in the saturated zone, transport can be near to conservative. Understanding and modelling PFAS migration through the unsaturated and saturated zone is of paramount importance for future risk assessment of PFAS contaminated sites.

3.3.1 Unsaturated zone

Over the past years efforts have been made to better understand PFAS behaviour in the unsaturated zone. The impression exists that this expertise is not widely used by the professional community. The unsaturated zone is porous soil material above the ground water level. Pores are partially filled with air and partially with water and in contaminated soil possibly with non-aqueous phase liquids (NAPL) as well. At high concentrations, micelles can be formed. PFAS transport through this multiphase zone is dictated by retention processes which in turn are functions of molecular PFAS properties, the degree of saturation in the unsaturated zone and geochemical properties of the soil. The relevant retardation processes (Brusseau et al., 2022) are:

- Water-solid interfacial adsorption
- Air-water interfacial adsorption
- NAPL-air interfacial adsorption
- NAPL-water interfacial adsorption
- Colloidal matter adsorption
- Vapor-phase processes

In the Netherlands research on this topic was done by Naod Negash in 2021 “Fate and Transport of Per- and Polyfluoroalkyl Substances in the Unsaturated Zone”. Based on this desk study a further study will be conducted into the feasibility of deriving generic (i.e. national) limit levels for the re-use of soil and sediment based on the risk of leaching. In this study a sensitivity analysis is conducted of the most important parameters such as sorption.

Modelling

The above mentioned processes control the distribution of PFAS in the porewater. Modelling the above processes will give insight in the rate and amount of PFAS migration from the unsaturated to the saturated zone. Brusseau also developed a PFAS mass distribution model relating the total PFAS in the soil to porewater concentration (Brusseau et al., 2022) in which the water-solid and air-water interfacial adsorption were considered the major retardation factors:

- Water-solid interfacial adsorption can either be measured or it can be estimated from a model. Strictly taken, water-solid interfacial is non-linear, thus the adsorptivity changes with concentration. In case of severe pollution (and thus higher PFAS concentrations) nonlinearity in adsorption becomes a major issue for modelling (Brusseau, 2019).
- Adsorption at the air-water interface is heavily dependent on the Air Water Interfacial Area (AWIA); the larger the interfacial area the higher the retardation factor. The AWIA can be estimated using various techniques upon which the outcome can vary greatly (Brusseau, 2021).

The developed model for the unsaturated zone (Brusseau, 2022) is a step forward that has experimentally proven to be accurate under applicable conditions but needs to be validated in practice. Also, specific situations with NAPL contaminated unsaturated zones and situations in which colloidal adsorption or vapor phase processes are important are not currently covered by a model. The need to address specific aspects of PFAS sorption behaviour in modelling depends on the specific goal of the modelling exercise and the scale.

Ambient levels and leaching

RIVM conducted research on ambient levels in soil and groundwater. At relatively low concentrations (ambient levels), no relationship was found between concentrations in soil and phreatic groundwater (Wintersen et al., 2020a). Sweco concluded likewise in a study on groundwater in coastal areas (Hollander et al., 2021).

Currently more research is being carried out on leaching by RIVM. The results are not expected before the end of 2023.

3.3.2 Saturated zone and solute transport modelling

PFAS are found to be able to form large plumes in the saturated zone. Compared with the unsaturated zone there is very limited air-water interface that could cause retention. NAPL-water interfacial adsorption was investigated for the saturated zone and turned out to be an important retardation factor (Brusseau, 2019). In general, retardation in the saturated zone is more heavily influenced by solid-water and NAPL-water adsorption compared to air-water adsorption.

In literature many references can be found for Koc, Kow or Kd values, (Li et al 2018, Higgins & Luthy et al. 2006, Wintersen et al. 2020a). Sorption depends on more factors than organic carbon content (pH, EC, clay), and some PFAS (e.g. PFOA) show a poor correlation with organic matter content (Wintersen et al., 2020a).

Moreover, the intervals of parameters are big, and too uncertain for reliable modelling. Batch experiments of RIVM (Wintersen et al., 2020a) indicated Kd values of 20 and more for PFOS and PFOA leading to retardation of over 100 times. In field cases retardation of PFOS is observed to be able to be less than 2 in Dutch aquifer systems (e.g. Arcadis 2022, Saneringsonderzoek Soesterberg). More reliable field data are needed to narrow down the intervals for specific aquifers.

3.4 Knowledge gaps and research needs

The knowledge on transport of PFAS through the subsurface is rapidly increasing, but still not fully understood. More research is needed to both understand the underlying processes as to validate that against field data. And perhaps more essential for practitioners is to develop guidance to understand and how to deal with this. A guidance that would need updating as the understanding improves. For risk-based approaches understanding the fate and transport is crucial. The following elements are crucial in this guidance:

- PFAS tend to accumulate at interfaces. The unsaturated or vadose zone knows many interfaces between air, water and solids. Sorption, retardation, and leaching are far from a simple equation based upon equilibrium sorption and carbon content:
 - In low concentrations (<10 µg/kg) there is currently no evidence of correlation between soil and underlying groundwater quality. There is no clear link between soil concentrations and groundwater concentrations in/near the unsaturated zone. Research is on its way (RIVM), but it is expected that more data are crucial, specifying soil and PFAS types. This is also important for assessing the risk of the ambient levels of PFAS that we have in the Netherlands (and worldwide).
 - At source sites, especially sites where highly contaminated water entered the subsurface, field data have shown that leaching out of the source areas can be significant and very difficult to predict. The tendency of many PFAS to accumulate at interfaces like the one between water and air leads to high retardation factors that are not in line with sorption parameters from literature based upon equilibrium or column tests.
- There is a need for practical guidance how to assess the risks of PFAS in the unsaturated zone, especially at concentrations just above target levels. Risk levels are often simply based on sorption coefficients, but retention in the unsaturated zone depends on many more processes than just linear sorption, and therefore, the actual risk might be lower than calculated. Leaching might last much longer.
- In literature many data and coefficients for sorption in saturated conditions can be found. However, the behavior of PFAS, due to their special properties, is less straight forwarded than the simple sorption models that are mostly used. There is a need for a more comprehensive overview of (Dutch) field data and literature.
- Research has mainly focused on PFOS and PFOA. Research on the transport of other PFAS is increasing, but is still poorly understood. Short chain PFAS show less sorption, and may represent a bigger risk for groundwater systems.
- Little is known on the consequences of biotransformation of precursors, e.g. what happens to the PFAS in the newer AFFF formulations in the subsurface, what risk do they represent?

Obviously, sorption under differing conditions is still poorly understood, and leaching from the unsaturated zone might be lower than anticipated using traditional approaches. When PFAS enters the saturated zone, transport can be significant. Whilst the impact on drinking water reserves can be and is large, there is an urgency for additional research, and above all practical guidance on how to deal with this on the short and long term. Some of these aspects are currently under investigation in Dutch research institutions. Not all of this work is already publicly available. To deal with PFAS in our groundwater it is essential to come to an accessible and robust understanding of PFAS transport in groundwater.

4 Risk assessment, legislation and policy

4.1 Risk assessment and health advisory levels

The EFSA opinion

In July 2020 EFSA published its opinion on the toxicity of PFAS (EFSA, 2020). Based upon epidemiological studies in Sweden it was found that low levels of PFAS intake by mothers breastfeeding their children, can lead to a reduced number of antibodies in the blood of 1-year old children after vaccination. Many other effects on humans were recognized in this study, but immunotoxicity was considered to be the most critical endpoint and based on this, the tolerable weekly intake (TWI) of PFAS was established at 4.4 ng/kg bw/week for the sum of 4 PFAS (PFOS, PFOA, PFHxS and PFNA), below which no effects are expected. This new TWI is a factor of 20 more stringent than the value derived in 2016 for PFOA by the RIVM, which was based on animal studies. Also, it is 200-2,000 times more stringent than the previous TWIs of the EFSA of the year 2008. In addition, it includes four PFAS, whereas the previously set health-based guidance values (HBGVs) were for one PFAS.

This scientific opinion on the human risks related to the presence of PFAS in food is currently being used in calculations of guideline values or advisory levels in the Netherlands (see 4.2), the EU and other European countries. Based on the low TWI, guideline values for soil, groundwater, surface water and drinking water have become more stringent since 2020.

The EFSA TWI has been adopted by the Netherlands on January 18, 2021 (RIVM, 2021c). On several levels, there is discussion about the consequences of adopting the EFSA tolerable weekly intake for PFAS.

WHO document on guidelines for PFOS and PFOA in drinking water

Only recently a draft for public review became available from the World Health Organization on "PFOS and PFOA in drinking water" (WHO, 2022). One of the main conclusions of this report was:

"WHO considered that the uncertainties in identifying the key endpoint applicable to human health following exposure to PFOS and/or PFOA are too significant to derive a HBGV with confidence. Although the reduced antibody response following vaccination has been considered by some agencies as the most robust end point based on epidemiological data, it is unclear whether this correlation results in increased rates of infection and hence the clinical implications are uncertain."

Statement UK Committee on Toxicity on EFSA opinion

In the UK The Committee on Toxicity of Chemicals in Food, Consumer products and the Environment (COT) have reviewed the EFSA opinion and considered the outputs alongside UK exposure data to assess the potential risks to the UK population from PFASs (predominantly through exposure via the diet) (CoT, 2022). The succinct summary of their conclusion can be found in paragraph 214:

"Whilst the COT is unable to suggest an alternative TWI at this time, there are strong caveats when comparing the [UK population] exposure estimates with the TWI established by EFSA. There is considerable uncertainty as to the appropriateness of the derivation of the TWI, and of the biological significance of the response on which it is based, which complicates interpretation of the possible toxicological significance of exceedances."

Although the COT is unable to suggest an alternative, it in general concludes that the EFSA TWI is too low and the underlying study being insufficient and the basis for choosing this as a point of departure is weak.

USEPA

On June 15th 2022 USEPA published new advisory levels for PFOS and PFOA in drinking water, also based upon epidemiological work and immune response. Values for GenX and PFBS remain to be based on toxicity observed in animal studies. The drinking water levels for PFOS and PFOA are even lower than calculated by RIVM based upon EFSA (4.4 ng/l). USEPA advises 4 pg/l for PFOA and 20 pg/l for PFOS (USEPA, 2022).

Resumé

Although tolerable weekly intake levels are arguably low, the EU Commission, based on the opinion of EFSA of 2020, and USEPA use the same endpoint for risk assessment. WHO and CoT assess this endpoint as being uncertain. This endpoint is the basis for advisory levels in the Netherlands and at EU level.

4.2 RPFs and RBFs

Relative Potency Factors (RPF)

Within the framework of the research program on PFAS of the Expertisecentrum PFAS in 2018, the Dutch RIVM first developed the Relative Potency Factor methodology (Zeilmaker et al. 2018). This approach gives an indication of the relative toxicity of different PFAS based on liver toxicity in animal tests (see Table 2).

The relative potency of a congener can be expressed as a PFOA equivalents, and is the basis for the conversion and reflection of a more complex mixture of congeners to the EFSA opinion on TWI (see above).

By now the RPF methodology is more and more adopted in other countries and is endorsed by the Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) of the European Commission. The use of RPFs in combination with EFSA's TWI can be questioned since the RPF methodology is based upon animal studies and liver toxicity, whereas the EFSA opinion is based upon immune toxicity in humans. However, as SCHEER indicates; as long as there is no alternative, this is their recommended approach.

For not all congeners accurate data could be found and RIVM opted for intervals based upon comparable congeners with shorter and longer carbon chains. In later studies RIVM added some more congeners and from a precautionary point of view used the upper end of the interval (see Table 3), whereas the EU uses the average value in the interval (EC, 2022).

Relative Bioaccumulation Factors

In surface water systems PFAS bioaccumulate in fish and shellfish. Based upon 4 field studies RIVM published Relative Bioaccumulation Factors that account for this (Smit & Verbruggen, 2022). In combination with the EFSA TWI this leads to advisory levels for surface water (Environmental Quality Standard) that are far lower than currently set by the EU. If these levels are accepted as standards, then for PFOS and PFOA this would mean that the annual average environmental quality standard (AA-EQS) would go down from 0.65 to 0.007 ng/l for PFOS and from 48 to 0.3 ng/l for PFOA. For PFDS, PFDoDA and PFTTrDA the levels would even go to sub picogram/l levels.

Currently the analytical techniques are not able to measure these levels. Furthermore, ambient levels of PFOA equivalents (PEQ) in the main Dutch Rivers is somewhere between 3 and 10 ng/l, which is **3 orders of magnitude higher** than the advisory levels presented.

Table 2. Relative potency factors (RIVM, 2018)

| Congener | RPF |
|--|--------------------------|
| Perfluorobutanesulfonate (PFBS, C4) | 0.001 |
| Perfluoropentane sulfonic acid (PFPeS, C5) | 0.001 ≤ RPF ≤ 0.6 |
| Perfluorohexanesulfonate (PFHxS, C6) | 0.6 |
| Perfluoroheptane sulfonic acid (PFHpS, C7) | 0.6 ≤ RPF ≤ 2 |
| Perfluorooctanesulfonate (PFOS, C8) | 2 |
| Perfluorodecane sulfonic acid (PFDS, C10) | 2 |
| Perfluorobutyrate (PFBA, C4) | 0.05 |
| Perfluoropentanoic acid (PFPeA, C5) | 0.01 ≤ RPF ≤ 0.05 |
| Perfluorohexanoate (PFHxA, C6) | 0.01 |
| Perfluoroheptanoic acid (PFHpA, C7) | 0.01 ≤ RPF ≤ 1 |
| Perfluorooctanoic acid (PFOA, C8) | 1 |
| Perfluorononanoic acid (PFNA, C9) | 10 |
| Perfluorodecanoic acid (PFDA, C10) | 4 ≤ RPF ≤ 10 |
| Perfluoroundecanoic acid (PFUnDA, C11) | 4 |
| Perfluorododecanoic acid (PFDoDA, C12) | 3 |
| Perfluorotridecanoic acid (PFTTrDA, C13) | 0.3 ≤ RPF ≤ 3 |
| Perfluorotetradecanoic acid (PFTeDA, C14) | 0.3 |
| Perfluorohexadecanoic acid (PFHxDA, C16) | 0.02 |
| Perfluorooctadecanoic acid (PFODA, C18) | 0.02 |

Table 3. Relative potency factors and relative bioaccumulation factors for surface water (Smit & Verbruggen, 2022)

| | PFAS | RPF | RBF |
|------------------|----------------|-------------------|-------------------|
| Carboxylzuren | PFBA | 0,05 | 0,005 |
| | PFPeA | 0,05 ^a | 0,02 |
| | PFHxA | 0,01 | 0,07 |
| | PFHpA | 1 ^b | 0,3 |
| | PFOA | 1 | 1 |
| | PFNA | 10 | 4 |
| | PFDA | 10 ^c | 10 |
| | PFUnDA | 4 | 60 |
| | PFDoDA | 3 | 200 |
| | PFTTrDA | 3 ^d | 100 |
| | PFTeDA | 0,3 | 40 |
| | PFHxDA | 0,02 | |
| | PFODA | 0,02 | |
| Sulfon- zuren | PFBS | 0,001 | 0,1 |
| | PFPeS | 0,6 ^e | 0,4 |
| | PFHxS | 0,6 | 2 |
| | PFHpS | 2 ^f | 6 |
| | PFOS | 2 | 20 |
| | PFDS | 2 ^f | 300 |
| Overige | HFPO-DA (GenX) | 0,06 | 0,3 ^j |
| | ADONA | 0,03 | |
| | 6:2 FTOH | 0,02 | 0,3 ^h |
| | 8:2 FTOH | 0,04 | 4 ^c |
| | 4:2 FTS | 0,05 ^g | 0,02 ^g |
| | 6:2 FTS | 1 ^h | 0,3 ^h |
| | 8:2 FTS | 10 ^c | 4 ^c |
| | PFOSA=FOSA | 2 ^f | 20 ^f |
| | EtFOSAA | 2 ^f | 20 ^f |
| | MeFOSAA | 2 ^f | 20 ^f |

4.3 Legislation and policy the Netherlands

In the Netherlands, the Soil Protection Act (Wet bodembescherming; Wbb) includes rules and limit levels of contaminants for the protection of the quality of soil and groundwater. Within the legal framework of the Wbb, the Soil Quality Decree (Besluit bodemkwaliteit; Bbk) includes legislation for the application and re-use of soil and dredged sediments and the Soil remediation Circular states rules for the remediation of contaminated soil and groundwater. It is important to note that the Wbb distinguishes between historical and new cases of contamination, where the rules concerning remediation requirements differ. In the case of a historical contamination a risk based approach is applied in which concentrations have to be lower than the site specific risk levels. For new contamination, the duty of care requires to restore the impact as far as reasonably possible. Contamination originating from after the 1st of January 1987 is considered to be new, whereas that originating from before this date is considered historical. Currently PFAS are considered a new contamination, but the Ministry is developing guidance on how to interpret “reasonably” since it is obvious that in many cases it will not be possible to go back to pristine conditions.

For groundwater, next to national legislation, EU legislation exists, being the Water Framework Directive (WFD) (2000/60/EC). Quality standards for substances in groundwater are listed in the WFD daughter directive, being the Groundwater Directive (GWD; 2006/118/EC). Another daughter directive of the WFD, the Environmental Quality Standards Directive (EQSD; 2008/105/EC) lists environmental quality standards for surface water. The environmental quality standards in the EQSD have been nationally implemented in the ‘Besluit kwaliteitseisen en monitoring waterkwaliteit’.

In near future the above mentioned legislation will be transposed into the Environment and Planning Act (Omgevingswet).

4.3.1 Soil reuse

The Netherlands is besides Belgium and Germany one of the few European countries with a policy on reuse of soil containing PFAS. This is described in “Handelingskader voor hergebruik van PFAS-houdende grond en baggerspecie” (I&W, 2021). Soil reuse is based upon the stand still principle, and local and regional soil quality.

4.3.2 Risk based advisory levels

Soil

For PFAS in soil no legislative norms exist on a national level. Instead, humane risk levels have been derived by the RIVM for PFOS, PFOA and GenX for soil and groundwater (including and excluding the use of raw groundwater as drinking water) which are given in Table 4. These humane risk levels are used as indicative levels for severe contamination (Indicatieve niveaus voor ernstige verontreiniging; INEVs) and serve as provisional intervention levels. INEVs and intervention values can be used as a first step in identifying whether a location possibly contains a contamination causing unacceptable human health risks. If these levels are exceeded, an additional location specific risks assessment is required to find out whether this is actually the case and whether remediation is necessary. Risk levels are calculated for ecological effects, indirect ecological effects and human health effects. For the latter the most recent EFSA TWI applies. The lowest risk level is used as INEV. Humane risk levels can be derived for specific soil functions with specific exposure scenario’s. The levels in table for have been derived for the soil function ‘Living with garden’ (Wonen met tuin).

Special attention is needed for the uptake through vegetables. For human exposure this has proven to be a major exposure pathway, that needs more attention towards vegetable gardens and agriculture.

Table 4. Humane risk levels for the derivation of intervention levels in soil, porewater and for direct consumption of groundwater (RIVM, 2021a).

| PFAS | Soil (µg/kg) | Porewater (ng/l) | C _{gw, max} (ng/l) |
|----------------|--------------|---------------------|-----------------------------|
| PFOS | 59 | 2.7x10 ³ | 9.9 |
| PFOA | 60 | 8.6x10 ³ | 20 |
| HFPO-DA (GenX) | 57 | 6.0x10 ⁴ | 3.3x10 ² |

Next to humane risk levels for the derivation of INEVs and intervention values, humane risk levels are calculated for the derivation of maximum levels (maximale waarden). Maximum levels can be used to assess whether the application of soil and dredged sediment on land complies with the chemical requirements in relation to the specific use of the soil or sediment.

Maximal values are based on 50% of the TWI (instead of 100% of the TWI at the INEVs), in order to take into account the exposure to PFAS through different routes than soil or dredged sediment. When assessing site specific risks, also the (direct and indirect) ecological risks have to be incorporated (RIVM, 2021b).

Table 5. Humane risk levels in soil and dredged sediment for the derivation of maximum levels in µg/kg (RIVM, 2021b).

| Use | PFOS | PFOA |
|--|------|------|
| Houses with vegetable garden | 2.4 | 2.3 |
| Houses with garden | 29 | 30 |
| Other green areas, infrastructure and industry | 480 | 930 |

Groundwater

Following the updated health-based guidance value by EFSA in 2020, the RIVM advised new risk levels for PFOS, PFOA and HFPO-DA (GenX) on which new INEVs could be based (Table 4). Only risk levels for the use of raw groundwater as drinking water, and the use of water in urban areas have been derived, and there is a difference of several orders of magnitude between these values. There is a need for integrated risk levels for groundwater at other uses (e.g. the use of groundwater in vegetable gardens), or when groundwater is discharged towards surface water.

Surface water

Water quality standards for PFOS, PFOA and HFPO-DA have been derived and are used in practice but currently only the standard for PFOS has been included in legislation (through the WFD, see 4.4.1)). For HFPO-DA, only an indicative level for has been derived by the RIVM (Smit & Verbruggen, 2022).

Table 6. Water quality standards for PFOS, PFOA and HFPO-DA in surface water.

| PFAS | AA-EQS (ng/l) |
|----------------|---|
| PFOS | 0.65 (fresh water) and 0.13 (salt water) ¹ |
| PFOA | 48 (fresh and salt water) ² |
| HFPO-DA (GenX) | 118 ³ |

¹ AA-EQS based on the EU Water Framework Directive.

² AA-EQS (Verbruggen et al., 2017).

³ Limit level derived by RIVM (RIVM, 2018).

4.4 International legislation and policy

4.4.1 European Union

Water Framework Directive – Groundwater and surface water

EU legislation exists for groundwater, being the Water Framework Directive (WFD) (2000/60/EC). Limit levels for substances in groundwater are listed in the WFD daughter directive, being the Groundwater Directive (GWD; 2006/118/EC). Currently, no limit levels for PFAS have been set for groundwater. Another daughter directive of the WFD, the Environmental Quality Standards Directive (EQSD; 2008/105/EC) lists limit levels for surface water. Currently, environmental quality standards apply for PFOS only, being 0.65 ng/l in inland surface waters and 0.13 ng/l in other surface waters for the annual average (AA) concentrations. The maximum allowable concentrations (MAC) are 36 and 7.3 µg/l for inland and other surface waters, respectively. However, these values are based at old TWI's, and at the time of writing this report, an amendment of the WFD is proposed which includes 24 PFAS in both the GWD and EQSD with a sum limit of 4.4 ng/l, using RPF-factors (EC, 2022).

Previously set limit levels in surface water will expire as soon as this amendment is put into effect. The average ambient level in phreatic groundwater is ~30 ng/l, which means that the proposed QS will not be met in the foreseeable future.

Drinking water directive

Current limit levels in water intended for human consumption are listed in the Drinking Water Directive (DWD; 2020/2184; EC, 2020). The directive contains two drinking water limit levels for PFAS, being 0.1 µg/l for the sum of subset of 20 PFAS and 0.5 µg/l for the sum of all PFAS. According to the DWD the first shall only apply once technical guidelines regarding methods of analysis for monitoring this parameter are developed by the EU Commission. These guidelines are to be established in early 2024. Member states may decide which limit to use.

Soil Strategy and Soil Health Law

In 2021, the European Commission launched the new EU soil strategy, including several soil mission objectives. For PFAS in soil and groundwater several objectives are relevant:

- Increase in the reuse of urban soils (circularity);
- Reduce soil pollution;
- Enhance habitat functions (biodiversity).

An EU Soil Health Law or Directive is being developed and is expected to come into force in 2023. The consequences of the EU Soil Missions and the EU Soil Health Law for the approach on PFAS are not yet clear but need attention (also see chapter 7, Sustainability and circularity).

4.4.2 Other Countries

Several countries in Europe have developed policies for PFAS in soil and ground water, including the neighboring countries of the Netherlands. A short description of this legislation is given here. Some other countries like the Nordic countries and Switzerland have also developed specific legislation for soil and groundwater. For most other EU countries, legislation on PFAS is limited to EU legislation.

Belgium

In Belgium, soil remediation levels for PFOS and PFOA for different land uses (agriculture, urban, recreation and industry) were recently updated by the Flemish Institute for Technological Research (VITO, 2022b). The levels have been adopted by the Flemish government December 16, 2022 (Flemish government, 2022). The EFSA TWI has been used for the evaluation.

Table 7. Soil remediation values for Flanders (Vrancken, 2022)

| Destination type | I/II | III | IV | V |
|------------------|------|-----|-----|-----|
| PFOS (µg/kg) | 3,8* | 4,9 | 110 | 268 |
| PFOA (µg/kg) | 2,5* | 7,9 | 632 | 303 |

*adjusted standard based on the value of free use (see below)

I/II = agriculture/nature, III = housing (urban areas), IV = recreation, V = industry.

For some types of uses (e.g. agriculture), a calculation of the risk levels based on the EFSA TWI resulted in target levels below the background values. This means that the background levels already cause an exposure that exceeds the EFSA TWI and a certain risk level is to be accepted. In these cases, the risk level was set on a pragmatic basis where the soil remediation value was set on the demands that the value of free use had to be 80% of the soil remediation value, and a factor two higher than the target value (equal to the background concentration). For these soil remediation value risk indexes were calculated in order to provide information on how large the health risk would be (risk indexes not shown here).

E.g. for agriculture, soil remediation levels and values for free use of soil for PFOS and PFOA are now based on ambient levels. To estimate how high this risk is at these levels, risk indexes were calculated that exceeded the EFSA TWI by a factor of 8,6 and 3,8 for PFOS and PFOA, accumulating to a potential exceedance of a factor 12,4.

Although this risk seems high at first, the VITO explained that this is a conservative risk estimation, as conservative assumptions are made in the exposure scenario for the agricultural environment. Therefore, the actual health risk of the soil remediation values set for PFOS and PFOA in agricultural fields is in reality likely to be lower than calculated and the need for location specific risk assessment was emphasized.

For other types of soil use (in urban and industrial environments) the EFSA TWI could be used in setting a soil remediation value. However, the EFSA TWI was fully attributed to both PFOS and PFOA separately, meaning that in soil containing high concentrations of PFOS and PFOA, the total exposure to these PFAS could be higher than the EFSA TWI. For soil in recreational environments, ecotoxicological levels were used for setting the soil remediation level.

For groundwater, a limit level of 0.1 µg/l for the sum of 20 PFAS and 0.5 µg/l for the sum of all PFAS is used. This is based on the EU Drinking Water Directive (2020/2184). For surface water, EU standards for PFOS apply.

Germany

In Germany, nationwide recommendations for soil and water contamination have been given in 2022, based on existing guidelines in some of the German states (e.g. Bavaria and Baden-Württemberg) (UBA, 2022). The derived values have been based on a tolerable daily intake (TDI) assessed in 2017. Whether the new EFSA TWI will be incorporated is being discussed.

For groundwater, threshold values have been derived for 13 PFAS. These values are also the basis for the assessment of soil, which is being assessed based on soil leachate values. Mixture toxicity can be assessed via a quotient index summation (risk index). Compounds with only a health advisory level (HAL) are not included in the summation.

Table 8. Insignificance threshold values and health advisory levels (HAL) for PFAS in groundwater (UBA, 2022)

| Substance | Insignificance threshold [µg/l] | HAL [µg/l] |
|---|---------------------------------|------------|
| Perfluorobutanoic acid, PFBA | 10.0 | |
| Perfluoropentanoic acid, PFPeA | | 3.0 |
| Perfluorohexanoic acid, PFHxA | 6.0 | |
| Perfluoroheptanoic acid, PFHpA | | 0.3 |
| Perfluorooctanoic acid, PFOA | 0.1 | |
| Perfluorononanoic acid, PFNA | 0.06 | |
| Perfluorodecanoic acid, PFDA | | 0.1 |
| Perfluorobutane sulfonic acid, PFBS | 6.0 | |
| Perfluorohexane sulfonic acid, PFHxS | 0.1 | |
| Perfluoroheptane sulfonic acid, PFHpS | | 0.3 |
| Perfluorooctane sulfonic acid, PFOS | 0.1 | |
| 6:2 Fluorotelomer sulfonic acid, 6:2 FTSA (H4PFOS) | | 0.1 |
| Perfluorooctanesulfonamide, PFOSA | | 0.1 |
| Other PFAS with R1-(CF2) <i>n</i> -R2, and <i>n</i> >3 | | 0.1 |

* Simultaneously serve as guidance values for drinking water pursuant to TrinkwV

For soil reuse three types of uses have been identified. The values are based on assessing leachate values at a liquid-solid ratio of 2.

- VK1. Soil can be used without restrictions.
- VK2. Restricted open emplacement, soils can be used, but only under certain conditions.
- VK3. Restricted emplacement in technical structures, soils can only be used in technical structures with safety measures.

Table 9. Preliminary maximum permissible concentrations in the liquid-to-solid 2:1 eluate in µg/l for the specific recovery classes (insignificance threshold based values) (UBA, 2022)

| | VK 1 Unrestricted open emplacement | VK 2 Restricted open emplacement in areas with elevated PFAS concentrations (*see notes) | VK 3 Restricted emplacement in technical structures with defined safety measures |
|---|---|--|--|
| Perfluorobutanoic acid, PFBA | ≤ 10.0 | ≤ 20.0 | ≤ 50 |
| Perfluorohexanoic acid, PFHxA | ≤ 6.0 | ≤ 12.0 | ≤ 30 |
| Perfluorooctanoic acid, PFOA | ≤ 0.1 | ≤ 0.2 | ≤ 1 |
| Perfluorononanoic acid, PFNA | ≤ 0.06 | ≤ 0.12 | ≤ 0.6 |
| Perfluorobutane sulfonic acid, PFBS | ≤ 6.0 | ≤ 12.0 | ≤ 30 |
| Perfluorohexane sulfonic acid, PFHxS | ≤ 0.1 | ≤ 0.2 | ≤ 1 |
| Perfluorooctane sulfonic acid, PFOS | ≤ 0.1 | ≤ 0.2 | ≤ 1 |

UK

In the UK, so called soil screening values for waste recovery to land based on the secondary poisoning of birds and mammals were set for PFOS and PFOA in soil, being 13 and 19 µg/kg respectively (Environment Agency, 2022).

For groundwater, a limit level of 1 µg/l applies for PFOS only, based on the danger of deterioration in the quality of the receiving groundwater (UKTAG, 2016).

For surface waters, the same AA-EQS and MAC-EQS for PFOS as in the EU EQSD apply, which are and AA-EQS of 0.65 ng/l in inland surface waters and 0.13 ng/l in other surface waters and a MAC-EQS of 36 and 7.3 µg/l for inland and other surface waters.

New WFD regulations based on the EFSA TWI and RPF-factors will not be adopted in the UK. The UK are planning to introduce new EQS for long chain PFAS in 2023.

4.5 Knowledge gaps and research needs

Uncertainty and decision making

The basis of the recent advisory levels for PFAS based upon EFSA is not undisputed (WHO, UK CoT: “endpoint too uncertain”). Combined with the fact that EFSA results in advisory levels that are often lower than ambient levels, detection limits and remediation capabilities, there is a need for a more robust underpinning, leading to regulatory requirements that are feasible and controllable. Challenges are big and both the positive and especially negative effects and consequences of stringent values can be huge.

Regarding high ambient levels of PFAS in soil, for some soil functions a certain risk is to be accepted when using the EFSA TWI and achieving concentrations leading to exposure below the EFSA TWI is not feasible. There is a need for decision making on which level of risk can be accepted (see example Riskindex VITO 2022 “Bindend normenkader voor PFOS en PFOA”).

Clear guidance

More study and guidance are needed on the influence of other exposure/intake routes for humans. Although much uncertainty remains and updates are on its way, the TWI for PFAS is already largely filled with other exposure routes than soil and groundwater. Currently the starting point is suggested by RIVM that 50% may be taken for exposure through soil and groundwater (Moestuinen onderzoek Dordrecht, Arcadis 2023).

There is a big difference between the values set for groundwater including drinking water consumption and excluding drinking water consumption. From a risk perspective, other values can be used for irrigation uses and cattle.

In surface water and drinking water, the advisory levels and maximum allowable levels are stringent, and tend to shift outside a feasible interval for chemical analyses or discharge levels. In the Netherlands these values often are below ambient levels. There is a need for a practical guidance on target levels in soil, water, and discharge criteria.

Relative toxicity

There is also a need for practical guidance for PFAS other than PFOS and PFOA. The current RPF method is developed for direct intake (e.g. drinking water, raw groundwater for drinking water, fruit and vegetables), but not very suitable to assess the risk of mixtures in soils and groundwater at urban use levels, risks that also depend on other endpoints than human toxicity such as ecotoxicity.

Furthermore, the RPF methodology for looking at the relative toxicity of different PFAS is a valuable tool but needs further development. The numbers used are not exact and not available for all congeners. In many cases they are the outcome of interpolation. There are significant differences between the RPFs used by RIVM and those from the EU, or that can be deduced from USEPA data.

The basis of the RPF methodology lies in animal studies whereas the TWI with which the outcome of a RPF calculation is compared is based upon epidemiological data.

5 Site investigation

5.1 Sampling

During sampling, storage and analysis it is of paramount importance to prevent cross-contamination. In general, products (clothing, tools, but also personal hygiene products etc.) potentially possessing PFAS should be avoided by the person who takes the samples. For storage, high-density polyethylene (HDPE) bottles are a safe choice, but attention should be paid to seals in the lids being PFAS free as well. PFAS are surfactants and can adsorb to different types of materials, to avoid loss of PFAS in the sample, some materials should be avoided during sampling and storage. For detailed instructions and recommendations in Dutch see the comprehensive overview of how to prevent PFAS cross-contamination *Handreiking PFAS bemonsteren* (Expertisecentrum PFAS, 2020).

When PFAS containing products are avoided, PFAS sampling in soil generally does not seem to be affected by cross-contamination. This is confirmed by the fact that soil samples from deeper layers often do not contain any PFAS. At high PFAS concentrations, cross-contamination could be an issue.

At this moment, it is not yet clear whether cross-contamination with PFAS actually occurs during groundwater sampling. Furthermore, guidance values for groundwater are already strict and might be set even lower. The lower the guidance values (and consequently the lower limits of detection), the more likely it will be that even very small amounts of cross contamination will have a noticeable impact on the sample. The risk on cross contamination or poor sample quality is higher when sampling deep groundwater tables, in case submersible or bladder pumps need to be used. A point of attention might be that during well construction the use of reused casing, if not cleaned thoroughly, might result in a (temporary) PFAS contamination in the groundwater). Another concern when sampling deep groundwater is that more tubing is required; it is quite possible that some PFAS compounds adsorb to the tubing material, resulting in an underestimation of the PFAS concentrations in the groundwater.

In (river) sediments there seems to be a larger spread in laboratory PFAS sampling results than in other matrices. This is something that should be taken into account when sampling (river) sediments for PFAS, sometimes it is worthwhile to reanalyze the sample when PFAS are present in concentrations above the background values.

5.2 Chemical analyses

Recent and future sharpening of PFAS regulations both in the Netherlands and abroad obviates the need for sensitive, cheap, fast and high-throughput PFAS detection methods in different matrices. Specifically, methods with the ability to measure the sum of all the PFAS in a sample are of interest for easy assessment of the regulations. However, the sheer number of different PFAS compounds challenges standardized analysis. This chapter gives an overview of the state-of-the-art PFAS detection methods.

5.2.1 Standard Analytical Techniques (LC-MS/MS)

Standard laboratory analysis in the Netherlands comprises a set of 28-30 individual compounds. This set can be expanded if necessary to roughly 40 individual PFAS substances including PFSA's, PFCA's, fluorotelomer sulfonic acids (FTS), polyfluoroalkyl phosphate esters (PaP), perfluoroethers and some other precursors. Expansion of this set of PFAS is limited due to the lack of appropriate internal standards of other PFAS compounds beyond this standard package.

Standard analysis is performed with liquid chromatography coupled to tandem-MS (LC-MS/MS). In this technique, the substances in a subjected sample are separated through liquid chromatography and subsequently identified using tandem MS. The limit of detection is typically 1 nanogram per liter (ng/L) in water and 5-10 microgram per kilogram ($\mu\text{g}/\text{kg}$) in soils. Recent efforts of some laboratories have led to lower detection limits of 1 ng/L for water and 0.1 $\mu\text{g}/\text{kg}$ for soils.

LC-MS/MS is a well-established method with a very low limit of detection. It has the advantage of both quantitative and qualitative characterization. Analysis of PFAS in soil and groundwater is nowadays mainstream and can be requested at the commercial laboratories, with a standard delivery time. However, LC-MS/MS is limited to only a standard set of PFAS compounds which makes it unsuitable for quantification of the total amount of PFAS in a sample.

5.2.2 Advanced Analytical Techniques

The suite of PFAS used in commercial applications like firefighting foam or used for oil and water repellency is much larger than the standard set of PFAS being analysed by LC-MS/MS. Which PFAS are used in which products is often not known due to proprietary information of the producers.

Quantification of other PFAS is more challenging and requires advanced analytical techniques. Three such advanced analytical techniques are discussed below.

Total Oxidizable Precursor Assay (TOP)

The TOP assay is the most common advanced analytical technique for detecting PFAS precursors. It is an indirect technique and involves precursor oxidation to PFAAs and subsequent quantification using LC-MS/MS (Bell, 2019). At elevated temperatures, persulfate ($S_2O_8^{2-}$) thermolysis generates sulphate and hydroxyl radicals. These radicals fully oxidize PFAA-precursors into PFAAs. The difference between the concentration of the sample before and after the TOP assay corresponds to the molar concentration of precursors in the sample.

The TOP assay has the advantage that analysis is performed with LC-MS/MS and thus no extra equipment is needed. A disadvantage is that the TOP assay takes about 6 hours extra compared to regular LC-MS/MS quantification. Besides, it does still not cover all the potential PFAS in a sample, but only the standard package plus the precursors that oxidize into species in the standard package.

Total Organofluorine (TOF)

In this technique organofluorine is mineralized to hydrofluoric acid by combustion at elevated temperatures (900-1000 °C). After combustion the concentration of fluoride is measured using ion chromatography (CIC). This anionic fluoride concentration is related to the amount of organofluorine in the pre-combustion sample. In order to obtain reliable results, it is of great importance to separate the organofluoride from fluoride before combustion.

For this purpose two methods are used:

- Extractable organofluorine (EOF) can be used for many different matrices such as water, soil, sediment and biological tissue (McDonough et al., 2019). For liquid samples, EOF concerns the separation of organofluorine fluoride by solid phase extraction. For solid matrices it concerns extraction of the fluorinated compounds from the matrix with methanol. The fluorinated compounds are incinerated, and the fluorine is quantified by CIC. The limit of detection of EOF is 10-100 µg/kg for solids depending on the matrix. (Held and Reinhard, 2020; Pancras, 2021).
- Adsorbable organofluorine (AOF) is only suitable for water samples. This assay depends on adsorption of organofluorides (and not fluoride) from the matrix on a synthetic activated carbon (AC). CIC is performed after elution of organofluoride from the AC. Recently, a limit of detection of 300-400 ng/L was reported for AOF (Han et al., 2021). A caveat of AOF is the difference in absorption of the various PFAS species. Especially short chain PFAS will remain partially undetected using this method. However, AOF is expected to cover a broad range of adsorbable cationic, anionic, neutral and zwitterionic organofluorine compounds, while the solid phase extraction of EOF covers mainly anionic compounds.

Neither EOF nor AOF can be used to identify specific PFAS species. However, these are useful methods for evaluating the total amount of PFAS in a sample. Further standardization will help rendering these methods applicable for routine monitoring of PFAS concentrations.

Particle-Induced Gamma Emission (PIGE) Spectroscopy

PIGE is a method that involves proton bombardment of a fluorine-holding sample. The feedback of the bombardment are Y-rays with a specific fluorine fingerprint. The intensity of the Gamma rays is proportional to the amount of fluorine present in the sample. Traditionally, this method has only been exploited for measuring the amount of fluorine in solids, but recently a procedure has been developed to apply this method to drinking water (Peaslee et al., 2021). In this procedure PFAS is adsorbed on an activated carbon felt which is subsequently subjected to the proton bombardment. This is a non-specific technique; any fluorine present in the sample is detected. In case elevated PFAS concentrations are measured, the activated carbon felt can be sent to a laboratory for further LC-MS/MS analysis.

The procedure developed has many practical advantages. It involves easy sample collection and only the activated carbon felt needs to be transported to the laboratory for PIGE assessment, not the whole water sample.

The detection limit is as low as 50 ppt (50 ng/L) for a 2L sample and can be lower by increasing the sample volume. Furthermore, if elevated concentrations of PFAS are detected, the carbon felt can be sent to a laboratory for further LC-MS/MS analysis without the need of complementary sample collection. A disadvantage of this techniques is that, just as with AOF, the recovery of short-chain PFAS's is low. Besides, it is only applicable to water matrices and to date it is mostly restricted to academic laboratories. Therefore, although promising, this method is not yet applicable in the Netherlands.

High-resolution mass spectrometry

Advanced analytical methods have shown a great discrepancy with the PFAS detected with LC-MS/MS. This raises the question what kind of substances these 'dark matter PFAS' are. For non-targeted and suspect PFAS screening, High-Resolution-Mass-Spectrometry (HRMS) in combination with computational methods has been developed to qualify unknown PFAS.

HRMS offers high spectral resolving power (RP) allowing for trace detection of ions. Subsequent data reduction is needed to distinguish trace ions from background signals for which various software are available. Advanced filtering, including diagnostic fractions, mass defects and homologue search, for specific features is used to search for suspected PFAS ions. Yet, this method has not fully matured to date. For broad applicability, further simplification and standardization is needed for sample preparation. At the same time, further automation in the identification of suspect PFAS will render this method practical for broad applicability.

5.2.3 Resumé analytical technologies

Measuring the sum of all PFAS's in a sample in a straightforward way is still a challenge. The detection of short-chain PFAS is a general gap in PFAS analyses. Table 10 gives an overview of the various techniques discussed. LC-MS/MS is a well-established and very sensitive method for PFAS detection. However, it only measures a fraction of all known PFAS's. The TOP assay, in which precursors are oxidized to PFAA many of which are detectable on LC-MS/MS, substantially increases the number of PFAS's detectable with LC-MS/MS. However, this method still doesn't cover all the PFAS's. TOF does theoretically cover all PFAS in a sample by combustion ion chromatography. However, adsorption and extraction of especially short-chain PFAS's is low which again results in an incomplete value for the sum of all PFAS's in a sample. PIGE is an elegant and promising technique in the field but again low recovery on the carbon felt of some PFAS's poses a challenge. All the techniques discussed have detection limits low enough for measuring legal values ($\mu\text{g/L}$).

Thus, TOF and PIGE are promising techniques for measuring the sum of all PFAS's but more work on increasing recovery needs to be done.

Table 10. Overview analytical technologies

| Technique | Scope | Detection limit | Applicability | Matrices |
|-------------------|---|---|---|----------|
| LC-MS/MS | Standard analytical package (~40 PFAS's) | 1 ng/l 0.1 $\mu\text{g/kg}$ | Standard analysis method, not all PFAS are covered | All |
| HRMS | Unknown PFAS | N/A, only qualification | | All |
| TOP + LC-MS/MS | Standard analytical package (28-40 PFAS's) plus their oxidizable precursors | Same as LC-MS/MS | TOP assay time demanding, not all PFAS are covered | All |
| CIC (EOF and AOF) | All organic fluorine | 10-100 $\mu\text{g/kg}$ 300-400 ng/l | Difference in adsorption and extraction among PFAS species. More standardization needed | All |
| PIGE | All organic fluorine | 50 ng/l | Mostly academic, more standardization needed | Water |

5.3 Knowledge gaps and research needs

Sampling

Sampling (if executed with care and according to protocols) is not considered as a major bottleneck, however research is considered necessary to test the influence of submersible pumps and tubing, necessary at deeper groundwater levels. Soil sampling at greater depth is sensitive for cross-contamination during sampling.

At very stringent target levels, cross contamination (or adsorption) can be an important issue.

Chemical analyses

There is a need for sensitive, cheap, fast and high-throughput PFAS detection methods in different matrices. Specifically, methods with the ability to measure the sum of all the PFAS in a sample are of interest. However, the sheer number of different PFAS compounds challenges standardized analyses.

The frontiers of detection limits are nearby. For clean soil a level of 0.1 µg/kg is possible for a standard set of PFAS. In clean water a level of 0.1 ng/l seems achievable for longer chain lengths but is challenging regarding reliability and reproducibility. The influence of cross contamination and other disturbances increases at lower concentrations. For shorter chains, recovery is more difficult than for long chain PFAS. Moving even lower towards the advisory levels in the order of magnitude of pg/l (picogram/l, or ppq) is expected not to be feasible in the short and midterm.

The TOP Assay is a very valuable tool for the identification of precursors and other compounds that are not identified with a PFAS target analyses, and gives insight in the chain length of the compounds. However, there is a need for more sophisticated technologies for the identification of this dark matter. This is especially important in case of newer PFAS contaminations (with precursors and other PFAS). For analyses that focus at assessing the total amount of PFAS, lower detection limits are necessary.

The discrepancy between Total organic fluorine and detectable, targetable PFAS compounds is too big. There is a need for explaining and exploring the difference between these two. It is expected that a more than significant amount of PFAS is present in the environment (and consumer products) that currently is not detected by means of a target analysis or a TOP assay.

Most technologies focus on anionic PFAS, cationic PFAS and zwitterionic PFAS are not included. Little is known about the presence and detection of cationic and zwitterionic PFAS.

The lack of internal standards limits the quantification of PFAS beyond the standard analytical package. For advanced analytical technologies validation and accreditation is necessary.

6 Soil remediation

6.1 Technologies and challenges

Treatment of contaminated soil or contaminated water starts with a good understanding of the boundary conditions of the site, the presence and behavior of the contamination, understanding of co-contaminations and the relevant receptors. A well-prepared conceptual site model is the basis for the selection of the treatment technologies.

Treatment of contaminated soil or contaminated water has multiple challenges:

- What is the appropriate remediation objective?
- How to remove the contaminant?
- How to reach the low target values for soil or discharge water?
- What to do with the waste?

Since PFAS are very recalcitrant and not prone to degradation, the amount of suitable remediation technologies is limited. PFAS properties vary depending on the perfluoroalkyl chain length and head group functionality which results in complex behavior within the subsurface, such as sorption to surfaces, partitioning to water/air interfaces and differential mobility. Overall remediation strategies should therefore consider how best to target PFAS sources.

For each technology, the ultimate fate of PFAS should be considered in terms of residual PFAS, byproducts and wastes. This is especially important in case of destruction technologies where a fluoride mass balance should be assessed to demonstrate complete destruction. This includes monitoring of potential byproducts such as partly fluorinated compounds and/or ultrashort PFAS, which may be toxic and recalcitrant. PFAS destruction requires aggressive methods typically involving high temperatures, pressures and/or electrical energy. Therefore, significant focus is currently directed toward developing more pragmatic, sustainable solutions.

For remediation of PFAS, the presence of precursors (which do not always show up in the general suite of PFAS being analysed), should also be considered. Under certain conditions, these precursors can be biotransformed into recalcitrant PFAS and so can represent a long-term source of PFAAs via leaching or runoff with concentrations of PFAAs observed to increase instead of decrease in some studies (Derksen and Baltussen, 2021).

6.1.1 Structuring technologies

Working principles

Remediation technologies can roughly be divided into the categories ex-situ and in-situ remediation. Within these categories, there are different working principles:

1. Ex-situ remediation: excavation and subsequent treatment or disposal
 - a. Separation (soil washing, landfilling, engineered containment)
 - b. Destruction (incineration, thermal treatment, ball-milling)
 - c. Immobilisation (stabilization/solidification)
2. In-situ remediation:
 - a. Immobilisation (injection activated carbon, stabilization/solidification)
 - b. Destruction (oxidation/reduction)
 - c. Separation (soil flushing)

6.1.2 Overview available technologies soil

Remediation of PFAS-contaminated soil in the Netherlands is currently focused at excavation and the disposal at a landfill site. In the Netherlands, for soils contaminated with PFAS-concentrations higher than 60-140-60 µg/kg (respectively PFOS, PFOA and other PFAS), can be declared not cleanable (“niet-reinigbaarheidsverklaring”), as well as soils with >40% fines (fraction <63 µm + organic matter). These soils are sent to a landfill site. Landfilling of soils is expensive, and leaching of the PFAS towards surface water at the landfill sites should be addressed. Engineered containment (e.g. within constructed cells) is similar to landfilling and may be undertaken on site, potentially involving pretreatment, but leachate management and containment lifespan should also be considered.

Soil washing is suitable for more granular soils, with relatively clean sand and gravels being separated (potentially for reuse) from the contaminated washing water and fines fraction. Techniques are being developed to expand the washing process to the fines fraction. Attention has to be given to the treatment of the washing water and appropriate management of fines, since most of the PFAS is transferred to these media. Water treatment technologies are discussed in the next chapter.

A related approach is soil flushing which aims to separate PFAS from soil surfaces either in situ or from leached 'heaps' above ground. These approaches are in their infancy and are not as aggressive as soil washing but may be applied over longer timeframes. Effective management of leachate is required.

Destructive technologies that can be applied to excavated soil include incineration at high temperatures (above ~1100 °C) which is costly, not very sustainable with limited suitable incineration capacity across Europe. Thermal desorption based approaches are similar to incineration but use lower initial temperatures with PFAS destruction achieved via off gas treatment. The ability and capacity to handle bulk soil volumes is higher than industrial incineration. A range of novel destructive technologies are being actively researched and developed to lower the energy costs and meet the needs for soil remediation.

Soil stabilization and solidification involving mixing soils with sorptive additives and cementitious binders (in situ or ex situ) to immobilize PFAS. It is increasing being assessed as a pragmatic, more sustainable approach with a focus on demonstrating long term durability and leachate reduction. In the Netherlands, there is not yet an accepted framework for soil stabilization. Stabilization prior to landfilling has been undertaken in Sweden and suggested in other countries. An additional in-situ remediation approach involves injection of activate carbons into soils to sorb PFAS and reduce mobility. Again, the focus is on demonstrating long term management of flux as well as ensuring effective distribution. Immobilization approaches do not destroy PFAS but look to manage leaching, mass flux and associated risks.

The research of biodegradation of PFAS is still in its infancy. PFAS's are very stable end products of biotransformation of PFAS-precursors, thus biodegradation of PFAS-contamination is not likely to be very effective. However, several plant based, bacterial and fungal species have been identified that are capable of degrading certain PFAS-compounds (Zhang et al., 2022). There are definitely research needs for sustainable PFAS remediation technologies, like biodegradation (or other technologies).

PFAS Treatment Technologies for Soil

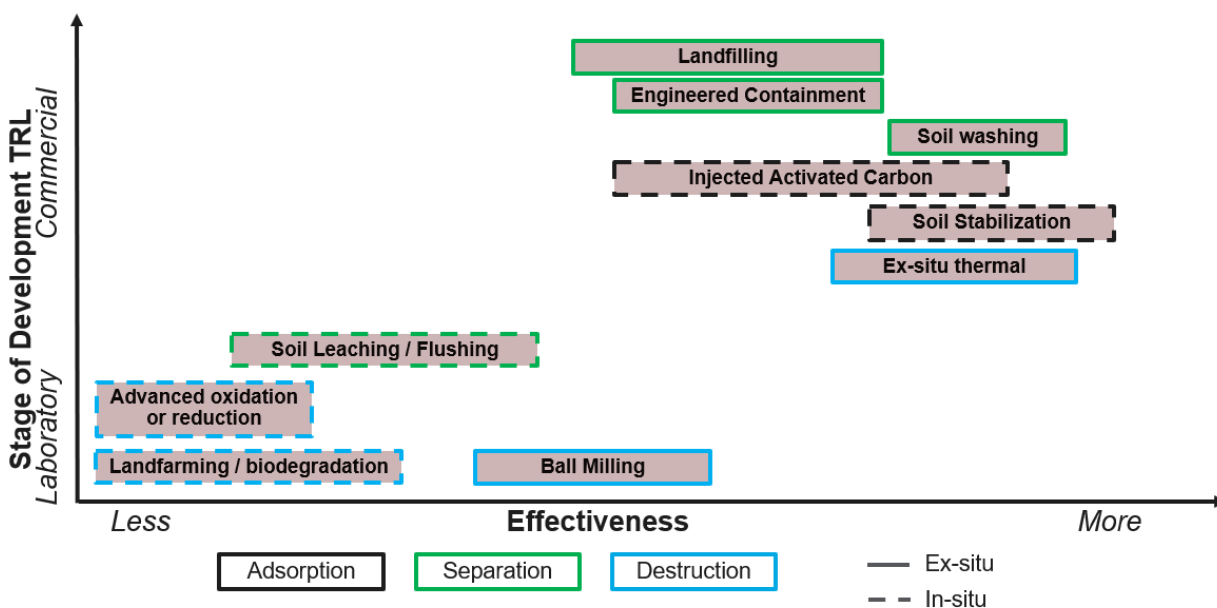


Figure 7: Treatment technologies for soil

6.1.3 Waste disposal and discharge

Ex-situ remediation technologies generate waste. Contaminated soil can be sent to a landfill when the concentrations are high enough, but the capacity at landfills in the Netherlands is limited and leachate treatment may be ineffective for PFAS. The capacity for incineration of PFAS-contaminated soils is very limited too, there are no high temperature incinerators in the Netherlands that can be used for incineration of PFAS-contaminated soils. There are a few incinerators across the borders, but also over there the capacity is limited, it requires a lot of transportation movements, and the fate of the PFAS during incineration is being questioned (although it looks like that the majority of the PFAS is being destructed, the mass balance is not 100% clear yet).

In case of soil washing, the fines fraction is usually sent to a landfill. The contaminated washing water needs treatment prior to discharge. The permitting process for the discharge of a water treatment unit has shown to be quite a challenge, due to strict threshold values. In 2020, uniform values for discharge of wastewater from soil treatment units have been established (500 ng/l for PFOS and PFOA, 1,000 ng/l for GenX, for a maximum of 4,000 m³) (Bodemplus, 2020). These values have not been reevaluated yet based on the latest insights (EFSA TWI and surface water criteria).

6.2 Knowledge gaps and research needs

Ex situ technology

Soil treatment (washing) is feasible and available in the Netherlands to desired levels of cleanup, also with higher initial concentrations than the formal not-treatability level (60 µg/kg). Dependent upon soil type even PFAS levels above 1 mg/kg can be treated to the reuse criteria. The management of fines from this process requires additional consideration.

The main bottlenecks for soil treatment in the Netherlands are the disposal of waste and the discharge of PFAS containing water. There is an urgent need for waste treatment options and clear regulation on discharge (see chapter 7). The uncertainty on discharge permits has slowed the development of soil treatment techniques.

Destruction of PFAS via high temperature incineration is expensive, unsustainable and not available in the Netherlands and also has some uncertainties:

- In recent years there have been issues with the reuse of thermally treated soils, concerning the chemical quality and applicability of the soil after treatment.
- Complete mineralization requires very high temperatures and the available treatment plants in the Netherlands do not operate at sufficiently high temperatures. Capacity across Europe is also limited.
- The mass balance at high temperature incinerators is not completely assessed yet, including monitoring of potential byproducts such as partly fluorinated compounds and/or ultrashort PFAS. It may also require hydrogen fluoride flue gas scrubbing, which is not universally present on incinerators, which may be toxic and recalcitrant.

To date, biological or chemical destruction techniques have not proven to be effective. Novel destruction techniques for soil require further development, investment and application to provide a lower cost, less energy intensive alternative to incineration.

In situ technologies and stabilization

At this moment there is not really an outlook towards in situ technologies, except for in situ adsorption by activated carbon or soil stabilization. In that case, the PFAS remains in the soil. PFAS cannot be destructed in-situ, and although the transport can be stimulated with thermal technologies, the readiness and effectivity of these techniques are not mature. There is a need for more perspective in the field of in situ.

At this moment there is not yet an accepted framework in the Netherlands for soil stabilization and it is not very common. However, immobilization approaches may benefit from further studies and field applications demonstrating effective long term treatment to gain stakeholder acceptance, either for remediation onsite or as pretreatment prior to landfilling.

7 Water treatment

7.1 Technologies and criteria

7.1.1 Inventories

PFAS are especially a threat to water quality and one of the major challenges is to find cost-effective technologies that are able to achieve the required discharge levels at reasonable cost levels. The world of water treatment on PFAS is dynamic.

Recently two inventories on technologies were started. The Flemish VITO is busy with an extended study on the Best Available techniques (VITO, 2022a). This draft was one of the inputs for a more concise memo of Witteveen+Bos and the Dutch Expertisecenter PFAS (Witteveen+Bos, 2023). For this memo also interviews were held in order to identify the major bottlenecks that are experienced in practice. Both of these studies are based upon many references. The view on the state of the art on treatment technologies is mainly based upon these studies, reflected against practical field experiences.

7.1.2 Structuring technologies

Working principles

Treatment technologies can roughly be divided with their mainly working principles:

1. Adsorption (activated carbon, resins, novel adsorbents);
2. Separation:
 - Coagulation;
 - Foam fractionation (air/ozone);
 - Membrane filtration (RO/NF);
3. Destruction:
 - Incineration;
 - Novel technologies e.g. super critical water oxidation (SCWO), electrochemical (EC), sonolysis, plasma, UV, biological degradation).

Varieties to these principles exist with technologies including many different products and providers, obviously with different specifications and effectivity. In this overview we restrict ourselves to the headlines. As an example, in a study of Concauwe, that was executed in 2021 a comparison was made between different types of adsorbents and separation techniques (Roest et al., 2021).

Technology readiness

Many technologies are in a state of development that is not yet suitable for field application. In the above mentioned studies the methodology of STOWA for the readiness level of the technologies is used (Stowa, 2019). The ranking methodology was developed for the removal of medicine residues out of Municipal wastewater. In appendix A an overview of treatment techniques is given, with a short description and impression of the development level.

Treatment performance

The removal efficiency of techniques in specific situations highly depends upon:

- Type of water (matrix), chemical composition, is it relatively clean or does it contain a high load of other substances.
- Type of PFAS, sorption and separation technologies are typically more effective for long chain PFAS than for shorter chain lengths. Straight chain PFAS adsorb better than branched PFAS.
- The treatment scenario and scale are important when considering whether technologies are cost effective over the long term.
- The presence of precursors. Precursor treatment is less well studied and complex. Aerobic processes can enhance the rates of biotransformation which may result in an increase in PFAA-concentrations.

- Concentration level in the water to be treated and the target levels that have to be reached. More than 95% reduction is feasible, but more than 99.99% is challenging and often not possible.
- When very low target levels are required, the efficiency drops dramatically. For instance, it is very difficult to reduce a concentration from 10 ng/l to 1 ng/l. A reduction from 1 ug/l to 0,1 ug/l is much more feasible.

Combination of technologies

In reality, only rarely technologies are used as a standalone technique given the range of PFAS and challenges associated with removal. Often an extended treatment train of multiple technologies is needed. An example treatment train may comprise pretreatment (e.g. sand filtration, flocculation, organics removal), then the main treatment step, followed by a polishing step (e.g. activated carbon, ion exchange resins) in order to achieve the required low levels.

7.1.3 Overview available technologies water

In the figure below a high-level summary of the level of development of a technology (TRL) and its effectiveness for PFAS removal. The level of readiness may differ over countries. There is overlap between technologies, and also the effectiveness highly depends upon the criteria regarding discharge. The placement is based on the standalone application.

Roughly, the technologies in the right-hand top quadrant are suitable for pilot testing or full-scale application and most demonstrated to be effective. Activated carbon, ion exchange resins, incineration and reversed osmosis / nano filtration (RO/NF) are most deployed and commercially available technologies. For foam fractionation, super critical water oxidation (SCWO) and biobased adsorbents the first full scale field applications have been successfully realized. The other technologies haven't reached a sufficient maturity level or are not sufficiently effective in removing PFAS.

PFAS Treatment Technologies for Water

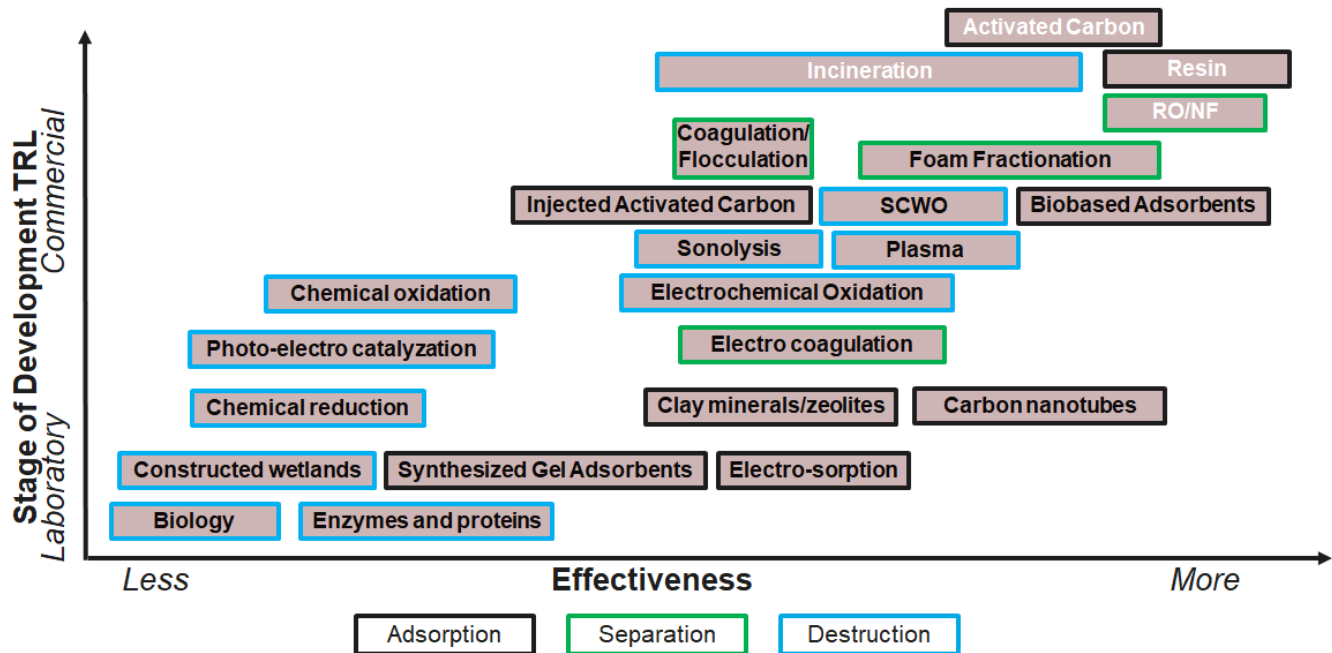


Figure 8: Treatment Technologies for Water (SCWO: Super critical Water Oxidation, RO/NF: Reversed Osmosis/Nano Filtration)

7.1.4 Waste and disposal

Effective destruction of PFAS via incineration needs very high temperatures and energy and is therefore expensive and not suitable for large liquid volumes. Capacity at high temperature incinerators is very limited. Also, the efficacy of incineration has been questioned in some locations.

Solid wastes from liquid treatment also require treatment with spent carbon, resins and other sorbents requiring high temperature incineration or regeneration or (less often) landfilling.

Commercially available options for onsite destruction are under fast development but have not yet been realized. For example, SCWO is being scale up in the US but remains expensive and not available in Europe.

7.2 Knowledge gaps and research needs

Barriers

There are technologies available that can treat PFAS contaminated water to required levels (ng/l). Activated carbon, resins, RO/NF are readily available and effective. However, if lower levels (picogram/l) are requested, these are considered not to be feasible, not on the short nor longer term. Moreover the cost of the application of these technologies are often expected to be beyond the cost interval of the BBT+ approach in the Netherlands (allowable cost per kg removal) (Ministerie IenW, 2018).

Foam fractionation, coagulation and flocculation are operational but usually need polishing steps. Destruction techniques SCWO, plasma, UV, electrochemical and sonolysis are upcoming but not yet fully operational. Nearly all other technologies mentioned in figure 5 need additional development to be sufficiently effective or commercially available.

The effectivity of treatment technologies highly depends on the quality and contamination degree of the water. Some techniques are very susceptible for matrix demand and need intensive pretreatment (e.g. activated carbon and RO/NF). Flocculation and fractionation techniques are less susceptible for contaminant matrix but need polishing steps. The wide range of PFAS (including precursors) and their different properties and removal efficiency is also a significant hurdle. Therefore, in most cases a treatment train of more than one technology is needed. The hunt is for the most cost- effective treatment train.

The required discharge levels, cost and impacts needed to achieve these levels are serious bottlenecks. Energy requirements and waste production can be big. More and more the disposal of this waste becomes an issue. There are no waste treatment facilities in the Netherlands that can destroy PFAS, the facilities abroad have limited capacity and the export of waste is currently under intensified control.

Another bottleneck lies in the uncertainty around discharge permits. Target levels for surface water and sewer systems differ over different authorities and are unstable. Often a precautionary, stringent approach is the chosen, leading to challenging levels or high cost and other negative impacts. For permitted activities in the Netherlands an emissiontest is being used, a test in which the amount of contaminant that will be discharged is reflected against the contaminant level in the water stream in which it is discharged¹¹. This approach unfortunately is not applicable for many remediation projects. Furthermore, the Water Framework Directive may drive discharge criteria to very low levels (sub ng/l, or even pg/l based on Smit en Verbruggen, 2022), that may prove to be beyond the technical possibilities of chemical analyses and treatment techniques.

Needs

From a technical viewpoint, treatment technologies need optimization to either increase the availability, effectiveness, or cost level. Additionally, there is a need in the Netherlands for waste treatment facilities that can destroy PFAS or increased possibilities abroad. A need more sustainable, less energy intensive technologies that can effectively destroy PFAS is clear.

From a policy and regulatory viewpoint, also an integrated feasibility and sustainability framework could be considered. It is obvious that the impacts of energy consumption, waste production can be significant and can be reflected against the level of risk reduction in case a negligible risk is not feasible (also see chapter 8).

¹¹ <https://www.immissietoets.nl/>

8 Sustainability and circularity

Sustainability and circularity are strongly linked. In this chapter sustainability is linked to remediation techniques, whereas circularity is discussed in relation to soil reuse.

8.1 Sustainability

Sustainable remediation

At present target levels for remediation of PFAS in soil and water are low. There are still many uncertainties on the exact toxicity and effects of PFAS, and for now PFAS are considered a new contaminant, meaning that as much as possible should be removed if reasonable and fair. This differs from a risk-based, function-oriented approach that can be used for historical contamination, where more residual contamination is accepted.

Far reaching removal puts high demands on remediation techniques and may cause negative impacts.

The impacts of soil transport, treatment, discharges or dumping, (energy consumption, emissions of CO₂ and dust, noise, cost, stagnation of societal developments etc.) can be significant and may outweigh the benefits of the undertaking.

Over the last two decades many decision frameworks, tools and policies were developed looking at sustainable remediation of (mainly) historical contaminated soil and groundwater, a few of them:

- Circular Soil Remediation 2013 (Circulaire Bodemsanering 2013, afweging baten en lasten).
- SuRF-UK, A Framework for Assessing the Sustainability of Soil and Groundwater Remediation, 2010.
- Cahier Duurzaam Saneren doe je zo, SKB-Bodembreedforum 2015.
- Joint Position Risk-informed and sustainable remediation, NICOLE-Common Forum 2013.
- Praktijkdocument ROSA, Handreiking voor het maken van keuzes en afspraken bij mobiele verontreinigingen, 2005
- ISO18504 Guidance on sustainable remediation, 2017.

In these methodologies key performance indicators (KPIs) have been developed to make sustainability measurable or to make remedial options comparable. PFAS contamination however is not considered historical, and these methodologies may not be applicable in the Netherlands. Also, remediation in our country nowadays mainly originates from redevelopment, where the aim often is to remediate to reuse levels, delivering optimal property value. Reuse levels are much lower than intervention levels and have a bigger impact. Sustainability of remediation is not considered up front in the planning process, but in the contracting phase, where in essence it should be considered as green remediation (not perse the most sustainable option).

Currently the Dutch Ministry is evaluating criteria that can be used to underpin “reasonable and fair”, and finally to give guidance to competent authorities.

From a sustainability viewpoint it is recommended to assess or investigate on a national scale (not on a site-specific level), the influence of using sustainability KPIs, criteria for fairness and reasonableness on the overall sustainability and risk reduction of the proposed approach. Given the fact that PFAS are omnipresent and the major exposure route for humans is food (not directly soil or groundwater), it can be expected that the gain of far-reaching removal is limited whereas the negative impacts can be significant. It is unclear to what extent PFAS in soil contribute to PFAS in food.

Easily accessible sustainability gains

Criteria for non-treatability of soil (60 µg/kgdw) were set 4-5 years ago and in the meantime knowledge and technologies have advanced. Landfilling as a final destination for contaminated soil is considered a less sustainable way forward than other options. It is recommended to reconsider the criteria for non-treatability.

8.2 Circularity

Regarding circularity of products and resources containing PFAS it is important to make a distinction between the reuse of soil and sludge, and circularity in general. For the reuse of soil and sludge in the Netherlands distinct policies exist; The decree on Soil Quality (Besluit Bodemkwaliteit, (BBK)), and the Guidance on PFAS in Soils and Sludge (Handelingskader PFAS (HK)).

Reuse of soil and sludge

The fact that there are clear ambitions on circular economy (CE) and sustainability and that PFAS can be found in many products, soils, sludge etc. implicates that there is a need on clear guidance and decision models. It is obvious that these tools need a solid basis in policy. Apart from perhaps a few countries in the EU like Belgium, the policy and regulation on soil reuse in the Netherlands is rather unique and well developed. For soil and sludge this offers a strict framework, in which the dominating starting point lie in the stand still principle based upon the chemical status of the soil. The BBK and HK don't offer a framework for the assessment of the suitability of the soil regarding:

- Physical properties and suitability of the soil for specific purposes (building, top layer for vegetation etc.);
- Biodiversity and vitality.

BBK and HK offer a framework for diffuse contamination, where a difference can be made between generic policy and an area specific policy. For more severe contamination currently the Soil Protection Law (Wet Bodembescherming) regarding remediation applies (see 8.1). In both the generic and area specific policy understandably, the chemical status dominates decision making whereas sustainability and circularity considerations might mean concessions to the current interpretation of stand still.

In the current situation the general perception is that (ToC session, 2022):

- There is a lot of unnecessary soil transport, that causes CO2 emissions and costs money and energy.
- Organic rich top-layers are excavated and removed.
- There is limited capacity for soil mining or for the disposal of soils qualified as soils of poor quality.
- Very often soil reuse is not possible because of other legislation.

In the policy letter "Water en bodem sturend" (Water and soil guiding; I&W, 2022) on November 25th 2022, the Secretary of State amongst others set out the strategy on soil for years to come, and regarding circularity mentioned:

- Reduce excavation, especially of organic rich soils.
- Reuse locally.
- Reuse in the same area.

Challenges

Considering the ambitions and bottlenecks and looking at the clear but strict interpretation of BBK, HK and adjoining legislation, it is recommended to investigate if more flexibility regarding PFAS can be incorporated in order to take into account sustainability or circularity principles and to better prepare on future ambitions on soil vitality. This may require a revisit on the definition of Stand-still (at what level), and a thorough study on possible risks involved.

Currently at best sustainability considerations are done during the contracting phase. Bigger sustainability gains are feasible if these considerations take place earlier in the decision of policy making process.

Circularity in general

In 2020 RIVM performed an inventory of available information that helps to reinforce the knowledge for the assessment of initiatives on circular economy (CE). This included websites, helpdesks and knowledge networks. The focus was on the interface of CE, emerging contaminants (EC) and sustainability. This study also gives a (still actual) view on the needs regarding PFAS and CE in general the Netherlands (mainly regarding PFAS in products and goods).

The major finding of RIVM in the was that knowledge is scattered over different sources of information. More in detail can be read that:

- Information is available on websites on separate topics, but there is hardly any attention for the intersection between CE, EC and sustainability. If there is any info, then it is hard to find.
- Information is more market push then on demand, and often difficult to access or understand for authorities.
- Information should be bundled on one spot, and then differentiated for different end users. Also, the existing helpdesks or front-offices need more cooperation and linking.
- Networks only scarcely focus on this topic and are all too often too homogeneous of composition (only municipal servants or Environment departments. More crosslinking is needed.

9 Resumé

This document provides an overview of the current state of the art of the knowledge necessary for sustainable management of PFAS contamination in soil and groundwater. The widespread presence of PFAS, the recalcitrance of the compounds, the complexity of the PFAS-compounds and fate and transport in combination with the very stringent target levels make the risk assessment and management of PFAS-contamination very challenging.

General findings

- Exposure and uptake out of many diffuse sources (food, dust) already exceeds the Tolerable Daily Intake level. Research and management strategies should be considered with this in mind. It demands an integral approach of dealing with PFAS and a shift from a negligible risk approach to an acceptable risk approach.
- Ambient values of PFAS in surface water and phreatic ground water (~30 ng/l) in the Netherlands are above the recent advisory level for drinking water (4.4 ng/l, RIVM 2022) and, more challenging, above the proposed Quality Standard (QS) in the amendment of the Groundwater Directive (also 4.4 ng/l). The goal of meeting the QS in ground water by 2033 is considered unfeasible. The relatively recent European drinking water target value (100 ng/l) however is not exceeded.
- A considerable contaminant load comes from outside the boundaries of our countries (rivers, sea spray, atmospheric deposition).
- The recent decrease of advisory levels to picogram level, puts these advisory levels beyond the range that can be achieved by chemical analyses and remediation technologies. Innovation and improvement are certainly possible to make the analyses and technologies more robust and reliable to the nanogram level. The picogram level will remain beyond reach.
- Prevention and restriction are above all the most important management options. PFOS and PFOA levels in rivers and human serum have shown to decrease significantly over the last 10-15 years.

Knowledge gaps, research needs and challenges

Understanding different PFAS

- Types and uses of PFAS vary significantly. For many PFAS there is not enough information available to be able to assess the behavior and risks. Especially shorter chain PFAS and precursors can be more mobile in soil and groundwater, and more difficult to detect.
- Study on the use and origin of PFAS in industrial processes, to understand potential sources and dispersion in the environment.
- Knowledge and expertise on the fate and transport of the different PFAS in the unsaturated and the saturated zone is increasing, but often misunderstood. Transport is dominated by interfaces processes and much less on linear sorption kinetics. More research and validation against field data is desired, but above all, practical guidance is needed for practitioners.
- Concerning analyses of PFAS, the frontiers of detection limits and cross contamination are near. Already in the standard suite, the recovery of the shorter chain PFAS is still an issue. But especially the analyses of other compounds than the standard suite of PFAS should be developed further, in order to be able to gain more insight in the PFAS that are currently not identifiable with target analyses, the so-called dark matter.

Risk Assessment and target levels

- Target levels for risk assessment are mainly based upon the EFSA TWI, which has been derived for 4 PFAS. The basis of this TWI is immunotoxicology. It is endorsed in Europe but is found to be too uncertain and unachievable by the WHO and the UK Committee on Toxicity. WHO acknowledges the reduced number of antibodies after vaccination but doesn't find actual health effects at this level. Given the impact of this TWI and the forementioned uncertainty, more research, communication and guidance is needed to put risks in perspective.
- The main exposure route for humans is intake. It is unclear to what extent soil contamination contributes to PFAS in food.
- Currently Relative Potency Factors (RPF) are used to estimate the toxicity of PFAS other than PFOS, PFOA, PFHxS and PFNA. The RPF approach is a very valuable tool but needs further development. The RPF factors are uncertain estimates and based on a different endpoint than EFSA (liver toxicity, not immunotoxicity). USEPA target values for drinking water indicate different RPFs, and also the EU SCHEER uses slightly different numbers. This is especially an issue when the other PFAS are driving the risk assessment.
- Target or advisory values are found to hinder the development and permitting processes for the treatment of PFAS containing soils and water. Often a precautionary, stringent approach is chosen, leading to practically unachievable levels or high cost and other negative impacts. Initially even pilot projects were not possible.

A clear and more flexible policy on discharge is necessary to make steps towards tackling PFAS contamination, and to enable efficient mass reduction.

Treatment Technologies and approaches

- There is a limited range of ex situ technologies that can be used for soil remediation. At present, no state of the art technologies for in situ remediation are known. For water treatment the range of technologies is wider. Common characteristic for most technologies is that the technologies require a lot of energy or generate waste that has to be dealt with. There is an urgent need for waste treatment facilities, where the mass balance of PFAS has been evaluated and is guaranteed.
- Treatment technologies for water need optimization. Although efficient technologies are available, they all have specific downsides. Cost, energy consumption and waste production can be high. And negative impacts are passed on to other environment compartments. The sensitivity for water chemistry and co-contaminants usually is high, especially because in most cases a treatment train is needed to reach the nanogram level. Furthermore, for most technologies, the efficacy differs between types of PFAS. Currently there are no techniques really operational for destruction of PFAS.
- There is a clear need for more sustainable approaches. In the context of stringent target levels, the costs and environmental impact of remediation and treatment are very high. There is a need for a comprehensive, sustainability framework for remediation objectives. In comparison with our policy renewal in the beginning of this century, we should take care that the cure is no worse than the disease.
- Also, the presence of PFAS in our soils and sludge is a threat or barrier for the circular economy. A high-level study can investigate options to reduce the potential barriers for circularity.
- Currently there are no waste destruction facilities in the Netherlands which are suitable for the treatment of PFAS containing waste. The need is obvious.

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Appendix A: Overview of Treatment Techniques (Dutch)

| Techniek | Schaal/Marktrijpheid/TRL | ACTIEPROGRAMMA PFAS (TRL 5 en hoger) | Verwijderingsrendementen (korte en lange ketens) | Type water | Reststroom | Investeringskosten | Operationele kosten | Techniek toelichting | Achtergrondinformatie |
|--|--|--------------------------------------|---|--|---|--|--|--|---|
| | | | | Industrieel afvalwater / Grondwater | | CAPEX, Kwalitatief | OPEX, Kwalitatief | | (verwijzing naar enkele niet-commerciële websites) |
| Adsorptie Activated carbon <i>Actief kool</i> - GAC - PAC | TRL9 (Iery, 2019) | Ja | PFOS >90% (Kucharzyk et al., 2017) PFOS/PFOA > 90% (Arcadis, 2021) Van 90 - >99% verwijdering Minder goede adsorptie van short chain en snellere doorslag (Kucharzyk et al., 2017; OVAM, 2021) Minder effectief voor kortere PFAA keten, maar kan gecompenseerd worden door een langere EBCT. Variabele precursor effectiviteit (Arcadis, 2021) PFAS < CS hebben een kortere doorbraak tijd (Iery, 2019) | Grondwater (Concawe), industrieel water (diverse praktijkinstallaties) | Reactivatie van verbruikte GAK. Hoeveelheid verbruik is matig bij focus op lange PFAS ketens, maar het verbruik is hoger als korte ketens verwijderd moeten worden | + (Concawe) | 0 (Concawe) | Actief kool is een microporeuze inerte koolstofmatrix, met een zeer groot intern oppervlak (700 tot 1 500 m ² /g). Dit intern oppervlak leent zich ideaal tot adsorptie (https://emis.vito.be/nl/bbt/bbt-tools/selectiesystemen/luss/technieken/actief-kool-adsorptie) | https://emis.vito.be/nl/node/19258 https://emis.vito.be/nl/node/19259 |
| Ionexchange resins <i>Ionenuitwisselingsharsen</i> - Anion exchange removal (AER) | TRL 9 (Iery, 2019 & OVAM, 2021) | Ja | PFOS/PFOA >90% (Arcadis, 2021) Hogere capaciteit dan GAC6x PFOA en 8x PFOS (Arcadis, 2021) Hogere capaciteit bij hoge concentratie en langere ketenlengte (some PFOS molecules were adsorbing to the resin without ion exchange occurring) (Boyer et al., 2021) ook afh van type resin Maar snellere adsorptiesnelheid voor korte keten PFAS (size exclusion long vs. short), maar kan ook omgekeerd afh van type resin (Boyer et al., 2021) Beter prestatie om kore PFAS keten aan te pakken tov GAK (Arcadis, 2021) Significant hogere adsorptie capaciteit tov GAK (Gagliano et al., 2020) (uit boyer et al., 2021) pH kan een rol spelen voor korte keten behalve voor PFAAs (Boyer et al., 2021) | Grondwater en afvalwater (Dixit Et al. 2021) | Brijn met PFAS; niet regeneerbare verzadigde ionenuitwisselingsharsen | + (Concawe) | - Hoge kosten voor verbruikt regenerant, ionenuitwisseling is een tweede optie als GAK niet mogelijk is (Verma Et al. 2021) | Een ionenwisselaar bestaat uit een behuizing gevuld met kunsthars, waarmee ongewenste ionen uit een waterige stroom worden verwijderd door ze uit te wisselen met minder schadelijke ionen. (https://emis.vito.be/nl/bbt/bbt-tools/techniefiches/ionenuitwisseling) | https://emis.vito.be/nl/node/19257 |
| Biobased adsorbentia - DEXSORB - ... | TRL 5 - 6 | Ja | Snellere adsorptie kinetiek dan GAK, dus kleinere installaties zijn mogelijk (Concawe) Hogere affiniteit voor lange PFAS keten dan voor korte ketens (Concawe) | Grondwater (Concawe), maar ook voor industrieel water | Twee reststromen Vervanging van adsorbent (DEXSORB* vastestof) en verbruikte regenerant (methanol (vloeibaar)). De hoeveelheid verbruikte stoffen is niet bekend (Concawe) | + (Concawe) | 0 (Concawe) | DEXSORB bestaat uit kuppjes cyclodextrine moleculen met crosslinkers. De verwijderingsmechanisme berust op de hydrophobische interactie van de binnenzijde van de kuppjes. (Concawe) | |
| Biochar | TRL 7 - 8 (Iery, 2019) | Ja | tot 100% PFAS uitloging reductie bij hoge dosering van 5% (OVAM 2021) 0-94% 7 dagen labtest. 22-58 % met biofilm pilot 22 weken. (Lenka et al. 2021) Werkt beter met long chain dan short chain (OVAM 2021) | Grondwater (OVAM 2021) Afvalwater (Lenka et al. 2021) | Niet nader beschouwd | Mogelijk hoger dan GAC, omdat meer materiaal nodig is voor zelfde rendement en dus grotere contactoren/reactoren | + 6x goedkoper om te produceren dan GAC (S. Garg et al. 2021) | Biochar is carbonrijk poreuze vaste stof dat gemaakt wordt door biomassa (zoals hout of mest) te verhitten onder lage zuurstof concentratie omgeving. (ITRC June 2022) | Biochar verwijderd PFAS minder efficiënt dan GAC. De hoeveelheid Biochar dat verwerkt moeten worden na verzadiging zal vermoedelijk hoger zijn dan wanneer GAC wordt gebruikt |
| Carbon nanotubes <i>Koolstof nanotubes</i> | TRL 3 (Kucharzyk et al., 2017) | Nee | Werkt goed (Li et al. 2020) Adsorbeerd lange ketens beter dan korte ketens (Li et al. 2020) | Grondwater (Santiago et al. 2022) (Kucharzyk et al. 2017) | Niet nader beschouwd | Niet nader beschouwd | - groot schalige productie is een uitdaging, verwacht hogere kosten (Santiago et al. 2022)(Wanninayake et al. 2021) | Koolstof nanotubes hebben unieke nanostructuur, conductiviteit en zeer grote oppervlak. (Santiago etl al. 2022) | Nanomaterialen in de grond injecteren kan uitloging in het grondwater vertraging (Wanninayake 2021) https://watercircle.be/publicaties/database-waterzuivering-en-behandelingstechnieken/acoustic-nanotube-technology/ https://watercircle.be/publicaties/database-waterzuivering-en-behandelingstechnieken/nanotechnology/ |
| Natural and surface-modified clay minerals/zeolites <i>Natuurlijke en oppervlaktemodificeerde kleimineralen/zeolieten</i> | TRL 3 (Kucharzyk et al., 2017, Iery, 2019) | Nee | Minder adsorptie capaciteit vergeleken met ionenwisselaar en GAK (Du et al., 2014) Kan PFOS and PFOA verwijderen (Verma et al. 2021) | Grondwater (ITRC June 2022) | Vaste reststroom, hoeveelheid inschatting is niet nader beschouwd | Niet nader beschouwd | Onbekend | Zeoliet is een aluminumsilicaat dat zowel natuurlijk voorkomt als synthetisch wordt aangemaakt. Het zeoliet heeft een driedimensionale structuur met poriën. Zeolieten en klei materialen kunnen PFAS uit het water verwijderen d.m.v. ionenuitwisseling en adsorptie mechanisme (https://emis.vito.be/nl/bbt/bbt-tools/techniefiches/zeoliet-adsorptie) (ITRC June 2022) | In batch testen, is een reductie van 95-99% anionische PFAS loging geobserveerd, inclusief PFOS and PFOA. De dosering in het verontreinigde grond is 0.5% tot 5% gewicht van een commercieel gemodificeerd klei oppervlak (Wang et al. 2021) https://watercircle.be/publicaties/database-waterzuivering-en-behandelingstechnieken/nanotechnology/ |
| Molecularly imprinted polymers | TRL 3 (Kucharzyk et al., 2017) | Nee | Deze techniek heeft een hogere adsorptie affiniteit voor PFO tov poeder actieve kool (Xiao et al., 2017a) Hoge adsorptie capaciteit voor PFOS door micell formatie in de poreuze materiaal (Wanninayake 2021) | Niet duidelijk in welke water getest is | Niet nader beschouwd | Niet nader beschouwd | Niet nader beschouwd | Selectieve adsorbent die synthetisch wordt gemaakt (Verma et al. 2021) | |
| Electrosorption <i>Elektrosorptie</i> | TRL 2 -3 | Nee | PFOA verwijdering >82.5% in secundaire afvalwater. PFOS/PFOA/PFNA/PFSA verwijdering >85%. The zuiveringstijd bandbreedte gaat van 0,5 tot 4 uur en soms boven de 5 uur (Garg et al. 2021) Vooral getest op lange ketens (Garg et al. 2021) | Getest in secundaire afvalwater en voornamelijk in demi water (Garg et al. 2021) | De elektrische polen omdraaien om de ionen terug in het vloeistof te drijven (Garg et al 2021) | Niet nader beschouwd | Niet nader beschouwd | Elektrosorptie is een proces waar opgeloste deeltjes zich aan het oppervlak bindt van de gepoliseerde elektrode d.m.v. een geïnduceerde elektrisch veld (Santiago et al. 2022) | Een handvol testen in deionized water en een paar met secundaire wafvalwater (Garg et al 2021) |

| Techniek | Schaal/Marktrijpheid/TRL | ACTIEPROGRAMMA PFAS (TRL 5 en hoger) | Verwijderingsrendementen (korte en lange ketens) | Type water | Reststroom | Investeringskosten CAPEX, Kwalitatief | Operationele kosten OPEX, Kwalitatief | Techniek toelichting | Achtergrondinformatie (verwijzing naar enkele niet-commerciële websites) |
|--|---|--------------------------------------|---|---|--|---|---|--|--|
| | | | | Industrieel afvalwater / Grondwater | | | | | |
| Coagulatie technieken | | | | | | | | | |
| Coagulation/flocculation <i>Coagulatie/flocculatie</i> | TRL 9 (Iery, 2019) | Ja | PFOA verwijdering >90% (PAC1 = 10mg/L) Verwijdering efficiëncie van korte ketens is uitstekend (PFBA > PFHxA > PFOA > PFDoA > PFOS) (Liu et al., 2022) | grondwater (Concawe) | Reststroom is slib met PFAS. De hoeveelheid reststroom hangt af van het afvalwater matrix, de dosering en de gewenste verwijderingsrendement | Niet nader beschouwd | Niet nader beschouwd | Coagulatie en flocculatie worden vaak in combinatie gebruikt. In sommige gevallen is het gebruik van louter coagulant of flocculant echter voldoende om goed bezinkbare of floteerbare vlokken te vormen. (https://emis.vito.be/nl/bbt/bbt-tools/selectiesystemen/wass/technieken/coagulatie-en-flocculatie) | https://emis.vito.be/nl/node/19223 |
| Electrocoagulation <i>Elektrocoagulatie</i> | TRL 4 Titanium (ITRC June 2022) TRL 6-7 Ijzeranode TRL4 (Periodically Reversing ElectroCoagulation) | Ja | Ti4O7 elektrode verwijderd meer dan 90% van de lange PFA ketens in 60min (Santiago et al., 2022) 99% PFOA verwijdering met ijzer anode (Santiago et al., 2022) Verwijdering van PFBS, PFHxS, and PFOS kan zo hoog zijn als 87.4%, 95.6%, and 100% respectievelijk (Liu et al., 2022) bijzonder goede adsorptie rendement voor korte ketens (Liu et al. 2022) | Grondwater (ITRC June 2022)(Liu et al. 2022) | Slib en gebruikte coagulant afzet (Garg et al. 2021), de hoeveelheid afzet is niet nader beschouwd. | Het ontwerp kan variëren van eenvoudig tot complex. Deze techniek is compact (ITRC 2june 2022) | Niet nader beschouwd | Het doel van elektrocoagulatie is het vormen van precipitaten en van bindingen tussen colloïden zodat deze stoffen gemakkelijk afgescheiden kunnen worden. Het vrijkomen van coagulant wordt bereikt door het elektrolytisch oplossen van een elektrode (anode, gewoonlijk Fe of Al). (https://emis.vito.be/nl/bbt/bbt-tools/techniefiches/elektrocoagulatie) | https://emis.vito.be/nl/node/19225 Reported to be relatively lowcost without specifying if that is regarded to CAPEX or OPEX (ITRC June 2022) |
| Scheidingstechnieken | | | | | | | | | |
| Reverse osmosis (RO) <i>Omgekeerde osmose (OO)</i> | TRL 9 (Iery, 2019) | Ja | PFOS >99% (polyamide membraan) (Kucharzyk et al., 2017) Verwijderd alle PFAS | RWZI (Lenka et al. 2021), niet voor grondwater (Wanninayake 2021) | Concentraat (vloeistof) | - Concentraat behandeling en hoge investeringskosten (Verma et al. 2021) Membranen onderhouden voor de inzet bij grondwater is economisch niet haalbaar (Wanninayake 2021) | - Concentraat behandeling en hoge investeringskosten (Verma et al. 2021) Membranen onderhouden voor de inzet bij grondwater is economisch niet haalbaar (Wanninayake 2021) | Omgekeerde osmose is een drukgedreven membraanproces dat een scheidingsbereik heeft tussen 0.1 en 1 nm. Hierdoor bezitten omgekeerde osmose membranen een hoge retentie voor bacteriën, virussen en microdeeltjes. Ook tweewaardige en sommige eenwaardige ionen worden goed tegengehouden door het membraan. (https://emis.vito.be/nl/bbt/bbt-tools/techniefiches/omgekeerde-osmose) | https://emis.vito.be/nl/node/19250 |
| Nano filtration <i>Nanofiltratie (NF)</i> | TRL 9 (Iery, 2019) | Ja | PFOS 90 - 99% (Kucharzyk et al., 2017) >95% PFAS (Arcadis, 2021) 69% voor kortere ketens (Liu et al., 2022) Inefficiënte NF verwijdering van korte PFAS keten (Arcadis, 2021) | grondwater (Kucharzyk et al. 2017), niet voor grondwater (Wanninayake 2021) | Concentraat (vloeistof) | - Membranen onderhouden voor de inzet bij grondwater is economisch niet haalbaar (Wanninayake 2021) | - Membranen onderhouden voor de inzet bij grondwater is economisch niet haalbaar (Wanninayake 2021) | Nanofiltratie is een drukgedreven membraanproces dat zich qua scheidingsgrens situeert tussen UF of ultrafiltratie (zie technische fiche 'Ultrafiltratie') en RO of omgekeerde osmose (zie technische fiche 'Omgekeerde osmose'). (https://emis.vito.be/nl/bbt/bbt-tools/techniefiches/nanofiltratie) | https://emis.vito.be/nl/node/19249 |
| Foam fractionation and ozo-foam fractionation Schuimscheiding en schuimscheiding met behulp van ozon | TRL 7 - 8 (ex situ)(Arcadis, 2021) TRL 3 - 4 (in situ) (Arcadis, 2021) | Ja | Ozon fractienatie heeft betere verwijderingsrendement dan gewone schuimscheiding (Meegoda 2020) Één dag pilot liet zien dat >C6 PFAS moleculen goed verwijderd worden (ITRC June 2022) | Grondwater (Wanninayake 2021) | concentraat volume is 0,5-2% of van het influent volume (Meegoda et al. 2020) | + lage apparatuur kosten voor schuimscheiding | Niet nader beschouwd. Mogelijk extra kosten voor concentraat behandeling | Deze techniek bestaat uit kolommen waarin het verontreinigde water doorheen gaat. Daarin worden fijne (ozon) bubbles ingebracht om de verontreinigingen te scheiden. De verontreiniging worden geconcentreerd in het schuim dat boven de waterkolom bevindt. (Ross et al. 2022) | |
| Chemische technieken | | | | | | | | | |
| Photocatalytische degradatie <i>Fotokatalyse / Elektrokatalyse / Fotoelektrokatalyse</i> | TRL 4 - 5 (OVAM, 2021) | Nee | PFOA, PFOS en andere PFAS zijn volledig afbreekbaar, maar het afbraakmechanisme is sterk afhankelijk van het type PFAS. (OVAM 2021) PFOA 0-23% verwijdering na 180 minuten (Lenka et al. 2021) Fotokatalyse reactie kan zowel lange als korte ketens afbreken. Lange ketens afbreken kost meer tijd (Li et al.2020) | Grondwater concentraat na membraan filtratie (Verma et al. 2021) | mineralisatie (Verma et al. 2021) | high-power UV lamps zijn kostbaar en hebben een beperkte levensduur (Leonello et al. 2021) | - Duurste chemicaliën verbruik kosten vergeleken met sonolyse en ARP. Het catalyst is ook kostbaar (Nzeribe et al. 2021) | Catalyst worden onderworpen aan specifieke lichtgolf om zeer sterke reductor en oxidator te produceren die de verontreinigingen kunnen breken. (Xu et al. 2017) | Voor de praktische inzet van deze techniek moet onderzocht worden hoe de katalisatoren vastgezet kunnen worden voor een langere inzet inclusief om ze te kunnen regenereren (Ahmed et al. 2020) https://watercircle.be/publicaties/database-waterzuivering-en-behandelingstechnieken/photocatalytic-water-purification-technology/ |
| Chemical oxidation <i>Chemische oxidatie</i> - Waterstofperoxide - natriumpersulfaat - Na/K-permanganaat - ozon - ozon/waterstofperoxide | TRL6 (Vito 2022) | Nee | Chemische oxidatie kan ineffectief zijn voor PFAS behandeling (ITRC June 2022)(Kucharzyk et al., 2017). | Niet duidelijk in welke water getest is | Niet nader beschouwd | Niet nader beschouwd | Niet nader beschouwd | Chemische oxidatie wordt toegepast op deelstromen die ongewenste stoffen bevatten die door oxidatie tot een onschuldige of gemakkelijker te verwijderen stof kunnen omgezet worden. (https://emis.vito.be/nl/bbt/bbt-tools/techniefiches/chemische-oxidatie) | https://emis.vito.be/nl/node/19231 |
| Electrochemical oxidation <i>Elektrochemische oxidatie</i> | TRL 4 (OVAM, 2021) TRL 5 (Liang et al. 2022) | Nee | Meerdere PFAS (incl. PFHxA) 76,6 - 99,7% (Arcadis, 2021) 92,1 - >99,9% (PFOA en PFOS) (Sherma et al., 2022) compleet mineralisatie van C4 tot C8 PFAAs (Iery, 2019) Minder effectief voor korte PFAS keten (Ross Et al., 2018) | Grondwater (Liang et al. 2022) | Mineralisatie (Ross Et al. 2018) | Niet nader beschouwd | Niet nader beschouwd | Electrochemische oxidatie is een proces waarbij hydroxyl radicalen geproduceerd worden door water te splitsen zonder chemicaliën toevoeging. (Santiago et al. 2022) | Kan geschikt zijn voor kleine volume met hoge concentratie (Ross et al. 2018) |
| Super critical water oxidation (SCWO) <i>Super kritische wateroxidatie</i> | TRL 4 - 6 (Arcadis, 2021) | Ja | 100% meerdere PFAS (Arcadis, 2021) Max 70% PFOS conversie naar HF en CO2 na 60 min op 500 oC (Pinkard et al. 2021) | Kan ook voor nonwater afval ingezet worden zoals slib (Berg et al.2021) | Mineralisatie (McDonough et al. 2021) | Niet nader beschouwd | - Hoog energie verbruik (Berg et al. 2021) | Water gedraagt zich als een oplosmiddel als hij de kritische staat heeft bereikt (boven de 374 graden Celsius en 22.11 Mpa). In deze staat worden chemische oxidatieve reacties versterkt door oxidanten als O2, lucht en H2O2. (Berg et al. 2022) | https://emis.vito.be/nl/node/19264 |
| Chemical reduction <i>Chemische reductie</i> - Zero valent iron (ZVI) - UV/sulfite system | TRL 3 | Nee | 86.8% PFHS reductie (Verma et al. 2021) Variabele PFOA and PFOS verwijderings efficiencies in labtesten (Ross et al. 2018) Fluor emissie is niet afhankelijk van de PFCA koolstofketen lengte, terwijl voor PFSA wel afhankelijk is (Nzeribe et al. 2019) | Grondwater (Nzeribe et al. 2019) | Niet nader beschouwd | Niet nader beschouwd | Hoge reactie temperaturen en kosten van nul valente ijzer (zero valent iron) (Verma et al. 2021) | Vergelijkbaar met oxidatieprocessen omvatten reductieprocessen directe elektronen overdracht als genereren van reactieve vrije radicalen om verontreinigingen af te breken. (Nzeribe et al. 2019) | De reductors worden snel door zuurstof en nitraat afgevangen, waardoor on-site applicatie uitdagend kan zijn (Ross et al. 2018) |

| Techniek | Schaal/Marktrijpheid/TRL | ACTIEPROGRAMMA PFAS (TRL 5 en hoger) | Verwijderingsrendementen (korte en lange ketens) | Type water | Reststroom | Investeringskosten CAPEX, Kwalitatief | Operationele kosten OPEX, Kwalitatief | Techniek toelichting | Achtergrondinformatie (verwijzing naar enkele niet-commerciële websites) |
|---|--------------------------|--------------------------------------|--|-------------------------------------|----------------------|---|---|---|---|
| | | | | Industrieel afvalwater / Grondwater | | | | | |
| Chemische technieken | | | | | | | | | |
| Plasma treatment technology <i>Plasmabehandelingstechnologie</i> | TRL 3 | Nee | Meerdere PFAS 93,6% (Arcadis, 2021) 90% mineralizatie van PFOA en PFOS (Strattonet al., 2017) 90% lange keten and 88% korte keten verwijdering (Santiago et al 2022) | Grondwater (Ahmed et al. 2020) | Niet nader beschouwd | - Duurder dan geavanceerde oxidatie proces en adsorptie technieken (Ahmed et al. 2020) | - Duurder dan geavanceerde oxidatie proces en adsorptie technieken (Ahmed et al. 2020) | Plasma is de vierde toestand van materie die gebaseerd is op een eenvoudige fysisch principe, en het bestaat uit ionen, atomen in hogere energie toestand, atoomfragmenten, vrije elektronen etc. Organische moleculen kunnen tegelijkertijd worden geoxideerd en gereduceerd door plasma elektrische ontladingen (Ahmed et al. 2020) | Kan toxische bijproducten en broeikasgas vrij komen (Ahmed et al. 2020) |

| Techniek | Schaal/Marktrijpheid/TRL | ACTIEPROGRAMMA PFAS (TRL 5 en hoger) | Verwijderingsrendementen (korte en lange ketens) | Type water | Reststroom | Investeringskosten CAPEX, Kwalitatief | Operationele kosten OPEX, Kwalitatief | Techniek toelichting | Achtergrondinformatie (verwijzing naar enkele niet-commerciële websites) |
|--|---|--------------------------------------|---|---|---|---|--|--|--|
| | | | | Industrieel afvalwater / Grondwater | | | | | |
| Biologische behandelingstechnieken | | | | | | | | | |
| Microbe-based bioremediation <i>Microorganismen-gebaseerde bioremediatie</i> - Mycologische destructie/degradatie - Bacteriële degradatie | TRL 1-3 (Kucharzyk et al., 2017) | Nee | Eerder polyPFAS dan perFAS. 30% PFOA 45% 6:2 FTOH (Kucharzyk et al., 2017). 60% eliminatie van PFOA en PFOS (Huang and Jaffé, 2019) (bact) PFOA en PFOS <7% (Xu et al. 2017) Beperkte biodegradatie studies en veel conflicterende resultaten (Kucharzyk et al., 2017). Zeer trage degradatie onder ideale lab condities (Wanninayake 2021) Korte PFAS vertoont sterke resistentie in actieve slib systeem (Liu et al. 2022) | Niet duidelijk in welke water getest is | Niet nader beschouwd | Niet nader beschouwd | Niet nader beschouwd | Afbraak van stoffen door microorganismen (Kucharzyk et al. 2017) (Garg et al. 2021) | |
| Constructed wetlands | TRL 3 - 4 | Nee | Accumulatie van 29.3-95.88% PFOS en PFOA in wortels en stelen. 82.8% PFAA is in een plant (Juncus Effusus) geaccumuleerd in 21 dagen. Accumulation in roots 48.8-95.8% for PFOS and 29.3-77.4% for PFOA in shoots (Garg et al. 2021) Bioaccumulation and translocation in roots and shoots of Juncus effusus varied with the carbon chain I+F31+F32 | Niet duidelijk in welke water getest is | Mogelijk PFAS houdende planten behandelen | Niet nader beschouwd | Niet nader beschouwd | Opname van PFAS in planten (constructed wetlands) (ITRC June 2022) (Garg et al. 2021) | |
| Enzymes and proteins for bioremediation <i>Enzymen en proteïnen voor bioremediatie</i> | TRL 2 - 3 | Nee | 98% PFOS degradatie met enzymen in 1 uur (Wanninayake 2021) | Niet duidelijk in welke water getest is | Niet nader beschouwd | Niet nader beschouwd | Niet nader beschouwd | Afbraak van stoffen door enzymen. Afbraak route afhankelijk van type enzym. (Garg et al. 2021) (Rose et al. 2018) | Enzymen van <i>Cannabissativa L.</i> is bewezen in staat te zijn om PFAS snel af te breken. Aerobe en anaerobe microben hebben meer dan 100 dagen nodig om 70-80% van de PFAS af te breken (Wanninayake 2021) Stabiliteit van enzymen waarborgen is belangrijk. Enzymen is uiteindelijk een goede bron van nutriënten voor andere bacteriën. (Rose et al. 2018) |
| Diverse technieken | | | | | | | | | |
| Sonochemical degradation <i>Sonochemische degradatie</i> | TRL 7-8 (Kucharzyk et al., 2017 / Jaleri, 2019) | Ja | PFOS 39 - 73% (Kucharzyk et al., 2017) PFOA: 44% (Kucharzyk et al., 2017) PFOS/PFOA: 28 - 100% (afh. energieverbruik en duur) (Arcadis, 2021) PFOA completely degraded at 370°C after 360 min (Liu et al., 2022) 44% PFOA and 39% PFOS afbraak (Verma et al. 2021) Lange koolstof ketens worden meer efficiënt afgebroken (Liu et al. 2022) | Grondwater (Verma et al. 2021) | Mineralizatie (Verma et al. 2021) | - Hoge investeringskosten (Wanninayake 2021) | 0 Relatief lage energie verbruik op kamertemperatuur en atmosferische druk (Ahmed et al. 2020)(Concawe) | Het sonolytische proces is afhankelijk van de voortplanting van akoestische golven in vloeistoffen met frequenties tussen 20 kHz en 1000 kHz, wat resulteert in cavitatie. Tijdens cavitatie, cyclische vorming, groei en instorting van microbubbel resulteren in een intense toename van temperatuur en druk (5000 K en 2000 atm), en het genereren van vrije radicalen. Hiermee kan stoffen afgebroken worden. (Nzeribe et al. 2019) | Voorstel om ultra-sonische techniek met geavanceerde oxidatie techniek te combineren voor een operationele simpele systeem die efficiënt is en goed op te schalen is. Het is verder economisch rendabel (Wanninayake 2021) |
| Thermal degradation and incineration <i>Thermische degradatie en verbranding</i> | TRL 9 | Ja | De enige bewezen techniek (Meegoda 2020) Werkt voor zowel korte als lange PFAS keten (Concawe) | Grondwater (Concawe) | Verbrandings resten/bodem assen | Niet nader beschouwd | - (Concawe) | inzet van zeer hoge temperatuur om stoffen af te breken (Kucharzyk et al. 2017) | |

Colophon

STATE OF THE ART PFAS
AN OVERVIEW OF KNOWLEDGE GAPS AND RESEARCH NEEDS - SOIL AND GROUNDWATER

AUTHORS

Arcadis

READERS GROUP

Witteveen+Bos
Arcadis UK
RWS
BASF
Arcadis D
RIVM

Many thanks to others who preferred to stay anonymous.

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www.arcadis.com

Arcadis Nederland B.V.

P.O. Box 264
6800 AG Arnhem
The Netherlands

T +31 (0)88 xxx xx xx

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